

Drag Reduction and Structural Turbulence in Flowing Polyox Solutions

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Synopsis

Structural turbulence has been detected in dilute aqueous solutions of Polyox Coagulant (also known to be a highly effective drag-reducing agent). The flow line which characterizes structural turbulence from its onset in the laminar region passes well into the fully turbulent region (Reynolds turbulence) with virtually no change in slope, implying that the same molecular oscillations or segmental motions responsible for structural turbulence are now operative in drag reduction. The persistence of structural turbulence at very low concentrations is rationalized on the basis of Busse's explanation of the role of polymer entanglements in viscosity and elastic turbulence.

INTRODUCTION

Ram and Tamir¹ have measured steady state capillary flow for solutions of polyisobutylene in kerosene and mineral oils at rates well below the critical Reynolds number for the laminar-to-turbulent transition ($R_n \cong 2300$). Their experimental results have indicated that structural turbulence—a term coined by Ostwald and Auerback² in 1926—can be observed in flowing polyisobutylene solutions at concentrations greater than 0.1% for polymers having molecular weights in excess of 1.7 million. According to Ram and Tamir,¹ the onset of structural turbulence is characterized by a sharp and steady rise of the apparent viscosity with increasing rates of shear while the flow is still well below that for the critical Reynolds number. For example, Ram and Tamir have observed early turbulence in the Reynolds number region of 1 to 1000 for polyisobutylene solutions in oil, dependent upon sample molecular weight and concentration.

Structural turbulence is considered to be characterized by a critical wall shear stress which has a unique value for a particular substance. Structural turbulence, as its name implies, is believed to result from the collapse of structure in the system observed when this critical shear stress is exceeded. In one study vortices were actually observed.³ It should be pointed out that structural turbulence is generally detected only in tubes of small diameter where the high shear stresses needed to produce the effect can be reached below the transition Reynolds number for Reynolds turbulence. In the case of polymer solutions, the probability of observing structural

turbulence increases as the polymer concentration increases to the point where networks of entangled molecules can be formed. Such entanglement is probable at concentrations above the polymer critical concentration, i.e., that concentration where random coils just begin to touch. It has been recently conjectured⁴ that, since the onset of drag reduction like the onset of structural turbulence scales with the wall shear stress, both shear stress values would be identical provided low enough concentrations could be studied. It is the purpose of this report to examine the structural turbulence-concentration relations for a known drag reduction agent—Polyox Coagulant—and to examine the possible relevance of structural turbulence to drag reduction.

EXPERIMENTAL

Materials

A special narrow-cut fraction of Polyox Coagulant was obtained from the Union Carbide Corporation. Its intrinsic viscosity was 22.6 in aqueous solution, which corresponds to a molecular weight of 7.0×10^6 by the intrinsic viscosity-molecular weight relation reported by Shin.⁵ Viscosity measurements were made in a Cannon-Fenske viscometer at $30.08^\circ \pm 0.04^\circ\text{C}$. Flow times were determined to within 0.1 sec. Freshly distilled water was used for the preparation of all solutions.

Treatment of Solution

The properties of dilute Polyox solutions may be altered by the procedures used in preparation and storage. For example, if a 5-ppm Polyox solution is heated at 95°C for 1 hr in contact with an air interface, or if it is stored at room temperature (27°C) for a week, all drag-reducing properties are lost.

Irreproducible mixing techniques cause large variations in solution properties. Good reproducibility of solution properties resulted when the following scheme was adopted for solution preparation. All dilute solutions were prepared by sprinkling the additive over a large surface of the fluid to avoid clumping of particles and to allow solution to take place by diffusion over a period of several days. An occasional gentle stirring with a glass rod ensured adequate dispersion of solute. In this way errors caused by variations in mixing technique were avoided. Solutions were immediately stored at 6°C and were used within four days of preparation. It was found that the drag-reducing properties of 5 ppm Polyox Coagulant were virtually unchanged when stored at 6°C for more than one week.

