# Degradation of semidilute polymer solutions in elongational flows*

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*(Received 30 April 1991; revised 13 August 1991; accepted 1 October 1991)*

Elongational flow techniques are applied to the examination of flow-induced chain scission of macromolecules in solution. An opposed-jets apparatus is used both to produce mechanical scission and to monitor the molecular-weight distribution of the scission products. Gel permeation chromatography is also used to complement the latter. In dilute solutions of almost monodisperse high-molecular-weight atactic polystyrene (aPS), degradation occurs as closely central scission of the molecules beyond a critical strain rate. As the concentration is increased to the semidilute regime, this preferential breaking near the centre of the molecule disappears (for 1.5% aPS/decalin solutions, $M_p = 5.8 \times 10^6$). Therefore, according to expectation, the scission is randomized as the number of entanglements per chain is greatly increased. The results also indicate that, once entanglements are present, the parameter that seems to be most relevant to the process of molecular fracture is the applied stress.

**(Keywords: degradation; semidilute solutions; elongational flows; chain scission; molecular-weight distribution; polystyrene)**

## INTRODUCTION

This work is a continuation of our study of flow-induced degradation of macromolecules in solution; preceding papers have been focused on the particular aspect of flow-induced chain fracture of isolated chains in solution[1–7]. Although the behaviour of semidilute solutions has been the subject of a number of publications of the present authors[2,8–13], the issue of degrading interacting chains during flow has only been mentioned on the basis of preliminary results[7,9–12]. In this article we will relate these previous results with ongoing new work on this subject matter. Since this paper arises from the study of chain extension by means of elongational flows, a very brief recapitulation follows. Extensive reviews have been published elsewhere on the merits and limitations of elongational flow techniques for the study of chain stretching in dilute and semidilute solutions[2,9,14].

### *Basic principles: dilute solutions*

To extend a long flexible chain in solution by flow the fluid must be persistently extending, i.e. the extensional component of the velocity gradient should dominate over the rotational component[15]. Preceding theory has also anticipated that, in order to extend fully a random coiled molecule, the molecule should be deformed at a stretching rate high enough to exceed its rate of relaxation, i.e. the strain rate should be higher than the critical value:

$$\dot{\varepsilon}_c \tau > 1 \qquad (1)$$

where $\tau$ is the longest relaxation time of the molecule[16,17]. The coil-to-stretch transition has been predicted as sudden because of the hysteresis of molecular relaxation time with chain extension. Furthermore, the coil should remain in the flow field at $\dot{\varepsilon} > \dot{\varepsilon}_c$ for a long enough time so that it can accumulate the required molecular strain[18].

In previous work this predicted sharp coil–stretch transition has been verified for a number of polymers using near-ideal extensional flow fields, such as opposing jets, crossed slots or four-roll mills. These devices incorporate a stagnation point at their centre of symmetry. The extension of molecules can be assessed from optical retardation in the solution. In dilute solutions, as the strain rate is increased a localized narrow birefringent line is observed around the stagnation point, signalling that the molecules are only being extended where large strains are available[2]. The presence of a stagnation point provides long residence times for the streamlines that pass close to it. Therefore a region of quasi-steady-state flow (QSSF), where steady-state molecular conformations can be achieved, surrounds the stagnation point[7,19].

The recording of optical retardation *versus* strain rate curves enables the direct assessment of $\tau$ of the isolated molecule. For flexible molecules $\tau$ is found to depend

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* Paper presented at 'Polymer Physics', 3–5 April 1991, Bristol, UK
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0032-3861/92/122598-07

upon molecular weight ($M$) as:

$$\tau \propto \eta_s M^{1.5}/kT \qquad (2)$$

where $\eta_s$ is the solvent viscosity, $k$ the Boltzmann constant and $T$ the absolute temperature. The validity of the exponent 1.5 for all of the polymer–solvent pairs examined irrespective of solvent quality has been the subject of theoretical debate[14,20]. In more pragmatic terms, it provides us with a ready method for determining molecular weights and in fact the full distribution[2].

If the chains are overstretched, that is $\dot{\varepsilon}$ increases much further than $\dot{\varepsilon}_c$, the already stretched-out chains become increasingly stressed until they rupture. It is then possible to stop the experiment and start again from $\dot{\varepsilon} = 0$, remeasure a new optical retardation *versus* $\dot{\varepsilon}$ curve and derive the resultant molecular weight. Thus, through our technique we can both break chains in a controlled fashion and characterize the resulting fracture products of the flow-induced chain fracture[3]. The main results of flow-induced degradation in dilute solutions by elongational flows are:

(i) The chains break into two closely equal halves, hence accurately at their centres.

