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Rheological properties of chiral liquid crystals possessing a cholesteric–smectic A transition

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We have measured the rheological properties of two cholesterol derivatives (cholesteryl myristate and cholesteryl nonanoate) in the vicinity of their cholesteric–smecticA transitions. The results for the two compounds differ qualitatively, and are in agreement with results based on optical observations of new defects in cholesteryl nonanoate showing that this material, traditionally considered as a typical cholesteric, in fact exhibits a TGBA phase between the cholesteric and smectic A phases.

1. Introduction

Chiral liquid crystals (CLCs) have been much investigated, from the discovery of the liquid crystal state in cholesterol derivatives [1] to the recent discovery of the TGB phases [2] and smectic blue phases [3]. Studies on chiral liquid crystals deal mostly with their structural properties and their interplay with electrical field or anchoring conditions, at the root of display applications. Their complex flow properties have long been recognized but yet scarcely studied [4]. We focus here on the flow behaviour of two cholesterol derivatives: cholesteryl tetradecanoate (CT) and cholesteryl nonanoate (CN), in the vicinity of their cholesteric to smectic A transition (N*–SmA). CT is known to display a clearly first-order transition [5] and CN presents a weakly first-order transition, as evidenced by investigating pretransitional effects in this compound: X-ray scattering measurements of the smectic order parameter [5], density [6], pitch and elastic constants measurements [7]. The specific pretransitional effects for CN were reported to result from pretransitional fluctuating smectic clusters in the cholesteric phase [5, 7].

In the frame of the superconducting analogy [8], two types of cholesteric can be distinguished (called type I or type II). In type I, twist deformations do not penetrate into the SmA ordering, the N*–SmA transition is direct, with no any intermediate state. In type II, twist deformations penetrate the SmA phase, as 'vortex' lines, more precisely screw dislocations; the N* and SmA states are separated by a TGBA phase in the phase diagram. The TGBA phase usually exists over a very narrow range of temperature and is experimentally difficult to identify. Following the considerations of Renn and Lubensky [9], and taking into account the arguments of Vigman and Filev [10] (who claimed that the analogue of the Landau–Ginsburg parameter for CN is exactly $1/\sqrt{2}$) and recent results on defects [11], CN could be a good candidate for a type II CLC, whereas CT is clearly of type I.

The aim of this study is to compare the pretransitional flow properties of CT and CN in the vicinity of their N*–SmA transitions and obtain further information to assign a type I or type II form to CN.

2. Experimental

CN (97% purity) and CT (99% purity) are commercially available and were obtained from Aldrich. In CT, solid crystals were observed in the isotropic phase at the phase transition. The CT material was therefore purified twice by recrystallization from ethanol; the crystals did not appear after purification. CN was used

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as obtained. Note that the purification procedure performed for CT does not remove soluble impurities.

Rheological measurements were performed using a rheometer DSR500 from Rheometrics with a cone and plate geometry (diameter 40 mm, cone angle 0.04 rad, minimum sample thickness between the truncated cone and the plate 51 μm). The shear cell was thermo-isolated in a home-made transparent chamber inside which hot air at a controlled temperature circulated. The sample was protected from direct air flow by a second smaller cell. This ensured an atmosphere close to the desired temperature around the shear cell. This desired temperature was imposed on the sample through the thermo-regulation system of the rheometer, a thermostated bath in contact with the lower plate. The rotor and stator temperatures were measured, the difference being controlled with an accuracy of 0.1°C; furthermore, shearing was expected to favour temperature homogenization throughout the sample. We checked the absence of a radial temperature gradient using a well-known property of CN [7]: near the N*–SmA transition, the cholesteric pitch increases sharply. When the pitch corresponds to an optical wavelength in the visible range, the cholesteric specimen shows colours on light reflection (Bragg reflections). This strong temperature dependence of the cholesteric pitch makes CN a sensitive indicator of thermal gradients. The upper plate of our set-up was transparent except at its central part (a disc of 22 mm diameter where the plate is linked to the rotor). We checked that a uniform colour was seen in the visible part of the sample, although very locally all the observed spectra revealed some defects. We started from a temperature deep in the isotropic phase then slowly cooled stepwise (steps of 0.2°C near the transition). At each step, after temperature stabilization, we imposed discrete increasing shear rates and then measured the steady-state response of the sample (the stress).

