Observation of a Frustrated Phase in Mixtures of Ferroelectric and Antiferroelectric Liquid Crystals

E. Gorecka,[1] D. Pociecha,[1] M. Glogarova,[2] and J. Mieczkowski[1]

[1]*Chemistry Department, Warsaw University, Al. Żwirki i Wigury 101, 02-089 Warsaw, Poland*
[2]*Institute of Physics, Academy of Sciences of the Czech Republic, Na Slovance 2, Prague, Czech Republic*
(Received 6 April 1998)

Continuous evolution of polar properties from ferro- to antiferro- has been observed in binary mixtures of compounds having antiferroelectric and ferroelectric phases. The dielectric constant in the antiferroelectriclike smectic phase increases continuously upon increasing the ferroelectric component concentration. The variations of antiferroelectric phase properties could be attributed to changes of the azimuthal tilt angle correlations, which result in frustration between antiferroelectric and ferroelectric interactions and formation of clusters of both phases. A strong difference between dielectric susceptibilities of zero-field-cooled and field-cooled samples was observed in a frustrated phase. [S0031-9007(98)07218-4]

It has been predicted that the transition between ferroelectric (FE) and antiferroelectric (AF) smectic phases under a temperature change [1] must be either of the first order or it occurs via ferrielectric phase [2]. However, we cannot exclude that the transition between FE and AF phases might also involve an intermediate state with weak correlation of azimuthal tilt angle between neighboring smectic layers. Such a structure has been recently assigned to a so-called thresholdless antiferroelectric state [3]. This state is most probably induced by surface interaction since so far it has been detected in thin samples only.

Here we report properties of binary mixtures of two successive homologues in which a continuous evolution of the AF phase into the FE one is observed when increasing the concentration of the compound with exclusive FE phase. Dielectric properties are studied to establish the polar character of the phase. Continuous variation of dielectric properties is related to diminished azimuthal tilt angle correlation between adjacent smectic layers causing frustration between ferro- and antiferroordering. No ferrielectric properties have been observed in this system.

The compounds studied belong to a homologue series of 4-(4′-alkoxy-biphenyl-4-yloxymethyl)-benzoic acid 2-octanol esters [4] exhibiting a strong discrimination of FE properties upon lengthening of a nonchiral terminal chain (Fig. 1). For a homologue with 13 carbon atoms in alkoxyl chain (C13) and longer ones only FE phases (SmC^* and hexatic SmI^*) have been detected. For compounds C12 and shorter, AF properties dominate and the FE SmC phase, preceding AF SmC and SmI phases, is very narrow ($\sim$1 K). Cells for measurements consisted of glass plates coated with indium tin oxide (ITO) transparent electrodes and parallel rubbed polyimid layer. Dielectric measurements were carried out with a 25 μm thick cell filled by a capillary action in the isotropic phase. A good sample planar alignment was obtained by slow cooling of the sample from the isotropic phase. The textures of

