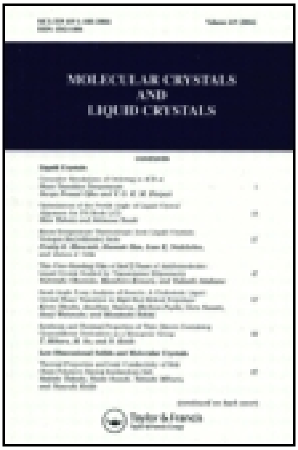

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STABILIZATION OF THE SMC* PHASE IN MIXTURES OF FERROELECTRIC AND NON-FERROELECTRIC HOMOLOGUES

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Stabilization of the SmC* Phase in Mixtures of Ferroelectric and Non-Ferroelectric Homologues

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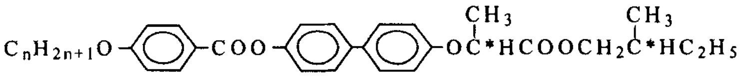
For a series denoted as HO n/** binary mixtures of ferroelectric, FE, (n=10, 12) and non-ferroelectric (n=8) homologues are studied. All homologues exhibit the SmA and SmB phases. With HO10/**- HO8/**mixtures, the FE phase exists only down to 90% of FE homologue. With HO12/**- HO8/** system the phase transition temperature to the FE phase is decreasing when decreasing the concentration of the FE compound, the width of the FE phase becoming gradually smaller. Spontaneous polarization as well as the tilt angle in FE mixtures is increasing with increasing FE component. We found a strong soft mode in all studied non-ferroelectric mixtures, which gives evidence of proximity of a hypothetical SmA-SmC* phase transition.

Keywords: ferroelectric liquid crystals; binary mixtures; spontaneous polarization

INTRODUCTION

Mixtures of ferroelectric (FE) and non-ferroelectric compounds are frequently studied when inventing FE materials for display applications. In those cases, the non-FE components are non-chiral. Here we study binary mixtures of FE and non-FE compounds that have very close molecular structure being from one homologue series. Investigation of stabilization of the FE phase in such systems and properties of FE mixtures is the aim of this contribution.

We choose a series recently reported [1] containing a lactate group with two chiral centers. General formula of these compounds denoted as HOn/** is:



$$C_nH_{2n+1}O\text{-}C_6H_4\text{-}COO\text{-}C_6H_4\text{-}C_6H_4\text{-}OC^*H(CH_3)COOCH_2C^*H(CH_3)C_2H_5$$

The homologues exhibit the phase sequence SmA-SmC*-SmB or directly SmA-SmB for compound with short alkyl chains. A well-pronounced soft mode has been detected in the SmA phase for all materials, suggesting proximity of a hypothetical SmC* phase even in the non-FE compounds [1].

EXPERIMENTAL

The sequences of phases of materials used in mixtures are shown in Table 1. We prepared binary mixtures of FE HO10/** or HO12/** with non-FE HO8/**.

TABLE 1 Phase transition temperatures in °C for materials used in the binary mixtures. The symbols show: • the phase exists, — the phase does not exist, m.p. is the melting point.

	m.p.	SmB	SmC*	SmA	N*	BP	Iso
HO8/**	58	•	—	55 •	65 •	82 •	84 •
HO10/**	52	•	53 •	58 •	65 •	84 •	86 •
HO12/**	59	•	45 •	63 •	66 •	77 •	80 •

The cells 25 μm thick were filled in the isotropic phase and composed of glass plates provided with transparent ITO electrodes and polyimide layers rubbed in the same direction, which ensures planar (bookshelf) geometry. Samples were aligned applying a.c. electric field (typically 5×10^6 V/m, 20 Hz). Temperature was changed and stabilized with accuracy ±0.1°C in the Linkam hot stage.

In the SmC* phase the dechiralization lines could not be seen in the polarizing microscope in all studied samples indicating the helical structure was unwound. In such a case, the director twist-bend along the sample plane normal is expected (twisted structure [2,3]).

Spontaneous polarization was measured using Sawyer-Tower circuit enabling compensation of d.c. conductivity and linear capacity. The tilt angle was determined from change of the extinction position between crossed polarizers under rectangular a.c. field. Frequency dispersion of the complex permittivity was studied in the frequency range from 10 Hz to 1 MHz. The dispersion data were analyzed using the Cole-Cole formula:

$$\varepsilon^*(f)-\varepsilon_\infty=\frac{\Delta\varepsilon}{1+(if/f_r)^{(1-\alpha)}}-\frac{\sigma^n}{2\pi\varepsilon_0 f} \qquad (1)$$

f_r, $\Delta\varepsilon$, α, σ, and n are relaxation frequency, dielectric strength, distribution parameter, conductivity, and exponent, respectively. The same parameters were used for fitting the real and imaginary parts of Eq. 1.