3. Results

3.1. *N*–SmA transition temperatures*

As mentioned above, the cholesteric pitch increases when approaching the transition and reaches values comparable to light wavelengths: the cholesteric specimen then shows corresponding colours due to selective light reflection that can be recognized with the naked eye.

For CT, the N*–SmA transition is strongly first order [5]. The cholesteric pitch increases slightly on cooling, then jumps at the transition point, from about 400 nm (Bragg reflection in blue colour/cholesteric phase) to infinity (transparent sample/smectic phase). The transition point is thus determined, by direct observation through the transparent shear cell, as the temperature at which the blue selective reflection disappears.

For CN, the cholesteric pitch is reported to 'diverge' for temperatures approaching the transition point, displaying selective reflection colours changing from blue to red and then infrared, very close to the transition [7]. The transition to the SmA phase is accompanied by marked changes of the texture, which can be recognized via polarizing microscopy [11]. Our polarizing microscopy observations out of the rheometer indicate that, on cooling, the transition to the SmA phase occurs 0.2°C below the temperature, T_{red}, at which the red colour (last *visible* selective reflection) disappears. This is in good agreement with literature reports [7]. The textural changes can even be recognized with the naked eye: the sample becomes less turbid in the smectic phase. We estimate the accuracy of such a measurement to 0.1°C.

We found that for CT the transition occurred at 78°C, which is in rather good agreement with the literature (between 78 and 80°C) [5, 12]. In the case of CN, we found $T_{\mathrm{N^*\text{–}SmA}}=70.1°\mathrm{C}$. The temperature range ($T_{\mathrm{N^*\text{–}SmA}}+1°\mathrm{C}$; $T_{\mathrm{N^*\text{–}SmA}}$) corresponding to the divergence of the pitch is in good agreement with literature results but the absolute value of $T_{\mathrm{N^*\text{–}SmA}}$ observed here is lower (it was reported to be between 74 and 75°C for purified samples [5–7]). This difference can be attributed to the presence of soluble impurities in our CN material. Although it is known that the effect of impurities on the pretransitional properties of cholesterics can be significant, we did not attempt to study such effects in this work, which was restricted to a commercially available material.

3.2. *Rheology*

The results of our measurements are presented as log–log plots of shear rate versus stress (figure 1 for CT, figure 2 for CN), to underscore the generally observed power law behaviours ($\dot{\gamma}\sim\sigma^m$); m is then directly obtained as the slope of the curve.† Each curve corresponds to one temperature. Note that when $m=1$, the system is Newtonian; when $m>1$, it is shear-thinning, i.e. its apparent viscosity ($\eta=\sigma/\dot{\gamma}$) decreases with increasing shear rate. Apparent viscosity for a given shear rate of $5\,\mathrm{s}^{-1}$ (figure 3) is presented as a function of the normalized temperature $T\text{-}T_{\mathrm{N^*\text{–}SmA}}$ for both CN and CT.

It should be noted that all the plots correspond to steady-states ($\dot{\gamma}$ was imposed and we waited for a

†Such power laws are reported for other liquid crystal phases and can be understood as defect-mediated regimes, adapting to liquid crystals the theory developed long ago by Orowan for the motion of line defects in solids [13].

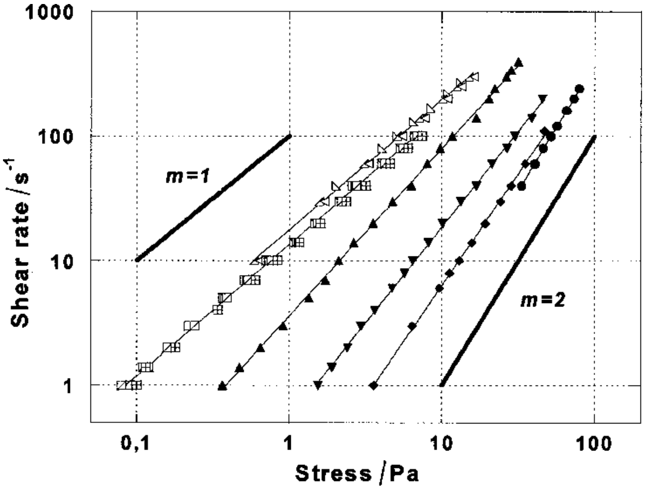

Figure 1. Shear rate versus stress at different temperatures for cholesteryl tetradecanoate (CT). Open symbols: cholesteric phase, $T=82$, 79, 78.7, 78.4, 78.2°C ($\dot{\gamma} \sim \sigma^m$, $m=1$). Filled symbols: smectic phase, $T=77.9$ ($m=1.35$), 77.6 ($m=1.55$), 77.1 ($m=1.8$), 76.8°C ($m=2$). To aid reading, bold lines with exact slopes corresponding to $m=1$ and $m=2$ are represented.

