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Enhanced smectic polymorphism of a cholesteric side chain co-oligosiloxane by blending with small molecule liquid crystals

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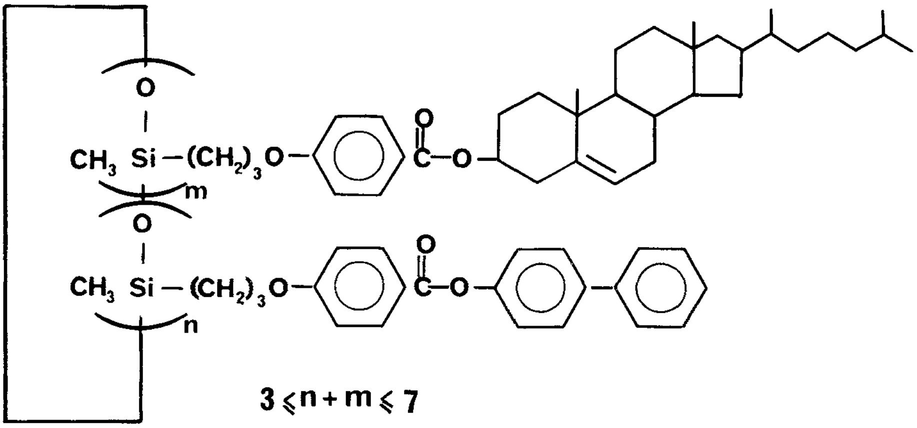
We have shown recently that a side chain chiral industrial co-oligosiloxane exhibits an original blue phase behaviour at the cholesteric–isotropic transition [1–3]. This same material has been studied dissolved in various polar small molecule nematic or cholesteric liquid crystals and it was shown that these associations are responsible for a large induced smectic domain. These systems allow the adjustment of the smectic A–cholesteric transition temperature from 180°C to room temperature, depending on the nature and concentration of the associated small molecule liquid crystal. Moreover the kinetics of this transition is strongly slowed down at high co-oligomer concentrations, suggesting, as confirmed by a preliminary X-ray study on the pure material, that the presumed glass transition allowing for the quenching of the Bragg optical properties at room temperature is in fact strongly associated with strong smectic correlations between the mesogenic parts.

1. Introduction

The industrial side chain siloxane co-oligomer is used in the manufacture [4] of decorative papers by a simple process consisting of shearing this material in the cholesteric phase, to obtain a planar orientation on the supporting paper, followed by a natural cooling to below its supposed glass transition, at about 50°C.

2. Materials and experimental set up

The side chain co-oligomer used in this work [4] was furnished by Wacker Chemie and is called SB in the following; it was the formula:



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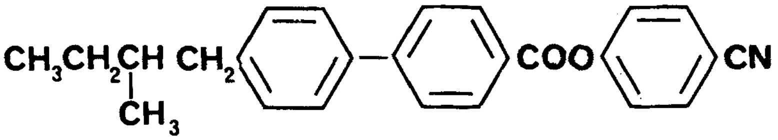
The mole ratio of mesogen to chiral side chain is about 50 per cent in the SB sample. After shearing SB gives cholesteric Bragg reflections in the visible optical domain, from 200°C to room temperature. The wavelength of normal incidence reflection undergoes a weak red shift when the temperature is slowly decreased; this effect is most observable in the vicinity of the isotropic transition [1]. The value of this wavelength in the lower part of this large mesomorphic domain ($T < 150°C$) is about 470 nm for an ordinary refractive index of 1·5.

The small molecule liquid crystals are commercial materials from Merck, Poole. The nematic one, K15 is 4-*n*-pentyl-4′-cyanobiphenyl, and the cholesteric CEI, has the formula:



The polymorphism of these compounds is: C + 99·5°C Ch 196°C I for CE1 and C 24°C N 35° I for K15. It is important to note that both molecules are strongly polar due to the C–N group and that the chiralities of CE1 and SB are in opposite sense, giving rise to a nematic racemic mixture at about 40 per cent (*w*/*w*) of CE1.

The differential scanning calorimetry measurements were performed on a Perkin–Elmer DSC7 calorimeter, the X-ray measurements, on a Rigaku rotating anode diffractometer, and a polarizing reflection or transmission Olympus microscope was used in association with a Mettler hot stage and a Jobin–Yvon monochromator for the observation of the textures and the determination of the reflected wavelengths.

