HETEROGENEITY OF DILUTE POLYMER SOLUTIONS *

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Summary

Dilute macromolecular solutions often exhibit flow characteristics which
are remarkably different from those of the Newtonian solvent. Drag may be
decreased in turbulent shear flow and increased in flow around cylinders and
through porous media. In dilute polymer solutions turbulent clouds will
disperse more slowly, jets become more stable, and Taylor and bath-tub vor-
tices may be supressed.

Some of these effects may be explained by assuming the macromolecules
stretch in strong flows. But often the effects occur in weak flows or flows
in which substantial stretching is incompatible with the kinematics, and
further the onset of the non-Newtonian behaviour often depends on polymer
concentration.

It is proposed here that "fresh" solutions of macromolecules are hetero-
geneous. When dilute solutions are prepared from concentrated master solu-
tions, strings are created by the mixing process and these strings form a net-
work in the fluid. The difficulty in obtaining repeatable experimental results,
as well as the disappearance of many non-Newtonian effects in aged solu-
tions which retain drag reducing ability in turbulent shear flow, may be
explained by this model.

If the strings of polymer solutions are sufficiently long compared with
their thickness, the network will move with the surrounding fluid. At low
rates of strain a dilute network will hardly affect the solvent properties.
Under high rates of strain, of sufficient duration, strain hardening will cause

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the elasticity of the strings to predominate; the fluid will behave like a concentrated polymer solution with "diluted" elastic properties. The similarity of the kinematics of concentrated and dilute solutions could be explained by such a liquid network model.

Rheological equations may be easily contructed for such polymer solution networks if those of the concentrated "master" solutions are known. Many rheological equations for concentrated polymer solutions are, however, found to have some deficiencies when the liquid network model is applied to the sink flow through an orifice.

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1. Introduction

Minute concentrations of dissolved macromolecules may have a dramatic affect on flow characteristics. In the Tom's effect for instance an 80% reduction in friction may be obtained in turbulent shear flow of water by adding as little as 10 parts per million in weight of high molecular weight Polyox.

It is evident that in order for such dilute solutions to exhibit significant non-Newtonian behaviour, the macromolecules must interact hydrodynamically. This can happen when the molecules are stretched by the flow from a r.m.s. coil size, a, to a stretched length, l. While the solution remains dilute in the sense that the volume fraction $c[\eta] < 1$, where c is the weight concentration and $[\eta]$ the intrinsic viscosity, there will be hydrodynamic interactions if $c[\eta](l/a)^2 > 1$. Under these conditions the "extensional" viscosity may be increased by a factor $c[\eta](l/a)^2$, or even $c[\eta](l/a)^3$ if the particles become rigid [1]. Such selective increases in elongational viscosity have been assumed to alter the structure of turbulent shear flow leading to an overall drag reduction [2]. A salient feature of this theory is that in order for the molecules to be stretched, the flow has to be strong, i.e. $\lambda|\nabla U| > 1$ where λ is the relaxation time of the molecule and $|\nabla U|$ the largest real part of an eigenvalue of the tensor ∇U where U is the velocity vector. Thus, as has been often experimentally verified, a uniform laminar shear flow of dilute macromolecular solutions, for which $|\nabla U| = 0$, behaves as the Newtonian solvent with an insignificant increase in shear viscosity. In turbulent shear flow a sharp onset of non-Newtonian behaviour becomes apparent at $\lambda|\nabla U| \sim 1$. This onset condition should be — and is often found to be in practice — independent of the polymer concentration.

With dilute polymer solutions in non-uniform laminar flow, extraordinary increases in drag have been observed. For example, in orifice flow, increases in Trouton viscosity by several orders of magnitude have been measured. Since the kinematics of laminar flows are seemingly easier to trace, it has often been suggested that their study might reveal the basic rheology of dilute polymer solutions, which in its turn may lead to an explanation of the Tom's effect.

