Insights on some chiral smectic phases

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Abstract. Combining layered positional order as smectic order and chirality can generate complex architectures since twist parallel to the layers is not allowed. This paper will review some new experimental results on different phases resulting from the competition between smectic positional order and twist orientational order. It concerns the TGB_A and the NL*, that is the liquid line phase as well as the SmQ phase. Chiral effects in the isotropic phase will also be discussed.

Keywords. Liquid crystals; smectics; chirality; frustrated phases; twist grain boundary phases.

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1. Introduction

The presence of one or several chiral centres in a mesogen molecule can deeply modify the organization of the mesophases. Indeed the chiral centre transforms local uniform orientational order into a twisted one. This local orientational order leads to the well-known cholesteric phase that corresponds to the original nematic phase. But twisting a smectic phase is not as simple as twisting a nematic phase. Due to smectic ordering, the molecules are more or less packed in layers and smectic phases can be seen as a stacking of fluid layers although permeation of molecules in between the layers is allowed. However, twisting the normal to a surface along any direction along the surface is geometrically impossible. Therefore in smectic phases, twist is easy only along the normal to the layers as in the SmC* phase in which the molecules are tilted with respect to the normal to the layers. But in the SmA phase, local twist is not compatible with the layered structure. Both order can only co-exist in complex architectures like the TGB_A phase [1]. In this phase, perfect smectic grains, with no twist inside each grain, are piled along a preferred axis parallel to the layers. Twist appears in between the grains and is concentrated in walls separating the grains. For low twist angle between the grains, these boundaries are just walls of screw dislocation regularly spaced in the boundary, and the architecture is more complicated for large twist angles [2]. In a more general way and in many cases, the only way to combine chiral orientational order and some smectic order requires the presence of defects like in the TGB phase. Complex architectures can then be observed. They imply permanent and stable structural defects and are generally observed close or not far from the isotropic phase where these defects do not cost too much from an energetical point of view. The aim of this paper is to sketch a few important features of some of these architectures

(the NL* phase, the SmQ phase) and some effects in the isotropic phase based on recent experimental results.

For the TGB_A phase, recent X-ray experiments [3] show the precise organization of the defects from the TGB_A phase to the cholesteric phase through the chiral liquid-line phase (or NL* phase). When Galerne and Liebert [4] discovered the SmC_A phase, first called SmO, they observed in the chiral compound between the isotropic phase and this smectic phase, a mesophase (called SmQ) exhibiting a high degree of ordering with many Bragg peaks in the X-ray patterns at low angle scattering but with a liquid signature at a large angle, that is at short distances. This phase disappears by adding a small quantity of the enantiomeric compound and is thus clearly related to chirality. Levelut *et al* [5] presented a detailed study of this phase exhibited by various compounds. Four different space groups have been reported: three of them are tetragonal ($I422$, $I4_122$, $P4_122$) and one is hexagonal ($P6_222$). Different geometrical models have been proposed to understand such 3D structures. Some recent X-ray and optical experiments on a new compound [6] exhibiting such a phase can discriminate between the two models proposed for one of the symmetry groups. The competition between smectic order and chirality also disturbs the isotropic phase. The clearing point of chiral compounds can be several degrees lower than the clearing point of the corresponding racemic compound when a direct transition from the isotropic phase to a smectic phase occurs, whatever the smectic phase is (SmA, SmC_A^*, SmC^*, ...). More surprising is the frequent presence of a bump in DSC measurements on the chiral compound located close to the clearing point temperature of the racemic one. This bump is clearly linked to changes in other physical features of the liquid phase such as the optical activity [7, 8]. This paper will also report a change in the local smectic order which is surprisingly different from the smectic order of the neighbouring smectic phase. This rules out the interpretation of the increase in optical activity in terms of fluctuations linked to the lower temperature phase.