3. Experimental results

3.1. *CE1–SB system*

3.1.1. *Polarized microscopy*

We initiated this study with polarizing optical examination of contact preparation between the co-oligomer and both the low molar mass materials. These preparations reveal the compatibility of these materials: no separation was observed with melts over the whole mesomorphic domain even after long annealing.

Even for concentrations as low as 5 per cent (*w*/*w*) of CE1, a drastic change of behaviour was observed relative to pure SB. At a variable temperature depending on the concentration ratio, a strong unwinding of the cholesteric helix can easily be observed. With an induced planar orientation of the samples (obtained with polyvinyl alcohol treated glass slides) and when the concentration of CE1 is low, this unwinding is seen between crossed polars by the strong red shift of the reflected wavelength, when the temperature was decreased. The microscopic observations revealed that this red shift is associated with the transverse displacement of disclination lines (figure 2) [5] (Grandjean lines) starting either from the border of the preparation or from impurities inside the sample. This leads to the progressive disappearance of the reflected colours and, at a critical temperature T_c, the grey, planar, small pitch cholesteric texture seen in the transmission polarized microscope transforms to a particular fan shaped, focal conic texture [6].

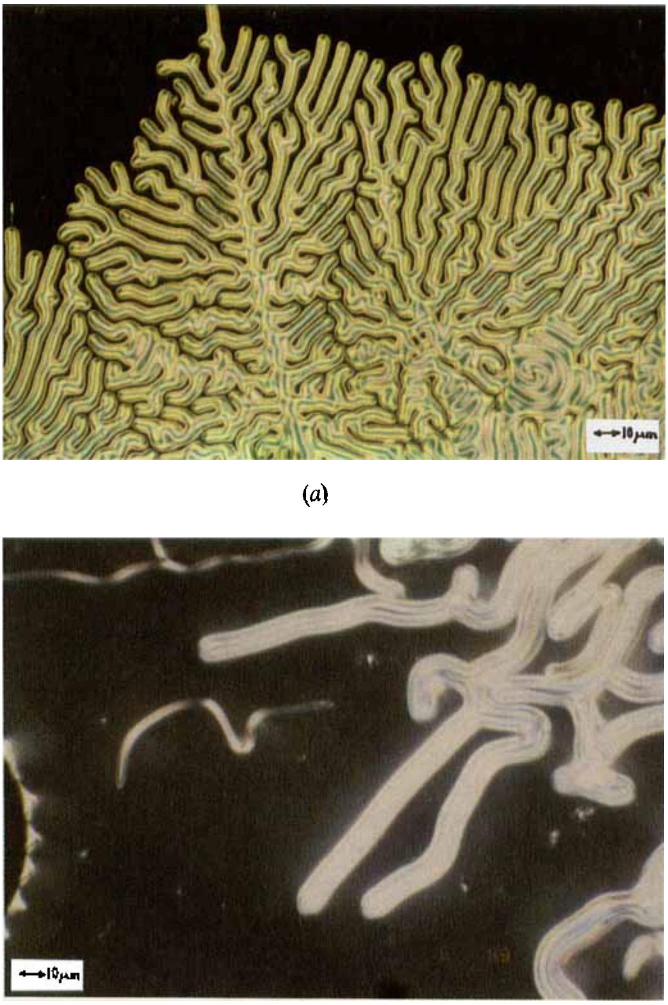
With the same melt sandwiched between untreated glass slides, an annealing, at a temperature of a few degrees lower than T_c, leads to a black texture characteristic of uniaxial media, with the symmetry axis parallel to the direction of light propagation. A weak shear on the upper plate produced the characteristic oily-streaks instability of the smectic homeotropic texture [7]. A rapid decrease in temperature gave rise to the appearance of the quadratic white domains corresponding to the dilation undulation of the smectic with the director normal to the layers [8], moreover, X-ray experiments made on these blends unambiguously reveal the S_A nature of this phase. When the temperature was increased above T_c, starting from this homeotropic texture, a spectacular transition was observed consisting of the nucleation and growth of strongly birefringent fingers: by changing experimental parameters such as concentration or the rate of heating, two very different fingers are observed. The first one (see figure 1 (*a*)), strongly coloured by Newton phenomenon, appearing at low concentration, or with fast heating rates, is identifiable to those described by Oswald *et al.* [9], and also observed during the unwinding of a cholesteric, induced by a decrease of the sample thickness [10]. The second one, with a white tint, never described to our knowledge, appears for a slow increase in the temperature and, for intermediate values of concentration ($C\% \approx 50\%$), gave the optical impression of cylindrical shaped objects which deviate the incident light strongly (see figure 1 (*b*)). It is of fundamental importance to underline here, that, in a temperature range of a few degrees, near T_c, it is possible to observe a thermodynamic coexistence of this second type of fingers and homeotropic smectic domains. This fact brings us to make the assumption of the presence of an intermediate phase between the lower S_A phase and the upper Ch one, analogous, in this particular glass slide geometry, to the Abrikosov phase, in the field of superconducting materials under magnetic fields. The nature of these phenomena is outside the scope of this work and a paper in preparation will be devoted to this.

