polymer papers

Viscosity as a consequence of dielectric dissipation: 1. General equation and applications

D. Porter
Dow Chemical (Nederland) B.V., PO Box 48, 4530 AA Terneuzen, The Netherlands

(Received 4 September 1986; accepted 20 October 1986)

A general equation is derived for the viscosity of a fluid. Viscosity is a consequence of dielectric loss by dipoles, which are forced to move relative to each other in a shear field. The viscosity equation is shown to be valid for the monomeric fluids of water and styrene. Finally, polymer melt viscosity is considered as a function of molecular weight and shear rate.

(Keywords: viscosity; dielectrics; elasticity; fracture; relaxation time)

INTRODUCTION

Viscosity is the macroscopic proportionality constant between shear stress and shear gradient in a fluid. On a molecular level, viscosity is usually considered as the consequence of complicated collision processes and intermolecular forces. Owing to their complex nature, these interactions are accounted for by introducing a 'unit frictional drag' factor, which is one of the building blocks of current reptation theory[1]. This does not, however, expose the physical nature of the viscosity mechanism.

Consider now an alternative hypothesis: viscosity is a direct consequence of intermolecular interaction energy, and viscosity is generated by the dissipation of energy during the relative motion of one molecule past another. The author starts with this hypothesis and goes through the intermediate step of monomeric fluid viscosity to apply the concept of energy dissipation to the case of polymer melt rheology.

GENERAL VISCOSITY EQUATION

Figure 1 shows the geometry used to derive the equations for fluid viscosity. Spherical molecules, of radius a and occupation area A, are close-packed into laminar layers of thickness d, which lie in a plane normal to a linear shear gradient, $\dot{\gamma}$. Molecules in adjacent layers move relative to each other with frequency ν:

$$\nu = \dot{\gamma} d/(2a) \tag{1}$$

The interaction energy ϕ between a single molecule and all the molecules in an adjacent layer is expressed in terms of the surface free energy S of the fluid[2,3]:

$$\phi = SA \tag{2}$$

The number of such interactions per unit volume, n, is the inverse of the volume per molecule:

$$n = 1/Ad \tag{3}$$

The total interaction energy per unit volume, Φ, in the direction of the shear gradient is, therefore:

$$\Phi = S/d \tag{4}$$

For each cycle of interaction, as one molecule passes another, the energy lost per cycle can be related to the interaction energy per cycle, ϕ, by the general loss tangent, $\tan\delta$. The power P dissipated per unit volume of sheared fluid becomes:

$$P = \Phi(\tan\delta)\nu \tag{5}$$

The power dissipation can also be expressed in terms of viscosity η:

$$P = \eta\dot{\gamma}^2 \tag{6}$$

By combining equations (1), (4), (5) and (6):

$$\eta = \frac{S}{d}\,\frac{\tan\delta}{\dot{\gamma}} \tag{7}$$

Equation (7) is the general equation for fluid viscosity. The power dissipation parameter, $\tan\delta$, must now be specified.

ENERGY DISSIPATION

As fluid molecules in the sheared layers are forced to move past each other with frequency ν, the dipole charge distribution in each molecule can be expected to lag in phase relative to ν. This phase lag means that electromagnetic radiation is produced by the dipoles, which then dissipates energy in the shear field. Thus, viscosity is a consequence of dielectric energy dissipation.

The dielectric loss tangent is expressed in terms of the real and imaginary parts of the complex dielectric constant, ε' and ε'' respectively[4]:

$$\tan\delta = \varepsilon''/\varepsilon' \tag{8}$$

0032-3861/87/071051-05$03.00

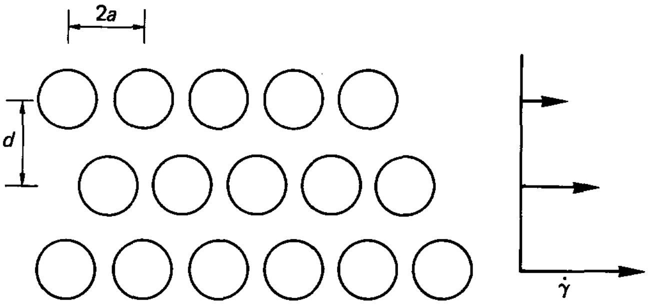

Figure 1 The geometry of molecules moving in a linear shear gradient, $\dot{\gamma}$

