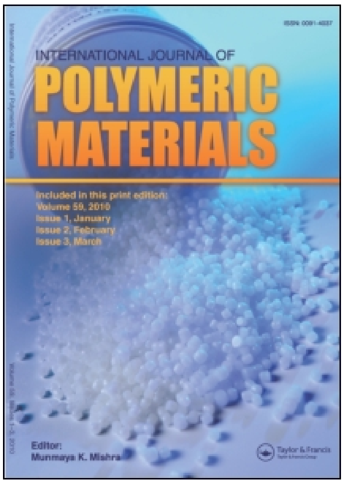

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

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To cite this Article Ferguson, J. and Hudson, N. E.(1993) 'Elongational Viscosity and Relaxation Processes in Polymer Solutions', International Journal of Polymeric Materials, 20: 3, 181 — 191

To link to this Article: DOI: 10.1080/00914039308048360

URL: http://dx.doi.org/10.1080/00914039308048360

Intern. J. Polymeric Mater., 1993, Vol. 20, pp. 181–191
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Printed in Malaysia

Elongational Viscosity and Relaxation Processes in Polymer Solutions

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(Received January 30, 1992; in final form June 26, 1992)

Problems associated with measurements and interpretations of elongational viscosities are reviewed.

KEY WORDS Elongational viscosity, polymer solutions, relaxation processes.

INTRODUCTION

The definition of elongational viscosity, $\eta_E = \sigma_E/\dot{\varepsilon}$, requires, on a strict theoretical basis, that the stress and strain rate are constant at the time of measurement. While it is more or less possible to achieve this state with very high viscosity fluids such as polymer melts, it is almost impossible with a low viscosity fluid. For many polymer solutions, and even such polymer melts as Nylon 66 and polyethylene terephthalate, it is necessary to use a "non-equilibrium" method. The resulting viscosity, $\eta_E(t)/\dot{\varepsilon}(t)$, will be an instantaneous or apparent value influenced by the technique and such experimental variables as stretch rate, flow history, etc. While this would tend to give a great degree of uncertainty as to how best to interpret the data from non-equilibrium flow, it has to be realised that the form of the flow curves may be a reasonable representation of the true flow. Münstedt and Laun[1] have shown that for low density polyethylenes (Figure 1), the maximum (peak) value, as well as the strain rate at which departure from Newtonian flow occurs, is a function of the breadth of the molecular weight distribution M_w/M_n, where M_w is the weight average and M_n is the number average molecular weight. In branched low density polyethylene, the peak height is also a function of the degree of branching.

Figure 2 shows data obtained with a solution of polybutadiene in decalin. The flow curve of this solution also exhibits a peak value and, most striking, a minimum followed by a rise to what would appear to be a limiting value of strain rate (or total strain). In this strain hardening region the fluid is spinnable, and the dominant mode of deformation is elastic rather than viscous.[2] In other words, the fluid showed solid-like elastic characteristics.

