Unusual pressure profiles and fluctuations during shear flows of liquid crystal polymers

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The spatial dependence of a stress tensor component has been measured for a liquid crystalline solution during cone-and-plate shear flows. The measured stress profile can be used to calculate thermodynamic pressure as a function of position within the flowing liquid crystal. At most shear rates, the pressure profile is highly unusual, with thermodynamic pressure below atmospheric pressure within the rheometer. However, the shape of the time-averaged pressure profile is consistent with the velocity field expected in the rheometer, even at shear rates for which the total thrust on the cone exhibits large time-dependent fluctuations. The measured stress profile can also be used to calculate the second normal stress difference (N_2). The magnitude of N_2 is often surprisingly large, with an unusual oscillatory dependence on shear rate.

(Keywords: rheology; liquid crystal polymers; nematic fluid; lyotrope; second normal stress difference; cone-and-plate rheometer)

INTRODUCTION

Main-chain liquid crystal polymers (LCPs) are materials which exhibit a thermodynamic fluid state with long range orientational order[1]. Numerous applications are foreseen for LCPs as load-bearing structural materials, provided that processing flows can be devised to control the direction of molecular orientation[2,3]. Therefore the rheological behaviour of these materials is a topic of much practical and scientific interest, particularly in the non-linear flow regime (high shear rates) where the Doi molecular theory[4] is expected to apply.

The goal of rheological studies has long been the measurement of material response to a known flow field imposed on the sample. In the widely used cone-and-plate (C&P) rheometer, the 'known' flow field is presumed to be a homogeneous viscometric shearing flow with position-independent rheological properties[5]. However, recently published versions of the Doi theory predict that it is impossible to impose such a velocity field on an LCP at moderate shear rates[6,7]. Instead, these theories predict that the average liquid crystal orientation (the director) 'tumbles' or 'wags' during flow, never achieving a steady value. If this prediction is true, rheological studies on LCPs with the C&P rheometer are impossible. In this paper, we report on our efforts to investigate the nature of the velocity field in C&P flows of LCPs by measuring the spatial dependence of a stress tensor component. The stress profile is also used to calculate the second normal stress difference (N_2), a rheological property which has not been previously measured for a liquid crystalline material.

MATERIALS

In this initial study on LCPs we report results for a widely studied lyotropic system: poly(γ-benzyl-L-glutamate) (PBLG) in *m*-cresol[8–11]. The PBLG sample was purchased commercially and characterized by gel permeation chromatography (g.p.c.) and viscometric methods. PBLG is a synthetic polypeptide which adopts a stiff α-helical form in *m*-cresol with a persistence length $\approx$ 100 nm (ref. 12). According to g.p.c. measurements, the polymer sample has an average molecular weight of 230 000, and a polydispersity ratio of 1.8. For PBLG in its α-helical form, this molecular weight corresponds to a contour length $L \approx 155$ nm. In *m*-cresol at 29°C, the intrinsic viscosity was measured to be $0.375\ \mathrm{m^3\ kg^{-1}}$. The measured intrinsic viscosity can be used to estimate an effective length (L_{eff}) for the polymer modelled as a rigid rod: $L_{\mathrm{eff}} \approx 150$ nm (ref. 13). Since $L_{\mathrm{eff}} \approx L$ for this polymer, it is reasonable to use a rigid-rod molecular theory to qualitatively describe its rheological behaviour. According to the Doi theory[13], rigid-rod solutions exhibit four concentration regimes. In order of increasing concentration these are: dilute, semi-dilute, isotropic concentrated and liquid crystalline. Here we are interested in the fourth regime, the first three regimes having already been discussed for the same polymer sample in reference 10. The onset of liquid crystal ordering occurs at a concentration $C_1 \approx 9.5$ wt%, as determined by viewing the birefringence of the solution with a polarizing microscope. The isotropic phase completely disappears for concentrations above $C_2 \approx$ 12.3 wt%. All liquid crystal results reported in this paper were measured on a wholly liquid crystalline solution with a concentration of 15.0 wt%. This solution has a polydomain morphology at rest, due to the presence of metastable defects in the director field of the liquid

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crystal[1]. Because these orientational defects are very difficult to remove, rheological studies to date have focused on polydomain LCPs. Orientational defects are not accounted for in most of the molecular theories of LCPs[6–7,13].

