Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Two unusual mesophases in chiral side chain polymers

P. Davidson[a]; K. Kühnpast[b]; J. Springer[b]; G. Scherowsky[c]
[a] Laboratoire de Physique des Solides, associé au CNRS, Bt. 510, Université Paris-Sud, Orsay, Cédex, France [b] Institut für Technische Chemie, Fachgebiet Makromolekulare Chemie, Technische Universität Berlin, Berlin 12, Germany [c] Institut für Organische Chemie, Technische Universität Berlin, Berlin 12, Germany

To cite this Article Davidson, P. , Kühnpast, K. , Springer, J. and Scherowsky, G.(1993) 'Two unusual mesophases in chiral side chain polymers', Liquid Crystals, 14: 3, 901 — 910
To link to this Article: DOI: 10.1080/02678299308027767
URL: http://dx.doi.org/10.1080/02678299308027767

LIQUID CRYSTALS, 1993, VOL. 14, NO. 3, 901–910

Two unusual mesophases in chiral side chain polymers

by P. DAVIDSON†*, K. KÜHNPAST‡, J. SPRINGER‡ and G. SCHEROWSKY§

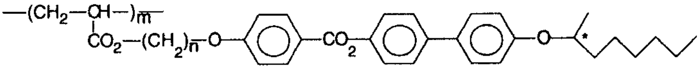
† Laboratoire de Physique des Solides, associé au CNRS, Bât. 510,
Université Paris-Sud, 91405 Orsay Cédex, France
‡ Institut für Technische Chemie, Fachgebiet Makromolekulare Chemie,
Technische Universität Berlin, D-1000 Berlin 12, Germany
§ Institüt für Organische Chemie, Technische Universität Berlin,
D-1000 Berlin 12, Germany

We have reported in a previous paper the synthesis, characterization, structural and electro-optic properties of a new family of chiral mesomorphic side chain polyacrylates. The most salient finding was that many of these polymers presented two S_C^* phases of similar structure, but differing in their switching properties. In addition, two unusual mesophases called U1 and U2 were also discovered in this family. We describe here in more detail the symmetries and molecular organizations for these U1 and U2 phases. We also discuss their relation, on the one hand, to the newly discovered antiferroelectric chiral $S_{C_A}^*$ and S_O^* phases, and, on the other hand, to the 2-dimensional fluid smectic $\tilde{A}$ and smectic $\tilde{C}$ phases displayed by strongly polar low molar mass mesogens. The occurrence of chevron-like ordering in the U1 and U2 phases may give a clue to an understanding of this peculiar S_C^* polymorphism.

1. Introduction

New chiral antiferroelectric phases ($S_{C_A}^*$ and S_O^*) derived from the S_C^* phase have recently been discovered and are presently attracting much interest [1–8]. In particular, the $S_{C_A}^*$ phase gives an unusual electro-optic switching behaviour [2]. A typical feature of these new fluid smectic phases lies in their chevron-like molecular organization [3, 5–7]. Such an antiferroelectric phase has also just been demonstrated in a chiral mesomorphic side chain polymer [8]. In a previous paper [9], we have recently reported the case of a family of chiral mesomorphic polymers which also exhibit a peculiar switching behaviour. These polymers display two different S_C^* phases of similar structure (as seen by X-ray diffraction on fibre samples, i.e. on samples of uniaxial texture, be they real fibres or magnetically aligned samples), but differing in their switching properties. The conditions for the appearance of the ferroelectric properties are not yet clear, but the observation of two unusual mesophases, called the U1 and U2 phases [9], in this system may help to shed some light on this situation and may possibly point to a connection with the new chiral phases.

In this context, this paper will only focus on the structures of the two new U1 and U2 phases and their relation to the antiferroelectric phases. The compounds are chiral side chain polyacrylates **1** of general formula:



* Author for correspondence.

It should be noted that the chemical structure of the side chain has some similarity to that of compound MHPOBC [2] which displays the chiral antiferroelectric $S_{C_A}^*$ phase.