2. From the TGB_A phase to the cholesteric phase through the NL* phase

An elegant analogy between superconductors and smectic liquid crystals was pointed out in 1972 by de Gennes [9]. A more spectacular illustration of this analogy was proposed in 1988 when Renn and Lubensky [1] theoretically worked out the structure of an intermediate phase between the smectic phase and the cholesteric phase associated with the type II limit. This new phase (figure 1), analogous to the flux phase of superconductors was called the twist grain boundary (TGB) phase. A twisted lattice of screw dislocations was proposed as the counterpart of the hexagonal lattice of flux lines. The complex structure of the TGB phase was experimentally discovered shortly afterwards and extensively studied [10–13]. In the same way as thermal fluctuations can cause the regular vortex lattice to melt producing a melted phase where the lines stay in average in the same common direction, the screw dislocation lattice is no longer expected to exhibit at higher temperatures long range positional order but only orientational one. In the TGB case, the orientational order of these defect lines is thus of cholesteric-type. This new twisted phase called NL* phase has been proposed first by Kamien and Lubensky [14]. It differs from the usual cholesteric phase only by the existence of strong local smectic A order.

In the $n = 10$ homolog of the series 3-fluoro-4[(S)-1-methylheptyloxy]-4$'$-(4$''$-alkoxy-2$''$,3$''$-difluorobenzoyloxy) tolane (nF2BTFO1M7 for short) compound, standard
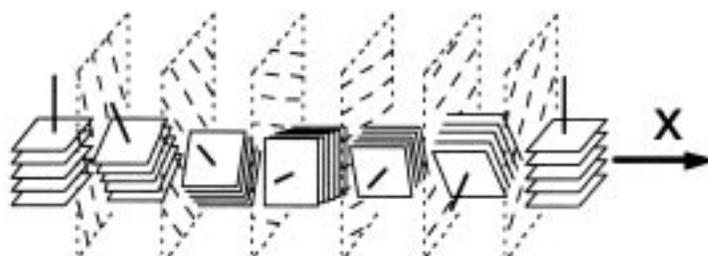
Figure 1. Schematic representation of a TGB phase. The pitch is along the *x*-axis.

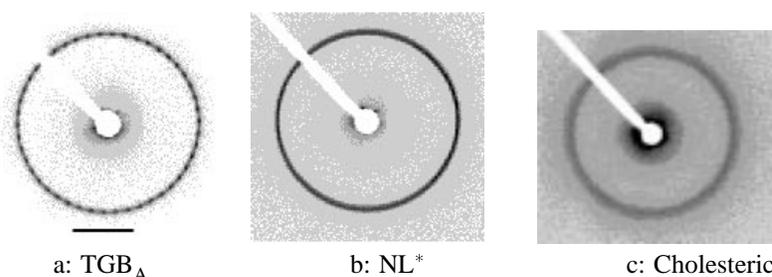a: TGB$_A$ b: NL* c: Cholesteric

Figure 2. X-ray scattering pattern observed on an oriented sample and with a beam parallel to the twist axis. Both TGB$_A$ and NL* phase exhibit long range smectic order since the smectic ring is thin. The dotted pattern in the TGB$_A$ phase clearly shows that the smectic slabs are tilted by a finite angle, which is not the case in the NL* phase (continuous ring). The line on figure 2a indicates the anchoring direction. Commensuration of the TGB$_A$ phase along the pitch could be explained by locking the structure on cholesteric-type defects [17].

calorimetric data show at 106.7°C a transition from the cholesteric phase to some ordered phase first depicted as the TGB$_A$ phase. Using a high calorimetric measurement set-up, Navailles *et al* [15] reported the presence of a new small peak in the TGB$_A$ phase temperature range at 102.8°C, the transition to the SmC* phase occurring at 99.7°C. This was the first experimental evidence of the eventual presence of a NL* phase in between the cholesteric and the TGB$_A$ phase. Navailles *et al* [16] revisited this phase sequence using synchrotron radiation on oriented samples and found that the organization of the TGB$_A$ phase as a regular stack of well-defined smectic A slabs was lost in the intermediate region, although the smectic order was still strong (figure 2). This was consistent with the disordered state of the Kamien– Lubensky model for the NL* phase.

