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Bilayer structures in cholesteric, cyclic-siloxane liquid crystals

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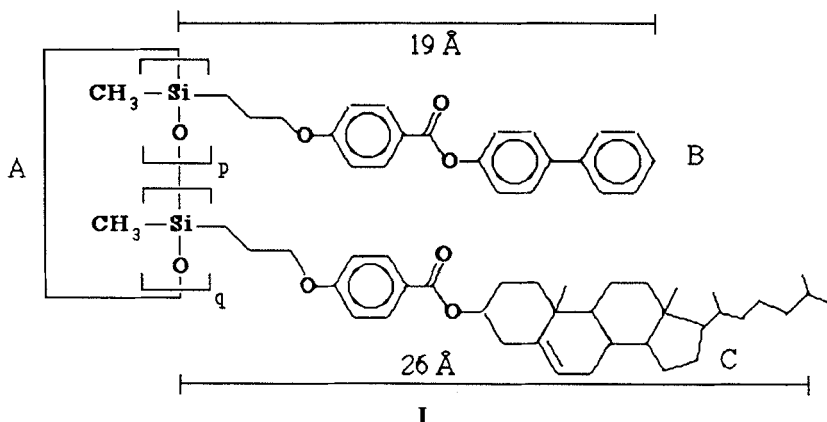
X-ray diffraction has been used to investigate a series of commercially available liquid crystals based on a cyclic penta(methylsiloxane) with combinations of cholesteryl-4'-allyloxybenzoate and biphenyl-4'-allyloxybenzoate mesogens pendant on the siloxane ring. A lamellar, (smectic-like) structure is indicated in the mesophase and quenched glassy solid state. Extended molecular dimensions of the mesogens generally account for the observed d spacings. The mesogens may interdigitate within lamellae but the packing and extent of interdigitation is dependent on the ratio of cholesteryl to biphenyl mesogens. There is probably also a structural contribution from the nano-aggregated (nano-phase separated), immiscible, siloxane-rich layer delineating the lamellae interfaces as this mesophase shows unusually good definition; diffraction patterns exhibit high order reflections (up to 6th order). The lamellae have a macroscopic helicoidal twist about an axis lying in the plane of the lamellae, a cholesteric supramolecular structure, which derives from the chiral, steroid mesogenic component. Surprisingly, this mesophase composed of low molar mass cyclic siloxanes may be drawn into fibres tens of metres in length, to give a morphology having the lamellae normal to the fibre axis.

1. Introduction

Most of the work to date on liquid-crystalline polysiloxanes has dealt with side-chain polymers with an aim towards incorporating greater flexibility into the polymer backbone via the siloxane moiety [1]. This increased backbone flexibility lowers the glass transition temperature and allows the characteristic properties of low molar mass liquid crystals to be realized near ambient temperature in these liquid-crystalline polymers. In such polymers, a flexible backbone in conjunction with decoupled mesogen side-chains (i.e. side-chains having a sufficiently long spacer) enables the rotational and translational motions of the mesogens to be dictated primarily by excluded volume interactions between (not necessarily topological) nearest neighbour mesogens. Such interactions are believed to be the dominant intermolecular interactions responsible for mesomorphism in low molar mass liquid crystals [2]. By contrast,

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a small siloxane ring having mesogenic units attached by short spacer chains might have intramolecular constraints that preclude certain kinds of intermesogen interactions. For example, within the cyclic siloxane unit, the motions of topologically neighbouring mesogens may be highly correlated. Computer simulations have predicted phases ranging from discotic to conventional nematic depending on the size of the siloxane ring and the rigidity and length of the spacer group used to attach the mesogens to the ring [3].



