Recently Champagne, Harris, and Corrsin (*2*) have measured turbulence properties in a nearly homogeneous shear flow where far downstream of a shear-turbulence generator, the turbulence has reached a nearly homogeneous asymptotic condition with constant values of the mean velocity gradient and the one-point turbulence moments. The present note interprets the experimental results in terms of Phillips' hypothesis. The experimentally measured value of the eddy viscosity ν_e is found to be 0.0144 sq. ft./sec. The Eulerian space-time correlation of the axial velocity fluctuations in the apparent convective frame was fit with an exponential curve. The convective integral scale L_τ was then read as the value of τ where the peak correlations dropped to the value of $1/e$. This procedure is identical to that followed by Phillips (*5*) in interpreting the jet mixing region data of Davis, Fisher, and Barratt (*3*) and by Baldwin and Haberstroh (*1*) in interpreting fully developed pipe flow data. Θ is found to be 0.098 sec. The value of A for nearly homogeneous shear flow was calculated from Equation (3) to be 0.55.

Three different experimental tests of Phillips' model give values of A of the same order and these values indicate the anisotropy of the energy-containing eddies for different turbulent shear flows as shown in Table 1.

The elongations of the energy-containing eddies are represented reasonably by the experimental A values. The descending degree of anisotropy for the turbulent shear flows that are considered in Table 1 shows that Phillips' mechanism, Equation (3), is consistent with the available experimental observations.

NOTATION

A = dimensionless constant, Equation (3)
e = Naperian logarithm base, 2.718
L_τ = convective integral scale of axial turbulent velocity from space-time data, sec.
U = mean velocity, ft./sec.
$\overline{v^2}$ = mean square of lateral turbulent velocity, sq.ft./sec.^{2}
y = lateral coordinate, ft.
Θ = convective integral scale of lateral turbulent velocity from space-time data, sec.
ν_e = kinematic eddy viscosity, sq.ft./sec.
τ = turbulent shear stress, lb.$_f$/sq.ft.
τ = time delay in space-time correlation data, sec.

LITERATURE CITED

1. Baldwin, L. V., and R. D. Haberstroh, *AIChE J.*, **14** 825 (1968).
2. Champagne, F. H., V. G. Harris, and S. Corrsin, *J. Fluid Mech.*, **41**, 81 (1970).
3. Davies, P. A., M. J. Fisher, and M. J. Barratt, *ibid.*, **15**, 337 (1963).
4. Miles, J. W., *ibid.*, **3**, 185 (1957).
5. Phillips, O. M., *ibid.*, **27**, 131 (1967).
6. ———, *Ann. Rev. Fluid Mech.*, 245 (1969).
7. Townsend, A. A., "The Structure of Turbulent Shear Flow," Cambridge Univ. Press (1956).
8. ———, *J. Fluid Mech.*, **41**, 13 (1970).

On the Stretching of Dilute Polymer Solutions

A. E. EVERAGE, JR. and R. J. GORDON

Department of Chemical Engineering
University of Florida, Gainesville, Florida 32601

In a recent communication, Denn and Marrucci examined the concept of a limiting stretch rate in viscoelastic liquids (*1*). Using as a basis a convected Maxwell model (*2*) with constant coefficients, these authors found that the manifestation of such a limiting rate is intimately connected with the total time the pure stretching deformation is imposed. Thus, for the well-known limiting condition $2\lambda\Gamma = 1$, where λ = relaxation time, Γ = stretch rate, Denn and Marrucci showed that a time $t = 15\lambda$ was required for the stress (in an initially unstressed fluid) to increase an order of magnitude above the Newtonian value. Such considerations are of especial importance in understanding turbulent drag reduction (*3*), as the concept of a limiting stretch rate has often been used to explain this phenomenon (*3* to *6*).