There is ample experimental evidence, in particular in laminar flows, that

dilute polymer solutions exhibit extraordinary effects while the flows are weak and the onset condition depends on concentration. In many such cases, like flow through porous media or around obstacles, the stretching ratio of fluid elements is insufficient to stretch the molecules to a length at which hydrodynamic interaction may occur.

It is this evidence, to be presented in the following section, which led us to a model involving a heterogenous macromolecular distribution in the fluid. With this model the non-Newtonian behaviour of weak flows may be explained as well as many contradictory experimental results.

2. Experimental background

Experimentalists have learned that in order to obtain a semblance of repeatability the utmost care has to be taken to prepare batches of solutions in a similar manner. In particular, the time between the preparation of the diluted solution and the experiment has to be kept the same. Since degradation is often appreciable in high-molecular-weight solutions, it has become an accepted procedure to use only "once through" solutions.

2.1 Turbulent shear flow

Early experiments with Guar Gum solutions in turbulent shear flow showed the onset of drag reduction not to depend on the concentration [3]. Some weak dependence was subsequently found with different polymers. A different behaviour was later found in studies in which the conformation of the macromolecules in quiescent solutions was artificially altered by adding inorganic salts or varying the pH of the solvent. From such studies Virk [4] concluded that there were two kinds of turbulent drag reduction, type A and B. In type A, in which the macromolecules start in a collapsed conformation, the onset condition is independent of concentration while the relative drag reduction depends on the concentration as well as on the rate of strain. In type B, in which the molecules start in an extended state, the flow remains laminar up to much higher Reynolds numbers but with very high apparent viscosities. The critical Reynolds number themselves are highly dependent on concentration. A type B behaviour has been observed with suspensions of fibres and with miscelles formed by inorganic soap solutions.

Stenberg et al. [5] found similar variations in friction coefficient, f, with freshly prepared Polyox solutions varying only the rate of mixing. Slightly mixed or unmixed solutions gave a type B behaviour while more vigorous mixing resulted in type A flow characteristics (Fig. 1). Since the solution was the same in the experiments, the molecular relaxation time should be the same, and thus the type B drag reduction occurred in weak flows.

2.2 Other turbulent flows

Weak free turbulent flows of dilute polymer solutions also exhibit changes in characteristics. Tulin and Wu [6] found appreciable suppression of turbu-
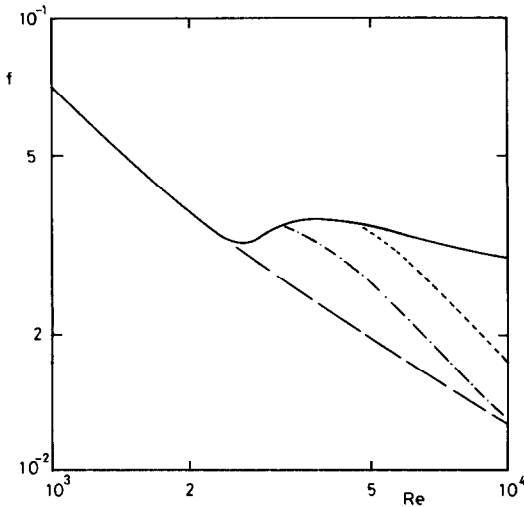
Fig. 1. Plot of friction coefficient versus Reynolds number: ——— water, with injection of 5 × 10⁻³ volume of 1% Polyox solution into water with mixer speed up to 20 rev/sec — — —, at 30 rev/sec · — · — · and at 40 rev/sec - - - - - - (redrawn from [5]).

lence in a 25 p.p.m. Polyox solution, by measuring the rate of spreading of a turbulent cloud. Similar damping effects are sometimes found in axisymmetrical jets. While a 500 p.p.m. drag reducing Guar Gum solution does not stabalize a jet, much lower concentrations of Polyox sometimes do, [7]. It is interesting to note that at breakup a jet of a solution of 200 p.p.m. Polyox seems to form long strings of fluid [8]. In fact pituity or the ability to form strings has been an observed property of fresh dilute polymer solutions and concentrated solutions alike. In external flows like that around a sphere, laminar separation can be delayed, reducing from drag with fresh Polyox but not with Guar Gum solutions. With aging of several days the Polyox solution loses its effect on the sphere drag but retains its skin friction reduction properties in turbulent shear flow [7].