In this series, polymer **1a** ($n=2$, $M_w=117\,000$ g/mol) gives the U1 phase below a $S_{C_2}^*$ phase, and polymer **1g** ($n=11$, $M_w=38000$ g/mol) gives the U2 phase below the two different S_C^* phases. The polymorphism of these two compounds is described by the following sequences [9]:

Polymer **1a**: g **74** U1 **192** $S_{C_2}^*$ **214** S_{A_2} **277** I
Polymer **1g**: g **40** $S_{F_2}^*$**84** U2 **123** $S_{C_{1,x}}^*$ **141** $S_{C_{1,y}}^*$ **158** I

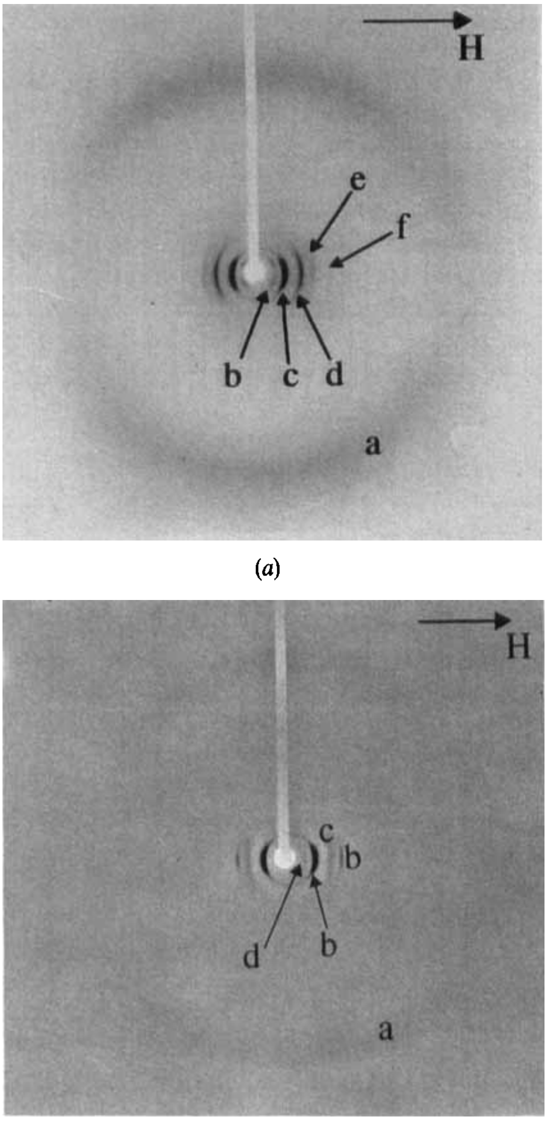
where g stands for glassy state and I for isotropic liquid. The subscripts 1 and 2 indicate the monolayer or bilayer character of the phase, the subscripts x and y label the two different S_C^* phases and the bold numbers represent the transition temperatures in °C. Of the two U1 and U2 phases, the U2 phase is the simpler and we shall describe its structure first.

2. Structure of the U2 phase

Figure 1 (*a*) shows the X-ray diffraction pattern of a magnetically aligned sample of polymer **1g** in the U2 phase and figure 1 (*b*) shows its diffraction pattern in the $S_{C_{1,x}}^*$ phase for comparison. This latter pattern is indeed characteristic of a S_C^* phase: the small angle Bragg spots arise from reflections from the smectic layers of periodicity, $d=35{\cdot}3$ Å. This value, compared with the side group length (+backbone segment, estimated using Stuart and Briegleb stereomodels with an extended conformation) $l_{11}=44$ Å, indicates a tilt angle of 37° at 130°C. The layers are perpendicular to the magnetic field direction (meridian). The wide angle diffuse ring has a large polar angular extension and its maxima lie in directions perpendicular to the field (equator); this shows that the magnetic field is not strong enough to unwind the helix. Altogether, this behaviour is very classical.

The X-ray diffraction pattern of the U2 phase is strikingly different from that of the S_C^* phase, as several other small angle reflections have appeared. In particular, four sharp reflections located off the meridian are clearly visible. The wide angle diffuse ring remains unchanged, still pointing to a uniaxial distribution of the side chains tilted away from the normal to the layers. The small angle reflections can be indexed in a 2-dimensional centred rectangular lattice. The two reciprocal lattice vectors are **c*** along the meridian of modulus $c=1/67{\cdot}5\,\text{Å}^{-1}$ and **a*** perpendicular to the meridian of modulus $a=1/85\,\text{Å}^{-1}$. The $(\pm1, 0\pm1)$, $(0, 0, \pm2)$, $(\pm1, 0, \pm3)$, $(0, 0\pm4)$ and $(\pm1, 0, \pm5)$ reflections are observed; although the $(\pm1, 0, \pm1)$ reflections are clearly split off the meridian on the pattern, the $(\pm1, 0, \pm3)$ and $(\pm1, 0, \pm5)$ reflections are merged into a single line. This effect can be explained classically by the influence of the mosaic nature of the sample. The $(\pm1, 0, l)$ reciprocal nodes are separated by the constant vector **2a**. The effect of the mosaic is to smear out the reciprocal nodes in a given constant mosaicity angle. The larger l is, the smaller is the angle between the $(\pm1, 0, l)$ reciprocal nodes. When this angle becomes comparable to the mosaicity angle, the $(\pm1, 0, l)$ reflections are merged together. Due to their high viscosity, samples of polymeric compounds are difficult to align and all attempts to obtain better aligned samples failed.

