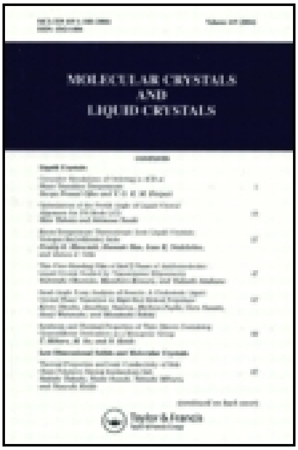

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Ferroelectricity in Tilted Smectics Doped with Optically Active Additives

L. A. Beresnev [a] , L. M. Blinov [a] , V. A. Baikalov [a] , E. P. Pozhidayev [a] , G. V. Purvanetskas [a] & A. I. Pavluchenko [a]

[a] Organic Intermediates and Dyes Institute, 103787, B. Sadovaya 1-4, Moscow, U.S.S.R.
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Ferroelectricity in Tilted Smectics Doped with Optically Active Additives†

L. A. BERESNEV, L. M. BLINOV, V. A. BAIKALOV, E. P. POZHIDAYEV, G. V. PURVANETSKAS and A. I. PAVLUCHENKO

Organic Intermediates and Dyes Institute, 103787, B. Sadovaya 1-4 Moscow, U.S.S.R.

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The spontaneous polarization (P_s) induced by chiral dipolar additives in non-chiral smectic C liquid crystals was investigated. High values of P_s are reported. A special type of smectic polymorphism was observed and novel phases, supposedly, of the anti-ferroelectric type were discovered. Fast linear electro-optical switching with low-temperature mixtures was demonstrated.

1. INTRODUCTION

Ferroelectric liquid crystals[1] are extremely interesting materials not only from the physical point of view, but for practical applications as well. The latter point is due mainly to the fast linear electro-optical response of these materials to low driving voltages.[2] It is also possible to use such materials in pyroelectric,[3] non-linear optical,[4] and some other devices.

Until recently, ferroelectric liquid crystals were rather exotic substances, for they seemed to have to satisfy simultaneously the following set of necessary conditions:

(a) the molecules have to form a lamellar structure;

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(b) the long axes of the molecules (i.e., the director) have to be deviated from the normal to the layer planes by an angle $\theta \neq 0$;

(c) the molecules have to be chiral;

(d) the molecular dipole moment should be directed perpendicular to the long axis of the molecule of the liquid crystal.

However, it has been shown[3,5] that the ferroelectric ordering is completely analogous to that for pure mesogens when the first two and the second two conditions are satisfied separately using an ordinary (non-chiral) tilted smectic, e.g., smectic C or G (S_C, S_G) and a chiral dipolar additive dissolved in it. Such an approach opens the possibility of having a large variety of liquid ferroelectrics, as there are hundreds non-chiral tilted smectics,[6] and, in addition, the chiral additives are allowed to be mesomorphic and non-mesomorphic alike.

The question arises, what magnitude of the spontaneous polarization (P_s) can be induced by a chiral additive in a tilted smectic? In the first experiments,[5] P_s did not exceed $6 \cdot 10^{-11}\ \mathrm{C \cdot cm^{-2}}$. For high additive concentrations we have obtained[3] the value $P_s = 1.6 \cdot 10^{-9}\ \mathrm{C \cdot cm^{-2}}$. In this paper we will present results of a search for some new mixtures with enhanced polarization. Moreover, we will show that inducing the polarization is a useful tool for the investigation of polymorphism and the discovery of new smectic phases. In addition, we evaluate the possibility of the application of smectics with induced polarization in linear electro-optical devices.