2.3 Visco-elasticity

In general, fresh solutions of most polymers exhibit viscoelastic characteristics, although these are not necessary to cause turbulent drag reduction. Gadd [9] found normal stress differences in shear flow of Polyox but not in Guar Gum solutions, while Brennan and Gadd [10] showed that the viscoelastic effects but not the drag-reducing ability disappeared after storing the solution for several days. James [11] also measured normal stresses in dilute polymer solutions.

2.4 Flow around cylinders

A typical example of concentration-dependent onset of non-Newtonian behaviour in laminar flow was shown in the experiments by James et al. [12, 13]. Heat transfer and drag coefficients were measured for uniform around thin cylinder over a range of flow Reynolds number of $0.1 < Re < 200$. The strain rate at onset was in the range $10 \text{ sec}^{-1} < V/D < 300 \text{ sec}^{-1}$, where V is the mean stream velocity and D the diameter of the cylinder, which with a molecular relaxation time $\tau \sim 10^{-3}$ sec indicates weak flow with $V\tau/D < 1$ at onset. In addition onset was found to depend on the concentration. Beyond onset, both heat transfer as well as drag coefficients were found to be essentially independent of the Reynolds number (Fig. 2). Analysis of the data indicates that beyond onset $C_D \propto c^{1/2}/D$ where C_D is the drag coefficient and c the average polymer concentration.

Piau [14] showed, from flow observations, that after onset an effective obstruction to the flow is created which may be orders of magnitude larger than the cylinder, as if the cylinder had a substantially larger diameter. This change in kinematics was found similarly for dilute as well as concentrated polymer solutions. The observed larger effective diameter is also substantiated by the independence of Nusselt number of Reynolds number, since heat transfer is then governed by the convection in the essentially stagnant flow around the cylinder. Pitot tube corrections for dilute polymer solutions are evidently related to similar changes in the kinematics.

Kit and Poreh [15] have also made drag measurements on cylinders but at higher Reynolds numbers. They found that the increase in the drag diminishes if there was a delay between the experiment and the preparation of the diluted solution from their 2% Polyox master solution, while skin friction reduction was not affected.
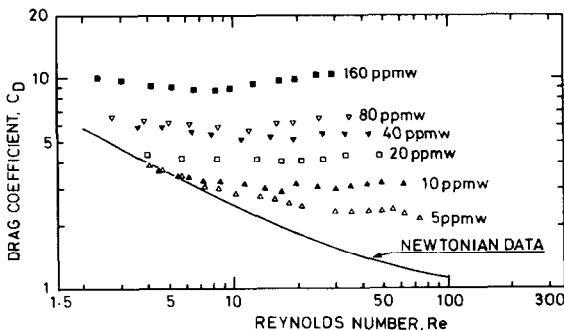

Fig. 2. Drag measurements of a circular cylinder ($D = 0.15$ mm) in solution of Polyox coagulant (from [13]).

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2.5 Flow through porous media

In flow of dilute polymer solutions through porous media a similar con-
centration-dependent onset was found in weak flow conditions [16]. Typical
strain rates at onset were found to be between 2 and 20 sec^{-1} depending on
concentration. From an analysis of these data and those of James and
McLaren [17], onset seems to occur at

$$c^{1/2}V_0/nD_p = \text{constant} \qquad (1)$$

for each kind of polymer solution where n is the porosity, V_0/n the effective
average velocity in the pores and D_p the diameter of the particles in the
porous bed (Fig. 3). The large increase in pressure drop was found to occur
mainly in the first upstream centimetres of the porous bed. Naudascher and
Killen [18] who found a similar correlation, also observed that a solution
aged beyond three days lost its drag enhancing properties.

