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Tilt angles and spontaneous polarization in induced S_c^* phases

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Induced S_c^* phases can be obtained by doping several non-chiral S_c-host phases (H) with chiral polar compounds (G). The tilt angle θ of such systems and their spontaneous polarization P_s were measured as a function of the mole fraction, x_G, of the optically active compounds.

In the S_c^* phase of a pure compound P_s and θ are expected to be closely related to each other. Consequently, a material constant P_0 can be defined as $P_s = P_0 \sin\theta$. In induced S_c^*-phases P_s depends on the concentration of the optically active guest compound. In several cases $P_s(x_G)$ deviates considerably from linearity. To investigate the origin of this non-linearity we measured θ and P_s as function of x_G. The question arises if P_0 depends on x_G and/or on the molecular structure of G and H: $P_s(x_G) = P_0(x_G)\sin\theta(x_G)$. Comparing the results of $P_0(x_G)$ for mixed systems with the same optically active dopant G we can make the following statements.

(*a*) The polarization is directly proportional to $\sin\theta$.
(*b*) $P_0(x_G)$ is linear within experimental error in the measured concentration range referred to a temperature 5 K below the transition S_c^* to chol or S_A.
(*c*) $P_0(x_G)$ only depends on the molecular structure of the optically active guest compound, but there is no dependence on the structure of the host phase.

As a result we can define a material constant, the polarization power ∂_p:

$$\partial_p := \left(\frac{\partial P_0(x_G)}{\partial x_G}\right)_{\Delta T},$$

which is an inherent material constant for a given polar chiral dopant.

1. Introduction

As is well known, tilted smectic phases composed of chiral molecules with transverse dipole moments exhibit ferroelectric properties [1]. In 1980 it was shown by Kuczynski and Stegemeyer that it is possible to induce S_c^* phases exhibiting ferroelectric properties by doping a non-chiral S_c host phase with a chiral polar compound [2].

In an S_c^* phase the polarization vector $\mathbf{P}_s$ stands perpendicular on the tilt plane defined by the layer normal $\mathbf{z}$ and the director $\mathbf{n}$ [3]

$$\mathbf{P}_s = P_0(\mathbf{z} \times \mathbf{n}). \tag{1}$$

The tilt angle of an S_c^* phase is the angle between the layer normal $\mathbf{z}$ and the director $\mathbf{n}$. So the absolute value of $\mathbf{P}_s$ is directly proportional to $\sin\theta$ with the material dependent coefficient P_0

$$P_s = P_0 \sin\theta. \tag{2}$$

Simple theories for S_c^* phases predict a strict proportionality between P_s and $\sin\theta$. It has been shown experimentally and theoretically that this is not correct [4, 5]. At temperatures near the transition S_c^* to S_A, P_0 is strongly dependent on temperature but at temperatures sufficiently far away from the phase transition a nearly constant value of $P_s/\sin\theta$ is observed.

However, in a pure substance P_0 is a material constant depending on the anisotropic distribution of the molecular dipoles and on steric effects.

In induced S_c^* phases P_s and θ depend strongly on the concentration of the optically active compound. This dependence must be considered in equations (1) and (2)

$$P_s(x_G) = P_0(x_G)\sin[\theta(x_G)], \tag{3}$$

where x_G is the mole fraction of the optically active compound.

Because the spontaneous polarization is responsible for the strong coupling of the tilt angle to an electric field, it is interesting to investigate the behaviour of P_s and θ in mixed systems composed of chiral and non-chiral S_c phases (see, for example [6–11]).

In this paper we present measurements on P_s and θ in mixed systems which exhibit an S_c^* phase over the whole concentration range and consist of compounds with non-chiral S_c phases and chiral S_c phases. In each mixed system we measured θ and P_s for several mixtures with different concentrations of the optically active compound.

2. Experimental

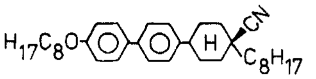
The structure and phase sequence of the compounds under investigation are listed in table 1. The chiral substances and the non-chiral S_c-phase N808 were made available by courtesy of E. Merck, Darmstadt.

The S_c phase 8008 was synthesized after Schubert and Weissflog [12]. The purity of each compound was checked by gas chromatography, by thin layer chromatography and by comparing the transition temperature with data from the literature.