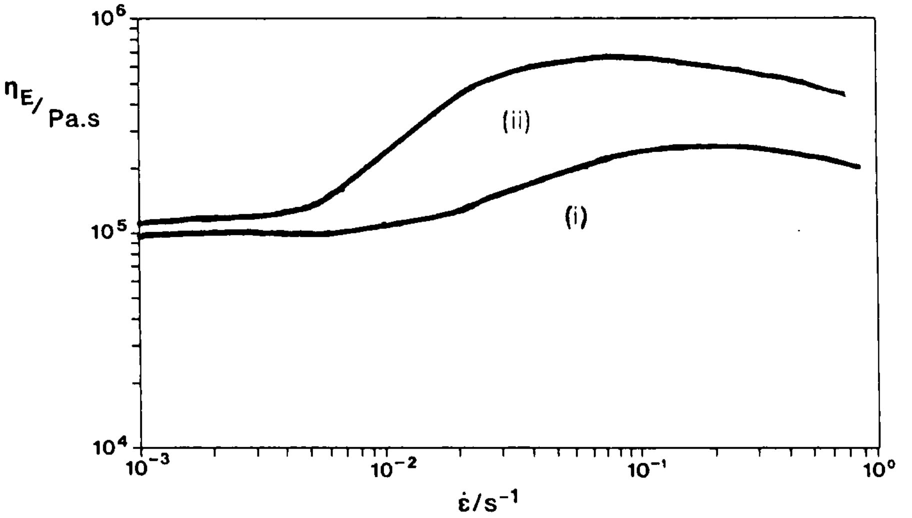

FIGURE 1 Elongational viscosity, η_E, as a function of rate of strain, $\dot{\varepsilon}$, for two low density polyethylenes of different molecular weight distributions at 150°C, from the data of Münstedt and Laun.[1] (i) M_w/M_n = 7.0 and (ii) M_w/M_n = 24.2.

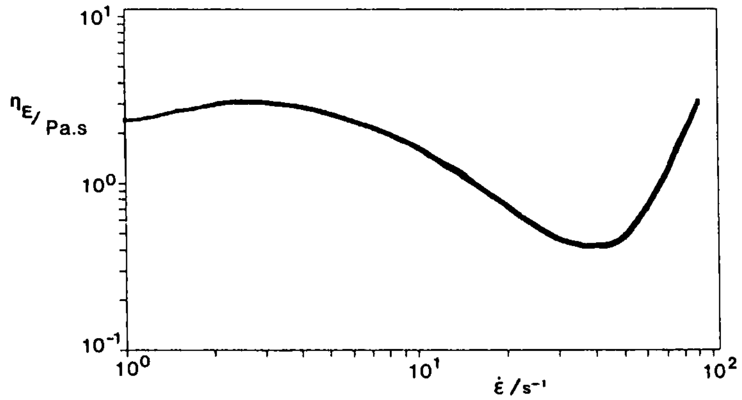

FIGURE 2 Apparent elongational viscosity, η_E, as a function of rate of strain, $\dot{\varepsilon}$, for a 6.4% (w/w) solution of polybutadiene in decalin.

Not all fluids necessarily follow the behaviour shown in Figures 1 and 2. Newtonian, strain thinning, or monotonic strain hardening are also possible.

The purpose of this paper is to examine the apparent elongational flow behaviour of polymer solutions under different conditions of measurement and show the influence of relaxation time on the mode of deformation in a stretching flow. Firstly, the different techniques presently used to measure elongational viscosity are described. Then, the results for test fluid using a number of these methods are compared. Thirdly, the effects of polymer conformation are examined. This is followed by a discussion of complexation effects in an elongational flow field. Finally, the topic of spinnability with respect to relaxation processes is considered.

EXPERIMENTAL METHODS

The techniques fall naturally into two classes.

Controllable Experiments

The sample is held at both ends by clamps or rotating gear wheels and is then elongated.

Homogeneous stretching method.[3] To maintain a constant rate of elongation as the sample stretches, the velocity of the movable grip must vary exponentially with time. The movement of the clamps determines the strain rate that can be attained, given that the motion must be sustained long enough for the stress to reach a steady state. Stress itself is measured by a strain gauge or a linear displacement voltage transducer attached to a spring. The experiment is done with the sample immersed in a fluid bath (usually silicone oil) to isolate it from temperature changes and gravity.

Constant stress devices. These are essentially of the creep experiment type.[4,5] They apply a constant stress by applying a force that decreases the load at the same rate as the cross section area of the extending polymer decreases.

The lubricated die.[6] In a flow channel of decreasing cross section there will be a considerable shear contribution as well as an elongational component to the resultant stress. The shear can be removed by coating the walls of the die with a low viscosity fluid. This creates slip at the wall and the fluid under examination then experiences a pure elongational flow.

Non-Controllable Experiments

The sample is not held at both ends. The motion depends on the flow of material.

