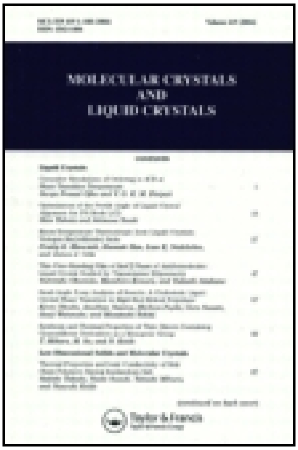

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

Induced Ferroelectric Liquid Crystalline Salicylidenanilines

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Induced Ferroelectric Liquid Crystalline Salicylidenanilines

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The helical twisting powers, temperature dependences of pitch and temperature/frequency dependences of the dielectric constants of low-temperature mixtures of smectic C liquid crystalline salicylidenanilines doped with non-mesogenic optically active compounds were measured.

Keywords: ferroelectric mesophases, chiral smectic phases, salicylidenaniline derivatives

INTRODUCTION

Induced chiral smectic C liquid crystals, *i.e.* systems composed of smectic C liquid crystals (Sm C) and optically active dopants (OAD) are (like induced nemato-chiral mixtures)[1] of growing importance for the solution of various scientific problems and for their applications.[2-4]

The nature of the helical twisting and ferroelectric properties of induced chiral Sm C systems is rather obscure, reflecting a scarcity of experimental data. In the present work the helical twisting power, temperature dependence of the pitch and the temperature-frequency dependence of the dielectric constant have been studied for different induced chiral Sm C systems, based on salicylidenaniline derivatives.

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MATERIALS

The following salicylidenanilines were used as host smectic C phase: 4-decyloxysalicilidene-4′-*n*-heptylaniline–Sm C-1, 4-heptyloxysalicilidene-4′-*n*-butylaniline–SmC-2, 4-heptyloxysalicylidene-4′-*n*-octylaniline–SmC-3 and a eutectic mixture of 4-butyloxysalicylidene-4′-*n*-octylaniline with SmC-3–SmC-4. Non-mesogenic tigogenin caprate (OAD-1), L-menthylnitrobenzoate (OAD-2) and 4-heptyloxysalicylidene-4′-(L-menthylbenzoate)aniline (OAD-3) were used as the most suitable optically active dopants.

TEMPERATURE DEPENDENCE OF SPIRAL PITCH

Two methods were employed to determine the pitches, of the chiral smectic C and the cholesteric phases: laser diffraction on the focal conic structure and measurement of the distance between stripes of monodomain samples.[5-6] The deformation of the helicoidal structure by wall anchoring was observed in cases where the cell thickness d was less than three or four times the undisturbed pitch (Fig. 1).

In the mixtures investigated, two types of the temperature dependence of pitch were observed. In the first case a monotonic increase of pitch with increasing temperature occurs (Fig. 2). In the

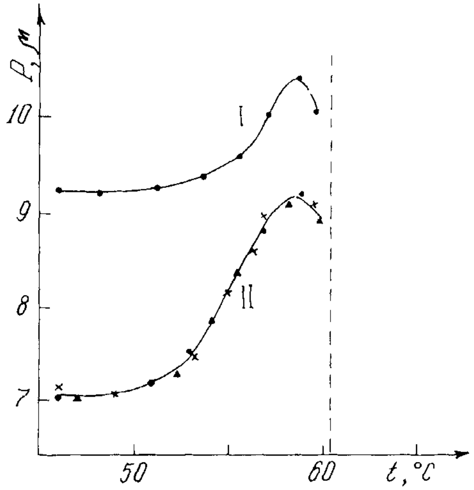

FIGURE 1 P(T) dependence for mixture 98% SmC-2 + 2% OAD-1 ■—d = 20 μm, ▲—d = 40 μm, ×—d = 60 μm, ●—d = 100 μm.

