Conformational relaxation time in polymer solutions by elongational flow experiments: 2. Preliminaries of further developments: chain retraction; identification of molecular weight fractions in a mixture

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Using a planar-flow cross-slot device the retraction of the molecules from full extension was followed through birefringence observations and the relaxation time associated with this process was found to be considerably larger than that for the extension from the coiled state found in Part 1. Thus in the first approximation a hysteresis is demonstrated together with further details (possibly a double relaxation) of the contraction process. Use of this flow geometry also facilitated exploitation of the relation between M_w and $\dot{\epsilon}_c$ of Part 1 for the method of distinguishing molecular weights in a mixture.

INTRODUCTION

In Part I we investigated the relaxation time associated with the stretching of isolated molecules in elongational flow fields in dilute solution. In part 2 we now report preliminary observations on the nature of the retraction of such molecules from full extension and the associated relaxation time. In addition, preliminary results are reported on the development of a technique, based on results reported in Part 1, for the identification of molecular weight fractions in a mixture.

EXPERIMENTAL

The cylindrical symmetric flow field of the opposed jets used in the past was replaced in the work reported here by a planar symmetric flow field of a cross-slot device (*Figure* 1) similar to that used by Scrivener *et al.*[1]. This new flow system has three main advantages.

(1) The planar flow channels ensure that there is a constant strain rate along the length of any optical path which is in the plane of the channel and perpendicular to the flow direction.

(2) The optical path length can be easily increased to improve sensitivity.

(3) The nature of the retraction of the molecule after extension can be observed through the decay of the birefringent line in the exit channels.

Dilute solutions of a narrow fraction ($M_w/M_n = 1.2$) of 2×10^7 molecular weight atactic polystyrene in *ortho*-xylene were sucked or blown through the slot device and the resulting molecular extension assessed through birefringence observations made with crossed polars oriented at 45° to the entrance and exit channels. Birefringence resulting from residual strains in the glass could be compensated when a quarter-wave plate was inserted before the analyser. For observations of birefringence in the exit channel a mercury vapour lamp was the light source. For the identification of molecular weight fractions in a solution containing a mixture it was necessary to have continuous intensity measurement of the birefringent line in the central region of the cross-slot with changing strain rate. A photodiode detector was used and the mercury lamp replaced by a He–Ne laser for these photometric measurements. The mixture used contained equal weights of narrow fractions ($M_w/M_n = 1.2$) of atactic polystyrene with molecular weights of 2×10^6 and 2×10^7 in 0.1% solution in *o*-xylene.

CHAIN RETRACTION

Figure 2a shows the birefringent line resulting from the extension of the molecules in the elongational flow field in the central region of the slot, and its subsequent decay as the molecules leave the device via the exit slot. *Figure 2b* represents diagrammatically the region shown in *Figure 2a*. *Figure 3a* is a photodensitometer trace of the biref-

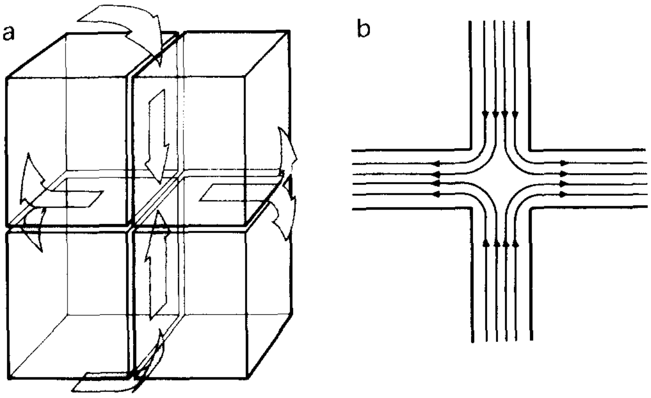

Figure 1 (a) Cross-slot device used to produce a planar elongational flow field. Slot cross-section is 4 x 0.3 mm; (b) idealized flow field in the cross-slot

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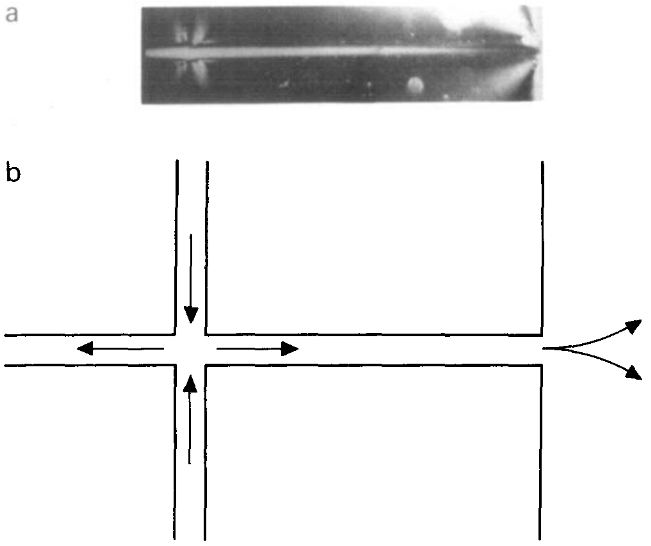