Spinning. A filament of polymer solution or melt is extruded from a die and is then caught and extended by a rotating drum or vacuum tube. The force generated is measured either at the die or at the take-up roller. Alternatively, changes in pressure drop across the die can be monitored. Since there is no control over the rate of elongation at any point along the filament, its diameter profile must be measured. This is done either photographically or by using a video camera connected through a digitizer to a desktop computer. The changing rate of elongation along the filament means that the elongational stresses generated are transient. The data should not, therefore, be compared directly with the apparently equilibrium results obtained from the controlled experiments. The problem is that although the flow may be steady in a Eulerian sense (i.e. the velocity at a particular point on the threadline does not change with time) it is unlikely to be steady in a Lagrangean sense (because the strain rate experienced by a given fluid element will generally change with time as it passes along the threadline). The spinning experiment illustrates the typical dilemma facing the rheologist interested in measuring elongational viscosity. These measurements are often easy to perform, the general kinematics can be determined simply and a suitable stress value can be found. However, their interpretation, as will be apparent from the results found so far, is still a matter of dispute. Nevertheless, two points can be made that illustrate the usefulness of the information:

(i) the technique resembles many processes involved in the fabrication of polymers into plastic articles; and
(ii) when experiments are carried out on Newtonian fluids the Trouton ratio of three is obtained at zero, and higher rates of extension, as predicted by theory.

The spinning technique certainly provides a convenient measure of the resistance experienced by a non-Newtonian fluid in a flow dominated by extension. The principle is now the basis behind a commercially available elongational rheometer.[2,7,8]

Contraction flows.[9] This method has the advantage of being useful for mobile fluids as well as for polymer melts. The fluid flows from a large diameter tube into one of much smaller diameter—the ratio of the diameters being about eight to one. The flow usually consists of a central core that is dominated by elongation and an outer shear dominated vortex region.

Because of the mixture of flow types, the interpretation of the data is difficult and like all other aspects of elongational flow is the subject of much current research.

Open siphon method.[10] This uses the ability of a highly elastic liquid to flow from a reservoir up into a nozzle (the open siphon effect). The problems of interpretation are the same as those of the spinning experiment and the system is often highly unstable.

Opposed jets.[11,12] When a fluid is extruded either into or out of two narrow diameter orifices held a small distance apart, then the flow field between the orifices contains a stagnation point at the centre. The region containing this stagnation point either parallel (for inflow) or perpendicular (for outflow) to the line joining the orifices is one of high extensional deformation. The extensional stresses generated can be determined from the deformation of the tubes containing the orifices, and the strain rate from the geometry of the configuration.

RESULTS FOR A TEST FLUID

At a meeting at Chamonix in January 1988,[13] it was apparent that the extensional data obtained from the many different instruments being used were significantly different. The organising committee suggested that a cooperative project be established for measurements to take place on a single fluid. The test fluid selected was a Boger fluid, prepared at Monash University (hence it was titled M1). This fluid was dispatched to participants in the summer of 1988. The project was brought to its conclusion at the special workshop held at Combloux during March 1989. A special issue of the *Journal of Non-Newtonian Fluid Mechanics*[14] has recently been published containing the papers presented at this meeting. One session concentrated on the simple and complex shear flow properties of M1. Steady shear and dynamic data from a wide range of instruments were presented. The results showed considerable agreement between the various laboratories. In particular, the dominant relaxation time for this fluid was found to be about 0.3 seconds. Flow rates in steady shear covered 6 decades while frequencies in oscillatory shear were over 5 decades. Substantial stress overshoots were found above a critical shear rate, suggesting a stability problem with the fluid (possibly connected to the unusual behaviour in extension noted below).

In the main session, the properties of M1 in extension were discussed. The majority of experiments could be placed in one of two categories, namely spin line or opposed jets. The apparent elongational viscosity, calculated from the full equations of motion, increased with strain up to a maximum, before falling slightly. The level of this maximum depended upon the speed of the take-up drum, showing that the elastic response of the fluid was the dominant feature. As shown in Figure 3, there is a variation of strain rate with distance along the spin line, which is typical of results with this type of rheometer. It has therefore become customary to use average values of stress and strain rate from each experiment. The envelope of results from spin line experiments from several authors is shown in Figure 4 as area (a). Also shown in this Figure is the envelope of results obtained with elongational rheometers which utilise opposing jets, as area (b). Apparent elongational viscosity increased with strain rates, resulting in Trouton ratios from 1–100, at least an order of magnitude below those of the fibre spinning technique. Müller *et al.*[15] carried out birefringence experiments simultaneously with pressure drop measurements and showed that for strain rates up to 7 s^{-1}, the extensional flow field was about one fifth of the width of the jet orifices. Therefore, although their

