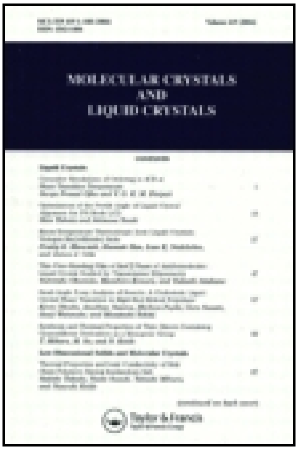

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Electrooptical Behaviour in Several Chiral Smectic Mesophases

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To cite this article: C. Destrade , C. Leon-latouche , H. T. Nguyen & P. Simeão Carvalho (1994): Electrooptical Behaviour in Several Chiral Smectic Mesophases, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 241:1, 289-297

To link to this article: http://dx.doi.org/10.1080/10587259408029765

Mol. Cryst. Liq. Cryst., 1994, Vol. 241, pp. 289–297
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Printed in the United States of America

Electrooptical Behaviour in Several Chiral Smectic Mesophases

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(Received February 22, 1993; in final form July 28, 1993)

Measurements of the tilt angle, response time τ_s and of the polarization were performed in compounds presenting several chiral smectic mesophases. The behaviour of these parameters under an a.c. electric field, make them interesting for electrooptical devices. We will show that the electrooptical measurements are good to identify the ferroelectric phases.

Keywords: Liquid crystals, chiral snectics, electrooptical, ferroelectric nesophases

INTRODUCTION

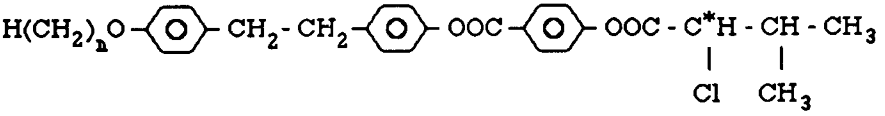
The traditional methods used to study smectic materials give us important information about their mesomorphic properties, such as transition temperatures and enthalpies, thickness of the smectic layers, molecular arrangements and the tilt angle of the molecules.

It is well known that the ferroelectric behaviour in certain chiral phases, such as SmC*, SmI*, SmF*, SmJ* and SmG* is related to their symmetry, that can enhance the molecular response to an external electric field. On the other hand, a paraelectric phase (for example, the smectic hexagonal SmB phase) is devoid of any ferroelectric properties. The uniaxial character of these paraelectric phases can be identified under an a.c. electric field.

In this paper we will show the importance of the electrooptical measurements in the study of ferroelectric phases, with a special interest to the SmI* and SmF* phases.

EXPERIMENTAL

Our results were obtained in a series of compounds that was recently published[1] having the general formulae:



with $n = 6, 7, \ldots, 12$.

The optical observations of the characteristic textures and the tilt angles of the molecules in the different liquid crystal (LC) phases were performed with an optical polarizing microscope Zeiss with polarized light. To obtain the values of the polarization, we used the well known polarization reversal current method.[2] This current was measured with an ammeter probe Tektronix AG 302 for a square wave of 3 kHz and with a built-in electronic circuit for a square wave of 200 Hz and below. The temperature was controlled with an accuracy up to 0.1°C, by an Apple IIe computer. The measurements were carried on at a stabilized temperature, from the high temperature phase to the crystal phase. All the LC samples were prepared and aligned under the same conditions, corresponding to the bookshelf geometry, using rubbed polymeric coating and shearing as previously described.[1]

RESULTS AND DISCUSSION

It has already been pointed out[1] that the optical observations of the textures corresponding to the LC phases, under a polarizing microscope, for the whole family of compounds, was good enough to identify the SmA, SmC* and SmB phases, but not adequate for the low temperature ferroelectric phases such as SmI* or SmF*, because no clear differences between them could be noticed. The inadequacy of this method is due to the structural similarity of these phases. As they are supposed to be ferroelectric, a careful study of the polarization (P) and of the tilt angle (θ) could help in identifying them.

