Phase Transitions, 1988, Vol. 12, pp. 247–262
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Printed in the United Kingdom

Temperature Dependence of Spontaneous Polarization and Tilt in a Homologous Series of Smectics C Doped with a Chiral Additive

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(Received 11 November 1987; in final form 7 December 1987)

The spontaneous polarization was measured in a homologous series of smectics C doped with a chiral additive. An unusual temperature dependence was found which can be well fitted using the generalized Landau model of ferroelectric smectics. The temperature dependence of the tilt angle was also determined and compared with present theories.

KEYWORDS: chiral smectic liquid crystals, ferroelectricity, Landau theory.

INTRODUCTION

Chiral smectic C (SmC*) liquid crystals have gained increasing interest during the last years because of delicate physical phenomena arising in these systems and the possibility of their practical application. Meyer, Liébert, Strzelecki and Keller (1975) have demonstrated that

SmC* materials may possess a spontaneous polarization which can be easily oriented by an applied electric field, i.e. they are ferroelectrics. The bistability character and the short switching times of surface-stabilized cells (Clark and Lagerwall, 1980) promise favourable usability for optical shutters, modulators, matrix displays etc. In this respect the study of the spontaneous polarization P_s, tilt angle Θ and helical pitch $L = 2\pi/q$ of the system are of upmost importance.

There are a great number of papers devoted to measurement of the temperature dependence of these physical quantities (Martinot-Lagarde, 1976; Ostrovskii, Rabinovich, Sonin, Strukov and Chernova, 1977; Yoshino, Uemoto and Inuishi, 1977; Uemoto, Yoshino and Inuishi, 1979; Loseva, Ostrovskii, Rabinovich, Sonin and Chernova, 1980; Ostrovskii, Rabinovich, Sonin, Sorkin, Strukov and Taraskin, 1980; Martinot-Lagarde, Duke and Durand, 1981; Takezoe, Kondo, Miyasato, Abe, Tsuchiya, Fukuda and Kuze, 1984; Wahl and Jain, 1984; Baikalov, Beresnev and Blinov, 1985; Sakurai, Mikami, Ozaki and Yoshino, 1986; Skarp and Andersson, 1986; Dumrongrattana, Nounesis and Huang, 1986; Mohr, Köhler, Worm, Pelzl, Diele, Zaschke, Demus, Andersson, Dahl, Lagerwall, Skarp and Stebler, 1987; Otterholm, Alstermark, Flatischler, Dahlgren, Lagerwall and Skarp, 1987; Patel and Goodby, 1987; Yoshino, Ozaki, Kishio, Sakurai, Mikami, Higuchi and Honma, 1987; Inukai, Saitoh, Inoue, Miyazawa, Terashima and Furukawa, 1987; Bahr and Heppke, 1987ab). These measurements have been performed on single compounds, on mixtures and on doped systems. As a first attempt to interpret experimental data a theoretical model based on a Landau expansion of the free-energy density has been used (Pikin and Indenbom, 1978; Pikin, 1981). According to this theory, the tilt angle and the spontaneous polarization is expected to possess a square-root type of temperature dependence near the SmA–SmC* phase transition, while the pitch and the ratio P/Θ ought to be temperature independent. In the majority of papers, experimental data on tilt and polarization have been presented without further analysis or fitted by the square-root curves, which show a rough agreement with the theory.

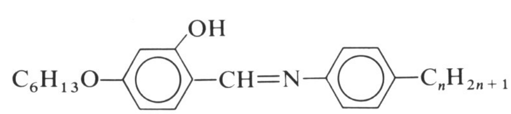
However, no such agreement was found concerning the pitch and the ratio P/Θ (Martinot-Lagarde *et al.*, 1981; Takezoe *et al.*, 1984). Recently, an anomalous temperature dependence of the spontaneous polarization has also been detected in DOBAMBC (Filipic, A. Levstik, I. Levstik, Blinc, Zeks, Glogarova' and Carlsson, 1987). In order to give a physical interpretation of these anomalies some extra terms were incorporated into the Landau expansion (Filipic *et al.*, 1987; Huang, 1987; Carlsson, Zeks, A. Levstik, Filipic, I. Levstik and Blinc, 1987; Zeks, Carlsson, Filipic and A. Levstik). These generalized thermodynamic models were able to describe a set of experimental data measured on DOBAMBC, at least in a qualitative way. Unfortunately DOBAMBC is not an ideal compound to check the performance of a theory because of its narrow SmC* range and chemical instability which does not allow good agreement between data measured by different authors.