2. SUBSTANCES AND TECHNIQUES

Smectic C liquid crystals investigated were: (1) the pentyl- and (2) the 4-hexyloxyphenyl ester of octyloxybenzoic acid (POPEOOBA ($\mathrm{Kr} \underset{37°\mathrm{C}}{\overset{58°}{\rightleftarrows}} S_C \overset{64°\mathrm{C}}{\longleftrightarrow} S_A \overset{66°\mathrm{C}}{\longleftrightarrow} N \overset{85°\mathrm{C}}{\longleftrightarrow} I$) and HOPEOOBA ($\mathrm{Kr} \underset{39°\mathrm{C}}{\overset{55°\mathrm{C}}{\rightleftarrows}} S_C \overset{66°\mathrm{C}}{\longleftrightarrow} N \overset{89°\mathrm{C}}{\longleftrightarrow} I$) resp.), (3) the 4-hexyloxyphenyl ester of decyloxybenzoic acid (HOPEDOBA ($\mathrm{Kr} \underset{44°\mathrm{C}}{\overset{63°\mathrm{C}}{\rightleftarrows}} S_C \overset{77.5°\mathrm{C}}{\longleftrightarrow} S_A \overset{83.5°\mathrm{C}}{\longleftrightarrow} N \overset{89.5°\mathrm{C}}{\longleftrightarrow} I$), (4) the 4-octyloxyphenyl ester of nonylbenzoic acid (OOPENBA ($\mathrm{Kr} \overset{53°\mathrm{C}}{\longrightarrow} N$; $\mathrm{Kr} \overset{37°\mathrm{C}}{\longleftarrow} S_C \overset{48°\mathrm{C}}{\longrightarrow} N$; $N \overset{64°\mathrm{C}}{\longrightarrow} I$), (5) 4-nonyloxybenzylidene-4′-amino-pentylcinnamate† (NOBAPC ($\mathrm{Kr} \overset{77.5°\mathrm{C}}{\longrightarrow} S_B \overset{94°\mathrm{C}}{\longleftrightarrow} S_C \overset{102.5°\mathrm{C}}{\longleftrightarrow} S_A \overset{137.5°\mathrm{C}}{\longleftrightarrow} I$)

† Pentyl 4-(4′-nonyloxybenzylidene)aminocinnamate.

Chiral additives used are:

(1) L-4-hexyloxybenzylidene-4'-amino-2-chloropropylcinnamate† (HOBACPC),

(2) L-4-hexyloxybenzylidene-4'-amino-2-cyanopropylcinnamate‡ (HOBACNCP),

(3) L-4-decyloxybenzylidene-4'-amino-2-cyanopropylcinnamate‡ (DOBACNPC).

The sample preparations and the measurement of the spontaneous polarization were reported earlier.[7] The P_s value was calculated upon integrating the temperature dependence of the pyroelectric coefficient $\gamma \equiv dP_s/dT$, measured from the pyroelectric response of a liquid crystalline layer to a heat pulse of a Nd-glass c.w. laser. The thickness of a layer and the dye concentration providing laser absorption were 1 mm and <0.2 wt%, respectively.

The circuit for the measurement of the electro-optical response is shown in Figure 1. The homogeneous (planar) orientation of smectic samples with an area 0.5 cm^2 was obtained with the help of cooling from the nematic phase. The geometry of the experiment was analogous to that in.[2] The director reorientation was controlled by an external voltage pulse of amplitude $U_{\sqcap} = \pm 50$ V and duration 1 ms. In its final position θ and $-\theta$, the director lay in the electrode plane. The thickness of the cell (d) was fitted in order to satisfy the condition $d \cdot \Delta n = \frac{1}{2}\lambda$ where $\lambda = 6328$ Å (He-Ne laser light) and $\Delta n = n_e - n_o$ is the optical anisotropy at this λ value. In such a case, the optical properties of the liquid crystalline layer are equivalent to those for a uniaxial $\lambda/2$-plate with optical axis along the $-\theta$ or θ directions for each polarity of the applied voltage.

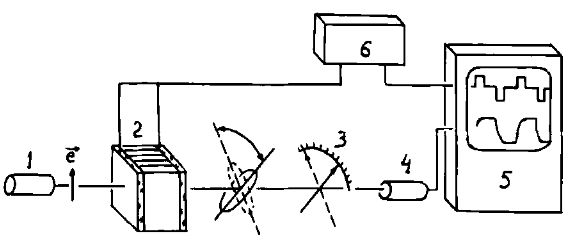

FIGURE 1 Electro-optical arrangement: 1—He-Ne laser; 2—cell, $d = 6\mu$; 3—rotating analyzer with a limb; 4—photomultiplier; 5—double-beam oscilloscope; 6—pulse generator.

