

This article was downloaded by:

On: 25 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Liquid Crystals

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713926090>

### Effect of enantiomeric excess on thermotropic and electro-optical properties of ferroelectric sulphinate liquid crystals

Mohammed Zoubair Cherkaoui; Jean-Francois Nicoud; Yves Galerne; Daniel Guillon

Online publication date: 06 August 2010

**To cite this Article** Cherkaoui, Mohammed Zoubair , Nicoud, Jean-Francois , Galerne, Yves and Guillon, Daniel(1999) 'Effect of enantiomeric excess on thermotropic and electro-optical properties of ferroelectric sulphinate liquid crystals', *Liquid Crystals*, 26: 9, 1315 – 1324

**To link to this Article:** DOI: 10.1080/026782999203986

**URL:** <http://dx.doi.org/10.1080/026782999203986>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

# Effect of enantiomeric excess on thermotropic and electro-optical properties of ferroelectric sulphinate liquid crystals

MOHAMMED ZOUBAIR CHERKAOUI, JEAN-FRANÇOIS NICLOUD,  
YVES GALERNE and DANIEL GUILLON\*

Institut de Physique et Chimie des Matériaux de Strasbourg,  
Groupe des Matériaux Organiques, 23 rue du Loess, 67037 Strasbourg Cedex,  
France

(Received 22 January 1999; accepted 25 March 1999)

The liquid crystalline behaviour and the electro-optical properties of mixtures of two pure ferroelectric enantiomers are studied as a function of the enantiomeric excess and compared with those of the corresponding racemate. It appears clearly that, depending upon the value of the enantiomeric excess, distinct thermotropic sequences are observed. The transition temperatures change significantly, and an additional SmB phase is observed for the racemate and for the mixtures of neighbouring concentrations. Moreover, the variation of the spontaneous polarization as a function of the enantiomeric excess is found to be strongly non-linear. All these experimental observations show unambiguously that the thermotropic behaviour, the polar order, and consequently all the related electro-optical properties of the ferroelectric liquid crystal materials studied in the present work depend significantly upon the optical purity of the materials.

## 1. Introduction

During the last two decades, the possibility of developing electro-optical devices by using ferroelectric smectic C\* liquid crystals has aroused much interest in these systems [1]. The first generation of these materials was designed in order to obtain a large spontaneous polarization, which generally leads to a short response time. In this context, a large number of smectic C\* compounds has been synthesized with various polar groups and chiral centres [2–6]. The respective positions of the polar group and of the chiral centre along the molecular long axis, in order to induce a large spontaneous polarization, were found to be optimal when they were close to each other in the proximity of the aromatic rigid core [7]. Let us remark, nevertheless, that actual ferroelectric mixtures used in displays contain only a small quantity of chiral material.

The interest in ferroelectric liquid crystals then became focused on the synthesis of stable, broad-range room temperature smectic C\* compounds. In this case, the expression stability relates mainly to the chemical stability. But the principal prerequisite for the ferroelectricity is the introduction of chirality into the SmC compounds, and the ferroelectric electro-optical para-

meters are quantitatively associated with their optical purity. So in addition to their chemical stability, great care should be taken about the optical stability and the enantiomeric composition of the mesogens. In other words, for a given smectic C\* compound, it is important to know at which enantiomeric excess (ee) the ferroelectric quantities have been measured, as has already been pointed out [8]. However, only a few publications have paid attention to this point, the general assumption being that the measured ferroelectric properties correspond to the optically pure material, at least when the starting materials come from natural chiral compounds. Several reasons may explain why ee values are not generally quoted in papers reporting the properties arising from chirality in liquid crystalline materials. (a) The classical method for the determination of ee (when the maximum specific optical rotation is unknown) is to prepare diastereomers that are quantitatively analysed by conventional methods (GLC, HPLC and NMR). However most chiral liquid crystal compounds cannot be easily derivatized into diastereomers, which renders this method most often inoperative. (b) The use of chiral stationary phases in GLC and HPLC analyses should in principle give satisfactory results. But the fact is that it takes much trial and error to find a good chiral phase, and once this phase is discovered, if any, it may not be good for other series of chiral LCs. The cost of such investigations is often too high for many laboratories.

\* Author for correspondence; e-mail: guillon@michelangelo.u-strasbg.fr

(c) The successful use of chiral shift reagents for the ee excess determination by NMR depends on the association of the chiral compound with the shift reagent. This does not occur for many chiral liquid crystalline compounds, so the method cannot be generalized. For all these reasons, most research papers on the mesomorphic and electro-optic properties of ferroelectric liquid crystals report results on materials where the ee values are assumed to be the same as those of the starting materials or of various intermediates. In fact, especially when studying a new series of chiral liquid crystalline materials, we consider that it is important to know the actual optical purity of the compounds whenever it is possible. It is also important to check if the chiral smectic C compound could undergo partial chemical or thermal racemization during the initial synthesis, or during the investigations of the mesomorphic and electro-optical properties. In the work reported here, the use of chiral NMR shift reagents proved to be the method of choice for the ee measurements on our sulphinate derivatives, both as optically pure compounds and as chiral mixtures.