Apparatus for Measurement of Structural Turbulence

Figure 1 is a diagram of the flow equipment used to detect structural turbulence in the laminar flow zone and to determine the extent of drag reduction in the turbulent region. Essentially the device is a motor-

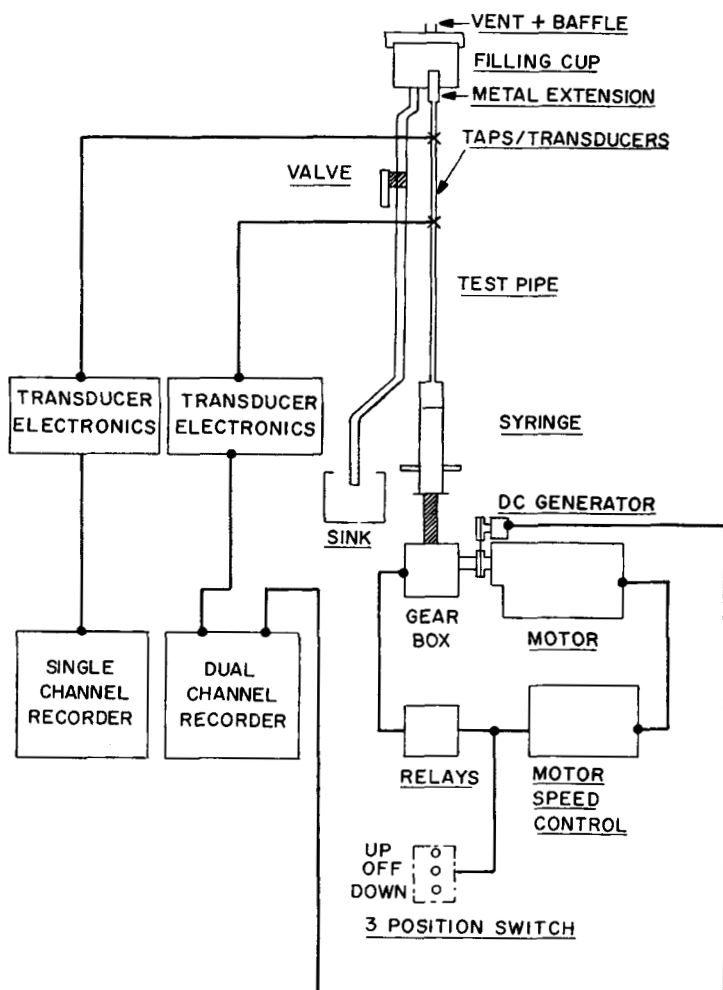


Fig. 1. Turbulent flow rheometer.

driven metal syringe (Becton, Dickinson and Company), the delivery rate of which is determined by a motor speed controller (Model S-30, G. K. Heller Company). The flow pipe is a Pyrex capillary tube with a diameter of 0.1575 cm. The first tap is placed 200 diameters from the entrance and the second tap is placed 100 diameters from the first. Statham universal transducers with 10 psi pressure diaphragms were used to determine the pressure drop between taps. The pressures were recorded on a Varian dual-channel recorder. The flow rate was monitored by a small dc generator (Electric Indicator Company) coupled to the motor drive. The generator output was proportional to motor rpm (and hence to flow rate) and was used to drive another recorder. The linear actuator (Airborn Sales Company) which directly drove the syringe plunger was coupled to

the motor. The travel limits of the actuator were set by microswitches within the actuator gear box. The actuator was driven by a $\frac{1}{4}$ -hp electric motor (nominal 3400 rpm). Motor coasting was avoided by taking advantage of the dynamic braking action of the S-30 Motor Controller through a minor circuit modification involving an additional pair of relays which were individually activated by the actuator microswitches. The apparatus is capable of operating in the Reynolds range of 500 to 14,000 for a fluid having the nominal viscosity of water. The natural transition point from laminar to turbulent flow for the 0.1575-cm capillary tube occurred at $R_n = 3000$. In essence, the apparatus is a modified version of a simpler device used earlier by Hoyt.⁶

RESULTS

Drag Reduction

Drag reduction appears to occur in two modes—at least in an analytical sense. Figure 2 presents data for a 1.03-ppm Polyox Coagulant solution in water. Note that the flow of the solution continues in a laminar-like fashion beyond the transition Reynolds number for Reynolds turbulence (circa 3000 for the capillary tube used). This extended laminar region has been previously observed⁷ for polyisobutylene solutions in cyclohexane.

