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Flow of monodisperse polystyrene solutions through porous media

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Abstract: In this work, we study the origin of the extension thickening commonly observed when solutions of flexible polymers flow through porous media and ideal elongational flows. We have used randomly packed beds of glass beads as porous media. We have performed experiments with closely monodisperse atactic polystyrene of different molecular weights dissolved in organic solvents. The use of a closely monodisperse polymer allowed us to make a more meaningful comparison between the results obtained using opposed jets and porous media flow, as compared to previous works on polydisperse polymers. The results indicate that the coil-stretch transition of isolated polymer molecules in solution cannot be the only mechanism responsible for the extension thickening. It is clear that part of the observed effect is due to the extension of isolated molecules, but the main factor causing a great increase in the elongation viscosity beyond a critical strain rate is the formation of transient entanglement networks.

Key words: Porous media – monodisperse polystyrene – elongational viscosity – entanglements – elongational flow

Introduction

The flow of polymer solutions through porous media is of great importance in practical applications that include filtration, chromatography and tertiary oil recovery from underground reservoirs.

The pioneering works of Dauben and Menzie [1] and Marshall and Metzner [2] reported dramatic increases in flow resistance when poly(ethylene oxide) (PEO) or hydrolysed polyacrylamide (HPAA) solutions were made to flow through randomly packed beds of spheres; in contrast with their shear thinning behaviour in simple shear flows. They postulated that the elongational nature of the flow field was responsible for the observed non-Newtonian effects. Flow through a porous medium contains substantial elongational components arising from the rapid changes of the cross-sectional areas of the pore space in the direction of the flow. It is well known that polymer solutions can exhibit extension thickening behaviour when they are exposed to elongational flow fields, an observation that has been reported for a variety of flow situations: flow through orifices, capillary entrances and converging channels, flow in four roll mills and flow through opposed jets devices [3, 4].

Figure 1 illustrates the typical hydrodynamic behaviour of a Newtonian fluid and a solution of a flexible polymer flowing through porous media. The figure shows how the resistance coefficient Λ varies as the Reynolds number (Re) is increased. The resistance coefficient is a measure of the flow resistance in the form of a dimensionless ratio of pressure drop to flow rate, and is defined, for a non consolidated porous medium, as:

$$\Lambda = \frac{\Delta P}{L} \frac{d^2 \phi^3}{\eta_s u (1-\phi)^2}, \tag{1}$$

where $\Delta P/L$ is the pressure drop per unit length of porous medium (including gravitational potential contributions), d is the particle diameter, ϕ is the

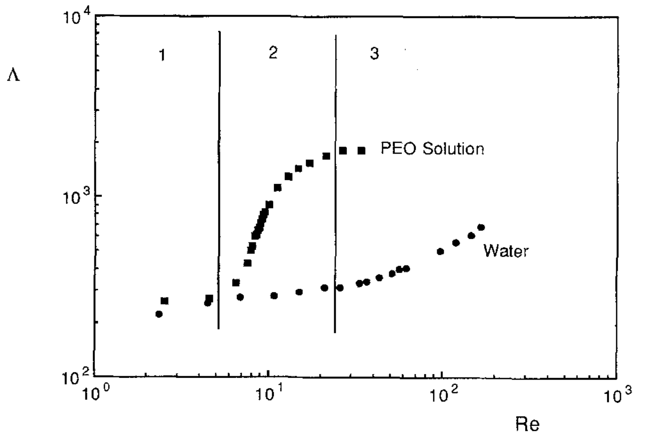

Fig. 1. Typical resistance coefficient vs. Reynolds number for a solution of a high molecular weight flexible polymer, 100 ppm poly(ethylene oxide) in water, $Mv = 4 \times 10^6$

porosity of the medium, η_s is the viscosity of the solvent, and u is the superficial velocity (volumetric flow rate per unit cross sectional area). The Reynolds number can be defined for uniform one-dimensional flow through the medium as:

$$\mathrm{Re} = \frac{\rho_s u d}{\eta_s(1-\phi)}, \tag{2}$$

where ρ_s is the solvent density. Figure 1 shows that the behaviour of a Newtonian fluid (water) can be described empirically by the Ergun equation:

$$\Lambda = A + B\mathrm{Re}, \tag{3}$$

where A and B are constants. Equation (3) indicates that in the low Re limit Λ is a constant, i.e., the pressure drop is directly proportional to the superficial velocity (a regime commonly referred to as Darcian). At high Re inertial effects in the pores dominate over viscous effects and the pressure drop becomes proportional to the square of the superficial velocity. The data in Fig. 1 were obtained by Müller et al. [5]. Equation (3) fits the data with $A = 250$ and $B = 2.54$. Macdonald et al. [6] recommend values of $A = 180$ and $B = 1.8$ after extensive analysis of published data, a deviation of 15% from the figures is quite common for one-dimensional uniform flow since the constants A and B vary according to the type of packing and particle roughness.

