This article was downloaded by:
On: *25 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK

Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Rheological properties in cholesteric and blue phases of cholesteryl isostearyl carbonate: viscosity and effect of electric field on the rheology

K. Negita

Online publication date: 06 August 2010

To cite this Article Negita, K.(1998) 'Rheological properties in cholesteric and blue phases of cholesteryl isostearyl carbonate: viscosity and effect of electric field on the rheology', Liquid Crystals, 24: 2, 243 — 246

To link to this Article: DOI: 10.1080/026782998207415

URL: http://dx.doi.org/10.1080/026782998207415

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

LIQUID CRYSTALS, 1998, VOL. 24, NO. 2, 243–246

Rheological properties in cholesteric and blue phases of cholesteryl isostearyl carbonate: viscosity and effect of electric field on the rheology

by K. NEGITA
Advanced Materials Research Group, Nissan Research Center, Nissan Motor Co., Ltd., Natsushima, Yokosuka 237, Japan

Rheological property (shear stress versus shear rate) of cholesteryl isostearyl carbonate (CISC) is measured as a function of temperature, finding that, like some other cholesteryl derivatives, CISC has blue phases (BPs) between the cholesteric (Ch) and the isotropic (I) phases. In the Ch and the BP phases, measurements of the electrorheological (ER) effect, of the electric field on the rheology, are made; a slight increase of the viscosity is observed in the BPs and no ER effect in the Ch phase, which is contrasted to the distinct ER effect in the nematic (N) and the smectic A (SmA) phases.

1. Introduction

In some colloidal suspensions, the application of an electric field of a few kV mm^{-1} induces a dramatic rheological change of the suspensions, characterized by a viscosity increase of 2–3 orders of magnitude. Such an electrorheological (ER) effect in colloidal suspensions has been studied following the pioneering work by Winslow [1] in 1947, and has been shown to be caused by a chain-like structure formed by a polarization induced at respective particles [1–5].

On the other hand, the study of the ER effect in liquid crystals has started more recently. In the nematic (N) phase, an increase or a decrease of viscosity is observed, depending on whether the dielectric anisotropy is positive or negative, respectively [6–8]. The change in viscosity and fluidity in the N phase upon application of an electric field has been successfully interpreted on the basis of the Leslie–Ericksen theory; an orientational change of the director is suggested to be responsible for the ER effect. In the smectic A (SmA) phase, a large decrease of viscosity is observed and is understood to occur as a result of a geometrical change of the smectic layer from a mixed to an aligned one [9]. The ER effect in other liquid crystalline phases, although there have been some studies [10, 11], is not well understood.

In the present study, firstly, rheological properties of cholesteryl isostearyl carbonate (CISC) were measured as a function of temperature, finding that, similarly to other cholesteryl derivatives, there exist BPs in CISC, indicated by an anomalous viscosity observed between the Ch and the I phases. Secondly, the effect of an electric field of a few kV mm^{-1} on the rheology was studied in the Ch phase and the BPs to clarify the ER effect in these phases, leading to the result that there appears to be no ER effect in the Ch phase and a slight viscosity increase in the BPs.

2. Experimental

The liquid crystal cholesteryl isostearylcarbonate (CISC) was obtained from Peboc Ltd (UK) and was used without further purification. The specimen at room temperature is a turbid fluid having a high viscosity. The rheological property, shear stress versus shear rate, was measured with a home-made viscometer of a double cylinder type in a shear rate region from 3·4 to 34 s^{-1} [12]. The measurement of the ER effect was made by applying an a.c. high voltage (20 Hz) of a few kV to the 1 mm gap between the inner and outer cylinders. The temperature of the sample was kept constant within 0·1 K using a chromel–constantan thermocouple and a heater attached to the outer cylinder. Liquid crystalline phases were identified by differential thermal analysis (DTA) with heating and cooling rates of about 0·5 K min^{-1}. In this paper, the amplitude of the electric field is expressed in rms.