(ii) The critical fracture strain rate ($\dot{\varepsilon}_f$) obeys the relation:

$$\dot{\varepsilon}_f \propto 1/M^2 \qquad (3)$$

(iii) It follows from a combination of equations (1) and (3) that there is a limiting upper $M$ beyond which the chains cannot be stretched out, unavoidably breaking in the process. This conclusion has been confirmed experimentally[3].

(iv) The strain-rate dependence of the scission rate beyond $\dot{\varepsilon}_f$ has been determined at room temperature. These results clearly indicate that in dilute solution only those molecules that are virtually fully stretched can undergo central scission[5].

Results (i) and (ii) can be accounted for qualitatively by applying Stokes' law to a stretched-out string of beads; in fact, the applicability of Stokes' law is possibly the clearest evidence that the chains are indeed close to their stretched-out state (other evidence is given in ref. 2). The fracture stress itself can be calculated, and it was found to correspond to that of the breaking strength of a C–C bond, within an order of magnitude. The fact that chain breakage is practically exactly central (whilst the stress distribution is parabolic) can be accounted for by a thermally activated barrier to scission (TABS) model. This model considers the fracture as a thermally activated process, where the exponential nature of the transition probability from the intact to the fracture state confines the probable fracture sites close to the centre of the stretched-out chain[4–7].

### *Semidilute solutions: previous results*

As the concentration increases, dramatic changes can be observed beyond a critical concentration $c^+ \ll c^*$ (see 'Discussion'). At low strain rates (long timescales) the semidilute solutions behave as for dilute solutions: the appearance of a narrow birefingent line beyond a critical strain rate $\dot{\varepsilon}_c$. The polymer chains can be stretched as if in isolation if they have enough time to disentangle from one another. At high strain rates (short timescales), the molecules will not have enough time to slip past each other and will form a transient network. The presence of such transient networks is evident from the delocalization of the birefringent line, which progressively develops an unstable pattern until it resembles a flame in motion or flare[9] (see *Figure 1*).

It is to be expected that the dramatic effects associated with the formation of transient networks will also have a corresponding influence on the macroscopic flow behaviour. A new technique was developed to enable the simultaneous assessment of macroscopic flow resistance and visual observations of molecular strain and flow fields[9–14].

In order to quantify flow resistance, the pressure drop across the jets was measured as the strain rate was increased, as described in ref. 8. *Figure 2a* shows the great difference in flow resistance upon flowing water or a 0.2% poly(ethylene oxide) (PEO)/water solution ($M_w > 5 \times 10^6$) through an opposed-jets apparatus. The non-Newtonian shear-thickening character of the semidilute PEO solution is evident when compared with the behaviour of the water (*Figure 2f*).

The curve of *Figure 2a* can be correlated with simultaneous visual observations of birefringence and flow field (by light scattered at 90° by tracer particles). The sharp rise in $\Delta P$ beyond a particular $\dot{\varepsilon}$ ($\dot{\varepsilon}_n \propto 1/\tau_n$ where $\tau_n$ is the disentanglement time of the molecules) corresponds to the appearance of the flare and the breakdown of the stagnation-point flow (see refs. 10–13). Thus, we have a correspondence between the visually registered development of transient entanglement formation and the macroscopic flow characteristics. Accordingly,