RESULTS

With HO12/**- HO8/** system, the phase transition temperature to the FE phase, T_c, is decreasing when decreasing the concentration of the FE compound, the width of the FE phase becoming gradually smaller. It is clearly demonstrated in Figure 1, where the temperature dependences of real part of the permittivity measured at 30 Hz are shown. Below the concentration of 40 weight % of HO12/** the FE SmC* phase is lost and a direct SmA-SmB transition takes place. The results are summarized in the phase diagram (Figure 2).

With HO10/**- HO8/** system, the FE phase exists down to the concentration of 90% of the FE compound only. At the transitions to the SmB phase a coexistence of phases within several K occurred, which prevented a systematic study in the very narrow SmC* phase.

The values of spontaneous polarization, P_s, in the FE mixtures gradually decrease under the decrease of the FE component. For pure HO12/** P_s =110 nC/cm^2, for the FE mixture containing the smallest amount of HO12/** P_s still reaches 50 nC/cm^2, for pure HO10/** P_s =60 nC/cm^2 only (all measured at 5 K below T_c). Temperature dependences of polarization for several mixtures of HO12/**- HO8/**

system exhibiting FE phase are in Figure 3. For the same compounds temperature dependences of the tilt angle, θ_s, are shown in Figure 4. The values of θ_s also decrease with decreasing concentration of FE component.

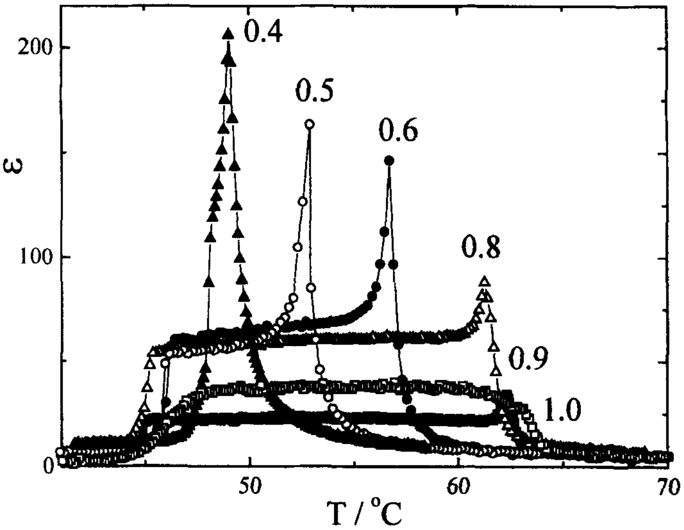


FIGURE 1 Temperature dependences of real part of permittivity measured at 30 Hz for indicated weight concentration of FE compound HO12/**.

The dielectric spectroscopy revealed a strong soft mode in the SmA phase of all studied homologues in the whole concentration region of the HO12/**-HO8/** system. The relaxation frequency of the soft mode exhibits a linear decrease when approaching T_c, the slopes of lines are the same for all mixtures except the compounds with highest concentrations of HO12/** (see Figure 5). The dielectric strength within the SmC* phase is constant except for the close vicinity of T_c, where the contribution of the soft mode is significant. The origin of the susceptibility in the SmC* phase is the "thickness mode" in correspondence with the twisted structure [4].

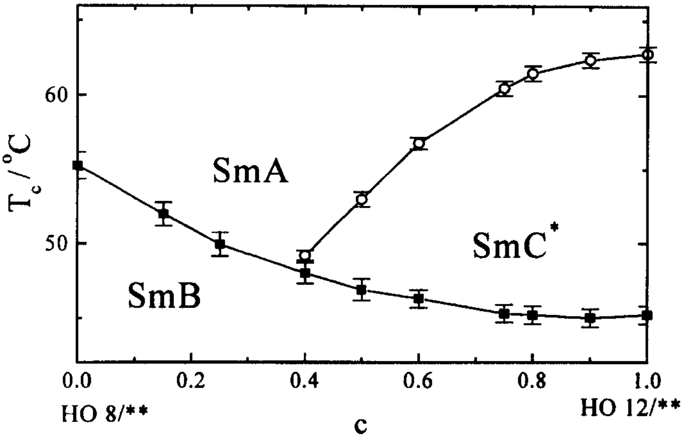


FIGURE 2 Phase diagram for binary mixtures HO12/**-HO8/**, *c* denotes relative weight concentration.

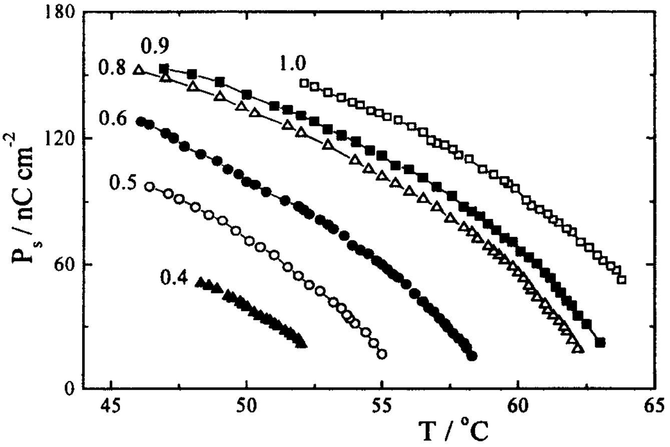


FIGURE 3 Temperature dependences of spontaneous polarization for indicated concentrations of FE HO12/**.