Neither in the convergent–divergent flow passages of a porous medium
nor in external flow are the stretch rates adequate to cause significant mole-
cular stretching. Even if such stretch rates in the kinematics of the New-
tonian flow would be sufficient to create hydrodynamic interaction between
the molecules and result in appreciable extra stresses, the kinematics would
change subsequently to avoid such stresses in the flow [16].

2.6 Flow through an orifice

The increased pressure drop in porous media is thought to be due to the
non-uniform flow of the visco-elastic fluid in the converging–diverging pas-
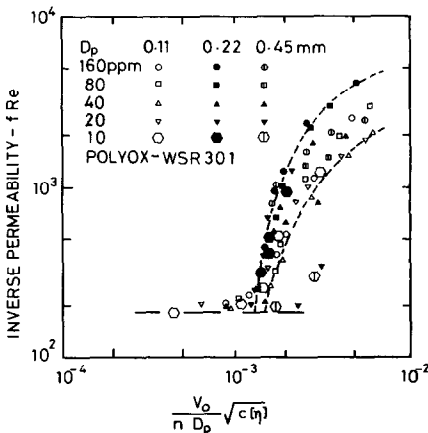sages. The converging flow upstream from a small orifice has similarly been

Fig. 3. Nondimensional plot of inverse permeability for solutions of Polyox WSR 301
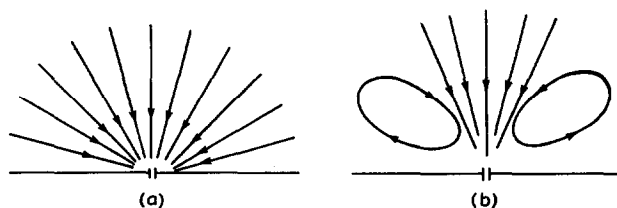(Fig. from [16], data from [17]).

Fig. 4. Sinkflow of Newtonian fluid (a) and polymer solutions (b).

found to exhibit a concentration-dependent onset [14]. From measurements of the thrust of a jet ejected from an orifice, Metzner and Metzner [19] deduced for a 100 p.p.m. solution of Separan, elongational viscosities 500—6000 times the shear viscosity. Their analysis was based on the observation that the main flow after onset is limited to a narrow cone with a vortex ring filling the remaining flow field upstream of the orifice (see Fig. 4). These kinematics were observed for dilute as well as concentrated solutions.

Similar measurements for pressure drop in orifice flow were made by Bilgen [20] who, for four different kinds of Polyox solutions with concentrations of $0 < c < 200$ p.p.m., found a remarkable consistent correlation of his data which can be rewritten as

$$\frac{\Delta p}{\frac{1}{2}\rho V^2} \propto \frac{\nu \lambda c}{D^2} \cdot \frac{\nu}{VD}, \tag{2}$$

where ν is the kinematic viscosity.

Balakrishnan and Gordon [21] observed that when the flow is suddenly stopped, the conical flow region upstream from an orifice will recoil upstreamwards. As remarkable, Gordon and Balakrishnan [22] found that a Bathtub vortex could be suppressed by adding as little as 3 p.p.m. Polyox.

Rubin and Elata [23] showed experimentally that the critical Taylor number increases with concentration of Polyox in solution. With 100 p.p.m., a 30% increase in the critical Taylor number was measured at shear rates in the Couette flow of around 30 sec^{-1}.

All these experimental results indicate first-order changes in flow characteristics of dilute macromolecular solutions under weak flow conditions. Thus an additional model is required to explain the remarkable non-Newtonian fluid characteristics, which encompasses interaction between the macromolecules which, if at all, are only slightly stretched.

3. The liquid network model

3.1 Origin of network

The evidence presented so far, leads us to a model for "fresh" dilute macromolecular solutions.