From another point of view, it is well known that a binary mixture of enantiomers in the crystalline state may generally lead to three fundamental types of mixtures according to whether the system is a conglomerate, a racemic compound or a pseudo-racemate [9]. The case of liquid crystals is more complicated because of the miscibility of the enantiomers in the mesomorphic state, even if the equimolar mixture of the two enantiomers of the liquid crystalline compound is a conglomerate or a racemic compound, and not necessarily a pseudo-racemate. From general observation of binary mixture phase diagrams in the solid state, it is well known that the racemate and its optically pure enantiomer are not equivalent thermodynamic systems. Indeed, apart from the case of ideal solid solution, the transition temperatures change as a function of the enantiomeric excess. This is due to the fact that the packing of chiral molecules differs for pure enantiomers on the one hand and for the racemate on the other, simply as a consequence of

geometry. In the former case, the crystal lattice is enantiomorphous. In the latter case, the crystal lattice generally possesses elements of inverse symmetry which transform an object into its mirror image. Therefore, the initial orientation of the molecules in the pure enantiomer may change upon decreasing the enantiomeric excess, leading to a change of the molecular packing. In the liquid crystalline state, this can additionally induce a modification of the molecular motions. Then, when changing the enantiomeric excess, the initial polar order which is driven by different kinds of interactions between neighbouring molecules, may be affected. Consequently, the anisotropic distribution of the effective transverse dipole moments, responsible for the spontaneous polarization, can also be affected. Hence, the extrapolation of the spontaneous polarization value from a given enantiomeric concentration to the optically pure form should take into account not only the linear dipole moment compensation effect (between *R* and *S* molecules), but also the behaviour related to the variation of the polar order.

Generally one can expect three kinds of variation of the spontaneous polarization when changing the enantiomeric excess, figures 1(a-c). The simplest is the linear variation, figure 1(a), which can be retained only in the case of the ideal solid solution, for which the variation of the enantiomeric excess has no influence on the thermodynamic properties. The two other possible variations, figures 1(b,c), illustrate the conjugated effects of compensation of the dipole moments when decreasing the enantiomeric excess and the variations of the polar order due to the change of interactions between molecules; indeed, depending upon ee, the environment of each molecule will vary (number of *R*(*S*) molecules around one *S*(*R*) molecule). Such a change may then induce a non-linear behaviour of the physical properties as a function of enantiomeric excess. In the first case—positive curvature, figure 1(b)—the spontaneous polarization increases slowly with ee (when ee is small) and then increases more and more rapidly when ee becomes close

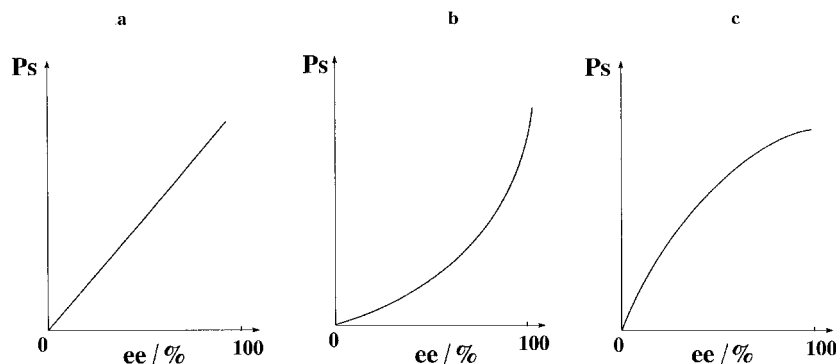


Figure 1. Three possible variations of the spontaneous polarization ( $P_s$ ) with enantiomeric excess (ee) (the curvatures are arbitrary).

to 100%; this is an example of a polar order which is very sensitive to the enantiomeric excess. In the second case—negative curvature, figure 1(c)— $P_s$  begins to increase strongly when ee is small and has a tendency to saturate when ee becomes close to 100%; the polar order can then be considered as optimized for high enantiomeric excesses, even if there is still a dipole compensation effect.

Only a few studies where the effect of the enantiomeric excess is mentioned have been reported [10–14]. The general view is that the transition temperatures are not strongly modified between the racemate and the optically pure compounds, and that the values of the spontaneous polarization vary linearly from 0 for the racemate to a finite value for the corresponding pure enantiomer [10, 13]. This linear extrapolation takes into account only the compensation effect of the overall molecular dipole moment. In addition, a simple theoretical model [15], based on steric and electrostatic interactions, predicts a linear dependence of the spontaneous polarization for chiral-racemic mixtures, as a function of enantiomeric excess when the variation of the smectic  $C^*$  to smectic A phase transition temperature is small enough when going from the optically active isomer to the racemate.

However, some more specific behaviours have been reported. In reference [11] a correlation between the thermodynamic behaviour and the spontaneous polarization is found, and it is stated that the variation of the polarization is responsible for the change of the transition temperatures between mesophases when varying the enantiomeric excess. But one can ask if such a behaviour is only due to ferroelectricity, since it can also be observed with non-ferroelectric phases [16]. On the other hand, a non-linear variation of the spontaneous polarization as a function of the enantiomeric excess (positive curvature) has been observed [12] for FLC mixtures of an *S*-enantiomer and its corresponding racemate, based on a leucine chiral group. In this case, the authors described the variations of the spontaneous polarization using a theoretical model based on different contributions induced by host–host, host–dopant and dopant–dopant interactions. Their model can lead to both linear and non-linear variations of  $P_s$  as a function of enantiomeric excess. Finally, one should also mention the case of optically active isomers where two additional ferroelectric mesophases are observed in comparison with the racemic mixture [14]. This behaviour has been interpreted for the chiral compounds in terms of different dipolar couplings in the ferroelectric phases.

In order to obtain further insight into the effects of enantiomeric excess on both mesomorphic and electro-optical properties of ferroelectric liquid crystals, we consider in the present work a pair of FLC enantiomers

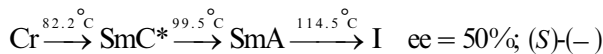
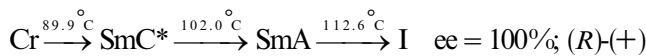
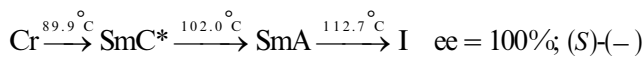
bearing a sulphinate functionality as the chiral group in the following *m*-BTS-*O*<sub>*n*</sub> series:



These materials were found to be thermally and optically stable and to exhibit the ferroelectric smectic  $C^*$  phase over a large temperature range [17]. They have been synthesized according to a method reported recently, involving an asymmetric synthesis which was developed to obtain optically pure enantiomers [18, 19]. These enantiomers were further recrystallized in acetone; the enantiomeric excess, the optical rotatory power and the transition temperatures were measured after each recrystallization until their values no longer varied. In this way, it can be reasonably assumed that the corresponding enantiomers were optically pure.