The transition temperatures of each mixture were determined by differential scanning calorimetry (Perkin Elmer DSC 2) and thermomicroscopy (Leitz Laborlux

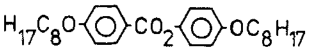
Table 1. Molecular structure, phase sequence and transition temperatures of the compounds investigated.

N808



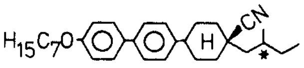
C (43) S_X (52) S_I 81 S_c 118 S_A 150 N 150·3 I

8008



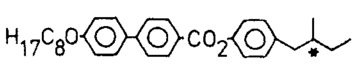
C 62·4 S_c 72·7 N 89·7 I

IS1912



C 66 S_c^* 107 S_A 112 CH 131 I

CE8



C 48 S_X^* 61 S_G^* 67 S_I^* 70 S_c^* 87 S_A 135 CH 140 I

12 polarizing microscope with Mettler FP 5/52 heating stage). The phase sequence was confirmed by optical investigations.

For the tilt and polarization measurements the probe was placed between two conducting polyimid coated glass plates. Sample orientation was achieved by slowly cooling (0·2 °C min^{-1}) from the isotropic phase to the S_c^* phase in an applied electric field.

The polarization was measured after Diamant *et al.* [13]. The cell thickness varied from 16 to 60 μm, depending on the pitch and the probe resistance [14].

The tilt angle θ was derived from the switching angle of the optical director measured in the same cell as was used for the polarization measurements.

3. Results

The C smectogenic compounds 8008 and N808 were mixed with the chiral compounds IS1912 and CE8. As seen in figures 1 (*b*) and 1 (*d*) the phase sequence of the systems containing N808 is S_c^*, S_A, chol and iso in the whole concentration range. A different behaviour is observed in the systems containing 8008 (figures 1 (*a*) and 1 (*c*)). In the systems with 8008 at higher concentrations of the chiral compound an S_A phase is inserted between the S_c^* phase and the cholesteric phase. In the systems with CE8 S_I^* and S_G^* phases were also observed at lower temperatures. If the concentration of the optically active compound exceeds a mole fraction of $x_G = 0{\cdot}6$ there are in addition up to three blue phases between the cholesteric and isotropic phase (not shown in the phase diagrams).

The polarization and tilt angle of each mixture were measured as a function of temperature. In figures 2 and 3, showing plots of P_s or θ versus x_G, the polarization or tilt angle is referred to a temperature 5 K below the transition $S_c^* \rightarrow$ chol or $S_c^* \rightarrow S_A$.

The mixed system 8008/CE8 shows a negative deviation from linearity in $P_s(x_G)$ (figure 2 (*a*)). At mole concentrations below $x_G = 0{\cdot}2$ it was not possible to measure the spontaneous polarization. The tilt angle plotted against x_G also shows a negative deviation from linearity, especially at low concentrations (figure 3 (*a*)).

At concentrations $x_{CE8} > 0{\cdot}2$ the mixed system N808/CE8 behaves similarly to the 8008/CE8 system, as shown by the plots of P_s against x_G and θ against x_G in figures 2 (*a*) and 3 (*a*). In this system it was also not possible to measure the spontaneous polarization at mole fractions below 0·2.

The mixed system 8008/IS1912 shows a positive deviation from linearity, and in addition the plot of P_s against x_G runs through a maximum (figure 2 (*b*)). The tilt angle θ plotted against x_G also exhibits a strong positive deviation and runs through a flat maximum (figure 3 (*b*)).

The behaviour of the mixed system N808/IS1912 is quite different. Both the polarization and the tilt angle show a negative deviation from linearity as a function of x_G (figures 2 (*b*) and 3 (*b*)).

Because of the corresponding concentration behaviour of P_s and θ, we plotted the ratio of $P_s(x_G)/\sin[\theta(x_G)] = P_0(x_G)$ according to equation (3) against x_G and obtained two interesting results (figure 4).

(*a*) For a given optically active compound $P_0(x_G)$ is a universal linear function within experimental error.

(*b*) This function does not depend on the structure or phase sequence of the non-chiral S_c phase.