This paper examines the packing and structure exhibited by commercially available [4], cholesteric, cyclic siloxane liquid crystals (Wacker LC-Silicones). This liquid crystal has been considered previously because of its attributes related to light processing media [5,6]. The cyclic siloxane liquid crystal has a general chemical structure (I) that enables the cholesteric wavelength of selective reflection [7], λ_{\max} , to be varied from the UV to the near IR by changing the molar ratio $p:q$ of the two mesogen units, biphenyl-4'-allyloxybenzoate (B) and cholesteryl-4'-allyloxybenzoate (C). The average ring size $\langle p+q \rangle$ is 5, and the approximate idealized dimensions of the extended mesogenic side-chains are indicated on the structural diagram (I). The primary commercial interest in this material derives from the fact that it can be readily shear-oriented and utilized in film form having a planar or Grandjean texture uniformly oriented over macroscopic dimensions wherein the cholesteric axis is normal to the film. Herein we show that the cyclic siloxane liquid crystals form a lamellae structure having the layers normal to the shear plane. A unique characteristic of this low molecular weight liquid crystal is that it may be drawn into fibres, a property that is usually found in polymeric systems. We use electron microscopy and X-ray diffraction techniques to study the nature of the structure in films and fibres of quenched glasses of several cyclic siloxane liquid crystals. We show that the lamellar structure exhibits unusually well-defined interlayer order giving rise to high order (up to 6th order) X-ray reflections.

2. Experimental

2.1. Materials

Wacker LC-Silicones (Consortium für electrochemische Industrie GmbH) with differing mole fractions of cholesteryl mesogen ($x_C = q/(p+q)$) were used as received; these materials probably contain a distribution of ring sizes with the average $\langle p+q \rangle$ equal to 5.

2.2. Electron microscopy

Scanning Electron Microscopy (SEM) was performed on a HP550B Coates and Welter field emission scanning electron microscope. A freeze-fracture technique was employed with both film and fibre samples. This consisted of immersing the sample in liquid nitrogen followed by fracturing along the desired axis. Annealed samples were prepared by floating the fibres on water at about 350 K until the desired shrinkage was obtained. The fibre was then cooled in ice-water and fractured.

2.3. X-ray diffraction

X-ray diffraction techniques were used to identify the packing characteristics of both the film and fibre forms of the cyclic siloxane mesogen at room temperature. X-ray reflections (Cu-K α radiation, graphite monochromator) were recorded with an evacuated Statton camera (sample-to-film distances were 50, 72.9 and 170 mm). Films were prepared by repetitive shearing of the heated (~ 415 K) liquid-crystalline melt between Teflon sheets (3.0 mm thick FEP polymer film, DuPont; obtained from American Durafilm Co., Inc.). Fibres were drawn from the liquid crystals near their clearing point (~ 450 K) and then quenched to room temperature in air. Diffraction patterns were recorded with the X-ray beam either parallel or perpendicular to the cholesteric axis (C-axis) which is normal to the film surface (see figure 1 (a)). These diffraction geometries are designated normal and edge, respectively; in fibre samples the incident X-ray beam was normal to the fibre axis (see figure 1 (b)). Intensities were extracted from the X-ray films using a Joyce-Loebl Scandig 3 densitometer. Only intensities from films having optical densities less than one were compared to ensure linearity in the measurements. Even so, the intensities should be viewed qualitatively as they have not been corrected for Lorentz polarization factors.

