Mol. Cryst. Liq. Cryst., Vol. 547: pp. 39/[1729]–45/[1735], 2011

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2011.572507

Rheological Properties of a Chiral Liquid Crystal Exhibiting Type-II Character

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We measured rheological properties of cholesteryl nonanoate and its mixture with 4′-octyloxy-4-cyanobiphenyl. In both systems, wider temperature range of blue phase under shear with anomalous increase in viscosity associated with non- Newtonian flow behavior has been observed. Shear thinning followed by Newtonian flow is found in cholesteric phase and non-Newtonian flow behavior at high shear rates is seen in smectic-A phase. In cholesteryl nonanoate a small peak in the viscosity at cholesteric to smectic-A transition along with a shear rate dependent viscosity at higher shear rate is attributed to the type-II character of the compound. We find that the type-II character of the compound is further enhanced by mixing a small amount (20 wt%) of 4′-octyloxy-4-cyanobiphenyl in cholesteryl nonanoate. No significant change in the temperature dependent rheological behavior is observed at the twist-grain-boundary-A to smectic-A transition. It is suggested that the small anomalous peak in the viscosity just above the twist-grain-boundary-A phase is due the existence of chiral line liquid phase.

Keywords Shear; type-II liquid crystals; viscosity

1. Introduction

Chiral liquid crystals have been studied since the time of their discovery. Since then a large number of chiral liquid crystals exhibiting cholesteric (N^*) phase are synthesized and characterized. The electrooptic properties of this phase have been studied extensively and in some cases they are exploited to make display devices. N^* to smectic-A (SmA) phase transitions in such materials have remarkable similarity with other systems in condensed matter like superconductor to normal metal and are fundamentally important. A formal similarity was first pointed out by de Gennes [1]. He predicted that like superconductors SmA liquid crystals can also be classified as type-I and type-II depending on their response to bending or twisting stress. Renn and Lubensky [2] showed that in such intermediate phase of highly chiral

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Address correspondence to S. Dhara, School of Physics, University of Hyderabad, Hyderabad 500046, India. Tel.: + 91-40-66794331 5684; Fax: +91-40-23010227; E-mail: sdsp@uohyd.ernet.in materials smectic blocks are separated by twist grain boundaries (TGB) and experimentally they were discovered by Goodby *et al.* in a highly chiral compound [3]. Subsequently, a variety of such TGB phases like TGB_A, TGB_C, $UTGB_{C^*}$ (undulated-twist-grain-boundary-C*) are also reported in many other compounds including mixtures of chiral and nonchiral compounds [4–6].

In this context, some of the studies suggested the presence of a TGB_A phase in cholesteryl nonanoate, though thermodynamically stable phase is not observed through optical polarizing microscopy or by calorimetric measurements. Nastishin *et al.* [7] suggested the existence of chiral line liquid (N^*_L) and TGB_A phase in this compound from the defect studies, and this was supplemented by the rheological measurements by Asnacois *et al.* [8].

In this paper we report the measurement of shear viscosity (η), storage (G') and loss (G'') modulus, as functions of shear rate and temperature in cholesteryl nonanoate (CN) and its mixture with 4′-octyloxy-4-cyanobiphenyl (8OCB). We report: (i) anomalous viscoelastic behavior of the blue phases, (ii) widening of the blue phase under shear and (iii) anomalous viscosity at N*-SmA transition.