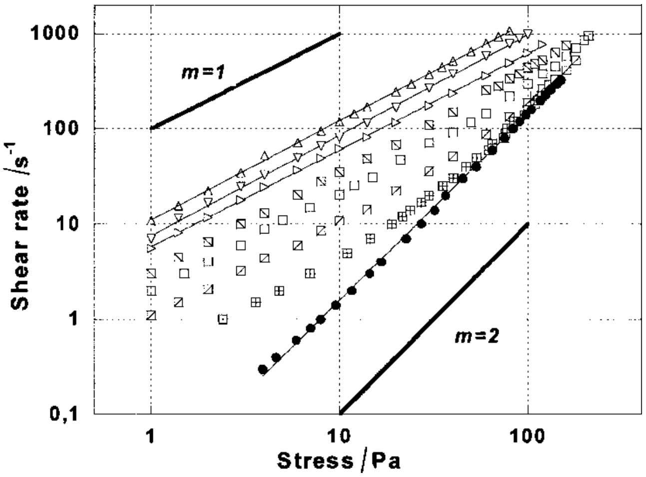

Figure 2. Shear rate versus stress at different temperatures for cholesteryl nonanoate (CN). Open symbols: triangles, for $T=75$, 72, 71.1°C ($T>T_{\mathrm{N^*\text{-}SmA}}+1$°C), $m=1$; squares for $T=70.9$, 70.7, 70.5, 70.3°C ($T_{\mathrm{N^*\text{-}SmA}}<T<T_{\mathrm{N^*\text{-}SmA}}+1$°C), from $m=1$ (low stresses) to $m=2$ (higher stresses). Filled symbols: smectic phase, 70°C, $m=2$. To aid reading, bold lines with exact slopes corresponding to $m=1$ and $m=2$ are represented.

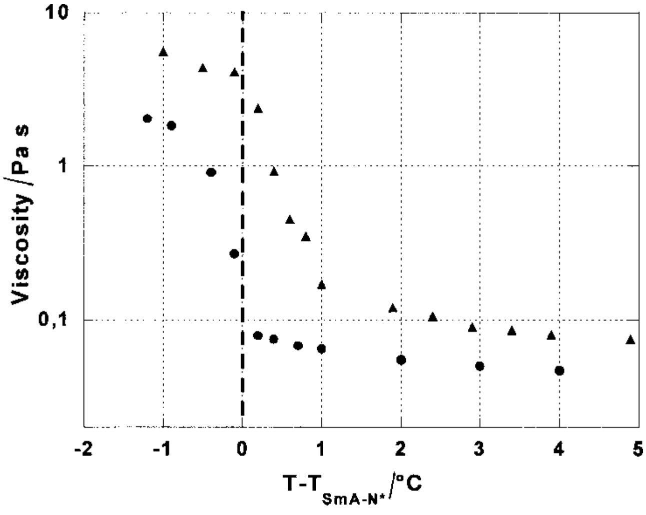

Figure 3. Viscosity ($\eta=\sigma/\dot{\gamma}$) versus T-$T_{\mathrm{N^*\text{-}SmA}}$ for CN (▲) and CT (●) for a shear rate of 5 s^{-1}.

stationary value of the stress). The results are reproducible as long as the temperature stabilization procedure, described above, is followed.

3.2.1. *Results for CT*

Figure 1 shows that the cholesteric ($T>78$°C) and smectic ($T<78$°C) phases exhibit different rheological behaviours. In the cholesteric phase, the rheological behaviour depends only slightly on temperature: it remains Newtonian (figure 1) in the range (82–78.2°C) and the viscosity smoothly increases on cooling to $T=78.2$°C (figure 3): it doubles from 0.047 Pa s (at 82°C) to 0.08 Pa s (at 78.2°C).

