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Nematic-Like Flow Behavior in a Non-Steroid Cholesteric Mesophase†

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Steady flow viscosity data were obtained on a compound which exhibits a cholesteric liquid crystalline mesophase but does not contain the steroid moiety. The compound is (+)-2-methylbutyl *p*-[*N*-(*p*-methoxybenzylidene)amino] cinnamate. This cholesteric liquid crystal rheology was found to be similar to that of the nematic class of liquid crystals. The material's liquid crystalline nature *lowers* its viscosity. A viscosity maximum is seen at the cholesteric-isotropic phase transition. This effect differs from that previously reported for cholesteric liquid crystals.

Nematic and cholesteric liquid crystals are generally considered to be similar except for a twist in the director field present in the latter.[1] On the local level the twist is quite small, and one would therefore expect these two liquid crystal types to exhibit similar rheological behavior. On the basis of data published to date, this appears not to be the case.[2–7] In this note, we report new data which partially resolves this discrepancy. We note that prior workers used nematics composed of more-or-less linear molecules, whereas all the cholesterics studied were steroid derivatives. By using a non-steroidal cholesteric liquid crystal, (+)-2-Methylbutyl *p*-[*N*-(*p*-Methoxybenzylidene)amino] cinnamate (MMBAC), we have observed viscosity vs. temperature curves more similar to those found for nematics. This lends strong support to the argument that the rheological behavior previously observed in cholesterics is not the result of the cholesteric twist alone, but is also the result of the presence of the steroid moiety.

Figure 1 shows generalized viscosity vs. temperature curves for nematic liquid crystals and for steroidal cholesteric mesophases. The nematic phase is

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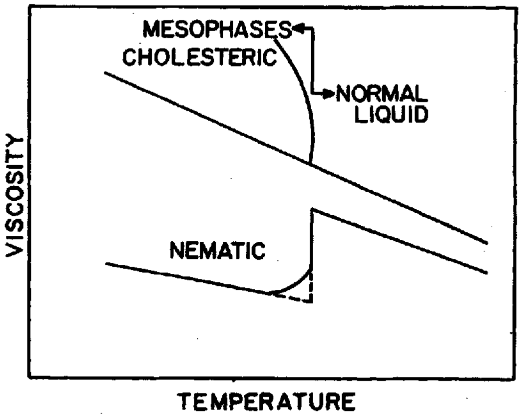

FIGURE 1 General flow of mesophase types. For the steroidal cholesteric mesophase the lower curve represents the limiting high shear Newtonian viscosity while the upper curve represents the viscosity at a much lower and arbitrary shear rate. (Reproduced, by permission, from Reference 7.) The dashed line for the nematic represents a possible additional orientation by electromagnetic field.

easily aligned by the flow, and its viscosity is lower than the extrapolation of the viscosity-temperature curve of the isotropic phase. One might expect similar behavior from a cholesteric. Even if alignment is more difficult than in a nematic, any partial alignment should still decrease the viscosity. The figure, however, does not support this argument. Apparently, the liquid crystalline nature of the material raises the viscosity instead of lowering it. Even at the highest shear rates, the viscosity of the liquid crystal never drops below the extrapolation of that of the isotropic.

A reason for a viscosity increase has been given by Pochan and Marsh.[8–10] From optical studies on materials under shear, they concluded that large domains of cholesteric order were first tipped by the shear field so that their axes of torsion were parallel to the flow direction. At higher rates of shear the domains began to break up. In other words, instead of the material undergoing a cholesteric to nematic transition as is seen under the influence of magnetic or electric fields, a cholesteric to isotropic transition is occurring.

Their explanation is certainly plausible, but the fact that *only* steroidal cholesterics have been used in obtaining viscosity vs. temperature curves is a limitation. Therefore, we have begun a study of the flow properties of non-steroidal cholesteric liquid crystals, which has already provided certain very surprising results.