where ε' and ε'' are functions of angular frequency $\omega = 2\pi\nu$, dielectric relaxation time τ, and the static and infinite-frequency dielectric constants, ε_s and ε_i respectively. At low frequencies, $\tan\delta$ becomes:

$$\tan\delta = \frac{\varepsilon_s - \varepsilon_i}{\varepsilon_s}\omega\tau \tag{9}$$

The dielectric constants ε_s and ε_i are obtained from Onsager's equation[4] for a polar fluid in terms of the permittivity of free space, ε_0, the dipole moment per molecule, μ, the number of dipoles per unit volume, n, Boltzmann's constant, k, and temperature, T. For a low-polarity fluid, Onsager's equation becomes:

$$\frac{\varepsilon_s - \varepsilon_i}{\varepsilon_s} = \frac{(\varepsilon_s + 2)^2}{3\varepsilon_s}\frac{n\mu^2}{3\varepsilon_0 kT} \tag{10}$$

Note that a local field correction factor must be used to calculate the actual relaxation time, τ, from an experimental value, τ_D, which might be taken from the position of the maximum value of ε'' in a plot against frequency, where $\omega\tau_D = 1$:

$$\tau = \tau_D \frac{\varepsilon_i + 2}{\varepsilon_s + 2} \tag{11}$$

MONOMERIC FLUIDS

Let the spheres in *Figure 1* be rigid monomeric units, such that $d = 2a$. By combining equations (7) and (9), an equation for the viscosity of a monomeric fluid is obtained:

$$\eta = \pi \frac{S}{a}\frac{\varepsilon_s - \varepsilon_i}{\varepsilon_s}\tau \tag{12}$$

Viscosity can be calculated as a function of temperature, since experimental data for the parameters S and a is readily available, and the dielectric constant parameters can be obtained from equation (10) if they are not already known. In order to predict τ as a function of temperature for a monomeric fluid, each monomer unit can be considered as an electrical tuned circuit[5], with a natural relaxation time, τ_0, in a totally isolated state. As the monomer units interact, with a negative potential energy of interaction, then the relaxation time must increase. In an electrical tuned circuit, where two separate circuits with inductances L interact with a mutual inductance m:

$$\tau = \tau_0\left(1 + \frac{m^2}{L^2}\right)^{1/2} \tag{13}$$

Similarly, for two interacting monomer units, whose negative energy of interaction decreases linearly with increasing temperature, then the ratio of relaxation times, τ_1 and τ_2, at temperatures T_1 and T_2 is given by the simplified expression, for $T \ll T_B$, where T_B is the boiling point of the fluid:

$$\frac{\tau_1}{\tau_2} = \left(\frac{T_B - T_1}{T_B - T_2}\right)^{1/2} \tag{14}$$

Example: water at 20°C

Experimental data points are available for all the parameters of equation (12) for water at 20°C[6]: $\varepsilon_s = 80$, $\varepsilon_i = 4.9$, $\tau_D = 10^{-11}$ s, $S = 0.073$ J m^{-2}, $a \simeq 1.9 \times 10^{-10}$ m. The value of τ is calculated from τ_D by using equation (11) as $\tau = 8.5 \times 10^{-13}$ s.

Equation (12) predicts $\eta = 9.6 \times 10^{-4}$ Pa s, which compares well with the standard experimental value of $\eta = 10^{-3}$ Pa s.

Example: styrene monomer

A general prediction of η against T is possible for the low-polarity styrene monomer. The parameter values[7] are: $T_B = 418$ K, $\varepsilon_s = 2.45$, $\mu = 4.3 \times 10^{-31}$ C m, $a = 3.4 \times 10^{-10}$ m, $\tau = 1.1 \times 10^{-10}$ s at $T = 258$ K, $S = 0.0645 - 0.00011T$ J m^{-2}.

