Second normal stress difference of a Boger fluid

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Measurement of the second normal stress difference for a highly elastic, constant viscosity 'Boger fluid' is reported. Two very different experimental techniques have been used: (1) measurement of the height of the free surface in rod-climbing flow; (2) measurement of the pressure distribution in cone-and-plate shearing flow. The second normal stress difference is at least 30 times smaller in magnitude than the first normal stress difference, and opposite in sign. The results should prove useful in distinguishing between the various constitutive equations proposed for Boger fluids.

(Keywords: rheology; polyisobutylene; model elastic fluid; rod-climbing; second normal stress difference)

INTRODUCTION

There is a great need for the development of numerical methods for predicting the flow behaviour of highly elastic liquids in polymer-processing type flows[1,2]. Such a development would allow the polymer engineer to rationally design processing equipment like extruders, thereby avoiding the numerous flow instabilities which have been observed in thermoplastic materials[3]. To this end, model elastic liquids have been studied experimentally[4–15] and simulated numerically[16–23], with the goal of achieving consistency between theory and experiment. A suitable model elastic liquid is both convenient to study experimentally, and has a known constitutive equation[24], without which numerical simulation is impossible. Once consistency between theory and experiment is achieved for these model systems, it will become plausible to attempt numerical simulations of more complex fluids like commercial polymer melts.

Perhaps the most widely studied model system for this application is the so-called 'Boger fluid', introduced by Boger in 1977[25]. For a discussion of the experimental advantages of Boger fluids, see reference 4. On the basis of their properties in simple shear flow[9,10,26,27], Boger fluids were historically believed to obey a rather simple constitutive equation, the Oldroyd-B equation[28]. Consequently the Oldroyd-B equation has been widely studied numerically and theoretically[16,20,22,29–35], and numerous experimental papers on Boger fluids[4–13,25–27,35–39] have appeared in the literature. Unfortunately, the consistency desired between numerical simulations and flow visualization experiments has not yet materialized. For example, the simulations are unable to predict the various vortex patterns observed in axisymmetric contraction flows of Boger fluids[20]. A possible cause of this discrepancy between theory and experiment is inadequacy of the Oldroyd-B constitutive equation. To salvage the use of Boger fluids as model elastic liquids, the Boger fluid constitutive equation must be further developed and tested. This can be accomplished via measurement of as many Boger fluid material functions as possible. In particular, the authors of a recent paper[39] have advocated second normal stress difference (N_2) measurements in order to distinguish between two possible constitutive equations for Boger fluids (i.e. the Giesekus equation[40] and the Bird–DeAguiar equation[41]). The value of N_2 also appears to be an important determinant of flow stability in certain types of flow[32,35,42].

For these reasons we have measured the second normal stress difference material function for a typical Boger fluid (polyisobutylene dissolved in oligomeric polybutene). Of the three material functions defined for polymers in simple shear flow[43], N_2 is least often reported in the literature, probably because it is the most difficult to measure. In our literature review, we have identified two earlier papers reporting N_2 values relevant to the data presented here. Keentok *et al.*[44] reported N_2 values close to zero ($-N_2/N_1 < 0.005$) for a Boger fluid consisting of polyacrylamide dissolved in maltose and water. Their results are consistent with our measurements, though we employed a different measuring technique on a Boger fluid of a different formulation. In recent years, Boger fluids containing polyisobutylene as the solute have replaced those containing polyacrylamide in popularity among rheologists, perhaps due to their decreased tendency toward solvent evaporation. For Boger fluids of this type, the only relevant N_2 study we have located is a recent rod-climbing paper by Hu *et al.*[45]. The fluid investigated by Hu *et al.* (fluid 'M1') has the same components as the Boger fluid that we studied, but with a higher polyisobutylene concentration (0.24 vs. 0.1%). This may be the reason why Hu *et al.* report a much higher N_2 value ($-N_2/N_1 = 0.11$–0.12) than our measurements indicate.

Apart from a desire to clarify the Boger fluid constitutive equation, we are also interested in comparing and

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evaluating different experimental techniques for N_2 measurement. An early survey of the various techniques is contained in reference 46. In the Results section N_2 measurements are presented for a standard polymeric liquid available from NIST[47]. For comparison's sake, it is hoped that other research groups involved in N_2 measurement will procure and investigate the same reference material from NIST. Two reasonably successful techniques for evaluating N_2 are measurements of the free surface height in rod-climbing flow[48], and measurements of the pressure distribution in cone-and-plate shearing flow. The latter technique was pioneered in our laboratory by the late E. B. Christiansen[49,50]. Application of both of these techniques to the same fluid is virtually without precedent. In 1983 an international effort was made to evaluate various techniques of N_2 measurement[51]. The evaluation was accomplished by applying the various N_2 measurement techniques to the same polymeric liquid (fluid 'D1') and comparing the results. Christiansen's pressure measurement technique was judged to be a superior method[51]; the use of rod-climbing measurements to estimate N_2 was not evaluated at that time. Recently rod-climbing results have been published for fluid D1[45]; the resulting N_2 estimates are in good agreement with the N_2 values determined in the 1983 study. In this paper we also demonstrate good agreement between N_2 estimates from rod-climbing studies and N_2 estimates from the pressure distribution in cone-and-plate shearing flow.

EXPERIMENTAL

Polymeric materials

Polymeric melts are characterized by large elasticities, and shear viscosities which may vary by three orders of magnitude, depending on the shear rate[24]. On the other hand, a suitably formulated Boger fluid is virtually non-shear-thinning, and yet has elasticity comparable to a polymer melt[27]. Hence by using Boger fluids in polymer-processing type flows, it is possible to separately assess the effects of elasticity and shear-thinning on the flow field. Reference 4 discusses the numerous experimental advantages of using Boger fluids as model elastic liquids. The prescription is now known for formulating Boger fluids[10,26] and this prescription may be varied in order to vary the level of fluid elasticity. Boger fluids typically consist of a trace amount of an ultra-high molecular weight polymer, dissolved in a very viscous Newtonian solvent. The relaxation time or elasticity of such a solution is qualitatively predicted by the Zimm theory[24], which is believed to describe the dynamics of the solution at low deformation rates[10,26]. According to the Zimm theory, the elasticity should increase as the second power of the solvent viscosity. The solvent used to formulate the Boger fluid reported on in this paper has a viscosity four orders of magnitude larger than the viscosity of a conventional solvent. Hence the Zimm theory explains why this Boger fluid is extremely elastic.

