

EXPONENTIAL SHEAR OF DILUTE POLYMER SOLUTIONS

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ABSTRACT

The stress generated in a simple shear field where the shear rate increases exponentially in time has been measured for dilute solutions of a high molecular weight polymer dissolved in a solvent of large viscosity. The viscosity in steady shear is slightly shear thinning for all the solutions tested. The results in exponential shear show that concentration affects the results even when a factor of four below the coil-overlap concentration. This result is not too surprising as the viscosity is affected by concentration in steady shear as it increases in a manner greater than usually predicted by dilute solution theories. However, in exponential shear the viscosity for smaller concentrations tends to stay near the zero shear asymptote even at large shear rates whilst higher concentrations stay near the high shear asymptote. This suggests that intermolecular interactions can "react" much faster than intramolecular interactions.

INTRODUCTION

Exponential shear where the shear rate increases exponentially in time was originally introduced by Doshi and Dealy (1987). They have argued that this flow is "strong" in nature by comparing the end-to-end distance of the macromolecule to its rest conformation as a function of time. They show that this stretching parameter tends to infinity as time increases for a simple dumbbell model. By their analysis the flow is strong in the sense of Tanner's (1976) classification scheme. However, Samurkas et al. (1989) have shown that this flow is neutrally aligning which indicates this flow is not truly "strong" (see Larson (1987)).

Thus far, all experimental results have been gathered for a handful of polymer melts using a sliding plate rheometer. This work investigates the stress response of polymer solutions of low concentration to this flow field by programming a rotational rheometer to have a rotation rate that increases exponentially in time. It is the purpose of this investigation to investigate what this flow field reveals for the stress response of these polymer solutions.

EXPERIMENTAL

The solutions were prepared by dissolving high molecular weight polyisobutylene (PIB, Vistanex MML 140) with a nominal molecular

weight of 10^6 Daltons in kerosene. The solutions were gently rotated in a closed vessel for one week. Low molecular weight poly(1-butene) (Hyvis 3) was then added and further rotated for a period of one week. The solutions were then allowed to rest for one to two weeks prior to testing. The concentrations are given below:

Soln.	PIB (wt%)	kerosene (wt%)	Hyvis 3 (wt%)
PIB00	0.0	7.500	92.50
PIB05	0.0502	7.500	92.45
PIB10	0.100	7.500	92.40
PIB20	0.200	7.500	92.30
PIB30	0.300	7.500	92.20

The steady shear viscosity was measured with a Rheometrics Fluids Spectrometer modified in house to measure torques as low as 0.25 $\mu\text{N}\cdot\text{m}$. The average of the torque for clockwise (CW) and counterclockwise (CCW) rotation was determined at each shear rate to eliminate hysteresis effects. The dynamic shear properties were also determined with existing testing procedures. All tests were conducted at 22 $^{\circ}\text{C}$ and with cone and plate geometry.

Exponential shear was performed by bypassing the existing VCVS low-pass second-order filter circuit in the rheometer. This filter had a time constant of order 10 ms which would seriously interfere with any transient torques measured. The motor on the rheometer was interfaced with a PC-AT clone with a function generator programmed in assembly language to increase the system response. A "noise killer" was also used which took the average torque at each time step of 10 ms. The signal to the motor (-10 to +10 V-DC) and from the torque transducer (-10 to +10 V-DC) were passed to a D/A and A/D 12-bit data acquisition board. To accommodate CW (positive voltage) and CCW (negative voltage) rotation the signal was modified by a signal conditioner to change the 0 to 10 V-DC signal accepted and generated by the computer to include the full range. An average of two CW and two CCW runs was taken for each test condition.

RESULTS

The solvent viscosity (PIB00) was found to be 1.337 Pa-s at small shear rates and decreased to 1,299 Pa-s at shear rates on the order of 50 s^{-1} and above. The viscosity at each shear rate was subtracted from each solution's viscosity to yield the steady state viscosity due the polymer at each shear rate as shown in Figure 1.

