Structural Characterization of New Ferroelectric Liquid-Crystalline Siloxanes

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Structural Characterization of New Ferroelectric Liquid-Crystalline Siloxanes

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Abstract. — In a previous paper [1] we reported the structural study of new smectogenic
molecules containing three distinct parts, an aromatic core, a central paraffin chain and a siloxane
endgroup. In the present paper we report the structural characterization of new ferroelectric
liquid crystalline siloxanes containing, in addition to these three parts, a branched aliphatic
tail. These low molar mass chiral organosiloxane mesogens and their racemic analogs have been
characterized using X-ray diffraction both on powder and oriented samples. The chiral (and
achiral) compounds exhibit enantiotropic ferroelectric smectic C* (or smectic C) mesophases
with high tilt angles at low temperatures and over a broad temperature range.
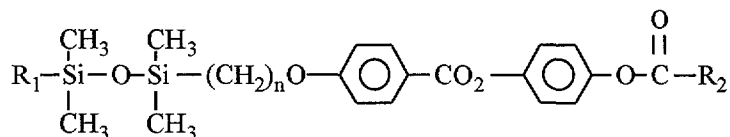
1. Introduction

Chiral low molar mass (LMM) smectogens exhibiting S_C^* phases have been studied extensively
because of their ferroelectric properties [2,3]. More recently, side-chain liquid-crystalline poly-
mers have been synthesised [4–6] and shown to exhibit S_C^* phases. The presence of the polymer
backbone increases the phase stability and improves the mechanical properties (stabilisation
of the layer structure ..), and the mesogenic side-group confers to the material its specific
electro-optical or ferroelectric properties. Recent results illustrate their potential for the fabri-
cation of rugged displays [7–9]. They also indicate that the response times of the polymers, in
the SmC* phase, are orders of magnitude slower than that of their LMM counterparts under
similar conditions. As a compromise between the advantages and the disadvantages of the
polymers, we have recently synthesised and characterized a number of LMM organosiloxane
mesogenic compounds [10]. Their special feature is that the molecules contain three, instead
of two, distinct parts incompatible with one another [1]. As a result the disiloxane moieties
locate themselves in separate sub-layers recalling the case of side-chain polymers where the
backbones are inserted between the smectic layers.

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2. Materials

The compounds studied in this work were synthesised by hydrosilylation and characterised as described in a separate paper [11]. Their chemical formula is :

$$R_1-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{Si}}-O-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{Si}}-(CH_2)_nO-\langle\!\langle O \rangle\!\rangle-CO_2-\langle\!\langle O \rangle\!\rangle-O-\overset{\overset{\displaystyle O}{\|}}{C}-R_2$$

and the compounds studied are:

Compound	n	R_1	R_2
C8A*B	8	CH_3-	$-\overset{*}{C}H-C_2H_5$ $\quad\ \ \|$ $\quad\ CH_3$
C10A$^{(\pm)}$B	10	CH_3-	$-CH-C_2H_5$ $\quad\ \|$ $\quad CH_3$
C10A*B	10	CH_3-	$-\overset{*}{C}H-C_2H_5$ $\quad\ \ \|$ $\quad\ CH_3$
C10A*Hexyl	10	$CH_3-(CH_2)_5-$	$-\overset{*}{C}H-C_2H_5$ $\quad\ \ \|$ $\quad\ CH_3$
C10C*B	10	CH_3-	$-\overset{*}{C}H-\overset{*}{C}H-CH_3$ $\quad\ \|\quad\ \ \|$ $\quad Cl\quad CH_3$
C10B*B	10	CH_3-	$-\overset{*}{C}H-\overset{*}{C}H-C_2H_5$ $\quad\ \|\quad\ \ \|$ $\quad Cl\quad CH_3$

3. Experiment

The thermotropic polymorphism of these compounds was studied by differential scanning calorimetry (DSC) and classical polarising optical microscopy suggesting the presence of smectic C (or C*) mesophases. The tilted nature of the smectic mesophases was confirmed by optical microscopy on free-standing thin films which exhibit typical schlieren textures (see Fig. 1). Table I summarises their mesomorphic behaviour.