RHEOMETRY

Figure 1 is a schematic diagram of the instrument used in this study. Miniature pressure transducers (diameter $\cong$ 2–3 mm) have been constructed in our laboratory, and mounted flush with the interior plate surface of a conventional C&P rheometer[14]. This modification allows us to measure Π_{22}, a diagonal component of the total stress tensor Π (here the 2 subscript denotes the velocity gradient direction in simple shear flow). The utility of this measurement is its use in connection with the following equation, which is derived from a rigorous momentum balance on the velocity field expected to be present in the rheometer during steady flow[5]:

$$-(\Pi_{22}+P_0) = -(N_1+2N_2)\ln(r/R) - N_2 \qquad (1)$$

Here P_0 is the atmospheric pressure, r is the spherical radial coordinate, R is the radius of the rheometer, and N_1 and N_2 are the primary and secondary normal stress differences, respectively. The left-hand side of equation (1) is the net upward vertical stress, a quantity which is measured at the locations of the miniature pressure transducers. Even in a homogeneous flow, this quantity varies with position, because it includes a contribution from the local thermodynamic pressure P (ref. 5). The P varies with r because no real fluid is truly incompressible, and thus fluid density varies slightly with position in such a way that the pressure balances the stresses generated by the flow. Therefore the measured variation in the upward vertical stress can be used to calculate the spatial variation in P:

$$P = -\Pi_{22} + N_2 \qquad (2)$$

Here we have assumed that $P \to P_0$ as $r \to R$. According to equations (1) and (2), P is a logarithmic function of r (N_1 and N_2 are constants within a homogeneous flow). Measurement of a pressure profile in violation of this prediction implies that the true velocity field in the rheometer is unknown. Suppose that liquid crystal rheological properties vary substantially in the direction normal to the rheometer plate. Then local values of N_1 and N_2, averaged across the gap, should depend on the radial coordinate r, because the rheometer gap varies linearly with r in a C&P apparatus. According to equations (1) and (2), radial variation in the value of N_1 or N_2 is inconsistent with a logarithmic pressure profile. Therefore observation of a logarithmic pressure profile provides indirect evidence that no large scale inhomogeneities are present in the flow, even in the direction normal to the rheometer plate.

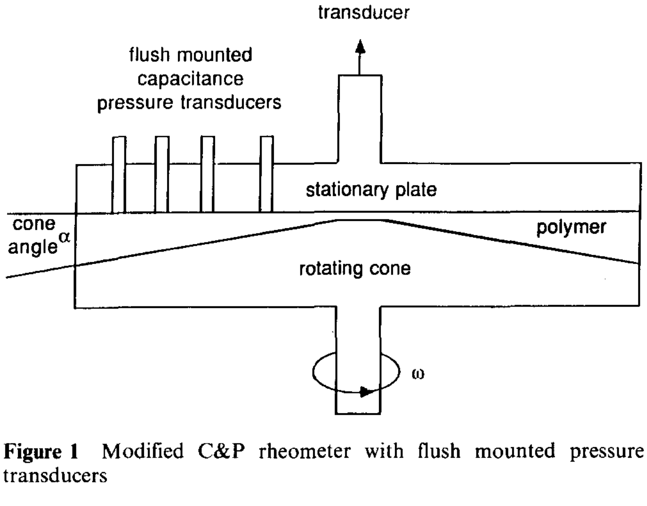

Figure 1 Modified C&P rheometer with flush mounted pressure transducers

For homogeneous viscometric flows, the value of N_2 can be accurately calculated from the measured stress profile[14–16]. Equation (1) indicates that a semi-logarithmic plot of the measured stress against radial coordinate r should yield a straight line, with slope equal to $-(N_1+2N_2)$. N_1 can be independently measured with the spring attached to the rheometer plate. Therefore, the value of N_2 can be calculated from the slope of the stress profile observed on a semi-logarithmic plot. This procedure assumes that the true stress profile can be estimated by drawing a smooth curve through the values of Π_{22} measured at the locations of the miniature pressure transducers. This assumption has been verified by integrating the stress profile so obtained, and comparing the result to the force calculated from the deflection of the rheometer spring[16].