By using a volume expansion coefficient of 0.001 K^{-1}, the following relation is obtained from equation (10):

$$\frac{\varepsilon_s - \varepsilon_i}{\varepsilon_s} = \frac{10.1}{T(1 + 0.001T)} \tag{15}$$

and the relaxation time, from equation (14), is:

$$\tau = 8.7 \times 10^{-12}(418 - T)^{1/2} \tag{16}$$

Figure 2 shows a plot of η against T for styrene monomer as predicted by equation (12). Experimental data points[7] are plotted for comparison.

POLYMER MELT VISCOSITY

Let the spheres of *Figure 1* be polymer macromolecules of radius R_0, but which deform in the linear shear gradient to the form of a prolate ellipse, with a long axis of length $2R$ and short axes of length $2D$: the long axis is in the direction of polymer flow. The constant volume condition for deformation in the molten state becomes:

$$RD^2 = R_0^3 \tag{17}$$

Each polymer macromolecule consists of N_T mer units in a chain, which is contained within the boundary of the elliptical volume elements. The energy of interaction per unit volume, Φ_p, is taken between macromolecular layers, of thickness $2D$, in the direction of maximum shear gradient. From equation (4), with subscript p used to specify a polymer parameter:

$$\Phi_p = S_p/(2D) \tag{18}$$

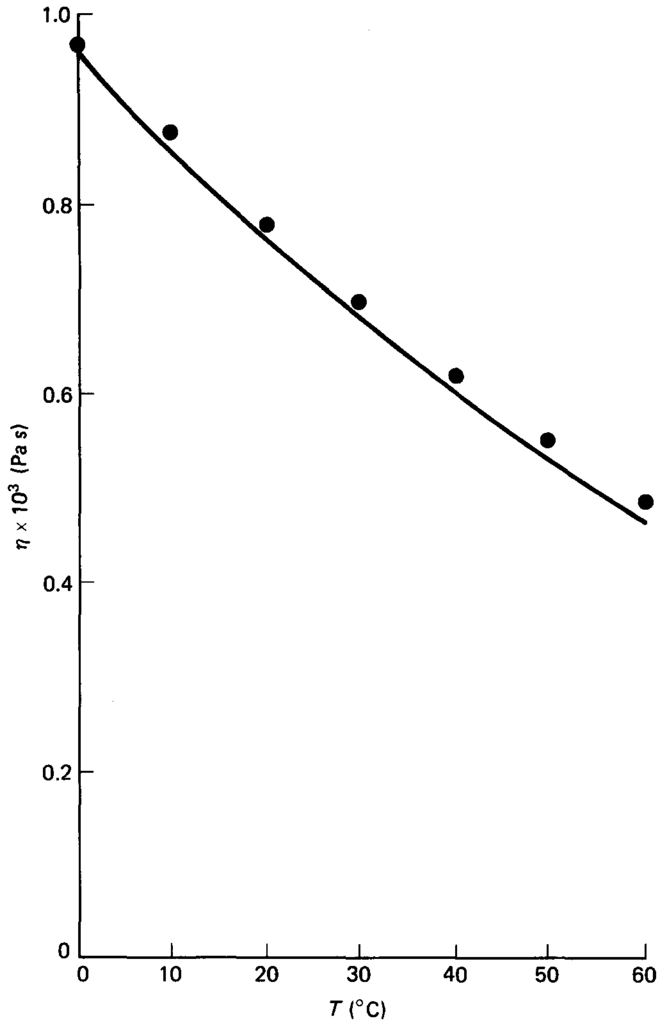

Figure 2 Viscosity, η, against temperature, T, for styrene monomer from equation (12). Points are experimental data[7]

The equation for polymer melt viscosity now takes the same form as equation (12): note, however, the change in geometry makes $v=\dot{\gamma}D/R$ and the dielectric equation (10) requires a scaling term D/a to account for the number of mer-unit dipoles which oscillate within the macromolecular layer:

$$\eta = \pi\frac{S_p}{a}\frac{\varepsilon_s-\varepsilon_i}{\varepsilon_s}\tau_p\frac{D^2}{R^2} \tag{19}$$