Figure 1 is a plot of P and θ as a function of the temperature, obtained with a

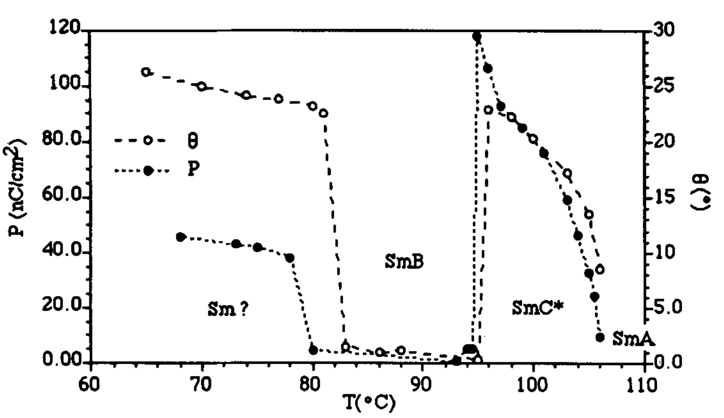


FIGURE 1 Temperature dependence of the polarization and of the tilt angle for the compound $n = 6$. The temperature deviations of the θ curve relatively to the P curve can be due to a slight decomposition of the compound, as a consequence of the length of the experiments.

saturation field of ±5 V/μm, between 60°C and 110°C, for the compound $n = 6$. We can see that the polarization increases sharply up to ~118 nC/cm^2, on cooling the sample in the high temperature phase. High values of θ and P_s confirm the existence of a ferroelectric SmC* phase, as previously reported.[1]

Below ~80°C, another ferroelectric phase, which we refer to as (Sm ?) can be observed, for an applied field of ±7 V/μm. The magnitude of the polarization in this phase is much lower than the value found in the SmC* phase. We will discuss this point later in the paragraph concerning the low temperature phases.

These two ferroelectric phases are separated by a non-ferroelectric one, characterized by small field induced values of P (~2 nC/cm^2) and θ (~1°). In fact, these values are typical of an electroclinic effect, which is always found in the uniaxial SmA phase and was also observed in the hexagonal SmB phase.[3] It is known that the LC molecules in the SmB phase are oriented perpendicular to the layers and possess a long range 3D positional and periodic order (crystal B phase[1]). This is consistent with the practically zero values of P and θ, as well as the mosaic-like texture found below the SmC* phase.

In the following we shall call compounds with $n = 7$ to 9 as group 1 and those with $n = 10$ to 12 as group 2. Each group shows a similar behaviour for the temperature dependence of the tilt angle and of the polarization, as can be seen in Figures 2a and 2b (group 1) and Figures 3a and 3b (group 2).

We find that both $\theta(T)$ and $P(T)$ are very similar for the compounds belonging to each group. Concerning the tilt angle curves, there is practically no difference between the groups, except in the magnitude of θ in the low temperature phase. A similar behaviour is observed in the polarization curves. In the SmC* phase the agreement is quite good, as we expected.

An interesting feature is observed in the $n = 6$ compound, below ~80°C. Although $\theta(T)$ is very similar to the tilt angle curves of group 1 compounds, this is not found in the polarization results. The polarization in this compound, in the low temperature phase, is much lower than in any other compound of its family. Moreover, this compound shows a paraelectric phase between two ferroelectric phases. So, it must be excluded from any of the two groups.

The differences between group 1 and group 2 are more visible if we compare one compound of each group, for instance the compounds with $n = 9$ and $n = 10$. In Figures 4a and 4b, the tilt angle and the polarization are plotted as a function of the temperature, respectively. In the SmC* phase, $\theta(T)$ and $P(T)$ does not differ much in shape and magnitude for both compounds. However, in the low temperature phase, the magnitude of both θ and P are lower for the compound $n = 10$.

It must be pointed out that the measured values of P in the low temperature phases do not probably correspond to the actual value of spontaneous polarization. This can be explained by the fact that, as the temperature decreases, the viscosity of the liquid crystal increases, in particular when it changes to a more ordered phase. In fact, as we can see in Figure 5, the response time τ_s of the molecules to an a.c. electric field (E), increases near the critical range of temperatures. To saturate the polarization we would need to apply fields higher than 20 V/μm, which short-circuit the sample. As the fields applied in all samples were the same at the same temperature, the only explanation for the different behaviours of $\theta(T)$ and