Figure 1 also shows the behaviour of a typical high molecular weight ($Mv = 4 \times 10^6$) flexible polymer, PEO, at a concentration of 100 ppm in water. Its behaviour is divided into three zones depending on the Reynolds number.

In zone 1, at low Re, the solution behaves as a Newtonian fluid following a trend almost indistinguishable from water. In zone 2, at higher Re, there is a sudden increase in the resistance coefficient beyond a critical Reynolds number usually denoted "onset Re" or Re_0. In zone 3, at even higher Re, the value of the resistance coefficient saturates, becoming constant with further increases of Re; this value will be denoted Λ_p in this work (where the subscript "p" stands for plateau). There have been reports in the literature of a fourth zone at very high Re found for very high molecular weight polymers, where after the plateau in the Λ versus Re curve, the Λ values drop upon increasing Re [7]. Such decreases in Λ have been interpreted as a consequence of the flow-induced mechanical degradation of the polymer.

Sudden increases in Λ similar to those shown in Fig. 1 have been reported for other solutions of high molecular weight flexible polymers. James and McLaren [8] suggested that such increases in flow resistance were a result of the increase in the elongational viscosity of the polymer solution, as a consequence of the extension of the molecules in the predominantly elongational flow field in the pores.

Theoretical considerations by de Gennes [9] and Hinch [10] predict that high molecular weight flexible molecules should undergo a coil-stretch transition in elongational flow fields, when the applied strain rate exceeds a critical value. This critical strain rate is of the order of the inverse of the longest relaxation time of the coil. A sudden transition is expected because of the hysteresis of molecular relaxation time with chain extension that arises, according to de Gennes, due to the draining characteristics of the coiled molecules changing as they become stretched out [9]. In other words, sudden extension implies a sudden conformational change with the statistical coils greatly aligned in the elongational flow direction changing their draining characteristics and causing the frictional contact of inner chain segments with the solvent to increase dramatically. Such behaviour is characteristic of highly flexible molecules like PEO, whose typical conformation in solution is that of a non free draining random coil. It is therefore expected that a coil-stretch transition will lead to an increase in the elongational viscosity of the solution, a fact that has been experimentally verified in idealised elongational flow situations such as in the flow through opposed jets [4]. Models like those based on the finitely extensible non-linear elastic (FENE) dumbbell have tried to reproduce theoretically such extension thickening behaviour [11].

Hoagland and Prud'homme [12] have recently studied the flow of flexible polymer solutions through porous media using a technique called hydrodynamic chromatography, where a pulse of the polymer solution is injected into a porous medium formed by small particle packing. The technique allows the indirect measurement of effective mean lateral size of the polymer molecules (in a direction perpendicular to the mean flow direction) as they flow through the pores. They found that the mean lateral size decreases as the flow rate through the medium increases, concluding that the molecules are orienting significantly in the mean flow direction. They interpret this observation in terms of the stretching of isolated macromolecules.

Based upon idealised flow studies, Odell et al. [13] proposed that the sudden onset of flow resistance in porous media flow could be due to other factors apart from the stretching of isolated molecules. It was argued that the criticality of the effect would not be expected in the context of coil-stretch transition since the polymers typically used were polydisperse PEO and HPAA. A polymer with a wide distribution of molecular weights will have a wide spectrum of relaxation times [14] and therefore should have a wide range of Reynolds numbers for the onset of increased flow resistance. Odell et al. also pointed out that the onset Re for the effect was highly dependent on the concentration following a trend more pronounced than a simple linear dependence with the solution viscosity. On the basis of these arguments, Odell et al. suggested that the coil stretch transition was not the only mechanism responsible for the increased flow resistance. They proposed that the formation of transient entanglements molecular networks, even at concentrations much lower than conventional overlap concentration (c*), could account for most of the experimental observations.

Recently, Rodriguez et al. [14] have studied the flow of polydisperse PEO (Mw/Mn estimated to be greater than 5) solutions through non-consolidated porous media. Their results also support the transient network hypothesis. They calculated that a polydispersity of less than 1.04 would have to be used in order to explain the observed criticality of the thickening effect in terms of only coil-stretch transitions of macromolecules.

In this work, we further explore the origin of the increase in flow resistance observed in the flow of polymer solutions through porous media, by studying the behaviour of closely monodisperse atactic polystyrene. Previous works have concentrated on polydisperse samples. The use of monodisperse polymers allows us to evaluate the contribution of narrow molecular weight fractions to the extension-thickening behaviour. We also assess the molecular orientation within a non-consolidated packed bed of glass beads through the measurement of optical retardation. Finally, we report some preliminary results on the flow-induced degradation of closely monodisperse aPS through porous media.