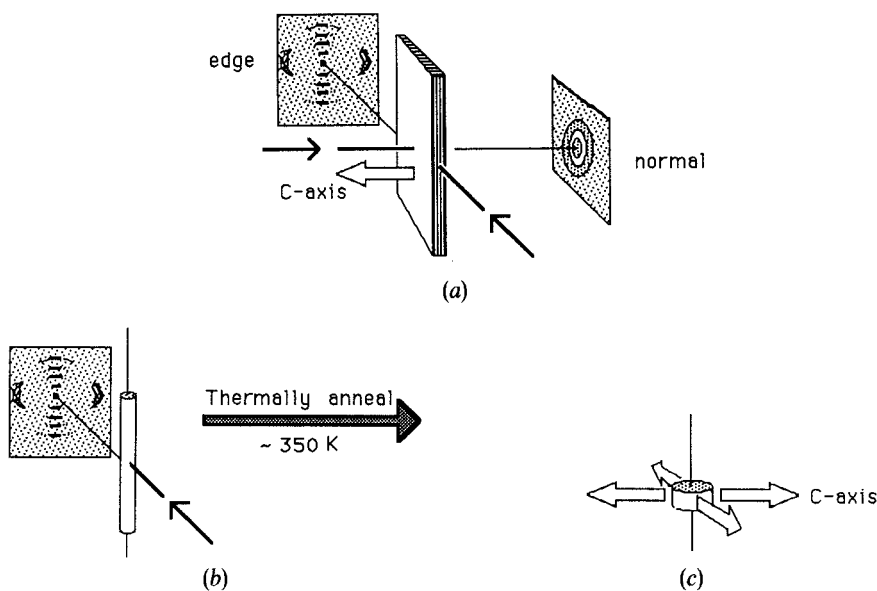


Figure 1. Schematic illustration of diffraction geometries for (a) the cholesteric film, (b) the uniaxial fibre (quenched) and (c) the annealed fibre of the cyclic siloxane liquid crystal glasses. The incident X-ray beam (bold arrows) are indicated and the orientation (distribution) of the cholesteric axes (open arrows) are shown. The cholesteric texture is absent in quenched fibres.

3. Results

Electron microscopy generally confirms the very good, macroscopic alignment of the cholesteric axis in films prepared by shearing the melts of I. Fracture surfaces tangent to the cholesteric axis (normal to the film surface) show vividly the Grandjean texture (see figure 2(a)) and they confirm the magnitude of the cholesteric pitch derived from visible reflection bands at λ_{\max} . No evidence for this texture is observed in thin, fractured fibres drawn and quenched from the melt; a featureless morphology is observed for cross-sectional fractures (see figure 2(b)). Fibres which are annealed do show that the cholesteric structure is restored. When viewed end-on a finger-print

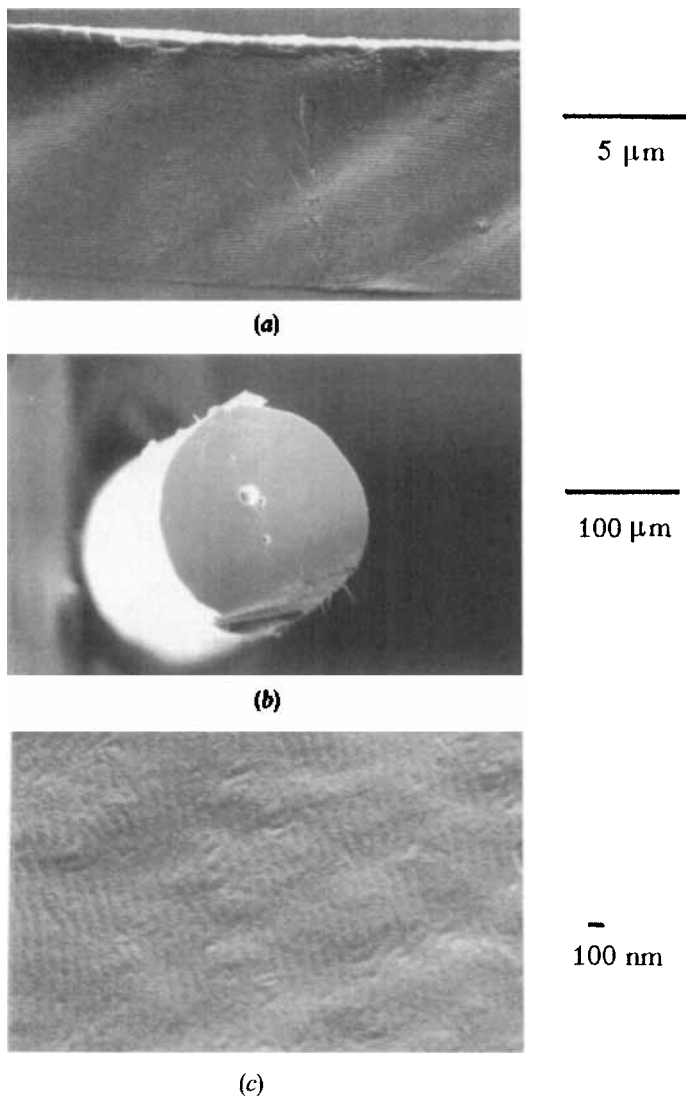


Figure 2. Electron photomicrographs of fractured cyclic siloxane glasses. (a) Grandjean texture; the cholesteric C-axis is approximately vertical and lies in the plane of the fracture surface; the C-axis is normal to the film-air and film-substrate interfaces; (b) end view of fractured fibre before annealing; (c) finger print texture in an annealed fibre showing random, uniplanar distribution of cholesteric axes.

texture is observed suggesting that the cholesteric axis is generally normal to the shrunken fibre axis, but its direction in a cross-sectional plane meanders randomly (see figure 2 (c)). Figure 1 summarizes the general textural morphology observed by electron microscopy in films and fibres of I; it shows the relative orientation of the cholesteric C-axis in these two specimen forms and the diffraction geometries used in the following discussion.