Fig. 1. — Typical schlieren texture of a free-standing thin film of C10A*B at 40°C.
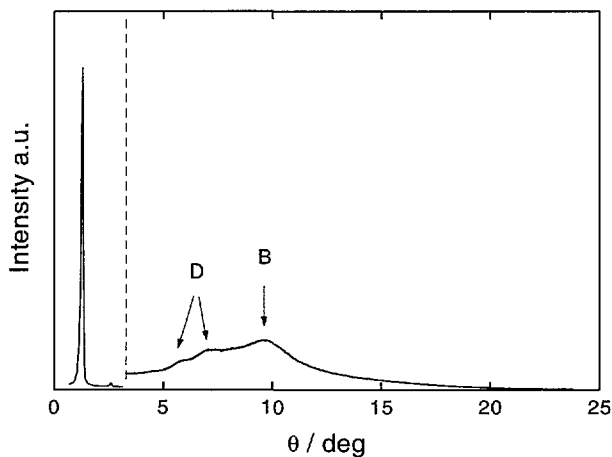

Fig. 2. — Typical example of an X-ray powder diffraction pattern of C10A*B in the smectic C phase, recorded at 40 °C with a curved position-sensitive detector as a function of the Bragg angle θ ($2d \sin \theta = n\lambda$). For clarity, small and wide-angle regions are represented separately; intensity in the wide-angle region is increased sixfold for convenience.

Powder X-ray diffraction studies were carried out with a set-up described elsewhere [1]. Typical powder X-ray patterns recorded are shown in Figures 2 and 3. For more quantitative investigations we have also studied oriented samples. The X-ray set-up consists of a Ni-filtered CuK_α beam from a rotating anode (Elliot) and a flat photographic film recording the patterns. The orientation was achieved by careful and slow cooling from the isotropic phase under a magnetic field of about 1.4 T. Despite the absence of a nematic phase, well oriented smectic samples could nevertheless be obtained. Typical X-ray diffraction patterns from oriented samples are shown in Figures 4 and 5.
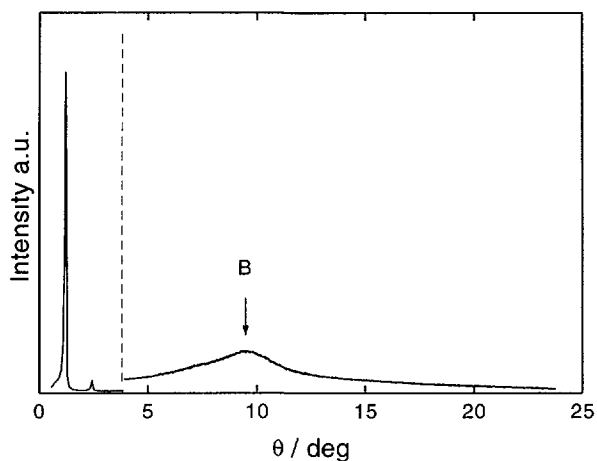
Fig. 3. — X-ray powder diffraction pattern of C10A*Hexyl in the smectic C phase, recorded at room temperature with a curved position-sensitive detector as a function of the Bragg angle θ $(2d \sin \theta = n\lambda)$. For clarity, small and wide-angle regions are represented separately; intensity in the wide-angle region is increased sixfold for convenience.
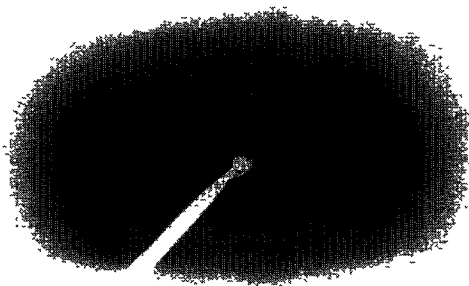

Fig. 4.
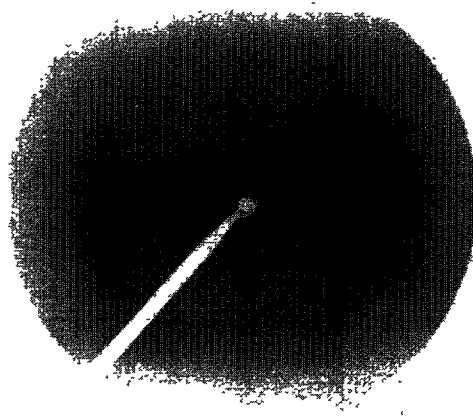
Fig. 5.