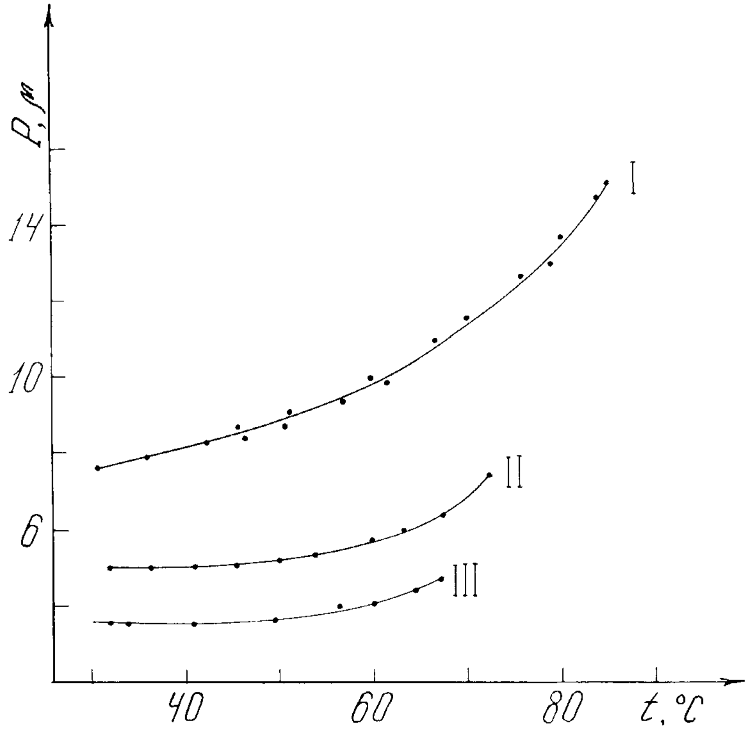

FIGURE 2 P(T) dependences for mixture SmC-1 + OAD-3: 1 c = 5%, 2 c = 10%, 3 c = 17%.

other case, near the smectic C phase transition the pitch increased steeply, to a relatively broad maximum and then decreased rapidly to a finite value at the phase transition point T_0 (Figs. 1 and 3). Such anomalous behaviour for a homologous series of *n*OBAMBC[7-9] has been explained in terms of the flexoelectric effect in the chiral Sm C.[10] The anomalous temperature dependence of pitch for room temperature ferroelectric liquid crystal has also been observed recently.[11] However this type of P(T) dependence was observed only at the smectic A–smectic C transition. It must be emphasized that we have observed this anomaly near the cholesteric–smectic C phase transition point also (Fig. 3). It is possible to observe the absence of anomalies, i.e. a monotonic increasing of pitch with temperature, near the smectic A–smectic C transition (Fig. 2). Thus, our measurements show that P(T) characteristics near the phase transition points are not understood quantitively. Perhaps, we may obtain relevant infor-

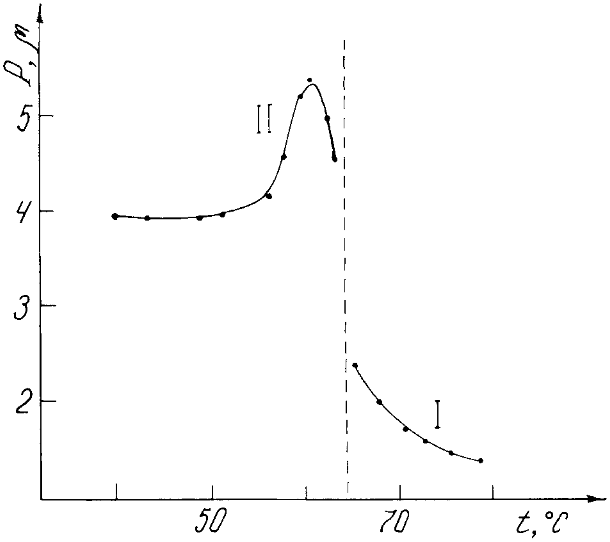

FIGURE 3 P(T) dependence for mixture 95% SmC-4 + 5% OAD-3 I—cholesteric phase, II—smectic phase.

mation from tilt angle (θ_c) measurement, since the anomalous temperature dependence of pitch is attributed to the thermal fluctuation effect on tilt angle.[9]

HELICAL TWISTING POWER

In Fig. 4 the concentration dependence of reciprocal pitch was plotted for a sample of SmC-4 doped with OAD-3. The same P^{-1} (c) (where c is the OAD concentration) dependences were observed as for other mixtures investigated. We determined values of pitches at temperatures 10 degrees below the phase transition points for each mixture. We take it, that at these temperatures all mixtures had more or less the same order parameter. Moreover, this temperature is appreciably from the region of the P(T) curve anomaly. The linear dependence P^{-1} (c) for cholesteric phases is observed up to a concentration of OAD, when the liquid crystal state is destroyed. At the same time, the linear dependence in smectic C phase may be broken for small concentrations (5 weight per cent) (Fig. 4). Thus, a linear dependence of P^{-1} on c, *i.e.* $P^{-1} = Ac$, is observed only at small concentrations

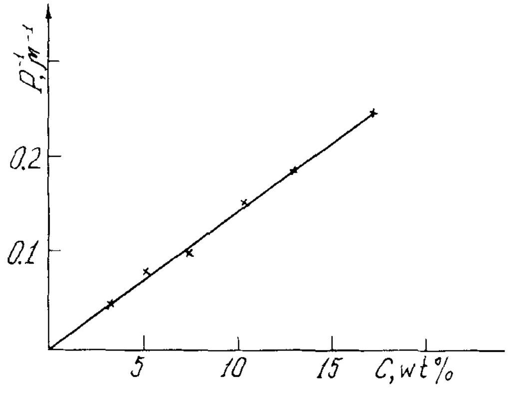

FIGURE 4 P^{-1} (c) dependence for mixture SmC-4 + OAD-3 I—cholesteric phase, II—smectic phase.

of OAD in induced chiral Sm C systems. The A parameter characterizes the helical twisting power (HTP) values for the mixtures investigated both for induced cholestric and chiral Sm C phases are given in Table I.