The preparation of dilute high-polymer solution is a tedious and time con-

suming procedure. Since vigorous stirring will cause molecular degradation the generally accepted method is to prepare a concentrated "master" solution by gently sloshing of the liquid with polymer powder suspension — allowing the polymer grains to swell until after several days a homogeneous solution is formed. From such a master solution the final required concentration of solution can be easily prepared by adding additional solvent under slow mixing. Such diluted solutions are visible homogeneous after a few minutes, and are often used in experiments immediately after preparation as "fresh" solutions. We assume here, however, that such solutions are not homogeneous but are heterogeneous. The slow mixing of a concentrated solution of entangled molecules with additional solvent will stretch the concentrated solution into long strings, creating a dispersed network. Hours or days may be required for the macromolecules to disentangle from these strands and create, through diffusion, a homogeneous solution. We have been unable to find the diffusivity of Polyox in a 1% solution, but if we estimate it as the dilute value reduced by the viscosity change then we obtain 10^{-14} m^2 s^{-1} which would predict a thread 0.1 mm dissolves in 10 days. Further studies could usefully examine the rate of dissolving of threads of concentrated polymer solutions.

It has been suggested previously that molecular chains in a homogeneous solution entangle during the flow to form larger macromolecular structures [24]. We think that this hypothesis is not feasible because the total volume concentration would remain fixed and so the hydrodynamic interaction between multimolecular structures would be less effective than between isolated molecules. Still, multimolecular structures have apparently been observed [5]. Electron micrographs of dilute Polyox solutions often show a fibrous network structure in the freeze-dried samples [25,26]. These pictures are a direct evidence for our model showing the dried strands of the network of concentrated solution, typically with a diameter of order 0.1 μm (James and Saringer [27]) to 1 μm [26]. Such a liquid network results from the preparation of the diluted solution and not as suggested by entanglement of flowing molecules. On the contrary, we may expect the networks to break up in flow.

Our model closely follows the visual observations of Stenberg et al. [5]. They showed that several centimeter long strings of a 200 p.p.m. Polyox solution could be maintained in an accelerating flow field at a thickness of $d \sim 10^{-1}$ mm. Such strings seem to fail and dissolve in a stringy fashion when extruded into an uniform flow field. The strands of concentrated solution will add marginally to the fluid viscosity in weak flows but under sufficiently persistent rates of strain, strain-hardening of the strands may become predominant making the fluid viscoelastic with "diluted" elastic properties.

3.2 Affine deformation

The friction force between liquid and network will be proportional to the length of the strings. If the length of the strings is sufficiently large com-

pared with their thickness, and as long as the network does not become too rigid, we may assume as a first approximation, that the relative velocity between network and fluid is negligible. Thus, an assumption of a large aspect ratio of the strings implies that it will deform affinely with the fluid. This assumption is most helpful in evaluating the contribution of the network to the bulk stresses in the fluid. Further studies need to be made to examine what happens when this asumption becomes invalid.

We assume a random three-dimensional network with threads of thickness d and average separation h. Comparing the amount of polymer contained in an h^3 volume we have

$$c_m \tfrac{3}{4}\pi h d^2 = c h^3, \tag{3}$$

where c is the average, homogeneous concentration in the "diluted" solution and c_m is the polymer concentration in the strands which we assume is equal to the value in the "master" solution (i.e. no swelling on mixing). The master solution will typically be "concentrated" with an effective volume concentration $c_m[\eta] > 1$ while $c[\eta] < 1$. Neglecting relative motion between network and fluid, as assumed, we may write in general for the average stress of the network liquid

$$\bar{\tau} = (1 - c^*)\tau_0 + c^*\tau_m, \tag{4}$$

where τ_0 and τ_m are the stresses in the fluid and strands respectively and $c^* = c/c_m = \tfrac{3}{4}\pi d^2/h^2$ is the ratio between the average cross-sectional area of strands and surrounding liquid. The extra stress above the Newtonian solvent stress caused by the presence of the network

$$\tau' = \bar{\tau} - \tau_0 \sim c^*\tau_m, \tag{5}$$

when $c_m[\eta] > 1$.