Using equation (17):

$$\eta = \pi\frac{S_p}{a}\frac{\varepsilon_s-\varepsilon_i}{\varepsilon_s}\tau_p\left(\frac{R_0}{R}\right)^3 \tag{20}$$

Equation (20) has the form:

$$\eta = \eta_0\left(\frac{R_0}{R}\right)^3 \tag{21}$$

The zero shear viscosity, η_0, is the viscosity with no deformation, such that $R_0=R$. The shear dependence of the polymer melt viscosity is contained in the deformation parameter $(R_0/R)^3$. The deformation parameter is calculated through a force balance between viscous drag and elastic reaction on an individual macromolecule. If G is the shear modulus of a molecule:

$$\eta\dot{\gamma} = G\frac{R-R_0}{R_0} \tag{22}$$

So,

$$\frac{\eta_0\dot{\gamma}}{G} = \left(\frac{R}{R_0}\right)^3\left(\frac{R}{R_0}-1\right) \tag{23}$$

By combining equations (20) and (23), the whole shear dependence of polymer melt viscosity can be predicted. Note also that equation (23) shows that the apparent real part of the complex elastic modulus, G', is frequency/shear-rate dependent, and its magnitude is controlled by the viscous drag forces on each molecule.

Example: polystyrene

Consider first the zero shear viscosity, η_0, which is predicted by making $R=R_0$ in equation (20). The dielectric constant terms are taken as being identical with those of styrene monomer, given in equation (15).

Figure 3 shows the data of various workers[4] for the dielectric relaxation time of polystyrene as a function of temperature. The data fit the empirical equation:

$$\tau_p = 3.4\times10^{-11}\exp\left(\frac{1236}{T-323}\right) \tag{24}$$

Data for S_p can be obtained by noting that the parameter S can be equated with the fracture energy per unit area of fractured surface[8] in a brittle fracture experiment. *Figure 4* shows the data collected by Kusy and Turner[9] for the brittle fracture energy of poly(methyl methacrylate) (PMMA) and polystyrene: a best-fit line of fracture

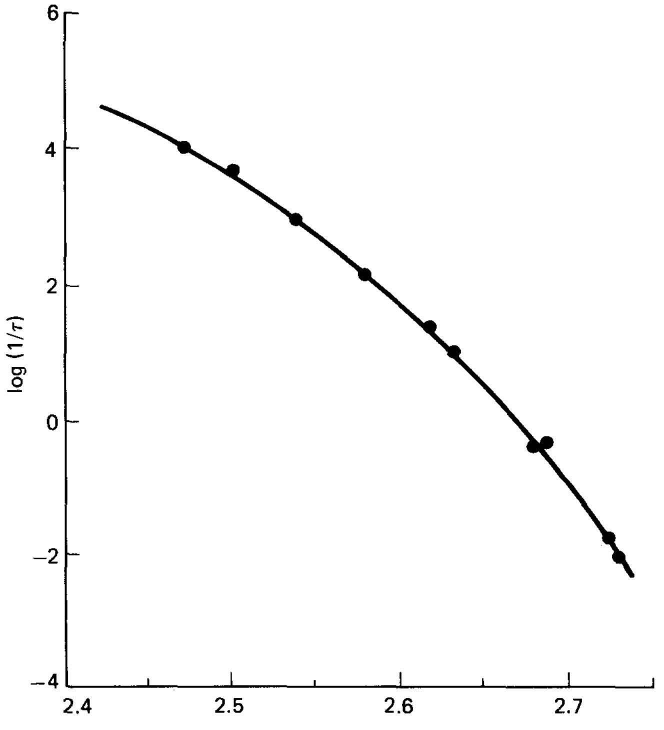

Figure 3 Experimental data[4] for dielectric relaxation time for polystyrene as a function of temperature. Plotted as $\log_{10}(1/\tau)$ against $10^3/T$