The constitutive equation used in the aforementioned study, namely

$$\tau^{ij} + \lambda \frac{\overline{D}\tau^{ij}}{Dt} = 2\mu d^{ij} \tag{1}$$

$$\frac{\overline{D}\tau^{ij}}{Dt} = \frac{\partial \tau^{ij}}{\partial t} + v^k \tau^{ij}{}_{;k} - \tau^{kj} v^i{}_{;k} - \tau^{ik} v^j{}_{;k} \tag{2}$$

$$T^{ij} = -pg^{ij} + \tau^{ij} \tag{3}$$

suffers from a number of limitations. In particular, Equations (1) to (3) predict both a constant viscosity and a zero secondary normal stress difference in steady shearing flow, in disagreement with generally accepted behavior (*7*, *8*). In light of these facts, and also the recent studies indicating the importance of the secondary normal stress difference in nonviscometric flows (*9* to *11*), it was felt worthwhile to repeat the Denn-Marrucci analysis, using a more realistic model.

CONSTITUTIVE EQUATION

Gordon and Schowalter recently presented a modification of the dumbbell theory of dilute polymer solutions (*12*), based on a structured fluid theory of Ericksen (*13*). Gordon and Everage used this result to obtain an explicit constitutive equation (*14*), namely

$$\tau^{ij} + \theta \frac{\overline{\overline{D}}\tau^{ij}}{Dt} = \frac{2Nc}{M} kT\theta(1-\epsilon) d^{ij} \tag{4}$$

Correspondence concerning this communication should be addressed to Professor R. J. Gordon.

$$\frac{\bar{\bar{D}}\tau^{ij}}{Dt} = \frac{\partial\tau^{ij}}{\partial t} + v^k\tau^{ij}{}_{;k} - \tau^{kj}v^i{}_{;k} - \tau^{ik}v^j{}_{;k} + \epsilon d^i{}_m\tau^{mj} + \epsilon\tau^i{}_m d^{mj} \quad (5)$$

$$T^{ij} = -pg^{ij} + \tau^{ij} + 2\eta_s d^{ij} \quad (6)$$

Here ϵ is a phenomenological constant subject only to the condition (12)

$$0 \leqq \epsilon < 1 \quad (7)$$

The Gordon-Schowalter-Everage (GSE) equation predicts both a non-Newtonian viscosity, and nonzero primary and secondary normal stress differences. The ratio of the secondary to the primary normal stress difference is given by

$$\frac{N_2}{N_1} = -\epsilon/2 \quad (8)$$

Recent measurements indicate N_2/N_1 to be about -0.2 (*7*, *15*), in agreement with Equations (7) and (8).

It is possible to specify θ explicitly in terms of molecular weight, temperature, and ϵ. To this end an expression for the intrinsic viscosity at zero shear rate $[\eta]_{G=0}$ is obtained from Equations (4) to (6):

$$[\eta]_{G=0} = \frac{NkT(1-\epsilon)}{M\eta_s}\theta \quad (9)$$

Combining this result with the well-known Mark-Houwink-Sakurada relation $[\eta]_{G=0} = KM^a$ (*16*), yields

$$\theta = \frac{\eta_s KM^{1+a}}{NkT(1-\epsilon)} \quad (10)$$

RESULTS

Following Denn and Marrucci, we consider a velocity field of the form $v^i = (\Gamma(t)x^1, -1/2\,\Gamma(t)x^2, -1/2\,\Gamma(t)x^3)$. Assuming the liquid to be unstressed at $t = 0$, the GSE equation gives for the axial stress $T^{11} = (\tau^{11} - \tau^{22}) + 3\eta_s\Gamma$

$$T^{11} = \frac{Nc}{M}kT(1-\epsilon)\int_0^t \exp\left[\frac{-(t-\xi)}{\theta}\right] \left\{2\exp\left[2(1-\epsilon)\int_\xi^t \Gamma(s)ds\right] + \exp\left[-(1-\epsilon)\int_\xi^t \Gamma(s)ds\right]\right\}\Gamma(\xi)d\xi + 3\eta_s\Gamma \quad (11)$$