At the point of the N*–SmA transition, the behaviour of CT switches from Newtonian, in the cholesteric phase, to shear-thinning in the smectic phase. Within the SmA phase, the slope m of the $\dot{\gamma}$ (σ) curves increase from 1.35 (at $T=77.9$°C) to 2 (at 76.8°C), and viscosity strongly increases with decreasing temperature: from 0.3 Pa s (at $T=77.9$°C) to 2 Pa s (at 76.8°C) for a shear rate of 5 s^{-1} (see figure 3). It transpires that steady states cannot be obtained for high shear rates ($\dot{\gamma}>400$ s^{-1}), and are thus not reported on the plot. The fact that steady states are not obtained might be related to a shear-induced transition towards another regime (see later). The measurements cannot be continued at temperatures lower than 1.5°C below $T_{\mathrm{N^*\text{-}SmA}}$: at $T_{\mathrm{N^*\text{-}SmA}}$–1.5°C, the viscosity strongly increases with time and the rotor finally stops: one can then observe a slow growth of solid nuclei in the sample and after a few hours the material is completely crystallized. This observation is reproducible. It was believed up to now that the LC smectic state for CT existed on cooling as far as 60°C. This is confirmed by DSC [14] and can be easily observed under the polarizing microscope. The shearing experiment on CT thus shows that the smectic phase below $T=T_{\mathrm{N^*\text{-}SmA}}$–1.5°C is a supercooled metastable state. It is known that the system can overcome the supercooling energy barrier when an external shear acts on it. In contrast to an induced phase transition, after overcoming the supercooled state, the transition is not reversible when the shear is switched off.

3.2.2. *Results for CN*

Our experiments show that two temperature ranges have to be distinguished for CN above $T_{\mathrm{N^*\!-\!SmA}}$, while CT exhibits the same rheological behaviour down to the point of phase transition. For CN, in the high temperature range, $T > T_{\mathrm{N^*\!-\!SmA}} + 1^\circ\mathrm{C}$, the behaviour of the cholesteric phase is Newtonian (see figure 2), with a viscosity slightly increasing on cooling (figure 3). In the range close to the phase transition, $T_{\mathrm{N^*\!-\!SmA}} < T < T_{\mathrm{N^*\!-\!SmA}} + 1^\circ\mathrm{C}$, the behaviour changes. First, the viscosity quite abruptly increases in comparison with the high temperature region. Second, the behaviour becomes clearly shear-thinning. Indeed, in figure 2, the slope m of the $\dot{\gamma}(\sigma)$ curves, between 71.1 and 70.3°C, changes continuously from about $m = 1$ at small shear rates to $m = 2$ at high shear rates, where the curves approach and then merge with the first curve of the smectic phase after the transition. This change from $m = 1$ to $m = 2$ occurs for smaller and smaller shear rates when cooling to the point of phase transition. Note that the merging of $\dot{\gamma}(\sigma)$ curves of two neighbouring phases is striking (see later).

Within the smectic phase ($T < T_{\mathrm{N^*\!-\!SmA}}$), the $\dot{\gamma}(\sigma)$ curves exhibit a slope $m = 2$ over the whole range of shear rates investigated. Below $T_{\mathrm{N^*\!-\!SmA}}$, measurements are possible only in a short temperature interval of about 1.4°C. Similarly, as was found for CT, CN crystallizes at $T = 68.7^\circ\mathrm{C}$, while polarizing microscopy and DSC indicate the existence of the smectic state down to 40°C. Again we point out that the smectic phase in CT below 68.7°C is a supercooled metastable state.

3.2.3. *Observations outside the rheometer at low shear rates*

To obtain complementary information, we have performed polarizing microscopy for both materials outside the rheometer. We find that shifting the upper slide induces *perpendicular* orientation of the helical axis with respect to the substrates for CT within the cholesteric phase down to the point of the phase transition ($T > T_{\mathrm{N^*\!-\!SmA}}$); also for CN, except in the immediate vicinity of the transition point. For CN, when the pitch approaches 1 μm, shifting the upper glass reorients helical axes along the shift direction, *parallel* to the substrates, even if before shearing it was oriented perpendicular. A regular stripe texture (figure 4) can be obtained in this way. We believe that these observations are in direct accord with the measured rheological behaviour.