2. Experimental Methods

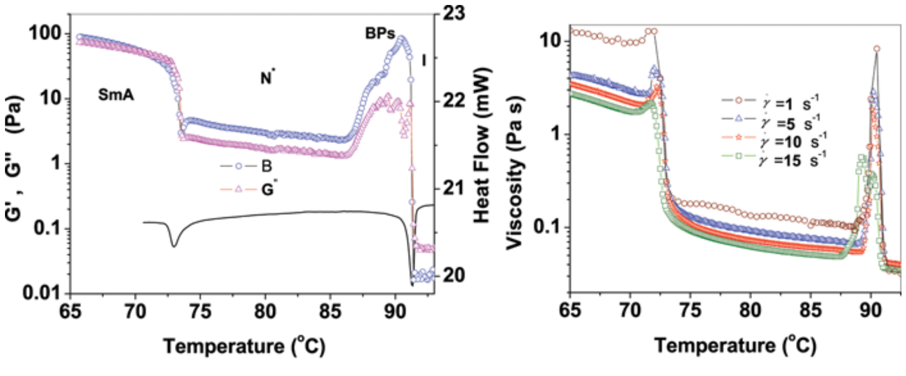
Cholesteryl nonanoate (CN) and 4′-octyloxy-4-cyanobiphenyl (8OCB) were synthesized in our laboratory, and have the following phase sequences observed on cooling: I 90.4°C N* 73.4°C SmA (CN) and I 79.5°C N 66.5°C SmA 54.5°C Cr. (8OCB). 80 wt% of CN and 20 wt% of 8OCB were dissolved in chloroform, and sonicated for several hours, and evaporated slowly to prepare the mixture. The measurement of transition temperatures and the heat of transitions were made by using a differential scanning calorimeter (DSC) (Perkin-Elmer), which was calibrated against the Indium standard. For each DSC measurement 6 mg of sample was used with a scanning rate 5°C/min. Textures were observed by using an optical polarizing microscope (Olympus BX-51) fitted with a digital camera and Mettler heating stage. Rheological measurements were performed using a Rheometer (Anton Paar MCR 501) with plate–cone geometry (diameter 25 mm, cone angle 1° and with a minimum gap of 50 μm between the plate and the truncated cone).

The temperature of the sample was controlled within an accuracy of 0.02°C by a Peltier temperature controller fitted with a hood for the uniformity of the sample temperature, and no measurable temperature gradient was observed. Calibration of the temperature controller was checked by measuring rheological properties of some standard liquid crystalline materials. All the measurements were made on cooling the sample from the isotropic phase.

3. Results and Discussion

The storage (G') and loss (G'') moduli were measured as a function of temperature and these are shown along with the calorimetric data in Figure 1(a).

Two clear peaks between I to N* except the blue phases and N* to SmA transitions are detected in the DSC measurements. In the isotropic phase, $G' < G''$ and both increases sharply as the temperature is lowered from the isotropic phase. In the cholesteric phase $G' > G''$ and they increase sharply at N*-SmA transition. Between the phases I and N* both $G'$and G'' exhibit broad peaks superimposed with multiple narrow peaks. Though the exact transition temperatures from I to BP and to N* could



(a) (b)

Figure 1. (a) Variation of storage modulus, G' (open circles) and loss modulus, G'' (open triangles) at strain amplitude $\gamma = 5\%$ and $\omega = 1$ rad/s and differential scanning calorimetric scan (solid line) of pure cholesteryl nonanoate (CN) as a function of temperature. **(b)** Variation of shear viscosity (η) of CN as a function of temperature at various shear rate ($\dot{\gamma}$).

not be detected from the present rheometric measurements nevertheless it is clear that under shear the temperature range between I and N* is broadened compared with the sharper transition (~0.7°C) as seen in the present DSC data or reported earlier [9]. The finer structure in G' and G'' data within this temperature region may be a pointer to the existence of multiple blue phases bound by the I and N* phases. The overall broadening without any fine structures of the blue phases with increasing shear rate was also reported by Negita *et al.* from the viscosity measurements [10].

Measurement of storage modulus of the blue phases using a torsional oscillation method was also reported by Kleiman *et al.* [9]. Transitions among the blue phases were detected even though no such broadening was reported. The stiffnesses of the blue phases are comparable to that of the SmA phase (i.e., $G'_{BPs} \sim G'_{SmA}$), and is attributed to presence of many dislocations in both the phases [9].