The molecular organization of the U2 phase in direct space can be confidently assumed on the basis of the reciprocal lattice. The important feature is the existence, if chirality is left aside, of mirror planes (due to the centred character of the lattice)



(*a*)

(*b*)

Figure 1. X-ray diffraction patterns of a magnetically aligned sample of polymer 1g. Flat film, sample-film distance: 120 mm, λCuKα = 1·541 Å. *H* is the direction of the magnetic field (0·7 Tesla) (meridian). (*a*) T = 110°C in the U2 phase. a is the wide angle diffuse ring, b the (101) reflection, c the (002) reflection, d the (±103) reflections, e the (004) reflection, and f the (±105) reflections. The (±103) and (±105) reflections are not split, because the sample mosaicity is too large. (*b*) $T = 130°C$ in the $S^*_{C_{1,x}}$ phase. a is the wide angle diffuse ring, b the small angle reflections from the smectic layers and c,d are additional diffuse streaks which are discussed in [9].

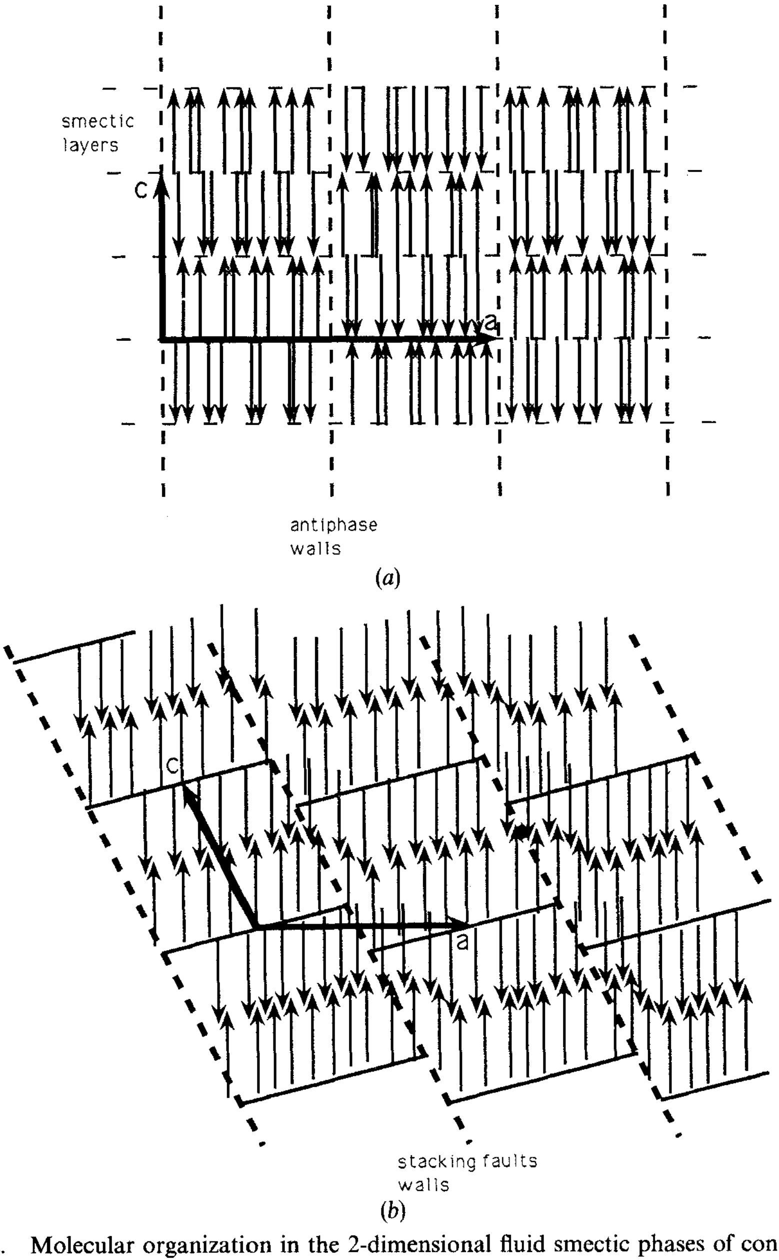


Figure 2. Molecular organization in the 2-dimensional fluid smectic phases of conventional polar mesogens. The molecules are represented by arrows and have an antiferroelectric ordering. Both structures are invariant under any translation in the direction perpendicular to the figure plane. (*a*) $S_{\tilde{A}}$ phase. The mesogens are perpendicular to the smectic layers which are periodically broken into ribbons by antiphase walls. The 2-dimensional unit cell is based on **a** and **c** and the lattice is centred rectangular. (*b*) $S_{\tilde{C}}$ phase. The molecules are tilted with respect to the smectic layers; the wall defects are no longer perpendicular to the layers. The 2-dimensional lattice based on **a** and **c** is oblique.