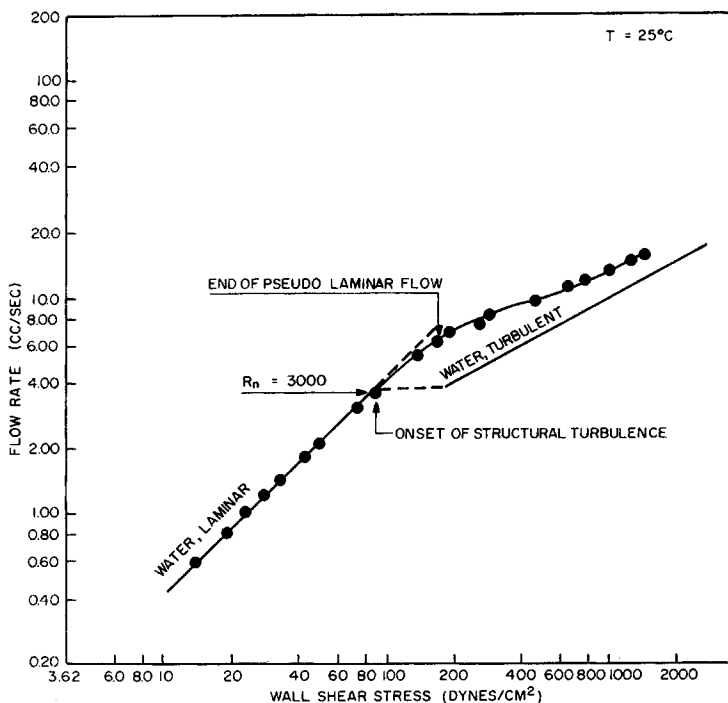


Fig. 2. Flow of 1.03 ppm Polyox Coagulant.

In the present case, when the shear stress value of 170 dynes/cm² is exceeded, the slope of the laminar-like or pseudolaminar line rapidly changes and ultimately appears to nearly parallel the turbulent flow line for water. This second kind of behavior suggests a less laminar-like flow and recalls the drag reduction flows observed in larger tubes.

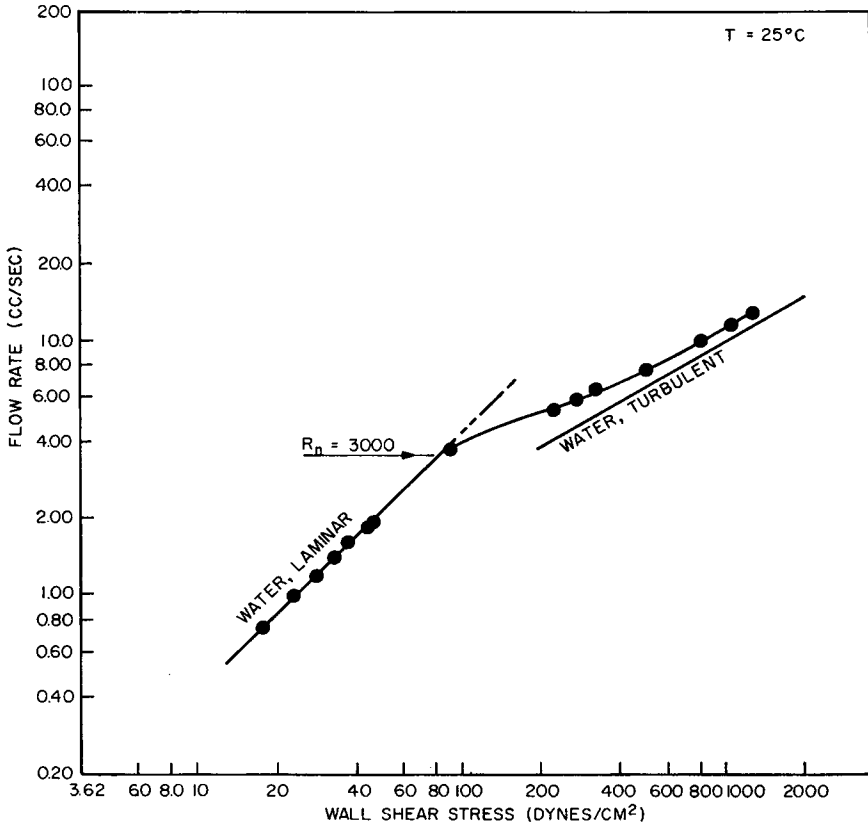


Fig. 3. Flow of 0.28 ppm Polyox Coagulant.