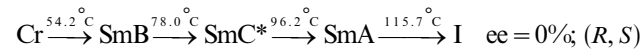
## 2. Thermotropic properties and enantiomeric excess

Comparison of the thermotropic sequences of the pure enantiomers 12-BTS-O8 ( $m = 12$ ;  $n = 8$ ) and their own mixture of ee = 50% revealed a notable difference in the thermal stability of the Sm $C^*$  and SmA mesophases as shown below:



For the optically pure compounds, the Sm $C^*$  and SmA mesophases are stable over a thermal range of 13 and 10.7 K, respectively. For the 50% enantiomeric mixture, a higher stability of the Sm $C^*$  and SmA mesophases is obtained (17.3 and 15 K, respectively). This suggests that the phase diagram between the two pure enantiomers does not exhibit the behaviour of an ideal solid solution. Furthermore, the DSC diagram of the above mixture shows a first order transition at 71.5°C, before the Cr–Sm $C^*$  transition (82.2°C) and could be attributed to the melting of a eutectic composition.

For the racemate, spectacular modifications of the thermotropic mesomorphism are evidenced:



In fact, this compound exhibits an additional SmB mesophase, stable over a large temperature range and easily characterized by its typical focal-conic texture when observed in the polarizing microscope. In the same way, the SmC–SmA and SmA–isotropic transition temperatures are affected. The X-ray diffraction patterns

show a classical variation of the lamellar spacing for the racemate (figure 2) when going from the SmA to the SmC mesophase, until a temperature of 77°C where the layer spacing increases abruptly to 42.7 Å and then vary slightly in the thermal range of the SmB mesophase. For the pure enantiomer (figure 3), no SmB mesophase is observed and the amplitude of the variation of the lamellar spacing in the SmC\* mesophase is higher compared with that observed for the racemate. For the former, the tilt angle deduced from the ratio  $d_{\text{SmC}}/d_{\text{SmA}} = \cos \theta$  is consequently smaller than for the pure enantiomer at the same distance from the SmA–SmC transition temperature ( $T_{\text{AC}}$ ) (figures 4 and 5). Here, it is interesting to point out that the thermal stability of the SmA mesophase is higher for the racemate than for the pure enantiomer, whereas it is intermediate for the mixture corresponding to  $ee = 50\%$ . These results seem to indicate that there is a tendency for the stabilization of the orthogonal mesophase as the enantiomeric excess decreases.

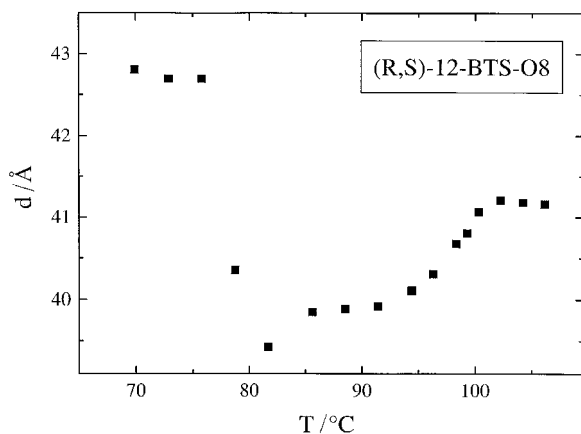


Figure 2. Smectic layer spacing as a function of temperature for the racemate.

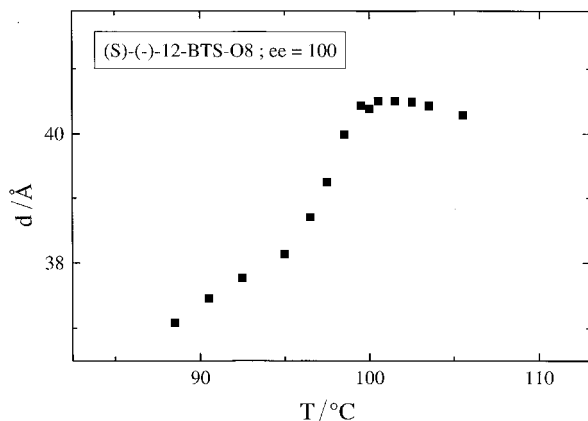


Figure 3. Smectic layer spacing as a function of temperature for the pure enantiomer.

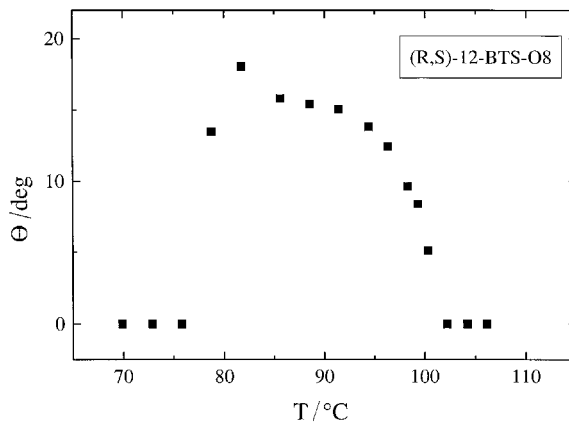


Figure 4. Tilt angle of the molecules as a function of temperature for the racemate.