perpendicular to the meridian. Since the side chains are tilted away from the layers normal, the presence of these mirrors implies some kind of chevron-like (also called herring bone) organization. The transverse modulation of the layers is brought about by antiphase walls perpendicular to the layers. All these characteristics are reminiscent of the so-called 2-dimensional fluid smectic phases, namely the $S_{\tilde{A}}$ and $S_{\tilde{C}}$ phases which appear with strongly polar molecules of low molar mass [10]. The $S_{\tilde{A}}$ and $S_{\tilde{C}}$ phases (see figures 2(*a*) and (*b*) are smectic phases in which the layers comprise antiparallel molecular pairs and are periodically cut into ribbons by wall defects. The U2 phase shares with the $S_{\tilde{A}}$ phase the centred rectangular lattice, and with the $S_{\tilde{C}}$ phase the existence of the tilt angle. This tilt angle can occur either in the (**a**, **c**) plane, as described in region A of figure 3, or perpendicular to the (**a**, **c**) plane as described in region B. In

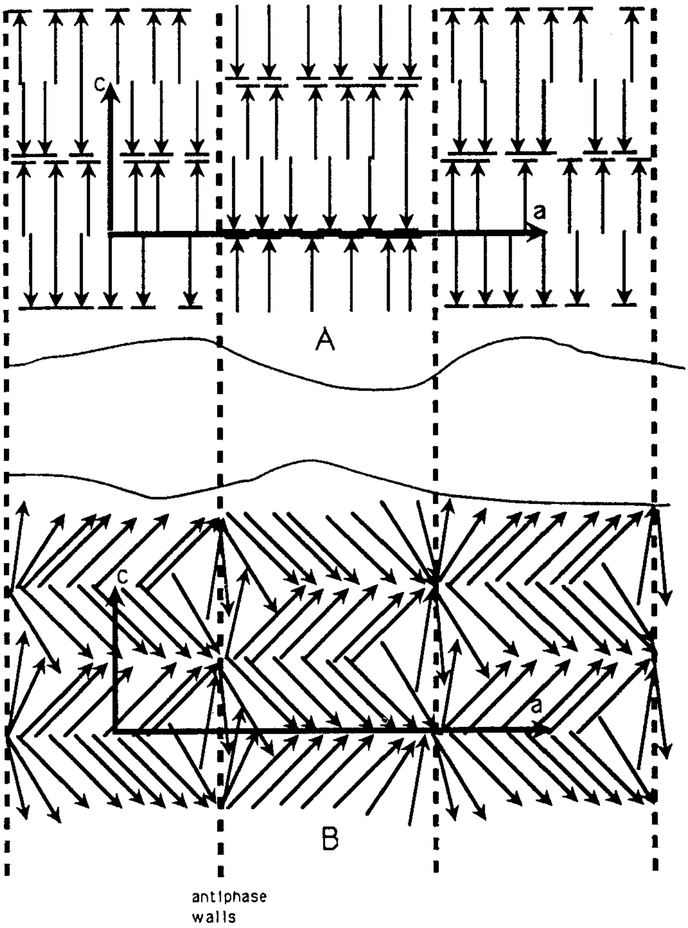


Figure 3. Molecular organization in the U2 phase of polymer 1 g. Though the side chains do not bear strong dipoles, they can still be represented by arrows because they are linked by one end to the polymer backbone. The side chains are tilted with respect to the smectic layers. In region A, they are tilted in a plane perpendicular to the (**a**, **c**) plane, and the nail representation is used. In region B, they are tilted in the (**a**, **c**) plane. If the U2 phase has a helical superstructure, then regions A and B are distant by $p/2$, where p is the helix pitch. If not, then only one region A or B prevails (see text). The 2-dimensional unit cell is based on **a** and **c** and the lattice is centred rectangular. For clarity, the backbones have not been represented.