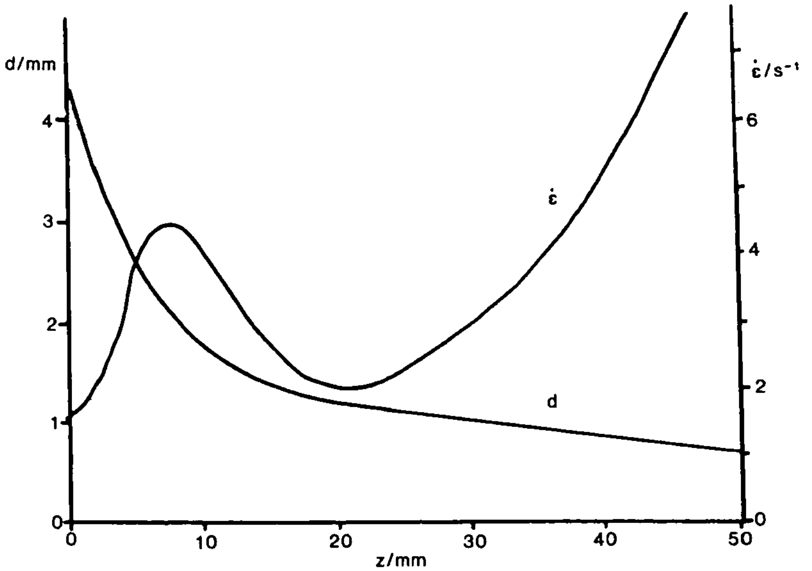

FIGURE 3 Typical data from a spin line experiment on test fluid M1. Filament diameter, *d*, and strain rate, $\dot{\varepsilon}$, as functions of distance, *z*, down the spin line.

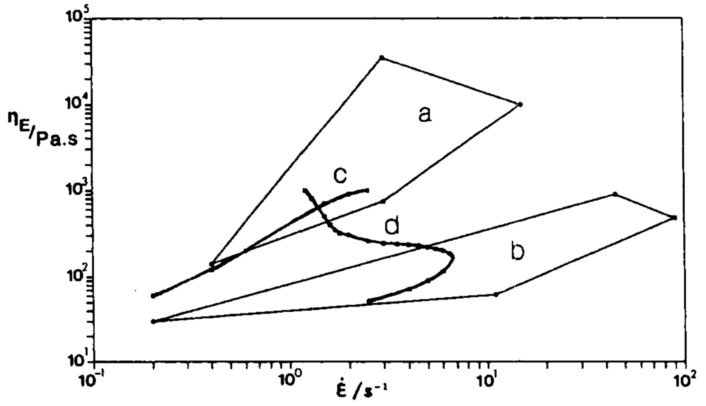

FIGURE 4 Resume of results from several laboratories on test fluid M1. Apparent elongational viscosity, η_E, as a function of rate of strain, $\dot{\varepsilon}$: (a) envelope of results from spin line experiments; (b) envelope of results from opposed jet experiments; (c) corrected results from opposed jet experiments[15]; and (d) results from the pendant drop technique.[17]

uncorrected results fell within the envelope (b), allowing for the width of the extensional field produced curve (c), which connects with the lower portion of envelope (a). They also showed that above this critical strain rate, the flow field became very erratic, so that great care had to be taken in interpreting results from an opposed jet system above this value. James and Chandler[16] used a converging channel extensional rheometer, the results from which fell within the envelope (b).

Jones *et al.*[17] showed results from pendant drop experiments, which illustrated quite dramatically the effects of the elasticity of the fluid, with the drop accelerating, decelerating almost to a stop, then accelerating again, as it pulled the filament from the upper capillary. The strain rate profile is shown in Figure 5. The calculated elongational viscosities are shown in Figure 4 as curve (d), where it can be seen that for short times the viscosity is within envelope (b), but as the flow time exceeded the relaxation time of the fluid, the extensional viscosity increased to finish within the envelope (a). The effect of flow time is more readily seen in Figure 5 where the elongational viscosity of the fluid generated by the falling drop is shown as a function of time.