The first Boger fluids introduced in 1977 consisted of dilute solutions of polyacrylamide in maltose/water. This aqueous type of Boger fluid has excellent rheological properties, but also has an unfortunate tendency for solvent evaporation. By employing 'organic' Boger fluids consisting of polyisobutylene dissolved in oligomeric polybutene, the evaporation problem can be eliminated, while retaining the desirable rheological properties. Consequently the frequency of investigation of organic Boger fluids has rapidly increased since their introduction in 1983[10,11,13,15,26,27,35,37–39,45]. Properties of three organic Boger fluids with varying polyisobutylene molecular weights were reported by one of the authors of this paper in a previous study[38]. In this earlier study, flow instabilities were observed for the two Boger fluids containing very high molecular weight polyisobutylenes. To avoid the complications of a flow instability, polyisobutylene of a lower molecular weight (nominal $M \cong 1 \times 10^6$) was used to construct the Boger fluid investigated in this paper. *Table 1* describes the composition of the Boger fluid formulated in this laboratory for N_2 measurement. Apart from the relative weight percentages of the components, this Boger fluid is identical to the least elastic polyisobutylene Boger fluid described in reference 38. As expected, no flow instabilities were observed for this Boger fluid in the cone-and-plate rheometer. Both polymer components are of broad and unknown polydispersity. Polydispersity is typical of virtually all Boger fluids discussed in the literature, and in fact polydispersity may contribute to the unusual rheological properties of Boger fluids. According to the suppliers, the polyisobutylene molecular weight is nominally 1.3×10^6. This nominal molecular weight was verified by intrinsic viscosity measurements[52] (*Table 1*) in a Ubbelohde viscometer with a wall shear stress of $\cong 1.5$ Pa. Intrinsic viscosity measurement cannot be performed to determine the polybutene molecular weight, which is nominally 950. However, rheological measurements on the oligomer are consistent with a molecular weight of this order of magnitude. In accordance with published formulations of Boger fluids[10,26,27], a polyisobutylene concentration of approximately 1000 ppm was chosen. Given the chemical similarity between the repeat units of polybutene and polyisobutylene, one would expect the oligomer to be a good or athermal solvent for the polyisobutylene. Based on the assumption of an athermal solvent, one estimates that the polyisobutylene overlap concentration c^* is approximately 0.1 g dl^{-1} (ref. 53). Since this is close to the actual polyisobutylene concentration, the characterization of Boger fluids as 'dilute'

Table 1 Polyisobutylene Boger fluid components

Component	Weight (%)	Molecular weight	Density (kg m^{-3})	Boiling point (°C)	Manufacturer
Polyisobutylene (PIB)	0.1	1.3×10^6 (nominal) 1.35×10^6 (viscosity-average)[a]	918.0	–	Aldrich
Polybutene (Parapol 950)	>98.5	950 (nominal)	890.4	–	Exxon
2-Chloropropane	<1.4	78.5	859	35	Aldrich

[a] The viscosity-average value is obtained from the intrinsic viscosity measurement for the PIB–toluene system at 30°C

polymer solutions may be somewhat questionable. However, by separately measuring the viscosity of the solvent (polybutene + 2-chloropropane) and the Boger fluid, it is estimated that the polyisobutylene intrinsic viscosity is only $\cong 5\ \mathrm{dl\ g^{-1}}$. This is less than one would expect for an athermal solvent[52], which suggests that c^* is greater than $0.1\ \mathrm{g\ dl^{-1}}$ ($c^* \cong 1$/intrinsic viscosity).

N_2 estimation from pressure distribution measurements

Complete specification of the state of stress of an isotropic fluid in shear flow requires the determination of three material functions: the viscosity (η), the first normal stress difference (N_1), and the second normal stress difference (N_2). The defining equations for these quantities are[43]:

$$\eta = \Pi_{12}/\dot{\gamma} \tag{1}$$

$$N_1 = \Pi_{11} - \Pi_{22} \tag{2}$$

$$N_2 = \Pi_{22} - \Pi_{33} \tag{3}$$

where $\dot{\gamma}$ denotes the shear rate, and Π_{ij} denotes the i,j component of the total stress tensor (i.e. shear stress + pressure). Following the usual rheological convention, a 1 subscript denotes the flow direction, a 2 subscript denotes the velocity gradient direction, and a 3 subscript denotes the neutral direction. For example, in the cone-and-plate rheometer, we define a spherical coordinate system with the origin located at the apex of the cone. In this geometry, the 1 direction corresponds to the azimuthal angle φ, the 2 direction corresponds to the polar angle θ, and the 3 direction corresponds to the radial coordinate r. The normal stress difference coefficients, Ψ_1 and Ψ_2, are defined by

$$\Psi_1 = N_1/\dot{\gamma}^2 \tag{4}$$

$$\Psi_2 = N_2/\dot{\gamma}^2 \tag{5}$$

Measurement of the first two material functions, η and Ψ_1, is easily accomplished on commercially available cone-and-plate rheometers. The N_2 measurement however, is much more difficult, and generally requires custom-designed equipment. One of the most reliable techniques of N_2 measurement is to infer its value from the measured pressure distribution in a cone-and-plate shearing flow[49–51]. The radial momentum balance equation can be used to derive a relationship between the pressure distribution and N_2[43]:

$$-\Pi_{\theta\theta} - P_0 = -(N_1 + 2N_2)\log(r/R) - N_2 \tag{6}$$

In equation (6), P_0 is the atmospheric pressure, R is the radius of the cone and $-\Pi_{\theta\theta} - P_0$ is the net vertical pressure force exerted by the liquid on the cone at a particular radial position r. For a given shear rate in the cone-and-plate rheometer, N_1 and N_2 are constants. Hence, equation (6) predicts that if we plot the net pressure force against the logarithm of the radial position, we should obtain a straight line with a slope of $-N_1 - 2N_2$. The slope of this line, in conjunction with an independent measurement of N_1, gives us an estimate of N_2. Alternatively, if we can extrapolate the pressure distribution to the rim of the cone, then the net pressure force at this location should equal $-N_2$. The assumptions which must be satisfied in order for equation (6) to apply are essentially the same assumptions which must be satisfied in order to measure the true polymeric viscosity in a cone-and-plate rheometer. In particular, a steady one-dimensional homogeneous shearing flow must be established when the polymer is sheared in the narrow gap between the cone and the plate. This is a reasonable assumption for most polymeric liquids; consequently, cone-and-plate rheometers are widely used in rheological research. If this assumption is satisfied, then it is not necessary to know the constitutive equation of the polymer in order to measure its three material functions η, Ψ_1, and Ψ_2.