For the case of constant stretch rate, Equation (11) reduces to

$$T^{11} = \frac{3\frac{Nc}{M}kT\theta(1-\epsilon)\Gamma}{[1-2\theta(1-\epsilon)\Gamma][1+\theta(1-\epsilon)\Gamma]} - \frac{2\frac{Nc}{M}kT\theta(1-\epsilon)\Gamma e^{-[1-2\theta(1-\epsilon)\Gamma]t/\theta}}{1-2\theta(1-\epsilon)\Gamma} - \frac{\frac{Nc}{M}kT\theta(1-\epsilon)\Gamma e^{-[1+\theta(1-\epsilon)\Gamma]t/\theta}}{1+\theta(1-\epsilon)\Gamma} + 3\eta_s\Gamma \quad (12)$$

The elongational viscosity,* $\bar{\eta} = (T^{11} - 3\eta_s\Gamma)/\Gamma$, is then

$$\frac{\bar{\eta}}{3(\eta_0-\eta_s)} = \frac{1}{[1-2\theta(1-\epsilon)\Gamma][1+\theta(1-\epsilon)\Gamma]} - \frac{2e^{-[1-2\theta(1-\epsilon)\Gamma]t/\theta}}{3[1-2\theta(1-\epsilon)\Gamma]} - \frac{e^{-[1+\theta(1-\epsilon)\Gamma]t/\theta}}{3[1+\theta(1-\epsilon)\Gamma]} \quad (13)$$

where $\eta_0 = \eta_s + \frac{Nc}{M}kT\theta(1-\epsilon)$ is the zero-shear viscosity.

Equation (13) is plotted in Figures 1 and 2 for various molecular weights of polyethylene oxide (a well-known drag reducer), dissolved in water at 30°C. In both figures the concentration is constant at 0.02% polyethylene oxide by weight, θ is calculated via Equation (10), using $K = 1.25 \times 10^{-2}$ cu.cm./g. and $a = 0.78$ (*16*), and ϵ is taken as 0.4. The stretch rate is 200 sec.$^{-1}$ in Figure 1 and 2,000 sec.$^{-1}$ in Figure 2. In both figures the value of $\bar{\eta}/3(\eta_0 - \eta_s)$ approaches a finite asymptote at molecular weights for which $2\theta(1-\epsilon)\Gamma < 1$. For higher molecular weights, no finite asymptote is approached. These results are in qualitative agreement with the findings of Denn and Marrucci.

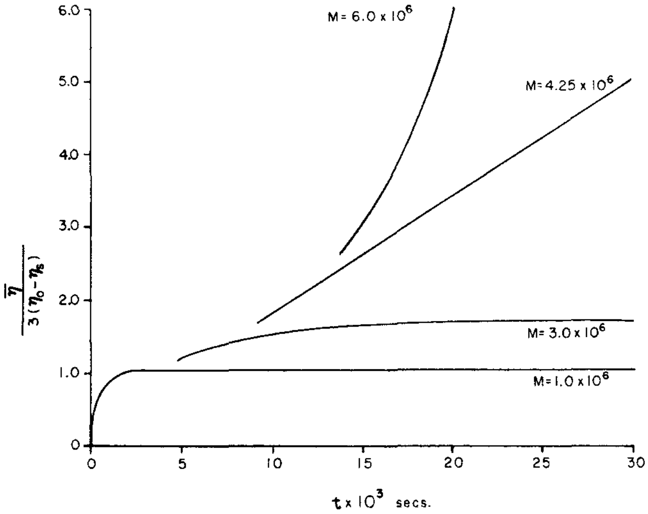

Fig. 1. $\bar{\eta}/3(\eta_0-\eta_s)$ versus time for various molecular weights of polyethylene oxide in dilute water solution and $\Gamma = 200$ sec.$^{-1}$.

