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The effect of pretransitional phenomena on the characteristics of induced ferroelectric liquid-crystalline systems

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The effect of different types of phase transition on the temperature dependence of the helical pitch and the spontaneous polarization is investigated for mixtures of smectic C liquid crystals and a chiral dopant, based on salicylidenanylene derivatives. The observed phenomena are explained by assuming that the temperature dependence of the pitch is connected with the growth of the disclination loops near the second order phase transition, and that the subsurface electric field can unwind the helix in chiral substances with strong piezoelectric effects which occur for large polarization values.

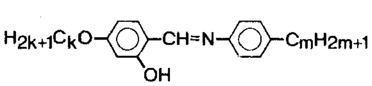
1. Introduction

It is well known that among a variety of smectic liquid crystals chiral smectics are distinguished by possible ferroelectric ordering [1]. These liquids crystals are of great practical interest because they possess the shortest switching times among liquid crystals [2]. One source of new ferroelectric liquid-crystalline materials is to induce a spiral twisting in smectics C by the addition of chiral dopants with transverse dipole moments [3–5], thus increasing the possibilities for the creation of ferroelectric systems and the variation of their properties. However, the properties of such mixtures have not been sufficiently well investigated despite the existance of a large number of induced ferroelectric systems. In particular, the effect of pretransitional phenomena on the properties of such ferroelectric systems (on spontaneous polarization, for example) has been studied little, if at all.

Here the results of our investigation of the effect of different phase transitions on the temperature dependence of the chiral pitch and their joint effect on the spontaneous polarization in induced ferroelectric liquid-crystalline systems are presented.

2. Materials

The salicylidenanylenes were used as smectic C solvents, they possess a variety of phase transitions: smectic C–nematic, smectic C–smectic A and smectic C–isotropic. Their structural formula is



traditionally designated as (k·0·m). Among them are:

1. 10·0·4

$$C \xleftrightarrow{45^\circ C} S_C \xleftrightarrow{76\cdot 8^\circ C} N \xleftrightarrow{88\cdot 8^\circ C} I$$

2. 6·0·6

$$C \xleftrightarrow{38\cdot 9^\circ C} S_C \xleftrightarrow{80\cdot 4^\circ C} N \xleftrightarrow{93\cdot 2^\circ C} I$$

3. 8·0·12

$$C \xleftrightarrow{50\cdot 5^\circ C} S_C \xleftrightarrow{101^\circ C} I$$

4. 5·0·5

$$C \xleftrightarrow{41\cdot 8^\circ C} S_C \xleftrightarrow{60\cdot 5^\circ C} N \xleftrightarrow{90^\circ C} I$$

5. Mixture (4·0·8 + 7·0·8)

$$C \xleftrightarrow{26\cdot 1^\circ C} S_C \xleftrightarrow{52\cdot 2^\circ C} N \xleftrightarrow{75\cdot 7^\circ C} I$$

6. 10·0·7

$$C \xleftrightarrow{41^\circ C} S_C \xleftrightarrow{100\cdot 6^\circ C} S_A \xleftrightarrow{101\cdot 40^\circ C} I$$

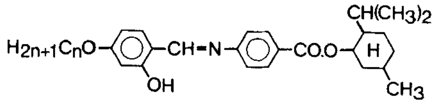
7. 6·0·8

$$C \xleftrightarrow{41\cdot 7^\circ C} S_C \xleftrightarrow{91\cdot 3^\circ C} S_A \xleftrightarrow{92\cdot 9^\circ C} N \xleftrightarrow{95\cdot 1^\circ C} I$$

8. 8·0·10

$$C \xleftrightarrow{52\cdot 2^\circ C} S_C \xleftrightarrow{100\cdot 9^\circ C} I$$

As twisting dopants the non-mesogenic alkoxysalicylidenanylene derivatives of *l*-menthol ($C_{10}H_{19}$) with n = 1–8 were used:



The choice of these compounds follows from their high solubility in the smectic solvents used. As a result we can obtain solutions of high concentration without significant narrowing of the temperature range of the smectic phases. It has been shown [5, 6] that it is possible to choose the compounds (as a matrix and as a dopent) with a similar chemical structure to create the induced ferroelectric system.