On the basis of experimental data on the dynamics of the pyroelectric response, Pozhidayev, Beresnev, Blinov and Pikin (1983) and Beresnev, Pozhidayev and Blinov (1984) proposed a simplified phenomenological model to interpret P/Θ anomalies. According to their idea, the polarization is composed of terms that are linear and cubic in the tilt.

It is the purpose of this paper to study the behaviour of the polarization and tilt in a homologous series of compounds having an SmC* phase in a broad temperature range and to analyze the experimental results on the basis of present theories.

COMPOUNDS

The smectic C phase formed by achiral molecules can be transformed into an SmC* phase by dissolving suitable chiral molecules. Such mixed systems have been published by Kuczynski and Stegemeyer (1980), Beresnev, Baikalov and Blinov (1982), Beresnev, Pozhidayev, Blinov, Pavluchenko and Etingen (1982), Beresnev, Blinov, Baikalov, Pozhidayev, Purvanetskas and Pavluchenko (1982), Pavel, Glogarová, Demus, Mädicke and Pelzl (1983) and Gerlach, Klappert, Fisher and Wahl (1986). In this paper we present results obtained on the homologous series of 6O.nSA (Allakhverdov, Terekhova, Zablotskaya and Etingen, 1981),



n	S_C^*		S_A		Ch		I
8	.	86	.		–	96	.
7	.	84	.	92	.	96	.
6	.	81	.	82	.	91	.
5	.	74	–			97	.

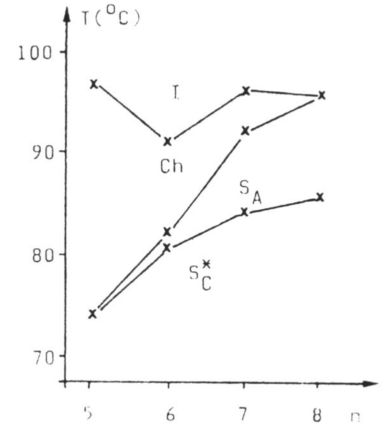
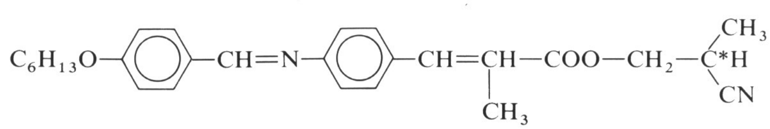


Figure 1 Phase transition temperatures of the homologous series of 6O.nSA doped with 5 w% of HOBACNPC.

doped with 5 weight % of HOBACNPC



The transition temperatures of these mixtures are shown in Figure 1.

EXPERIMENTAL TECHNIQUE

The spontaneous polarization was studied by two independent methods, the pyroelectric technique (Blinov, Beresnev, Shtykov and Elashvili, 1979; Beresnev and Blinov, 1981; Blinov, Baikalov, Barnik, Beresnev, Pozhidayev and Yablonsky, 1987) and the Sawyer-Tower method (Diamant, Drenck and Pepinsky, 1957). According to the pyroelectric technique the spontaneous polarization is obtained upon graphical integration of the $\gamma_p(T)$ pyroelectric coefficient, i.e.