EFFECTS OF POLYMER CONFORMATION

It is well known that the addition of acid to aqueous solutions of polyacrylamide, reduces the degree of ionisation of those acid groups formed by partial (approximately 10%) hydrolysis of the amide groups. This allows the polymer to form a tight coil with a reduction in the viscosity of the solution. Conversely, addition of alkali increases the degree of ionisation, the coil expands, and the solution viscosity is enhanced. A polyacrylamide of molecular weight about 5 million dalton was used in aqueous solutions of various concentrations. The reagents used for varying the pH of the solutions were hydrochloric acid and sodium hydroxide. The steady state apparent viscosities of one of these solutions at various values of pH and

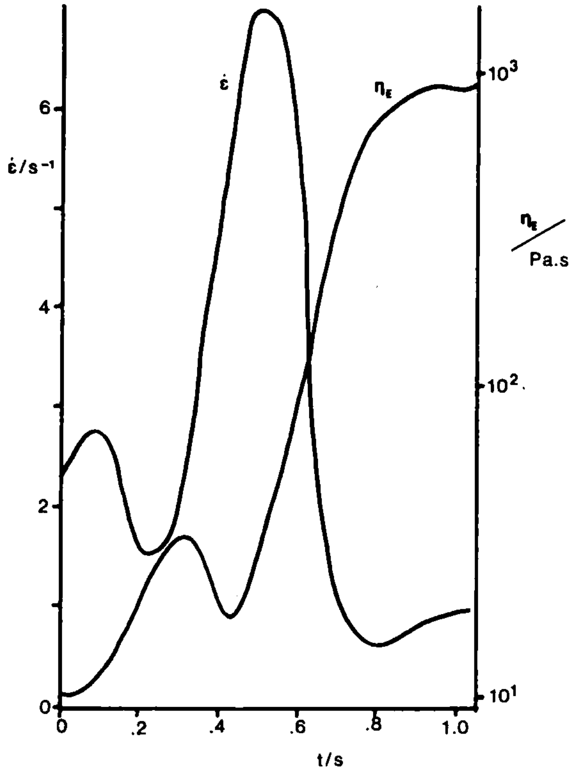

FIGURE 5 Rate of strain, $\dot{\varepsilon}$, and apparent elongational viscosity, η_ε, as functions of time of fall, t, from the pendant drop technique,[17] for test fluid M1.

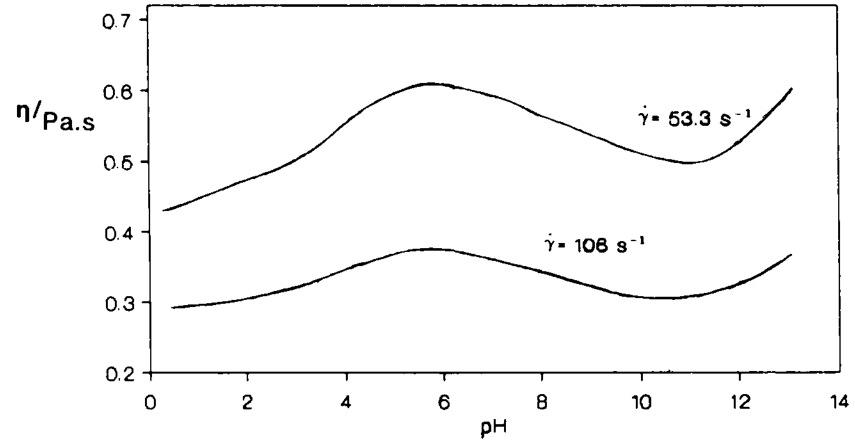

FIGURE 6 Steady state apparent shear viscosity, η, at two values of the applied shear rate, γ, as functions of the pH of a 2% (w/w) solution of polyacrylamide in water.

shear rate are shown in Figure 6. As pH increases, apparent viscosity increases, passes through a maximum, decreases slightly, then rises rapidly at high pH due to further hydrolysis of the amide groups.