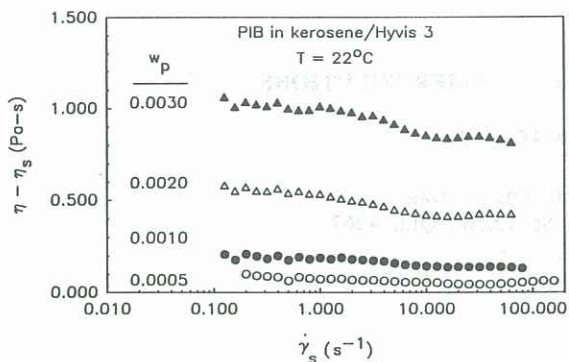


Figure 1 Viscosity of the polymer as a function of shear rate.

The dynamic properties are shown in Figure 2. These agree with results for similar fluids studied by Mackay and Boger (1989). Note that the solvent is slightly elastic with a relaxation time on the order of 10^{-4} sec. and the dynamic modulus for the solvent was subtracted from that of the solution.

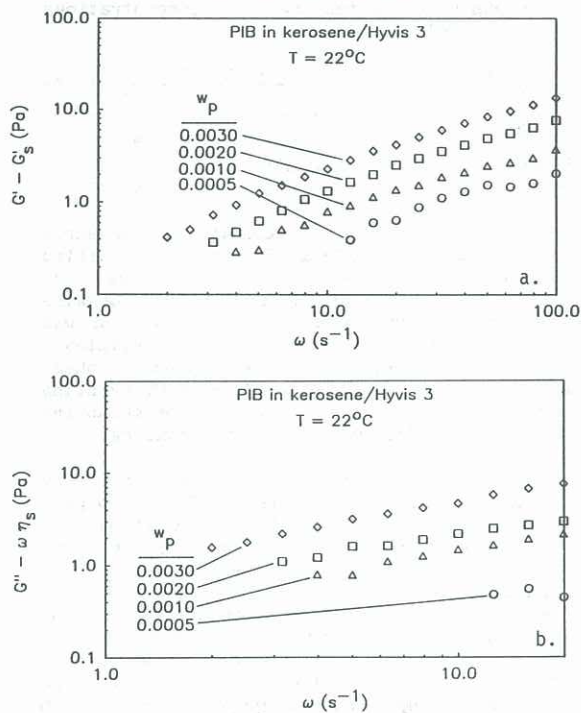


Figure 2 Dynamic properties of the solutions: (a.) storage modulus minus that due to the solvent versus frequency; (b.) loss modulus less that due to the solvent versus frequency.

The intrinsic viscosity was determined in the usual manner as shown in Figure 3. The value for this polymer/solvent system is 86.5. This is lower than that for the system studied by Mackay and Boger (1989) and is probably due to differences in the molecular weight and solvent.

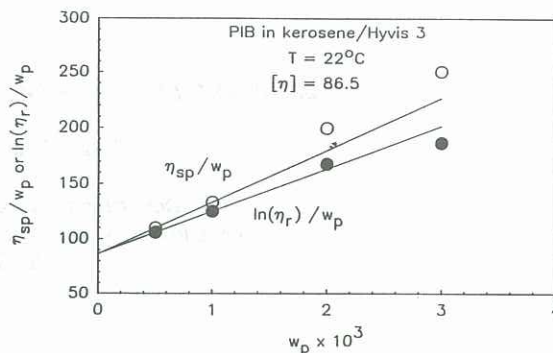


Figure 3 Plot to determine the intrinsic viscosity.

The relaxation time for the polymer was found from the intrinsic viscosity and other parameters (Larson (1988)) by:

$$\lambda = \frac{[\eta] M \eta_s}{N_A k_B T} \quad (1)$$

The density of the solution was assumed to be 0.87g/cc (Mackay and Boger (1989)). This yielded λ equal to 0.054 sec. Using this relaxation time and the polymer viscosity at small shear rates the dynamic moduli were calculated by assuming an Oldroyd-B fluid model. The results are shown in Figure 4 for two solutions.