Experimental

The polymers used in this study were closely monodisperse fractions of atactic polystyrene of Mp values 4, 8, 12.25 and 20×10^6 (Mw/Mn typically equal to or less than 1.2) supplied by Polymer Laboratories Ltd.

Figure 2 shows a schematic of the apparatus used to control the flow of solution through the test cell, measure the pressure drop across the cell and simultaneously observe or measure transmitted intensities of birefringence. A detailed description of the set-up can be found elsewhere [15].

Two test cells were used. The first one was a porous medium cell, it consisted of a glass parallelepiped of dimensions: 2.5 cm × 2.5 cm × 10 cm filled with randomly-packed glass spheres of

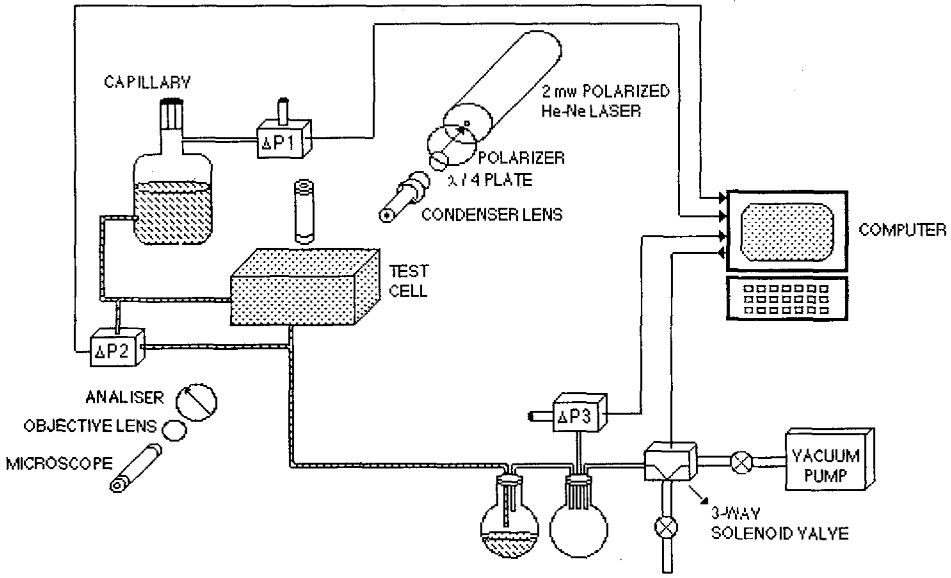

Fig. 2. Experimental apparatus

5 mm diameter. The porous medium had a porosity of 0.4. The spheres were made of high content borosilicate glass and were monodisperse in size. Such high quality spheres were essential for the optical measurements. The solvent for the aPS was chosen as a mixture of organic solvents that, blended in the right amount, would have a refractive index as close as possible to that of the glass beads. That solvent mixture was 80.5% by volume dioctylphtalate (DOP) and 19.5% tricresylphosphate (TCP). The laser beam was expanded to 1 cm diameter in order to average a path of 1 cm diameter by 2.5 cm length so that at least several pores were being illuminated. The intensity of the optical retardation recorded was the average value over the area.

The second test cell used was an opposed jets set-up identical to the one reported in ref. [4]. The opposed jets had an internal diameter of 0.57 mm, and the jet separation was 0.35 mm. The solvent used for these experiments was pure decalin. All measurements were performed at 24 °C.

Results and Discussion

Mechanisms behind the thickening of polymer solutions in pore flow

The effect of polymer concentration on the resistance coefficient versus Reynolds number curves can be seen in Fig. 3 for an $Mp = 12.25 \times 10^6$ aPS solution. The values of Λ are very high, even at very low Re (i.e., in the Newtonian limit of Λ values). This is a consequence of the fact that the shear viscosity of the solution is higher than that of the solvent, and that the flow distribution is not uniform. The flow is not uniform due to the limited size of the cell used. The fact that entrances and exits have a cross-section that is smaller than the 2.5 cm × 2.5 cm section of the cell implies that the average velocity field in the porous medium is not completely one dimensional.