Figure 3 displays the flow behavior of a very dilute 0.28-ppm Coagulant solution. In this case there appears to be little or no extension of the laminar flow line. Instead, after passing through the transition region, the flow lies above and nearly parallel to the turbulent flow line for water. This kind of flow is again reminiscent of flows observed in larger tubes where drag reduction effects are presumed to occur solely within the viscous sublayer of the flow.

Structural Turbulence

Figures 4 to 6 display evidence for the onset of structural turbulence (detected as a sudden increase in the apparent viscosity) over a 100-fold range of concentration. For example, the 10.3-ppm Coagulant solution of

Figure 4 shows a sudden increase in apparent viscosity at a wall shear stress value of 35 dynes/cm². Above the wall shear stress value of 110 dynes/cm², the flow exceeds the critical Reynolds number for Reynolds turbulence, and the 10.3-ppm Coagulant solution then operates as an effective drag-reducing fluid.

A number of determinations were made of the onset of structural turbulence as a function of polymer concentration. Figure 7 shows the ex-

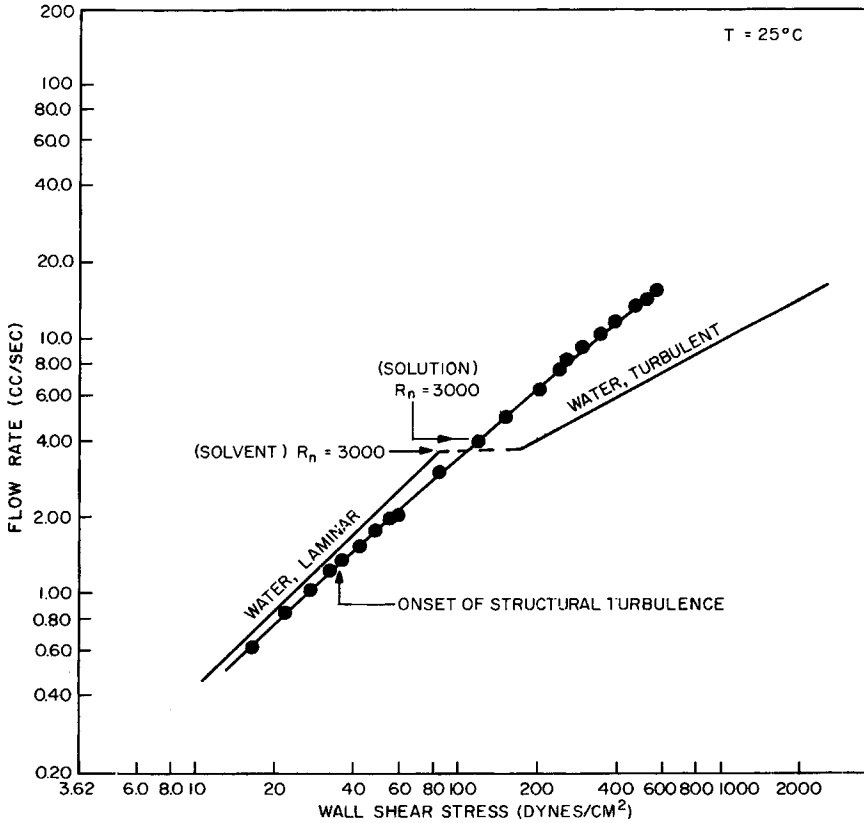


Fig. 4 Flow of 10.3 ppm Polyox Coagulant.

perimental results in graphic form. The curve has two legs. The right leg of the curve qualitatively corresponds to the trend previously reported by Ram and Tamir¹ for flowing polyisobutylene solutions in which they observed that the critical wall shear stress characterizing the onset of structural turbulence decreases with decreasing concentration. It should be noted that below a certain concentration, circa 10 ppm, the critical wall shear stress rises toward that of the solvent and generates the left leg of the curve.