$$P_s(T) = \int_{T_c}^{T} \gamma_p(T)dt$$

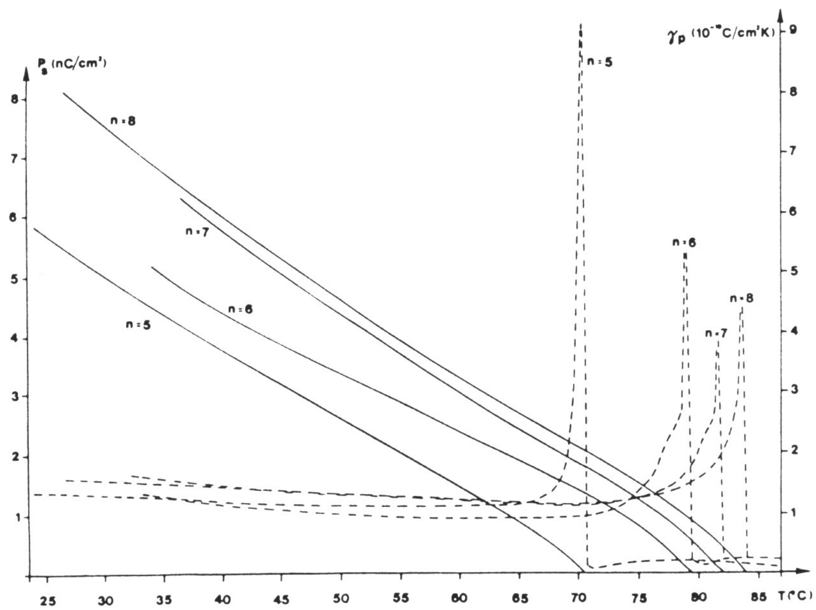


Figure 2 Temperature dependence of the pyroelectric coefficient γ_p (dashed line) and the spontaneous polarization P_s (continuous line) for the homologous series of mixtures 6O.nSA/HOBACNPC.

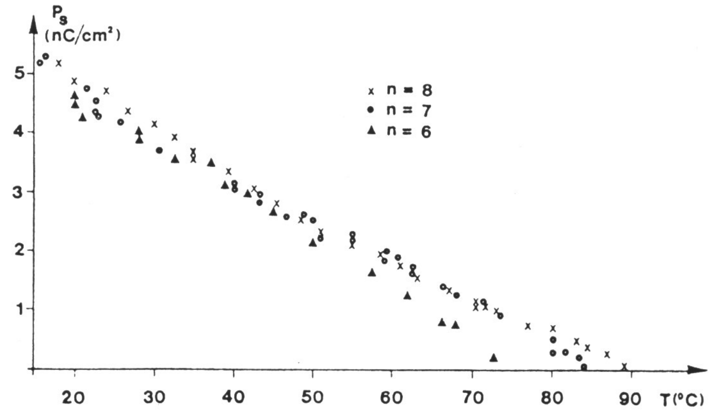


Figure 3 Spontaneous polarization measured by the bridge method for the homologous series of mixtures 6O.nSA/HOBACNPC.

The pyroelectric coefficient is calculated from the voltage developed between the transparent electrodes of the liquid crystal cell when it is irradiated with laser pulses of different duration. The radiation ($\lambda = 1.06\,\mu m$) of a YAG: Nd pulsed laser is absorbed within the liquid crystalline layer which contains a small amount ($< 0.5\%$) of a soluble light-absorbing dye. The temperature dependence of γ_p and the calculated P_s are shown in Figure 2. Since the laser beam causes only a local heating by the pyroelectric method we studied only a small region of the sample which was irradiated. Therefore the temperature of this region can be determined with relatively high precision. The calculation of γ_p requires a calibration of the optical and thermal properties of the cell.

By the Sawyer-Tower method we measured the usual P–E hysteresis curve. Our loop tracer consisted of a Diamant bridge (Diamant *et al.*, 1957) which was connected to a microcomputer allowing measurements at low frequencies (1–10 Hz). The temperature dependence of the spontaneous polarization measured by this method is shown in Figure 3. For such measurements one has to prepare a planar oriented sample (smectic layers are perpendicular to the bounding surfaces). We oriented the sample by the shear method (Bata, Buka, Éber and Jákli). The quality of orientation of the whole sample is important in this case, because any deterioration of the alignment leads to an effective decrease of the polarization. In Figure 4 we compare the temperature dependences of the spontaneous polarization measured by the two methods.

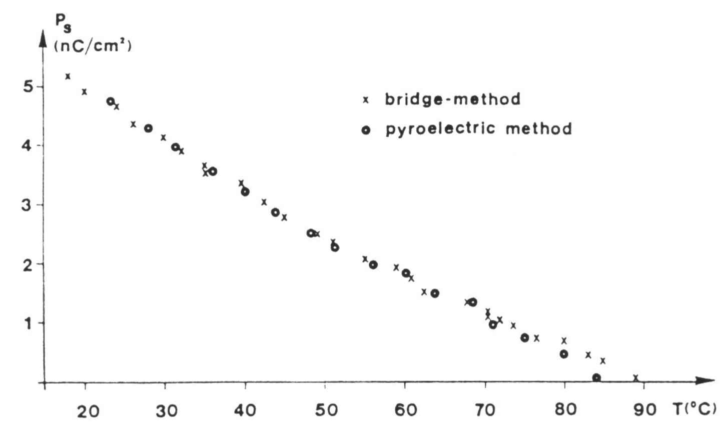


Figure 4 Comparison of the spontaneous polarization measured by two methods for the mixture 6O.8SA/HOBACNPC.