3. Measurement technique

The pitch of the helix p was determined by light diffraction on the natural overmolecular spatial lattice in the focal conic texture of a chiral smectic by the technique proposed by Kahn [7]. The pitch p was also determined by measuring the distance between neighbouring periodic strips in the mono-domain part of a sample by observation through the crossed polarizers of a microscope [8].

The spontaneous polarization P_S measurements were made according to the oscillograms of the polarization reversal in the alternating electrical field (by a modified Sawyer–Tower method [9, 10]) at frequencies of 20–200 Hz. The homeotropic alignment of the samples was microscopically controlled by observation of the cyclic reorientation of the samples in an electric field. The cells were prepared by coating their surfaces with a thin layer of polyvinyl alcohol and by rubbing. However, perfect director orientation could not be achieved in this way; the samples contained some focal conic domains. Nevertheless, as our investigations show, such imperfections had no essential influence on the spontaneous polarization values.

4. Experimental results

Investigations of the induced ferroelectric liquid crystalline systems were carried out in two ways: (*a*) the same optically active dopant was introduced into different solvents, and (*b*) all homologues of the optically active dopant were introduced into the same smectic solvent (see tables 1 and 2). Our observations allow us to draw the following conclusions.

Table 1. Characteristics of the mixtures 90 per cent 8·0·12 and 10 per cent alkoxysalicylidenanylene derivative of *l*-menthol.

Optically active homologue number	Value of spontaneous polarization, P_S/nC cm^{-2}	Behaviour of the pitch–temeprature dependence
1	1·36	Non-monotonic
2	0·35	Non-monotonic
3	0·75	Non-monotonic
4	1·80	Non-monotonic
5	2·04	Monotonic
6	3·0	Monotonic
7	2·0	Monotonic
8	0·37	Non-monotonic

Table 2. Characteristics of mixtures with 20 per cent heptyloxysalicylidenanylene derivative of *l*-menthol.

Smectic solvent	Value of spontaneous polarization, P_S/nC cm^{-2}	Information about the smectic A phase	Behaviour of the pitch–temperature dependence
10·0·4	2·5	Absent	Monotonic
5·0·5	30·0	Induced	Monotonic
Mixture (4·0·7 + 7·0·8)	8·0	Induced	Non-monotonic
10·0·17	0·1	Present	Non-monotonic
6·0·8	10·0	Present	Non-monotonic
8·0·10	6·0	Absent	Monotonic

4.1. *The temperature dependence of the helical pitch*

Two types of temperature dependence were observed in the chiral induced smectics investigated, these dependences differed by the shape of curves. The first type of function, $p(T)$, is shown by curve *a* of figure 1: the non-monotonic behaviour with a pronounced maximum is observed in the 10°C temperature range below the transition with decreasing temperature. The second type of function, $p(T)$, is represented by curve *b* of figure 1: the monotonic decrease of the pitch with decreasing temperature

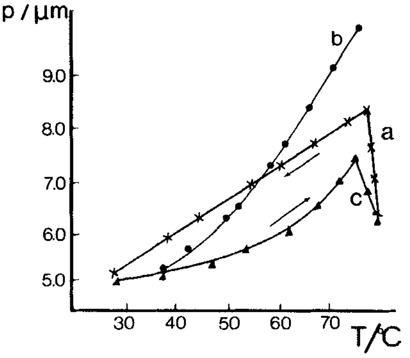


Figure 1. $p(T)$ dependences for mixtures 90 per cent 8·0·12 and 10 per cent alkoxysalicylidenanylene derivative of *l*-menthol: (*a*) $n = 2$ (cooling), (*b*) $n = 5$ (cooling) and (*c*) $n = 2$ (heating).

is observed over the whole chiral smectic C range. It was found that the monotonic dependence $p(T)$ is observed if the first order phase transition, chiral smectic C–chiral nematic, occurs in the mixture. The non-monotonic function $p(T)$ is observed if the second order phase transition, chiral smectic C–smectic A, occurs, the smectic A phase also being induced by doping with an optically active compound. However, the presence of the phase transition chiral smectic C–smectic A does not obviously correspond to the non-monotonic temperature dependence of the pitch. For example, any homologue from the alkoxysalicylindenanylene series induces the smectic A phase in the solvent 8·0·12, the function $p(T)$ is non-monotonic on doping with homologues with $n = 1, 2, 3, 4$ or 8, but is monotonic on doping with homologues with $n = 5$, 6 or 7 [11].