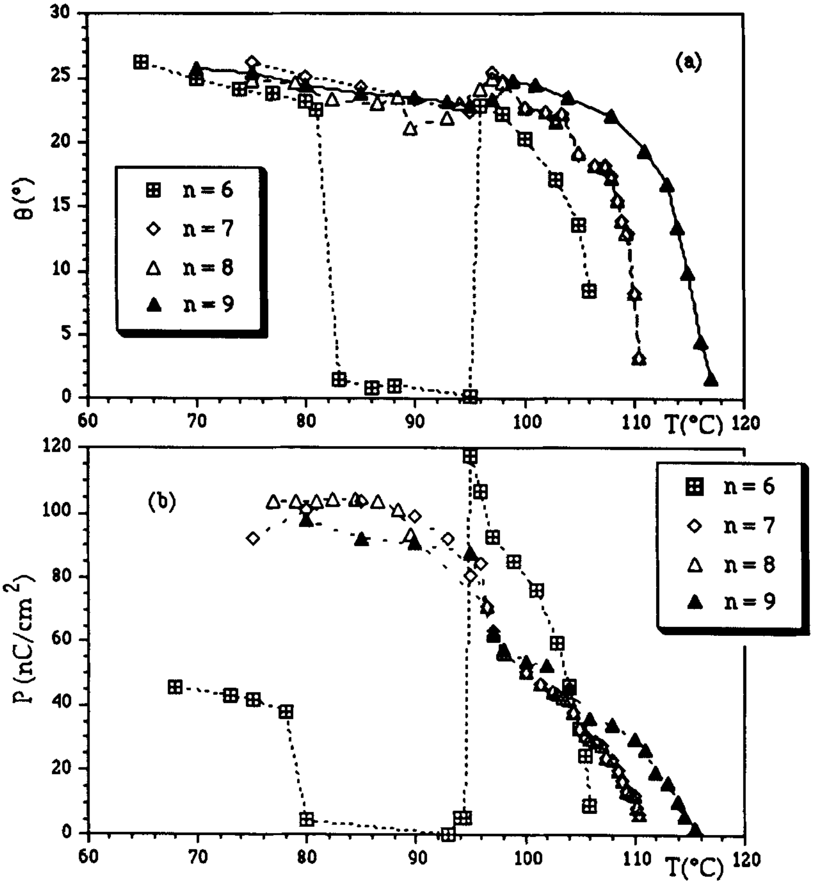


FIGURE 2 (a) θ(*T*) and (b) *P*(*T*) for the compounds of group 1 (*n* = 7, 8, 9) and for the compound *n* = 6.

P(*T*), in the low temperature phase of group 1 and group 2 compounds, is that we are in the presence of two ferroelectric phases of different nature.

Low Temperature Phases

Based on the referred results, we shall try to identify the low temperature phases, by taking into account the viscosity and the local symmetry.

It is known that in the SmI* phase, as well as in the SmC* phase, there is no correlation between the molecular positions of two successive layers. However, the local structure of the SmI* phase is much more rigid so the viscosity is higher than in the SmC*; this is directly connected to the steep increase of the response time τ_s at the transition temperature. The existence of a small coupling between neighbouring layers in the SmF* phase determines an increase of the viscosity in relation to the SmI* phase and so the dipoles must have to be oriented with stronger fields.

As seen in Figure 4b, in the low temperature phases, the polarization for the compound of group 2 is clearly lower than the one of group 1. Although the applied