One remaining question was the range of the smectic order in the NL* phase compared to the TGB$_A$ phase. Indeed, in the experiments reported in [16], the width of the smectic diffusion ring was resolution limited and this question could not be experimentally solved. In an oriented sample [16], this width gives information on the smectic correlation length perpendicular to the pitch axis. In a cholesteric phase, as in the nematic phase, the correlation length ξ of the smectic order is finite and the width of the smectic ring is related to $1/\xi$. The maximum correlation length of any object linked to smectic order as a screw dislocation cannot exceed ξ. In a TGB or a NL* phase, in which the smectic order is long range, the distance between the dislocations can be simply estimated from the
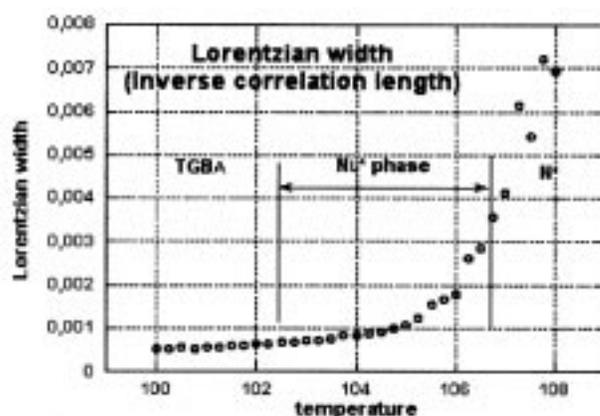
Figure 3. Inverse correlation length as a function of temperature from the TGB$_A$ to the cholesteric phase through the NL* phase.

Renn–Lubensky model to be $\ell \approx \ell_d \approx \ell_b \approx \sqrt{dP/2\pi}$ in which d is the layer spacing and P the helical pitch. In the TGB$_A$ phase this distance corresponds to the distance between the grain boundaries and in between the screw dislocations inside each boundary. In the NL* phase, this distance is just the most probable distance between the screw dislocations. The Kamien–Lubensky model of a cholesteric twist is produced by a set of screw dislocations and hence requires ξ to be significantly larger than ℓ. Recent high resolution X-ray diffraction experiments [3] have brought a new insight on the smectic correlation range from the TGB$_A$ to the cholesteric phase. Figure 3 shows the main results reported in [3]. The measured inverse correlation length (in $\mathring{A}^{-1}$) is plotted as a function of temperature. In the smectic A phase the width of the smectic ring depends on the sample and is probably limited by the size of the monodomains which can be grown. In the best sample, this size was about 0.2 μm. No discontinuity is observed at the transition from the TGB$_A$ to the NL* phase, which means that the smectic order in the NL* phase remains as long range as in the TGB$_A$ phase, at least at lower temperatures. The only change is in the spatial organization of the defect lines: long range ordered in the TGB$_A$ phase, only short range ordered in the NL* phase.

Throughout the NL* phase, the smectic correlation length decreases with increasing temperature. Transition to the cholesteric phase then occurs when the smectic correlation length becomes shorter than the distance between the defects, that is about 25 nm. This is in good agreement with the estimated distance between screw dislocations inside the boundaries. Indeed, at the TGB$_A$ to NL* transition, about 40 grains per pitch are observed. The twist angle θ between neighbouring grains is then $2\pi/40$. As the smectic period d is 3.8 nm, the distance between the screw dislocations, $\ell_d = d/\theta$, is about 24 nm. The size of the blocks, given by the ratio of the pitch P (0.95 μm) by the number of blocks in one pitch, is also of the same order of magnitude.

Nevertheless, it is important to recall that NL* and N* phases share the same symmetry and have to be considered as a single phase. The broad and rounded heat capacity peak seen in calorimetric data and first interpreted as due to a cholesteric to TGB$_A$ transition can now be associated with the change in the range of smectic order. It can also be seen as a gas to liquid transition in a fluid of screw dislocations.
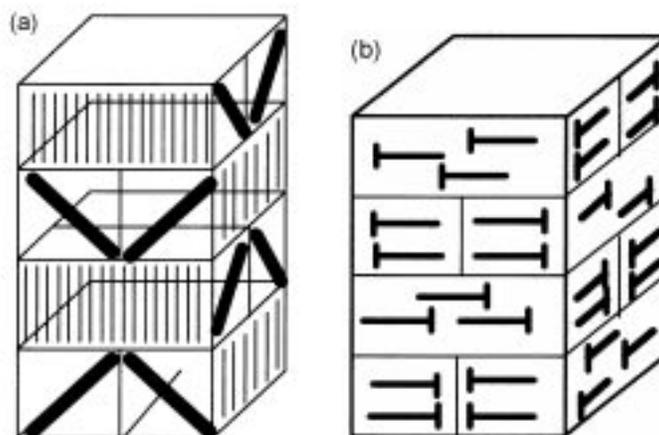
Figure 4. (**a**) Schematic representation of the quadratic cell of the $I4_122$ structure (model I). The molecules are tilted compared to the three main axes. (**b**) Schematic representation of the quadratic cell of the $I4_122$ structure (model II). The molecules are represented by their projection as nails on the faces of the cell. They are perpendicular to the c-axis, but tilted compared to the a- or b-axis.

