Shear-Induced Texture Changes in Cholesteric Liquid-Crystal Mixtures

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Rheological studies on a 23/77 wt% cholesteryl chloride–cholesteryl oleyl carbonate liquid-crystal system show isothermal shear-induced texture changes. The shear-induced textures show non-Newtonian behavior at shear rates below ~ 5 $\sec^{-1}$ and Newtonian behavior above this value. These textures have been optically characterized as the Grandjean and focal conic. At shear rates in excess of ~ 1000 $\sec^{-1}$, non-Newtonian behavior is observed and identified with the homeotropic texture. The first normal-force measurements on a liquid-crystal system are reported.

A number of previous rheological studies on cholesteric liquid-crystal systems have shown that materials in the cholesteric state are non-Newtonian up to a critical shear stress, and show Newtonian limiting viscosity behavior thereafter.[1,2] The rheological transitions reported are temperature-induced phase changes between various liquid-crystalline states and the isotropic state (e.g., smectic → cholesteric; cholesteric → isotropic).[2] We report here shear-induced texture changes and associated viscosity changes within the cholesteric state involving the Grandjean, focal conic, and homeotropic textures at a single temperature. We have used standard microscopic procedures (conoscopic figures and surface texture determinations) in the identification of these textures.[3] Our findings show that previously observed cases of limiting viscosity behavior in the cholesteric mesophase involve the formation of shear-induced focal conic texture from the Grandjean texture. The observations, which have been made rheologically and optically, will be reported in more detail later.

Most cholesteric liquid crystals exist over a limited temperature range. The compositions studied provide a broad temperature range of the cholesteric mesophase. The (room-temperature) cholesteric system studied consisted of mixtures of cholesteryl oleyl carbonate and cholesteryl chloride. Similar mixed cholesteric systems have been studied optically in this laboratory.[3,4] All systems were prepared by melt mixing. Data presented in this paper are for a 23/77 wt% mixture of cholesteryl chloride and cholesteryl oleyl carbonate.

The Weissenberg Rheogoniometer model R18 was used throughout this study. Behavior in both the rotational oscillatory modes was examined, and measurements included viscosity, shear moduli, and normal force.

The normal-force measurements are believed to be the first made on a liquid-crystal system. Normal-force values range from 10^4 to 10^5 dyn/cm^2 over the shear-rate range 10^2–10^4 $\sec^{-1}$.

An example of the viscosity behavior can be seen in Figure 1. Two transitions in flow behavior have been observed and characterized by optical measurements and movies. These transitions are the Grandjean→focal conic (low-shear transition), and the focal conic to homeotropic (high-shear transition). We have labeled these dynamic states on the basis of the texture to which each relaxes when the system is taken to zero shear from the shear rate indicated.

In part of our study, we replaced the normal 2.5-cm cone and plate of the Rheogoniometer with 6-in. diam transparent glass plates in order to make rheo-optical measurements as a function of shear rate. These measurements included spectral reflectance studies to establish the apparent helix orientation with shear, light scattering during shear to determine the orientation and relaxation behavior of the liquid-crystal entities, and motion pictures to record permanent-

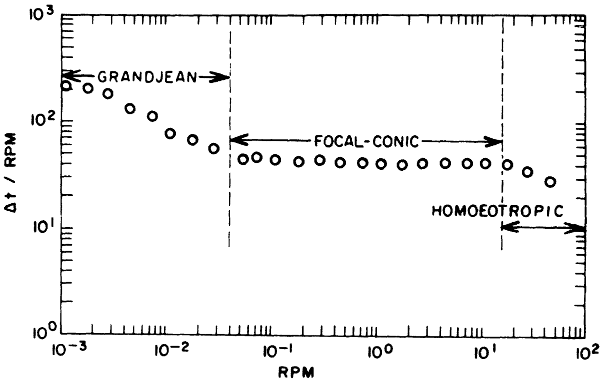

FIG. 1. Logarithm of relative viscosity versus relative shear rate for the double glass-plate configuration in the Weissenberg Rheogoniometer. Axes are given in terms of the instrument parameters: Δ_T is torsional transducer response and rpm is rev/min.

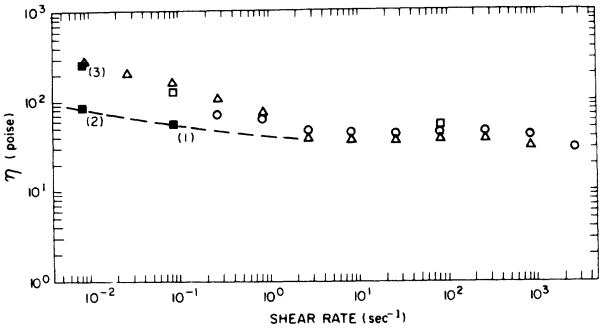

FIG. 2. Logarithm of viscosity versus logarithm of shear rate for a (77/23) mixture of cholesteryl oleyl carbonate and cholesteryl chloride. The open points depict different runs on the same sample starting from the Grandjean texture in each case. The solid points (1) and (2) are for shear-induced focal conic texture as described in the text. Point (3) is obtained on relaxation from the focal conic texture by removing the surface constraints as described.

ly the generation of the various textures. The irreversible nature of the transitions under the experimental conditions allowed verification of the textured states by microscopic studies using polarized light.

The use of large-radius, flat glass platens with narrow spacing allowed higher effective shear rates than for the cone and plate configuration. This enabled us to follow the transition to the homeotropic texture. On prolonged shearing (minutes) at shear rates greater than 1000 sec^{-1} we also observed the transition to the isotropic state ($T_{\mathrm{chol}\rightarrow\mathrm{iso}} \sim 32°\mathrm{C}$) apparently due to viscous heating. Care was taken to obtain viscosity measurements at each shear rate at short times so as to minimize the effects of viscous heating at the higher shear rates. Additional experiments on prolonged high-speed shearing showed quite different behavior from that reported here.

The results in Fig. 1 are given in terms of instrument parameters Δ_T, the torsional response, and rpm, the radial frequency. While no direct calculation of the viscosity is possible from these data, the results in Fig. 2 (obtained with the cone and plate configuration) show steady-state viscosity–shear-rate behavior essentially the same as in the glass platen case.

A nonreversible nature of the limiting viscosity is apparent. The darkened points labeled (1) and (2) depict viscosity levels at low shear rates on return from the high-shear-rate region. Once the limiting viscosity is established at high shear rates, the viscosity behavior depicted by the dashed line is reversible. The system was allowed to rest for periods up to 15 h with no apparent relaxation to the original non-Newtonian state.

Surface effects are most certainly involved. This is shown by the datum point (3) which was obtained by opening the platens and releasing the surface constraints induced at the high-shear-rate condition. This return of viscosity to the initial state upon reclosing the platens is accompanied by a change to the Grandjean texture.

We have studied the viscoelastic and rheological behavior, normal force, spectral reflection, viscous heating effects, and dynamic light scattering of this system. We expect that the description of the similarities and differences between this and other cholesteric systems whose flow properties have been reported will provide new information and insights into the basic flow mechanisms and structure of these fluids.

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