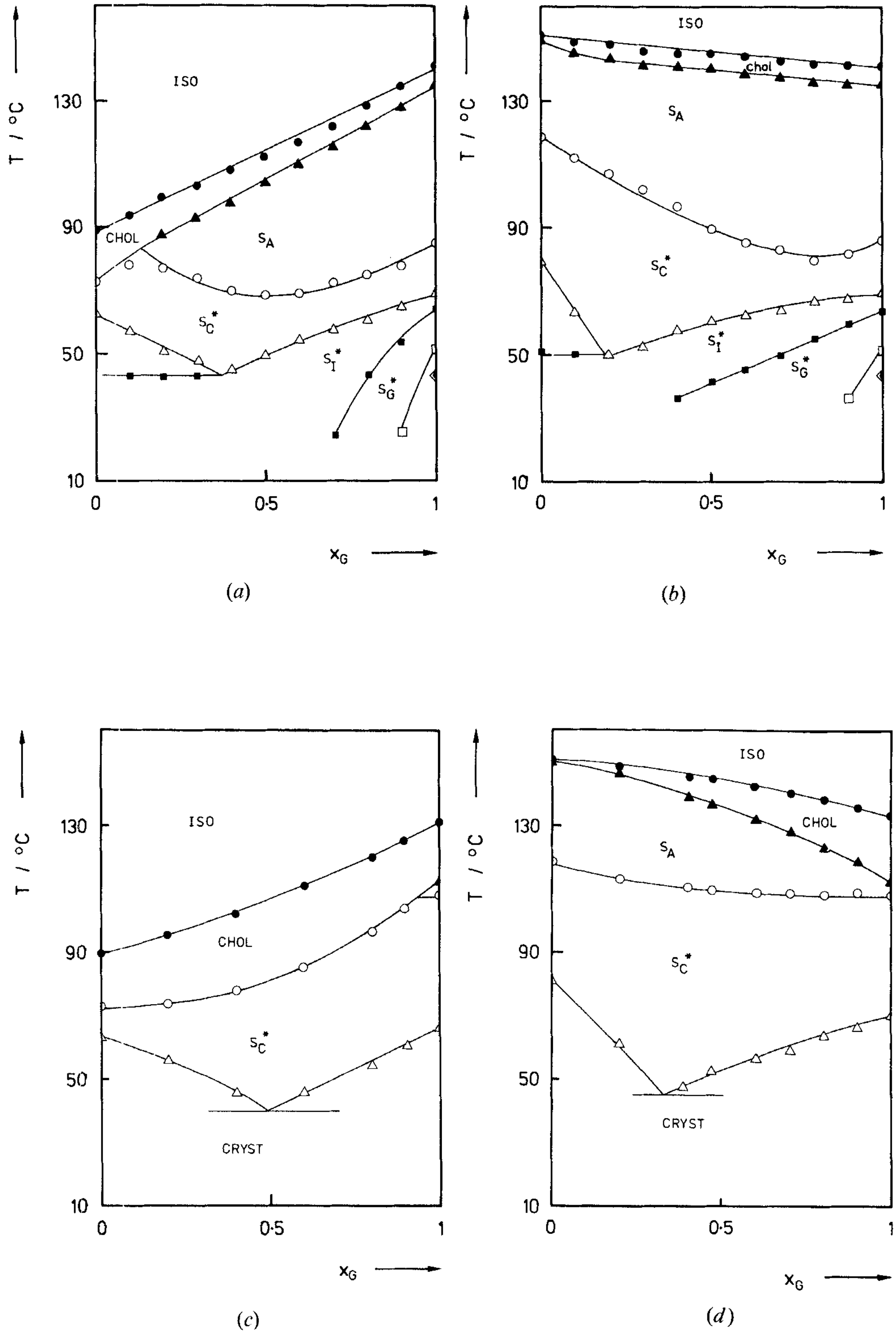
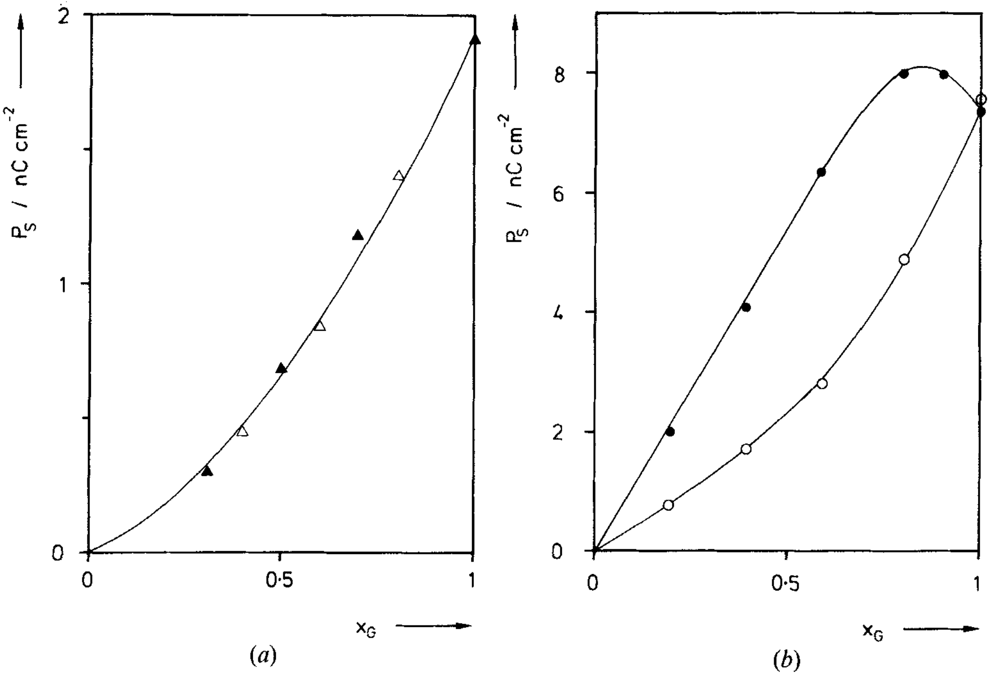