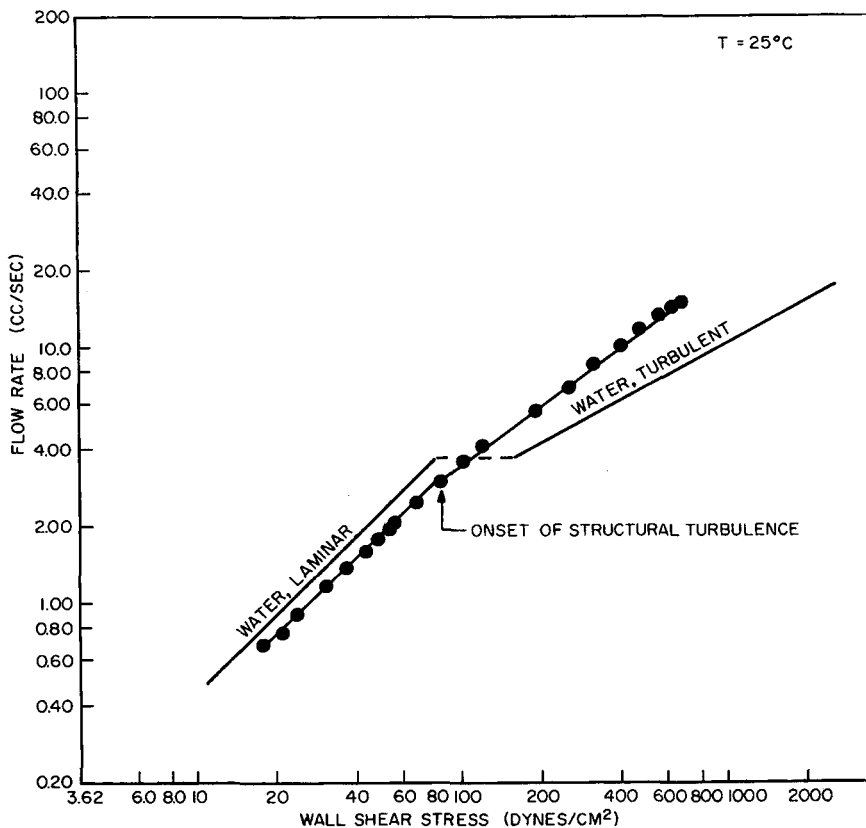


Fig. 5. Flow of 100 ppm Polyox Coagulant.

DISCUSSION

Conditions for the Observation of Structural Turbulence

In order to observe structural turbulence in a given tube, it is necessary that sufficient wall shear stresses be developed to promote the effect below the usual transition point corresponding to Reynolds turbulence (circa 2300 for most tubes). Tabulated literature data¹ suggests that the wall shear stress which characterizes the onset of structural turbulence is roughly independent of tube diameter. If this is true, it may be possible to estimate the maximum diameter of tube in which structural turbulence might be observed, provided the critical wall shear stress value for the onset is known for the particular fluid or agent concentration in a smaller tube. The usual definitions apply:

$$\tau_{\omega} = \frac{fu^2\rho}{8}$$

$$f = \frac{64}{R_n}$$

$$R_n = \frac{\rho u D}{\eta}$$

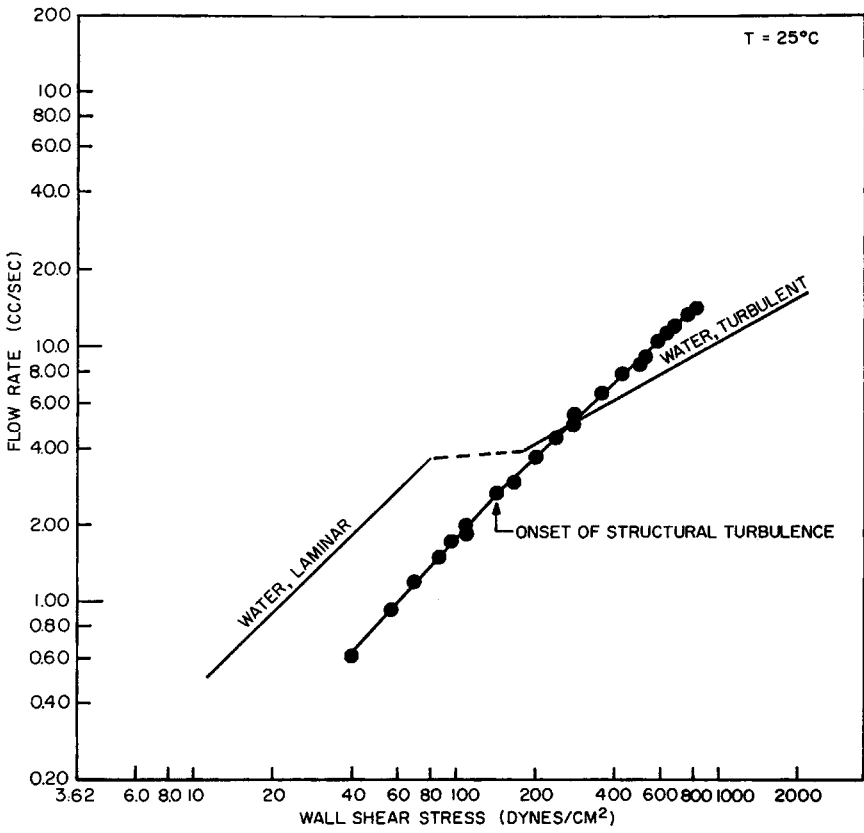


Fig. 6. Flow of 1010 ppm Polyox Coagulant.

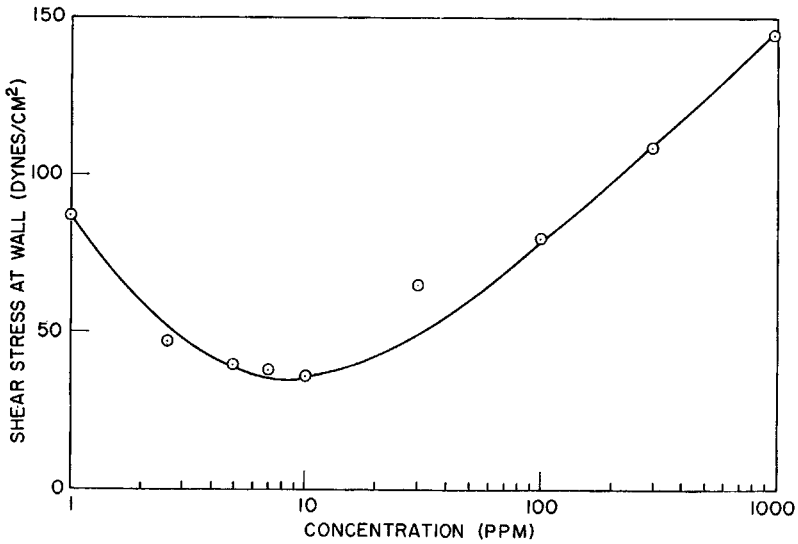


Fig. 7. Critical shear stress. Concentration effect for onset of structural turbulence in Coagulant solutions.

where τ_ω = wall shear stress, u = mean velocity of fluid, ρ = density of fluid, R_n = Reynolds number, f = friction factor, D = diameter of tube, and η = viscosity of fluid.

By appropriate combination of the above definitions one obtains

$$D_{\max} = 2\eta \sqrt{\frac{2R'_n}{\tau_\omega^* \rho}} \quad (1)$$

where D_{\max} = maximum diameter to observe structural turbulence, R'_n = transition point for Reynolds turbulence, and τ_ω^* = wall shear stress value which characterizes the onset of structural turbulence. If the above condition can be met, both drag reduction and structural turbulence can be observed in the same tube.

It is not surprising that structural turbulence had not been observed for flowing Polyox solutions. Noting that the minimum shear stress for the observation of structural turbulence is 35 dynes/cm² and assuming that the transition Reynolds number is normally 2300 for Reynolds turbulence, it is found that the largest pipe diameter for the observation of structural turbulence in Polyox Coagulant solutions would be 0.205 cm using eq. (1). All previous data collected on Polyox solutions—with the exception of Hoyt's work⁶ done at one fixed flow rate—have been in tubes of larger diameter.