RESULTS

Figure 2 shows the time dependence of the apparent value of N_1, as measured for a wholly liquid crystalline PBLG solution during what is ostensibly steady shear flow. Each curve in *Figure 2* corresponds to a different shear rate, and high frequency noise has been removed with a low pass filter (cut-off frequency $\approx$ cone rotational frequency). For shear rates near $50\,\mathrm{s}^{-1}$, the apparent value of N_1 fluctuates chaotically about its time-averaged value, and the fluctuations are surprisingly long-lived. Nonetheless, the time-averaged value of N_1 is quite consistent with N_1 values measured at neighbouring shear rates, shear rates at which no fluctuations are observed. *Figure 3* shows the shear rate dependence of time-averaged N_1 values. The sign of N_1 exhibits the remarkable oscillatory dependence on shear rate first reported by Kiss and Porter[8]. The fluctuations observed in *Figure 2* occur near the shear rate at which N_1 first becomes negative in *Figure 3*. This observation suggests a connection between the fluctuations and the Doi molecular theory, because the theory predicts the onset of a 'wagging' motion for the liquid crystal director near this shear rate[7]. To test this hypothesis, we are currently investigating rheological fluctuations in LCPs at lower concentrations, where the tendency for director tumbling and wagging is predicted to be at its strongest level. Additional evidence for director tumbling or wagging has already been provided by dichroism measurements on PBLG[9,11], and birefringence measurements on polybenzobisthiazole (PBT)[17]. However, areas of disagreement remain between the theory and the observations. For example, the PBLG sample of this study is predicted[7] to exhibit unstable flow behaviour for all shear rates below $300\,\mathrm{s}^{-1}$. In practice, large rheological fluctuations are only observed within a narrow band of shear rates centred about $50\,\mathrm{s}^{-1}$. This discrepancy between theory and experiment may possibly be attributable to orientational defects in the sample, defects which are not accounted

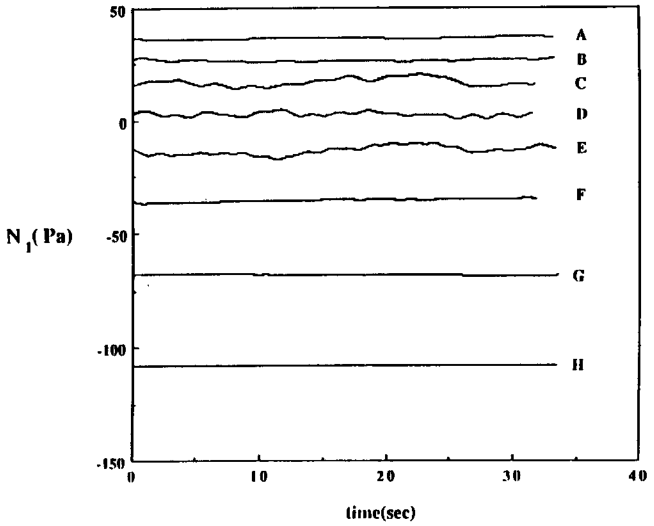

Figure 2 Time dependence of the primary normal stress (N_1), as measured for a wholly liquid crystalline PBLG solution at 15.0 wt%. Shear rates (s^{-1}): 14.6 (A); 29.1 (B); 36.6 (C); 46.0 (D); 58.0 (E); 73.0 (F); 91.9 (G); 116.0 (H)

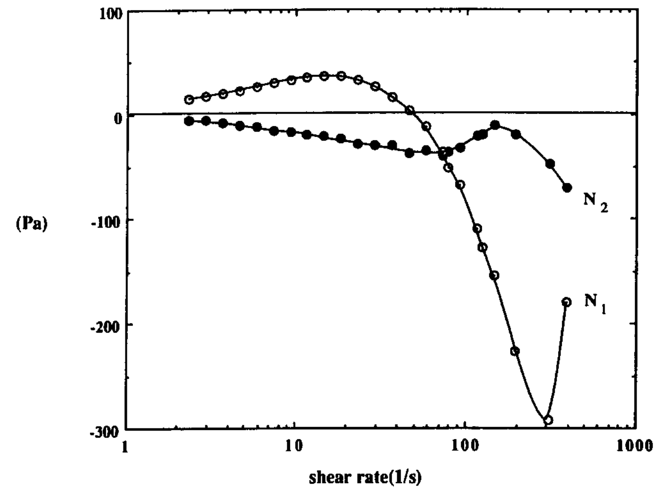

Figure 3 Shear rate dependence of the primary (N_1) and secondary (N_2) normal stresses, for a wholly liquid crystalline PBLG solution at 15.0 wt%