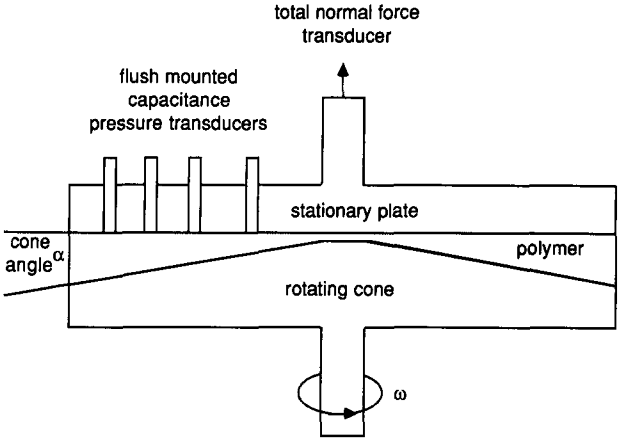

Figure 1 Cone-and-plate rheometer with flush mounted pressure transducers

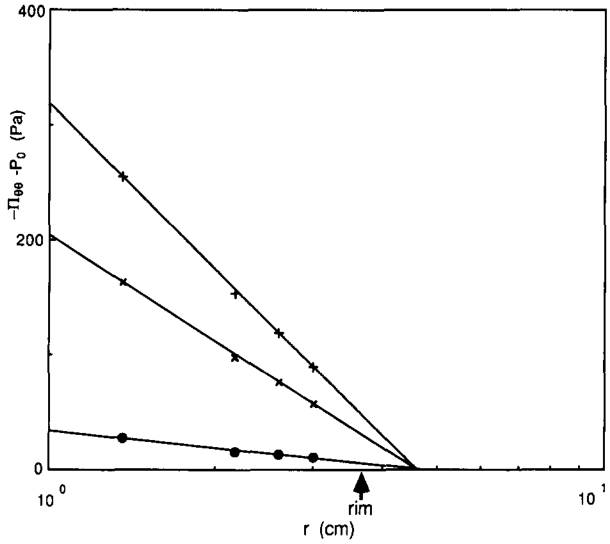

Figure 2 Net vertical pressure force as a function of radial position in cone-and-plate rheometer for NIST rheology standard. Shear rates ($\mathrm{s^{-1}}$): 1.16 (●); 5.8 (×); 9.2 (+)

The schematic diagram in *Figure 1* shows how the pressure distribution is measured in the cone-and-plate rheometer used in this study. Four miniature pressure transducers are located at four different radial positions on the rheometer plate. The transducers are mounted flush with the interior surface of the plate, thereby avoiding the 'hole pressure errors' documented in early investigations of this type[46]. The pressure transducers were custom-built in our laboratory over the last year, following the design of the late E. B. Christiansen and a patent by Dimeff and Harrison[54]. For details of the transducer design, the detection circuit, and the data acquisition system, see reference 55. The data presented in *Figure 2* indicates that these transducers are small enough (diameter $\cong 3.0$ mm) relative to the size of the rheometer plate (diameter = 74.0 mm) to allow measurement of the 'local' pressure at a given radial position, as required by equation (6). Despite their small size, these transducers are extremely sensitive, capable of measuring pressures as low as 1 Pa.

Because equation (6) for the pressure profile is derived without recourse to a particular constitutive equation, this N_2 measurement technique is not restricted to a particular shear rate regime. This should be contrasted with the rod-climbing method (see below), which is only valid in the second-order flow regime[48]. In practice, the lower shear rate limit for applying equation (6) to N_2 measurement is determined by our ability to measure the 'true' pressure distribution in the flowing polymeric fluid. Fortunately, two consistency checks are available to judge the accuracy of the measured pressure profile. First, the net pressure force measured must exhibit a logarithmic dependence on radial position, in accordance with equation (6). Second, the integral of the measured pressure profile over the surface of the rheometer plate can be used to obtain an estimate for N_1. This estimate can then be compared to an independent measurement of N_1 with the extremely sensitive normal spring attached to the plate of our R-17 Weissenberg rheometer. The N_2 values are reported here only at shear rates for which both of these cross-checks are satisfied. Using these criteria, the minimum shear rate for N_2 measurement on the Boger fluid of this paper is 2.3 s^{-1}. At this shear rate, the Boger fluid N_1 value is $\cong 15$ Pa, which exceeds considerably the sensitivity of the miniature pressure transducers. This N_2 measurement technique appears to be limited by the accuracy of the alignment of the transducers with the rheometer plate, and not by the transducer sensitivity[55].

N_2 estimation from rod-climbing measurements

One of the earliest and most convincing demonstrations of polymer elasticity is the tendency of the free surface of a polymeric liquid to climb the shaft of a rotating rod (*Figure 3*)[24,43]. In 1973 Joseph *et al.*[48] analysed the equations of motion via a perturbation scheme, and successfully related the height of the climb to the fluid material functions in shear flow. This analysis takes into account fluid inertia and surface tension, and is essentially rigorous, subject to certain restrictions discussed below. Subsequently rod-climbing measurements have been used to infer the values of fluid material functions in shear flow, especially N_2[45,56]. The theoretical analysis can be simplified considerably by choosing rod diameters small enough to make inertial effects negligible. In this case, the theory predicts that the height of the free surface h (at the rod) depends on the rod angular velocity ω in the following fashion[48]:

$$h = h_s + \frac{4a\hat{\beta}\omega^2}{2\sqrt{\rho g}(4\sqrt{\gamma} + a\sqrt{\rho g})} \tag{7}$$

where $\hat{\beta}$ is the 'climbing constant' $(=0.5\Psi_1^0 + 2.0\Psi_2^0)$, h_s is the static climb at $\omega = 0$, γ is the liquid surface tension, ρ is the liquid density, a is the rod radius and g is gravitational acceleration.

A zero superscript on a rheological property such as Ψ_1 denotes the limiting zero shear rate value. If one can accurately measure the height of climb as a function of rod rotation speed, then equation (7) can be used to calculate the fluid climbing constant $\hat{\beta}$. The calculated climbing constant can then be used in conjunction with an independent measurement of Ψ_1^0 to calculate N_2 (or its equivalent, Ψ_2^0).