We show the variation of shear viscosity as a function of temperature at various shear rate ($\dot{\gamma}$) in Figure 1(b). Two distinguishable viscosity peaks between the I to N* and N* to SmA transitions are observed. Viscosities (η) of BPs and SmA phases are much larger compared with that of N* phase. For example, η at 91°C, 80°C and 65°C are 3 Pa s, 0.1 Pa s and 4.2 Pa s respectively. Further, at higher $\dot{\gamma}$ e.g., $\dot{\gamma} = 15\,\mathrm{s}^{-1}$, splitting of I-N* peak and a small shifting of the N*-SmA viscosity peak towards the lower temperature is observed. Temperature dependent $\dot{\gamma}$ versus shear stress of CN was also studied by Asnacios *et al.* [8] and they suggested the possibility of existence of a $\mathrm{TGB_A}$ phase between the N* to SmA transition and of course no such phase was observed through polarizing microscopy.

Furthermore we prepared a mixture of 80 wt% of CN and 20 wt% of 8OCB and interestingly found that it exhibits the following phase sequences: I 82.4°C N* 62.3°C $\mathrm{TGB_A}$ 61.8°C SmA on cooling, as seen under a polarizing microscope. Textures of $\mathrm{TGB_A}$ phase in planar and homeotropic cell are shown in Figure 2. In planar cell, a typical texture of $\mathrm{TGB_A}$ phase with relatively large pitch is seen (Fig. 2(a)). The helix axis is perpendicular to the glass plate and different colours appear due to

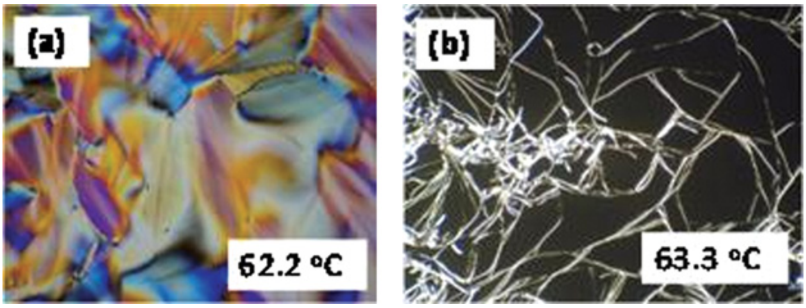
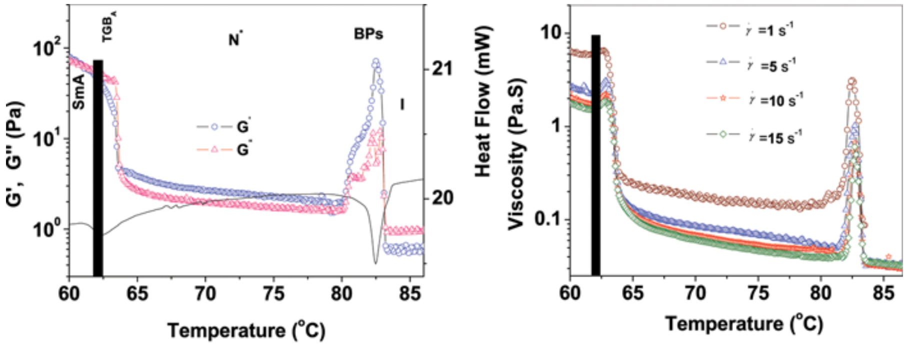


Figure 2. Photomicrographs of TGB_A phase (a) in planar cell at 62.2°C on cooling (b) in homeotropic cell at 63.3°C during heating from the SmA phase. (Figure appears in color online.)

the coexistence of different twisted states under cooling. In homeotropic cell (Fig. 2(b)) SmA planes are parallel to the substrate and appear dark. The SmA phase was then heated slowly and bright filaments started growing in the dark background. Similar textures in homeotropic cell in the case of other compounds showing TGB_A phase were also reported [5].