In previous works [5, 14], we have studied the influence of non-uniform flow distributions on the flow of PEO solutions through porous media. The results have shown that a sudden increase in flow resistance is still observed, but displaced to higher values of Λ and lower values of Re as compared to uniform flow values [14]. It should be noted that the values of Λ and Re were calculated using a superficial velocity based on the total available cross-sectional area of the porous medium. We carried out flow visualisations using methylene blue solutions and noted, in the non-uniform flow case, that there were preferential flow paths through the medium. Since, for non-uniform flow, the superficial velocity of the fluid is not constant over the whole flow section there are regions of locally high fluid velocities, which cause increases in the total pressure drop and decreases in the Re for the onset of inertial

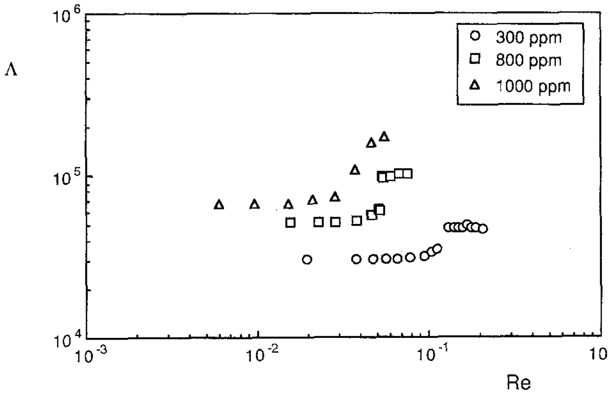

Fig. 3. Resistance coefficient vs. Reynolds number for $Mp = 12.25 \times 10^6$ aPS solutions in a viscous solvent (80.5% DOP/19.5% TCP v/v) at various concentrations

and non-Newtonian effects. On a more quantitative basis, we were able to show that the presence of polymer modifies the macroscopic flow field, increasing the total porous medium volume swept by the fluid, and effect that increases for higher polymer concentration.

In view of our previous results, we can treat the data presented here as qualitatively similar to uniform flow data (for instance, the solvent behaviour is accurately described by Eq. (3) but with different values of the constants A and B [14]).

The general trend of changes of Λ with concentration observed in Fig. 3 is similar to that reported for other flexible polymer solutions [7, 14]. However, the curves of Fig. 3 exhibit a more critical thickening behaviour than any other curve previously reported using polydisperse polymers, a fact clearly related to the narrow molecular weight distributions of the samples of aPS used here. It should be pointed out that the behaviour of solutions of 300 and 800 ppm was perfectly critical within the sensitivity range of our measuring devices; that is, there was a sudden jump in pressure drop at a particular Reynolds number and that is the reason why there is a discrete step in Λ values, with no intermediate values recorded. When the concentration of 1000 ppm was used, we were able to record a data point in the middle of the range where the pressure drop increases, thus indicating a somewhat less than critical behaviour that we attribute to flow-induced degradation (see the next section).

The fact that the curves in Fig. 3 do not converge at the same values of Λ at low Re is a consequence of the differences in solution shear viscosity. It should be remembered that the solvent viscosity was used in Eqs (1) and (2) in order to calculate Λ and Re. If the solution shear viscosities were used instead, all the curves would start at low Re with identical Λ values.

Another important fact gathered from Fig. 3 is that the absolute change in Λ is not as large for aPS solutions as it is for PEO solutions of roughly comparable polymer molecular weight and solution concentration [14]. This is to be expected on the basis of the much greater contour length of the PEO molecules (about 2.3 times longer) as compared to aPS of the same molecular weight.

An interesting point that emerges from Fig. 3 is that the onset Reynolds number decreases with increasing concentration. Such an effect cannot be accounted for by the increase in shear viscosity. It can be seen that the Re_0 decreases by a factor of two upon changing the concentration from 300 ppm to 800 ppm. The shear viscosity, however, only changed by a factor of 1.3 as indicated by the change in Λ values at low Re. We have found similar results using polydisperse PEO solutions (see ref. [5] and Fig. 7 below). The formation of transient entanglement networks would explain the observed tendency since it is expected that the flow rate for the onset of such an effect change very rapidly with varying concentration [15–16].

If the increase in flow resistance were due to the coil-stretch transition of the polymer molecules, then the strain rates at which this happens (which are proportional to Re_0) should be inversely proportional to the longest relaxation time of the coil. For flexible molecules, the longest relaxation time is found to depend on the viscosity of the solution and on the molecular weight according to:

$$\tau \propto \frac{\eta_{\mathrm{so}} M^{\mathrm{a}}}{kT} , \tag{4}$$

where η_{so} is the solution viscosity and "a" has a value of 1.5 for non-free draining flexible coils such as aPS. The relaxation time τ is inversely proportional to the critical strain rate for the coil-stretch transition and Eq. (4) has been verified experimentally using purely elongational flow techniques such as opposed jets and cross slots [17].

The effect of polymer molecular weight on the resistance coefficient versus Reynolds number curves at a constant concentration is shown in Figs 4 and 5. Figure 4 shows the available data for 300 ppm. The data for the $M\mathrm{p} = 20 \times 10^6$ aPS suggest that the Λ versus Re curve is not so critical (in its increase part), as that corresponding to the $M\mathrm{p} = 12.25 \times 10^6$ polymer. We believe that the reason behind this behaviour is the fact that, due to the very high molecular weight of the $M\mathrm{p} = 20 \times 10^6$ polymer, it degrades as it is being passed through the porous medium. This explanation was corroborated by repeatedly circulating the solution through the porous medium as shown in the following section.