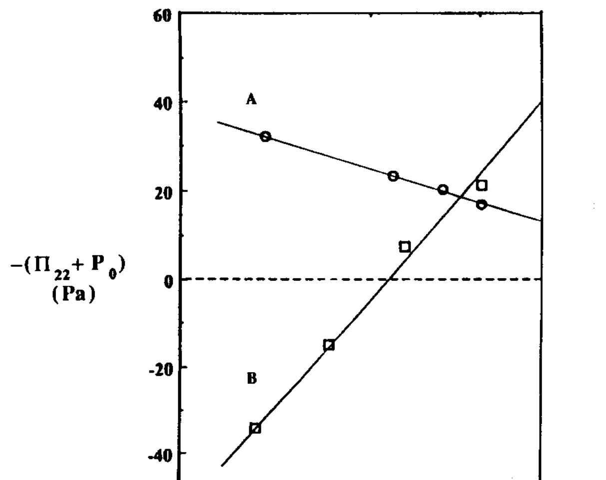

Figure 4 Net vertical stress exerted on the rheometer plate during flow, as a function of radial position: A, isotropic PBLG solution at 7.5 wt% (shear rate = 2.3 s^{-1}); B, wholly liquid crystalline solution at 15.0 wt% (shear rate = 46.0 s^{-1})

for in the theory. The occurrence of these defects is expected to give rise to Frank elastic stresses opposing the tumbling motion of the director[11].

Not surprisingly, measurements with the local pressure transducers show large fluctuations in the same shear rate range within which N_1 fluctuates. However, the time-averaged stress profile is highly reproducible, and conforms within experimental error to the theoretical stress profile (equation (1)). *Figure 4* contains a semi-logarithmic plot of the time-averaged stress profile, as measured within the liquid crystalline solution at a shear rate of 46 s^{-1}. At this shear rate, the value of N_1 is slightly positive with large time-dependent fluctuations (*Figure 2*). Despite the fluctuations, the measured stress profile is approximately linear on a semi-logarithmic plot, as expected from equation (1). No clear violation of equation (1) has been observed at any shear rate over the entire accessible shear rate range for this fluid (2–400 s^{-1}). As discussed earlier, this result implies that the liquid crystal polymer achieves a homogeneous and viscometric velocity field within the C&P rheometer. Recently Grizzuti has arrived at a similar conclusion with regard to planar Couette flow of LCPs, provided that the amount of strain is sufficiently large[18].

Thus large strain values of N_2 can be calculated from the measured stress profile at each shear rate, using the procedure described above. The N_2 values thus calculated are plotted against shear rate in *Figure 3*. We have already noted the oscillatory dependence of N_1 on shear rate, first reported in 1978[8]. The new result in *Figure 3* is that N_2 is also an oscillatory function of shear rate, with the oscillations in N_2 phase-shifted with respect to the oscillations in N_1. This is probably the first time that a non-monotonic dependence of N_2 on shear rate has been measured for any fluid. However, such a shear rate dependence is predicted by the Doi theory[7], and thus we are currently preparing a careful comparison between this theory and experiments over a wider range of experimental conditions[16].

For comparison, *Figure 4* also contains a typical stress profile observed in an isotropic solution of the same polymer. Both stress profiles in *Figure 4* are approximately linear. However, a positive slope is observed only for the stress profile in the liquid crystal, a result which implies that the thermodynamic pressure decreases as the tip of the cone is approached (equation (2)). Assuming that the pressure is near atmospheric at the rheometer rim, then pressure must be below atmospheric within the rheometer. This surprising result is also true at most other shear rates for this liquid crystal. For polymeric fluids which are isotropic at rest, thermodynamic pressure within the C&P rheometer invariably exceeds atmospheric pressure[5,14,15].

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