Figure 3 shows typical X-ray diffraction patterns of glassy films (see figures 3 (a) edge and (b) normal), and fibres (see figure 3 (c)). The most striking attribute of these diffraction patterns is the good alignment (see figures 3 (a) and (c)) and multiple order reflections. There is a systematic change in the progression of layer-line intensities and d spacings with x_C . A simple alternation in diffraction intensity for x_C of 0.14 in figure 3 (a) may be seen qualitatively in the optical densitometer trace in figure 4 (a) (a radial trace along the meridian). As indicated in figure 4 (b), for x_C of 0.40 there is a loss of layer-line intensities (weak 2nd, 3rd, and 4th order reflections) and the appearance of a low-angle diffraction peak ($\sim 50 \text{ \AA}$) as the mole fraction of steroid mesogen increases. Diffraction patterns of both film and fibre samples exhibit the same general features.

The multiple order layer-lines are the signature of a well-defined lamellar or smectic A structure in these materials. Note that for the fibre geometry the layers are normal to the fibre axis. Table 1 contains a summary of the primary d spacing observed for four samples that differ in the mole fraction of the cholesteryl mesogen; data is shown for both fibres and films. Evidence that the primary d spacing is a function of x_C (mesogen composition within the cyclic siloxane) is indicated, as a small increase in the d spacing occurs when the content of the steroid mesogen is increased. Table 2 contains all of the observed diffraction spacings for two materials examined in figure 4. Frequently multiple order (5th- and sometimes 6th-order) layer-lines are seen in the diffraction patterns for low x_C . These multiple order reflections are attributed to well-defined, translational order from layer to layer in a smectic A-like structure [8–11]. This good layer definition was observed in both films and fibres and table 2 shows that the calculated higher order diffraction spacings are in very good agreement with the observed d spacings. A diffuse equatorial reflection with a broad azimuthal intensity distribution corresponds to the nominal, lateral intermolecular distances within a single layer; this reflection ($4.2\text{--}6.0 \text{ \AA}$, increasing somewhat as x_C increases) is present in all diffraction patterns.

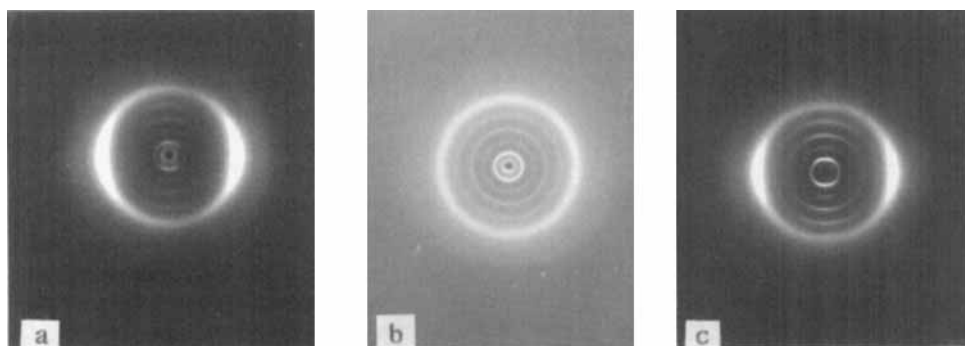
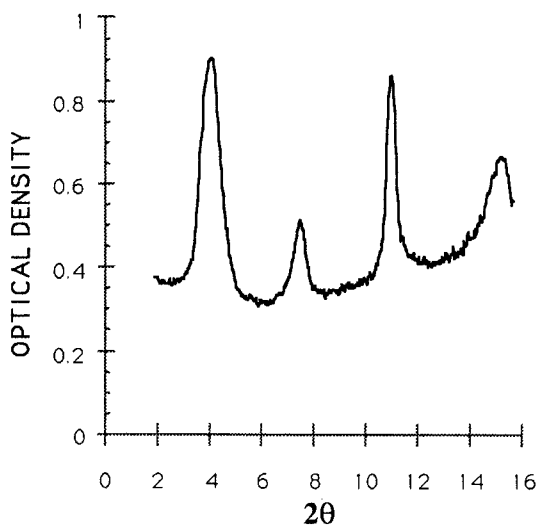
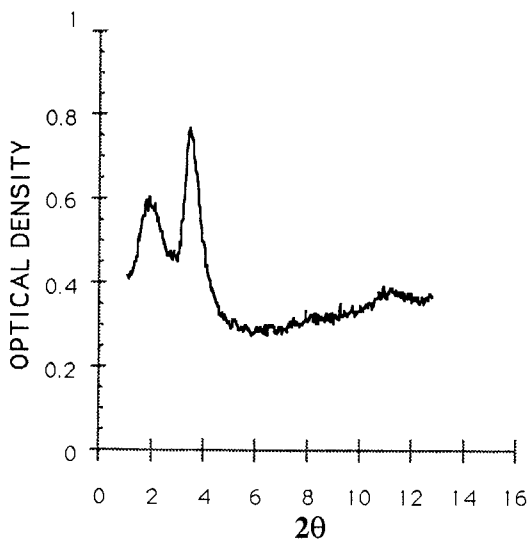