3.3 Effective (zero strain) viscosity

From (4) we can calculate the "zero shear" bulk viscosity of the liquid network system. The viscosity in a homogeneous solution at zero rate of strain is in general

$$\eta = \eta_0[1 + c[\eta] + kc^2[\eta]^2 + ...], \tag{6}$$

where η_0 is the solvent viscosity and $k \sim 0.5$ almost independent of molecular weight [28]. Since the rate of strain is the same in the network and fluid the measurable average viscosity will be

$$\bar{\eta} = (1 - c^*)\eta_0 + c^*\eta_m, \tag{7}$$

where η_m is the viscosity of the master solution from which the network is created. Substituting eqn. (6) into (7) we obtain for our heterogeneous solution

$$\bar{\eta} = \eta_0[1 + c([\eta] + kc_m[\eta]^2) + ...], \tag{8}$$

which is similar in form to the viscosity of a homogeneous dilute polymer solution, but with an effective instrinsic viscosity

$$[\eta]_e = [\eta](1 + kc_m[\eta]). \tag{9}$$

Taking as an example 0.5% master solution of Polyox with $[\eta] = 2000$ cm^3/gram and $\eta_0 = 10^{-2}$ poise, then $\eta_m = 0.61$ poise and $[\eta]_e = 12000$ cm^3/gram.

3.4 Onset criterion

If we assume for a moment that the material properties of the master solution are defined by its viscosity and a single relaxation time λ_m, each of the components of the stress tensor will have the form

$$\tau_m \propto \eta_m \Gamma f(\lambda_m \Gamma), \tag{10}$$

where Γ is a measure of the strain-rate. The extra stress will be from eqn. (5)

$$\tau' \propto c^* \eta_m \Gamma f(\lambda_m \Gamma).$$

If we assume onset of non-Newtonian behaviour to occur when $\tau' = \tau_0$ where $\tau_0 \propto \eta_0 \Gamma$ we find

$$(c^* \eta_m / \eta_0) f(\lambda_m \Gamma) = \text{constant},$$

or

$$\lambda_m \Gamma g(c^* \eta_m / \eta_0) = \text{constant}, \tag{11}$$

as a condition for onset.

Thus our model predicts that two distinct limit configurations will exist depending on the preparation and age of the diluted solution: a network of concentrated strands in "fresh" solutions and a homogeneous dispersion of single molecules in aged ones. From this we may expect in the limits, two distinct types of fluid behaviour. For the transient network system, onset will depend on polymer concentration and the time constant of the network will be the ratio between shear modulus and viscosity of the concentrated solution of entangled molecules, from which the network was created. In the homogeneous solution onset is independent of concentration, and its time constant is typically the maximum molecular relaxation time. The above model does explain the various, often contradictory experimental results.

3.5 Interpretation of experimental data

It was sheer luck that some of the early experiments in turbulent shear flow were carried out with less effective drag reducers like Guar Gum. These solutions could be pumped around a circulation system for weeks without seeming to suffer from degradation. In the light of the present model, we now understand that in this case the solution was homogeneous with sepa-

rated single molecules. Thus not surprisingly, onset was found not to depend on concentration and velocity profiles could be measured with pitot tubes without the need for visco-elastic corrections.

Aged, homogeneous solutions of separated molecules will give a type A drag reduction with concentration independent onset at $\lambda|\nabla U| \sim 1$. Networks will have a longer time constant such that onset of non-Newtonian behaviour in turbulent shear flow will be at lower shear rates, so low as to correspond to subtransitional Reynolds numbers. With a network relaxation time $\lambda_m \sim 1$ sec "onset" in a $1''$ pipe flow will be at $Re \sim 625$, and for smaller piper at correspondingly lower Reynolds numbers. Thus we may expect a "swamped" onset as found in type B drag reduction.