3. Results and discussion

3.1. *Temperature dependence of the viscosity*

Temperature dependence of the shear stress τ, which is proportional to the viscosity, was measured at a shear rate $\dot{\gamma}$ of 3·395 s^{-1}. The result is shown in figure 1, where two series of the data with increase and decrease in temperature are given. As this figure shows, with increase in temperature the shear stress gradually decreases until a discontinuous jump takes place at 297·1 K. Above this temperature a plateau appears up to ~298·0 K, followed by a gradual decrease continuing to around 300·8 K and a normal decrease in the I phase. The behaviour on

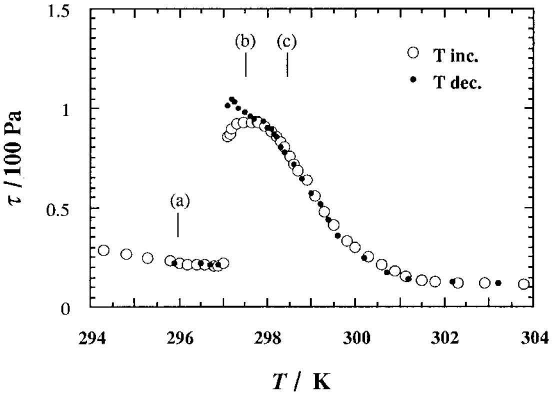

Figure 1. Temperature dependence of the shear stress measured at a shear rate of 3·295 s^{-1}. An anomalous viscosity due to the formation of BPs is observed between 297·1 and 300·8 K. The temperatures at which the measurement of the ER effect is made are indicated by solid bars.

cooling almost coincides with that on heating except for the temperature region between 297·1 and 297·6 K, where an increase in the shear stress is observed when approaching 297·1 K.

The anomalous viscosity observed in CISC is similar to that observed in the BPs of some other cholesteryl derivatives [13–15], suggesting the possibility that the observed anomaly is due to the formation of the BPs. To confirm the existence of the BPs, DTA and an observation of the visual appearance were carried out. Figure 2 shows the result of DTA. On heating, there appear a small peak at 298·4 K and a λ type peak at 300·8 K. On cooling, the λ type anomaly is reproduced with its position being ~0·3 K lower than that on heating and the small anomaly (298·4 K) on heating is not detected. The existence of the BPs is further confirmed by the measurement of visual appearance. On heating, the sample is opaque below 298·4 K, transparent with a bluish colour from 298·4 to 300·8 K, and colourless transparent above 300·8 K. On cooling, it changes from colourless transparent to bluish transparent at 300·5 K and the bluish colour is maintained down to room temperature. These results show that, on heating, the quiescent CISC exhibits the BPs with the Ch–BP and the BP–I transition points being 298·4 K and 300·8 K, respectively. The observed anomalous viscosity is thus attributed to the formation of the BPs. The difference of the BP region between the quiescent and the sheared specimens would be due to the effect of the steady shear flow, which is confirmed in the BPs of some other cholesteryl derivatives [16].

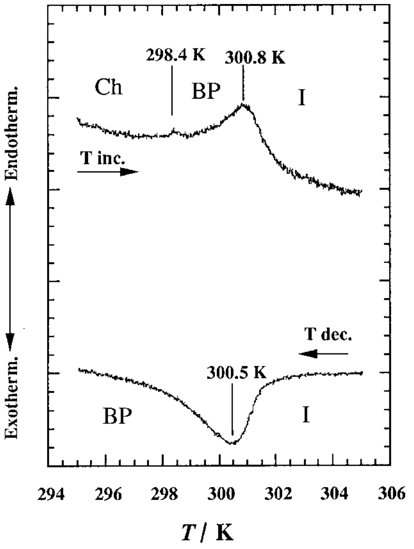

Figure 2. The result of DTA between 295 and 305 K. With increasing temperature, a small peak appears at 298·4 K and a λ type peak at 300·8 K, which are due to the Ch–BP and the BP–I phase transitions, respectively. On cooling, the transition from the I phase to the BP occurs at 300·5 K and the BP phase supercools to room temperature.

3.2. *The ER effect in the Ch phase*

Shear stress versus shear rate at 296·0 K in the Ch phase is depicted in figure 3, where the result under application of an electric field (20 Hz, 3 kV mm^{-1}) is also presented. The fluidity in the Ch phase is Newtonian as is evidenced by the linear relationship between shear stress and shear rate. As this figure shows, the application of the electric field does not affect the rheological property, indicating that the ER effect does not appear in the Ch phase.

As has been reported, the ER effect is observed in the N phase of 5CB and 8CB [8, 9]; the viscosity increases with the electric field and saturates at a high enough field with its magnitude a few times that without electric field, which is successfully understood to occur as a

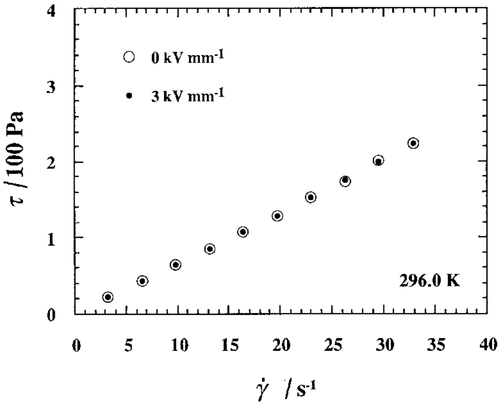

Figure 3. Shear stress τ versus shear rate $\dot{\gamma}$ at 296·0 K, at (*a*) in figure 1, in the Ch phase. The result under the application of an electric field (3 kV mm^{-1}, 20 Hz) shows the absence of the ER effect at this temperature.

consequence of the orientational change of the director. The result in the N phase indicates that for the appearance of the ER effect an orientationally changeable director is necessary.