† L-2-chloropropyl 4-(4'-hexyloxybenzylidene)aminocinnamate.
‡ An L-2-cyanopropyl 4-(4'-alkyloxybenzylidene)aminocinnamate.

3. RESULTS ON THE SPONTANEOUS POLARIZATION

The temperature behavior of the pyroelectric coefficient characteristic of binary mixtures of smectic C matrices with chiral additives is shown in Figure 2. The values of the spontaneous polarization calculated from the curves $\gamma(T)$ for different mixtures with the same concentration (5 wt%) of an additive are shown in Table I.

From our experiments it follows that the value of P_s induced by chiral additives in smectic C matrices depends upon several factors. It is nearly proportional to the concentration of chiral additive and the molecular tilt angle of the matrix. In addition, P_s increases with increasing rigidity of the molecular skeleton of an additive, and, lastly, approximate equality of the molecular dimensions of a matrix and an additive is favorable for the maximum values of P_s.

Having in mind these four factors, we have in fact managed to obtain a P_s value[8] which exceeds the record value of P_s measured pre-

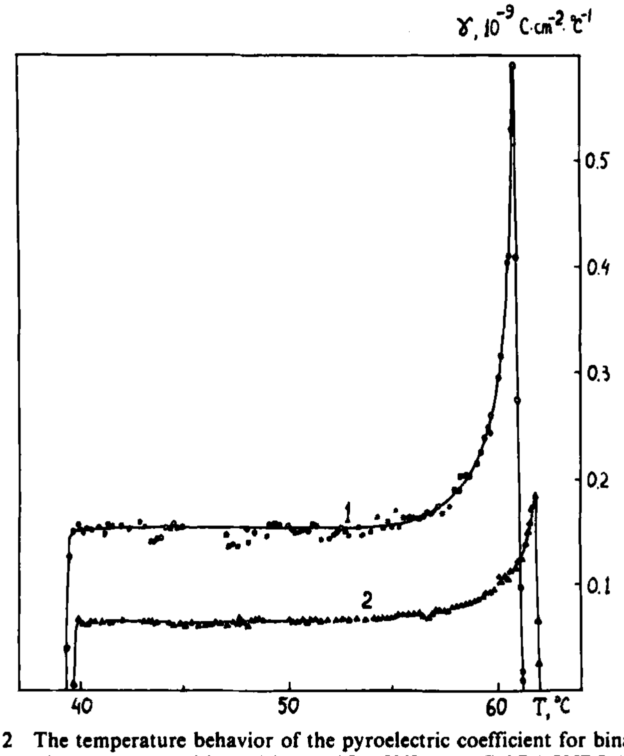

FIGURE 2 The temperature behavior of the pyroelectric coefficient for binary mixtures based on HOPEOOBA with additives HOBACNPC (1), DOBACNPC (2) at the same concentration (5 wt%).

TABLE I

No	Matrix	Additive (Conc., wt%)	T_{CA} °C	$\gamma(T)_{max}$ 10^{-10} C·cm^{-2}·°C^{-1}	P_s 10^{-9} C·cm^{-2}
1	HOPEOOBA	HOBACNPC (5%)	61.0	5.9	3.7 (39.5°C)
2	POPEOOBA	HOBACNPC (5%)	51.8	3.9	1.8 (37.5°C)
3	HOPEOOBA	DOBACNPC (5%)	62.0	1.9	1.6 (39.7°C)
4	HOPEDOBA	HOBACNPC (5%)	64.7	1.9	1.25 (41.6°C)
5	HOPEDOBA	DOBACNPC (5%)	64.8	0.8	0.8 (41.5°C)

viously for the pure chiral smectic C* phase of HOBACPC[3] and which exceeds the values in Table I by an order of magnitude.