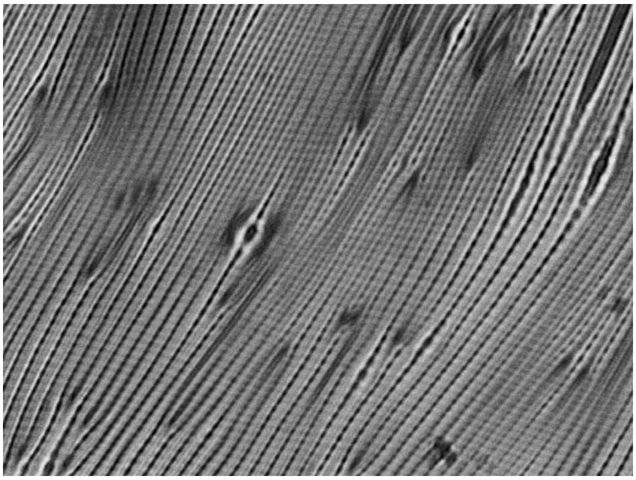

Figure 4. Texture of CN under low shear at $T = T_{\mathrm{N^*\!-\!SmA}} + 0.3^\circ\mathrm{C}$. The regular stripe texture indicates a reorientation of the helical axis parallel to the substrates.

4. Discussion

4.1. *Cholesteric phases*

We recall that, for CT in the whole temperature region of the cholesteric phase and for CN at $T > T_{\mathrm{N^*\!-\!SmA}} + 1^\circ\mathrm{C}$, the cholesteric phase appears to be Newtonian in the investigated shear rate range (1–$400\,\mathrm{s^{-1}}$), with viscosity slightly increasing on cooling. These results are in good agreement with the work of Sakamoto *et al.* [12] measured for CT. They found a strong shear-thinning behaviour for shear rates lower (10^{-3}–$10\,\mathrm{s^{-1}}$) than in our experiment, and a Newtonian regime for higher shear rates ($\dot{\gamma} > 10\,\mathrm{s^{-1}}$). Our results are thus in a shear rate range corresponding to the tail of the shear-thinning regime and thus mainly toward the Newtonian regime.

The observed shear-thinning which saturates to a Newtonian regime at high shear rates has been explained by a flow-induced reorientation of the helical axis perpendicular to the boundaries [4]. High viscosities are expected when the helical axis is not perpendicular to the flow, since the cholesteric director is blocked: the director in a flowing element must rotate as it moves to comply with the helical director pattern. The reorientation effect saturates at higher shear rates for which gliding of the 'cholesteric layers' becomes possible. This is in agreement with our polarizing microscopy observations mentioned above.

For $T_{\mathrm{N^*\!-\!SmA}} < T < T_{\mathrm{N^*\!-\!SmA}} + 1^\circ\mathrm{C}$, CN behaviour exhibits specific features that are not observed for CT: increase of the viscosity and merging of the 'cholesteric curve' with the 'smectic curve', characterized by an exponent $m = 2$ at the highest shear-rates.

The merging of the rheological behaviours of both phases in the vicinity of the transition has been documented for 8CB at the smectic A–nematic transition [15]: approaching the transition *on heating*, the SmA phase switches from a shear-dependent to a Newtonian behaviour with a viscosity value characteristic of the nematic phase just above the phase transition. In our case it is different: *on cooling*, the cholesteric phase adopts the rheological behaviour of the smectic phase. Indeed, the exponent $m=2$ is a characteristic feature of the smectic phase: we obtain $m=2$ for the whole temperature range of the CN smectic phase. Furthermore, the same exponent has been obtained by Panizza *et al.* [15], over a broad range of temperature, for the smectic phase of 8CB.‡ Under shear, X-ray measurements performed on 8CB [15, 17] showed two main orientations of layers, known in the literature as 'a' and 'c' orientations (see figure 5). We argue that the appearance of the exponent $m=2$ in the temperature range which is considered to be cholesteric reveals a long-range smectic order, with these two main layer orientations.

At least two explanations of the pretansitional anomalous rheological behaviour of CN can be considered. The first is based on the effect of shear on pretransitional fluctuating clusters pointed out by de Gennes [18] and Onuki [19]: because the relaxation time of a collective fluctuation cluster increases when approaching the transition, the cluster becomes amenable to distortion by the shear and thus may contribute to the rheological response. This explanation is plausible since CN is documented as exhibiting fluctuating smectic clusters in a temperature range about 1°C above the transition [5,7]. Furthermore, the smectic clusters that can be distorted by the shear into an extremely anisotropic shape, (exhibiting a quasi-long-range order), have either 'a' or 'c' orientation, as shown by Safinya *et al.* [17]. One could then expect the fluctuating smectic clusters to be responsible for the rheological behaviour characterized by an exponent $m=2$. However, for 8CB a strong shear-induced distortion of the smectic clusters was observed only in a narrow temperature range of about 0.2°C above the transition, although fluctuating clusters exist in a larger temperature range (1°C). Furthermore, such a hypothesis does not explain the reorientation of the helix axis parallel to the flow, which we observed in the vicinity of the transition (see the discussion below).