The dielectric anisotropy $\Delta\varepsilon$ of CISC is expected to be negative, similar to other cholesteryl aliphatic esters [17], indicating that unwinding of the helical structure does not occur even at a high electric field. This suggests that there is no orientationally changeable director like that in the N phase, thus leading to the absence of the ER effect in the Ch phase.

3.3. *The ER effect in BPs*

The rheological property at 297·5 K is given in figure 4. The fluidity is non-Newtonian as is obvious from the non-linear relationship between the shear stress and the shear rate. The shear stress extrapolated to the value at $\dot{\gamma}=0$ is expected to show a finite value, indicating that there exists a yield stress which gives evidence of the solid-like property of CISC at this temperature. When an electric field ($3\,\mathrm{kV\,mm^{-1}}$) is applied, the effective viscosity does not show a dramatic change but a slight increase of viscosity. Similar results are obtained at 297·3 and 297·7 K. With increase in temperature the ER effect becomes smaller, and disappears around 298·0 K. Figure 5 shows the result at 298·4 K; the non-Newtonian flow is maintained, but a change of the rheology upon application of the electric field is not seen. Such a behaviour is also seen at 299·4 K. The measurement at 303·4 K in the I phase shows a Newtonian flow with no ER effect.

With respect to the BPs, three types of phase have been identified; BP I and BP II are crystals having a body centred cubic O^8 ($I\,4_132$) and a simple cubic O^2 ($P\,4_232$) symmetries, respectively, and BP III is probably amorphous, sometimes called 'fog phase' [18, 19]. When the compound has a negative dielectric anisotropy, the structural change of the BPs under the application of an electric field is not so complicated as that for the compound having a positive dielectric anisotropy [20–22]. In a mixture of chiral and nematic compounds, having a negative $\Delta\varepsilon$, it is clarified that phase transitions of BP I–BP I$^{\mathrm{d}}$–BPH–Ch and BP II–BP II$^{\mathrm{d}}$–BPH–Ch occur with increase in the amplitude of the electric field, where the BP I$^{\mathrm{d}}$ and BP II$^{\mathrm{d}}$ are tetragonally distorted BPs and BPH is a hexagonal BP (D_6^4 or D_6^5) [20]. In other studies, field induced phase transitions BP I–BPEx–Ch, BP II–BPi–Ch, and BP III–BPi–Ch are reported, where BPEx is a structurally unknown phase and BPi is a phase resembling BP II [21].

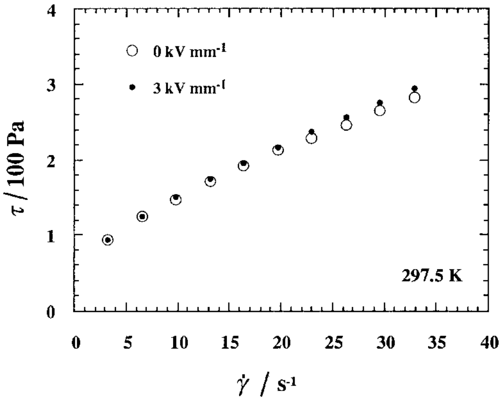

Figure 4. Shear stress τ versus shear rate $\dot{\gamma}$ at 297·5 K, at (*b*) in figure 1, in the BP. The flow is non-Newtonian as is shown by the non-linear relationship between shear stress and shear rate. A slight increase of the viscosity is confirmed under the application of the electric field ($3\,\mathrm{kV\,mm^{-1}}$, 20 Hz).