Figure 3. X-ray diffraction patterns from glasses of cyclic siloxane liquid crystals $x_C=0.14$; (a) edge diffraction of film sample; (b) normal diffraction of film sample; (c) fibre diffraction pattern. (Refer to figure 1 for geometry definitions.)



(a)



(b)

Figure 4. Radial optical densitometer traces along the meridian of edge diffraction patterns
(a) $x_c=0.14$, (b) $x_c=0.40$.

Table 1. Observed λ_{\max} and 1st order d spacings for cyclic siloxane liquid crystals.

x_c	$\lambda_{\max}/\text{\AA}$	$d(\text{film, edge})/\text{\AA}$	$d(\text{fibre}\dagger)/\text{\AA}$
0.40	4400	25.4	25.6
0.36	5150	25.0	25.0
0.31	6100	24.0	24.0
0.14	11900	22.3	22.6

† Drawn from the melt.

Table 2. X-ray diffraction data.

Meridional spacings/Å	Diffraction order	Calculated spacings†/Å
$x_c = 0.40$ film (edge)		
49 (small angle)		
25.4	1	25.0
12.2 (weak)	2	12.5
8.2	3	8.3
6.4 (weak)	4	6.3
Broad equatorial crescent—5.1 Å		
$x_c = 0.14$ film (edge)		
—(no small angle maximum)		
22.3	1	23.2
11.6	2	11.6
7.8	3	7.7
5.8	4	5.8
4.7	5	4.6
3.9	6	3.9
Equatorial crescent—4.5 Å		

† Calculated from average d spacing obtained from observed layer lines.