The pyroelectric data were normalized at one point to the data obtained using the Diamant bridge.

The difference in the absolute values may be connected with calibration problems of the pyroelectric cell and/or insufficient orientation of the cell used in the bridge method. The tail at the phase transition on bridge data may be connected with the fact that in large-area samples, a thermal gradient is usually present, leading to an averaging over regions of slightly different temperature which is the more pronounced the higher the dP/dT. Thus the pyroelectric method yields a more precise temperature dependence especially near to the SmA-SmC* phase transition.

The coincidence of the two temperature dependences is striking. A similar behaviour has been found, in addition to the other members of the same homologous series, also for other doped systems (Blinov, private communication), indicating that the unusual temperature dependence of the spontaneous polarization shown in Figures 2–4 is not an occasional feature of these substances.

The interpretation of this significant deviation from the square-root law may be a good way of checking the performance of different theoretical models.

COMPARISON WITH THEORETICAL MODELS

Novel theoretical models of the ferroelectric SmC* phase are based on a generalized Landau expansion. The free-energy density of the system is expanded in two order parameters, the tilt Θ and the polarization P (Carlsson *et al.*, 1987; Zeks *et al.*).

$$g_0 = \tfrac{1}{2}a\Theta^2 + \tfrac{1}{4}b\Theta^4 + \tfrac{1}{6}c\Theta^6 - \Lambda q\Theta^2 + \tfrac{1}{2}K_3 q^2\Theta^2 + \frac{1}{2\varepsilon}P^2$$
$$- \mu qP\Theta - CP\Theta - \tfrac{1}{2}\Omega P^2\Theta^2 + \tfrac{1}{4}\eta P^4 - dq\Theta^4 \qquad (1)$$

Only the coefficient $a = \alpha(T - T_0)$ is assumed to be temperature dependent. T is the temperature of the system, T_0 a specific temperature, b, c, d and η constants, K_3 an elastic modulus, Λ the Lifshitz constant, μ and C the coefficients of the flexo- and piezo-electric bilinear coupling, ε the dielectric permittivity and Ω the coefficient of the biquadratic coupling term inducing transverse quadrupole ordering.

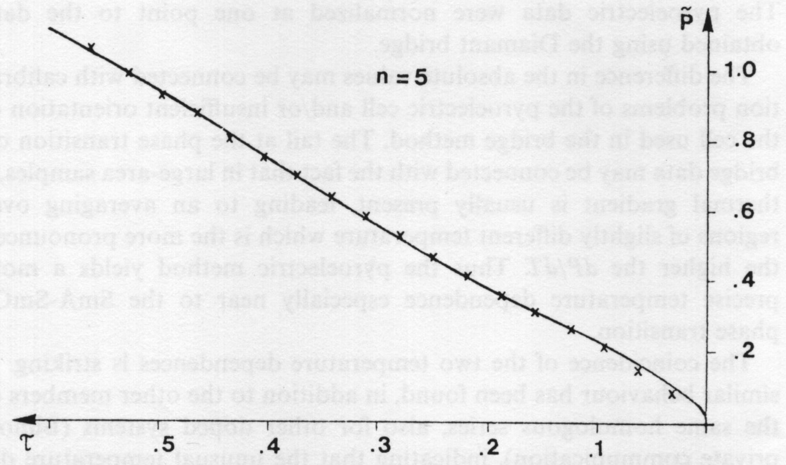


Figure 5 Dimensionless polarization versus dimensionless temperature for the mixture 6O.5SA/HOBACNPC. Crosses are the measured points renormalized by $P^* = 5.32\ \mathrm{nC/cm^2}$, $T^* = 80°\mathrm{C}$. Continuous line is the fitted curve with parameters $\beta = 0.5$, $\gamma = 1.35$, $\rho = 0$, $\nu\delta = 0$.