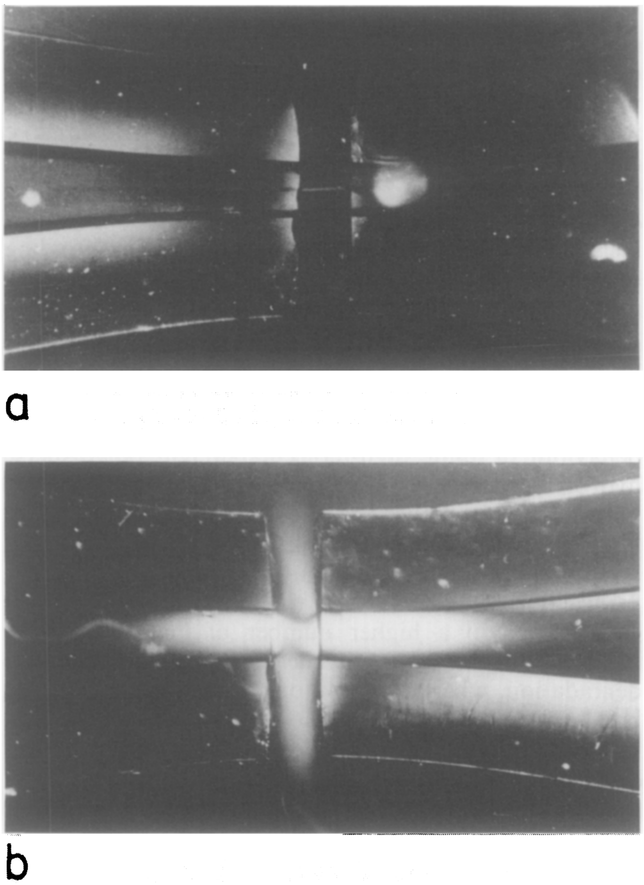

**Figure 1** (a) A narrow birefringent line observed between the opposed jets (crossed polaroids) in a semidilute solution with $\dot{\varepsilon}_c < \dot{\varepsilon} < \dot{\varepsilon}_n$ (0.2%, aPS/decalin, $M_p = 7.2 \times 10^6$). (b) Flaring of birefringence in the same solution with $\dot{\varepsilon} > \dot{\varepsilon}_n$

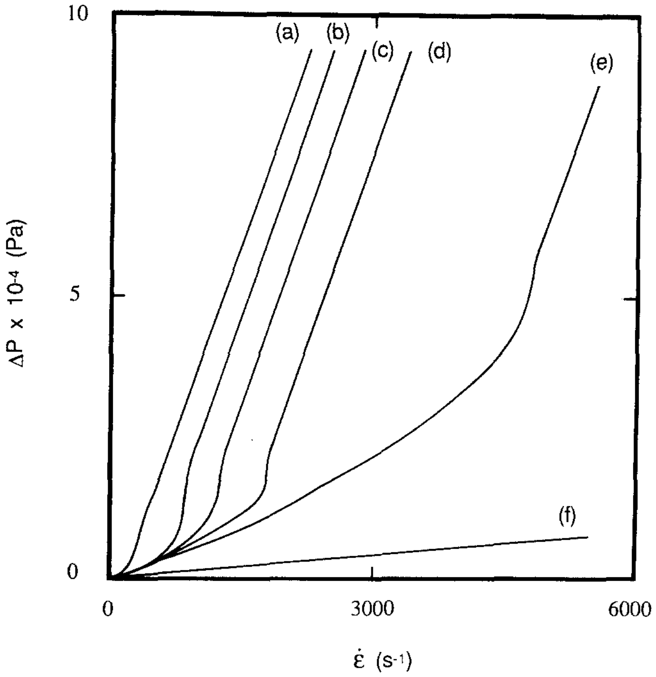

**Figure 2** Pressure drop across the jets *versus* strain rate for a 0.2% PEO/water solution ($M_w > 5 \times 10^6$). Number of runs: (a) 1; (b) 2; (c) 3; (d) 5; (e) 15. Curve (f) is for water

entanglement formation is associated with an increase in flow resistance, leading to a massive increase (the region where the slope has a maximum value) when the network becomes infinite as signalled by the flare[9,10].

The degradation of interacting molecules was first detected by studying the reversibility characteristics of a curve such as *Figure 2a*. The $\Delta P$ *versus* $\dot{\varepsilon}$ plot is perfectly reproducible for reruns up to the onset of the sudden increase in $\Delta P$, which roughly corresponds to the flare effect. However, once the flare stage has been reached, the same plots for subsequent consecutive reruns show (see *Figure 2a–e*) that the sudden increase in flow resistance is shifted to higher strain rates corresponding to a progressive reduction in molecular weight, as chains are broken by stretching beyond $\dot{\varepsilon}_n$. Such chain scission is confirmed by gel permeation chromatographic molecular-weight measurements (g.p.c.), which show a progressive destruction of the high-molecular-weight tail[9,10]. Very similar results were found when the behaviour of dilute high-molecular-weight polydisperse hydrolysed polyacrylamides (HPAA) were examined[11].

It must be said that the degradation progressed very fast, as can be seen from *Figure 2*. A difference in the $\Delta P$ *versus* $\dot{\varepsilon}$ curve (reflecting degradation) could be observed for each single run above the flare condition. This corresponds to a higher number of molecules being broken per pass than in the case of dilute-solution degradation, where typically only 1% of the molecules break in a single pass[7].