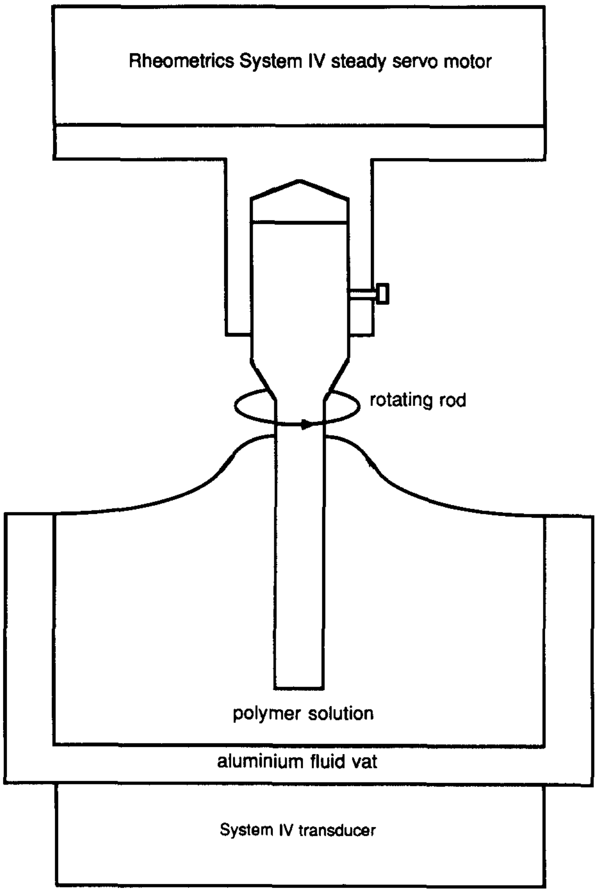

Figure 3 System IV as modified for rod-climbing measurements

The simplicity of this method is one of the principal advantages of rod-climbing measurements. Disadvantages to this technique arise from the necessity of ensuring that the theoretical assumptions made in deriving equation (7) are satisfied in the experiments. Equation (7) is derived assuming that the rod/liquid contact angle is 90°, and also that the measurements are made in the 'second-order' flow regime[48]. The latter restriction appears to be more serious, since it implies that N_2 cannot be measured at high shear rates. In fact, for higher shear rates a 'heuristic' criterion has been proposed to qualitatively predict rod-climbing flows[57]. Isotropic liquids with 'fading memory' are expected to exhibit a second-order flow regime at low deformation rates[24]. But, it is impossible to predict a priori the maximum allowable rotational speed of the rod (ω_{max}) without knowing the constitutive equation of the polymer. In practice one needs to judge from the experimental data itself the rotational range over which the measured climb is quadratic in ω, as predicted by equation (7). One must hope that within this rotational speed range, the height of the polymer climb is large enough to measure.

Clearly it is experimentally convenient if the polymer exhibits large climbs within the second-order flow regime, and this is a major reason for applying this technique to Boger fluids. Boger fluids are believed to exhibit an unusually large second-order flow regime. In the rod-climbing measurements, care was taken to make sure that h does, in fact, exhibit quadratic dependence on ω.

As anticipated, it was observed that the rod-climbing technique works well with Boger fluids. For a given fluid at a fixed rod rotation speed, equation (7) also predicts the climbing height as a function of rod size. This prediction was used as an additional check on our data, to ensure that ω did not exceed $\omega_{\max}$ (see Results).

Though determination of the climbing constant $\hat{\beta}$ is relatively simple for Boger fluids, separation of $\hat{\beta}$ into Ψ_1^0 and Ψ_2^0 contributions is considerably more difficult. If rod-climbing is to be used as an N_2 measurement technique, then Ψ_1^0 must be independently determined on another rheometer, which implies a different flow geometry. Often the rheometer used to measure Ψ_1 cannot probe shear rates as low as those present in the rod-climbing experiments. This can be a serious limitation if Ψ_1 is a strong function of shear rate, because Ψ_1 must then be extrapolated to zero shear rate.

The Rheometrics Systems IV rheometer in this laboratory was modified to function as a rotating rod viscometer (*Figure 3*). Precisely machined steel rods were attached to the steady servo motor of the System IV. The Boger fluid was contained in a cylindrical aluminium vat of diameter 6.35 cm and depth 3.3 cm. The rods were immersed in the fluid to a depth of 2.0 cm, with careful attention to the rod alignment and concentricity with respect to the vat. The steady servo motor uses an air-bearing, and its rotational speed has been carefully calibrated. Climbing heights of the fluid free surface were measured from photographs taken with a Nikon F camera, with a five-fold magnification. The depth of the rod was found to have little effect on the measured climb. Equation (7) for the height of the climb was derived assuming a semi-infinite fluid container[48]. In these experiments, the ratio of the vat diameter to the rod diameter (λ) was varied between 8 and 20. Joseph *et al.*[56] recommend that λ be at least 10, and λ values as low as 10.5 have been reported in the literature[45]. Consequently, we believe that edge effects are minimal with our smallest diameter rod. However, to our knowledge, no systematic study of edge effects in rod-climbing flows has ever been published.

In order to use rod-climbing measurements to determine fluid material functions, the rod-rotation speed must not exceed the limit of the second-order flow regime. At the lower end, the measurements are limited by the ability to measure small climbing heights. Based on a photographic magnification of 5, one would estimate a resolution of 0.1 mm in height measurement. A more serious source of measuring error is attributable to the large static rise of a Boger fluid ($h_s \cong 0.5$ mm). High viscosity polymers are notorious for hysteresis and a slow approach to equilibrium in surface tension measurements[58]. Consequently it was decided to restrict our measurements to flow regimes for which the measured climb is significantly greater than the static rise. For the Boger fluid studied, this restricts measurements to rod-rotation speeds greater than 0.8 Hz. Strictly speaking, in order for the theory to apply, the static rise should be zero. However, past investigations have shown that this is not a serious limitation[48]. The temperature of the experiments was carefully monitored but not controlled. Experiments were discontinued if the temperature departed from 25°C by more than 0.1°C. Based on measurements of the temperature dependence of Ψ_1 in a cone-and-plate rheometer, we do not believe that temperature fluctuations are a major source of error.

