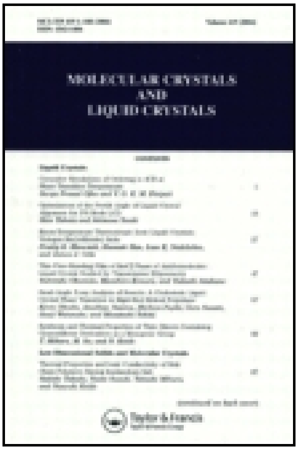

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Keishi Negita [a]
[a] Advanced Materials Research Group, Nissan Research Center, Nissan Motor Co., Ltd., Natsushima, Yokosuka, 237, Japan

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Anomalous Viscosity in the Blue Phases of Cholesteryl Nonanoate

KEISHI NEGITA

*Advanced Materials Research Group, Nissan Research Center,
Nissan Motor Co., Ltd., Natsushima, Yokosuka 237, Japan*

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Rheological property, shear stress *vs.* shear rate, of cholesteryl nonanoate (CN) is measured in a temperature region including the blue phases (BPs). From the measurement of the temperature dependence, an anomalous increase in the viscosity, accompanied by a non-Newtonian flow, is observed between 363.4 K and 367.5 K. The anomalous temperature region of 4.1 K obtained from the rheological measurement is wider than the BP region of 0.8 K determined from the thermal analysis, suggesting that the BP region is enlarged under an application of the steady shear flow.

Keywords: Blue phase; phase transition; cholesteryl nonanoate; viscosity; rheology

INTRODUCTION

It has been clarified that some of cholesteric liquid crystals having a high chirality exhibit blue phases (BPs) in a narrow temperature region (~ 1 K) just below the isotropic (Is) phase. According to the difference in the structure, three types of BPs, BP I, BP II and BP III, are identified; BP I and BP II are crystals having a body centered cubic $O^8(I\ 4_132)$ and a simple cubic $O^2(P\ 4_232)$ symmetries, respectively, and the BP III is probably amorphous called "fog phase" [1-3]. The BPs are observed in some cholesteryl derivatives, of which cholesteryl nonanoate (CN) explored in the present study has been clarified to show a phase sequence of Ch - BP I - BP II - BP III - Is from the measurements of texture [4], optical transmission and reflectance [5, 6], optical rotary power [7], Bragg scattering [8], heat capacity [9] and mechanical properties [10].

One of the interesting phenomena of the BPs is their fluidity, and some viscosity measurements on various cholesteryl derivatives have been made, showing that there appears a viscosity peak just below the Is phase [10, 11 – 15]. However, the correspondence between the viscosity anomaly and the respective phases, and the effect of the shear deformation on the phase stability are not well understood. In the present study, rheological measurements have been made on CN to shed light on the fluidity of the BPs and the effect of the shear deformation on the stability of the BPs.

EXPERIMENT

The liquid crystal cholesteryl nonanoate (CN) was obtained from Peboc. Ltd. (UK) and was used without further purification. The phase transition points for the quiescent specimen were determined from DTA; the Ch - BP I and the BP III - Is transitions on heating were 363.8 K and 364.6 K, respectively, which are comparable to those obtained from the heat capacity measurement [9]. Probably owing to the small and sharp heat capacity peaks for the BP I - BP II and the BP II - BP III phase transitions [9, 10], these phase transitions were not detected in DTA . The rheological properties were measured with a home made viscometer of a double cylinder type in a shear rate region from 13.18 to 329.5 s^{-1}. The temperature of the specimen was controlled within 0.1 K using a chromel-constantan thermocouple and a heater attached on the outer cylinder. The accuracy of the temperature measurement is about 0.2 K.

RESULTS AND DISCUSSION

With increasing temperature, temperature dependence of the viscosity (η) is measured at a shear rate ($\dot{\gamma}$) of 329.5 s^{-1} and the result is given in Figure 1. The viscosity at 362.0 K is 42.9 mPa s, which is smaller than that obtained indirectly from the torsional oscillation method [10]. Below 363.4 K. the viscosity decreases with temperature, and above this temperature it gradually increases. After a small decrease above 364.3 K a discontinuous jump is observed at 364.7 K, which is followed by a gradual decrease with a change of the slope at 365.4 K. The anomalous viscosity continues up to c.a. 367.5 K. In this figure the BP region, 363.8 K $\sim$ 364.6 K, determined from DTA is specified by the shaded area. The viscosity on cooling is almost coincide with that on heating with some deviation in the temperature region,