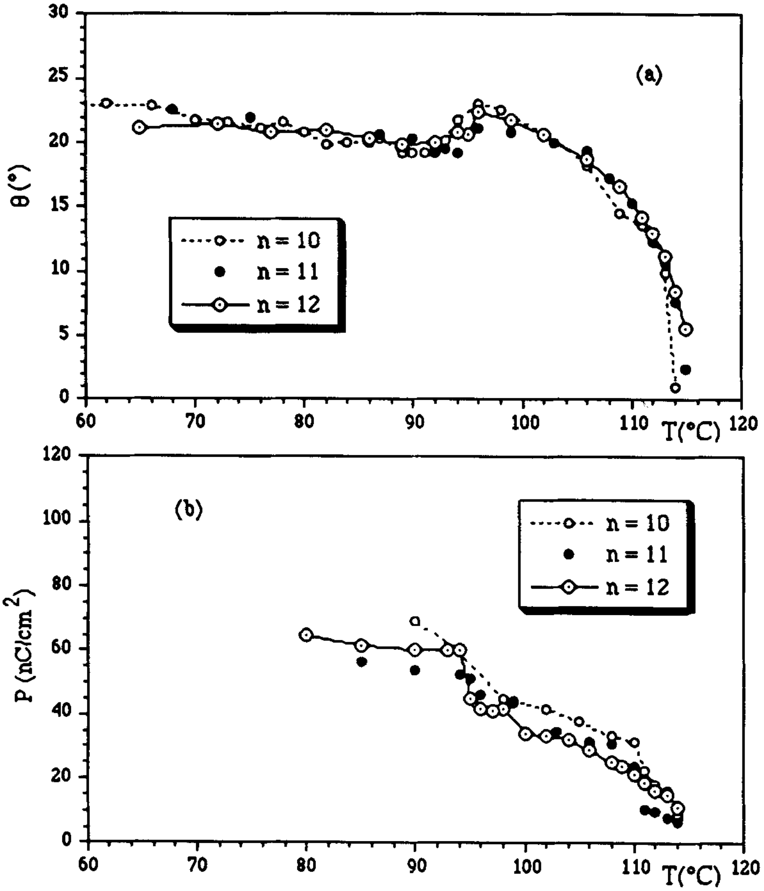


FIGURE 3 (a) $\theta(T)$ and (b) $P(T)$ for the compounds of group 2 (n = 10, 11, 12).

fields are practically the same (near the limits of the short-circuit conditions . . .), the tilt angle is also lower for the compound of group 2 (Figure 4a). Anyway, previous X-ray measurements[1,7] have shown an increase of the layer spacing for the compounds of group 2 which is consistent with a SmI* or a SmF* phase, while with one compound of group 1 (compound $n = 9$) a decrease of the layer spacing is observed,[1] so it is not possible to know the exact nature of the low temperature mesophase in group 1 (for this reason, we shall call it SmX*); high resolution X-ray measurements may be necessary to clarity this point.

Apparently the length of the aliphatic chain is responsible for the onset of the viscous SmF*, SmI* or SmX* phases, those being thermodynamically stable for certain numbers of carbon atoms.

Anomalous Behaviour in the SmC* Phase

An interesting feature was observed in the SmC* phase at least for some compounds, both for polarization and tilt angle curves. Figure 6 shows this anomalous behaviour in $P(T)$ and in $\theta(T)$ for the compounds $n = 7$ and $n = 10$. The anomaly

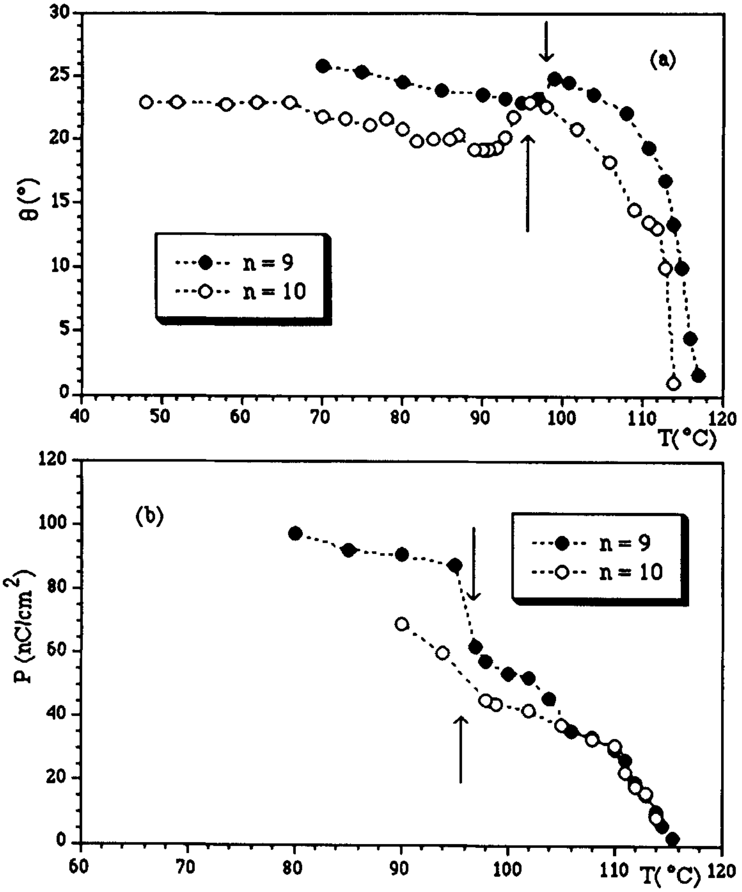


FIGURE 4 Differences and similarities in (1) $\theta(T)$ and in (b) $P(T)$ between the compounds $n = 9$ (group 1) and $n = 10$ (group 2). The arrows indicate the transition from the SmC* phase to the low temperature phase.

appears as a "shoulder" in $\theta(T)$ and it is related to a small increase of the spontaneous polarization. This behaviour has not been detected with the microscope because no change was observed in the LC texture. There was also no evidence of structural change in X-ray measurements and no threshold field was detected on electrooptical measurements. Defects must be excluded as the alignment in the samples was very good.