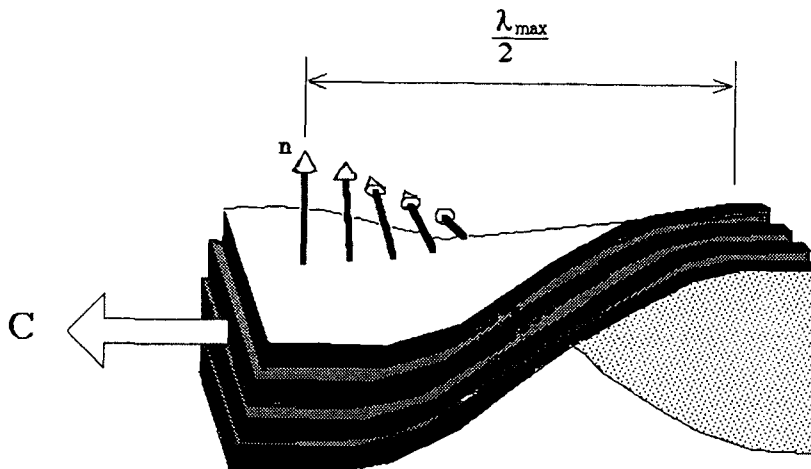
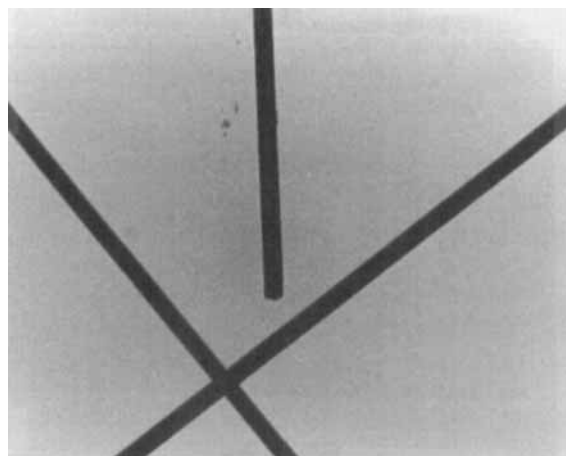
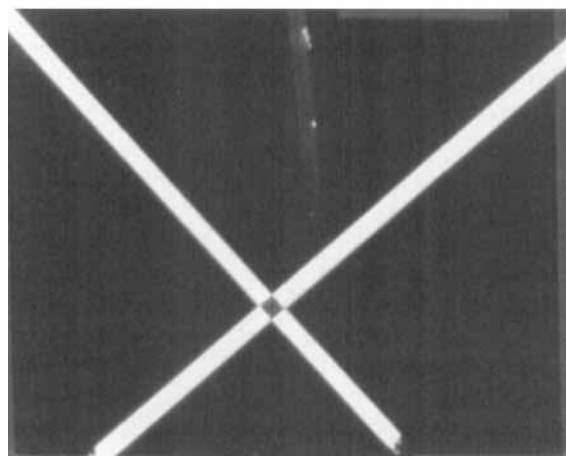


Figure 5. Schematic illustration of the cholesteric structure; lamellae (ribbons) of mesogenic side-chains having their axes perpendicular (on average) to the lamellae and defining the local director \mathbf{n} (normal to the ribbon surface). The stack of lamellae twists so that the set of local directors traces out a helicoidal path. The cholesteric axis (C) is normal to the surface of the macroscopic film samples; the magnitude of the one half of the pitch ($=\lambda_{\max}/2$) is illustrated in the figure.

X-ray patterns taken with the beam parallel to the cholesteric axis (normal to the film surface) show uniform azimuthal intensity rings with the same d spacings as in the edge patterns (see figure 3(b)). This azimuthal intensity distribution is expected if the lamellae twist in a helicoidal arrangement with the twist axis in the plane of the lamellae; this arrangement generates a cholesteric texture with the twist axis perpendicular to the long axes of the mesogenic side-chains and the macroscopic film surface. A schematic illustration of the cholesteric structure compatible with our data is shown in figure 5; in the illustration the alternating strata correspond to variably



(a)



(b)

Figure 6. Optical photomicrographs of drawn fibres of a cyclic siloxane liquid crystal; (a) unpolarized light (b) crossed polars (parallel to photo edges).

interdigitated mesogens (hydrocarbon-rich stratum) possibly segregated from a siloxane-rich interface comprised of the cyclic siloxane part of the mesogens. The normal to the smectic-layers (the local director \mathbf{n}) traces out the cholesteric helix.

Surprisingly this twisted supramolecular structure may be mechanically deformed, i.e. fibres may be drawn with retention of the lamellar arrangement. Figure 6 shows photomicrographs of fibres ($x_c=0.40$, diameter $\approx 100\ \mu\text{m}$) which exhibit strong birefringence. X-ray diffraction (see figure 3(c)) shows that the lamellar structure is perpendicular to the fibre axis, and electron microscopy shows no evidence of a mature cholesteric twist in the quenched fibres. The quenched glassy fibres are quite brittle; in the mesophase, however, they maintain their integrity while being drawn to lengths of tens of metres.

4. Discussion

We present evidence for an unusually well-ordered, smectic-like helicoidal supramolecular structure in cyclic siloxane mesogens. The lamellar structure deduced from X-ray diffraction exhibited by quenched glasses (see figure 3) persists in the mesophase also. X-ray diffraction patterns obtained with a microheater at a series of elevated temperatures show that the highly ordered lamellar structure is retained up to the clearing temperature [12].