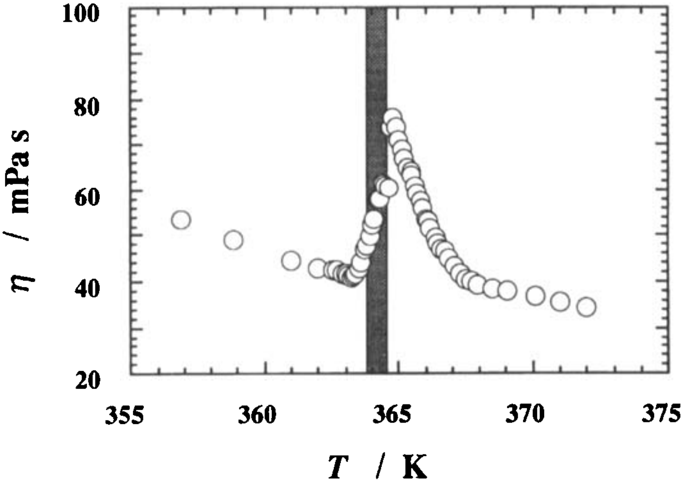

FIGURE 1 Temperature dependence of the viscosity of CN measured at a shear rate of 329.5 s^{-1}. The BP region determined from DTA is shaded.

364.3 K ~ 364.7, near the peak, which is contrasted to the behavior of the quiescent specimen, where a supercooling of the BP down to about 355 K is confirmed.

In Figure 2, a rheological property, viscosity vs. shear rate, at various temperatures is depicted. At 359.7 K (Ch phase) and 369.4 K (Is phase) the flow is Newtonian, which is evidenced by the fact that the viscosity is independent of the shear rate. At other temperatures, the viscosity depends on the shear rate with a stronger shear rate dependence at lower shear rates, indicating that the flow in the anomalous viscosity region is non-Newtonian.

In these rheological measurements, interesting is the fact that the anomalous viscosity region is wider than the BP region determined from DTA as shown in Figure 1. If we consider that the ordered structure in the liquid crystals reflects in the viscosity with its magnitude being related to the order parameter [16], it is most probable to understand that the anomalous viscosity is caused by the formation of the BPs. The BP region under a shear flow, thus, can be estimated to be 4.1 K with the Ch - BP I and the BP III - Is transition points being 363.4 K and 367.5 K respectively.

For understanding the difference in the BP region, temperature dependence of the shear stress (τ) is obtained at some shear rates (Fig. 3). In this figure it is confirmed that the anomalous viscosity region becomes narrower when lowering the shear rate; at the shear rate of 13.18 s^{-1} the shear stress discontinuously changes at the Ch - BP phase transition point,

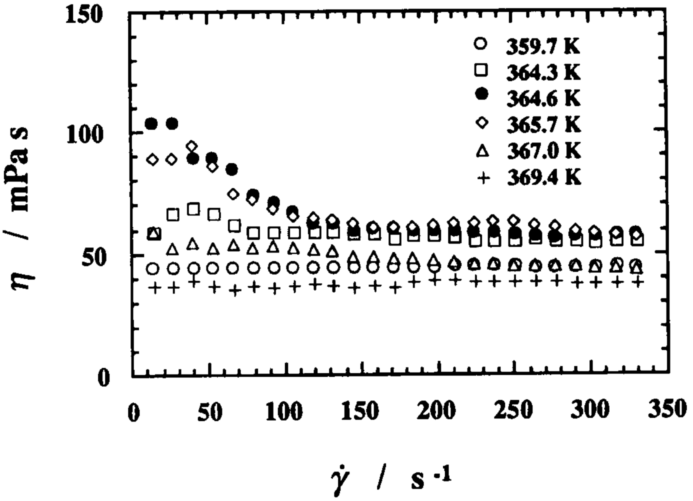

FIGURE 2 Rheological property, viscosity vs. shear rate, at various temperatures including the BP region. The flow is Newtonian at 359.7 K and 369.4 K and is non-Newtonian at other temperatures.

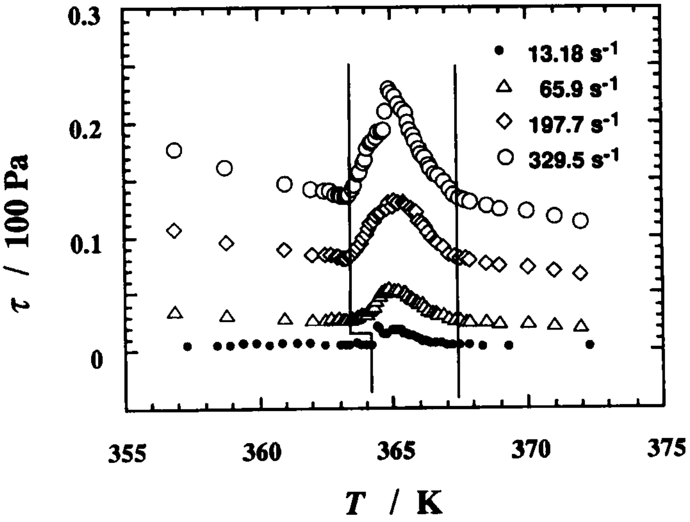

FIGURE 3 Temperature dependence of the shear stress measured at some shear rates. The anomalous viscosity region is specified by two solid lines.