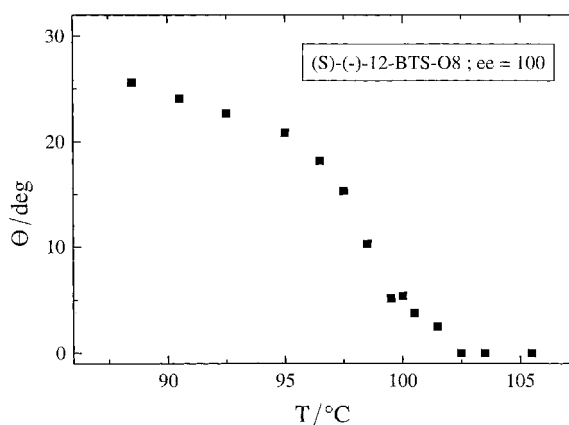


Figure 5. Tilt angle of the molecules as a function of temperature for the pure enantiomer.

In order to understand more explicitly the occurrence of the SmB mesophase for the racemate and at the same time to examine the effect of the enantiomeric excess on the polymorphism, the binary mixture phase diagram of the two 12-BTS-O8 enantiomers has been investigated. As shown above, by studying the thermotropic sequence of the pure enantiomers, of the  $ee = 50\%$  mixture and of the racemate, useful information is already available for describing the general aspects of the binary mixture phase diagram. First, the melting points of the pure enantiomers are higher than that of the mixture corresponding to  $ee = 50\%$ . Second, this latter mixture shows a first order transition peak before the transition to the SmC\* phase, which is not observed in the case of the pure enantiomers or in the case of the racemate. We then anticipate the presence of a eutectic point in the phase diagram which is consequently not consistent with the existence of a solid solution of the two enantiomers.

The determination of the transition temperatures was performed mainly by differential scanning calorimetry (DSC) which is considered as the best adapted technique

for the construction of the phase diagrams. Concerning the determination of the enantiomeric excess of the binary mixtures, it was found that the preparation of mixtures for the construction of binary phase diagrams by using a weighing method (currently employed in the literature) may induce errors, especially when the weighed substances are below 100 mg. In this work, the direct determination of the enantiomeric excess by  $^1\text{H}$  NMR, using a chiral shift reagent [17–19], was adopted. Enantiomeric excesses of the investigated mixtures were then measured before and after experiments and were found to be the same. We considered a 100% ee was reached when only one enantiomer was detected in the NMR spectrum in the presence of a chiral shift reagent. Let us note, however, that for such an observation, there may in fact remain 1 to 2% of the other enantiomer.

The phase diagram so obtained in this manner is represented in figure 6. The racemate is a racemic compound, since its clearing point is higher than that of the pure enantiomers. The composition corresponding to  $ee = 33.4\%$  presents a eutectic point which defines the stability domain of the SmB mesophase on each side of the racemate for which the SmB–SmC\* transition temperature is maximal. The SmC\*–SmA transition temperature ( $T_{AC}$ ) is maximal for the pure enantiomer and decreases continuously with decreasing enantiomeric excess, while the clearing temperature increases at the same time. The highest stability of the SmA mesophase is obtained for the racemate and is an indication of the stabilization of the non-tilted mesophases as previously shown by the X-ray diffraction experiments (figures 2–5). Furthermore, it is interesting to note the large effect on the stability of the SmC\* mesophase induced by the enantiomeric excess. Thus, at the eutectic point ( $ee = 33.4\%$ ), the smectic SmC\* mesophase is stable over

a large temperature range up to 27 K. This stability decreases considerably (13 K for the pure enantiomer) with increasing the enantiomeric excess. On the contrary, for the compositions between the racemate and the eutectic point, the stability of the SmC\* mesophase decreases with decreasing enantiomeric excess. This behaviour can be attributed to the occurrence of the smectic B phase. Indeed, thermodynamical fluctuations of the SmB phase start at the eutectic point, and by decreasing the enantiomeric excess the tendency to stabilize the non-tilted mesophase increases.

The thermotropic behaviour shown in the binary mixture phase diagram can be qualitatively deduced from optical microscope observations on a contact preparation sample. The experiment consists in putting the two enantiomers on opposite sides of a microscope cell. The two samples are allowed to melt and gradually penetrate into the cell by capillarity until each enantiomer occupies approximately half the cell area. They are in close contact with one another in the middle (contact region). The enantiomers are then allowed to cool until the whole preparation crystallizes. The preparation is made of pure *S* enantiomer (left side), pure *R* enantiomer (right side), and all possible intermediate mixtures in between (contact region). It is then slowly heated while being observed in the polarizing light microscope.

The results obtained are in perfect agreement with those deduced from the binary mixture phase diagram. In fact, at a temperature of  $68^\circ\text{C}$ , the two pure enantiomers are in the crystalline state (figure 7.1), while the contact region appears as a vertical liquid crystalline zone with a focal-conic texture characteristic of the SmB mesophase. Moreover, at the same temperature and by using a homeotropic alignment, it is possible to obtain the contact zone (figure 7.2) in an extinct state, indicating that the smectic mesophase is characterized by a layered

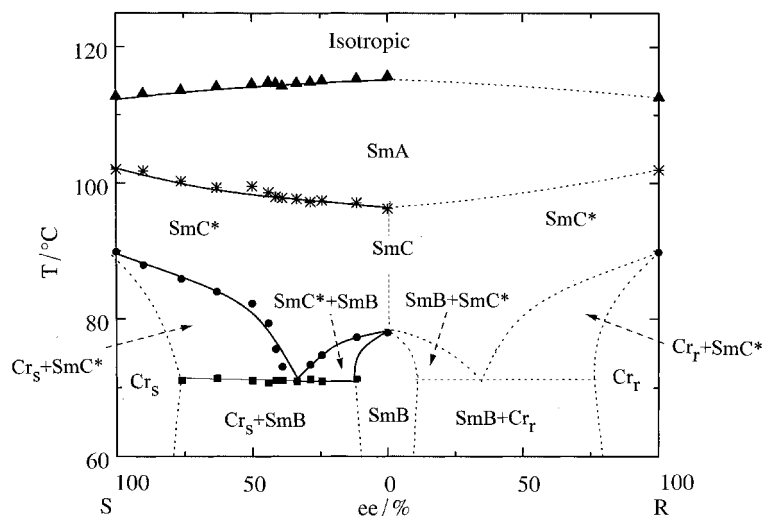


Figure 6. Binary phase diagram between the two pure enantiomers.