region A, the antiphase walls are twist-walls, whereas they are splay-walls in region B. These two limiting situations A and B do not necessarily have the same energies, but since the elastic constants are unknown, it is not easy to tell which region has the smallest energy.

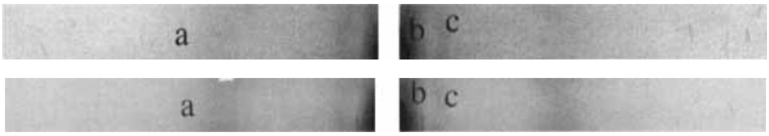
At this point, let us recall that the U2 phase is made of chiral molecules, so that it may or may not present a helical superstructure. If it does, then as the **a** lattice vector must be kept constant from one layer to the next, we must assume that the director and only the director describes a helix along the layer normal. Then the helix relates the two regions A and B separated by $p/4$ or $3p/4$ along the **c** axis; p is the helical pitch, and is much larger than c. As regions A and B have *a priori* different energies, the helix should not be uniform. Conversely, if one of these two regions has an energy much lower than the other, then the helix may spontaneously unwind, and the U2 phase may no longer present a helical superstructure. However, all the samples (either magnetically aligned or quenched fibres) have uniaxial symmetry, so that it is not possible, on the basis of X-ray diffraction, to tell whether the phase really presents a helical superstructure or if the samples are made of a uniaxial distribution of unwound domains. A measure of optical rotatory power would be needed to answer this question.

If we leave chirality aside, we can compare the symmetry of the U2 phase with those of other mesophases. The structure of the U2 phase is intermediate between those of the $S_{\tilde{A}}$ and $S_{\tilde{C}}$ phases of polar mesogens [10] (see figure 2 (*a*), (*b*). The U2 phase is a 2-dimensional fluid phase in which the mesogenic side chains are tilted with respect to the layers. Consequently, in terms of nomenclature, it can be labelled $S_{\tilde{C}}$. However, the organization of the U2 phase differs from that of the $S_{\tilde{C}}$ phase reported in [10]. When chirality is left aside, the U2 phase has 3-dimensional space group Cmm2 (3-dimensional space group No. 35 of the International Tables of Crystallography [11] with the proper axes setting), whereas the $S_{\tilde{C}}$ phase of [10] has 3-dimensional space group P2/m (3-dimensional space group No. 10 of the International Tables of Crystallography [11]). In fact, the definition of the $S_{\tilde{C}}$ phase as a 2-dimensional fluid phase, in which the mesogenic molecules are tilted with respect to the layers, is not restrictive enough since it does not state the respective orientations of the tilt angle, the wall defects and the normal to the layers. Altogether, the most important feature of the U2 phase is the existence of a chevron-like ordering modulated by antiphase walls.

3. Structure of the U1 phase

Figure 4 (*a*), (*b*) shows the X-ray diffraction patterns of a powder sample of polymer **1a** in the U1 and $S_{C_2^*}$ phases respectively. The diffraction pattern in the $S_{C_2^*}$ phase is very simple: it displays only the small angle smectic reflections (first and second orders) and a wide angle diffuse ring. The comparison between the smectic period $d = 52$ Å at 200°C and the side chain length $l_2 = 31$ Å proves the bilayer character of the $S_{C_2^*}$ phase and provides a value of 33° for the tilt angle. The X-ray diffraction pattern of the U1 phase is very different, as many new small angle reflections are now present: up to 10 diffraction lines ranging from $d = 88$ Å to $d = 23{\cdot}3$ Å have been observed with a classical Guinier camera. These numerous small angle reflections could only be indexed (see table) in the 3-dimensional monoclinic system with the parameters: $a = 120$ Å, $b = 74$ Å, $c = 63$ Å and $\beta = 133°$ at 150°C.