4. SMECTIC POLYMORPHISM AND ANTI-FERROELECTRIC PHASES

For symmetry reasons,[1] spontaneous polarization occurs only in tilted smectic phases. Therefore, its appearance can be used for the identification of the molecular tilt in smectic layers. Here, we would like to demonstrate a very intriguing example of smectic polymorphism for mixtures of NOBAPC with different chiral additives. According to Demus *et al.*[6] the smectic C phase of NOBAPC changes to the orthogonal smectic B phase at temperatures decreasing below $t = 94.5$°C. Doping NOBAPC with chiral additives results in the following unusual facts:

(a) With an orienting electric field applied to a sample, the pyroelectric effect is observed not only for the smectic C* phase, but also for the low-temperature phase as well (let us call it the S_2^*-phase). For example, in Figure 3 the second (low-temperature) maxima of $\gamma(T)$ correspond to the transitions to that phase.

The value of the pyroelectric signal is markedly (two orders of magnitude) higher than that associated with the field induced electroclinic effect in the orthogonal smectic A phase and hence, we are dealing with a non-orthogonal phase. For high concentrations of the additives HOBACNPC and HOBACPC we observe not only that S_2^*-phase, but other low-temperature phases (the S_3^* to S_7^* phases in Figure 4); it should be noted, that there is no helical structure for any of the S_3^* to S_7^* phases.

(b) It may be thought, that the chiral additives induce in NOBAPC one of the known ferroelectric tilted phases (e.g., S_G^* or S_H^*). However,

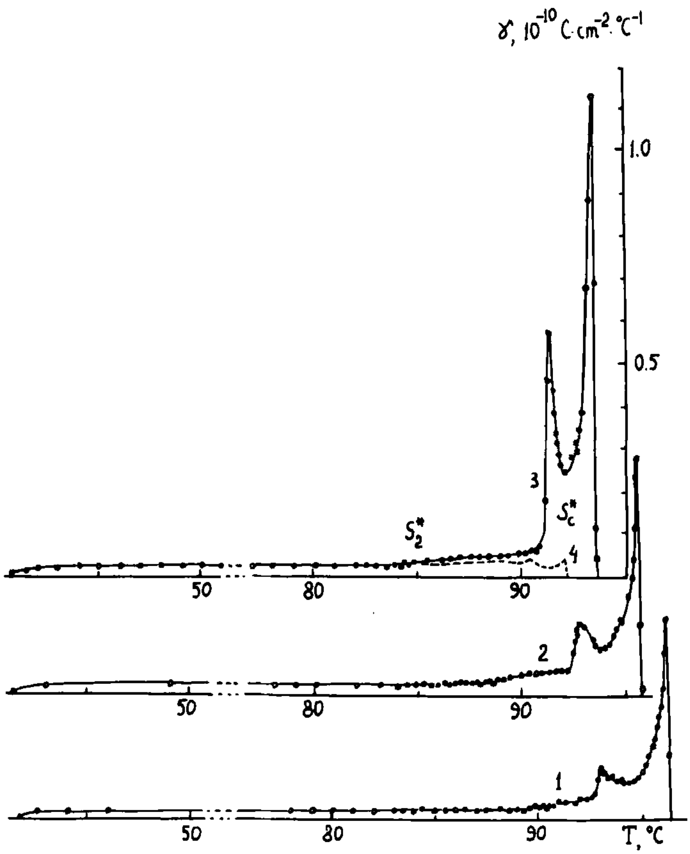

FIGURE 3 The temperature behavior of the pyroelectric coefficient for NOBAPC doped with DOBACNPC (concentration 4.5 (curve 1), 6.8 (curve 2), and 10 (curve 3) (wt%), and HOBACNPC (10 wt%, curve 4).

there are some differences in the field behavior of the S_3^* to S_7^* phases from the ordinary case. Though, the curve for the pyroelectric coefficient against inducing voltage has a saturation typical of liquid crystalline ferroelectrics (Figure 5), for the S_2^* and S_3^* phases the polarization quickly disappears after switching the field off, while for an ordinary S_G^* (or S_H^*) phase it remains for several hours.

(c) The absence of the electro-optical response is characteristic of all the S_2^* to S_7^* phases, even for fields markedly higher than those used in our electro-optical investigations described in the next paragraph. Such a behavior is typical for orthogonal phases.