We verified that the whole SmC* phase is easily polarized and the anomaly is more visible for weak fields. Higher fields tend to suppress (or mask) this behaviour. The existence of a ferrielectric (SmC^*_{fi}) phase and a ferroelectric (SmC^*_{fe}) phase, below the paraelectric SmA phase, may be a reasonable explanation for what we have observed.

Low Temperature Phase for the $n = 6$ Compound

As we have already pointed out, at low temperature, the polarization values in the $n = 6$ compound are the lowest in the family of the studied compounds (see

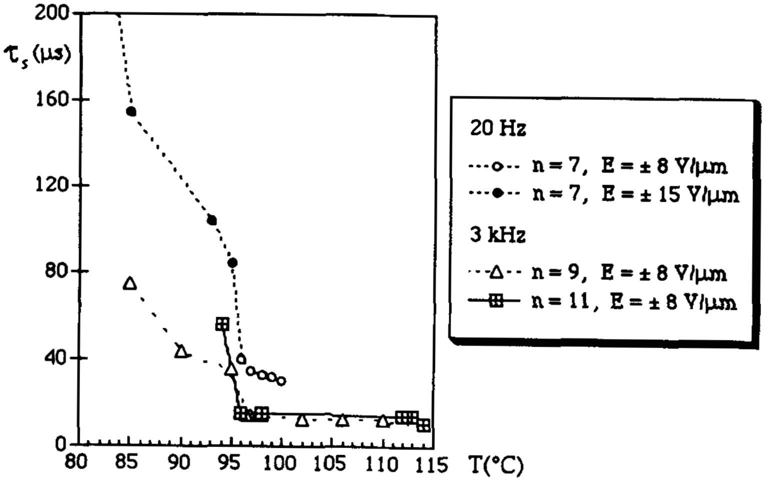


FIGURE 5 Response time τ_s for the compounds $n = 7$, 9 and 11, near the transition to the low temperature phase. τ_s was measured in the compound $n = 7$ with a signal frequency of 20 Hz, while the signal frequency for the compounds $n = 9$ and $n = 11$ was of 3 kHz.

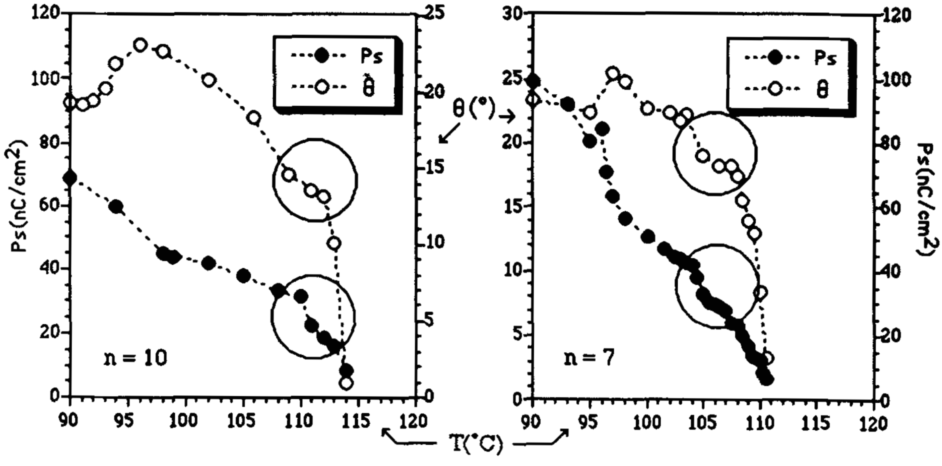


FIGURE 6 Anomalous behaviour in P_s and θ for the compounds $n = 7$ and $n = 10$, here identified by large opened circles. The "shoulder" in the tilt angle is accompanied by a steep increase in the polarization.