3.1.2. *DSC study*

Figure 3 shows the DSC traces obtained for different concentrations of CE1: a high temperature peak, depending very weakly on concentration is observed, corresponding to the Ch–I (N–I, for the racemic mixture) transition. In the extreme concentration regions of the phase diagram see figure 4), this peak corresponds in fact to the complex blue phase behaviour described for both pure compounds. Nevertheless, no remarkable change is observed for the simple large pitch Ch–I transition and its enthalpy remains of the same order ($\approx 2\,\mathrm{J\,g^{-1}}$). At lower temperatures, the middle composition mixtures clearly exhibit a second, low enthalpy peak, appearing approximately at the same temperature at which the optical observations reveal the S–Ch transition. This temperature is a maximum in the vicinity of the racemic blends, and decreases when the concentration is moved in both possible ways. In fact, this peak becomes hardly observable when the concentration of CE1 is decreased, probably due to the slowed transition kinetics, as easily verified by optical observations. For relatively low concentrations of low molar mass liquid crystals, ($0\% < C\% < 40\%$) the crystallization tendencies of CE1 are suppressed, so the possibilities of quenching either the coloured films in the planar configuration, or the finger textures in the homeotropic one, are maintained if reasonable fast cooling rates, depending on concentration, are used. We return in the following discussion to the important experimental and applied interest of this property.

3.2. *K15–SB system*

As in the preceding case the compatibility of the mixtures obtained with these strongly polar mesogens is complete. As we observed in some preliminary studies, this compatibility is not limited to the lower component of the alkyl cyanobiphenyl homologous series but seems to be very general and applies to alkoxy-cyanobiphenyls



(b)

Figure 1.

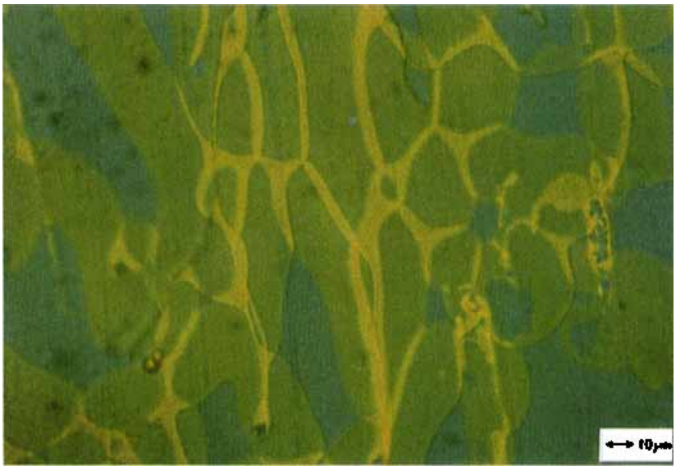


Figure 2.

and other related nematogens. This allows a very useful method for adjusting the temperature and kinetic properties of the resulting blends. Limiting here our presentation to the K15, we observe in the blends with low concentration of K15, a behaviour very similar to that for CE1 a decrease of chirality, induced by a progressive introduction of K15, leads to an enhancement of the smectic tendencies and then, a S–Ch transition becomes clearly observable.

The main differences with the CE1 phase diagram are, as foreseeable, observable when the K15 content becomes important. The isotropization transition temperature follows a quasi linear behaviour from the pure SB 200°C Ch–I value down to 35°C corresponding to the N–I transition of the pure K15, and the S_A–Ch transition temperature is progressively moved. This fact is of great experimental interest, leading, for an approximate content of 65 per cent of K15 (*w*/*w*), to a S_A–Ch transition at room temperature, with optical characteristics very similar to those of the CE1 blends.