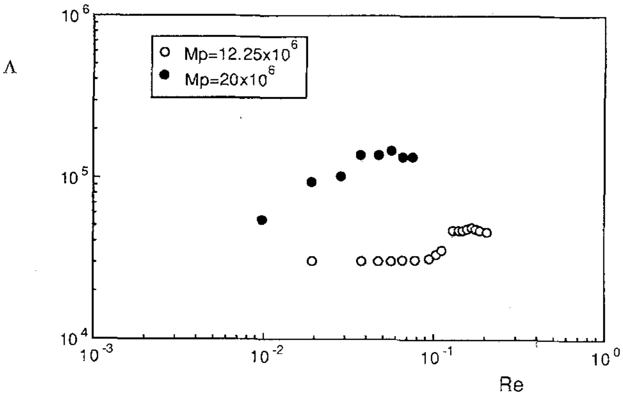

Fig. 4. Resistance coefficient vs. Reynolds number for 300 ppm aPS solutions in a viscous solvent (80.5% DOP/19.5% TCP v/v) for various molecular weights

The molecular weight dependence of the onset Re for thickening is shown in Fig. 6, where the Re_0 from Figs. 4 and 5 has been compiled. Here, Re_0 was taken as the Reynolds number at which Λ increases beyond it Newtonian value. It should be obvious from the previous discussion that if the coil-stretch transition is the mechanism responsible for the non-Newtonian behaviour, then Eq. (4) should be obeyed and the Re_0 should scale with M as:

$$\mathrm{Re}_0 \propto M^{-b}\,, \tag{5}$$

where b is 1.5 for aPS. The data points seem to follow a much greater exponent (of the order of 3.0 to 4.0), even allowing for a shear viscosity correction. An exponent greater than 2 is not compatible with the coil-stretch hypothesis and would probably indicate that molecular interactions are taking place and this would then give support to the transient network hypothesis.

Kulicke and Haas [7] also studied the molecular weight dependence of Λ versus Re behaviour in porous media flow of polyacrylamide (PAA) solutions. They found that their Re_0 scales with polymer molecular weight according to the expectations of the coil-stretch transition theory (i.e., with $b = 1.5$ in Eq. 5). However, they used PAA of polydispersities of 2.5. This is a low value compared to commercial samples but it is difficult to draw definite conclusions using such polydispersities, since the corresponding distribution of relaxation times would be extremely wide. As a matter

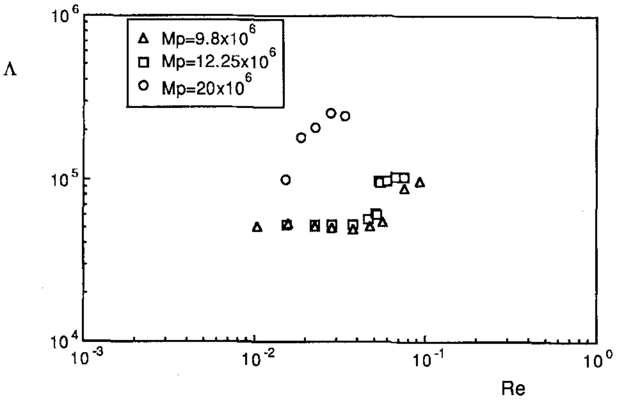

Fig. 5. Resistance coefficient vs. Reynolds number for 800 ppm aPS solutions in a viscous solvent (80.5% DOP/19.5% TCP v/v) for various molecular weights

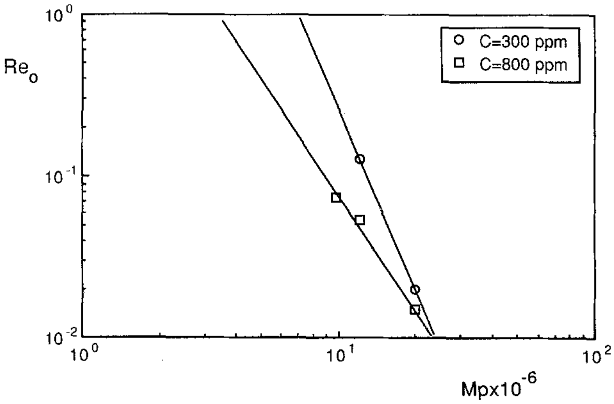

Fig. 6. Onset Reynolds number vs. molecular weight for aPS solutions in a viscous solvent (80.5% DOP/19.5% TCP v/v)

of fact, the only available data we have on different molecular weight polydisperse flexible polymers corresponds to two polydisperse PEO samples of *Mv* equal to 4 and 5 million respectively (determined by capillary viscometry). The Re_0 data on these two polymers shows an approximately 3.5 power law scaling between Re_0 and *Mv*, as can be appreciated in Fig. 7.