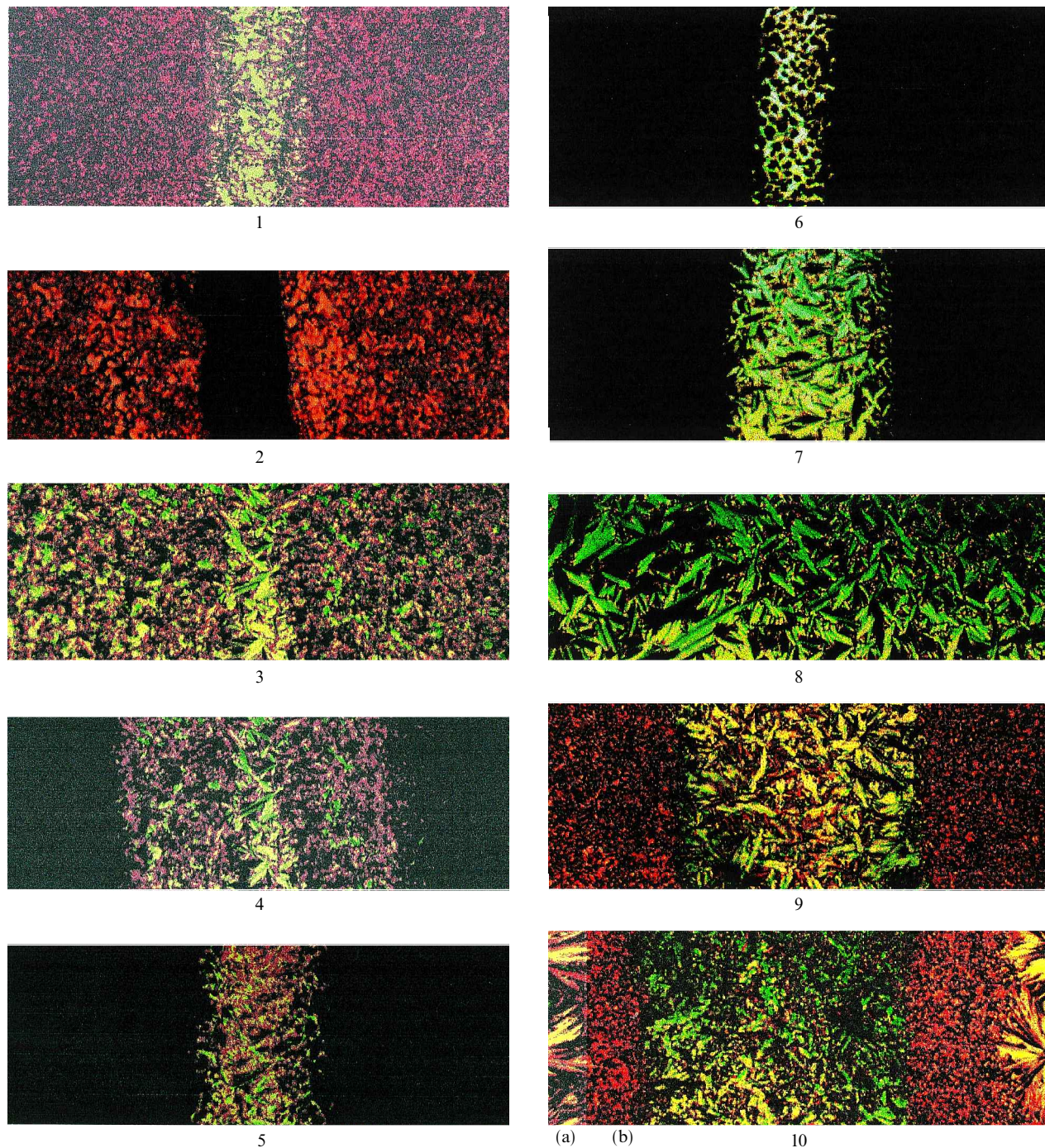


Figure 7. Individual photomicrographs (1–10) at particular temperatures (see text for details) of the contact zone in a contact preparation prepared from the two pure enantiomers.

structure where the molecules are normal to the smectic planes (A or B orthogonal smectic phases). By increasing the temperature to 105°C the whole sample exhibits the SmA mesophase. Nevertheless, the contact zone can be optically distinguished from the left and the right zones (figure 7.3). This is due to the fact that the thermotropic sequences of the mixtures included between the

racemic compound and the eutectic point and that of the mixtures of higher enantiomeric excess are not the same. For the former case the thermotropic sequence is SmB–SmC\*(SmC)–SmA while for the latter the sequence is Cr–SmC\*–SmA. By gradually increasing the temperature from the SmA mesophase to the isotropic phase (figures 7.4 and 7.5), the transition starts simultaneously

on the left and right sides (high enantiomeric excess) of the sample and progresses continuously toward the contact zone (low enantiomeric excess). On the contrary, by slowly decreasing the temperature from the isotropic liquid to the SmA mesophase (figures 7.6 to 7.8), the transition begins at the contact zone (low enantiomeric excess) and progresses continuously and simultaneously to the left and right (high enantiomeric excess). These observations reproduce exactly the liquidus curves of the binary mixture phase diagram. In fact the clearing point increases as the enantiomeric excess decreases. In addition, it is interesting to point out that contrary to the situation illustrated in figure 7.3, the SmA phase texture developed by cooling from the isotropic liquid (figure 7.8) is regular, without any distinction between the contact zone and the left and right sides. Here, all the enantiomeric mixtures exhibit the same isotropic–SmA transition.