A difference in scission rate was thus detected depending on the concentration regime. This was found to hold for polydisperse PEO and HPAA solutions but also for monodisperse aPS solutions. Nevertheless, there was a big difference between polydisperse PEO (and HPAA) and monodisperse aPS solutions. When compared on the basis of equivalent concentration and flow rate, the aPS solutions were more degradation-resistant (i.e. the scission rate was lower). The monodisperse aPS solutions were found to resist scission by modifying the flow, annihilating the stagnation point even before the appearance of the flare and therefore earlier than in the polydisperse PEO and HPAA cases.

In spite of the differences observed regarding scission rate between the dilute and the semidilute degradation, the type of scission remained closely central against all expectations of randomized breakage with increasing concentration (at least up to the highest concentrations examined: 0.35% aPS/decalin, $M_p = 8.1 \times 10^6$ (ref. 5)). Random scission is to be expected in a highly entangled network where the forces are transmitted to other chains via junctions instead of viscous energy dissipation.

In this work we extend the concentration range to higher values than before using closely monodisperse aPS and the scission products are characterized by both g.p.c. and elongational flow.

## EXPERIMENTAL

The experimental procedures used in this work have been described in detail previously[7]. The opposed-jets apparatus used allowed simultaneous observation of birefringence, flow resistance measurements and flow field examination.

The molecular-weight distributions were obtained by gel permeation chromatography (g.p.c.) and by elongational flow. The elongational flow technique is particularly sensitive to high molecular weights and its upper limit is determined by the molecular weight at which $\dot{\varepsilon}_c = \dot{\varepsilon}_f$ ($M_p \simeq 3 \times 10^7$ (aPS) (ref. 3)). It has, however, a lower limit that is determined by the maximum achievable strain rate (for the present set-up, it is $M_p \simeq 2 \times 10^6$ for aPS/decalin solutions). The g.p.c., on the other hand, is best suited for molecular weights that are lower than $M_p = 4 \times 10^6$, since resolution is usually very poor beyond around $4 \times 10^6$ and chain scission can occur depending on the pumping rate used[5].

In view of the above, the g.p.c. was mainly used in order to examine that part of the molecular-weight distribution that was not covered by the elongational flow technique, i.e. $M < 2 \times 10^6$.

The sample used was a nominally $M_p = 6 \times 10^6$ closely monodisperse ($M_w/M_n < 1.2$) aPs supplied by Polymer Laboratories. The sample was found to possess a $M_p = 5.8 \times 10^6$ by elongational flow and a polydispersity index of 1.117; we will use these values.

A solution of 1.5% weight by weight aPS/decalin was prepared by dispersing the aPS powder in the solvent and letting it dissolve slowly in an oven at 30°C with no stirring at all. After 4 weeks the polymer was completely dissolved. The solution was intentionally not degassed in order to leave enough oxygen in it as a radical scavenger that will prevent any possible chain recombination reaction. The concentration of 1.5% is very high considering that the $c^+$ (minimum concentration for chain interaction in elongational flow) for a $M_p = 5.8 \times 10^6$ is approximately 0.05%, according to previous results[12].

The procedure used was to flow the solution through the jets at the degrading conditions specified below and then a sample was collected. The sample was then diluted to determine its molecular-weight distribution in a separate elongational flow experiment (see sections 2.1 and 3.1 in ref. 7). A similar sample was used for g.p.c.

but in this case the polymer was recovered by solvent evaporation and then dissolved in toluene.

## RESULTS

The degradation conditions used are summarized in *Table 1* and the results are displayed in *Figures 3–6*. *Figure 3* shows the $\Delta P$ *versus* $\dot{\varepsilon}$ curves, while *Figure 4* shows optical retardation *versus* $\dot{\varepsilon}$ for selected samples. Their derived molecular-weight distributions are plotted in *Figure 5*, and *Figure 6* shows g.p.c. traces of these samples.

The degradation sequence is somewhat complex and this is related to the search for the real parameter that could characterize the scission process. By analogy to the dilute case, we started the experiments by trying to degrade the polymer solution at constant $\dot{\varepsilon}_{\mathrm{deg}}$. There is a major difficulty with this approach: when the solution is semidilute it only degrades after the breakdown of the stagnation-point flow (this was demonstrated for closely monodisperse aPS semidilute solutions in section 3.4 of ref. 12). Therefore, the values of $\dot{\varepsilon}$ (at $\dot{\varepsilon} > \dot{\varepsilon}_{\mathrm{n}}$) are changing with the unstable flow field and in our experiment we can only guarantee that the total flow rate is constant.