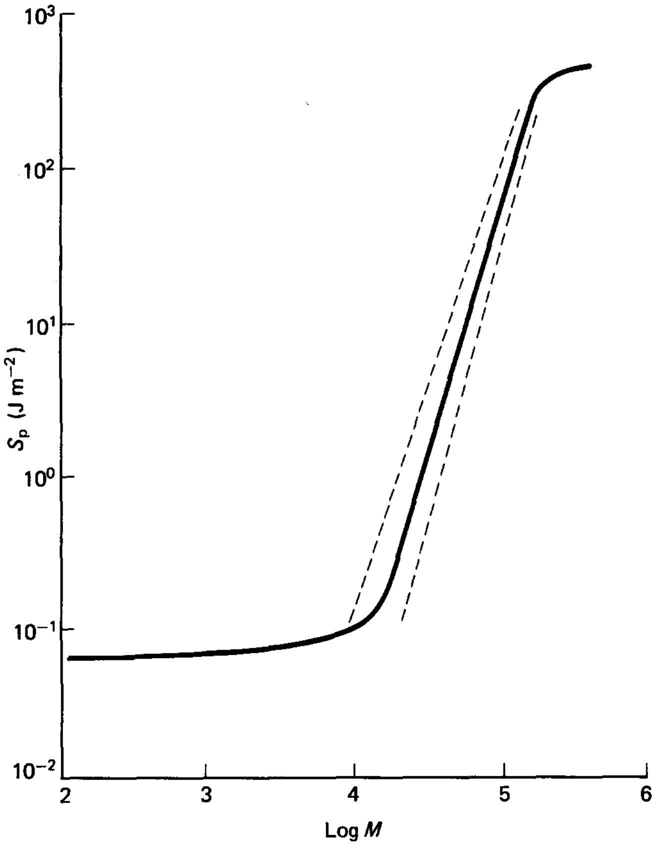

Figure 4 S_p against M for PMMA and polystyrene, taken from the data of Kusy and Turner[9]. Broken lines give experimental error bands

energy per unit area against molecular weight, M, is shown with experimental error bands. The fracture energy of polystyrene falls within the error bands for PMMA, as might be expected from such similar mer units in terms of S, M and molecular volume. The temperature dependence of S_p is ignored for the moment, since the main temperature dependence of η is expected to come from the exponential of equation (24).

Figure 5 shows a plot of the predicted values of η_0 against molecular weight at 490 K, using $a = 3.6 \times 10^{-10}$ m. The experimental data of Fox and coworkers[10] is also plotted for comparison. The broken line on *Figure 5* is an extrapolation of the Kusy and Turner data, with a slope of about 3.33. *Figure 5* demonstrates clearly that the molecular weight dependence of zero shear viscosity comes directly from the interaction energy parameter, S_p.

The shear dependence equation (23) has been tested by measuring viscosity as a function of shear rate for two narrow molecular weight distribution polystyrenes of $\eta_0 = 900$ Pa s and $\eta_0 = 6.3 \times 10^3$ Pa s at $T = 490$ K. A value of $G = 10^5$ N m^{-2} was used in equation (23)[11] and a comparison of predicted and experimental values of η against $\dot{\gamma}$ is shown in *Figure 6*.

DISCUSSION

The author has avoided direct suggestions about the fundamental nature of the parameters of the viscosity equations, particularly S_p, τ_p and G: experimental values of these parameters were used successfully to predict viscosity. Entanglement and reptation concepts might be invoked to explain the dependence of S_p and G upon molecular weight, which subsequently dictate the dependence of viscosity upon molecular weight. However, the simple ball-in-space molecular geometry used throughout this paper implies that the author attributes the physical properties of a polymer to intermolecular potential energy of interaction: the model for polymer viscosity would be invalid if this were not the case. This concept will be extended in part 2, since it is beyond the scope of the current report. One simple practical consequence of interaction energy effects upon polymer viscosity is the use of incompatible plasticizing agents in a polymer matrix to reduce polymer viscosity. This effect can be understood by reducing the surface free