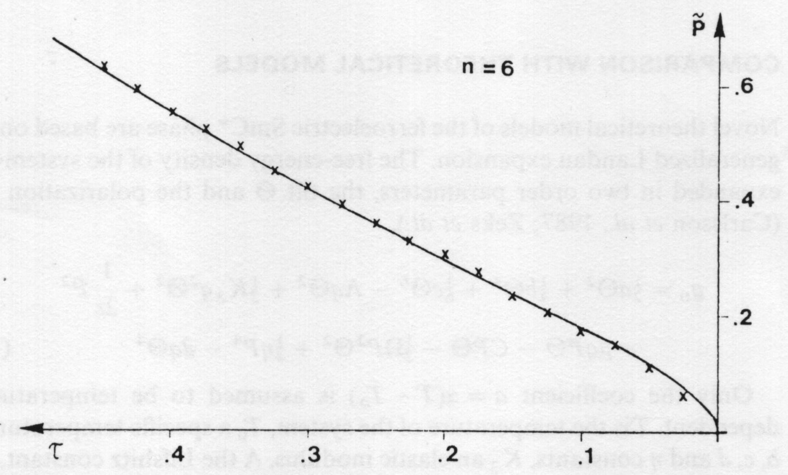


Figure 6 Dimensionless polarization versus dimensionless temperature for the mixture 6O.6SA/HOBACNPC. Crosses are the measured points renormalized by $P^* = 8.02\ \mathrm{nC/cm^2}$, $T^* = 100°\mathrm{C}$. Continuous line is the fitted curve with parameters $\beta = 0.447$, $\gamma = 1.6$, $\rho = 0$, $\nu\delta = 0$.

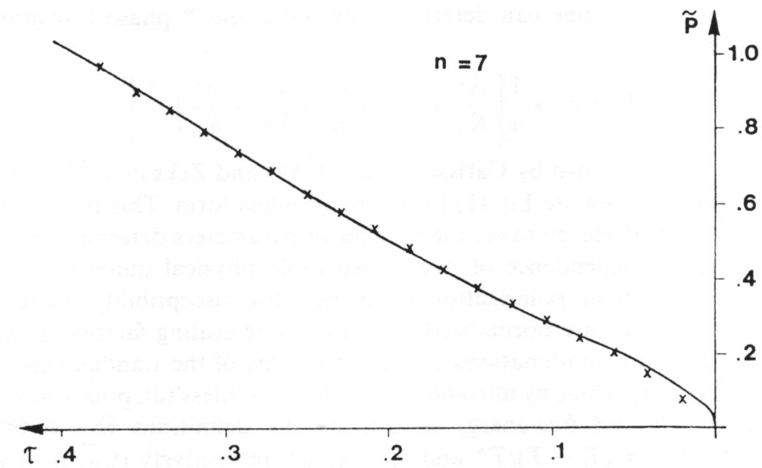


Figure 7 Dimensionless polarization versus dimensionless temperature for the mixture 6O.7SA/HOBACNPC. Crosses are the measured points renormalized by $P^* = 6.4\,\text{nC/cm}^2$, $T^* = 120°\text{C}$. Continuous line is the fitted curve with parameters $\beta = 0.548$, $\gamma = 1.2$, $\rho = 0$, $\nu\delta = 0$.