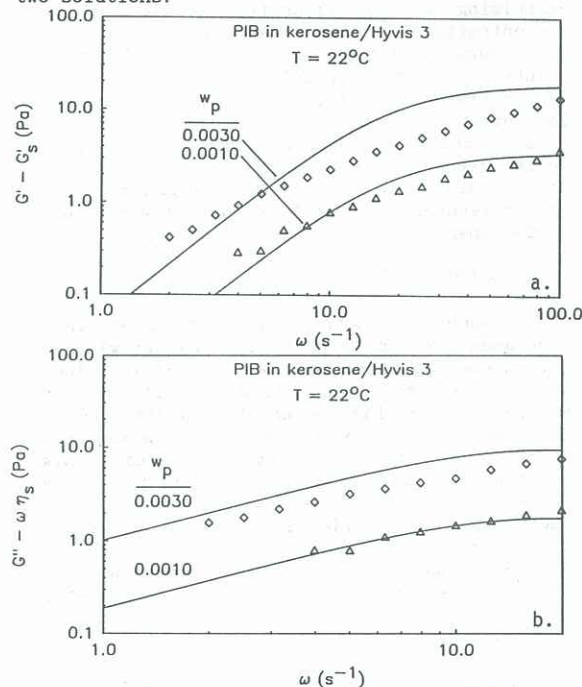


Figure 4 Prediction of the dynamic storage modulus (a.) and loss modulus (b.) for solutions PIB10 and PIB30 using the Oldroyd-B model.

A Newtonian fluid was used to check the accuracy of the exponential shear test. The shear rate was programmed to increase in the following manner:

$$\dot{\gamma}_s = A \alpha \exp(\alpha t) \quad (2)$$

An example of a test is shown in Figure 5. The system achieves equilibrium quite fast and shows no evidence of inertial effects. Although the data is "noisy" the mean taken in time steps from 0 to 1 sec. is within four significant figures of the overall mean.

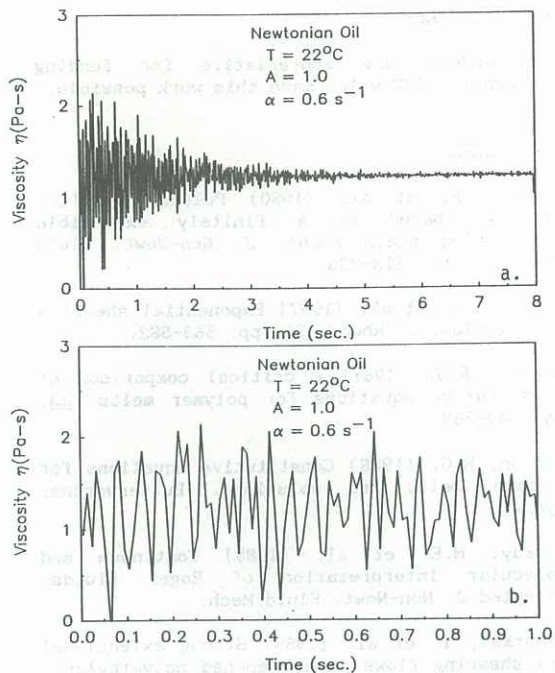


Figure 5 Exponential shear of a Newtonian oil with $A = 1$ and $\alpha = 0.6 \text{ s}^{-1}$. Instantaneous values of the viscosity were calculated at each time step of 10 ms and plotted versus time: (a.) total test; (b.) first 1 sec.

The polymer solutions were then tested and the results are shown in Figures 6 and 7. The torque was measured and converted to an instantaneous solution viscosity. The upper and lower bounds for the solution viscosity are also displayed in the figures. The FENE-P modification for the Oldroyd-B model (Bird et al. (1980)) was used to calculate the response of this model to exponential shear. The results for this model are shown in the figures. b is a macromolecule flexibility parameter and as it tends to infinity the Oldroyd-B model results. Note b has no influence on the dynamic storage and loss moduli.