studied samples were monitored using a polarizing microscope (Nikon-Optiphot2). The dielectric measurements were performed in heating runs to avoid the overcooling effects at the first order phase transitions. Frequency dispersion of the complex permittivity $\varepsilon^*(\omega) = \varepsilon' - i\varepsilon''$ has been measured in a range of 20 Hz–300 kHz as a function of temperature using Wayne Kerr impedance analyzer. The strength of the dielectric mode $\Delta\varepsilon$ and its relaxation frequency f_r were obtained from fitting of complex permittivity to the Cole-Cole equation $\varepsilon^* - \varepsilon_\infty = \frac{\Delta\varepsilon}{1+(if/f_r)^{1-\alpha}} - i\frac{\sigma}{2\pi\varepsilon_0 f}$. The spontaneous polarization has been determined by integrating the electric current during the sample switching at the frequency
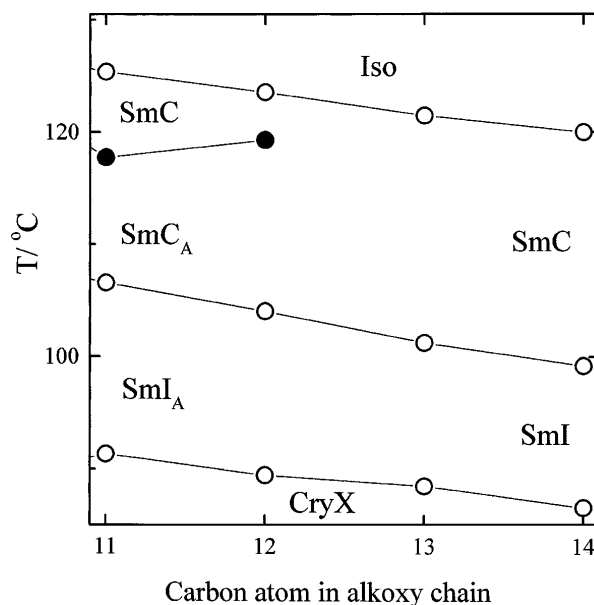

FIG. 1. Part of the phase diagram of studied homologue series. Phase transition temperatures are taken from DSC scans at 5 K/min.

100 Hz. The spontaneous tilt was measured from the angle difference between minimum transmission positions of a planar sample placed between crossed polarizes under opposite dc electric fields. Selective reflection was measured using a Nikon microspectrometry system in ~10 μm thick one surface free homeotropic samples.

In mixtures with a low concentration of the compound C13 the phase transition between smectic C (FE and AF) phases was clearly observed, similarly as in the pure compound C12. At the transition temperature T_o a small peak on DSC thermograms was detected and the phase transition was also observable under microscope as the texture change. In the AF-like phase the typical tristable optical switching was found with characteristic domain boundary movement and double current peak. Also at dielectric measurements the transition was clearly visible as a jump of low frequency dielectric constant, from about 500 in FE to about 5 in AF phase. The helical pitch being in visible light wavelength range in FE phase, becomes infinite in AF phase which is signified by the appearance of a periodic net of defects, e.g., stripes or squares in thick (>5 μm) free suspended film or schlieren texture in thinner samples. The periodic net

of defects was attributed to an existence of the in-layer bend modulation of director in helix free samples [5]. The existence of these defects prevents the conoscopic study. As a mole fraction of C13 increased the phase transition temperature T_o slightly decreased. Along with it the relevant transition enthalpy abruptly decreased, being undetectable in mixtures with a mole fraction of C13 higher than ~0.5. When increasing the fraction of C13 the properties of the phases (SmC and SmI) below T_o became less AF-type, which was manifested in a monotonous increase of dielectric constant in these phases. Consequently, the jump in dielectric constant at the transition point T_0 decreased as the system moved toward the pure FE compound C13 (Fig. 2). Also the texture changes observed in planar cells at the AF-FE transition became less pronounced. For mixtures with a concentration of C13 higher than 0.9 mole fraction, the AF-FE phase transition was lost. With increasing the concentration of the FE component, also the threshold field for the switching of spontaneous polarization and apparent tilt decreased monotonously (Fig. 3). The helix as observed in homeotropic samples becomes unwound below T_o for mole fraction of C13 $x < 0.85$. For higher x only a small maximum of pitch was observed at T_o, and for pure C13 no anomaly of pitch occurs in the SmC* phase.