The exact details of the cyclic siloxane's global molecular conformation and the possible intermolecular arrangements among the pendant mesogens in the liquid crystal phase have not been deduced in the present work. Nevertheless, it is intriguing to examine the types of molecular conformations that are compatible with the lamellar arrangement shown in figure 5. For example, the arrangement of pendant mesogenic cores relative to one another around the siloxane ring may assume some rather different global shapes (see figure 7). In figure 7 (a), a disc-like shape is depicted where the pendant mesogens are splayed out radially about a siloxane rich centroid. However, in order to fit the cyclic siloxane molecule into lamellae keeping the pendant mesogens normal to the layers (and, perhaps, the siloxane and hydrocarbon components separated), the uniform radial splay of the mesogens in figures 7 (a) would have to be distorted. Figure 7 (b) and (c) show possible distortions; figure 7 (b) shows a cylinder-like shape. Admittedly this is an extreme global conformation in that it shows the steroid and biphenyl units separated on opposite ends of the cylinder. Such intramolecular aggregation might derive from intermesogen packing preferences discussed later. In this asymmetric (with respect to mesogen type) cylinder, the two mesogen-rich ends are separated by a siloxane interface. A conical shape (with a siloxane-rich nose-cone) is also a possible conformation for the cyclic siloxane liquid crystal (see figure 7 (c)). The cylinder shape (and the conical shape) would permit the observed mesogen packing into lamellae and allows for a siloxane-rich interface. Moreover, the cylinder shape would provide the continuity from layer to layer (via interdigitation of the mesogens) needed to account for the fibre forming characteristics of this mesophase.

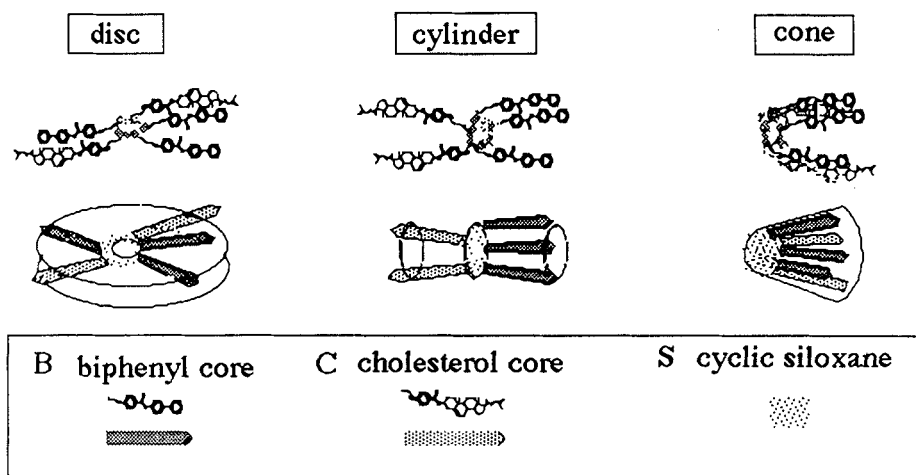


Figure 7. Coarse global shapes which may be adopted by the cyclic siloxane liquid crystal; the partitioning of mesogens and siloxane and the mesogen head-to-tail sense is illustrated.