By rapid cooling from the SmA mesophase to a temperature of 68°C (figure 7.9), the same initial situation of the preparation is recovered (figure 7.10). In fact, in agreement with the phase diagram, crystallization starts simultaneously from the left and right sides and progresses continuously toward the median line of the sample, then stops, delimiting the two sides of the contact zone. This latter has become larger than it was initially. This is not surprising in the sense that the previous heating of the sample for some hours in the isotropic state has induced a better diffusion of the two enantiomeric forms from one to the other, yielding therefore a larger contact zone. Nevertheless, further successive heatings of the preparation into the isotropic state do not further alter the width of the contact zone. This means that the diffusion is stopped at the heterogeneous domain of coexistence of the crystalline and SmB phases. In fact, by slowly cooling the SmA mesophase to 68°C, two distinct crystalline zones (a) and (b) are observed

(figure 7.10) on the left and right sides of the contact area zone containing focal-conic textures. The first crystalline zone (a) corresponds to the beginning of the crystallization, and exhibits a spherulitic texture. This corresponds to the crystallization of pure enantiomers and of high enantiomeric excess mixtures. In the second zone (b), the texture is not as well developed and is attributed to a heterogeneous zone of coexistence of the crystalline and SmB phases. In this latter zone the mixtures crystallize like the eutectic system.

### 3. Electro-optical properties as a function of the enantiomeric excess

The enantiomeric excess dependence of the spontaneous polarization  $P_s$  at different  $T_{AC}-T$  for the binary mixtures of (*R*)- and (*S*)-12-BTS-O8 is shown in figure 8. For the mixtures of ee below 30%, the measured values of the spontaneous polarization are small. In fact, for three compositions (ee = 6, 11 and 27%) the values of  $P_s$  do not exceed 3 to 4 nC cm<sup>-2</sup>, even near the SmC\*–SmB transition; it is interesting to note that the critical electric field was relatively high and increased as the enantiomeric excess was lowered. Indeed it was not possible to apply an electric field higher than 10V μm<sup>-1</sup>, because of the occurrence of important ionization of the samples. For the pure enantiomer, a high spontaneous polarization of about 270 nC cm<sup>-2</sup> was measured near the transition to the crystal (12.5°C). Here, it is important to stress that a decrease of the enantiomeric excess of only 10% induces a large decrease of the spontaneous polarization of about 50%.

As shown in figure 8, the variation of the spontaneous polarization is not a linear function of the enantiomeric excess. This result is not surprising since the mixture of the two sulphinate enantiomers is not ideal. In fact, as was shown in the phase diagram, the thermotropic properties are greatly dependent on the enantiomeric

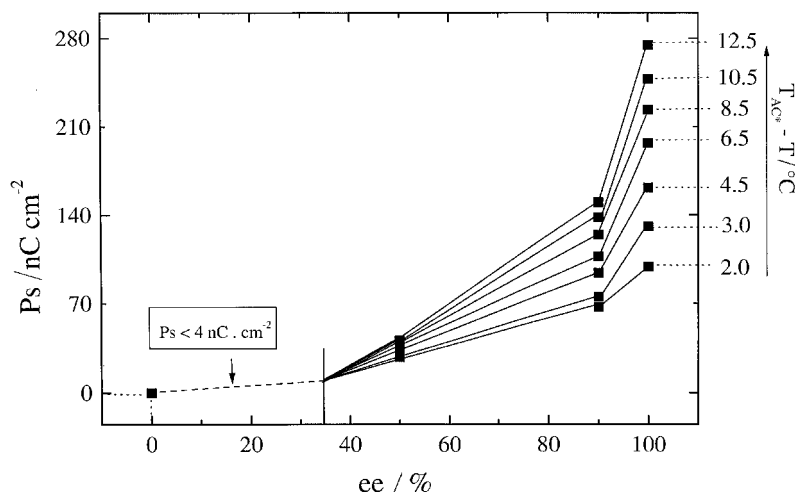


Figure 8. Spontaneous polarization as a function of the enantiomeric excess at different temperatures.



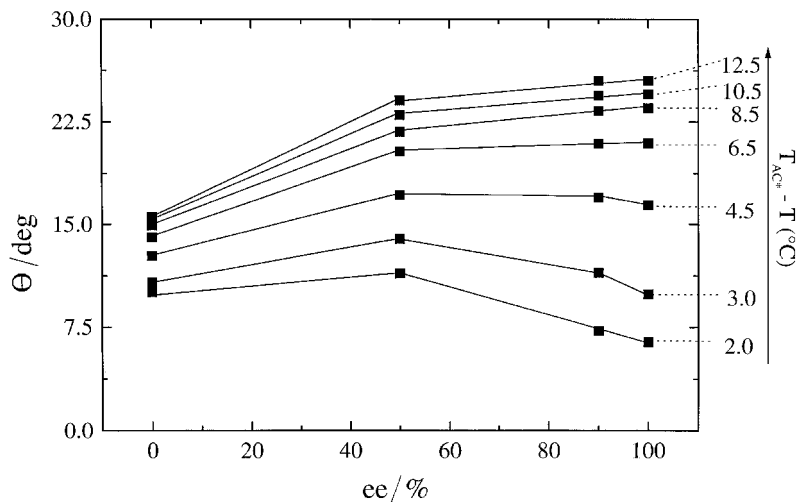


Figure 9. Tilt angle of the molecules within the smectic C\* phase as a function of the enantiomeric excess at different temperatures.