In FE SmC* phases the Goldstone mode [6] was detected. In the AF phase of pure C12 homologue no dielectric mode was found within the studied frequency
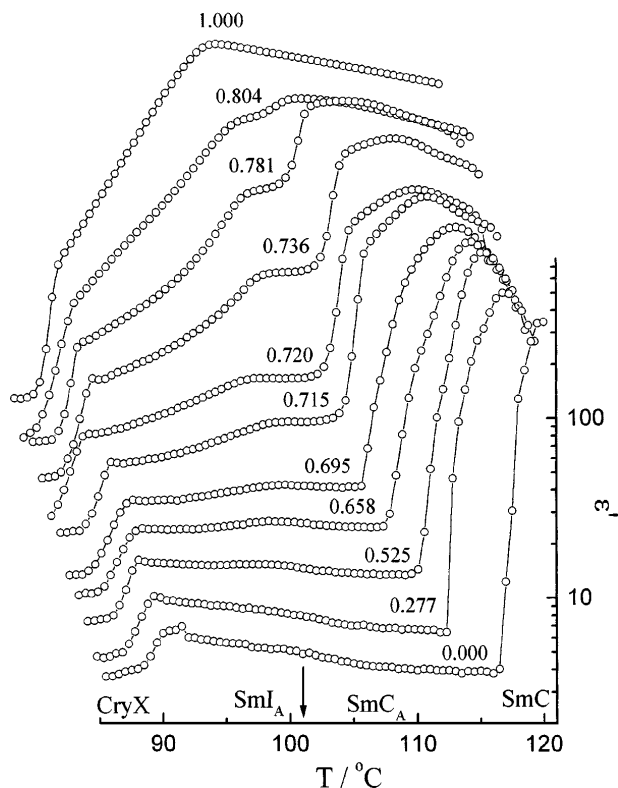

FIG. 2. Dielectric constant (obtained at frequency 120 Hz) vs temperature for binary mixtures of homologues C12 and C13. The curve parameters show the concentration of C13. The arrow indicates the temperature of the phase transition into hexatic smectic phase, which only slightly depends on mixture composition. The vertical axis labels are valid for the pure C12 only. Other curves are shifted up, keeping the same scale.
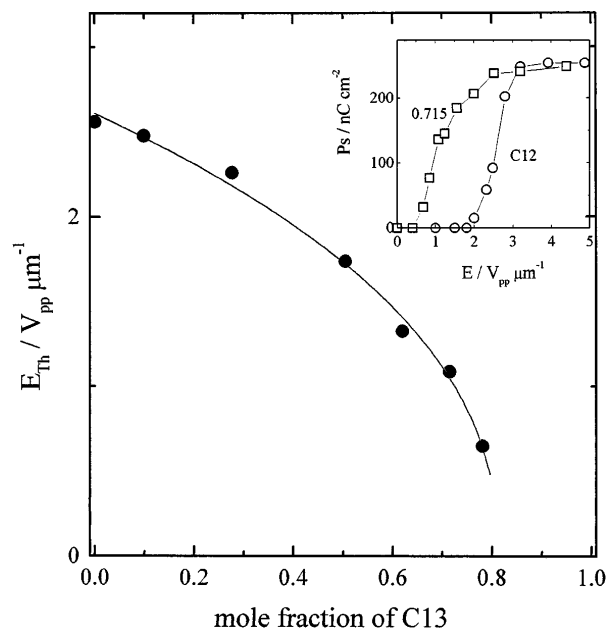

FIG. 3. Threshold electric field for spontaneous polarization switching vs concentration of C13 measured at 4 K below FE-AF-like phase transition temperature. In the inset Ps vs electric field for homologue C12 and mixture with $x = 0.715$ mole fraction of C13.

range. However, as the concentration of C13 increased the Goldstone mode appears in the AF-like phase and became gradually stronger. The relaxation frequency of this mode, f_G, gradually decreases with decreasing temperature in the SmC^* phase, but remains in the frequency range of about a few kHz. Slight anomalies of f_G occur at AF-FE phase transition T_o temperature, which have the form of a decrease or an increase depending on the concentration of C12. In the SmC^* phase range, the temperature dependence of the strength of the Goldstone mode is the same as that of the low frequency permittivity, exhibiting a jump up at T_o on heating, which is stronger for more AF-like mixtures (cf. Fig. 2).

In the hexatic SmI^* phase f_G suddenly decreases by one order. Thus, the permittivity measured at the frequency of 120 Hz in this phase can differ from the static one. This causes the decrease in permittivity below the SmC^*-SmI^* phase transition observed with compounds of high concentration of C13 (see Fig. 2).