As seen in Figure 7, the elongational viscosity of these solutions increases with strain rate, passes through a maximum and then a minimum, finally increasing rapidly for the reason given above. The values obtained also increased with pH as the solution was changed from acid to neutral.

COMPLEXATION EFFECTS IN EXTENSIONAL FLOWS

Recent work on extensional flow of polymers in a variety of solvents has indicated that polymer-polymer complexation can be induced in strong flow fields.[18] In the extreme case, phase changes have been shown to occur, both in shear and, more recently, in elongation.[19] Similar phenomena are known to occur in solutions at rest, particularly where strongly interacting high molecular weight polymers are present. Such interactions can be highly selective, both in terms of species taking part, and in terms of molecular weight. In one review, Kabanov and Papisov[20] generalised the experimental and theoretical information about the formation of complexes between complementary synthetic polymers in dilute solution. They summarised their results as follows:

a. A strong dependence of the stability of the polycomplex on the length of the oligomer unit.
b. The high selectivity of these reactions to the length of the oligomer chain, which enables polydisperse polymers of relatively low molecular weight to be separated into narrow fractions.
c. An exceptionally high selectivity of reaction between the macromolecules with respect to the chemical structure of the reactants, as indicated by the fact that among chains of different structure, a macromolecule almost without fail finds the "strongest" partner and combines in a polycomplex only with this.

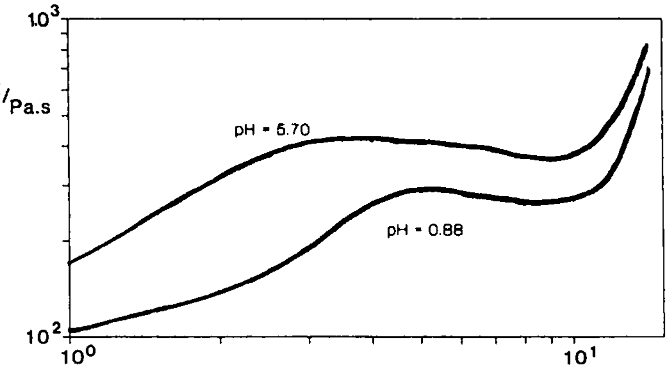

FIGURE 7 Apparent elongational viscosity, η_E, as a function of rate of strain, $\dot{\varepsilon}$, for a 2% (w/w) solution of polyacrylamide in water at two values of the pH.

All of the papers in this review essentially dealt with solutions at rest, although it should be noted that dilute solution capillary viscometry is frequently used to monitor the changes occurring. This itself may well influence the rate and extent of complexation. In elongational flow it would appear likely that the extensional process would affect such polymer-polymer interactions in several ways. Firstly, since polymer-polymer entanglements increase significantly in lifetime as the molecular weight of the entangled species rises, the molecular weight effects may well be enhanced. Secondly, because of the alignment of polymer molecules at high stretch rates, interactions normally not sufficient to cause complexation in random coil polymers, will become important. The rate at which interactions will occur can be expected to be greatly enhanced. The elongational flow behaviour of a number of polymer-solvent systems are now described and discussed in terms of the above effects.

Throughout this series of experiments, the laboratory was at a constant temperature of 18 ± 0.5°C. In order to test the accuracy of the commercial elongational viscometer (EV) with a vacuum tube take-up, the first fluid tested was Silicone Fluid, graded 250cS, supplied by Hopkin and Williams. Using a Weissenberg Rheogoniometer, its viscosity in shear was found to be constant at 0.4 Pa.s (4.0 Poise). In the modified EV, the filament length was kept at approximately 10 mm. The flow rates were found to be linear with applied pressure, even when large variations of applied vacuum were used (i.e. there was no enhancement of flow rate with applied vacuum). Elongational force readings were noted, and a series of photographs taken. The results showed that within experimental error, the slope of stress to strain rate had a value 1.2, so the elongational viscosity was 3 times the shear viscosity, signifying a Newtonian fluid. Strain rates of up to 312 s^{-1} were achieved. Next, a series of aqueous solutions (500, 1000, 2000, 3100 ppm) of polyethylene oxide, ($M_w \approx 4 \times 10^6$ dalton) supplied by BDH, were used. All had zero shear viscosities, measured on a Weissenberg Rheogoniometer, of between 5 and 40 mPa.s. On the EV, there was a slight enhancement of flow rate below free flow and that under applied vacuum. Filament lengths were varied from 5 to 14 mm. Trouton ratios, varying with strain rate, of between 6 and 50 were obtained. Strain rates up to 2000 s^{-1} were achieved. The results for all four solutions are shown in Figure 8, where it can be seen that elongational viscosity appears to rise, pass through a maximum at a strain rate of 100 to 200 s^{-1}, decrease, and then at a strain rate of about 700 to 900 s^{-1} rise sharply. These results compare very favourably with those given by Keller *et al.*[11] for similar solutions tested on their opposed jet system.