Another explanation is suggested by the results reported in [11] showing that, in the very same temperature region ($T_{\mathrm{N^*\text{–}SmA}} < T < T_{\mathrm{N^*\text{–}SmA}} + 1°\mathrm{C}$), CN has a TGBA phase. The TGBA phase consists of smectic A slabs, rotating discontinuously around the helical axis. The slabs are separated by parallel walls of screw dislocations such that the smectic layers are everywhere parallel to the helical axis [9].

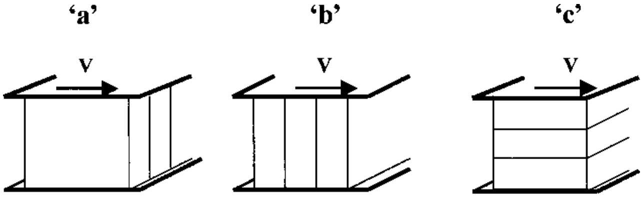

Figure 5. Schematic representation of 'a', 'b' and 'c' orientations of the smectic layers with respect to the plate boundaries and to the flow (V).

If the helical axis χ is perpendicular to the flow direction V and to the boundaries, see figure 6 (*a*), some of the smectic slabs have their layers oriented perpendicular to V (known as orientation 'b' in the literature). This 'b' orientation implies an energetically costly permeation mechanism for the flow of molecules perpendicular to the smectic layers, whereas for 'a' and 'c' orientations, molecules flow parallel to the layers [17].

If $\chi \| \mathrm{V}$, figure 6 (*b*), there is no 'b' orientation; in all the smectic slabs, the layers appear to be parallel to the flow with molecules flowing parallel to the layers. Hence it is reasonable to expect that the flow will reorient χ parallel to V. The reorientation cannot be expected for fluctuating clusters, because the geometry $\chi \perp \mathrm{V}$ is more favourable than $\chi \| \mathrm{V}$ for two reasons. First, Safinya *et al.* [17] have theoretically shown that for $\chi \perp \mathrm{V}$, the fluctuating clusters of the 'b' orientation are suppressed by the shear, whereas the 'a' clusters grow; thus molecules glide along the 'cholesteric layers' and parallel to the smectic layers within the clusters. Second, the geometry $\chi \| \mathrm{V}$ implies permeation of the molecules through the helical director pattern, which for the cholesteric is energetically costly. The same problem with permeation through the helical director pattern appears for a TGBA phase in the $\chi \| \mathrm{V}$ geometry. This would lead to increased viscosity, which is indeed observed in our experiment. In TGBA the reorientation of the helical axis parallel to the flow avoids permeation through the smectic layers but not through the helical structure. Note that the geometry $\chi \| \mathrm{V}$ implies the presence of 'a' and 'c' orientations of smectic slabs and is compatible with the exponent $m=2$. In such a case, the merging of the TGBA curves with smectic curves appears natural and thus supports the existence of a TGBA phase. Note that, in the frame of our interpretation of the rheological results, namely the presence of a TGBA phase for CN in the range ($T_{\mathrm{N^*\text{–}SmA}} + 1°\mathrm{C}; T_{\mathrm{N^*\text{–}SmA}}$), the selective Bragg reflections observed for CN near the transition to the SmA phase

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‡The exponent $m=2$ has also been reported for nematic polymers in solution and was recently explained as a defect-mediated regime [16], following Kléman and co-workers [13]. Nevertheless $m=2$ has never been reported for a thermotropic nematic to our knowledge.