Further evidence that supports the hypothesis of the formation of transient networks is provided by Fig. 8. Here, we show for the first time (as far as we are aware) simultaneous results on the measured transmitted intensity, due to flow induced birefringence, through crossed polars and resistance coefficient. It should be remembered that the intensity that is reported in Fig. 8 is an average value in arbitrary units of the optical retardation through several pores since the refractive index of the glass was matched to that of the solvent. Perhaps the most striking feature of Fig. 8 is the almost perfect criticality of both the increase in Λ and the simultaneous increase in the intensity. Figure 8 demonstrates that when a major increase in flow resistance occurs, a major change in the molecular orientation is also occurring. However, the criticality of the effect is such that it resembles a step function, a perfectly monodisperse polymer would be required to rationalise these results in terms of the stretching of isolated molecules. Even though the polymer standard used here is closely monodisperse, its residual polydispersity ($M\mathrm{w}/M\mathrm{n} = 1.2$) is enough to invalidate this explanation [14]. Again, we find that the formation of transient entanglement networks could better explain the criticality of the effect.

We have studied the behaviour of closely monodisperse aPS solutions in stagnation point elongational flows produced by opposed jets [4]. In these experiments, we measure the pressure drop across the jets while simultaneous birefringence visualisations of induced molecular strains are performed.

Figure 9 shows pressure drop versus strain rates curves for the $M\mathrm{p} = 12.25 \times 10^6$ aPS in

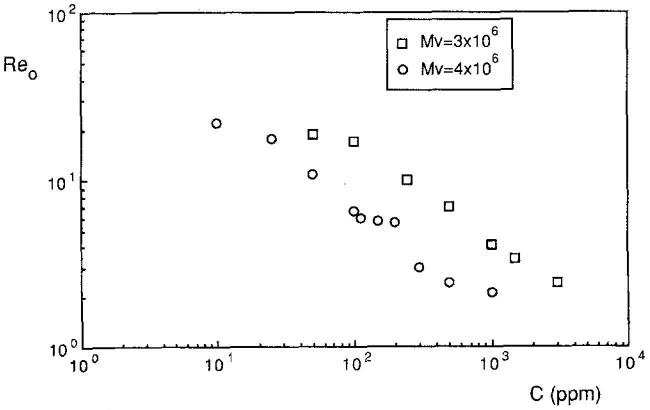

Fig. 7. Onset Reynolds number vs. concentration for aqueous solutions of polydisperse PEO of the indicated average viscometric molecular weight

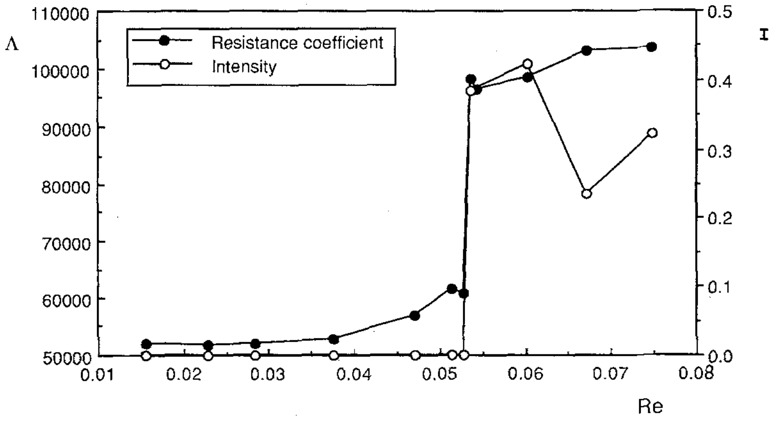

Fig. 8. Resistance coefficient and intensity of optical retardation as a function of Reynolds number for a 800 ppm $M\mathrm{p} = 12.25 \times 10^6$ aPS solution in a viscous solvent (80.5 DOP/19.5% TCP *v*/*v*)