4.2. *Measurements of the spontaneous polarization*

The typical temperature dependence of the magnitude of the spontaneous polarization is shown in figure 2: the magnitude P_S is saturated in the 10°C temperature range below the transition with decreasing temperature. The data in tables 1 and 2 represent the P_S saturation value. It is seen from the results in table 2 that the

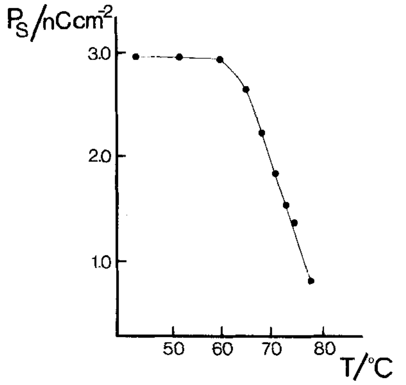


Figure 2. $P_S(T)$ dependence for mixture 90 per cent 8·0·12 and 10 per cent alkoxysalicylidenanylene derivative of *l*-menthol ($n = 6$).

spontaneous polarization of the system depends on the ratio of the molecular length of the solvent to the molecular length of the chiral dopant. The P_S value increases when these lengths are equal.

Table 2 shows that large values of the spontaneous polarization correspond to systems with an induced smectic A phase. However, the existence of the phase transition smectic C–smectic A in the solvent has no influence on the P_S value. We can conclude this by comparing data obtained for solvents 10·0·4. and 10·0·7.

We can also see the correlation between the temperature dependence of the pitch and the magnitude of the spontaneous polarization. For example, in systems with the solvent 8·10·12 (see table 1) the increase of P_S is accompanied by the appearance of the monotonic dependence $p(T)$. Thus, we expect the systems with the induced smectic A phase and the monotonous dependence $p(T)$ to be characterized by the largest values of the spontaneous polarization. Indeed, the maximum P_S values for the systems investigated are obtained for the solvents 5·0·5 and 6·0·6, where the induction of the smectic A and the monotonic function $p(T)$ are observed by doping with an optically active compound.

5. Theoretical discussion

We can draw theoretical conclusions about the character of the temperature dependences mentioned previously on the basis of the following qualitative notions related to a competition between the unwinding effect of some subsurface electric field and the twisting effect of some disclination system which is energetically favourable in twisted structures [12]. It is assumed that there is an electric field, $\mathbf{E}_S$, near the surface. This field is due to the existence, for example, of a double electrical layer (of thickness r_D) near the smectic surface. The existence of some system of orientational defects (disclinations) was observed experimentally [13]. The number of linear disclinations (or disclination loops of a large size) per unit length n can be estimated from

$$n = n_0 \exp(-p/\xi),$$

where n_0 is a phenomenological parameter, $\xi \approx (T/K\theta^2)$, K being the elastic constant in the phenomenological expression for the free energy of a smectic C related to the azimuthal director deviations [14] and the quantity $Tp/\xi \approx K\theta^2 p$ is a characteristic potential barrier which must be overcome to widen the disclination loop. The presence of such defects gives the energy gain which has the order of magnitude

$$-K\theta^2 n/p = -K\theta^2 (n_0/p) \exp(-p/\xi).$$

The electric field $\mathbf{E}_S$ causes the unwinding of the polarization helix. The larger the thickness r_D is, the stronger the effect: the corresponding critical value of the field is $E_{SC} \approx (E_C/\Delta)$, where $\Delta = (r_D/d)$, d being the thickness of the smectic film and $E_C \approx (K\theta/\mu p_0^2)$ [15], where μ is the piezoelectric coefficient and p_0 is the undisturbed value of the pitch (or the value of the pitch far from the phase transition T_C). We can imagine the formation of a helix as the appearance of walls (of thickness $\eta \approx (K\theta/\mu E_S)^{1/2}$) in which the polarization orientation changes sharply. The effect is similar to helix formation in cholesterics [12, 15]. At $E_S < E_{SC}$ the number of such walls becomes large. The number of walls per unit length is of the order of p^{-1}, the corresponding energy gain is a value of order $r_D \mu(E_S - E_{SC})(p_0/p)$. The loss in energy conditioned by the mutual repulsion of the walls is proportional to $\frac{1}{2} dK\theta^2 p^{-2} \exp(-p/\eta)$ since the wall interactions decrease rapidly as a function of the interwall distance, p, with a correlation length η [12].