DSC scan along with the measurements of G' and G'' of the mixture as a function of temperature are shown in Figure 3(a). Temperature dependence of G' and G'' are almost similar to that of the pure compound as discussed earlier. In the DSC thermogram the blue phases could not be resolved between I to N^* transition. Similarly individual peaks of N^*-TGB_A-SmA transition were not detected through DSC; instead the profile was a single broad peak. Such broad peaks bracketing the transition N^*-TGB_A-SmA were also reported for pure compounds [11,12]. It is anticipated that this broad peak is due to the occurrence of a TGB_A-like short range order called chiral line liquid (or N^*_L) phase. Further, in a high resolution a.c calorimetric study [11], a slight slope change superimposed on the broad peak was



(a) (b)

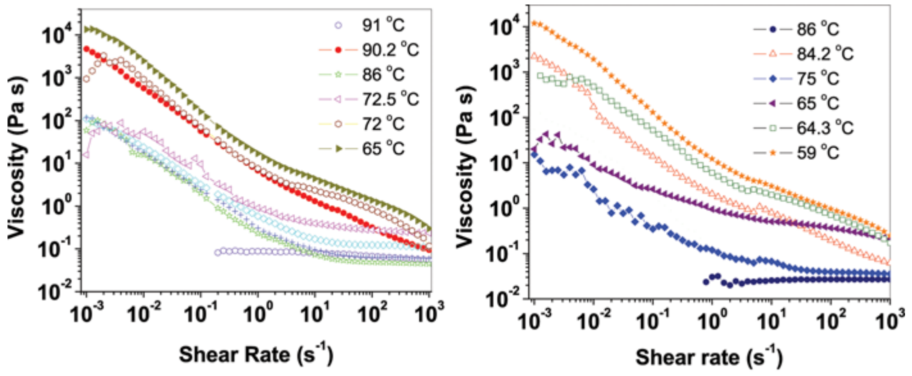
Figure 3. (a) Variation of storage modulus, G' (open circles) and loss modulus, G'' (open triangles) at strain amplitude $\gamma = 5\%$ and $\omega = 1$ rad/s and differential scanning calorimetric scan (solid line) of the mixture (20 wt% 8OCB and 80 wt% CN) as a function of temperature. (b) Variation of shear viscosity (η) of the mixture as a function of temperature at various shear rate ($\dot{\gamma}$). Black bars indicate the temperature range of TGB_A phase.

reported, suggesting a phase sequence: N^*-N^*_L-TGB_A-SmA. Variation of η with temperature of the mixture is presented in Figure 3(b). The viscosity decreases with increasing $\dot{\gamma}$ and N^* exhibits Newtonian and SmA phase exhibits non-Newtonian flow behavior at higher $\dot{\gamma}$. Distinguishable viscosity peaks between I to N^* and N^* to SmA transition are observed. Similar temperature dependent viscosity of cholesteryl myristate (CM) with pronounced peaks at the transitions were also reported [13]. However, occurrence of TGB_A is not known in CM. In the present mixture we note that the TGB_A appears reasonably below the anomalous viscosity peak with no significant change in the viscosity across N^*_L-TGB_A-SmA transitions.

The variation of η with $\dot{\gamma}$ for both the pure and the mixture at various temperatures is shown in Figure 4. The viscosities of the I phase (91°C in Fig. 4(a) and 84.5°C in Fig. 4(b)) is independent of shear rate showing a Newtonian behavior. At 86°C (Fig. 4(a)) and at 73.5°C (Fig. 4(b)) the N^* phase exhibits shear thinning followed by a Newtonian flow behavior beyond $\dot{\gamma} \approx 40\,s^{-1}$. The shear thinning is due to the strong shear induced alignment of the liquid crystal director. In cholesteric liquid crystals in the absence of field the director commonly tend to be parallel to the shear (flow) direction and hence the measured viscosity represent Miesowicz viscosity η_2 [14].