3.3. *X-ray, DSC, and optical measurements on the pure cooligomer* [11]

Figures 5(*a*) and (*b*), show respectively X-ray $\theta - 2\theta$ traces obtained with an unoriented sample of SB at different temperatures, and the diffractogram measured at room temperature with fibres of the same material stretched in the mesomorphic Bragg reflecting phase. At room temperature, the presence of a thin ring at low angle, demonstrates the smectic A nature of the small scale ordering, with a smectic layer thickness of 26·5 Å, comparable with the mesogen side chain length. (A correlation length for smectic ordering extending over seven layers is obtained from the width of the peak via the Sherrer formula.) The asymmetric diffracted intensity, observed in figure 5(*b*) around the incident beam direction, corresponds to the average stretching induced orientation of the molecules parallel to the fibres. Concerning the temperature dependence, the low angle peak (see figure 5(*a*)) shows the progressive disappearance of the smectic correlations starting from the supposed T_g ($\approx$ 50°C), up to more than 150°C. A reversed temperature variation shows the reappearance of the same correlations by a progressive narrowing of the low angle peak without significant hysteresis at the low temperature variation rate used.

Figure 1. (*a*) Starting from the homeotropic smectic texture of a 50 per cent (*w*/*w*) CE1–SB, ($\approx$20 µm sample thickness, between untreated glass slides) at about 170°C, a rapid increase of the temperature leads to the growth of the coloured branching fingers, as observed here, which rapidly invade all the plate and coalesce, to form a cholesteric, large pitch, texture. The characteristic width of these fingers depends strongly on the kinetics used and on the region of the slide observed. (*b*) Two dimensional type fingers observed under the same conditions as in figure 1 (*a*), but with a slower increase of temperature: these fingers are of a calibrated size (depending only on the sample thickness) and never branched. They can either be stabilized if the temperature is maintained constant or grow by increasing their length or bending when the temperature is increased. They longitudinally associate with themselves, to form larger fingers. The unfavourable point defect that they present at their end when isolated, can be removed by this kind of association.

Figure 2. Transmission textures observed at room temperature with planar anchoring treatments, 20 µm thick, of slowly cooled (0·1°C) samples of pure SB (textures also observed at the temperature of cholesteric unwinding of CE1 low content samples): successive Grandjean–Cano lines separating different coloured regions are visible on the slide. In the second case, the displacement of these lines can be observed and their successive propagation leads to the successive lowering of the number of half pitches in the constant thickness of the sample, associated with the successive red shifts of a given region.

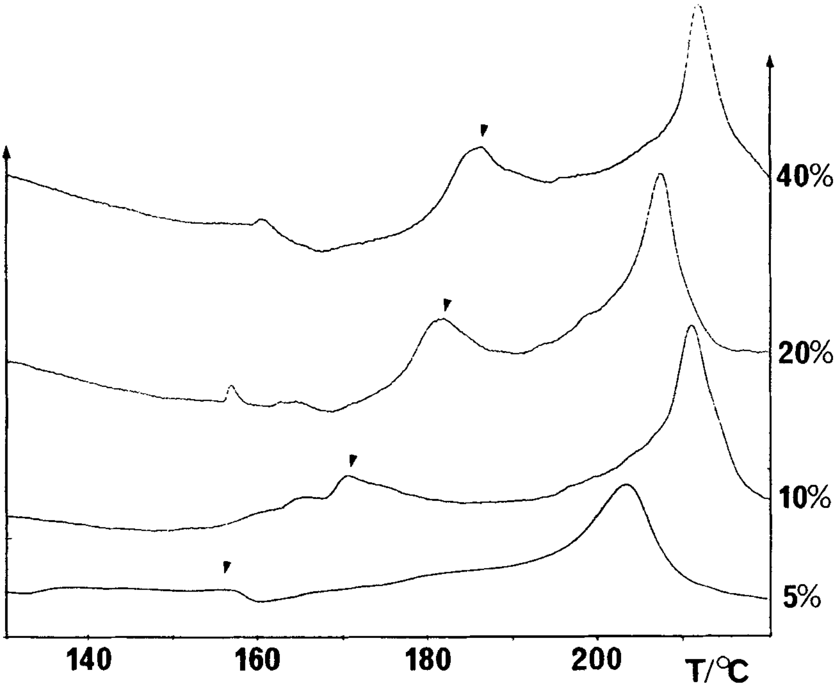


Figure 3. Differential scanning calorimetry traces obtained at a 20°C m^{-1} increasing temperature rate, for different CE1 concentrations (*w*/*w*) (indicated on the right). The higher temperature peak of $\approx 2\,\mathrm{J\,g^{-1}}$ enthalpy, corresponding to the Ch–I transition, depends only weakly on the CE1 content. The low temperature peak, corresponding to the optical observations of the S–Ch transition, indicated by arrows, moves towards low temperatures and becomes less observable when this content is decreased.