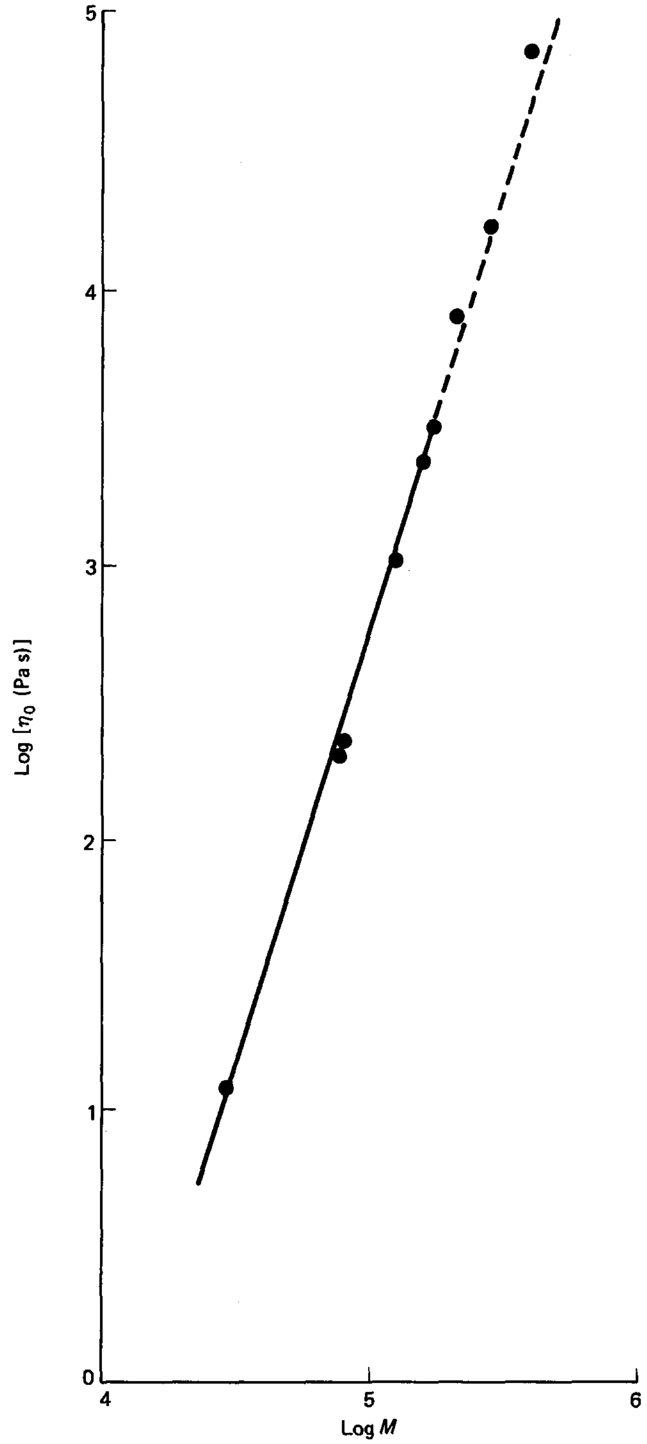

Figure 5 Prediction of zero shear viscosity, η_0, against molecular weight, M, for polystyrene at $T = 490$ K. Points are experimental data of Fox and coworkers[10], and broken line an extrapolation of the data for S_p