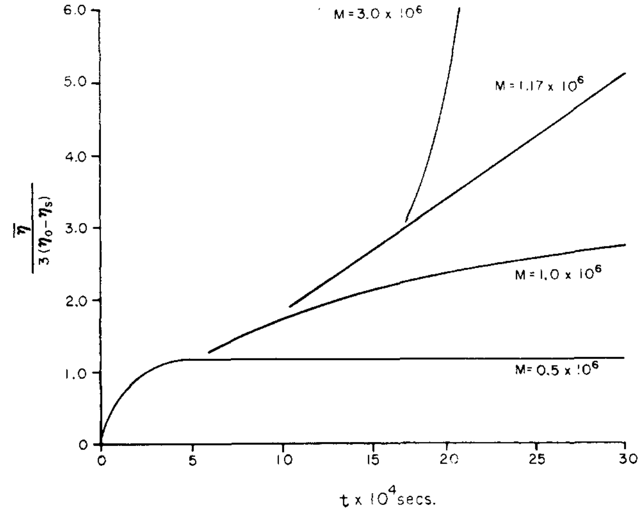

Fig. 2. $\bar{\eta}/3(\eta_0-\eta_s)$ versus time for various molecular weights of polyethylene oxide in dilute water solution and $\Gamma = 2{,}000$ sec.$^{-1}$.

---

* Relative to that of the solvent.

TABLE 1. EFFECT OF MOLECULAR WEIGHT ON INTRINSIC VISCOSITY AND ELONGATIONAL VISCOSITY

$M \times 10^{-6}$	θ, sec.	$[\eta]_{G=0}$, dl./g.	$\bar{\eta}/3(\eta_0 - \eta_s) = \bar{\eta}/(3c\eta_s[\eta]_{G=0})$ ($\Gamma = 2{,}000$ sec.$^{-1}$, $t = 0.008$ sec.)
1.0	3.17×10^{-4}	5.98	3.01
2.0	1.09×10^{-3}	10.3	5.76×10^4
3.0	2.24×10^{-3}	14.1	9.28×10^5
4.0	3.73×10^{-3}	17.6	2.14×10^6
5.0	5.56×10^{-3}	21.0	2.79×10^6
6.0	7.69×10^{-3}	24.2	2.94×10^6

DRAG REDUCTION

Our results are also interesting from another point of view, namely, in explaining some aspects of turbulent drag reduction. Recently, Seyer and Metzner proposed a phenomenological explanation of drag reduction, based on the unusually high resistance of polymer solutions to pure stretching motions (*3, 4*). According to these authors, the turbulent eddy structure near a pipe wall may be considered roughly as such a stretching motion, and the drag reduction results from the resistance of the solution to this motion. They conclude, therefore, that high elongational viscosity is synonymous with good drag reduction.

Seyer and Metzner calculated Γ to be about 2,000 sec.$^{-1}$ for a dilute water solution (0.01 wt. %) of a high molecular weight polyacrylamide, at a Reynolds number of 144,000, in a 1-in. tube. Our results in Figure 2 are for Γ = 2,000 sec.$^{-1}$, and indicate the effect of changes in molecular weight on elongational viscosity. This is demonstrated more clearly in Table 1, where values of $[\eta]_{G=0}$, $\bar{\eta}/3(\eta_0 - \eta_s)$ and θ are tabulated for various molecular weights. The values of $\bar{\eta}/3(\eta_0 - \eta_s)$ are calculated for $t = 0.008$ sec., which is roughly the order of magnitude of the time scale characteristic of energy-containing eddies (*3*). The effect of molecular weight on elongational viscosity is seen to be extremely large, while changes in intrinsic viscosity are rather small. Consequently, our results (considered in light of Seyer and Metzner's work) imply that molecular degradation should have a catastrophic effect on drag reduction, while affecting intrinsic viscosity only slightly. This has recently been observed experimentally by Patterson and Abernathy (*6*). Their results indicate that the drag reduction phenomenon depends very strongly on the concentration of the highest molecular weight species present. Molecular degradation was found to be most severe for these high molecular weight polymers, resulting in large changes in drag reduction, but small changes in $[\eta]$.