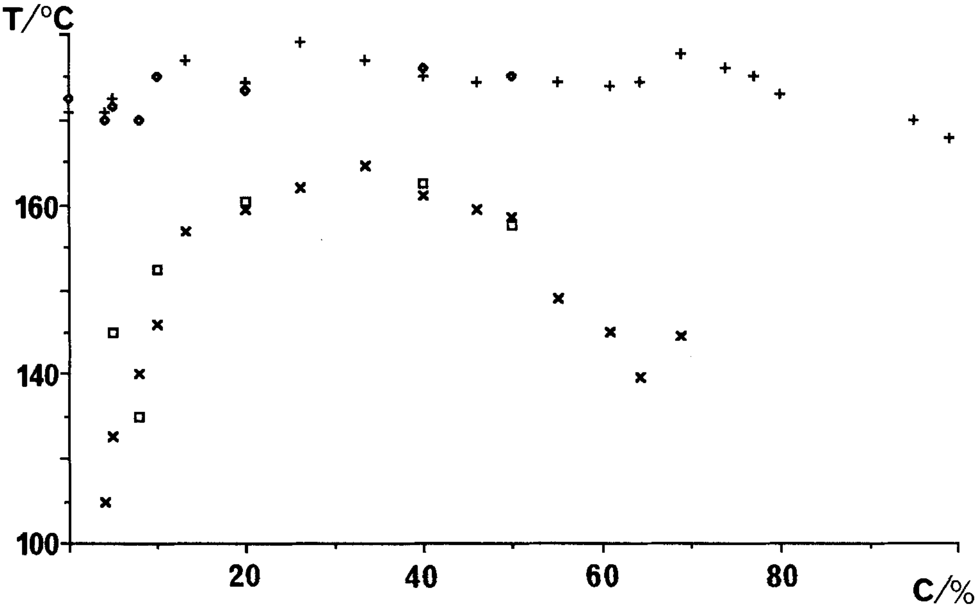


Figure 4. Phase diagram of the CE1–SB mixture obtained by optical and differential scanning calorimetry: right, at high CE1 content, crystallization of the blends takes place at low temperatures. (×) T_{sch} (opt), (+) T_{ChI} (opt), (□) T_{SCh} (DSC), (◇) T_{ChI} (DSC).

The DSC study (see figure 6) made directly on the as furnished SB, without temperature treatments, reveals a strong peak ($\approx 9\,\mathrm{J/g^{-1}}$) at the T_g temperature indicated by the technical notice of the manufacturer. This peak is obtained only for the first increasing temperature cycle and is not observed when the temperature is decreased. Moreover, immediate subsequent increasing temperature scans do not reveal a particular thermodynamic transition (first or second order, at the indicated glass transition). However, a few days annealing at room temperature allows a progressive reappearance of the peak (see figure 6) indicating a very slow reorganization of the mesophase at room temperature.

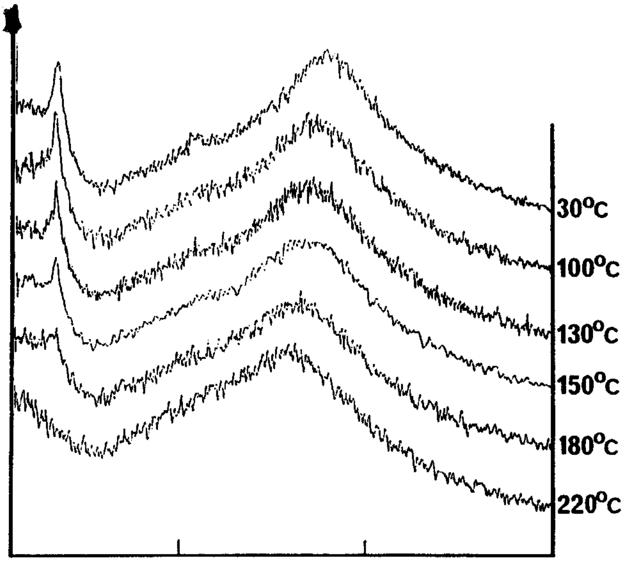
The use of a computer driven hot stage allows the study of the optical reflection under normal incidence of SB between glass slides treated for planar anchoring, at extremely low rates of temperature decrease (a few tenths of degree/h). These observations reveal, in fact, the same tendency of the cholesteric helix to unwind as seen for the low CE1 content blends. This unwinding is strongly dependent not only on the kinetics used but also on the thickness of the sample. Thick samples ($>10\,\mu$m) lead easily to a red coloured reflection under normal incidence, while thinner ones quench the violet-blue colour (the same as obtained in the industrial process described previously) even at cooling cycles as low as 0·1°C/h. The observation of the quenched red-shifted thick samples (see figure 2) clearly shows the Grandjean lines separating differently coloured planar domains: the number of half pitches as contained in the thickness of the sample, changes at the crossing of these lines [5].