Strain hardening in even these dilute solutions is not necessarily due to entanglements, but may also be due to strain induced complexation. It is worth noting that for these solutions, sudden cessation of elongational strain produced the type of droplet formation described previously[19] and which is indicative of phase change resulting from complexation.

The phenomenon, i.e. complexation, has also been shown to occur[18] in solutions of anti-misting agent FM9 in dipropylene glycol monomethyl ether (DPM). To investigate the influence of the solvent quality on complexation, solutions of FM9 in both DPM and Paraffin have been subjected to shear and elongational flow.

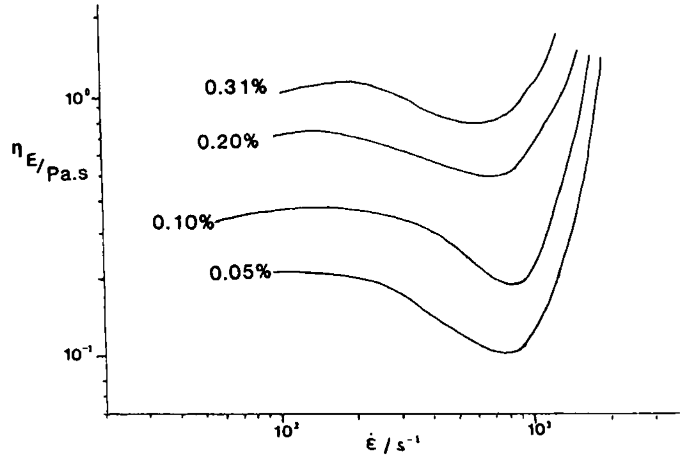

FIGURE 8 Apparent elongational viscosity, η_E, as a function of rate of strain, $\dot{\varepsilon}$, for solutions of polyethylene oxide (WSR-301) at four different concentrations (w/v).

Using a Weissenberg Rheogoniometer, solutions of FM9 in DPM were tested at various shear rates. It was found that these solutions were not only shear thinning, but were also thixotropic.

The extensional viscosity of a 2% solution was found using the pendant drop method[21] and the results indicated monotonic strain hardening. Solutions of FM9 in Paraffin were tested on a controlled stress rheometer. Below a critical shear stress (different from each concentration) the polymer solutions were slightly shear thinning. Above this shear stress, the shear rate dropped dramatically, indicating a rapid rise in viscosity. Examining the solution after testing revealed that it had separated into two phases. One was gel-like in appearance, and the other had similar superficial properties to the solvent. These two phases were subjected to infrared analysis. The peaks for the gel-like phase corresponded to adsorptions due to dissolved polymer. The fact that these were so much stronger than those in either the unsheared solution or the low viscosity phase showed that the concentration of polymer is considerably higher in the gel phase than in the unsheared solution. This is unequivocable proof that the shearing action had produced two phases with different concentrations of dissolved polymer. It should be noted that a similar gelling was induced in elongation.

SPINNABILITY AND RELAXATION PROCESSES

It will be clear from the results presented here that extensional flow characteristics are closely controlled by the relaxation processes in the fluid. In particular, the relaxation time appears to play a critical role. This is certainly the case in determining whether or not the fluid will be spinnable. The condition for spinnability is that the elongational viscosity must rise faster than the rate of decrease of the cross section area of the extending filament. The fluid must, therefore, be strain hardening. This can only be achieved where the lifetime of the entanglement chain junctions is long relative to rate of extension (high Deborah No).

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