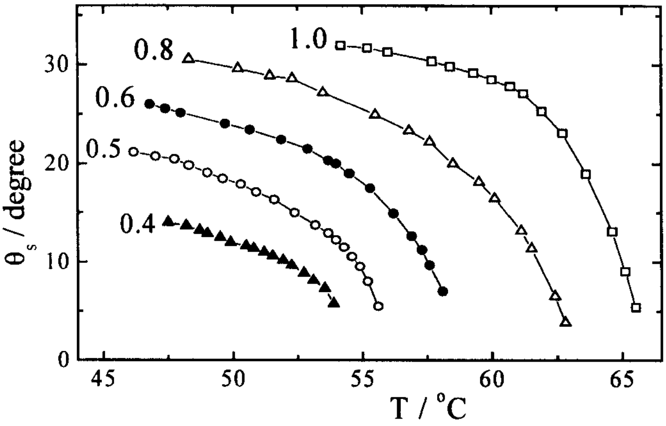


FIGURE 4 Temperature dependences of tilt angle for indicated concentrations of FE HO12/**.

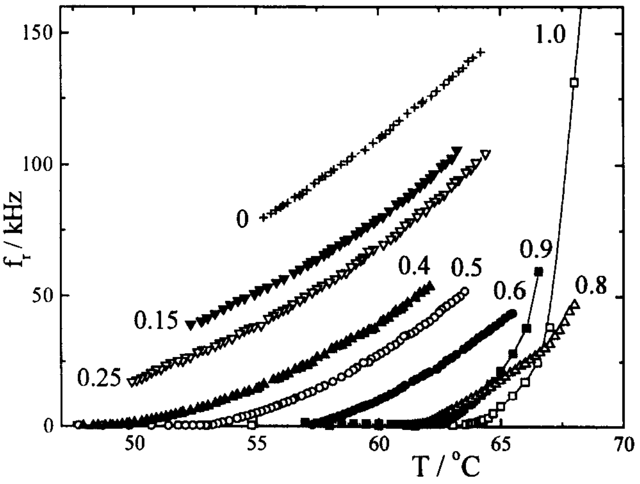


FIGURE 5 Temperature dependences of relaxation frequencies for indicated concentrations of HO12/**.

DISCUSSION AND CONCLUSIONS

The results show that the FE phase is more easily stabilized in the mixtures with FE HO12/** than with FE HO10/**. The reason is that HO10/** is only weakly ferroelectric material, as it has very narrow FE phase (5 K) and relatively low spontaneous polarization.

When increasing the concentration of the FE HO12/** compound, the spontaneous polarization as well as the tilt angle increase (see Figures 3,4,6). On the opposite, the permittivity decreases (see Figure 1).

Concentration dependences of spontaneous quantities are rather natural, as the FE compound raises both the spontaneous polarization and tilt angle, but the last dependence seems to be rather unexpected.

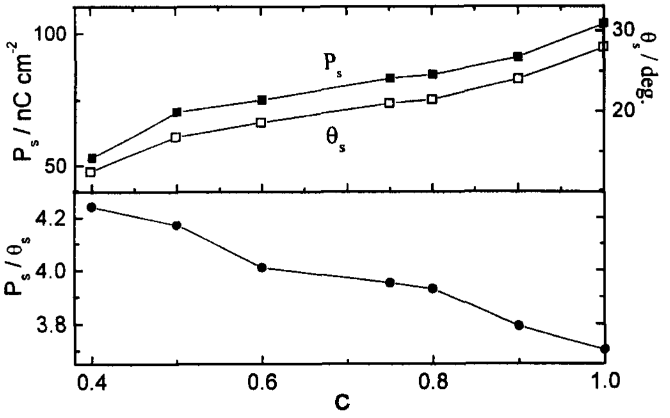


FIGURE 6 Spontaneous polarization, tilt angle, and their ratio P_s/θ_s (measured 5 K below the phase transition to the FE phase) versus concentration of the FE HO12/**.

It can be understood considering the thickness mode properties, which is the origin of the dielectric response in the SmC* phase of the studied samples. The susceptibility, χ, of this mode is [5]

$$\chi = \frac{\mu^2/2}{K_1(\pi/d)^2 + L\,\mu^2/2} \qquad (2)$$

where $\mu \equiv P_S/\theta_S$, K_l is an elastic constant and L is a depolarization factor. From Eq. 2 one can see that if the terms in denominator are comparable and K_l and L constant, the change of χ are essentially driven by changes of μ. Then one can expect that if μ is decreasing with increasing concentration of FE HO12/** (see Figure 6), the permittivity can also decrease.

The soft mode is detected in the SmA phases of all mixtures, even in those, which do not exhibit the SmC* phase (see Figure 5). On cooling of those mixtures, the transition to the SmB phase occurs before the softening of the mode is completed. The same phenomenon has been found in non-FE HO8/** [1].

Acknowledgements
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