4. Discussion

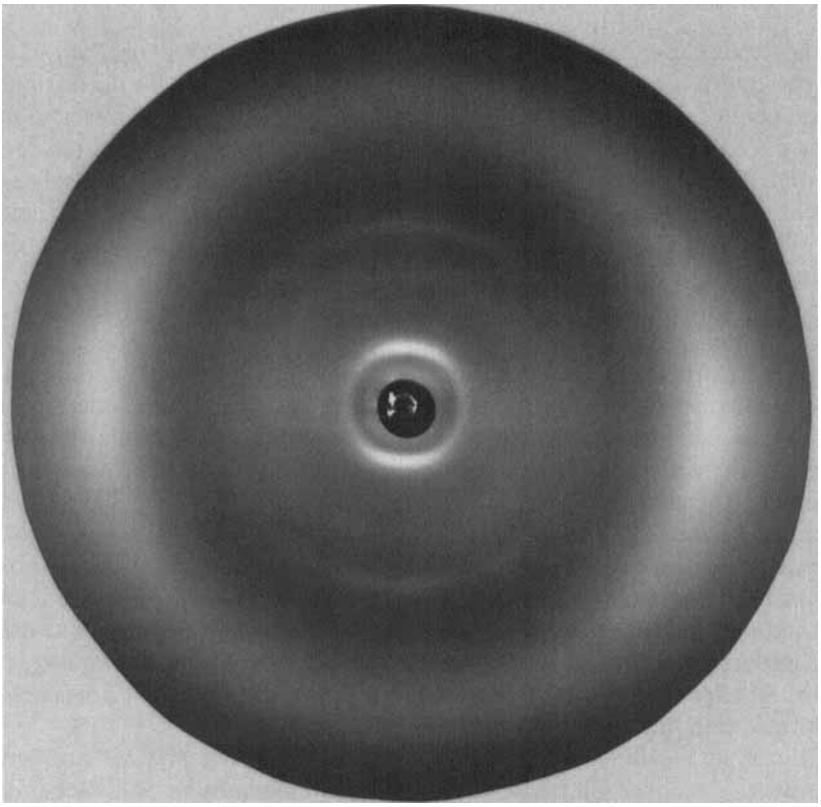
It becomes clear, now, that the particularly high rotational viscosity of this side chain cholesteric is probably responsible for a strong damping of the nucleation and the displacement of these lines. They have to propagate in successive waves to obey the smectic director tendencies, excluding the twist progressively when the temperature is decreased. The permeation [12] across them is needed, alone, without displacement of the molecular centres of gravity. The attachment of the mesogens and chiral units to the main siloxane chain makes this process very slow, as seen also in the dielectric experiments on comparable materials [13].

The CE1 phase diagram indicates a considerable change in the temperature and kinetics of the S_A–Ch transition strongly associated with the natural pitch of the mixture, illustrating here the topological incompatibility of chirality and layering. But, due to the rather different lengths involved in both the cholesteric and smectic organizations, the smectic ordering remains possible at a molecular level without incompatibility with the high scale level of the helical structure. The pioneering work of de Gennes [14] and more recently of Renn and Lubensky [15], have shown in a Ginzburg–Landau equilibrium thermodynamic frame, the existence of a partial analogy between the S_A–N transition in the presence of induced elastic deformations (our problem here is concerned with twist) and the superconductor–non-superconductor transition in the presence of an external magnetic field. Notwithstanding the important differences of symmetries of the two problems, this analogy predicts as in the superconductor case, the possibility of two very different processes for the S_A–Ch transition, depending on the Ginzburg parameter.