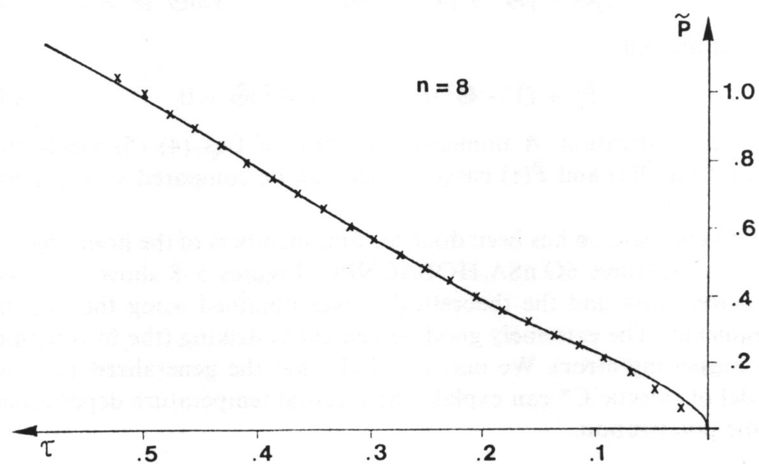


Figure 8 Dimensionless polarization versus dimensionless temperature for the mixture 6O.8SA/HOBACNPC. Crosses are the measured points renormalized by $P^* = 7.87\,\text{nC/cm}^2$, $T^* = 110°\text{C}$. Continuous line is the fitted curve with parameters $\beta = 0.5$, $\gamma = 1.3$, $\rho = 0$, $\nu\delta = 0$.

From Eq. (1) one can determine the SmA–SmC* phase transition temperature as

$$T_c = T_0 + \frac{1}{\alpha}\left[\frac{\Lambda^2}{K_3} + \left(C + \frac{\Lambda\mu}{K_3}\right)^2\left(\frac{1}{\varepsilon} - \frac{\mu^2}{K_3}\right)^{-1}\right] \tag{2}$$

It has been shown by Carlsson *et al.* (1987) and Zeks *et al.* that it is convenient to rewrite Eq. (1) in a dimensionless form. This procedure decreases from eleven to six the number of parameters determining the temperature dependence of five measureable physical quantities (tilt angle, spontaneous polarization, pitch, dielectric susceptibility and heat capacity) which are normalized by appropriate scaling factors. These parameters are combinations of the coefficients of the Landau expansion in Eq. (1). Thus, by introducing the dimensionless tilt, polarization, temperature and free-energy density by the definitions $\tilde{\Theta} = \Theta/\Theta^*$, $\tilde{P} = P/P^*$, $\tau = (T_c - T)/T^*$ and $\tilde{g}_0 = g_0/g_0^*$, respectively (Carlsson *et al.*, 1987)

$$\tilde{g}_0 = \tfrac{1}{2}(\beta^2 - \gamma\tau)\tilde{\Theta}^2 + \tfrac{1}{4}\gamma\tilde{\Theta}^4 + \tfrac{1}{6}\rho\tilde{\Theta}^6 + \tfrac{1}{2}\tilde{P}^2 + \tfrac{1}{4}\tilde{P}^4 \\ -\beta\tilde{P}\tilde{\Theta} - \tfrac{1}{2}\tilde{P}^2\tilde{\Theta}^2 - \nu\delta\tilde{\Theta}^3\tilde{P} \tag{3}$$

Minimizing $\tilde{g}_0$ with respect to $\tilde{\Theta}$ and $\tilde{P}$ one can obtain the equations

$$(\beta^2 - \gamma\tau)\tilde{\Theta} - \gamma\tilde{\Theta}^3 + \rho\tilde{\Theta}^5 - \tilde{\Theta}\tilde{P}^2 - (\beta + 3\nu\delta\tilde{\Theta}^2)\tilde{P} = 0 \tag{4}$$

for the tilt and

$$\tilde{P}^3 + (1 - \Theta^2)\tilde{P} - (\beta + \nu\delta\tilde{\Theta}^2)\tilde{\Theta} = 0 \tag{5}$$

for the polarization. A numerical solution of Eqs (4)–(5) yields the theoretical $\tilde{\Theta}(\tau)$ and $\tilde{P}(\tau)$ curves which can be compared with experimental data.

This comparison has been done for four members of the homologous series of mixtures 6O.nSA/HOBACNPC. Figures 5–8 show both the measured data and the theoretical curves obtained using the best fit parameters. The extremely good agreement is striking (the fit is within the measuring error). We may conclude that the generalized Landau model of smectic C* can explain the unusual temperature dependence of the polarization.

TILT ANGLE

Since the temperature dependence of the tilt can also be obtained from the model, a further check would be to compare it with the measured tilt angle.