**Table 1** Degradation conditions applied to a 1.5% aPS/decalin solution of $M_{\mathrm{p}} = 5.8 \times 10^6$

| Sample no. | $\dot{\varepsilon}_{\mathrm{deg}} \times 10^{-3}$ ($\mathrm{s}^{-1}$) | $\Delta P_{\mathrm{deg}}$ (atm) | $t_{\mathrm{deg}}$ (h) |
|---|---|---|---|
| 0 | 0 | 0 | 0 |
| 1 | 4 | 1 | 2.8(8)[a] |
| 2 | 4 | 1 | 5.7(24) |
| 3 | 5 | 1 | 14.2(64) |
| 4 | 18 | 2 | 2.6 |
| 5 | 26–30 | 2 | 12.8 |
| 6 | 30–50 | 2 | 10.0 |

[a] Numbers in parentheses indicate the total number of runs through the jets for that sample

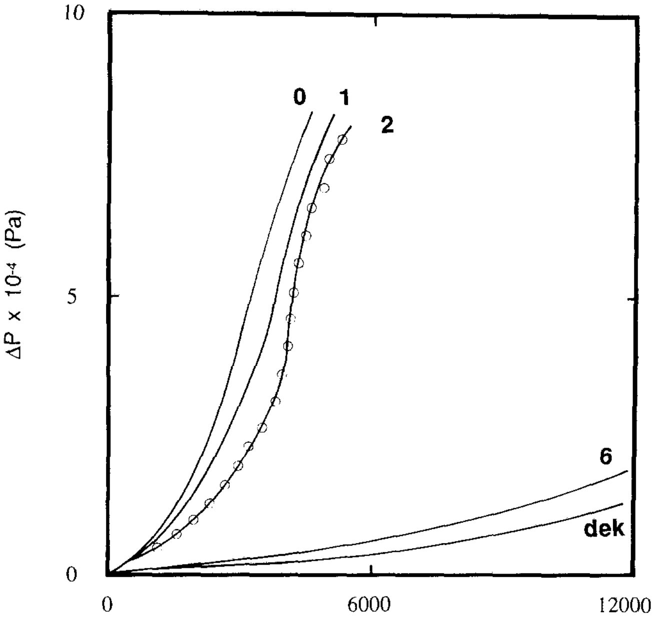

**Figure 3** Pressure drop across the jets *versus* strain rate for: sample 0, sample 1, sample 2, sample 3 (○○○), sample 6 and decalin

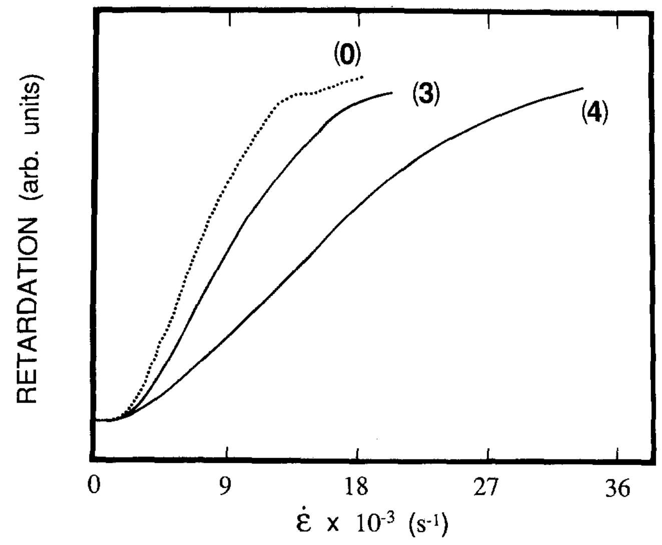

**Figure 4** Optical retardation *versus* strain rate for: sample 0, sample 3 and sample 4

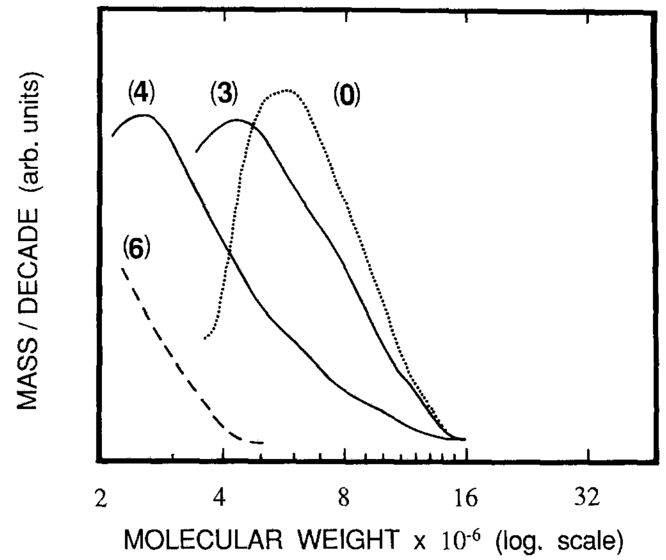

**Figure 5** Molecular-weight distributions derived from *Figure 4*. The result for sample 6 was derived from visual observations of birefringence *versus* strain rate