The total free energy per unit length can then be written as

$$f = K\theta^2\left[\frac{\tau}{p} + \frac{1}{2p^2}\exp\left(-\frac{p}{\eta}\right) - \frac{n_0}{p}\exp\left(-\frac{p}{\xi}\right)\right], \tag{1}$$

$$\tau = \frac{E_S - E_{SC}}{p_0 E_{SC}} = \frac{1}{p_0\theta}\left(\frac{\mu E_S p_0^2 \Delta}{K} - \theta\right).$$

The value of the pitch is found from the equation $\partial f/\partial p = 0$. If the field, E_S, and defects are absent (i.e. $\eta \to \infty$ and $n_0 \to 0$) the minimization of the free energy gives the expected result $p = p_0$. It follows from equation (1) that in the presence of defects the helix must be unwound (i.e. $p \to \infty$), if $\tau \geqslant n_0$, i.e. in a stronger field. The equation $\tau \approx n_0$ determines the temperature T^* above which the helix is unwound. The tilt angle

$$\theta^* \approx \frac{\mu E_S p_0^2 \Delta}{K(1 + n_0 p_0)}$$

corresponds to temperature T^*. For a second order phase transition we have the limits $T^* \to T_c$ and $\theta^* \to 0$, if $E_S\Delta \to 0$.

For a first order ferroelectric phase transition, for example for the transition chiral smectic C–cholesteric, the T^* point should correspond to the ratio

$$\theta^*\psi^* = \frac{\mu' E_S p_0^2 \Delta}{K'(1 + n_0 p_0)},$$

where ψ is the smectic order parameter, $\psi^* = \psi(T^*)$, $\mu = \mu'\psi$ and $K = K'\psi^2$. If the jumps θ_c and ψ_c in the magnitudes of θ and ψ at T_c are such that the inequality

$$\theta_c\psi_c > \theta^*\psi^* \tag{2}$$

is fulfilled beforehand, then the point T^* is absent at temperatures $T < T_c$ and we find the pitch as

$$p \approx p_0\left(1 + n_0 p_0 - \frac{E_S}{E_{SC}}\right)^{-1}. \tag{3}$$

Equation (3) shows that, in the presence of the inequality (2), the pitch of the helix must increase monotonically at all temperatures right up to T_C. If the temperature T^* is slightly larger than T_C, i.e. the values $\theta^*\psi^*$ and $\theta_c\psi_c$ are almost equal, then the increase of p near the phase transition must be sharp:

$$p \approx \eta^* \ln\frac{1}{\theta\psi - \theta^*\psi^*}, \tag{4}$$

where $\eta^* = \eta(T^*)$. We have observed experimentally a similar monotonic temperature behaviour of the pitch for several materials which have a first order ferroelectric phase transition. An example of such behaviour is shown on figure 1 (curve *b*).

For a second order phase transition the minimization of the free energy, f, with respect to the pitch, p, results in expressions for p which are similar to those in equations (3) and (4) in different temperature intervals:

$$p \approx \begin{cases} p_0\left(1 + n_0 p_0 - \dfrac{\mu E_S p_0^2 \Delta}{K\theta}\right)^{-1}, & \text{at } T < T_m(\theta > \theta_m), \\ \eta \ln\dfrac{1}{2(n_0 - \tau)}, & \text{at } T_m < T < T^*(\theta_m > \theta > \theta^*). \end{cases} \tag{5}$$

These expressions show that below the temperature T_m determined by the equation $p \approx \eta\, \theta(T_m)$ is

$$\theta_m = \theta^*/\Delta(1 + n_0 p_0),$$

the pitch increases smoothly with increasing temperature and reaches a maximum value at $T = T_m$ (see figure 3). At $T > T_m$ the pitch decreases according to the law $p \approx \eta \approx \theta^{1/2}$ with the temperature rise practically up to T^*, but in the narrow range near T^* the pitch increases sharply according to the law in equation (4) (see figure 3). Such behaviour of the pitch must take place if $\theta_m > \theta^*$. The T_m and T^* points can be very close to T_c if $n_0 p_0 \gg 1$ and $\Delta \ll 1$. The equality $\theta^* \approx \theta_m$ is fulfilled if $n_0 p_0 \Delta \approx 1$, in this case the local minimum in the dependence on $p(T)$ must disappear: the pitch increases monotonically with increasing temperature up to T^*, at which p jumps discontinuously to infinity. The latter case is possible if the thickness r_D is sufficiently large, r_D being dependent on the concentration of free charges and the dielectric permeability. We expect that this situation is possible in materials with a strong piezoelectric coupling, μ.