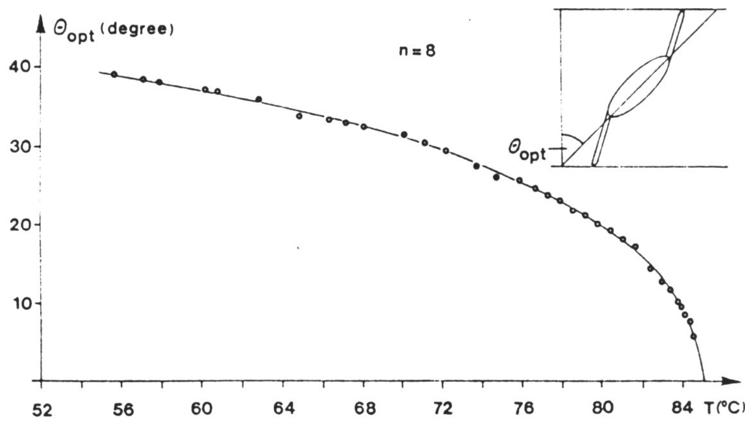


Figure 9 Temperature dependence of the optical tilt angle for the mixture 6O.8SA/HOBACNPC.

We used two methods to measure the tilt angle: an optical one (Baikalov *et al.*, 1985) and X-ray scattering. The measured temperature dependence is shown in Figures 9 and 10 for the mixture 6O.8SA/HOBACNPC. The difference in the absolute values of the tilt angle measured by the two methods are worth noting! According to the usual interpretation by the optical method we measure the tilt of the core of

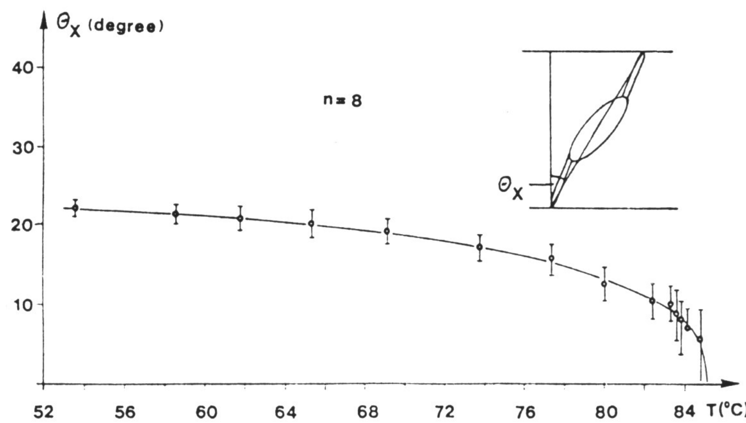


Figure 10 Temperature dependence of the X-ray tilt angle for the mixture 6O.8SA/HOBACNPC.

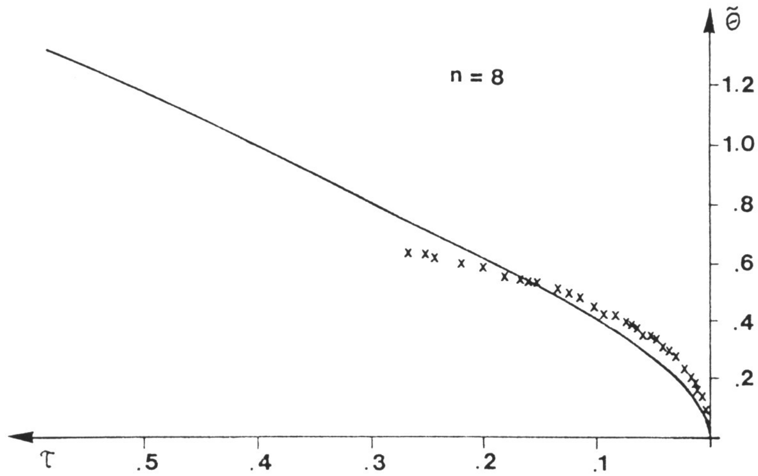


Figure 11 Dimensionless tilt versus dimensionless temperature for the mixture 6O.8SA/HOBACNPC. Crosses are points measured by optical method and renormalized by $\Theta^* = 61.6$ degrees, $T^* = 110°C$. Continuous line is the calculated curve with parameters $\beta = 0.5$, $\gamma = 1.3$, $\rho = 0$, $v\delta = 0$.