The bias electric field has the same influence on dielectric properties below and above T_0. A monotonous decrease of the strength of the dielectric mode is observed with increasing bias field.

Summarizing, all observed changes in dielectric as well as in the switching properties of lower temperature phase suggest that its behavior evolves continuously from AF-like to FE-like when changing the composition of the mixtures.

Besides, the polar properties of the low-temperature phase strongly depend on the history of the system. An interesting "learning of ferroelectricity" phenomenon was observed in the AF-like phase, which means that treating the sample by dc electric field of the strength above the switching threshold brings about FE-like behavior. This effect is illustrated in Fig. 4(a), where one can see that the threshold electric field for tilt angle switching measured in fresh sample is significantly higher than that in a sample treated by electric field before the study. Likewise, the permittivity of the samples cooled in dc electric field reaches the FE values even below T_o in contrast to zero-field cooled samples, which exhibits a strong decrease of permittivity below T_o [see Fig. 4(b)]. It is also worth mentioning that the AF state was not restored in field treated samples. The decrease in dielectric constant was found to be less than 10% over a period of a few days, and is probably due to the small chemical degradation of the sample.

The polar properties of the phase below T_o were also affected by strong boundary interactions. It was found that surfaces favor FE alignment. With decreasing sample thickness the strength of Goldstone-mode in AF-like phase increases, the effect being more pronounced for less AF-like mixtures. This behavior of the Goldstone mode in phase below T_o is reversed to that detected in FE phase in which the mode is suppressed by decreasing cell thickness. In cells of thickness $\sim 3~\mu$m apparent
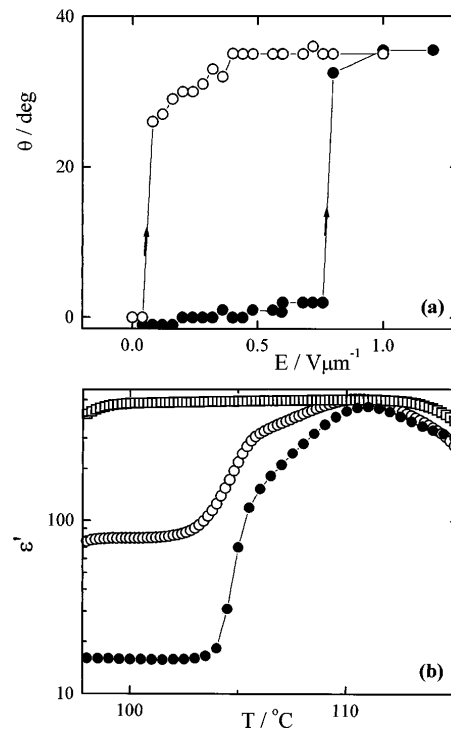

FIG. 4. Apparent tilt angle changes under electric field at 102 °C (a) and dielectric constant obtained at 120 Hz on heating run (b) in mixture 0.715 mole fraction of C13. Filled circles—changes observed for zero-field sample. Open circles—after applying dc electric field. Squares in (b)—the dc electric-field-cooled dielectric constant.

thresholdless switching, similar to that reported in Ref. [3], was detected.

As mentioned above, two different ways in which the system can change from AF type to FE type have been considered so far. One possibility is a first order transition line separating FE and AF regions in the temperature-concentration phase diagram. This line would close the AF phase region existing for mixtures with low concentration of FE component and should terminate at the triple point on the line of phase transition to the low temperature crystalline phase. The other possibility involves the intermediate ferrielectric phases. Under suitable conditions the evolution from FE to AF phase through the ferristates can be observed as apparently continuous since the changes in order parameter might be very small [7].