accompanied by the narrowing of the BP region. Such an effect of the shear deformation on the BP phase is confirmed in some other studies. (1) In CN, the BP III - Is phase transition point determined from the shear elasticity is higher than the temperature at which the heat capacity peak appears [10]. (2) A shear induced birefringence, which is indicative of the formation of the BP I, is observed in other cholesteryl derivatives [17]. (3) In cholesteryl isostearyl carbonate (CISC), similar result is obtained with the anomalous viscosity region of 3.6 K and the BP region of 2.4 K for the quiescent specimen [18]. These results suggest that the application of a steady shear flow would enlarge the BP region with its region depending on the shear rate.

In the viscosity measurements in cholesteryl oleate (CO) and cholesteryl oleyl carbonate (COC), an increase in the viscosity is observed when lowering the temperature from the Is phase, and the anomaly is interpreted, on the basis of the Ch - Is phase transition point for the quiescent specimen, as a pretransitional divergence in the Is Phase [14]. However, such a viscosity divergence has not been known in the Is phase emerging as a result of Ne - Is and Ch - Is phase transitions, and in some cholesteryl derivatives the anomalous viscosity does not appear in the Is phase [12, 15]. These facts may suggest that the shear flow enlarges the BP region in CO and COC and the anomaly which is understood as a pretransitional effect is due to the formation of the BP phase, probably BP III. In CN, this type of the anomaly is observed at the high temperature side of the peak and extends over a few Kelvin. As shown in Figure 3, its region is not affected by varying the shear rate. However, the anomaly in this temperature region would also be understood to appear as a result of the shear induced enlargement of the BP region, since such a large anomaly is not observed in the viscosity obtained from the torsional oscillator method [10], where a torsional shear deformation less than 0.01 % is applied.

In the present study, an enlargement of the BP region under a steady shar flow is suggested. The rheological measurement, however, is not enough to determine the phase sequence and the phase transition points. Structural investigations under a steady shear flow are desired on the BPs.

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References

[1] D. C. Wright and D. Mermin, *Rev. Mod. Phys.*, **61**, 385 (1989).
[2] T. Seideman, *Rep. Prog. Phys.*, **53**, 659 (1990).
[3] P. G. de Gennes and J. Prost, *The Physics of Liquid Crystals* (Clarendon Press, Oxford, 1993), 2nd Ed., Chap. 6.

[4] H. Onusseit and H. Stegemeyer, *Z. Naturforsch*, **362**, 1083 (1981).
[5] S. Meiboom and M. Sammon, *Phys. Rev. A*, **24**, 468 (1981).
[6] V. A. Belyakov, E. I. Demikhov, V. E. Dmitrienko and K. Dolganov, *Sov. Phys. JETP*, **62**, 173 (1986).
[7] P. J. Collings, *Phys. Rev. A*, **37**, 1754 (1988)
[8] V. A. Kizel' and V. V. Prokhorov, *Sov. Phys. JETP*, **60**, 257 (1985).
[9] J. Thoen, *Phys. Rev. A*, **37**, 1754 (1988).
[10] R. N. Kleiman, D. J. Bishop, R. Pindak and P. Taborek, *Phys. Rev. Lett.*, **53**, 2137 (1984).
[11] W. Ostward, *Trans. Faraday Soc.*, **79**, 78 (1931).
[12] K. Sakamoto, R. S. Porter and J. Johnson, *Mol. Crys. Liq. Crys.*, **8**, 443 (1969).
[13] T. Yamada and E. Fukuda, Jpn. *J. Appl. Phys.*, **12**, 68 (1973).
[14] P. H. Keyes and D. B. Ajgaonkar, *Phys. Lett.*, **64A**, 298 (1977).
[15] H. Stegemeyer and P. Pollman, *Mol. Crys. Liq. Crys.*, **82**, 123 (1982).
[16] H. Imura and K. Okano, Jpn. *J. Appl. Phys.*, **11**, 1440 (1972).
[17] D. Armitage and R. J. Cox, *Mol. Crys. Liq. Crys.*, **64**, 41 (1980).
[18] K. Negita, to be published in *Liq. Crys.*, (1997).