CONCLUSIONS

1. The results of the GSE constitutive model are in qualitative agreement with those of Denn and Marrucci, thus confirming the conclusions of these authors regarding limiting stretch rates in viscoelastic fluids.
2. Assuming $\epsilon = 0.4$ as suggested by available data, we calculated the elongational viscosities of monodisperse aqueous solutions of polyethylene oxides of varying molecular weights. These calculations clearly illustrate the strong dependence of elongational viscosity (and hence drag reduction) on molecular weight.
3. The findings of Patterson and Abernathy, which are essentially that intrinsic viscosity is a very poor measure of degradation, have been tentatively explained.

ACKNOWLEDGMENT

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

NOTATION

a = exponent in Mark-Houwink-Sakurada relation, $[\eta]_{G=0} = KM^a$
b^2 = $3/(2\langle r^2\rangle_0)$
c = concentration
d^{ij} = deformation rate tensor
g^{ij} = metric tensor
G = shear rate
k = Boltzmann's constant
K = coefficient in Mark-Houwink-Sakurada relation, $[\eta]_{G=0} = KM^a$
M = molecular weight
N = Avogadro's number
N_1 = primary normal stress difference
N_2 = secondary normal stress difference
p = isotropic pressure
$\langle r^2\rangle_0$ = mean square end to end distance of macromolecule at rest
t = time
T = absolute temperature
T^{11} = tensile stress
v^k = velocity

Greek Letters

Γ = stretch rate
ϵ = phenomenological constant
$\bar{\eta}$ = elongational viscosity
η_s = solvent viscosity
η_0 = zero shear rate viscosity
$[\eta]_{G=0}$ = zero shear rate intrinsic viscosity
λ = relaxation time
τ^{ij} = extra stress tensor
θ = relaxation time = $\zeta/4b^2kT$
ζ = frictional coefficient

LITERATURE CITED

1. Denn, M. M., and G. Marrucci, *AIChE J.*, **17**, 101 (1971).
2. White, J. L., and A. B. Metzner, *J. Appl. Polymer Sci.*, **7**, 1867 (1963).
3. Seyer, F. A., and A. B. Metzner, *AIChE J.*, **15**, 426 (1969).
4. Gordon, R. J., *J. Appl. Polymer Sci.*, 14, 2097 (1970).
5. Lumley, J. L., *Ann. Rev. Fluid Mech.* (1969).
6. Patterson, R. W., and F. H. Abernathy, *J. Fluid Mech.*, 43, 689 (1970).
7. Ginn, R. F., and A. B. Metzner, *Trans. Soc. Rheol.*, **13**, 429 (1969).
8. Kaye, A., A. S. Lodge, and D. G. Vale, *Rheol. Acta*, **7**, 368 (1968).
9. McIntire, L. V., and W. R. Schowalter, *Trans. Soc. Rheol.*, 14, 585 (1970).
10. Ginn, R. F., and M. M. Denn, *AIChE J.*, **15**, 450 (1969).
11. Denn, M. M., and J. J. Roisman, *ibid.*, **15**, 454 (1969).
12. Gordon, R. J., and W. R. Schowalter, paper presented at Soc. Rheol. meeting, Princeton, N. J. (1970). *Trans. Soc. Rheol.*, to be published.
13. Ericksen, J. L., *Kolloid Z*, 173, 117 (1960).
14. Gordon, R. J., and A. E. Everage, Jr., *J. Appl. Polymer Sci.*, to be published.
15. Tanner, R. I., *Trans. Soc. Rheol.*, 14, 483 (1970).
16. Brandrup, J., and E. H. Immergut, Eds., "Polymer Handbook," Interscience, New York (1967).