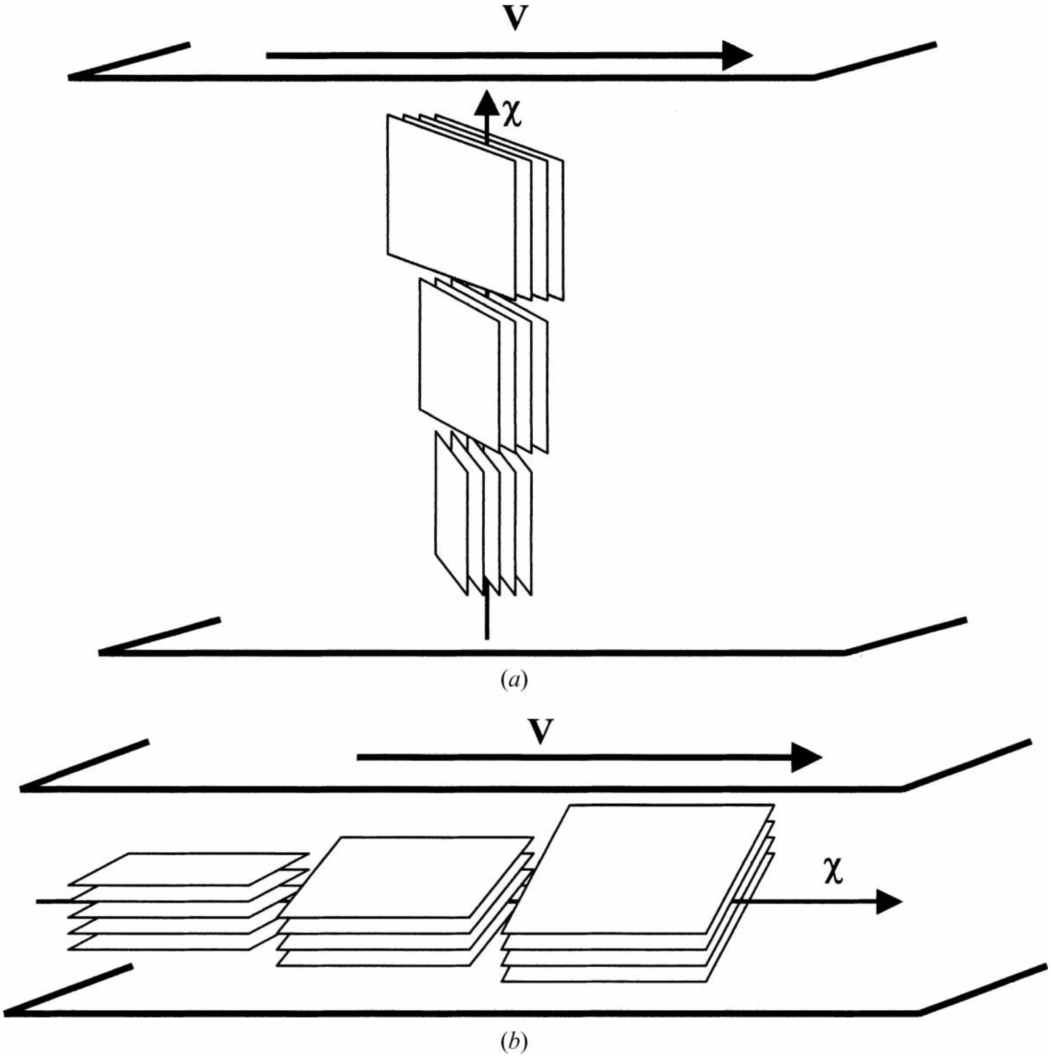

Figure 6. Schematic representation of a TGBA phase. (*a*) Helical axis perpendicular to the flow; it contains smectic slabs of 'a' and 'b' orientations. (*b*) Helical axis parallel to the flow; it contains smectic slabs of 'a' and 'c' orientations, but no 'b'.

are then explained by a divergence of the pitch of the helical axis of the smectic slabs of the TGBA instead of the cholesteric pitch.

4.2. *Smectic phases*

The SmA phase of 8CB exhibits a shear-induced transition between a low shear rate regime characterized by $m=2$ to a high shear rate Newtonian regime [15]. This shear-induced transition occurs for lower and lower shear rates when approaching the N–SmA phase transition, so that in the vicinity of the transition 8CB is Newtonian in the whole shear rate range. Our results on CN and CT do not show the Newtonian regime for either of the two smectic phases. In the case of CT, the smectic phase just after the transition is shear-thinning but with m continuously increasing from 1.35 (at 77.9°C) to 2 (at 76.8°C). For CN, the SmA phase just below the transition only shows the shear-thinning regime ($m=2$) in the investigated shear rate range. However, the difficulty of obtaining steady states at higher shear rates may indicate the transition towards the Newtonian regime (mentioned below in the case of 8CB), but the rheometer limits did not allow us to investigate a higher range of shear rates. The main difference with 8CB would then be the need of a much higher shear rate to provoke the transition of orientation from ('a–c', $m=2$) to ('a', $m=1$).