3. High chirality and antiferroelectric smectic order: The SmQ phase

Contrary to SmA, SmC and SmC* type structures for which clear experimental evidence of TGB phases have been reported, $TGBC_A$ seems to be still puzzling and subject to controversy. Nevetheless, a complex phase has already been observed in chiral antiferroelectric compounds. This phase, called SmQ, which disappears when chirality decreases, has been first seen by Galerne and Liebert [4] when they observed the SmC_A phase (called SmO at that time) for the first time. The SmQ phase was then extensively studied by Levelut *et al* in several compounds [5]. Four different SmQ phases have been found close to isotropic phase and mainly in the vicinity of smectic antiferro-phases. These phases are really liquid crystalline phases exhibiting liquid order of the paraffinic chains. But X-ray scattering patterns show intense and numerous Bragg spots revealing large density modulations with 3D symmetry. Four different space groups have been identified: three are tetragonal ($I4_122$, $P4_222$, $I422$), and one is hexagonal ($P6_222$). The lattice parameters of the $I4_122$ space group are typically $2d$ in the plane perpendicular to the four-fold symmetry axis and $4d$ along this axis, where d is the smectic layer thickness. In all the cases, the distances involved are just a few times d and this is clearly not a TGB phase. Different geometrical models (figure 4) have been proposed to explain these large density modulations. They involve complex organizations of small SmC_A grains, small meaning that the width of each grain is two layers and its lateral size of the same order of magnitude. In these structures there is no length which would be intermediate between the smectic period and the pitch as in the TGB phase.

In the first model, the molecules are tilted by a fixed angle compared to the four-fold axis (called z-axis), alternatively in the x–z plane or in the y–z plane. The four-fold axis is thus perpendicular to both the smectic layer normal and the local polarization direction. In the second model, the molecules are parallel to the x–y plane and tilted compared to both
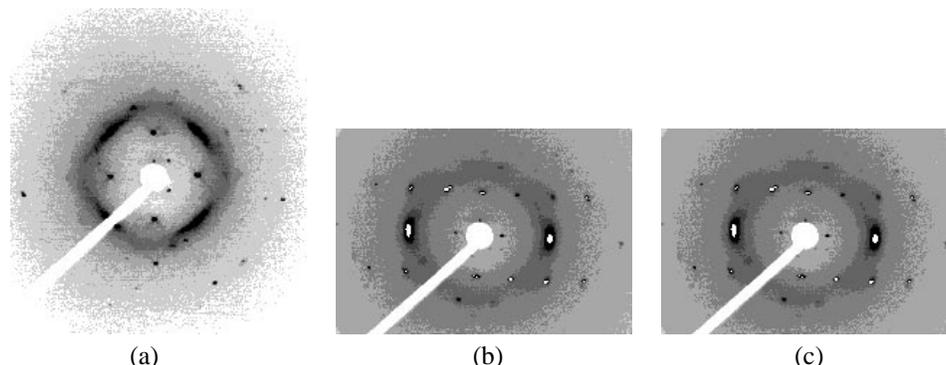

(a) (b) (c)

Figure 5. (**a**) X-ray scattering pattern of a monodomain of SmQ phase. The beam is perpendicular to the four-fold axis. The four intense spots are the $200, \bar{2}00, 200, 0\bar{2}0$ Bragg reflections. These intense spots correspond to the smectic layer spacing. The layer normal is thus directed along either the a- or the b-axis. (**b**) Plane containing the 110 and the 001 directions. The more intense spots are the 400 and $\bar{4}00$ reflections. Some spots appear white because of saturation. (**c**) Plane containing the 110 and the 111 directions. Some spots appear white because of saturation.

the x and the y axes. The four-fold axis, that is the z-axis, is perpendicular to both the layer normal and the molecular axes, but is parallel to the local polarization direction.