All the facts mentioned above can be accounted for by assuming that (at least in the cases of the S_2^* and S_3^* phases) we are dealing with true

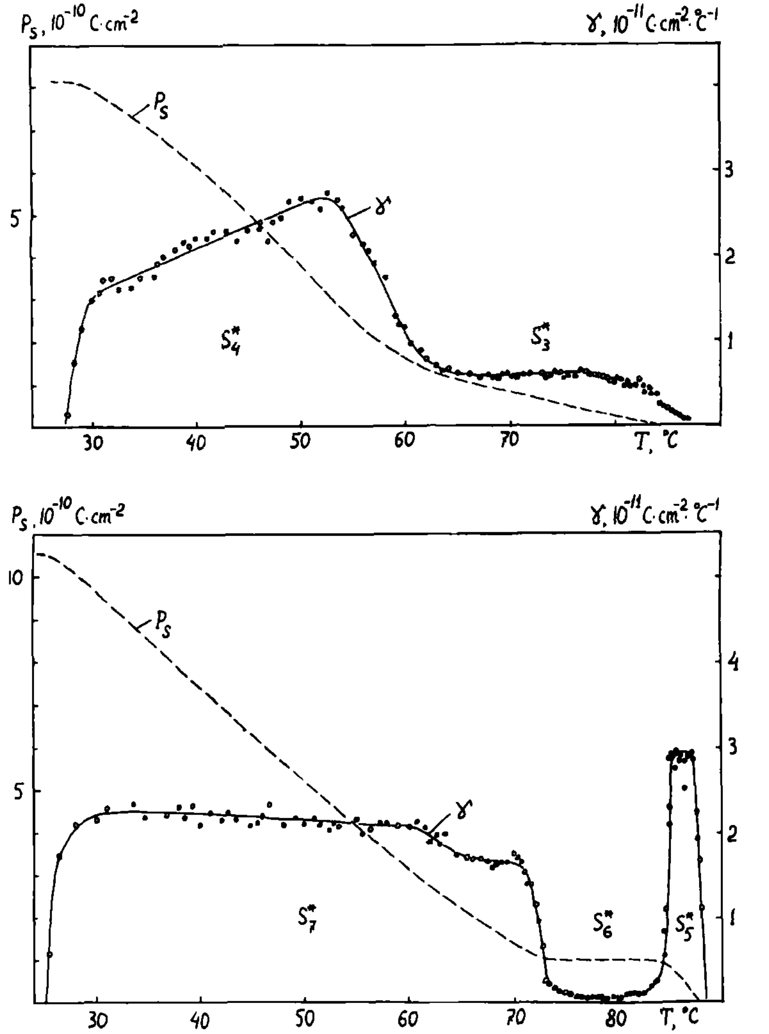

FIGURE 4 Smectic polymorphism in NOBAPC doped with 20 wt% of HOBACNPC (upper curves) and HOBACPC (lower curves). The appearance of new S_3^* to S_7^* phases are easily seen.

(in contrast to Ref. 9) anti-ferroelectric phases. A hypothetical structure is shown in Figure 6. Supposedly, a chiral additive gives rise to the molecular tilt in smectic layers of NOBAPC with angles θ and $-\theta$ alternating from one layer to another (such an alternation could, in principle, exist even before doping in pure smectic C matrix[10]). Then, the overall structure appears to be uniaxial, though spontaneous polarization, being compensated for the whole sample, occurs in each layer.

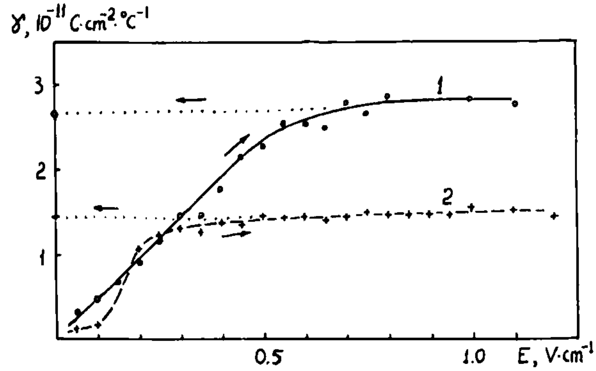

FIGURE 5 The pyroelectric signal *vs.* an inducing electric field in NOBAPC doped with 20 wt% of HOBACPC; curve 1: 86°C, curve 2: 67°C.