5. Conclusion

The first detailed study of the rheological properties of two liquid crystal materials in the immediate vicinity of their N*–SmA phase is reported. The flow behaviours of cholesteryl nonanoate and cholesteryl myristate differ. In the range $T_{\mathrm{N^*\text{–}SmA}} < T < T_{\mathrm{N^*\text{–}SmA}} + 1°$, CN presents an anomalous flow behaviour exhibiting two main features: increase of viscosity and merging of the 'cholesteric curve' with the 'smectic curve', characterized by an exponent $m=2$ at the highest shear rates. Moreover, a shear-induced reorientation of the helical axis is observed in this temperature range. We considered two possible mechanisms to explain these results: a shear-induced distortion of fluctuating smectic clusters, or the presence of a TGBA phase between the cholesteric and smectic phases. We found that the second explanation fits our results more satisfactorily. This work leads, as in [11], to revisiting the origin of the so-called 'pretransitional' effects measured for CN [5–7] which reveals the presence of a TGBA phase between the cholesteric and the smectic phase rather than pretransitional smectic fluctuations.

References

[1] PLANER, P., 1861, *Liebigs Ann*, **118,** 25; REINITZER F., 1889, *Monatsh. Chem.,* **9,** 421.

[2] GOODBY, J. W., WAUGH, M. A., STEIN, S. M., CHIN, E., PINDAK, R., and PATEL, J. S., 1989, *Nature*, **337,** 449.

[3] GRELET, E., PANSU, B., LI, M. H., and NGUYEN, H. T., 2001, *Phys. Rev. Lett.*, **86,** 3791.

[4] LARSON, R. G., 1998, *The Structure and Rheology of Complex Fluids* (Oxford University Press).

[5] MCMILLAN, W. L., 1972, *Phys. Rev. A*, **6,** 936.

[6] DUARTE, E. L., PALANGANA, A. J., ITRI, R., SAMPAIO, A., and BARBOSA, A. A., 1998, *Eur. Phys. J. B*, **5,** 835.

[7] PINDAK, R. S., HUANG, C., and HO, J. T., 1974, *Phys. Rev. Lett.*, **32,** 43.

[8] DE GENNES, P. G., 1972, *Solid State Commun.*, **10,** 753.

[9] RENN, S. R., and LUBENSKY, T. C., 1988, *Phys. Rev. A.*, **38,** 2132.

[10] VIGMAN, P. B., and FILEV, V. M., 1976, *JETP*, **42,** 4, 747.

[11] NASTISHIN, Y. A., KLÉMAN, M., MALTHÊTE, J., and NGUYEN, H. T., 2001, *Eur. Phys. J. E*, **5,** 353; KLÉMAN, M., NASTISHIN, Y. A., and MALTHÊTE, J., 2002, *Eur. Phys. J. E*, **8,** 67.

[12] SAKAMOTO, S., PORTER, R. S., and JOHNSON, J. F., 1969, *Mol. Cryst. liq. Cryst.*, **8,** 443.

[13] MEYER, C., ASNACIOS, S., BOURGAUX, C., and KLEMAN, M., 2000, *Rheol. Acta*, **39,** 223; MEYER, C., ASNACIOS, S., and KLEMAN, M., 2001, *Eur. Phys. J. E*, **6,** 245.

[14] MALTHÊTE J., and NASTISHIN YU., (unpublished results).

[15] PANIZZA, P., ARCHAMBAULT, P., and ROUX, D., 1995, *J. Phys. II Fr.*, **5,** 303.

[16] COLBY, R. H., NENTWICH, L. M., CLINGMAN, S. R., and OBER, C. K., 2001, *Europhys. Lett.*, **54,** 269.

[17] SAFINYA, C. R., SIROTA, E. B., and PLANO, R. J., 1991, *Phys. Rev. Lett.*, **66,** 1986; BRUISMA, R. F., and SAFINYA, C. R., 1991, *Phys. Rev. A*, **43,** 5377.

[18] DE GENNES, P. G., 1976, *Mol. Cryst. liq. Cryst.*, **34,** 91.

[19] ONUKI, A., and KAWASAKI, K., 1979, *Ann. Phys.*, **121,** 456.