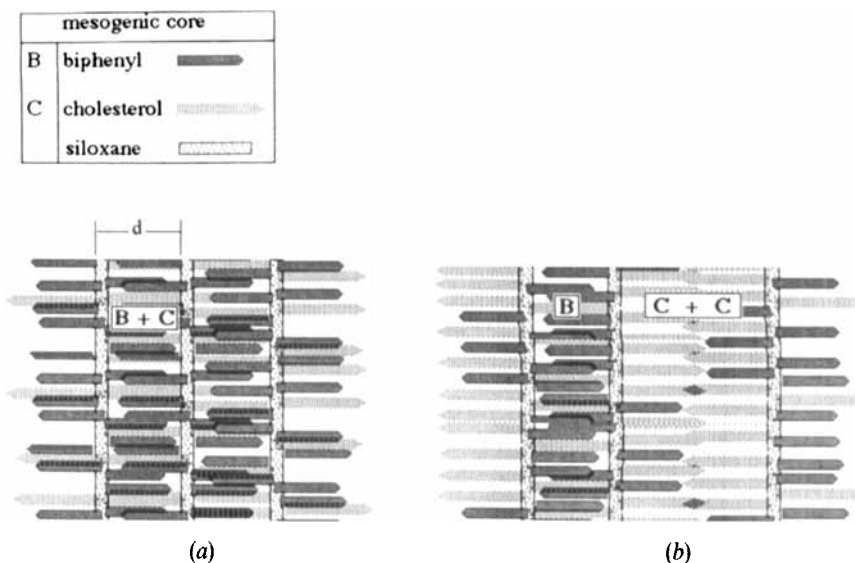


Figure 8. Classical smectic A structures which are compatible with the cyclic siloxane liquid crystal; (a) S_{Ad} bilayer with extensive association; (b) S_{Ad} bilayer (biphenyl mesogens) together with S_{A2} bilayer (cholesteryl mesogens); the latter have antiferroelectric ordering of mesogen head-to-tail sense.

Having suggested that the cylindrical global molecular shape for the cyclic siloxane liquid crystal is most compatible with experimental observations, we may speculate further about incorporating this shape into lamellae. To this end we examine the possible smectic-like structures that could be constructed with the cylindrical conformation. We restrict attention to smectic A structures. In figure 8(a), the classical smectic A structure is shown wherein the biphenyl (B) and cholesteryl (C) moieties mix (interdigitate) forming a single layer (B+C). If we insist that such mixed layers are separated by a thin interface ($< 5 \text{ \AA}$) of siloxane-rich material, this gives the pendant mesogen a head-to-tail sense in the layer (where the head is arbitrarily identified with the mesogen end closest to the siloxane junction; the tail is indicated by the arrow in the schematic illustrations of figures 7 and 8). Thus the extensive interdigitation of mesogens in the (B+C) (bi-) layer separated by a siloxane-rich interface (see figure 8(a)) might be more appropriately designated S_{Ad} , a semi-bilayer with extensive mesogen association, rather than S_{Ab} , (mono) layers with completely random head-to-tail disorder.

At low cholesteryl contents ($x_C < 0.15$) S_{Ad} would appear to be most compatible with the X-ray data; multiple orders of a single d spacing ($\sim 25 \text{ \AA}$) correspond to nearly complete mesogen interdigitation. At higher x_C , however, the multiple orders vanish and a small angle spacing ($\sim 50 \text{ \AA}$) appears. This spacing is consistent with partial interdigitation of cholesteryl mesogens reported [13] in side-chain polymers. Insertion of a smectic A_2 bilayer with antiferroelectric ordering of mesogen head-to-tail sense into the S_{Ad} structure (see figure 8(b)) may account for X-ray data in high cholesteryl content mesogens. Herein antiferroelectric ordering does not imply opposing dipolar ordering, rather, antiparallel ordering of mesogen head-to-tail sense in the bilayer. Such steric/flexibility driven antiparallel bilayer phases were originally suggested in modeling by Dowell [14]. (See [15] and [16] for recent reviews referring to this phenomenon.)

Recent observations [12] on the newly synthesized limiting cases $x_C=0$ and $x_C=1$, suggest that there are major organizational and packing (interdigitation) differences between these limiting cases, and that a transformation between highly interdigitated biphenyl mesogens to negligibly interdigitated steroid mesogens is responsible for the trends observed with x_C in the mixed pendant mesogen liquid crystals studied therein.

5. Concluding remarks

We propose a structural interpretation of electron microscopy and X-ray diffraction data wherein cyclic siloxane mesogens organize into a twisted (helical) lamellar arrangement having hydrocarbon-rich bilayer-like strata that may be reinforced and delineated by the (immiscible) siloxane component of the cyclic mesogen; such nano-aggregation (or phase separation on a molecular scale) of hydrocarbon and siloxane has been proposed before [17]. The helical structure is reminiscent of that originally proposed by Freidzon *et al.* [13] for cholesteryl containing acrylate and methacrylate side-chain liquid crystal polymers. A similar type of arrangement was subsequently proposed by Goodby *et al.* [18]. We find unusually good lamellae definition which exhibits high order diffraction. Moreover, we demonstrate that the lamellar structure is retained in fibres drawn from the mesophase. In the latter, the orientation of the lamellae normal to the fibre axis is very distinct from the transverse orientation generally exhibited by polymeric liquid crystals [19]. This normal orientation may confer unique optical properties to light propagating in such fibres.

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Note added in proof.—Related work by Kreuzer *et al.* has recently appeared [20].

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