A viscosity vs. temperature curve for MMBAC is shown in Figure 2. The shear rate was held constant while the temperature was continuously varied and the viscosity continuously monitored. (The experimental details are

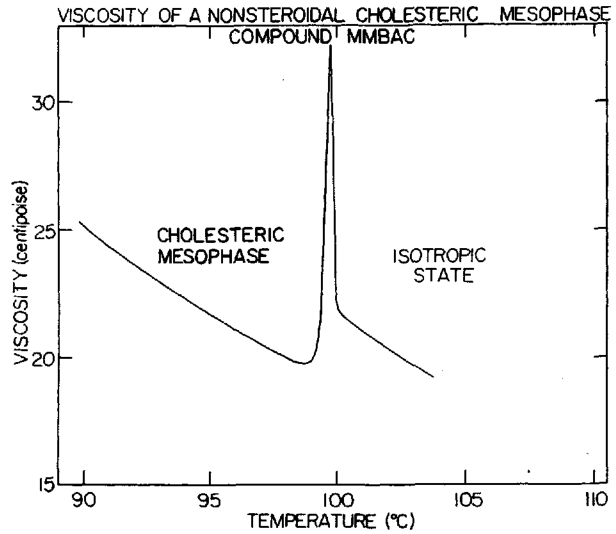

FIGURE 2 MMBAC viscosity vs. temperature. The temperature was monotonically increasing at approximately 0.5°C/min. The shear rate was 339 sec^{-1}. The curve was redrawn from the chart recorder output, and is typical of the results obtained at various shear rates and for heating and cooling.

described below.) The most significant feature of the curve is that the viscosity of the cholesteric phase is *lower* than that obtained by extrapolating the viscosity of the isotropic phase. Thus, the rheology previously considered as typical of cholesteric liquid crystals, must be considered to be typical only of the steroid derivative variety. As with the nematics, the viscosity of a non-steroidal cholesteric decreases with decreasing temperature in the region of the isotropic to cholesteric transition.

It is of interest to know whether the flow in the cholesteric region is Newtonian. Since there is a constant viscosity error in each viscosity-temperature run which gives rise to a run-to-run variation of as much as 2 or 3 centipoise, direct comparison of the viscosity at different shear rates was not helpful. However, we can assume the isotropic to be Newtonian and compare, at different shear rates, the difference between the viscosity of the cholesteric and the viscosity obtained by extrapolating from the isotropic region. Doing this, we see that the cholesteric is Newtonian to within 2 or 3 per cent over the measured range. This is, again, comparable to the behavior exhibited by nematic liquid crystals[2–4,7] and is in marked contrast to that exhibited by steroidal cholesteric liquid crystals.[3,5–7]

Another interesting feature is the viscosity peak seen at the cholesteric to isotropic transition. Apparently, this peak is characteristic of cholesteric liquid crystals in general, since it has also been observed in the steroid derivatives, but has never been reported for nematics. The magnitude of the peak increases with decreasing shear rate, which is also consistent with the steroid derivative results.[6,7] Further work is planned in an attempt to understand this phenomenon.

Viscosities were obtained on a Weissenberg Rheogoniometer, Model R17, using a 5 cm diameter plate and a 2° cone. The shear rates used were: 135 $\sec^{-1}$, 339 $\sec^{-1}$, and 1070 $\sec^{-1}$. The gap width was adjusted as the temperature changed, to correct for thermal expansion of the equipment, as described previously.[6,7] The curve shown in Figure 2 was redrawn by hand from the chart recorder output and is typical of the results obtained. Curves obtained were similar whether the temperature was increasing or decreasing. The peak height exhibited no systematic dependence upon whether the temperature was increasing or decreasing.

The MMBAC was used as obtained from Eastman Organic Chemicals (Catalogue No. 11236). The transition temperatures, as measured via differential scanning calorimetry are indicated below, where "EK" refers to the temperatures quoted by the supplier:

	THIS WORK	*EK*
Cholesteric-Isotropic	101.0°C	97°C
Smectic-Cholesteric	80.0	78
Solid-Smectic	—	53

The smectic-cholesteric transition was rather broad, having a width at half-height of at least 1°C. No transition was observed near 53°C. A transition was observed at 59.4°C, but its source is uncertain. A study to elucidate this is planned by others in the Materials Research Laboratory.

The rheologically-observed transition temperature of 99.8°C was reproducible to within ±0.2°C and independent of shear rate, so long as the runs were all made within about 12 hours of loading a fresh sample into the viscometer, and a nitrogen atmosphere maintained. Noticeable changes in the transition temperature (1°C or more) were observed in samples left overnight in the viscometer. A color change, from slightly iridescent bright yellow to black, is observed as the viscosity peak is traversed.

The conclusion to be drawn from this work is that there are two distinct types of cholesteric liquid crystal. There is the type studied here. It is a nematic-like liquid crystal with a twist in the director field, and has rheological properties similar to those of the nematics. There is also the type studied by prior workers. It has markedly different rheological properties which presumably result from the presence of the steroid moiety.

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