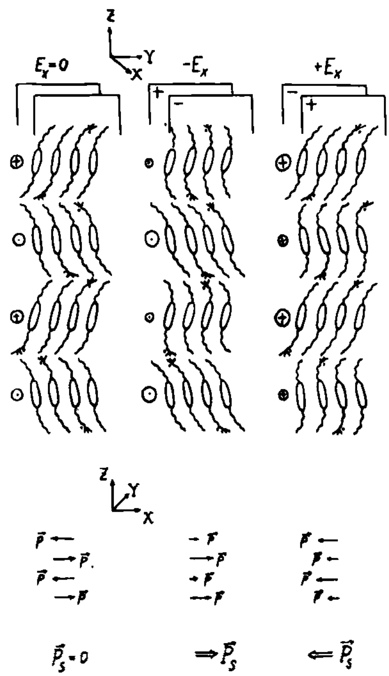

FIGURE 6 A model structure for an antiferroelectric and its field behavior (*Z* is the normal to smectic layers).

The direction of the P_s-vector is shown in Figure 6 for $E_x = 0$. The external field causes the reorientation of the unfavorably directed P_s-vectors along E_x and, as a result, the net sample polarization $\langle P_s \rangle$ appears which tends to the saturation value $\langle P_s \rangle = P_s$ with increasing field. After switching the field off in the S_2^* and S_3^* phases, the net polarization relaxes. The net polarization remains in the S_4^* to S_7^* phases, probably because of the large viscosity of these phases. The absence of the electro-optical response can be accounted for either by a small value of the tilt angle θ, or by the reorientation of only alkyl tails which are responsible for the P_s value in a layer. The model presented is analogous to a classical anti-ferroelectric.

5. THE ELECTRO-OPTICAL BEHAVIOR

Tilted smectics with spontaneous polarization induced by chiral additives seem to be very interesting materials for fast electro-optical devices. We have measured the switching times (t_0) for the director reorientation, by an electric field of changing polarity, from the $-\theta$ to $+\theta$ position. The parameters of the polarization ellipse for a light beam transmitted through an electro-optical cell under on and off conditions were also measured. Using these data and taking into account the angles between the director and the analyzer axis, we can calculate the molecular tilt angle θ for various temperatures.[11]

The temperature behavior of t_0 for two mixtures with induced polarization is shown in Figure 7 (the t_0-values were taken on the 0.9-level from the leading edge of the electro-optical response oscillogram). In Figures 7 and 8a it is easily seen that the response times are inversely proportional to the polarization. The form of the $t_0(T)$ curves approximately corresponds to the temperature behavior of the dynamic viscosity $\gamma_1(T)$. Indeed, let us substitute the linear term P_sE for the quadratic term $\epsilon_a \cdot E^2$ in the formula for the field-induced director reorientation in nematic liquid crystals, $\tau = \gamma_1/\epsilon_a \cdot E^2$. Then, assuming a small director reorientation by angle ξ, we have the corresponding time for the smectic C* phase:

$$t_\xi \sim \frac{\xi \cdot \gamma_1}{P_s \cdot E} = \frac{\xi \cdot \gamma_1}{P_s^\theta \cdot \theta \cdot E}$$

where P_s^θ is the P_s-value reduced to a unitary tilt angle. In fact, even the 0.9-level of the leading edge of an oscillogram corresponds to a rela-