A new compound, (R),(R) 4-(2-methylheptyloxycarbonyl) tolanyl 4-(2-methyl hepty-loxycarbonyl) tolan-4′-carboxylate recently synthesized by Nguyen, presents such a SmQ phase between the isotropic phase (115.5°C) and some crystalline phase (90°C). It has been been studied using both X-ray scattering and optical experiments [6]. To determine precisely the structure of the SmQ phase, monodomains have been grown in a small oven (± 0.5°C) mounted on a goniometric head and X-ray scattering experiments were performed on the D43 beamline at LURE (Laboratoire pour l'Utilisation du Rayonnement Electromagnétique, Orsay, France) using synchrotron radiation. The beam was monochromatized with a curved Ge monochromator ($\lambda = 1.44$ Å) and then focused on the detector (imaging plate or CCD camera) which was located at about 300 mm from the sample. The final beam size at the sample position was defined by a $500 \, \mu$m collimator. The symmetry group can then be easily determined from patterns like that of figure 5. From the absence of some peaks, one can conclude that the symmetry group is $I4_122$, one of the four groups already seen by Levelut *et al*. The period in the (a, b) plane has been measured to be 7.589 nm that is twice the smectic period. The period along the four-fold axis is $c = 12.724$ nm $= 1.68a$. The ratio c/a is very close to that previously measured in other compounds.

Two different models have been proposed as interpretation of the architecture of this SmQ phase. We have performed optical experiments in order to discriminate between these two models (figure 4). In the first model, there are four different orientations of the molecules along the four main directions of an elongated tetrahedron. In the second model, the molecules are always perpendicular to the c-axis and the molecules lie along four directions all lying in the same plane. Therefore for these two different structures, the optical properties and especially the birefringence should be very different. For the second model, the birefringence should be of the same order of magnitude as for a smectic phase whereas the first model, from an optical point of view, is closest to a cubic phase and
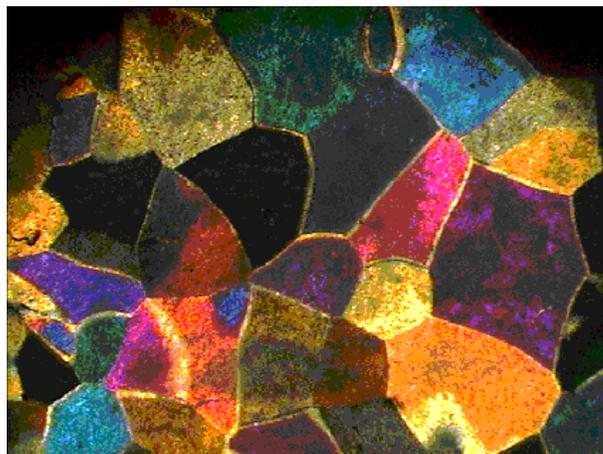
Figure 6. Optical textures of SmQ observed by transmission (in a 0.1 mm thick flat capillary). The colours of the platelets are due to low birefringence.

shoud exhibit a much lower birefringence. Thus optical study is certainly a good way to discriminate between the two models.

The material in the SmQ phase was examined under a polarization microscope in three different sample geometries: freely suspended droplets, samples sandwiched between two glass substrates, and free standing films. Slowly cooling (0.001°C/s) the material from the isotropic phase between glass substrates one can obtain perfectly black texture even for thickness as large as 75 μm. This is the distinctive texture of uniaxial liquid crystals with homeotropic orientation of the optic axis on which light conoscopy can be performed if the birefringence is high enough. Although under the polarization microscope with crossed polars the sample of a thickness of 75 μm had a uniformly extinguished texture, the light conoscopy does not produce any sign of isogyres or isokhromes indicating that the birefringence of the SmQ phase is essentially lower than 10^{-2}.

If the sample is cooled from the isotropic phase quickly, the SmQ texture observed between crossed polars is composed of coloured platelets (figure 6). This fact indicates that the optic axis is tilted or parallel to the substrates. There are platelets of different colours from black to red. We checked that these interference colours are of first order. Simple estimation gives that the birefringence is smaller than 5×10^{-3}. This result is in agreement with the estimation obtained from the light conoscopy experiment.