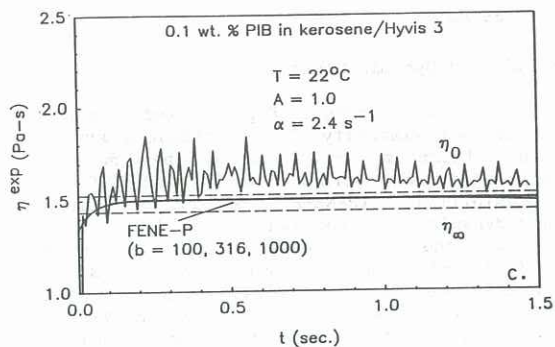
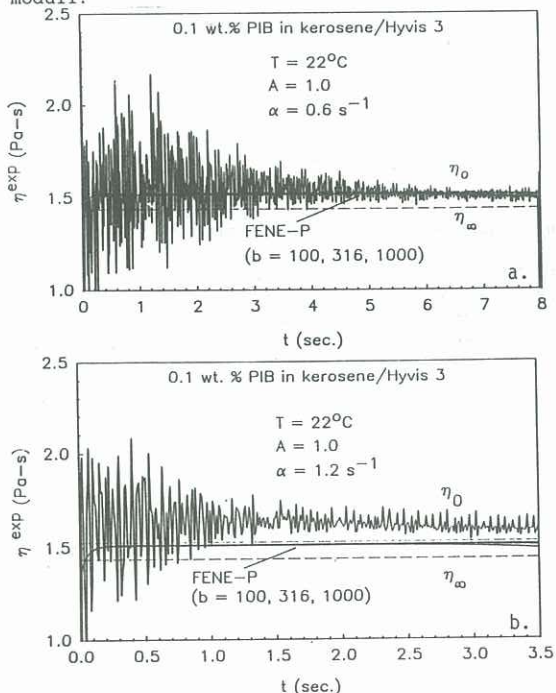


Figure 6 Exponential shear viscosity with $A = 1$ for solution PIB10: (a.) $\alpha = 0.6 \text{ s}^{-1}$; (b.) $\alpha = 1.2 \text{ s}^{-1}$; (c.) $\alpha = 2.4 \text{ s}^{-1}$

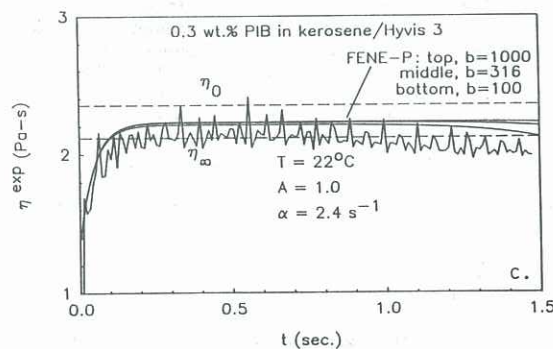
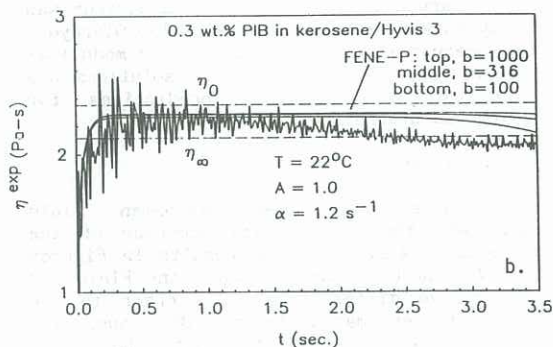
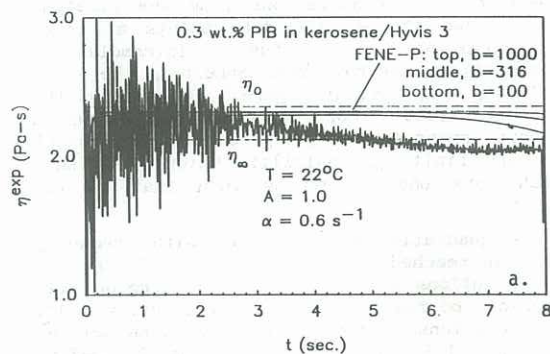