The 001 reflection, $d = 46{\cdot}7$ Å, which is the strongest one, can be continuously followed up to the $S_{C_2^*}$ phase where it turns into the first order of reflection from the smectic layers. This behaviours shows the close connection between the two phases. The



(*b*)

Figure 4. Guinier powder X-ray diffraction patterns of polymer **1a**. $\lambda CuK\alpha_1 = 1{\cdot}5405$ Å, sample-film distance: 115 mm. a represents the wide angle diffuse ring, b the small angle reflections and c the artefactual diffuse scattering due to the mylar windows of the set-up. (*a*) $T = 190$°C in the U1 phase and $T = 200$°C in the $S^*_{C_2}$ phase.

Measured and calculated *d*-spacings in the U1 phase.

hkl	d_{meas}/Å	d_{calc}/Å
100	88·6	88·0
010	73·9	74·0
−101	62·2	62·4
001	46·7	46·6
200	44·3	44·0
020	36·9	37·0
101	33·1	32·9
300	29·1	29·3
030	25·3	24·7
002	23·3	23·3

0*k*0 reflections have a relatively low intensity which means that the modulation along **b** is rather weak. No *hkl* reflection (i.e. reflection with $h \neq 0$, $k \neq 0$ and $l \neq 0$ simultaneously) could be detected. This observation, together with that of the wide angle diffuse ring, demonstrates that the U1 phase is still a fluid phase.

Figure 5 shows the X-ray diffraction pattern of a drawn fibre of polymer **1a** in the U1 phase. The small angle reflections aligned in a row perpendicular to the fibre axis are those of the (**a***, **c***) plane. The **b** axis is therefore oriented along the fibre axis, but the (010) reflection cannot be observed because the sample-film distance is too small. The important point obtained from this pattern is that the wide angle diffuse ring is slightly modulated with maxima in directions oriented at about 45° with respect to the (**a**, **c**) plane. Therefore, the side chains are tilted by that angle out of this plane.

Of course, it is difficult to establish precisely the structure of the U1 phase (i.e. the unit cell content) on the basis of the unit cell symmetry and dimensions alone, but some assumptions can be made by comparison with the $S_{C_2^*}$ and U2 phases present in the homologous series. The U1 phase is different from the U2 phase essentially for two reasons. Firstly, it is important to remark that (even leaving chirality aside) the U1 phase does not have mirror planes perpendicular to the **c** axis, so that the wall defects which induce the modulation along **a** are not antiphase walls any more, but simple wall defects. Therefore, in this respect, the U1 phase is much more similar to the $S_{\tilde{C}}$ phase reported in [10] (see figure 2 (*b*)). Note also that this latter phase can be regarded as a 2-dimensional stacking of ribbons of bimolecular pairs [12]. Secondly, the U1 phase presents, in addition, a long-range modulation along the direction (**b** axis) of the

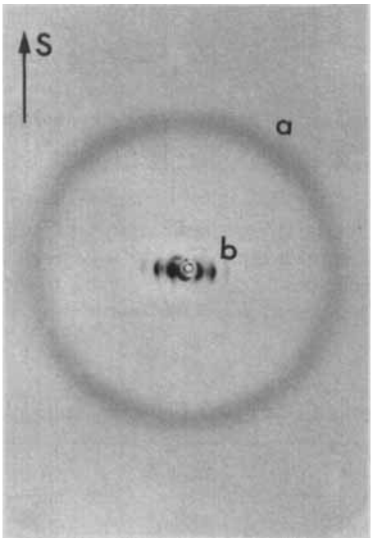


Figure 5. X-ray diffraction pattern of a fibre sample of polymer **1a** quenched to room temperature in the U1 phase. Sample-film distance: 85 mm, λCuKα = 1·541 Å. S is the stretching direction and a denotes the wide angle diffuse ring and b the small angle reflections of the (**a***, **c***) plane.