excess. When this decreases from 100 to 33.4%, a significant decrease of the Cr–SmC\* transition temperature is induced. This result can be explained by the increase of steric and polar effects leading to the occurrence of the eutectic point. Therefore, the decrease of the enantiomeric excess can also influence the polar order in the SmC\* mesophase in the same way as the dipole moment compensation. These two conjugated negative effects then induce a dramatic decrease in the spontaneous polarization. For the mixtures ranged between the eutectic (33.4%) and the racemic compound (0%), even if the steric and polar effects are minimized, the tendency in this range is for the stabilization of the orthogonal mesophase to the disadvantage of the tilted one. These effects are illustrated by non-equivalent variations of the tilt angles as a function of temperature and of enantiomeric excess. As shown in figure 9, the tilt angles are globally smaller for the racemic compound far from the SmC\*—SmA transition temperature ( $T_{AC}$ ) whereas they increase when the enantiomeric excess increases. Near  $T_{AC}$  the tilt angles are on the contrary decreasing. Therefore the coupling between the spontaneous polarization and the tilt angle is not linear as a function of the enantiomeric excess. The origin of this non-linearity may be the anisotropy of the interactions between molecules of the same handedness ( $R,R$  or  $S,S$ ) and of opposite handedness ( $R,S$ ), as proposed recently [20].

Finally the response times,  $\tau$ , measured for three compositions (50, 90 and 100%) also show a non-linear variation as the enantiomeric excess changes (figure 10). For the 50% mixture and under an electric field of  $10 \text{ V } \mu\text{m}^{-1}$ , the switching process is relatively slow and reaches  $50 \mu\text{s}$  near the transition to the crystal. For the enantiomers of  $ee = 90$  and  $100\%$ , shorter response times are measured; particularly for the pure enantiomer,  $\tau$  is  $20 \mu\text{s}$  near the transition to the crystal and only a few  $\mu\text{s}$  near the transition to the SmA phase.

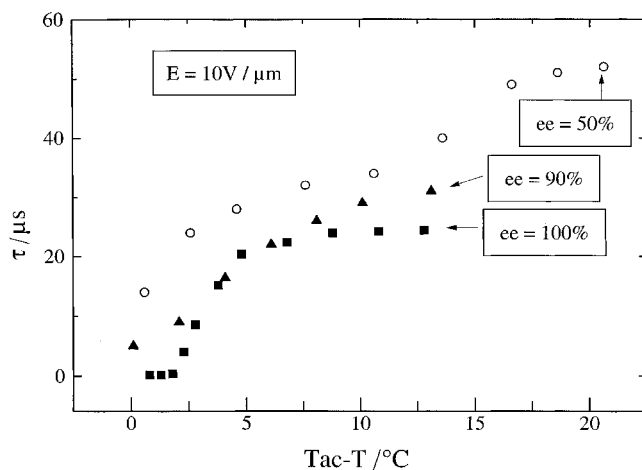


Figure 10. Switching response times as a function of temperature for three values of enantiomeric excess.

#### 4. Conclusion

We have shown that the variation of the enantiomeric excess has large effects on the thermodynamic properties of the ferroelectric chiral sulphinyl compounds investigated. These effects manifest themselves by distinct thermotropic sequences over all the enantiomeric concentration range. The transition temperatures are in fact greatly affected, and an additional SmB phase is observed for the racemate and its neighbouring compositions. This latter behaviour could be explained by a loss of asymmetry and by a tendency to stabilize the orthogonal phases as the enantiomeric excess decreases. The polar order is consequently greatly affected and in turn, leads to a non-linear dependence of the electro-optic quantities upon enantiomeric excess. Finally, the most important conclusion of this study is that the thermotropic behaviour, the polar order, and consequently all the related electro-optical properties of

ferroelectric liquid crystals may depend significantly on the optical purity of the materials.

In conclusion, it should be mentioned that Girard and Kagan recently published a review of ten years of investigation of non-linear effects in asymmetric synthesis and stereoselective reactions [21]. When using a chiral catalyst with a given enantiomeric excess, the chiral product finally obtained does not necessarily have the same enantiomeric excess as the chiral auxiliary of the catalyst. In many enantioselective reactions, the enantiomeric excess of the product is not proportional to the enantiomeric excess of the chiral auxiliary. Both (+)-non-linear and (-)-non-linear effects have been observed. Our study of the non-linear dependence of the physical properties of FLCs ( $P_s$ , tilt angle, response time) with the enantiomeric excess of the mesogen, is an addition to such observations of non-linear effects in experiments using chiral auxiliaries.

### 5. Experimental

Thermodynamical values of the phase transitions were measured by differential scanning calorimetry using a Perkin-Elmer DSC-7 apparatus and by polarized optical microscopy using a Leitz microscope equipped with a Mettler hot-stage.

X-ray diffraction experiments were carried out on powder samples in Lindemann capillaries. Diffraction patterns were recorded either photographically or using an INEL CPS-120 curved position-sensitive detector, with radiation from an INEL X-ray generator. Photographic detection was made using a Guinier focusing camera equipped with a bent quartz monochromator (Cu  $K_{\alpha}$  radiation).

The measurements of the spontaneous polarization,  $P_s$ , of the tilt angle,  $\theta$ , and of the response times,  $\tau$ , were carried out with a cell consisting of two polytetrafluoroethylene (teflon)-coated ITO-conducting glass plates [22]. The cell thickness was determined by capacity measurements. The liquid crystalline compound was then introduced into the cell by capillarity in its isotropic phase. A good orientation was achieved by slowly cooling from the isotropic state to the SmC\* phase without an applied electric field. The spontaneous polarization measurements were made on a calibrated standard bench by applying a triangular voltage across the cell with a wave frequency of 500 Hz. The ferroelectric signal (current versus time) was recorded on a HP 54501A oscilloscope connected to a microcomputer. Knowing the active area of the cell, the values of  $P_s$  were obtained through the integration of the characteristic peak.