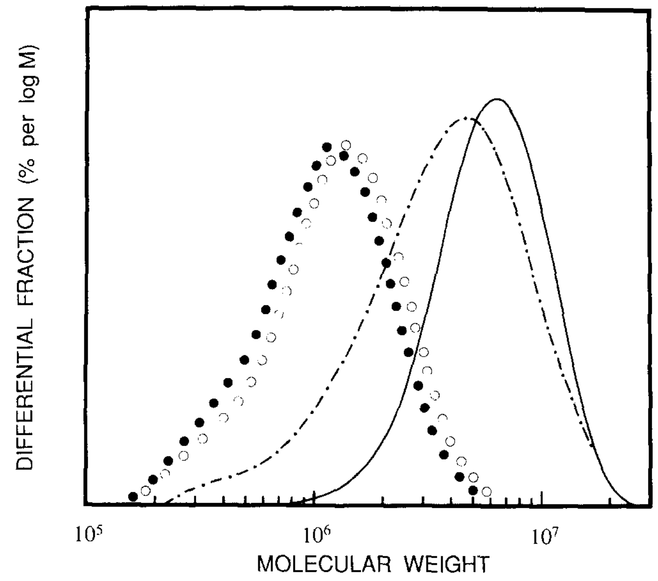

**Figure 6** G.p.c. molecular-weight distribution curves for: sample 0 (——), sample 4 (—·—), sample 5 (○○○), sample 6 (●●●)

The $\dot{\varepsilon}$ values of *Table 1* should be considered only as nominal values reflecting a variation in volumetric flow rate.

Nevertheless, the degradation was started by flowing the polymer through the jets at a flow rate where the pressure drop across the jets was nearly 1 atm and the birefringence displayed the flare effect. After 2.8 h (sample 1) a change was detected in the $\Delta P$ *versus* $\dot{\varepsilon}$ curve (see *Figure 3*) with respect to the undegraded sample (sample 0). Such a shift in the $\Delta P$ *versus* $\dot{\varepsilon}$ curve normally reflects a change in molecular weight. The g.p.c. trace of this sample, however, was very similar to the trace of the undegraded sample (*Figure 6*).

After 8.5 h (sample 2) at the same flow rate there was no further shift in the $\Delta P$ *versus* $\dot{\varepsilon}$ curve whilst the g.p.c. curve was still not showing noticeable signs of degradation. Because of the shift in the $\Delta P$ *versus* $\dot{\varepsilon}$ curve, the $\Delta P$ value at the initial strain rate had dropped to 0.8 atm. The flow rate was then increased to an equivalent nominal $\dot{\varepsilon}$ of 5000 $s^{-1}$ in order to restore the $\Delta P$ across the jets to 1 atm. Even so, the polymer did not degrade any further, as no change was detected in the flow resistance curve (sample 3).

The g.p.c. could not detect any appreciable change in the molecular-weight distributions of samples 2 and 3 as compared to the undegraded material (sample 0). However, the elongational flow method did slightly show degradation (*Figures 4* and *5*), confirming that the shift in the $\Delta P$ *versus* $\dot{\varepsilon}$ curve can indeed be associated with a molecular-weight change. It is clear that the flow resistance measurements are extremely sensitive to degradation (even more than g.p.c. measurements, at least in this high-molecular-weight range).

At this stage, since no further degradation was occurring, the $\Delta P$ across the jets was increased to 2 atm, and the flow rate increased accordingly to an equivalent $\dot{\varepsilon}$ value of 18 000 $s^{-1}$.

Sample 4 was analysed after 2.6 h running at the $\Delta P$ of 2 atm. *Figure 5* demonstrates how effective the degradation was; this is also shown by the corresponding g.p.c. trace (*Figure 6*). It is very important to note that, in contrast to dilute-solution degradation, only one peak is shown in the molecular-weight distribution. There are no signs of chain halving, only of a significant reduction in molecular weight and a substantial broadening of the molecular-weight distribution (see *Table 2*).