In the type 1 case, the transition is rather first order, and for an increase of temperature, the upper Ch phase processes, with unfavourable walls separating the domains. The case studied in a particular geometry in [9] from the dynamical point of view seems to be very close to this model. A considerably more complex situation



(*a*)



(*b*)

occurs in the type 2 case, and a true intermediate thermodynamically stable phase is expected even in the infinite three dimensional case. This phase is stabilized by the presence of now favourable walls (or defects), allowing for the coexistence of alternating regions of different order parameters. This case described theoreticaly in [15] leads probably, in confined geometries as our glass slide samples, to new situations involving strongly the double twist cylinder model developed for the blue phases and the concept of edge dislocation.

This useful approach will be elaborated in future papers and here we just want to focus our attention on the planar induced situation of the small pitch case which allows for the industrial uses described previously. Are the films, quenched at room temperature, associated with a type 1 or 2 situation? In addition is there a possible difference between them?

If we neglect in a first step the probable non-equilibrium nature of the quenched films and deal with infinitely slow rates of temperature change, the unwinding of the helical structure under the influence of the fluctuating cybotactic clusters [16] in the vicinity of T_c probably always takes place for sufficiently thick samples as demonstrated in our experiments. The problem is to know how far this equilibrium state unwinding can take place. The last half pitches being particularly hard to unwind (even impossible for orthogonal planar anchoring directions on the two slides), due to the singular high energy defects required in this case [17]. We can remark here that the free surface case involved in the industrial decorative paper described previously seems to lead to easier simple unwinding by rotating orientations of the director at the air interface during the cooling process. But we have to take into account a probable fast cooling at this interface which supposedly inhibits this process and brings the unwinding mechanism very close to the glass slide case studied here.

For a certain low number of half pitches comprised between the glass slides, we must try to imagine how the molecular smectic tendencies could be made compatible with the helical mesoscopic organization. Large domains of perfect smectic A structure are probably formed, alternating in the sample thickness, with strongly twisted cholesteric walls, parallel to the glass slides and unable to relax under the achoring conditions. Depending now on the Ginzburg parameter of the medium these walls are (case 2) or are not (case 1) able to transform to the regular screw dislocation array described in [15]. The situation in our low kinetic systems is complicated by the quench, at room temperature, of non-equilibrium states and the experiments previously described make us ask two questions:

(i) Are the thin optically stable Bragg reflecting films obtained at room temperature associated with case 1 or 2 or with a non-equilibrium cholesteric situation [16] (this last possibility cannot be completely disregarded due to the

Figure 5. (*a*) X-ray diffraction intensity of a powder pure SB sample at different temperatures, indicated on the right of the diagram, versus detection angle ($\theta-2\theta$ experiment): the low angle peak observable at low temperatures corresponds to the smectic layers correlation length, with a 26·5 Å distance and progressively disappears as the temperature is increased. The high angle diffuse peak corresponds to the liquid-like order between side chains. (*b*) Diffraction pattern of a fibre of the pure SB sample at room temperature: the low angle ring indicates, as in figure 5 (*a*), the smectic layering of the molecular order. The asymmetry of the intensity, around the incident beam direction, indicates an average orientation of the side chains parallel to the fibre stretching direction.