Free standing films were prepared using electron microscopy grids with square holes of 42 μm edge [18]. In many cells of the grid, the film is uniformly monodomain. One can also find some cells composed of two or three domains separated by grain boundaries. The brightness of the film changes when rotating it around the microscope axis, showing that the optic axis is essentially tilted or parallel with respect to the film surfaces. No interference fringes are seen when observing between crossed polars. The thickness of the film is quite uniform as shown by microscopy observations in reflected unpolarized light and can be estimated from the thickness of the grid $d = 20$ μm. Between crossed polars the film looks gray, indicating that the phase retardation between ordinary and extraordinary waves is much smaller than 90°. Assuming that the optic axis is in-plane of the film,

the Senarmont technique gives the value of the birefringence $\Delta n = 1.4 \times 10^{-3}$. This is in good agreement with the estimations presented above. This is an unusually small value when compared with the birefringence of thermotropic smectic liquid crystals. This fact indicates that in the SmQ phase the molecules are tilted with respect to the optic axis. The tilt angle is presumably close to the so-called magic angle at which the birefringence is zero.

Summarizing we conclude that the optical observations show that the SmQ is a liquid crystalline phase. It is optically uniaxial, and exhibits small birefringence. The molecules are essentially tilted with respect to the optic axis (about $50°$). Our conclusion is that the SmQ can be described by the fist model as described in figure 4a. From this model, one can explain the relationship between the two cell parameters. If the tilt angle compared to the optical axis is θ, then the two cell parameters a and c in this simple model are related by $\tan\theta = 2a/c$. If θ is equal to $54°$, then the ratio c/a should be close to 1.4. Even if the ratio which is experimentally found is not 1.4 but 1.68, the basic idea is that the three directions of the space are coupled through the tilt of the molecules. However representing the molecules by simple rods, which is what we have done in these simple computations, is a very crude approximation.

Moreover, the simple model of figure 4a cannot explain properly why so many Bragg peaks are observed. This small drawing cannot explain the density modulation which is certainly more complex. The next step consists in improving this model in order to fit with the experimental X-ray data.

4. Chiral effects in the isotropic phase

In many chiral compounds exhibiting a direct isotropic to smectic transition, the clearing point temperature is lower than in the racemic one and a broad diffuse 'bump' is often seen by differential scanning calorimetry (DSC) in the isotropic domain. As noticed by Goodby *et al* [19], this could suggest another 'phase transformation' within the temperature range of the liquid, i.e., a so-called isotropic to isotropic liquid conversion. Recent experiments [7] also show such an effect in antiferroelectric liquid crystals but at the isotropic to SmA transition. The authors clearly report the correlation between the bump in the DSC and the increase of the optical activity between this bump and the isotropic to smectic transition. They introduce the term 'L-phase', referring to this region of the phase diagram as 'some anisotropic liquid'. Baretto *et al* [8] have observed an important increase of the optical activity in the liquid phase of antiferroelectric liquid crystals close to the isotropic to SmC_A transition. They attributed this effect to SmC_A fluctuations linked with the underlying SmC_A phase. The presence of a bump in the DSC data occurs also for other smectic phases. For instance it can clearly be seen at the isotropic to SmC* transition in a chiral compound for which the racemic mixture shows an isotropic to SmA transition [19]. One can suspect that the presence of the bump observed in the DSC for the few examples given above is in fact more common since DSC measurements are usually stopped at only a few degrees above the clearing point whereas this bump can occur several degrees above the clearing point.