In general we showed that onset can be expected at

$$\lambda_m \Gamma g(c^* \eta_m / \eta_0) = \text{constant},$$

where the function g would depend on the particular type of flow. Re-examining the cylinder drag data from James et al. [12,13] we find this form. Over the range of Reynolds numbers of the experiments we would expect in Newtonian flow

$$C_D = F_D / \tfrac{1}{2} \rho V^2 D \propto R^{-1/2}, \tag{12}$$

where F_D is the drag force per unit length of cylinder, and R the Reynolds number based on the diameter. If we assume that, in order to avoid excessive elongational stresses above onset the flow changes its kinematics by simply creating a larger effective diameter of the cylinder, D_e, then using (12) for a Newtonian flow around the enlarged cylinder

$$C_D \propto \nu^{1/2} D_e^{1/2} / V^{1/2} D.$$

But from eqn. (11)

$$\Gamma^{-1} = D_e / V = \lambda_m g(c^* \eta_m / \eta_0) \tag{13}$$

and so

$$C_D \propto (\nu \lambda_m g)^{1/2} / D, \tag{14}$$

which is the dependence found in James and Gupta [13] with

$$g(c^* \eta_m / \eta_0) = c^* \eta_m / \eta_0, \tag{15}$$

for flow past cylinders.

Similarly in orifice flows, the jump from wide-angle axisymmetric sink flow to a restricted, conical flow, indicates a change in kinematics to avoid elongational stresses close to the orifice. Not surprisingly the same non-dimensional number (as was found in eqn. (14)) was successfully used as a correlation factor of flow of dilute polymer solutions in an orifice flow by Bilgen [20] as can be seen from eqn. (2). In the flow through porous media a comparison between the experimentally found onset condition and eqn.

(11) would lead to

$$g(c^*\eta_m/\eta_0) = (c^*\eta_m/\eta_0)^{1/2}, \tag{16}$$

for flow through porous media. Our model indicates that a liquid string network system will behave just as a concentrated solution but with the extra stress reduced by the factor c^*. The similar kinematics found in the flow of dilute and concentrated solutions, as in orifice flows and flow around cylinders, is further indirect support of our model.

3.6 Degradation

The model leads also to a new appreciation of the degradation of fresh polymer solutions and we may now distinguish between three kinds of observations:

(1) Flow disintegration of the network into individual molecules. The solution will lose its drag enhancement properties in non-uniform laminar flow and will change from type B to type A drag reduction in turbulent shear flow at high strain rates.

(2) Breakage of the network by overstressing into individual clusters of strands of molecules. Similar clusters have been observed by Stenberg et al. [5]. The fluid will no longer enhance drag in flow around obstacles but may retain some capability for effective clogging of orifice flow or flow in porous media.

(3) Degradation of individual molecules — causing a fall-off in molecular weight. The fluid will lose its drag reduction capabilities.

3.7 High-shear viscosity

It is obvious from the model for separated stretchable molecules that no abnormal shear viscosities should ever be expected in uniform laminar shear flow since the macromolecules, rotating with the flow, will only stretch marginally. The affinely moving network, however, will be stretched with the flow in shear flow as well as in pure straining motion, and should therefore exhibit considerably high shear viscosities as well as elongational viscosities upon strain hardening. Such shear-thickening behaviour may have been found in some cases [26,29]. Usually high shear viscosity measurements are taken in rotating apparatus after waiting for the measuring system to come to "equilibrium", by which time the network may be destroyed. Alternatively, viscosity measurements may be made in Poiseuille flow in which the network may be eliminated in the converging entrance region which is appropriately taken into account in "entrance" corrections. In general, measurements of the viscosity increment in dilute solutions, are erratic and intrinsic viscosities are determined from extrapolation of viscosity measurements of concentrated solutions. Many of the inconsistencies in reported experimental data have been blamed on the non-uniform molecular-weight distribution in

polymer samples and on molecular degradation acting selectively on the higher-molecular-weight end of the spectrum. In the light of our model such inconsistencies may be due to the presence of a transient string network, and the unlikelihood that such networks will have the same mechanical properties in different samples. A major conclusion is that since the liquid network model is of a transient nature all the non-Newtonian effects resulting from it will disappear with ageing of the solution. We suggest that further experiments should compare the rate of loss of the non-Newtonian effects with the rate at which threads dissolve.