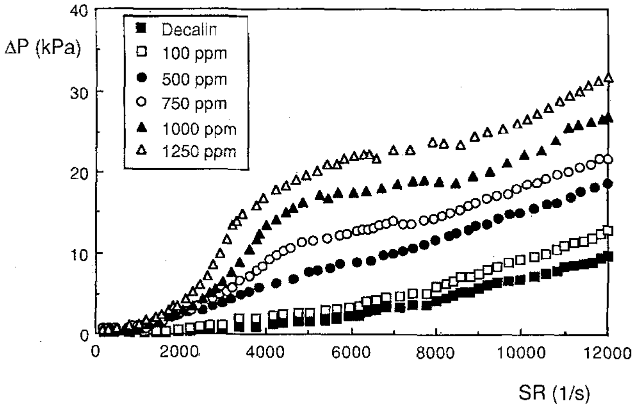

Fig. 9. Pressure drop across the jets as a function of strain rate for pure decalin and $Mp = 12.25 \times 10^6$ aPS solutions in decalin

decalin solution. When the solution is nearly dilute (i.e., 100 ppm, Fig. 9), there is a small increase in the pressure drop as compared to pure decalin only after the isolated molecules become stretched. The small pressure drop is consistent with a higher degree of stretching of isolated molecules over a small area surrounding the stagnation point [4]. Optical detection of the coil-stretch transition for this solution occurs at $\dot{\varepsilon}_c = 1500\,\mathrm{s}^{-1}$. Large increases in pressure drop, however, are found only beyond a critical concentration and strain rate that are associated with the stretching of transient entangled molecules, as demonstrated elsewhere [4, 18]. We have also shown that large increases in pressure drops cause significant perturbation of the flow field leading ultimately to the loss of stagnation point flow [4, 18].

We have developed a method of determining the overlap concentration necessary to produce the network behaviour in the opposed jets [4]. It consists of subtracting the solvent behaviour to all the polymer curves of Fig. 9 and then differentiating in order to obtain an effective excess elongational viscosity:

$$\eta_e' = \frac{d(\Delta P)}{d(\dot{\varepsilon})} \tag{6}$$

All the curves of effective elongational viscosity vs. strain rate above a critical concentration exhibit a pronounced maximum that diminishes in size as the concentration is lowered. If the value of that maximum is plotted as a function of concentration, a plot like that of Fig. 10 is generated. Fig. 10 shows how, by extrapolating to zero, we can calculate a value of concentration below which this extension thickening is not observed. As can be seen from Fig. 10, this overlap concentration for the formation of transient entanglement networks (c^+), as detected viscometrically and optically in flow through opposed jets of the same Mw aPS in decalin (a theta solvent), is approximately 335 ± 34 ppm (see ref. [4] for more details on this calculation). This concentration is much lower than the conventional c*, values of which would range from 50 to 70 times higher than 300 ppm, depending on the method used to assess it. The observation of molecular interactions at concentrations much lower than c* has been attributed to weak molecular entanglements which are active only on extremely short time scales, such as those that arise in strong elongational flows (see refs. [4, 13, 15–19]).

The Λ vs. Re curve in Fig. 8 shows a small continuous rise in Λ at low Re, from 0.04 until 0.05, then at a Re of 0.053 a sharp increase in Λ occurs. It is tempting to interpret the first small rise in Λ as the contribution of the coil-stretch transition to the value of Λ, and the big rise as caused by the formation of transient networks. Such an explanation would parallel the experimental results found measuring pressure drops through the opposed jets (Fig. 9). It should be

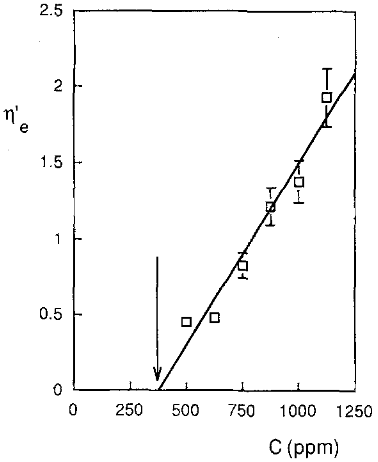

Fig. 10. Maximum value of excess effective elongational viscosity (in arbitrary units) for $Mp = 12.25 \times 10^6$ aPS solutions in decalin. (The extrapolated value of c^+ of approximately 335 ppm is indicated by an arrow.)

mentioned that a direct comparison is not strictly valid since the Λ value is a non-dimensional parameter that is proportional to the pressure drop divided by the strain rate. In this work, we have measured the pressure drop through the porous medium and the birefringent intensities, but the strain profiles were not determined since in a porous medium such visualisations are experimentally more difficult to perform. However, we are currently trying to perform this.

Flow induced degradation

The performance of almost all polymers that show high degrees of thickening in porous media flows is restricted by thermo-mechanical degradation, which acts to reduce the length of the molecule and therefore its effectiveness at increasing elongational viscosity.

We have performed experiments to analyse the degradation of the polymers in flow through porous medium. The basic nature of the experiments is to pass a solution through the porous medium several times, recording the resistance coefficient, and looking for changes in this parameter. Degradation can then be characterised in terms of the observed reduction of flow resistance.