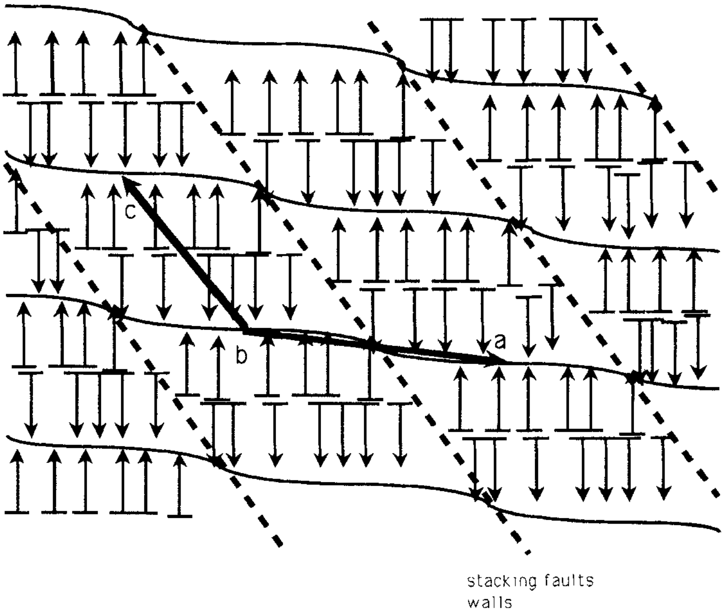


Figure 6. Tentative representation of the molecular organization in the U1 phase of polymer **1a**. The side chains are represented by arrows; they are tilted in the plane perpendicular to the (**a**, **c**) plane and the nail representation is used. The structure is modulated with a period **b** in the direction perpendicular to the (**a**, **c**) plane. The wall defects are no longer perpendicular to the smectic layers so that the 3-dimensional unit cell is monoclinic. For clarity, the backbones have not been represented.

ribbons, perpendicular to the (**a**, **c**) plane. The ribbons are periodically modulated, but adjacent ribbons are not in phase, since no *hkl* reflection is observed: the ribbons are decorrelated and free to slide over one another. As the U1 phase is a 3-dimensional phase of rather low symmetry, it is very unlikely to present a helical superstructure. However, here also, we lack the experimental information to answer this question definitely. In the following, we shall not take into account an eventual large pitch helical superstructure. All these considerations lead us to propose a tentative scheme of the molecular organization in the U1 phase (see figure 6). We still assume a chevron-like ordering on the basis of figure 5, of the existence of the $S_{C_2^*}$ phase above the U1 phase, of the epitaxial relations between these two phases. Note that the shift along the **c** direction of two ribbons distant by **a** takes no particular value (it is equal to $c/2$) in the case of the U2 phase inducing the centred character of the lattice). The space group of the U1 phase is P2 (3-dimensional space group No. 3 of the International Tables of Crystallography [11]). Altogether, the period c is related to the molecular length, the period a appears as a typical distance between wall defects (just like the U2 phase) and the period b is possibly due to the polymeric nature of the compound, since the **b** direction is oriented along the fibre axis. The origin of this modulation might come from the mechanical properties of the backbones themselves. The modulation can also be coupled to the chevron-like ordering through small variations of the tilt angle. The very complex side chain distribution in the U1 phase might be regarded as the remnants of the helical superstructure of the S_C^* phase distorted by the low symmetry. Due to the very special character of this phase, and because it is only seldom encountered in liquid-crystalline materials (here for the first time to our knowledge), we feel that there is no purpose served in coining a new symbol for it.

4. Discussion

In this section, we shall try to site the two unusual U1 and U2 phases with respect to the 2-dimensional fluid smectic $S_{\bar{A}}$ and $S_{\tilde{C}}$ phases and to the newly discovered $S_{C_A}^*$ and S_O^* phases. In the previous sections, it was shown that the structures of the U1 and U2 phases can be derived from those of the $S_{\bar{A}}$ and $S_{\tilde{C}}$ phases of strongly polar, small molecular weight mesogens. By the way, note that, generally, the dipoles which these mesogens bear are longitudinal ones. These latter phases appear as a means of relieving frustration in situations where density and molecular orientations are coupled. This is also the case with mesomorphic side chain polymers which are known not to need strong dipoles to exhibit the rich polymorphism of polar, small molecule mesogens [13]. Indeed, in these polymers, the density problem arises from the possible difference between the packing density of the side chains within the smectic layers and the grafting density on the backbone. The orientation problem arises because all the side chains are linked by one of their ends to the backbone so that they do not need a strong longitudinal dipole to be asymmetrical. Therefore the occurrence of related structures in the polymorphic sequences for polymers **1a** and **1g** is not so surprising. The common feature of all these phases (namely, $S_{\bar{A}}$, $S_{\tilde{C}}$, U1 and U2) is the existence of bilayers made of molecular (or side-chain) pairs, broken by periodic wall defects.