Fig. 4. — Typical X-ray diffraction pattern of a magnetically oriented sample of C10A*B, in the smectic C phase, recorded at 40 °C.

Fig. 5. — Typical X-ray diffraction pattern of a magnetically oriented sample of C10A*Hexyl, in the smectic C phase, recorded at room temperature.

4. Results and Discussion

The powder X-ray patterns recorded are in perfect compliance with the optical observations describing the mesophases as disordered smectic in nature. They contain indeed two (or three) equidistant sharp Bragg reflections in the small-angle region, corresponding to the smectic

layering. In the wide-angle region, they contain one diffuse band (B) at about 4.6 Å (Figs. 2 and 3), corresponding to the liquid-like conformation of the paraffin chains and to the lateral correlation of the aromatic cores, and one much more diffuse band at about 8.6 Å (as clearly confirmed using photographic film), which corresponds to the liquid-like arrangement of the siloxane moieties. Apart from the case of the C10A*Hexyl compound, the X-ray patterns contain two additional diffuse reflections (D) at about 6.3 and 7.5 Å (see Fig. 2).

Table I. — *Transition temperatures for the chiral (*) and the achiral* [±] *(AB organisiloxanes) determined using DSC. ([ ] indicates monotropic transition).*

Sample	K − SC*/°C	SC*−I/°C	K − I/°C
C8A*B	[-11.3]	[28.9]	38.1
C10A[±]B	-7.4	49.5	——
C10A*B	-8.4	51.7	—
C10C*B	-4.2	56.2	—
C10A*Hexyl	-1.0	26.9	——
C10B*B	-4.2	49.0	——

Table II. — *Smectic period (d), molecular lengths, L (measured by molecular simulation using Sybyl software from Tripos), tilt angle, θ, of the aromatic cores (calculated through equation* $\cos^{-1}(2\sigma_{ar}/S)$*), and deduced molar volumes (V) of the compounds studied. [ ] indicates the tilt angles determined using electrooptical measurements [14].*

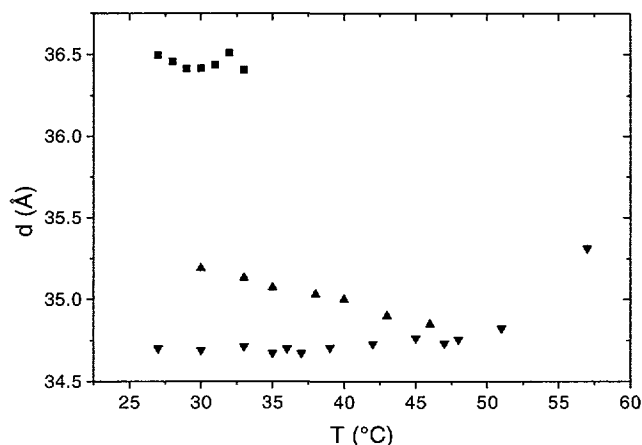| Compound	d/Å	L/Å	θ/deg	V/Å^3
C8A*B	32.5	33	38 [39]	927
C10A[±]B	35.0	36	36	981
C10A*B	34.9	36	36 [36]	981
C10A*Hexyl	36.5	43	37 [37]	1116
C10C*B	34.7	36	[28]	1008
C10B*B	35.2	37	——	1035

Fig. 6. — Smectic period of C10C*B (down triangle), C10B*B (up triangle) and C10A*Hexyl (square) as a function of temperature.