Figure 11 shows how the pressure drop (normalised by dividing the measured ΔP by the initial pressure drop before degradation, ΔP_0) decreases after each pass of the solution through the porous medium at a constant flow rate. The most significant drops in ΔP occur during the first five passes, after which the ΔP decreases only slightly on each pass. This indicates that the polymer is being degraded on each pass, until further degradation is not possible at the circulating Re of 0.08. It should be noted that the Re value chosen to examine the flow induced degradation corresponds to the resistance coefficient plateau of the undegraded solution. Figure 12 shows the Λ vs. Re curve of the fresh solution (termed *original*) as it flows through the porous medium.

After the solution was degraded by repeated passes (11 times, see Fig. 11), the degraded solution, was then passed again through the porous medium to record its resistance coefficient as a function of Reynolds number (curve termed *Degraded* 1 in Fig. 12). It can be seen in Fig. 12 that this solution exhibits an onset of the sudden increase in flow resistance that occurs approximately at the Reynolds number at which the polymer was being degraded (Re = 0.08). This suggests that all of the polymer molecules that participated in the non-Newtonian behaviour of the original solution were degraded in the experiment. Repeating the same procedure yields similar results: curve *Degraded* 2 was obtained by repeatedly flowing the *Degraded* 1 solution at an increased Reynolds number of 0.12.

Results qualitatively similar to those discussed above were obtained in our studies of degradation of PEO solutions [5, 14], as well as in previous works [20 and references therein], [21], indicating that this behaviour is characteristic of flexible polymers. The observation that for such polymers

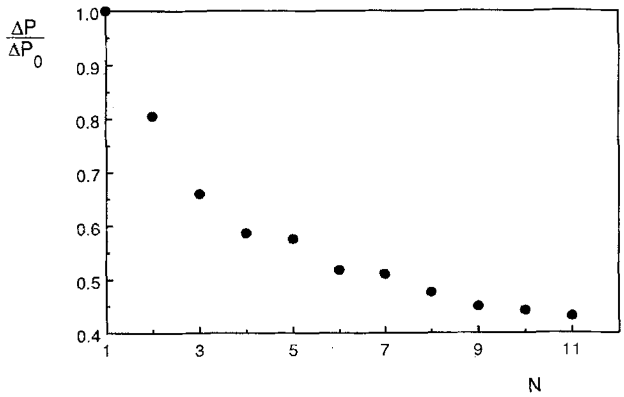

Fig. 11. Decrease of normalised pressure drop during repeated passes through the porous medium of a 300 ppm $Mp = 20 \times 10^6$ aPS solution in a viscous solvent (80.5 DOP/19.5% TCP v/v)

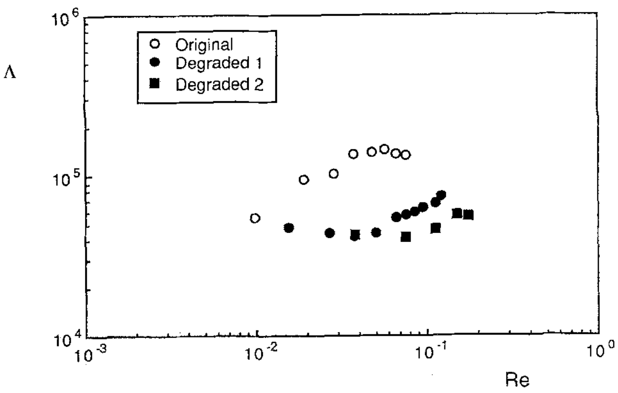

Fig. 12. Resistance coefficient for a 300 ppm $Mp = 20 \times 10^6$ aPS solution in a viscous solvent (80.5 DOP/19.5% TCP v/v) before and after flow-induced degradation

large viscosification effects are always accompanied by degradation is in itself not consistent with the coil-stretch hypothesis. For isolated molecules the fracture strain rate scales with molecular weight with a higher exponent than the coil-stretch strain rate, so that at these molecular weights fracture should only occur at much higher Reynolds number than stretching [22, 23].

Haas and Kulicke [20] have performed degradation experiments with solutions of high molecular weight polystyrene in toluene flowing through a porous medium. They took samples of the solutions as it passed through the medium, and determined their molecular weight by light scattering. Their results show that the polystyrene degrades only at Reynolds numbers higher than the onset value. Our results are consistent with these observations.

Conclusions

By using closely monodisperse flexible polymers, we have collected experimental evidence that supports the hypothesis that the mechanism responsible for the phenomenon of extension thickening in the flow of polymer solutions through porous media is not only the stretching of isolated molecules in solution. The molecular weight dependence of the effect, its criticality in strain rate, its concentration dependence and the degradation behaviour of the polymer through the porous media are best explained in terms of the formation of transient entanglement networks in addition to the coil-stretch transition of the polymer molecules that flow through the system.

Acknowledgements

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