We have also shown that a chevron-like ordering prevails in the U1 and U2 phases which gives them a common feature with the newly discovered chiral antiferroelectric S_O^* and $S_{C_A}^*$ phases. Note now that, in contrast to the $S_{\bar{A}}$ and $S_{\tilde{C}}$ phases of polar small molecule mesogens, the dipoles relevant to the S_O^* and $S_{C_A}^*$ phases are now transverse. This raises the question of the role of dipolar interactions in the occurrence of U1 and U2 phases. A piece of information lies in the following observation [7, 14]: in the same system in which the S_O^* phase was discovered, racemic mixtures also form the S_O phase. But, in the absence of segregation, the average dipole in each layer vanishes, showing that the chevron-like ordering results more from a mechanical interaction at the interface between layers than from a dipolar coupling. This mechanical interaction is certainly affected and possibly enhanced by the polymeric nature of our materials. It is now well known that the polymer backbones, in smectic phases, most probably lie at the interface of sublayers of mesogenic cores. In addition to their specific mechanical properties, the backbones, according to their tacticity, also tend to induce correlations of the mesogenic cores chemically linked to them [13].

The U1 phase is a 3-dimensional fluid phase which makes it at first sight similar to the S_Q^* phase of tetragonal symmetry found in the same system as the S_O^* phase [4]. However, this analogy is not very significant, because the S_Q^* phase, which occurs just below the clearing point, is closer to Blue Phases and may also be regarded as a complex ordering of twist-defects. Compound **1a**, probably because of the presence of the backbones, cannot adopt such a solution. On the contrary, the U1 phase is a low temperature phase in which only the *a* period appears as an equilibrium distance between defects, whereas the *b* period appears related to the backbones.

Finally, though the present work points to the influence of chevron-like ordering in the rich polymorphism of the chiral polymers **1**, it does not provide any direct conclusive evidence about the natures of the two $S_{C_x}^*$ and $S_{C_y}^*$ phases. Actually, very recent mixing experiments [15] seem to prove that the $S_{C_A}^*$, the S_O^* and the $S_{C_x}^*$ phases are of the same nature, but other experiments must be made in order to improve our understanding of the $S_{C_x}^*$ and $S_{C_y}^*$ phases. For instance, the influence of chirality may be studied by mixing enantiomers; measurements of optical rotatory power and piezoelectric tests could also be helpful.

The authors are deeply indebted to Dr. A. M. Levelut for helpful discussions and for kindly communicating to us a preprint of [7].

References

[1] Chandani, A. D. L., Hagiwara, T., Suzuki, Y., Ouchi, Y., Takezoe, H., and Fukuda, A., 1988, *Jap. J. appl. Phys.*, **23-5,** L729.

[2] Chandani, A. D. L., Ouchi, Y., Takezoe, H., Fukuda, A., Terashima, K., Furukawa, K., and Kishi, A., 1989, *Jap. J. appl. Phys.*, **28-7,** L1261.

[3] Gorecka, E., Chandani, A. D. L., Ouchi, Y., Takezoe, H., and Fukuda, A., 1990, *Jap. J. appl. Phys.*, **29-1,** 131.

[4] Levelut, A. M., Germain, C., Keller, P., Liébert, L., and Billard, J., 1983, *J. Phys., France*, **44,** 623.

[5] Galerne, Y., and Liébert, L., 1990, *Phys. Rev. Lett.*, **64-8,** 906.

[6] Galerne, Y., and Liébert, L., 1991, *Phys. Rev. Lett.*, **66-22,** 2891

[7] Hamelin, P., Levelut, A. M., Martinot-Lagarde, P., Germain, C., and Liébert, L., *J. Phys., France* (submitted).

[8] Bömelburg, J., Heppke, G., and Hollidt, J., 1991, *Makromolek. Chem. rap. Commun.*, **12,** 483.

[9] Kühnpast, K., Springer, J., Davidson, P., and Scherowsky, G., *Makromolek. Chemie* (in the press).

[10] Hardouin, F., Levelut, A. M., Achard, M. F., and Sigaud, G., 1983, *J. Chim. phys.*, **80,** 53.

[11] International Tables for Crystallography, 1983, Vol. A (Reidel).

[12] Hardouin, F., Tinh, N. H., Achard, M. F., and Levelut, A. M., 1982, *J. Phys. Lett., France*, **43,** L327.

[13] Davidson, P., and Levelut, A. M., 1992, *Liq. Crystals*, **11-4,** 469.

[14] Levelut, A. M. (private communication).

[15] Bömelburg, J. (private communication).