Structural Turbulence and Drag Reduction

It appears that for the first time both drag reduction and structural turbulence have been observed within the same apparatus for a given fluid (see Figs. 2 and 4, for example). Moreover, these effects have been demonstrated in extremely dilute solutions in the present case. Referring to Figure 4 specifically, it is of some interest to note that the 10.3-ppm solution flow line passes well beyond the transition point for Reynolds turbulence with virtually no change in slope. That is, the same kind of viscoelastic behavior responsible for structural turbulence appears to be now operative in drag reduction. There is no change in slope to suggest any changes in polymer oscillations or conformation. The data appear to suggest that once sufficiently high shear stresses have been developed (in the laminar zone) to set the polymer coils (or structures) into viscoelastic vibrations or oscillations, they are immediately available in these behavioral modes to effectively interact with turbulence. These observations seem to strengthen Ram's recent suggestion that structural turbulence and drag reduction are both controlled by viscoelastic behavior.⁸

The onset of drag reduction, like the onset of structural turbulence, is characterized by a critical wall shear stress which is essentially independent of tube diameter over the range observed. The lowest shear stress (see Fig. 7) which can initiate structural turbulence is 35 dynes/cm² for a 10-ppm Coagulant solution, flowing in the 0.1575-cm tube. For the onset of drag reduction, one can estimate a value of approximately 4 dynes/cm² for

a polyethylene oxide polymer close to the molecular weight of Coagulant (~ 6.1 million) using the data of Virk et al.⁹ taken in a 3.21-cm pipe. The observation that the onset of drag reduction can occur at shear stresses an order of magnitude lower than the onset of structural turbulence might imply that either the appearance of turbulence eddies (Reynolds turbulence) triggers the oscillation of polymer molecules or that a pipe diameter effect is involved so that the two sets of data cannot be directly compared.

Structural Turbulence— Polymer Concentration Effects

The appearance of the curve in Figure 7 might be explained qualitatively in the following manner. Starting from the point of highest concentration, as the polymer concentration decreases the shear stresses needed to disrupt the structure of the polymer-thickened fluid become less since the number of polymer entanglements decreases with concentration. Ultimately the point is reached concentration-wise where further entanglement is improbable, the structural turbulence then becoming a function of the oscillations of individual coils rather than the disruption of entangled coil networks as before. Below this characteristic concentration, the critical wall shear stress characterizing the onset of structural turbulence appears to rise ultimately to that of the solvent as polymer coils become increasingly isolated from each other and the disturbance caused by polymer oscillation becomes less detectable.

While this view seems qualitatively satisfying, it is somewhat in opposition to the expected observations, i.e., the minimum in the plot should occur at the polymer critical concentration where random coils just begin to touch to form entangled networks. This is computed to be 260 ppm for Coagulant solutions rather than the experimentally observed 10 ppm. The appearance of this minimum at a concentration much lower than the computed critical concentration (which is determined under rest conditions) might be rationalized on the basis of Busse's explanation of the role of entanglements in viscosity and elastic turbulence.¹⁰ Busse cites the experimental results of Peterlin et al.^{11,12} on flowing dilute solutions of poly(methyl methacrylate) ($\sim 0.1\%$) in a high-viscosity solvent (Aroclor). He notes that these workers found visual evidence that a nominally uniform shearing deformation can change a homogeneous solution into a macroscopically heterogeneous system of gel particles dispersed in a solution of lower concentration. Busse proposes that the greater the diameter of a random coil molecule, the greater the average velocity range that it will span (in laminar flow) and the greater the probability that its path will intersect those of other molecules and form long-chain entanglements. Busse further suggests that at very high shear rates one can expect most of the molecules to be tied up in clusters. If this explanation is accepted, the downward displacement of the minimum concentration from that expected at rest conditions (260 ppm) to that observed under flow conditions (10 ppm) becomes more credible. Finally, it has been recently suggested⁴ that drag reduction (the Toms effect) may also result from the formation and/or

the action or breakup of macromolecular entanglements in turbulently flowing polymer solutions.

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