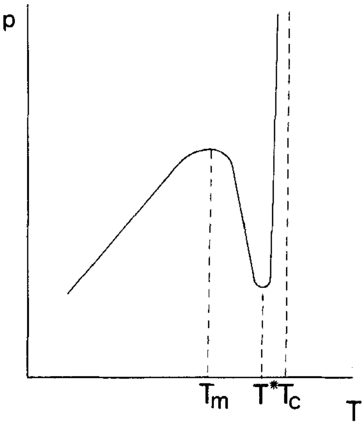


Figure 3. $p(T)$ dependence, obtained from the theoretical model.

The characteristic feature of the temperature dependence, mentioned previously, is the existence of a narrow temperature range near T_c (the interval T_c–T^*) in which the helix is unwound and, correspondingly, the defects disappear. Details of the temperature dependence in the interval T_c–T_m are determined by the parameters n_0, E_S and Δ, which are characteristics of a defect system and of a subsurface field. Unfortunately, at present no direct experimental data on these parameters are available. However, we can draw some conclusions about them from the observed $p(T)$ function. Our experiments show that the difference $T_c - T^*$ is smaller than 1 K, the difference $T_c - T_m$ is of the order of several degrees. In the interval T^*–T_c the helicoidal structure of the chiral smectic C phase was not observed, nor was the texture of the smectic A phase observed. In addition the calorimetric measurements had shown that the transition temperature T_c differs from the optically observed T^* and the difference is about 1 K.

The definition of θ^* and θ_m shows that the ratio

$$\left(\frac{\theta^*}{\theta}\right)^2 = \frac{T_c - T^*}{T_c - T_m} = \Delta^2(1 + n_0 p_0)^2$$

in our experiments is about 1/5. The n_0 value cannot exceed, from the physical point of view, the inverse thickness of the wall η^{*-1}, where $\eta^* \approx \Delta^{1/2}(1 + n_0p_0)^{-1/2}p_0$. Thus, at large values of n_0p_0 we can conclude that $n_0 < (p_0\Delta)^{-1}$ and $p(T^*) \approx \eta^* \approx (p_0\Delta/n_0)^{1/2} > p_0\Delta$, in the limit $n_0 \approx (p_0\Delta)^{-1}$ we have $\theta^* \approx \theta_m$, the local minimum of the function $p(T)$ being absent. At $n_0p_0 < 1$ we have $(\theta^*/\theta_m) \approx \Delta$, $p(T^*) \approx \Delta^{1/2}p_0$, $p(T_m) \approx p_0$, i.e. in this case we must observe the pronounced minimum in the $p(T)$ dependence that has been observed for certain materials. In our experiments (see figure 1, curves *a* and *c*) the minimum was not pronounced, thus we can conclude that $n_0p_0 > 1$, i.e. $p_0^{-1} < n_0 < (p_0\Delta)^{-1}$, in fact we have $(n_0p_0\Delta)^2 \approx 1/5$. We can speculate that $\Delta < 10^{-2}$, then $n_0 > 10^2p_0^{-1}$; at $\mu \approx 10^{-4}\,\mathrm{C\,m^{-2}}$, $K \approx 10^{-10}\,\mathrm{N}$, $p_0 \approx 5 \times 10^{-6}\,\mathrm{m}$, $\theta^* \approx 10^{-1}$ and we can estimate the field $E_S > 10^7\,\mathrm{V\,m^{-1}}$.

The hysterisis-like behaviour of the pitch due to defects should also be mentioned. The function $n(T)$ increases monotonically with increasing temperature, if the pitch changes slowly right up to the jump. As the temperature decreases from T_c, the jump-like appearance of defects occurs at T^*. Below T^* the defects cannot disappear if they are anchored to the boundaries of a sample. Therefore, generally, the reverse change of $p(T)$ must differ from the normal one. We expect an annealing of some defects at sufficiently high temperatures. In the last case the number of loops can be smaller and correspondingly the pitch can be larger on cooling than on heating. Probably this is the reason for curves *a* and *c* on figure 1, where we can see the hysterisis-like behaviour of the pitch.

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