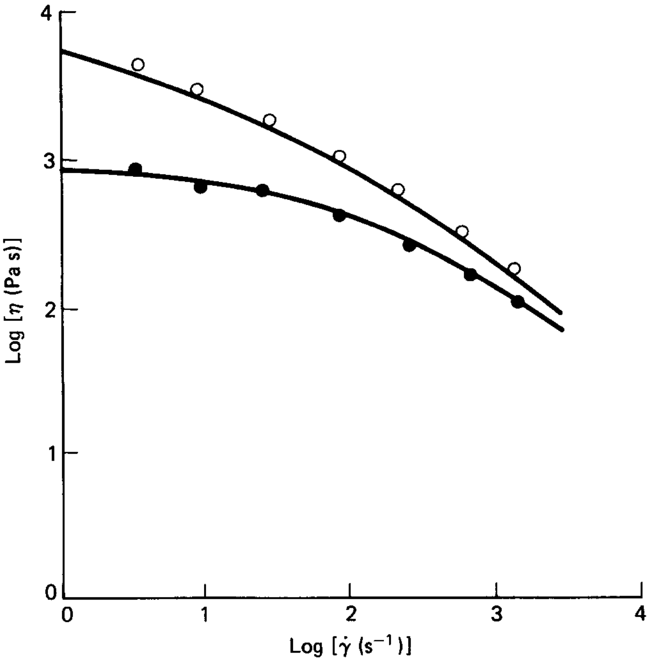

Figure 6 $\log_{10} \eta$ against $\log_{10} \dot{\gamma}$ for two narrow molecular weight distribution polystyrenes: ○, $\eta_0 = 6.3 \times 10^3$ Pa s; ●, $\eta_0 = 900$ Pa s

energy term in all the viscosity equations by an interfacial energy[12].

The motivation for this work was to examine the stability of a polymer flow, to predict the critical shear rate for the onset of spiral flow and eventually the 'shark-skin' effect. Preliminary results, obtained with a numerical simulation of the flow profile in a capillary tube, indicate that instability is associated with the shear rate in any part of the flow achieving the condition $\omega = 1/\tau$. This condition represents the maximum in the curve of loss tangent against frequency. Since the system tries to achieve a minimum energy condition, the shear field will adjust itself to values of shear rate above and below this critical condition to attain the same final average shear rate. The geometrical model of a macromolecule used in this report is similar to that of Lumley[13] in his discussion of turbulent flow.

CONCLUSIONS

The mechanism behind the viscosity of a fluid has been shown to be dielectric energy dissipation as molecular dipoles move relative to each other in a shear field. A general equation for fluid viscosity has been derived and shown to be valid for simple monomeric fluids, by using the examples of water and styrene monomer.

The concept has been extended to the case of a polymer melt by considering the simplified geometry of non-entangled discrete polymer macromolecules. Equations were derived to predict the viscosity of a polymer melt, and experimental values of the equation parameters were used successfully to predict the viscosity of polystyrene. The work strongly suggests that consideration of the intermolecular potential energy of interaction between polymer macromolecules would be fruitful for the understanding of all physical properties of a polymer.

ACKNOWLEDGEMENTS

The author wishes to thank Dow Chemical for permission to publish this work, and thanks Dr Klaas Vos for his support and helpful discussions. Thanks are also due to Dr John Daly for his helpful suggestions.

REFERENCES

1 Doi, M. and Edwards, S. F. *J. Chem. Soc., Faraday Trans. II* 1978, **74**, 1789
2 Girifalco, L. A. and Gilmore, G. D. *J. Appl. Phys.* 1949, **20**, 502
3 Oh, Y. and Jhon, M. S. *J. Colloid Interface Sci.* 1980, **73**, 467
4 McRum, N. G., Read, B. E. and Williams, G., 'Anelastic and Dielectric Effects in Polymeric Solids', Wiley, New York, 1967
5 Pain, H. J. 'The Physics of Vibrations and Waves', Wiley, London, 1970
6 Bleany, B. I. and Bleany, B. 'Electricity and Magnetism', Oxford University Press, Oxford, 1965
7 Boundy, R. H. and Boyer, R. F. 'Styrene: its Polymers, Copolymers and Derivatives', Reinhold, New York, 1952
8 Wake, W. C. 'Adhesion and the Formulation of Adhesives', Applied Science, London, 1970
9 Kusy, R. P. and Turner, D. T. *Polymer* 1976, **17**, 161
10 Fox, T. G., Gratch, S. and Loshaek, S. in 'Rheology' (Ed. F. R. Eirich), Academic Press, New York, 1956, Vol. I, p. 440
11 Ferry, J. D., 'Viscoelastic Properties of Polymers', Wiley, New York, 1980
12 Wu, S. *J. Polym. Sci. (C)* 1971, **34**, 19
13 Lumley, J. L. *Macromol. Rev.* 1973, **7**, 263