Since there was no way to perform this experiment at constant $\dot{\varepsilon}_{deg}$ or even at constant flow rate, we decided to control $\Delta P_{deg}$. In order to do this, the flow rate had to be increased every time $\Delta P$ dropped due to degradation (i.e. shifting of the $\Delta P$ *versus* $\dot{\varepsilon}$ curve). This is the reason for the range in nominal $\dot{\varepsilon}$ values reported in *Table 1* for samples 5 and 6.

The severe degradation suffered by the polymer solution repeatedly forced through the jets at $\Delta P_{deg} = 2$ atm is reflected in the $\Delta P$ *versus* $\dot{\varepsilon}$ curve of sample 6 (*Figure 3*). Its flow resistance is now only slightly higher than pure decalin. It showed no flare at all, only a very weak birefringent line, which was too dim to be recorded noise-free. Visual observation of this birefingent line enabled part of the high end of the molecular-weight curve to be constructed (*Figure 5*). The g.p.c. trace of this sample can be seen in *Figure 6* and it qualitatively matches *Figure 5*. *Figure 6* also shows a g.p.c. trace of sample 5 that indicates that most of the degradation had already occurred after 15.4 h at $\Delta P = 2$ atm (see *Table 1*).

**Table 2** Results of g.p.c. analysis

| Sample no. | $M_w$ | $M_n$ | $M_w/M_n$ |
|---|---|---|---|
| 0 | $6.73 \times 10^6$ | $5.02 \times 10^6$ | 1.34 |
| 4 | $5.05 \times 10^6$ | $2.50 \times 10^6$ | 2.00 |
| 5 | $1.51 \times 10^6$ | $0.96 \times 10^6$ | 1.57 |
| 6 | $1.31 \times 10^6$ | $0.85 \times 10^6$ | 1.54 |

## DISCUSSION

Polymer degradation in solution can be thermal, mechanical or thermomechanical in origin. Mechanical degradation can be subdivided according to the concentration regime into two types:

(i) Dilute-solution regime: where the forces required to break the chains are transmitted through viscous energy dissipation due to friction between solvent and polymer molecules. In this regime, chain breakage can be induced by overstretching at $\dot{\varepsilon} > \dot{\varepsilon}_f$, whilst the flow field remains purely elongational with a well defined stagnation point. Here the degradation can be carried out by flowing the solution at a constant strain rate (beyond $\dot{\varepsilon}_f$) and circulating the solution as many times as necessary, since degradation is limited to a small region surrounding the stagnation point (the molecules must stretch completely before breaking). Chain scission in this regime always yields central breakage because maximum loading is in the molecule centre as predicted by the TABS theory[7].

(ii) Semidilute-solution regime: where the forces required to break the chain are transmitted primarily by valence bonds, i.e. network chains and junctions. It is reasonable to anticipate marked differences in the degradation behaviour of stretched interacting molecules, the most obvious expectation would be the disappearance of preferential breaking near the centre of the molecule as higher concentrations are approached. At concentrations beyond $c^+$ and at timescales shorter than the disentanglement time of the chains ($\dot{\varepsilon} > \dot{\varepsilon}_n$), dramatic increases in the flow resistance are observed with concomitant degradation and distorted flow fields. However, it seems that the concentration has to be increased well above $c^+$ in order to get a more random scission.

Degradation experiments performed on a 0.35% aPS/decalin solution of $M_p = 8.1 \times 10^6$ (aPS) yielded central scission. In that case $c^+ = 0.04\%$, so that the solution was nearly 10 times that value.

As we have argued before, the elongational flow-induced extension registers a much lower degree of coil overlap than implied by the conventional $c^*$ criterion for semidilute solutions. Therefore, just above $c^+$ the number of such tenuous entanglements on the periphery of the coils may not be high enough to randomize scission. It thus seems necessary to increase the number of entanglements per chain in order to have a random distribution of molecular lengths in between junction points.

The concentration of 1.5% used in this work for a $M_p = 5.8 \times 10^6$ aPS/decalin solution is 30 times higher than $c^+$ (=0.05%). With this solution the results are consistent with non-central scission; $M_p$ shifts progressively to lower values (see *Figures 5* and *6*) with no indication of a residual peak at the original molecular weight or at half the original. The peak also broadens dramatically, the polydispersity index increasing to around 2 on going from sample number 0 to 4 (*Table 2*) during the initial stages of degradation. It narrows again to around 1.5 during the final stages of degradation (samples 5 and 6).