The high HTP values observed for mixtures of SmC-3 and SmC-4 with OAD-3 appear to indicate a structural similarity between host matrices and guest OAD molecules. The difference in HTP values for OAD-3 in SmC-1 and SmC-4 is connected with the fact, that SmC-1, in contrast to SmC-4, does not form a nematic phase, *i.e.* it is characterized by greater translational ordering. Thus, the appearance of the additional ordering hinders the induction of helicity. This is why the HTP value of a particular OAD in a nematic host may be an order of magnitude greater than its value in a smectic C host.

TABLE I

No.	Mixture	A_{chol}	A_{smec}
1.	SmC-1 + OAD-3	—	0.015
2.	SmC-2 + OAD-1	0.2	0.05
3.	SmC-2 + OAD-2	0.18	0.013
4.	SmC-3 + OAD-3	—	0.03
5.	SmC-4 + OAD-3	0.16	0.05
6.	SmC-4 + OAD-2	0.07	0.03

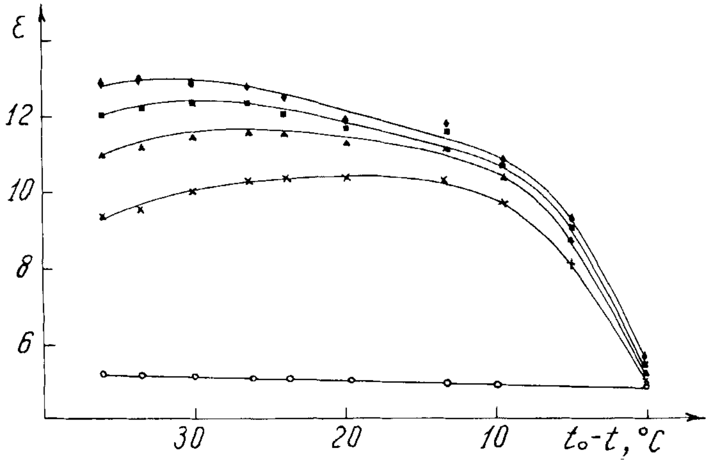

FIGURE 5 ε(T) dependences for mixture 80% SmC-1 + 20% OAD-3 ♦—100 Hz, ■—200 Hz, ▲—300 Hz, ×—500 Hz, ●—5 kHz.

TEMPERATURE-FREQUENCY DEPENDENCES OF DIELECTRIC CONSTANT

The dielectric constant (ε) was measured in a cell 40–100 μm thick. A homogenous orientation was produced by application of an electric field, rubbing and shear. However our samples were not perfectly monodomain and contained small regions with focal conic orientation. But we suggest that this does not influence the characteristics of ε. For all the mixtures a typical ferroelectric liquid crystal dependence ε(T,f) was observed. In Fig. 5 the ε(T) dependence at different frequences for mixture 80% SmC-1 + 20% OAD-3 is presented. Our experimental set-up ensures that measurements are made at the simultaneous application of a d-c unwinding field. It was experimentally shown that the d-c unwinding field was $\sim 5.10^4$ V/cm and relaxation frequency $\sim 5.10^3$ Hz. In the supercooled state, ferroelectric properties for the induced chiral Sm C investigated were observed up to room temperatures. Detailed investigations of spontaneous polarization will be published elsewhere.

CONCLUSION

Ferroelectric liquid crystals with a wide-temperature range consisting of salicylidenanilines doped with non-mesogenic OAD were obtained. The pitches of these systems vary over a wide range, and it is possible to supercool them to room temperatures. It was shown that the HTP depends on the geometrical similarity of the guest and host molecules and on the tendency of host liquid crystal matrix to assume translational ordering. The first results for P(T) and $\varepsilon(T,f)$ dependences cannot be explained in terms of existing theories.

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SmC-1	Cryst 41.0°C SmC 100.6°C SmA 101.4°C Isotrop
SmC-2	Cryst 20.0°C SmC 64.2°C NLC 86.8°C Isotrop
SmC-3	Cryst 20.0°C SmC 97.5°C Isotrop
SmC-4	Cryst 26.1°C SmC 52.2°C NLC 75.7°C Isotrop