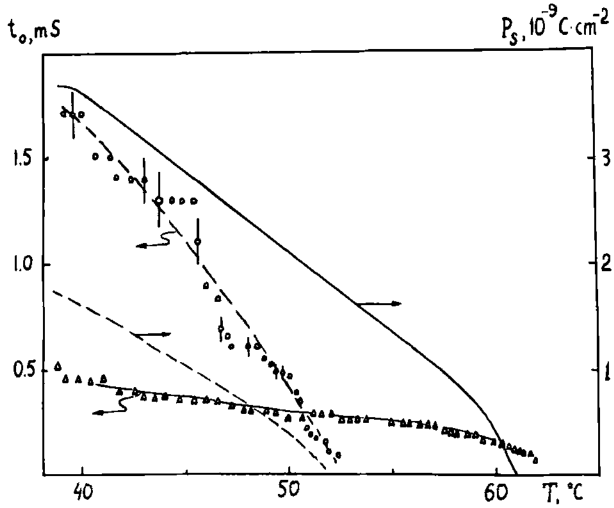

FIGURE 7 Times for electro-optical response and the spontaneous polarization *vs.* temperature for POPEOOBA (solid curves) and HOPEOOBA (dashed curves) doped with HOBACNPC (5 wt%).

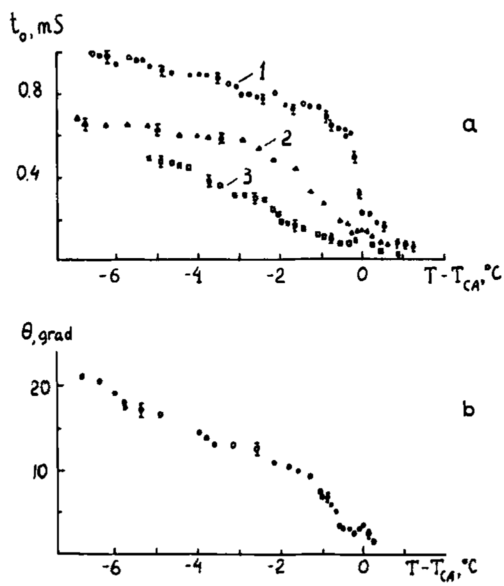

FIGURE 8 (a) Response times of OOPENBA doped with HOBACNPC for concentrations 3 (1), 5 (2), and 6 (3) wt%, (b) molecular tilt angle *vs.* temperature for OOPENBA.

tively small $\xi:\xi_{0.9} \simeq 13.3° = 0.59\theta$ for $\theta = 22.5°$.[11] Considering the simplified movement of the director in the layer plane we have

$$t_0 = t(\xi_{0.9}) \simeq \frac{0.59 \cdot \theta \cdot \gamma_1}{P_s^\theta \cdot \theta \cdot E} \sim \frac{\gamma_1}{P_s^\theta \cdot E}$$

i.e., $t_0(T) \sim \gamma_1(T)$, since P_s^θ can be considered to be temperature independent.

The electro-optical response above the smectic C*–smectic A transition seen in Figure 8a is due to the electroclinic effect, and the small maxima of t_0 and θ (Figure 8b) just at the transition point are caused by an increase in the molecular relaxation time,[12,13] and susceptibility,[12] respectively, at the second order phase transition.

According to Figure 8b the tilt angle in OOPENBA tends to $\theta > 20°$ at $T_{CA} - T > 5°C$. The depth of light modulation in this case reaches 95% for a cell thickness $d = 6\ \mu$. This figure agrees with the optical transmission of the cell $T = 95\%$ in the off state. The experimental values of the modulation depth and contrast are in accord with those calculated for uniaxial $\lambda/2$-plate for $\Delta n(\lambda = 0.63\ \mu) = 0.14$, with two possible directions ($-\theta$ and $+\theta$, resp.) of the optical axis.

Let us note that the presence of the spontaneous polarization in the smectic C* phase results in a two orders of magnitude faster linear electro-optical response than that for its quadratic counterpart in the nonchiral smectic C.[14]

6. CONCLUSION

It has been shown that inducing spontaneous polarization in tilted smectic C phases by chiral additives enables us

(a) to have high values of the polarization, P_s exceeding that for known pure chiral ferroelectric phases,

(b) to reveal novel, supposedly, anti-ferroelectric phases,

(c) to achieve high speeds of electro-optical response at rather low temperatures.

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