The above results are therefore consistent with *almost* random scission along the chains. Perfect random scission would require a polydispersity index of 2. The scission is non-central, as might be expected for a model where stress is transferred at discrete entanglement points rather than by hydrodynamic interaction by stretched molecules with the moving solvents.

As degradation proceeds, the average molecular weight gets much lower, which corresponds to a lower effective degree of entanglement. We would therefore expect, from earlier results, a return to non-random (i.e. more central) scission. This could explain the narrowing of the distribution in the final stages of degradation. In order to get perfectly random scission, we would have to increase the concentration even more.

Another major difference between type (i) and type (ii) scission is the impossibility of carrying out degradation experiments at constant strain rate when using semidilute solutions. This arises because of the flow modification induced by the presence of entanglements. The deformation of a network is incompatible with stagnation-point flow (infinite strains) and therefore the flow field loses its point of singularity and is very unstable, changing constantly with time. On the other hand, if the macroscopic volumetric flow rate is kept constant, then the degradation process will be halted when the dilatancy observed in flow resistance is eventually shifted to higher flow rates. This is because the solution will only degrade whilst in the entangled state (at $\tau < \tau_n$). Therefore, it is better to carry out the degradation experiment at a constant stress per molecule since we are dealing with a network. Comparison with previous preliminary results[12] at other concentrations and molecular weights suggests that it is the level of stress per chain in solution that determines degradation.

Regarding scission rate, two facts are now clear. First, the scission rate increases when changing from dilute solution (type (i) regime) to semidilute solution (type (ii) regime). This might be a result of the change in degradation conditions: in type (i) only a small percentage of the molecules have a chance to break (those molecules that pass close to the stagnation point) whereas in type (ii) nearly all of the molecules that pass through the jets are participating in the transient network formed. Nevertheless, it should be pointed out that it is difficult to compare scission-rate results when the degradation conditions are so different. Information on the concentration dependence of scission rate within each regime is still fragmentary in elongational flow, a subject at present under investigation.

Secondly, within the semidilute regime, it is more difficult to degrade a closely monodisperse polymer solution than a polydisperse one. This can be readily demonstrated by qualitatively comparing the change in the $\Delta P$ *versus* $\dot{\varepsilon}$ curve with the number of runs for polydisperse polymer solutions[9–12]. Compare, for instance, *Figure 2* with *Figure 3*. Just one run through the jets of a semidilute PEO/water solution (0.2%, $M_w > 5 \times 10^6$) is enough to shift the curve from *Figure 2a* to *Figure 2b*, indicating a certain amount of degradation. At least eight runs are necessary for an equivalent dilatancy change in a semidilute aPS solution (*Figure 3*). A dramatic shift in the PEO curve is obtained by 12 runs at $\Delta P_{\text{deg}} = 1$ atm (see *Figure 2e*), while 64 runs only produce a moderate shift in the aPS case (*Figure 3*).

Because the aPS solution is more concentrated, the comparison might not be fair. If, however, *Figure 2* is compared with previous results obtained with almost equivalent concentrations and molecular weights[12], a very similar situation is found, namely that the almost monodisperse polymer solution resists degradation more than the polydisperse one. We still lack a comparison between a polydisperse and a monodisperse sample of the same polymer. Even so, since PEO, HPAA and polyisobutylene seem to behave almost identically, we feel that a generalization could be in order.

The origin of the difference in degradation resistance outlined above may lie in the fact that all the molecules in the monodisperse case have the same relaxation times and therefore resist the flow in unison, forming a stronger network than in the polydisperse case, where the molecules will be selectively broken from a distribution one by one, starting from the longest.

## CONCLUSIONS

The flow resistance measurements are extremely sensitive to degradation of high-molecular-weight polymers.

According to expectation the degradation of polymer molecules in elongational flow is very closely central for dilute solutions but is increasingly randomized as higher concentrations are approached. These results might be expected for a change in degradation mechanism where stress is transferred at junction points in a transient network instead of the stress being transferred to hydrodynamic interaction of stretched molecules with the moving solvent molecules.

As a result of the change in degradation mechanism, the relevant parameter that seems to determine the degradation of a transient network is the stress per chain in solution.

The ability of monodisperse aPS to resist degradation whilst in the entangled state seems to be far greater than that of polydisperse PEO or HPAA. This could be a general feature of monodisperse systems, where all the molecules possess identical relaxation times and therefore resist the flow in concert, whereas polydisperse distribution molecules get 'picked off' one by one from the longest.

## ACKNOWLEDGEMENT

We are pleased to acknowledge the generous support of the Venture Research Unit of BP International.

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