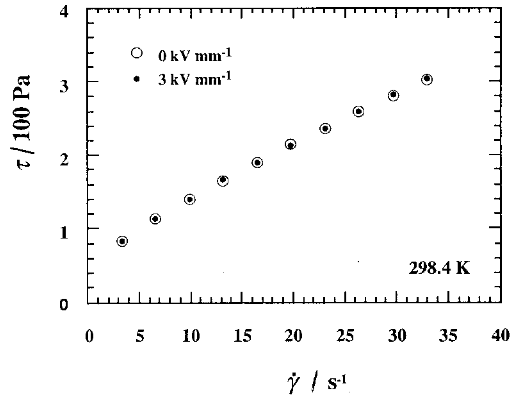

Figure 5. Shear stress τ versus shear rate $\dot{\gamma}$ at 298·4 K, at (*c*) in figure 1, in the BP. The flow is non-Newtonian and the application of an electric field ($3\,\mathrm{kV\,mm^{-1}}$, 20 Hz) does not induce a rheological change.

Considering these results, it is possible to understand that the slight increase of viscosity is associated with the formation of the field-induced BPs. In our measurement on the BPs of other cholesteryl derivatives, a similar field-induced increase of the viscosity is observed in cholesteryl oleyl carbonate, while in cholesteryl nonanoate, a small decrease of the viscosity is observed. Although further structural studies under both electric field and steady shear flow are necessary, it can be suggested that in BPs the application of an electric field induces a small rheological change associated with the field-induced phase transitions, which is in contrast to the dramatic rheological change observed in the N and the SmA phases [7–9].

4. Summary and conclusion

The present study shows that cholesteryl isostearyl carbonate exhibits BPs between the Ch and the I phases, which is evidenced by anomalous viscosity between 297·1 and 300·8 K. The formation of the BPs is confirmed by measurements of thermal properties and visual appearance. The application of an electric field does not affect the rheology in the Ch phase and induces a slight increase of viscosity in the BP. The absence of an ER effect in the Ch phase is attributed to the non-unwinding nature of the liquid crystal having a negative dielectric anisotropy. The small ER effect in the BP is suggested to be associated with the field-induced BP. In a recent study, it has been suggested that shear flow affects the phase transitions of the BPs [16]. Structural studies under shear and an electric field are required for further understanding of the properties of the BPs.

The author would like to thank Mr H. Takao, the former director of this laboratory, for his continuing interest in this work.

References

[1] Winslow, W. W., 1947, *J. appl. Phys.*, **20,** 1137.

[2] Klass, D. K., and Matrinek, T. W., 1967, *J. appl. Phys.*, **38,** 67.

[3] Gast, A. P., and Zukoski, C. F., 1989, *Adv. Colloid Interface Sci.*, **30,** 153.

[4] Block, H., and Kelley, J. P., 1988, *J. Phys. D*, **21,** 1661.

[5] Halsey, T. C., 1992, *Science*, **258,** 761.

[6] Yang, I.-K., and Shine, A. D., 1992, *J. Rheol.*, **36,** 1079.

[7] Negita, K., 1995, *Chem. Phys. Lett.*, **246,** 353.

[8] Negita, K., 1996, *J. chem. Phys.*, **105,** 7837.

[9] Negita, K., 1997, *Mol. Cryst. Liq. Cryst.* (to be published).

[10] Fukumasa, M., Yoshida, K., Ohkubo, S., and Yoshizawa, A., 1993, *Ferroelectrics*, **147,** 395.

[11] Kishi, R., Kitano, T., and Ichijo, H., 1996, *Mol. Cryst. Liq. Cryst.*, **280,** 109.

[12] Negita, K., 1995, *Netsu Sokutei*, **22,** 137 (Japanese).

[13] Stegemeyer, H., and Pollman, P., 1982, *Mol. Cryst. Liq. Cryst.*, **82,** 123.

[14] Porter, R. S., Griffen, G., and Johnson, J. F., 1974, *Mol. Cryst. Liq. Cryst.*, **25,** 131.

[15] Yamada, T., and Fukuda, E., 1973, *Jpn. J. appl. Phys.*, **12,** 68.

[16] Negita, K., 1997, *Mol. Cryst. Liq. Cryst.* (to be published).

[17] de Gennes, P. G., 1993, *The Physics of Liquid Crystals*, 2nd Edn (Oxford: Oxford University Press).

[18] Wright, D. C., and Mermin, D., 1989, *Rev. mod. Phys.*, **61,** 385.

[19] Seideman, T., 1990, *Rep. Prog. Phys.*, **53,** 659.

[20] Jerome, B., and Pieranski, P., 1989, *Liq. Cryst.*, **5,** 799.

[21] Heppke, G., Jerome, B., Kitzerow, H.-S., and Pieranski, P., 1989, *Liq. Cryst.*, **5,** 813.

[22] Niggemann, E., and Stegemeyer, H., 1995, *Ber. Bunsenges. phys. Chem.*, **99,** 789.