The oriented X-ray patterns show clearly that the molecules are tilted with respect to the smectic layers (Figs. 4 and 5). In the small angle region they contain two (or three) equidistant Bragg spots. The average direction of the long axes of the molecules lies along the field and the position of the layer spots with respect to the field direction gives directly the tilt angles (see Tab. II). It is of interest to note that the layer spots are aligned in only one direction, indicating that, within the volume of sample explored by the X-ray beam, the smectic layers are all oriented in the same direction. In the special case of compound C10C*B, the oriented patterns show the layer spots to lie parallel to the field direction making it hard to determine the tilt angle with accuracy. In the wide angle region, the X-ray patterns contain two diffuse equatorial crescents at 4.5 and 8.6 Å. The first corresponds to the liquid like state of the aliphatic parts and the second, much more diffuse, to the siloxane parts. Away from the equatorial plane, the patterns contain in addition two arcs at 6.4 and 7.5 Å, as already seen with polymers [12] and interpreted as resulting from intramolecular correlations [13]. In our case, they are probably related to the position of the siloxane part as an endgroup of the molecules as they are absent for the C10A‾Hexyl compound (see Figs. 3 and 5) where the siloxane carries a terminal hexyl group.

The smectic periods measured at 30 °C are given in Table II, along with the corresponding molecular lengths estimated from molecular modelling (Sybyl software from Tripos). As illustrated in Figure 6, the smectic period does not vary with temperature, showing the tilt angles to be constant in agreement with previous electrooptical measurements [14].

5. Structural Model

The mesophases of the compounds studied in the present work are clearly smectic C (or C*) in nature, the tilt angle of the molecules being in the range of 30-40 deg. The value of the smectic period, of about one molecular length, is then quite unexpected and deserves special consideration. To discuss this point and to describe the detailed molecular structure of these phases, it is useful to calculate the molecular areas S using the molar volume of the molecules. The limited amount of samples at our disposal prevented us from measuring molar volumes by dilatometry. However, with the usual assumption of additivity of the partial molar volumes of
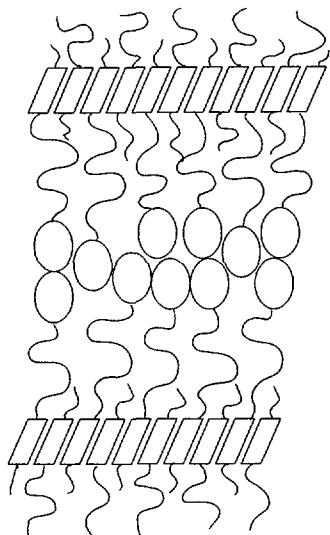
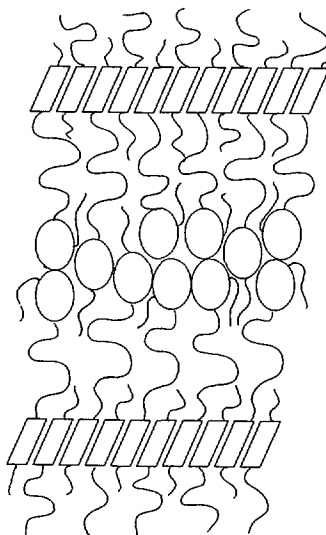Fig. 7.   Fig. 8.

Fig. 7. — Schematic representation of the smectic C layers of organosiloxane compounds. The central part of the smectic layers is arbitrarily chosen to be formed of the siloxane sublayers, with the disiloxane groups (ellipses) arranged in a partially bilayered structure. This central part is fringed with the disordered paraffin chains (wavy lines) arranged in single layers. The aromatic cores (rectangles) are located within distinct sub-layers in a mono-layered arrangement and tilted with respect to the normal layers.

Fig. 8. — Schematic representation of the smectic C layers of the C10A*Hexyl compound. See Figure 7 for the representation.

the constituent parts of the molecules, we were able to obtain an estimate of the molar volumes (see Tab. II) using the available volume data [1, 15]. Because of the mutual incompatibility of their constituent parts, the molecules must pile up in layers pointing alternately up and down (Fig. 7). As a result of the two-sided symmetry of the smectic layers, the molecular areas calculated ($S = 2V/d \cong 56 - 60$ Å^2) correspond to the area occupied in the smectic planes by two molecules.