Figure 7 Exponential shear viscosity with $A = 1$ for solution PIB30: (a.) $\alpha = 0.6 \text{ s}^{-1}$; (b.) $\alpha = 1.2 \text{ s}^{-1}$; (c.) $\alpha = 2.4 \text{ s}^{-1}$.

DISCUSSION

Steady and Dynamic Shear

The results shown in Figure 1 indicate that the polymer viscosity shows a slight amount of shear thinning which could be due to intramolecular forces such as: finite extensibility (FENE-P model), variable hydrodynamic interaction, excluded volume effects and/or internal viscosity (Larson (1988)). Since the intrinsic viscosity is 86.5 the coil-overlap concentration is given by the inverse of this value or 1.2 wt. %. A value of one-tenth of this is probably acceptable to define a truly dilute solution so solution PIB10 may be considered "dilute". Solutions PIB20 and PIB30 may exhibit some concentration effects, particularly on inspection of Figure 3 where they show deviations from the straight line drawn through the data points at lower concentrations. Thus, intermolecular interactions may have some effect on the shear thinning displayed in Figure 1 for some of the concentrations. None of these effects which produce shear thinning may be ruled out except perhaps finite extensibility which would show much more shear thinning than that in the figure.

A quadratic region for G' with frequency was not reached at low frequencies for any of the solutions in Figure 2a. This region will probably be reached at lower frequencies. All the solutions tend to a limiting slope between $2/3$ and $1/2$ in accord with the Rouse-Zimm theory (Larson (1988)). Similar behaviour was seen by Mackay and Boger (1989). The Oldroyd-B model adequately predicts the dynamic moduli as shown in Figure 4. Thus, these solutions are in accord with existing predictions for "dilute" solutions.

Exponential Shear

The results with the Newtonian fluid demonstrate the utility and accuracy of the technique (Figure 5). The results in Figures 6 and 7 show that the two solutions PIB10 and PIB30 behave differently. The error in the results is estimated to be 4%, thus, the results seem to indicate that the lower concentration solution, where intermolecular interactions are probably not present, has a instantaneous viscosity which hovers near the low shear steady state viscosity. The opposite is true for solution PIB30 where intermolecular interactions are probably present. The instantaneous viscosity hovers near the high shear asymptote suggesting that the intermolecular interactions can react much faster to the flow than intramolecular interactions.

CONCLUSION

The results in exponential shear show that concentration affects the instantaneous viscosity even when a factor of four below the coil overlap concentration. The intermolecular interactions react much faster to this flow than intramolecular interactions. These results will be checked with a more "well defined" system such as a narrow molecular weight polystyrene in various solvents and a more rigid macromolecule such as Xanthan gum.

ACKNOWLEDGEMENT

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NOMENCLATURE

- A Parameter in exponential shear
- b Flexibility parameter
- G' Storage modulus
- G'' Loss modulus
- k_B Boltzmann constant
- M Molecular weight
- N_A Avogadro's number
- t Time
- T Temperature
- w_p Weight fraction of polymer
- α Parameter in exponential shear
- $\dot{\gamma}_s$ Shear rate
- η Solution viscosity
- η_r Reduced viscosity
- η_s Solvent viscosity
- η_{sp} Specific viscosity
- η_0 Low shear solution viscosity
- η_∞ High shear solution viscosity
- η^{exp} Viscosity in exponential shear
- $[\eta]$ Intrinsic viscosity
- λ Polymer relaxation time
- ω Frequency