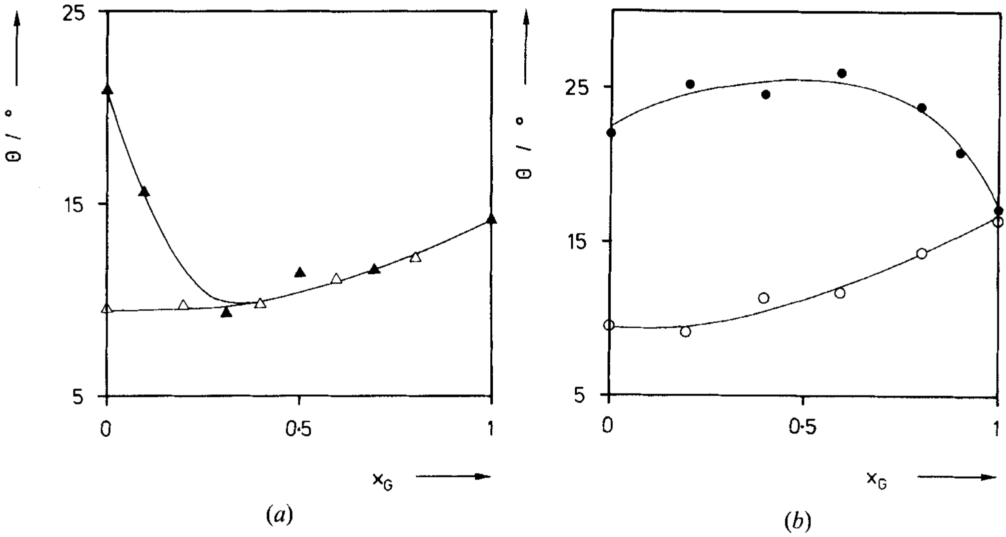