4. Rheological description

The extra stress in an affinely moving liquid network has been related to the concentrated polymer stress in the strands in eqn. (5). Assuming the network strands behave as a continuum, it remains to decide on the rheological description of the concentrated master solution.

Let us first assume it can be described by the simple Maxwell equation

$$\tau_m + \lambda_m \; \delta\tau_m/\delta t = 2\eta_m e \tag{17}$$

where $\delta/\delta t$ is the Oldroyd upper convected derivative and e the strain rate. In axisymmetric sink flow eqn. (17) gives in eqn. (5) a first normal stress difference

$$\tau' \propto \begin{cases} c^* \eta_m \Gamma & \text{at } \lambda_m \Gamma \ll 1 \\ c^* \eta_m \lambda_m^{1/3} \Gamma^{4/3} & \text{at } \lambda_m \Gamma \gg 1. \end{cases} \tag{18}$$

The Newtonian relation is of course $\tau_0 \propto \eta_0 \Gamma$. In the experiments with orifice flows, which may be approximately described by sink flow, we found a sharp onset depending linearly on concentration as would be described by eqn. (11) with g linear whereas eqn. (18) predicts g is cubic. While the stresses predicted by the simple Maxwell model in a sink flow increase faster than a Newtonian fluid, they do not increase fast enough to explain the orifice experiments. The 4/3 power-law increase in the stress for the Maxwell equation corresponds to the stress tensor being deformation with the fluid $\delta\tau/\delta t = 0$.

We have considered various modifications to the Maxwell constitutive equation. Many of the usual modifications to forms of Oldroyd equations are unable to give the required behaviour in sink flow while still behaving satisfactorily in steady simple shear flow. Adding to the right hand side of (17) 1 or $\delta e/\delta t$ changes τ_m by a Newtonian stress and is therefore not interesting. Changing the time derivative on the left hand side to

$$\frac{\delta\tau}{\delta t} + a(\tau \cdot e + e \cdot \tau) + b \, 1 \, (\tau : e) + ce(1 : \tau) \tag{19}$$

fails to give the correct behaviour in sink flow without also producing an infinite viscosity in simple shear flow at a finite shear-rate. The coefficient

of the first term on the left hand side of (17) can be made to depend on τ. Such a modification of the relaxation process is useful in limiting the infinite viscosity in steady extensional flow, but can not increase the stress growth in sink flow.

We could produce the required stress growth in sink flow by adding to the right hand side of (17) a term $8\eta_m \beta e^3 / \lambda_m^2$, $\beta > 0$. This modification produced in steady simple shear flow a thinning viscosity (instead of an infinite viscosity at a finite shear rate) so long as $\beta < 2a - a^2$, using the time derivative (19) with $b = c = 0$ and $0 < a < 1$. Before adding such an e^3 term to the right hand side of (17), one would expect first to include an e^2 term. An e^2 addition merely increases the second normal stress difference and causes a limited shear thickening.

We found an alternative modification to (17) which could give the required behaviour was to multiply the right hand side by a function of τ. E.g. if the time derivative (19) is used with $b = c = 0$, then the correct behaviour in sink flow is obtained with a multiplying factor $1 + (1 + 2a) \times (1 : \tau)$, while the steady shear flow behaviour remains satisfactory so long as $(\frac{2}{3})^{1/2} < a < 1$. The modification of multiplying the right hand side of (17) by a function of τ is necessary for a material whose microstructure is deformed according to a simple Maxwell model, but which then produces from this deformed microstructure a stress which increases more rapidly than linearly through a stiffening spring.

Our difficulty in obtaining the required behaviour in sink flow leads us to suggest that new constitutive equations should be tested for a satisfactory performance in this particular flow.

Acknowledgement

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