Since Baretto *et al* suspected some smectic fluctuations, we have performed X-ray scattering experiments on different compounds exhibiting isotropic to various smectic transitions. In this paper, I shall focus on the following compound: 4-(1-ethylheptyloxycarbonyl) phenyl 4-tetradecyloyloxytolane-4′-carboxylate (14CTBB9 for short). This compound
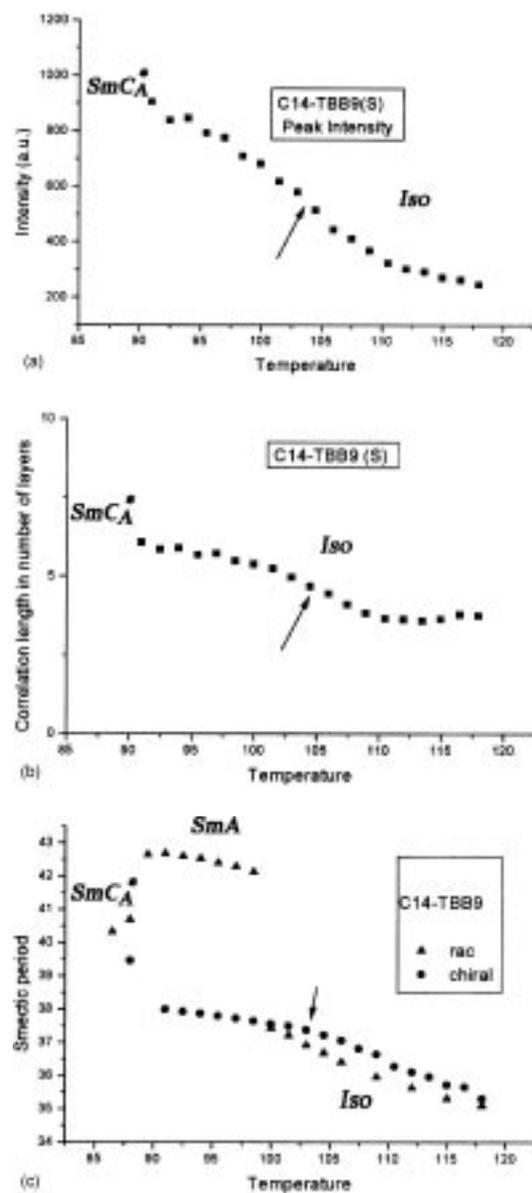
Figure 7. (**a**) Smectic peak intensity as a function of temperature in the isotropic phase of the C14-TBB9. The position of the bump in the DSC thermograms is indicated approximately by the arrow. (**b**) Correlation length of the smectic order in the isotropic phase of the C14-TBB9 as a function of temperature. The position of the bump in the DSC thermograms is indicated approximately by the arrow. (**c**) Smectic period in C14-TBB9 as a function of temperature. The position of the bump in the DSC thermograms is indicated approximately by the arrow.

exhibits an isotropic to SmC^*_A transition and a bump in DSC in the isotropic phase about 15°C above the clearing point. The racemic compound exhibits the following sequence upon decreasing temperature: isotropic phase-SmA-SmC$_A$. Experiments have been performed in LURE using the set-up described in [20]. Figure 7 shows some results on this compound. Smectic fluctuations are seen clearly 15° above the clearing point as expected but are of short range order. The correlation length extends to a few layers in that temperature range and the scattered intensity increases significantly. There are clearly smectic fluctuations but, as can be seen from the layer spacing, they are not smectic fluctuations of the lower temperature smectic phase. For instance, at the isotropic to SmCA transition, a jump in the smectic period is clearly observed. The racemic compound exhibits a SmA phase corresponding exactly to the temperature range where the isotropic phase presents this strange behaviour. Just by comparing the smectic period in the different phases with the smectic period of the racemic SmA phase, one can estimate the tilt angle in each phase: it would be about 20° in the SmC^*_A and 28° in the isotropic phase of the chiral compound. The shift of the smectic period at the transition from isotropic to SmC$_A$ phase shows that the smectic fluctuations cannot then simply be attributed to SmC$_A$ fluctuations. This seems to be also the case for the isotropic to SmC* transition for which a shift of the smectic period, but smaller, is also observed. Many questions thus remain unsolved. What is the local order above the clearing point? Is it the same even if the smectic phase at the lower temperatures is different...?

5. Conclusion

These new experimental results concerning chiral smectic phases prove once again the high degree of complexity observed when chiral orientational ordering competes with smectic positional ordering. Even the isotropic phase may be disturbed by this competition. Complex architectures such as the TGB phases can appear as resulting from these two conflicting orders. The TGB$_A$ phase is now well-understood, but for other phases like the SmQ phase, many questions remain still unsolved. Some answers should certainly come from the variety of the new compounds that the imaginative liquid crystal chemists will synthesize.

Acknowledgements

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