Figure 1. Phase diagrams of the mixed systems: (*a*) 8008–CE8, (*b*) N808–CE8, (*c*) 8008–IS1912 and (*d*) N808–IS19128.



(*a*) (*b*)

Figure 2. P_s as a function of the mole fraction x_G of the optically active compounds (*a*) CE8 and (*b*) IS1912 at a temperature 5 K below the transition S_c^* to chol or S_A. (▲) 8008-CE8, (△) N808-CE8, (●) 8008-IS1912, (○) N808-IS1912.



(*a*) (*b*)

Figure 3. θ as a function of the mole fraction x_G of the optically active compounds (*a*) CE8 and (*b*) IS1912 at a temperature 5 K below the transition S_c^* to chol or S_A. (▲) 8008-CE8, (△) N808-CE8, (●) 8008-IS1912, (○) N808-IS1912.

Consequently, the non-linearities in $P_s(x_G)$ originates from the non-linearities in $\theta(x_G)$.

4. Discussion

From the measurements presented above we draw the following conclusions.

(*a*) The spontaneous polarization P_s induced by an optically active compound is directly proportional to $\sin\theta$ of the mixture according to equation (3).

(*b*) $P_0(x_G)$ is a universal linear function for each chiral dopant referred to a constant temperature difference to the transition temperature S_c^* to S_A or S_c^* to chol.

(*c*) $P_0(x_G)$ is determined only by the molecular structure of the chiral substance. There is no influence of the non-chiral S_c host phase or the phase sequence on $P_0(x_G)$.

As shown in figure 4, $P_0(x_G)$ reflects the pure concentration dependence on P_s because the influence of the tilt on P_s is eliminated. To explain the non-linearities of $P_s(x_G)$ one has to explain the interactions between chiral and non-chiral compounds leading to the non-linearities in $\theta(x_G)$.

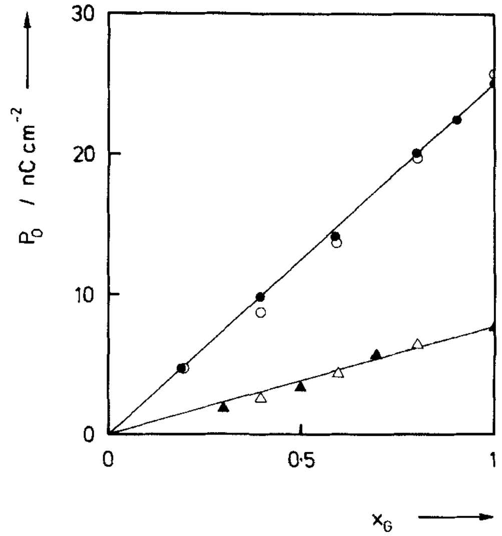


Figure 4. P_0 as a function of the mole fraction of the optically active compound. (▲) 8008-CE8, (△) N808-CE8, (●) 8008-IS1912, (○) N808-IS1912.

Because it has not hitherto been obvious which molecular properties lead to a tilted arrangement in smectic phases, the nature of the interactions between the chiral and non-chiral substances resulting in non-linearities of $\theta(x_G)$ are also not known.

However, the deviation from linearity in $\theta(x_G)$ can be explained by different solute–solvent interactions having their origin in the different structure of the chiral and non-chiral S_c compounds. As can be seen from figures 3(*a*) and 3(*b*), the deviation of $\theta(x_G)$ from linearity is larger the more the mixing compounds differ in their molecular structure.

To characterize the ability of a chiral polar compound to induce a spontaneous polarization in a non-chiral S_c phase we have defined a new material constant [11], the polarization power ∂_p:

$$\partial_p := \left(\frac{\partial P_0(x_G)}{\partial x_G}\right)_{\Delta T}. \tag{4}$$

The polarization power ∂_p is an inherent material constant for each given chiral polar compound. Values of ∂_p for the optically active substances under investigation are listed in table 2. ∂_p is governed by the molecular structure of the chiral compound.

Table 2. Values of ∂_p for several optically active compounds.

Compound	∂_p/nC cm^{-2}
IS1912	25
CE8	8
C7D [11]	42
S811 [11]	121

It must be pointed out that ∂_p is independent of the structure of the non-chiral S_c compound and the phase sequence. Thus, at small concentrations of the chiral compound the S_c host phase merely builds a matrix to orientate the chiral molecules with transverse dipole moments. The interactions between chiral and non-chiral compounds seems to have no influence on ∂_p.

The correlation between ∂_p and molecular structure is less straight forward. As P_0 is the component of the macroscopic dipole moment per unit volume, ∂_p should be related to an effective value of the transverse dipole moment $\mu_{\perp\text{eff}}$ [15] taking into account that the rotation around the long molecular axis is restricted but not frozen in.

Further on the relative position of the chiral centre with respect to the polar group and/or the core have a strong influence on ∂_p: the closer the distance between the two, the larger the spontaneous polarization is [16].

This general discussion shows that the influence of the molecular structure on ∂_p requires further investigation.

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