On these well aligned samples, the tilt angle measurements were made as a function of temperature using a microscope with crossed polarizers, by application of a rectangular wave voltage of frequency about 0.1 Hz.

The tilt angle is equal to half the angle between the two extreme optical directions corresponding to the two polarities of the applied electric field. The electro-optical response times,  $\tau$ , were measured simultaneously with the spontaneous polarization. They correspond to the time delay of the ferroelectric peak with reference to the electric field applied in the rectangular waveform.

The authors wish to thank Mr Benoît Heinrich for his assistance in the X-ray diffraction measurements.

### References

- [1] CLARK, N. A., and LAGERWALL, S. T., 1991, in *Ferroelectric Liquid Crystals* (Gordon and Breach Science Publishers), p. 409.
- [2] (a) WALBA, D. M., VOHRA, R. T., CLARK, N. A., HANNDSCHY, M. A., XUE, J., PARMAR, D. S., LAGERWALL, S. T., and SKARP, K., 1986, *J. Am. chem. Soc.*, **108**, 17 424. (b) HANNDSCHY, M. A., JOHNSON, K. M., MODDEL, G., and PAGANO-STAUFFER, L. A., 1988, *Ferroelectrics*, **85**, 279.
- [3] SCHEROWSKY, G., and GAY, J., 1989, *Liq. Cryst.*, **5**, 1253.
- [4] (a) WALBA, D. M., GAY, J., EIDMAN, K. F., and HALTIWANGER, R. C., 1989, *J. org. Chem.*, **54**, 4939; (b) KUSUMOTO, T., HANAMOTO, T., HIYAMA, T., TAKEHARA, S., SHOJI, T., OSAWA, M., KURIYAMA, T., NAKAMURA, K., and FUJISAWA, T., 1991, *Chem. Lett.*, 311.
- [5] SIERRA, T., ROS, M. B., OMENAT, A., and SERRANO, J. L., 1993, *Chem. Mater.*, **5**, 938.
- [6] (a) NAKAUCHI, J., UEMATSU, M., SAKASHITA, K., KAGEYAMA, Y., HAYASHI, S., IKEMOTO, T., and MORI, K., 1989, *Jpn. J. appl. Phys.*, **28**, L1258. (b) KODEN, M., KURATATE, K., FUNADA, F., AWANE, K., SAKAGUCHI, K., SIOMO, Y., and KITAMURA, T., 1990, *Jpn. J. appl. Phys.*, **29**, L981. (c) SAKASHITA, K., SHINDO, M., NAKAUCHI, J., UEMATSU, M., KAGEYAMA, Y., HAYASHI, S., IKEMOTO, T., and MORI, K., 1991, *Mol. Cryst. liq. Cryst.*, **199**, 119.
- [7] (a) GOODBY, J. W., and LESLIE, T. M., 1984, *Mol. Cryst. liq. Cryst.*, **110**, 175. (b) GOODBY, J. W., PATEL, J. S., and CHIN, E., 1987, *J. phys. Chem.*, **91**, 5151.
- [8] GOODBY, J. W., 1991, in *Ferroelectric Liquid Crystals*, (Gordon and Breach Science Publishers), p. 158; Goodby, J. W., invited lecture (C1-I1) at 17th International Liquid Crystal Conference, Strasbourg (19-24 July 1998).
- [9] JACQUES, J., and COLLET, A., 1991, *Enantiomers Racemates and Resolution* (Malabar, Florida: Krieger Publishing Company).
- [10] BAHR, C. H., HEPPKE, G., and SABASCHUS, B., 1988, *Ferroelectrics*, **84**, 103.
- [11] BAHR, C. H., HEPPKE, G., and SABASCHUS, B., 1991, *Liq. Cryst.*, **9**, 31.
- [12] DÜBAL, H. R., ESCHER, C., and OHLENDORF, D., 1988, *Ferroelectrics*, **84**, 143.
- [13] CHANDANI, A. D. L., OUCHI, Y., TAKEZOE, H., and FUKUDA, A., 1988, *Jpn. J. appl. Phys.*, **27**, L276.
- [14] GOODBY, J. W., and CHIN, E., 1988, *Liq. Cryst.*, **3**, 1245.
- [15] GINZBURG, V. V., SHAO, R., CLARK, N. A., and WALBA, D., 1994, *SPIE Proc.*, **2175**, 102.
- [16] LECLERCQ, M., BILLARD, J., and JACQUES, J., 1969, *Mol. Cryst. liq. Cryst.*, **8**, 367.

- [17] CHERKAOUI, M. Z., NICOUD, J. F., and GUILLON, D., 1994, *Chem. Mater.*, **6**, 2026.
- [18] CHERKAOUI, M. Z., and NICOUD, J. F., 1995, *New J. Chem.*, **19**, 851.
- [19] NICOUD, J. F., and CHERKAOUI, M. Z., 1995, *Tetrahedron Asymmetry*, **6**, 1941.
- [20] OSIPOV, M., and GUILLON, D. (to be published).
- [21] GIRARD, C., and KAGAN, H. B., 1998, *Angew. Chem. Int. Ed.*, **37**, 2923.
- [22] (a) CHERKAOUI, M. Z., 1993, PhD thesis, University Louis Pasteur, Strasbourg, France; (b) HUBERT, P., DREYFUS, H., GUILLON, D., and GALERNE, Y., 1995, *J. Phys. II Fr.*, **5**, 1371.