RESULTS AND DISCUSSION

Cone-and-plate rheometer

In this section, data is presented as measured on a Weissenberg R-17 cone-and-plate rheometer, suitably modified for N_2 measurement as described in the Experimental section. The Weissenberg temperature bath was used to fix the Boger fluid temperature at 25 ± 0.1°C. *Figure 4* and *5* present the shear rate dependence of the viscosity η and the first normal stress difference N_1. As expected, the Boger fluid is virtually non-shear-thinning, with a zero-shear-rate viscosity $\eta_0 = 23.7 \pm 0.2$ Pa s. *Figure 5* demonstrates that N_1 is approximately a quadratic function of shear rate, $\dot{\gamma}$. Because *Figures 4* and *5* are very similar to figures appearing in previous reports on

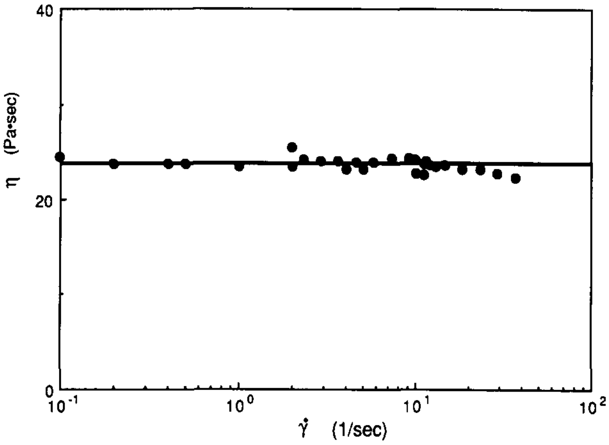

Figure 4 Steady shear viscosity as a function of shear rate for the Boger fluid

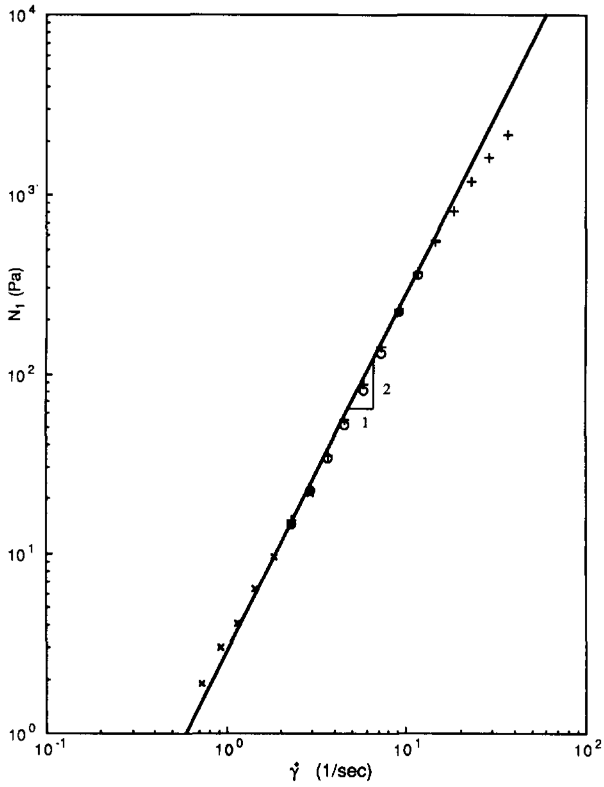

Figure 5 First normal stress difference as a function of shear rate for the Boger fluid: before rod-climbing (+); after rod-climbing (○); low shear rates (×)

Boger fluids, it is concluded that this fluid is rheologically typical of polyisobutylene Boger fluids as a class.

At low shear rates, all isotropic liquids with 'fading memory' are expected to show a second-order flow regime[24] where $N_1 = \Psi_1^0 \dot{\gamma}^2$. If the approximate quadratic behaviour of N_1 in *Figure 5* is taken as an indication of second-order flow behaviour, then the important fluid property Ψ_1^0 can be easily calculated. Logarithmic plots like *Figure 5* have long been used by Boger fluid investigators[9,10,26,27] to estimate Ψ_1^0.

However, the authors of a very recent paper argue that this method underestimates the true value of Ψ_1^0. According to Quinzani *et al.*[39], previous researchers have been misled because they have not investigated sufficiently low shear rates. This assertion is largely based upon data from dynamic oscillatory measurements of polyisobutylene Boger fluids.

It is beyond the scope of this paper to attempt to resolve this controversy concerning the correct value of Ψ_1^0 for Boger fluids. Nonetheless some subtle N_1 trends will be presented which may have a bearing on this question. One cannot discern these subtle trends in a logarithmic plot like *Figure 5*, hence *Figure 6* contains a semi-logarithmic plot of Ψ_1 against shear rate. Recall that Ψ_1 should be constant in the second-order flow regime. Contrary to the impression generated by *Figure 5*, it is noted in *Figure 6* that Ψ_1 is not truly a constant in any measurable shear rate range. Nonetheless, there is a plateau shear rate regime (2–15 s^{-1}) where Ψ_1 is relatively constant (within 20%). The plateau value of Ψ_1 is 2.65 ± 0.1 Pa s^2. At higher shear rates, Ψ_1 shows the expected sharp decrease associated with the finite length of the polymer chains. Closer inspection of the data in the plateau region reveals that the various Ψ_1 values are not randomly scattered about the mean. Instead, both data sets in *Figure 6* exhibit an inflection point at a shear rate of approximately 6 s^{-1}. Remarkably similar results, including the inflection point, were reported for the Boger fluids studied by Quinzani *et al.*[39].

If the predictions of Quinzani *et al.*[39] are correct, then the value of Ψ_1 should increase above its plateau value at very low shear rates. Consequently we pushed our measurements of Ψ_1 to the lowest shear rates possible at 25°C. In *Figure 6* the Ψ_1 values clearly do rise as the shear rate drops below 2.0 s^{-1}. However, N_1 is barely 5 Pa for the lowest shear rate reported. With such low stresses, we found that it was impossible to check our Ψ_1 measurements with the local pressure transducers flush-mounted on the rheometer plate (*Figure 1*). Consequently the Ψ_1 values for shear rates below 2.0 s^{-1} are considered to be less reliable than the values at higher shear rates.