Viscosities are much higher in the SmA phase in both the samples compared to the N^* phase. For example, $\dot{\gamma}$ at $0.1\,s^{-1}$ $\eta_{SmA}/\eta_{N^*} \sim 80$, (at 86°C and 65°C) and $\eta_{SmA}/\eta_{N^*} \sim 310$ (73.5°C and 57.5°C) where η_{SmA} and η_{N^*} are the viscosities of the SmA and N^* phase (Fig. 4(a) and Fig. 4(b)), respectively. Further it is noticed that in the N^* phase, $\dot{\gamma}$ above which the sample becomes non-Newtonian is decreased as the temperature is reduced towards the SmA phase. For example, Newtonian flow is observed above $\dot{\gamma} \approx 40 s^{-1}$ at 86°C and $\dot{\gamma} \approx 10 s^{-1}$ at 72.5°C respectively in Figure 4(a). Similar phenomena are observed in Figure 4(b). This is attributed to the larger pitch at lower temperature. Similar pitch-dependent shear thinning behavior is known for other cholesteric liquid crystals [15].

In the SmA phase viscosity decreases steadily with increasing shear rate showing non-Newtonian flow behavior up to $\dot{\gamma} = 10^3\,s^{-1}$ in both the cases. In the blue phases



(a) (b)

Figure 4. (a) Variation of shear viscosity of CN as a function of shear rate ($\dot{\gamma}$) at various temperatures. (b) Variation of shear viscosity of the mixture as a function of shear rate ($\dot{\gamma}$) at various temperatures. Before every measurement the sample was heated to isotropic phase and cooled to the desired temperatures.

(90.2°C in Fig. 4(a) and 82.7°C in Fig. 4(b)) the viscosities decrease rapidly accompanied by a non-Newtonian behavior, and their values become almost comparable to the values of viscosity of the N* phase indicating that the flow behavior of blue phases is similar to the N* phase. An interesting shear rate dependent viscosity is observed in both the samples at the N*-SmA transition temperatures. At low shear rate it exhibits shear thinning accompanied by the Newtonian behavior with viscosity similar to the values of SmA phase (72.5°C in Fig. 4(a) and 63.5°C in Fig. 4(b)), suggesting the existence of an intermediate phase that possesses higher viscosities like SmA and flow behavior similar to N* phase. This intermediate phase was identified as twist grain boundary (TGB_A) by Nastishin *et al.* from the observation of defects in freely suspended droplets [7]. This observation was also supported by other rheological measurements [8]. However, in our mixture we clearly observe that the viscosity peak appears at the N*-SmA transition (Fig. 3(b)) and TGB_A phase appears at lower temperature with a very narrow (~0.5°) range. We believe that the peak of the viscosity is associated with the fluctuations of the TGB_A-like short range order, identified as N^*_L. No significant difference in the viscosities and mechanical properties (G' and G'') are observed between the TGB_A and SmA phases suggesting that these two phases are almost similar from the viscoelastic point of view.

4. Conclusions and Perspectives

In conclusion, we measured viscoelastic properties of cholesteryl nonanoate (CN) and its mixture with 4′-octyloxy-4-cyanobiphenyl (8OCB). Our measurements show the broadening of the blue phases under shear. We find that in the mixture type-II character is enhanced. It appears that the flow behavior of BPs is similar to that of the N* phase. The anomalous increase in viscosity near N* to SmA transition is due to the presence of the N^*_L phase. Viscoelastic properties of SmA and TGB_A seem to be similar. These results suggest that work on compounds exhibiting large temperature range of TGB_A phase can be very rewarding.

Acknowledgment

We thank Mrs. K. N. Vasudha, from Raman Research Institute, Bangalore for helping us to do DSC measurements. MR thanks UGC-CAS fellowship.

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