Figure 2b). On the other hand, we can see in Figure 2a that the tilt angle values are very similar to the one of group 1 compounds. As the system changes from the almost crystalline SmB phase to a ferroelectric phase, some disorientation is possible (the SmB phase itself is not always homogeneously oriented in the whole sample), so the alignment at low temperature is poor and higher fields are needed to align the molecules. The behaviour of $\theta(T)$ point out for the existence of a SmI*, but only a microscopic analyses can confirm this assumption. To avoid speculations, in the plot of Figure 1 we referred to this phase as Sm ?.

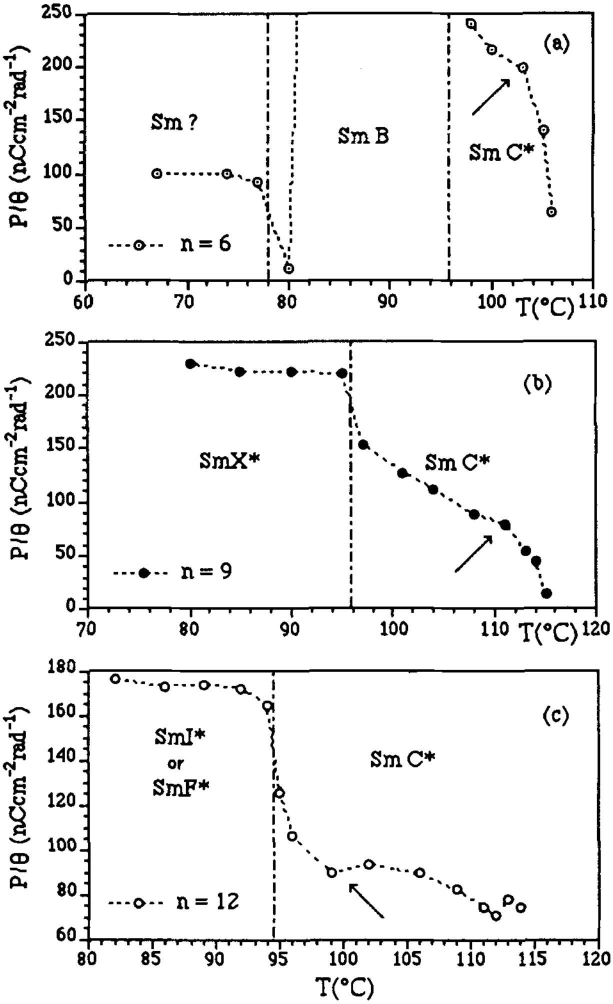


FIGURE 7 Temperature dependence of P/θ for the compounds (a) $n = 6$, (b) $n = 9$ and (c) $n = 12$. The arrows point to the anomaly in the SmC* phase, which is associated to an hypothetical transition between a ferrielectric phase (SmC^*_{fi}) and a ferroelectric phase (SmC^*_{fe}).

Coupling Between the Polarization (*P*) and the Tilt Angle (θ)

To investigate the coupling between these two parameters, we have calculated the ratio P/θ for all the compounds of the studied system. Figure 7 depicts P/θ for the compounds $n = 6$, 9 and 12. From these plots we can see that there is a slight tendency for a linear coupling in the low temperature phases (SmI* and SmF*), although this was not observed in all compounds. A pronounced temperature dependence is visible in the SmC* phase, which does not agree with the experimental results[4] or the theoretical models[5,6] presented in the literature. It is also possible to distinguish the anomaly in the SmC* phase (arrows in the figure), surely connected to the SmC^*_{fi} and to the SmC^*_{fe} phases previously mentioned.

For this serial of compounds it is clear that this analysis, still qualitative, is helpful to detect the different phases and it supports the results found for $\theta(T)$ and $P(T)$.

CONCLUSIONS

The importance of the electrooptical measurements in ferroelectric liquid crystals is well evidenced in this work, as we were able to study in detail the liquid crystal phases exhibiting a spontaneous polarization. The classification of groups of ordered ferroelectric smectic phases was possible, such as SmI* or SmF*, Sm ? and SmX*, as well as the study of the polar properties of the SmC* phase.

Acknowledgment

The authors are very much indebted to Professor Maria Renata Chaves for helpful discussions and revising the manuscript. This work was partially supported by "Instituto Nacional de Investigação Científica" and "Service Culturel Scientifique et de Coopération de l'Ambassade de France au Portugal."

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