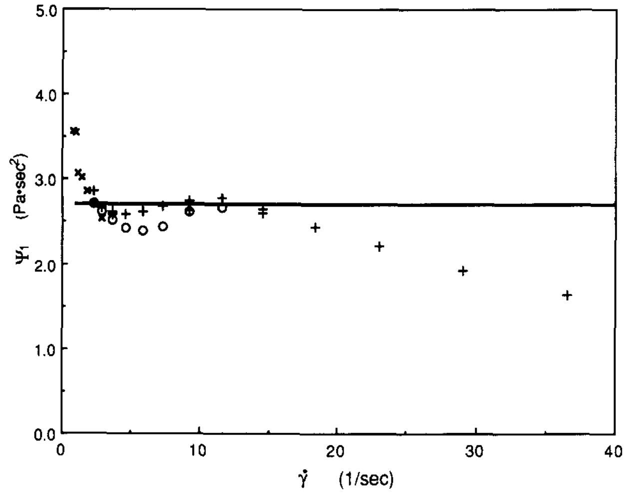

Figure 6 First normal stress difference coefficient as a function of shear rate for the Boger fluid: before rod-climbing (+); after rod-climbing (○); low shear rates (×); plateau value (——)

The rise in Ψ_1 at low shear rates is reproducible, with the data points in *Figure 6* below 2.0 s^{-1} representing the average of several data sets. This of course does not rule out the possibility of a systematic error. Such low stress measurement is possible only because the rheometer is equipped with large plates ($R = 37$ mm), a computerized data acquisition system, and a sensitive light spring specifically designed to measure small normal forces. Even with these experimental advantages, we have been unable to clearly determine the zero shear rate limit of Ψ_1. The prediction of Quinzani *et al.*[39] concerning the true value of Ψ_1^0 appears to be very difficult to verify via steady shear measurements at a single temperature.

To complete a determination of the polymer material functions in shear flow, one needs to measure N_2. There are previous reports of N_2 data from this laboratory[49–51]. However, this paper contains the first reported results obtained with our rheometer after redesigning it last year (see Experimental). To test our new design, we first investigate a standard polymer solution with known N_1 values certified by NIST for various shear rates[47]. We would prefer a fluid with known N_2 values, but to our knowledge no such fluid exists. *Figure 2* displays the pressure that we measure as a function of radial position during shear flows of the NIST standard material. As expected, the pressure is greatest near the tip of the cone—this is a manifestation of the Weissenberg effect which is also responsible for the rod-climbing phenomenon. For each shear rate, it is observed in *Figure 2* that the data points fall along a single straight line, in concordance with equation (6). Two very important conclusions can be drawn from this simple observation. First, the NIST material does achieve a homogeneous, one-dimensional shear flow in the cone-and-plate rheometer. Second, the pressure transducers are sufficiently small to justify the approximation that they measure the local pressure. For each shear rate, one can integrate the measured pressure distribution over the surface of the plate to obtain an estimate of N_1. The N_1 values thus obtained are compared to the NIST certified values in *Figure 7*, with excellent agreement over a wide shear rate range. Since the data satisfies both of the consistency checks discussed in the Experimental section, it is concluded that we can measure the true pressure distribution during shear flows of the NIST reference material. The Experimental section also describes how one can estimate N_2 by extrapolating the measured pressure distribution to the rim of the cone-and-plate. *Figure 8* contains the normal stress ratio $\psi = -N_2/N_1$ as a function of shear rate. Ignoring a possible weak dependence of ψ on shear rate, it is estimated that $\psi = 0.15 \pm 0.02$. NIST describes this standard material as a solution of polyisobutylene in cetane, and we have found no evidence that ψ has ever been measured previously for this fluid. From molecular theory, one would expect $\psi \cong 0.28$ for a highly concentrated, fully entangled polymer solution[24], and $\psi \cong 0$ for a dilute polymer solution[59,60]. The fact that the measured ψ

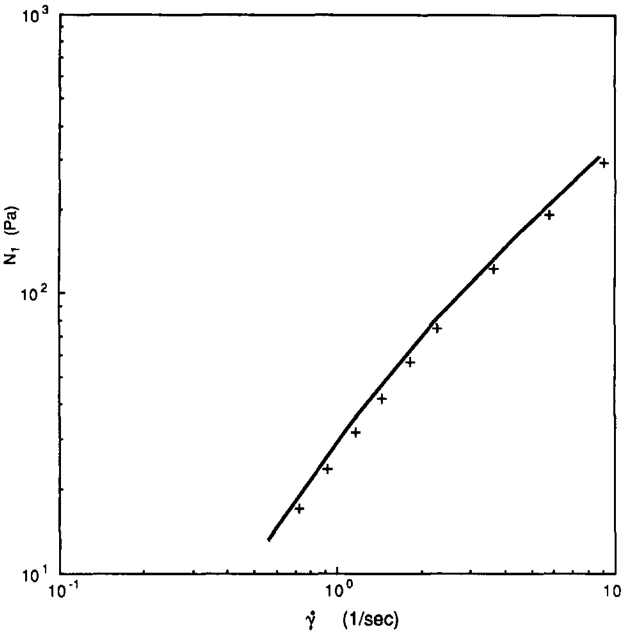

Figure 7 First normal stress difference as a function of shear rate for NIST rheology standard: estimated from measured pressure distribution (+); NIST certified values (——)

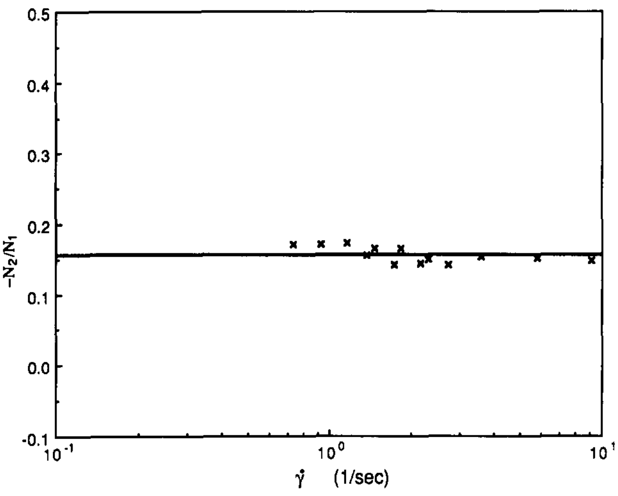

Figure 8 Negative ratio of second to first normal stress difference as a function of shear rate for NIST rheology standard

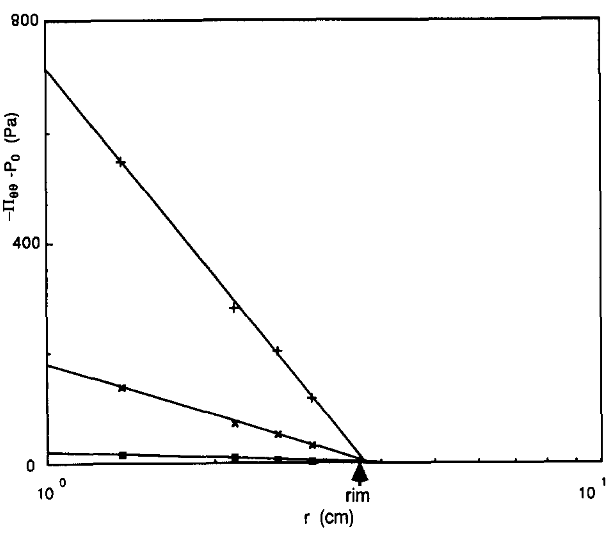

Figure 9 Net vertical pressure force as a function of radial position in cone-and-plate rheometer for the Boger fluid. Shear rates (s^{-1}): 2.31 (■); 7.3 (×); 14.6 (+)

value is intermediate between these two limits is consistent with our impression that the material is a moderately concentrated solution.