This value suggests the following comments regarding the molecular packing in each one of the three sub-layers of the smectic C structure (Fig. 7). Concerning the aromatic sublayers, the S value is larger than twice the molecular area of the aromatic cores ($\sigma_{ar} \cong 22 - 24$ Å^2 [16]). Clearly, this suggests a monolayered arrangement of tilted aromatic cores, with a tilt of about $\cos^{-1}(2\sigma_{ar}/S) \cong 31 - 40$ deg., in complete agreement with the values measured experimentally (Tab. II). Concerning the siloxane sub-layers, the S value is intermediate between one and twice the molecular area of a dimethylsiloxane polymer chain ($\sigma_{si} \cong 43$ Å^2 [17]). This suggests a partially bilayered arrangement of the siloxane endgoups, with a degree of bilayering ($\tau = 2 - S/\sigma_{si}$ [18]) of about $0.6 - 0.7$. Finally, concerning the paraffin sublayers, the S values are in agreement with what is known of the lateral expansion of paraffin chains in a disordered conformation and are therefore consistent with the single layered arrangement shown in Figure 7.

In our previous work concerning the structural characterization of three-block smectogens [1], molecules of which the aromatic cores carry a CN polar group, their head to head association gives arise to a partially bilayered smectic A mesophase as the calculated molecular areas ($S \cong 32 - 39$ Å^2) lie between one and two times the molecular area of the aromatic cores. In the present case, the aromatic core carries a branched and bulky aliphatic chain ($S \cong 29$ Å^2 [19]) which segregates in the paraffin sublayer and consequently increases their area. Thus being larger than the area of two aromatic cores, it induces a tilt of the aromatic cores, which in turn increases the area of their sublayers, so as to be adequate for superposition.

Now concerning the smectic period ($d \cong L$), the value obtained results from the contribution of the three sublayer thicknesses ($d = 2d_{\text{paraffin}} + d_{\text{aromatic}} + d_{\text{siloxane}}$). It is clear that the tilt of the aromatic cores decreases d_{aromatic} and consequently d. The bilayering of the siloxane parts, however, increases d_{siloxane} and of course the addition of a branched aliphatic tail increases the smectic period. Thus the value of the smectic period results from the competition between the effects of the tilt angle, the bilayering of the siloxane parts and the addition of the branched aliphatic tail. In the present case, these effects are compensated with each other to give rise to a value of d close to the molecular length. As for the C10A*Hexyl compound which contains an additional hexyl part, the change of the molecular architecture may change the balance between these effects and consequently the value of the smectic period compared to the value of the molecular length.

Finally, in the case of the C10A*Hexyl compound which contains in addition an hexyl end group covalently bonded to the siloxane part, one may have thought that it would perturb the internal structure of the siloxane groups and therefore their partial bilayering. Because of the nearly globular shape of the siloxane groups, the hexyl parts can arrange themselves in the paraffin sub-layers as shown in Figure 8 preserving the same kind of molecular arrangement as for the other compounds.

6. Conclusion

The present work deals with the mesomorphic behaviour of a new class of ferroelectric molecules containing three distinct parts : a phenylbenzoate aromatic core, paraffin chains (linear and chiral branched) and a siloxane group. It describes the smectic C structure observed as resulting in the superposition of three separate sublayers formed of the three molecular moieties. The main conclusion drawn is related with the necessity to combine different techniques to determine the structure and the nature of the mesophases. In the classical case of only two types of constituent parts, aromatic cores and paraffin chains, the structure of the smectic C phases is usually described in terms of the layer thickness and the tilt of the molecules with respect to the layer normals. The tilted nature of the smectic C phase can easily be deduced from a simple comparison between the smectic period and the molecular length. In the case of polyphilic molecules, containing more than two constituent parts which are incompatible with one another and out of proportion from the standpoint of their lateral molecular areas, the simple comparison between the smectic period and the molecular length is not a sufficient criterion in determining the tilted nature of the smectic mesophase, and a knowledge of the molecular area is necessary to describe the detailed arrangement of the molecules in the smectic layers.

Acknowledgments

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[19] Using the calculated volume of the squalane at room temperature ($V \cong 867$ Å^3: the corresponding density is 0.81 (see "Aldrich" catalogue)) and its molecular length in an extended conformation ($L \cong 30$ Å), we can calculate an estimate value of the molecular area of a branched aliphatic chain $S = V/L \cong 29$ Å^2