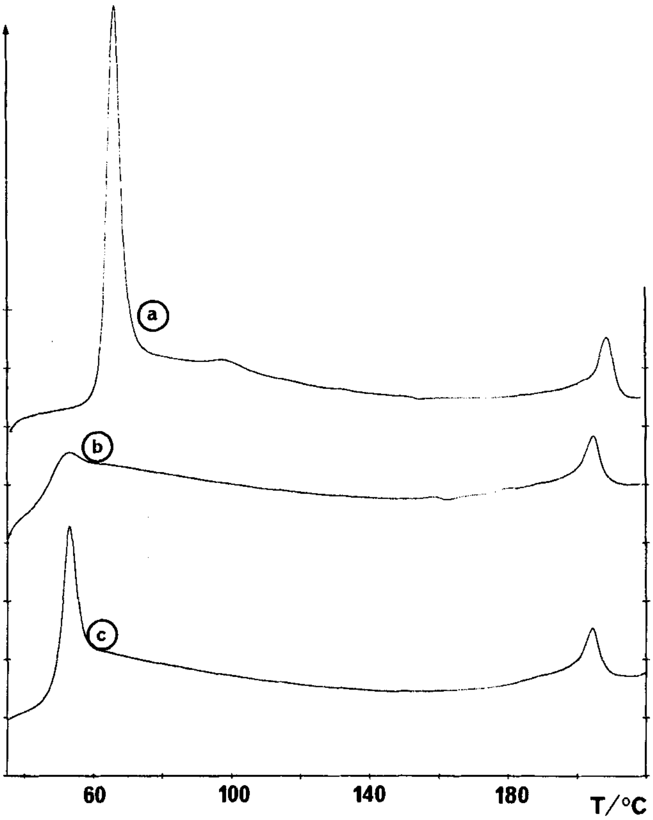


Figure 6. Differential scanning calorimetry traces obtained at a 20° min^{-1} increasing temperature rate, for a pure SB sample. (*a*) For the compound coming directly from the manufacturer or after long annealing at room temperature, a $\approx 9\,\mathrm{J\,g}^{-1}$ enthalpy peak is observed at 65°C; (*b*) Just after the first temperature cycle: the strong low temperature peak disappears. (*c*) After one day annealing at room temperature, the peak reappears at a lower temperature with a $\approx 2\,\mathrm{J\,g}^{-1}$ enthalpy. Traces with longer annealed samples demonstrate the progressive recovery of the original peak. The higher temperature peak of $\approx 2\,\mathrm{J\,g}^{-1}$ enthalpy corresponds to the Ch–I transition.

bulk sample nature of the X-ray experiments)?: an accurate optical study of the high order reflections seems, in that case, able to distinguish the differently distorted and undistorted helices [18].

(ii) Is the low kinetic transformation observed by DSC at low temperatures in the bulk sample related to the formation or transformation of the walls?: another possible explanation could be the existence of a highly ordered smectic phase appearing slowly at room temperature but in this case the X-ray pattern of annealed samples should present some characteristics of the in-plane molecular ordering [11]. The appearance of this peak is probably related to the concept of enthalpy relaxation developed in the domain of glassy materials (see, for example, [19] for non-mesomorphic polymeric materials). The explanation of the overshoot in T_g is based on a time distribution of the relaxation mechanisms of the polymer chain in the glassy state. In fact, no general microscopic description of this mechanism in terms of the chain conformational changes exists. In the particular case of our side chain materials, the probable strong coupling of the mesogens to the cyclic main chain suggest that these relaxation mechanisms involve slow reorganization of the side chains.

Different experimental studies are actually undertaken by us, to answer these questions and to increase the understanding of these original liquid crystal materials:

(i) X-ray and neutron scattering on the pure and blended materials will enhance our knowledge of the smectic phase encountered.
(ii) Associated with the quenching possibilities of these systems, the usefulness of electron transmission studies, demonstrated by us in the blue phase case [3], could also be of great interest here, having in mind the objective of direct observations of walls, defects or finger structures.
(iii) An accurate kinetic study of the quenching conditions of the blue phase, and intermediate S_A–Ch phase will also be of great interest to develop these last previous experiments as well as from a fundamental and applied point of view.

To conclude this discussion we want now to focus on some applied aspect of this work [20]. Taking into account the industrial nature of the material involved, it seems to us that blending low molar mass liquid crystals opens a new field of application. By varying the amount of liquid crystal introduced allows the adjustment not only of the colour variation domain, but also of the rate of this variation. The first possibility can bring, for processing comparable to that, actually used (described in the Introduction) the possibility of quenching different colours from the same mixture, just by changing the temperature before cooling the paper. Both these associated adjustments can also lead to interesting possibilities in the ground of low cost thermal indicator papers taking into account not only the temperature but also the time.

5. Conclusion

Initiated from the blue phase aspect our interest in this co-oligomer has been extended to the previously unknown smectic characteristics of this material. On the one hand this new point of view is probably necessary to understand the enormous supercooling possibilities of BP1 demonstrated by our recent electron microscopy observations of this phase, quenched at room temperature. On the other hand this original system seems also of great interest for investigating the poorly understood rich aspects of the S_A–Ch transition. This material interest is mostly due to its particular intermediate situation between low molecular weight crystalline, liquid crystal and high molecular weight amorphous polymers. Moreover, the blending of this co-oligomer with low molar mass liquid crystal gives us the possibility to adjust and modify in a large way the transitional and kinetic properties of the pure material, thus enlarging considerably the field of experimental investigation and allowing prospects for new applications in the field of temperature dependent optical properties.

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