The results obtained for the studied system are inconsistent with both assumptions. First, the line of FE-AF phase transition in the temperature-concentration phase diagram is nearly horizontal; it has no tendency to turn down to the line of transition to the crystalline phase. Moreover, a continuous variation from AF to FE properties is observed when the concentration is changed. The idea that this effect is due to the phase coexistence caused by slow kinetic of FE-AF phase transition was ruled out. Also the existence of the intervening ferrielectric phase (C and I type)

between AF and FE phases should be excluded, because no traces of that phase have been detected. The DSC results have not exhibited any peak for AF-ferri or ferri-Fe phase transitions, nor did microscope observation show any phase transition involving ferrielectric phase or phase coexistence region typical for these phase transitions. Moreover, no characteristic properties of the ferrielectric phase, e.g., nonmonotonous changes of the strength of Goldstonelike mode under a bias electric field, neither stepwise tilt nor Ps switching [8–10], were detected in any of the binary mixtures. Also observed not reversible "learning of ferroelectricity" effect after applying electric field is inconsistent with the formation of the ferrielectric phase which equilibrium structure should not depend on the system history.

One can point out that similar properties to that observed in the studied system, namely the continuous evolution from the AF to FE phase under a concentration change, have been found in binary mixtures of solid ferroelectrics and antiferroelectrics. For example, mixtures $Rb_{1-x}(ND_4)_x D_2PO_4$ exhibit this behavior for concentration x between about 0.3 and 0.7. It has been suggested that within this concentration range a glassy state occurs composed of nanometric size clusters of AF and FE phases; the proportion of which depends on x parameter [11]. This behavior is explained on the basis of broken translational and competing FE and AF interactions.

A similar model might be used to explain the behavior of mixtures composed of liquid crystals exhibiting AF and/or FE phases as established in this contribution. The formation of clusters that appear in mixtures in a certain temperature range might be allowed because of lowering of the strength of azimuthal angle correlation, which results in frustration between AF and FE phases. The concentration of FE clusters may be influenced not only by a mixture composition but also by surface interactions or the electric field treatment. The increase of FE cluster number in electric field is reminiscent of the deuteron glasses behavior [12].

[1] A. Fukuda, Y. Takanishi, T. Isozaki, K. Ishikawa, and H. Takezoe, J. Mater. Chem. **4**, 997 (1994), and references therein.

[2] E. Gorecka, A. D. L. Chandani, Y. Ouchi, H. Takezoe, and A. Fukuda, Jpn. J. Appl. Phys. **29**, 131 (1990).

[3] S. S. Seomun, Y. Takanishi, K. Ishikawa, H. Takezoe, and A. Fukuda, Jpn. J. Appl. Phys. **36**, 3586 (1997).

[4] J. Mieczkowski, D. Pociecha, E. Gorecka, and M. Glogarova, Ferroelectrics **212**, 357 (1998).

[5] E. Gorecka, M. Glogarova, L. Lejcek, and H. Sverenyak, Phys. Rev. Lett. **75**, 4047 (1995).

[6] J. W. Goodby, in *Ferroelectric Liquid Crystals*, edited by G. W. Taylor (Gordon and Breach Science Publishers, Philadelphia, 1991), p. 99.

[7] M. Yamashita and S. Tanaka, Jpn. J. Appl. Phys. **37**, L528 (1998).

[8] S. Inui, N. Iimura, T. Suzuki, H. Iwane, K. Miyachi, Y. Takanishi, and A. Fukuda, J. Mater. Chem. **6**, 671 (1996).

[9] Yu. P. Panurin, O. Kalonovskaya, J. K. Vij, and J. W. Goodby, Phys. Rev. E **55**, 4345 (1997).

[10] J. Hou, J. Schacht, F. Giebelmann, and P. Zugenmaier, Liq. Cryst. **22**, 401 (1997).

[11] R. Korner, Ch. Pfammatter, and R. Kind, Phys. Rev. Lett. **70**, 1283 (1993).

[12] A. Levstik, C. Filipic, K. Kutnjak, I. Levstik, R. Pirc, B. Tadic, and R. Blinc, Phys. Rev. Lett. **66**, 2368 (1991).