For the Boger fluid, *Figure 9* shows the measured pressure distribution as a function of radial position. Once again the pressure is a logarithmic function of position, in accordance with equation (6). Integrating the pressure distribution yields N_1 values very close to those already presented in *Figure 5*. There is a very informative difference between *Figures 2* and *9* which is immediately apparent. The net pressure force ($-\Pi_{\theta\theta} - P_0$) extrapolated to the rim of the cone is very close to zero for every shear rate in *Figure 9*. By contrast, the net pressure force at the rim systematically increases with shear rate in *Figure 2*. Equation (6) indicates that the net pressure force at the rim is given by $-N_2$. Thus by visually comparing *Figures 2* and *9*, one can immediately conclude that N_2 is much smaller in magnitude for the Boger fluid than for the NIST material. The measured pressure distributions are next used to calculate the normal stress ratio ψ displayed in *Figure 10*. All of the data points indicate that N_2 is negative, and very small in magnitude relative to N_1. The best estimate is that $\psi = 0.01 \pm 0.01$, with no discernable shear rate dependence over the range 2–15 s^{-1}.

This low value of ψ is consistent with the N_2 measurements reported for a polyacrylamide Boger fluid by Keentok *et al.*[44]. However, as discussed earlier, Hu *et al.*[45] estimate a much higher value of ψ for a polyisobutylene solution which may or may not be a Boger fluid. Modern molecular theories appropriate to dilute solutions of monodisperse polymers also predict that ψ is close to zero[59,60]. This is relevant because dilute solution molecular theory is often assumed to describe Boger fluids at low deformation rates[10,26]. The normal stress ratio ψ has never been measured for a conventional dilute polymer solution.

Rotating rod viscometer

The Boger fluid readily climbs the shaft of a rotating rod at 25°C, achieving a height of over 1 cm at a rotational speed of only 2 Hz. It is observed that other polymeric liquids such as power law fluids climb considerably less. Consequently we have much greater confidence in the relative accuracy of the rod-climbing method when

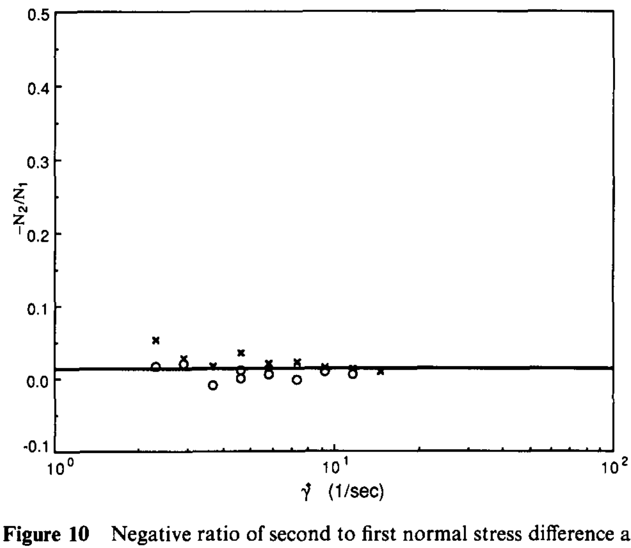

Figure 10 Negative ratio of second to first normal stress difference as a function of shear rate for the Boger fluid: before rod-climbing (×); after rod-climbing (○)

it is applied to the Boger fluid. One disadvantage of the Boger fluid is that it exhibits a rather large static climb h_s. As discussed in the Experimental section, the value of h_s determines the lower limit of the rotational speed range that we investigate. We rearrange the theoretical rod-climbing equations into a form in which h_s does not appear (see below). Consequently, uncertainty in the value of h_s does not affect the calculated Boger fluid properties.

In order to calculate the Boger fluid material functions appropriate to shear flow, the rod-climbing measurements must be performed in the second-order regime where equation (7) applies. Here ω_{max} is defined as the rod-rotation speed below which second-order behaviour is observed. To estimate ω_{max}, we first follow a procedure similar to that employed in previous rod-climbing studies[45,48,56]. *Figure 11* contains a plot of $h-h_1$ against ω^2 for two different rod sizes ($a=3.175$ and 1.588 mm). Here h_1 is the height of climb at a conveniently chosen low rod rotation speed. According to equation (7), this plot should yield a straight line. A departure from linearity at large ω may then be attributed to higher order terms in the equations of motion. Following this procedure with the data shown in *Figure 11*, it is estimated that $\omega_{max} \cong 2.4$ Hz. An alternative procedure was also employed which provides a more sensitive test for second-order behaviour. Assuming only that $h-h_s$ has a power law dependence on ω, the data itself is used to determine the power law exponent m which best fits the data. When m is close to 2.0, it is concluded that second-order theory applies. To apply this procedure, a power law version of equation (7) is used to predict the difference in h between two different rod-rotation speeds, ω_1 and ω_2:

$$h(\omega_2)-h(\omega_1)=C(\omega_2)^m-C(\omega_1)^m \tag{8}$$

where C is equal to:

$$C=\frac{4a\hat{\beta}}{2\sqrt{\rho g}(4\sqrt{\gamma}+a\sqrt{\rho g})} \tag{8a}$$

Note that the static climb h_s does not appear in equation (8). By choosing various ω_1 and ω_2 values below ω_{max}, one can determine the m value which allows equation (8) to best fit the data. Considering the data of *Figure 11*, we estimate $m=2.1\pm0.2$ for the smaller rod, and $m=2.0\pm0.1$ for the larger rod. Thus second-order theory predicts the dependence of the measured climb on rod-rotation speed. Equation (7) also predicts the dependence of the climb on the rod radius. To test this prediction with the data of *Figure 11*, we require the surface tension of the Boger fluid, which was measured by the Wilhemy plate technique[58,61] ($\gamma=0.027\pm0.001$ N m^{-1}). For a given rod-rotation speed, equation (7) predicts that $h-h_s$ increases with rod diameter (provided inertial effects are negligible). In *Figure 11*, it is clear that the Boger fluid does more readily climb the larger rod. Equation (7) predicts that the climb should be 69% greater for the larger rod in *Figure 11*, and the actual experimental difference is 60%. In summary, then, all tests that we can devise indicate that the Boger fluid does obey the second-order theory over a rather large rotational speed range. Within this range, the data for the smaller rod in *Figure 11* is used to estimate that the climbing constant in equation (7) has the value $\hat{\beta}=1.28\pm0.01$ Pa s^2. Because the λ value for this rod is over 20, edge effects on the data should be minimal (see Experimental).