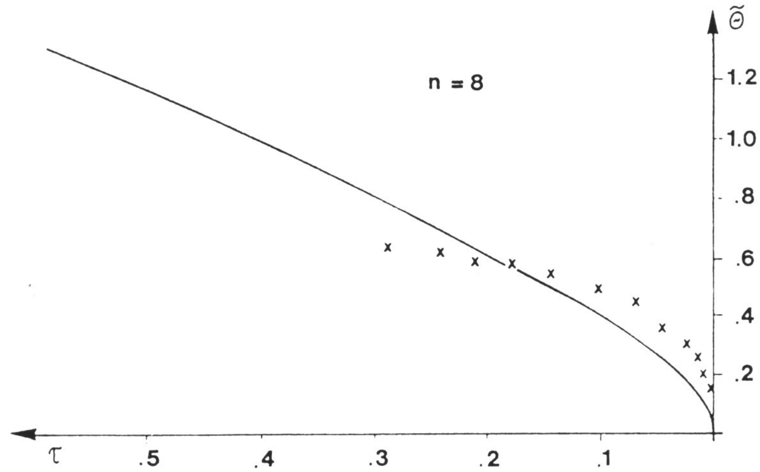


Figure 12 Dimensionless tilt versus dimensionless temperature for the mixture 6O.8SA/HOBACNPC. Crosses are points measured by the X-ray method and renormalized by $\Theta^* = 34.7$ degrees, $T^* = 110°C$. Continuous line is the calculated curve with parameters $\beta = 0.5$, $\gamma = 1.3$, $\rho = 0$, $v\delta = 0$.

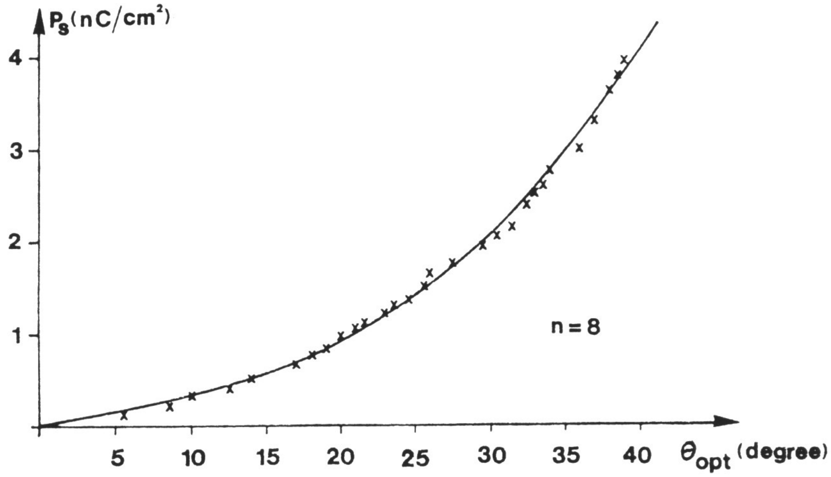


Figure 13 Spontaneous polarization versus optical tilt angle for the mixture 6O.8SA/HOBACNPC. Crosses are measured points, continuous line is the fitted polynomial ($P = a_1\Theta + a_3\Theta^3$). Parameters: $a_1 = 0.0266$ nC/cm^2 degree, $a_3 = 4.68 \times 10^{-5}$ nC/cm^2 degree^3.

the molecules. By X-rays we determine the layer spacings in both the SmA (d_A) and SmC* (d_C) phases and supposing that the configuration of the molecules does not change at the phase transition the tilt angle is calculated by the formula $\Theta = \cos^{-1}(d_C/d_A)$.

We compare the tilt angles measured by the two methods with the ones calculated using the parameters we obtained from the best fit of the spontaneous polarization in Figures 11 and 12. The fit is far from good in both cases. These results show that though the model contains the most important interactions some effects are not taken into account properly.

Now we focus on the direct relation between the spontaneous polarization and the tilt angle. In Figure 13 we plot the measured spontaneous polarization as a function of the measured optical tilt angle. We approximated this curve by a third-order polynomial $P = a_1\Theta + a_3\Theta^3$, as proposed by Pozhidayev *et al.* (1983) and Beresnev *et al.* (1984).

As it can be seen that a good fit is now obtained. It is now the task of theoreticians to incorporate the ideas of this simple model into a generalized thermodynamic model of Landau type in order to get a simultaneous fit for the temperature dependence of both the tilt and the polarization.

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