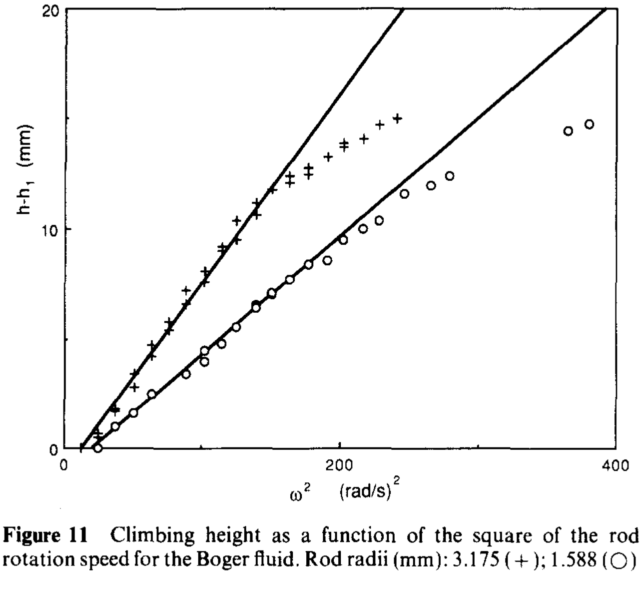

Figure 11 Climbing height as a function of the square of the rod rotation speed for the Boger fluid. Rod radii (mm): 3.175 (+); 1.588 (○)

Next an attempt is made to use the measured climbing constant to estimate the Boger fluid material functions in shear flow. According to second-order theory:

$$\hat{\beta}=0.5\Psi_1^0+2.0\Psi_2^0=0.5\Psi_1^0(1-4\psi^0) \tag{9}$$

where

$$\psi^0=-\Psi_2^0/\Psi_1^0$$

We now encounter the principal difficulty with the rotating rod viscometer—the need to independently estimate Ψ_1^0. Furthermore, as described in the preceding section on cone-and-plate measurements, there is a controversy in the literature concerning the true value of Ψ_1^0 for Boger fluids. Consequently the material functions that are calculated via equation (9) will depend on the position one takes with respect to this controversy.

Recall that the value of Ψ_1 has been accurately determined in the shear rate range 2–15 s^{-1} via cone-and-plate measurements. Within this range, the plateau value of Ψ_1 is 2.65 ± 0.1 Pa s^2. Substituting the plateau value of Ψ_1 into equation (9), one calculates that the normal stress ratio $\psi^0=0.01\pm0.01$. This value is in excellent agreement with the independent measurement of ψ via the flush-mounted pressure transducers.

However, less reliable cone-and-plate data for shear rates below 2.0 s^{-1} indicates that the true value of Ψ_1^0 is greater than the plateau value (*Figure 6*). This data is less reliable because of the low stress measurements required, and because we could not independently check these measurements with our flush-mounted pressure transducers. If one nonetheless assumes that this low shear rate data is accurate, then it is clear from *Figure 5* that Ψ_1^0 is at least 3.5 Pa s^2. Substituting this value of Ψ_1^0 into equation (9), one calculates a normal stress ratio $\psi^0=0.07$.

To summarize, estimates of N_2 from the rotating rod viscometer vary considerably, depending on the estimated zero shear rate limit of Ψ_1. Consequently we have more confidence in the N_2 values measured with the cone-and-plate rheometer than with the rotating rod viscometer. Assuming the N_2 values determined via the cone-and-plate rheometer are correct, there are three possible interpretations of the rod-climbing results. First, one might reject the low shear rate data in *Figure 6* as being unreliable. In this case, both N_2 measurement techniques predict that $-N_2/N_1$ is very close to zero. Second, one can retain the low shear rate data in *Figure 6*. In this case, the rotating rod viscometer predicts that $-N_2/N_1$ is >0.07 in the limit of zero shear rate. However, this possibility seems unlikely, because the data for $-N_2/N_1$ in *Figure 10* shows no evidence of approaching this limit at low shear rates. A third possibility is that we have not investigated low enough rod-rotation speeds to observe the true second-order flow regime. The most appropriate method for determining the limit of the second-order regime is from the rod-climbing data itself[48], and this data is entirely consistent with second-order theory. Alternatively, the limit of the second-order theory can be roughly estimated using cone-and-plate data, if it is assumed that the rod-climbing flow is equivalent to shear flow on a local level*. Also assuming that the Boger fluid viscosity is constant, then one can easily show that the maximum shear rate in a given flow is twice the rod angular velocity ω. The minimum value of ω studied was 0.8 Hz, due to the large static climb of the Boger fluid. Thus the minimum value of the shear rate at the rod places the rod-climbing flow within the plateau region for Ψ_1 in *Figure 6*. According to Quinzani *et al.*[39], the plateau region is not the true second-order regime, but a 'pseudo-second-order' regime. Thus perhaps the rod-climbing measurements reflect this pseudo-second-order regime observed in the cone-and-plate rheometer. One might further speculate that the second-order theory still describes rod-climbing in the pseudo-second-order regime, provided one replaces Ψ_1^0 with the plateau value of Ψ_1 in equation (7). Such an interpretation would explain why the rod-climbing data is consistent with the predictions of second-order theory. This interpretation of the rod-climbing data would also yield an estimate for N_2 very close to the value independently measured with the cone-and-plate rheometer.

CONCLUSIONS

A rheometer has been constructed which can accurately estimate N_2 by measuring the pressure distribution during shear flow. Second normal stress data is reported for a typical Boger fluid, and for a standard polymer solution supplied by NIST. Comparing these two polymer solutions, one finds that the Boger fluid has the much smaller $|N_2|$ value: $-N_2/N_1=0.01\pm0.01$. The rod-climbing method is also applied to the same Boger fluid, with comparable results for N_2. However, the rod-climbing estimates of N_2 are subject to larger uncertainties, due to difficulties in extrapolating Boger fluid properties to zero shear rate.

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* This is similar to the 'heuristic' treatment of rod-climbing discussed in reference 57

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