Figure 2 (a) Birefringent line seen in centre of cross slot and one exit channel for 0.1% solution of polystyrene ($M_w = 2 \times 10^7$) observed with monochromatic light and crossed polarizer and analyser at 45° to channels; (b) diagram of region seen in (a)

ringent line along the symmetry plane of an exit channel. For small retardations,

$$I/I_0 \sim B/B_0 \qquad (1)$$

where I_0 and B_0 are respectively, the intensity and birefringence corresponding to full chain extension. The end-to-end distance, l, can be related to the birefringence through the expression (2):

$$B/B_0 = [1 - 3l/L\,\mathscr{L}^{-1}(l/L)] \qquad (2)$$

where L is the contour length of the molecule and $\mathscr{L}^{-1}$ represents the inverse Langevin function. *Figure* 3*b* shows a plot of l/L against distance along exit channel which can be expressed as time from entering this channel. In order to relate distance to the time from entering the channel, a parabolic velocity profile has been assumed. Later, it is hoped a detailed plot of velocities within the slot will be obtained from photon-correlation experiments currently being undertaken. These measurements may also provide an explanation for the width of the birefringent line (*Figure* 2*a*) which is greater than would be expected from previous work[1-4]. We see two stages in the decay of the intensity, hence chain elongation. The initial slower decay can be fitted to an exponential of the form

$$l = L\exp^{-t/\tau}$$

where τ has a value of 0.018 s. If it is assumed that the molecule retracts freely in the solvent and it travels at uniform velocity along the exit channel, that is, the velocity gradient along the central line of the channel is zero, then this value of τ is the relaxation time associated with the retraction of the molecule from the fully-stretched state. This relaxation time is considerably larger than the corresponding relaxation time associated with extension from the coiled state, found in Part 1 to be 7.5 $\times 10^{-4}$ s for $M_w = 2 \times 10^7$.

The clearest suggestion which comes to mind is that the chain in the fully stretched state is in contact with the streaming solvent along its entire length; in other words it will approximate a free-draining chain[4] as opposed to a non-free-draining[3] one in the initial coiled state, the frictional coefficient, hence the relaxation time being correspondingly larger. Accordingly, the original extension would be governed by the fast non-free-draining (as established in Part 1) while the following retraction by the much slower free-draining relaxation. Indeed, a hysteresis in chain extension, has been predicted by de Gennes[5] and Hinch[6] which, as we have just seen, has become amenable to experimental observation.

Curves as in *Figure* 3 may convey more. It will be noted that the slow retraction is followed by a much faster process at the long time end completing the chain recoil, on a time scale of the order of 10^{-3} s. While it may be premature to place too much weight on these preliminary results, which require consolidation using a longer slot to avoid end effects, it is tempting to suggest that at a sufficient level of contraction the free-draining behaviour changes over to a non-free-draining one, at which point the chain 'snaps' back to its undeformed state with the correspondingly faster relaxation time.

It was implicit in the above argument that the retraction occurs in a flow field of zero velocity gradient corresponding to that of a completely free chain. We recognize that this cannot be taken for granted without

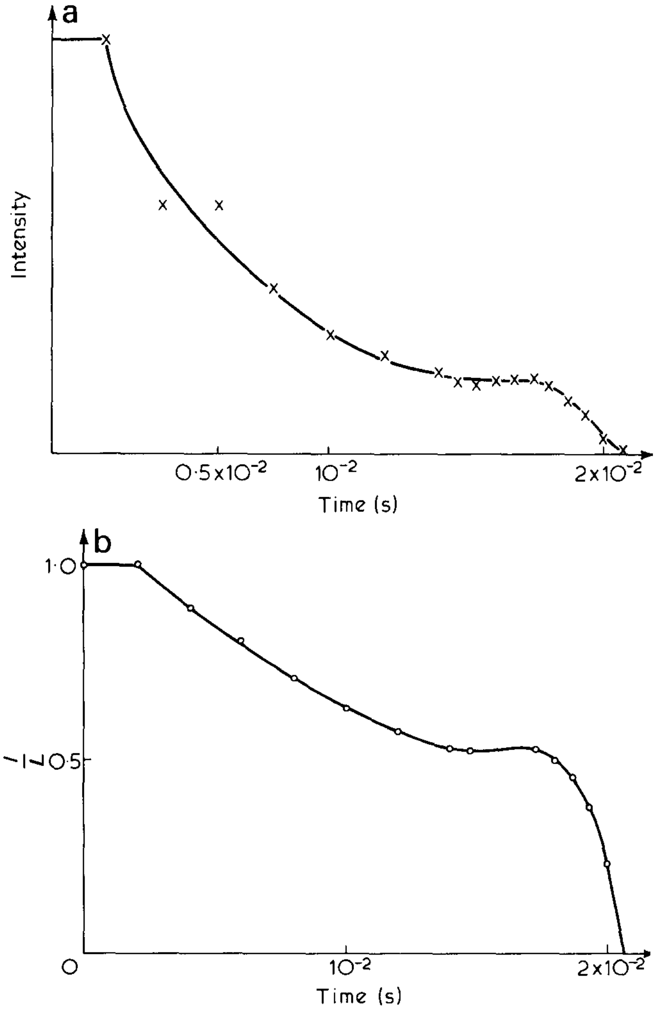

Figure 3 (a) Photodensitometer trace of centre of decaying birefringent line in an exit channel against time from entering the channel; (b) plot of l/L, derived from birefringent intensity, against time in exit channel where l is the end-to-end distance and L the contour length of the molecule

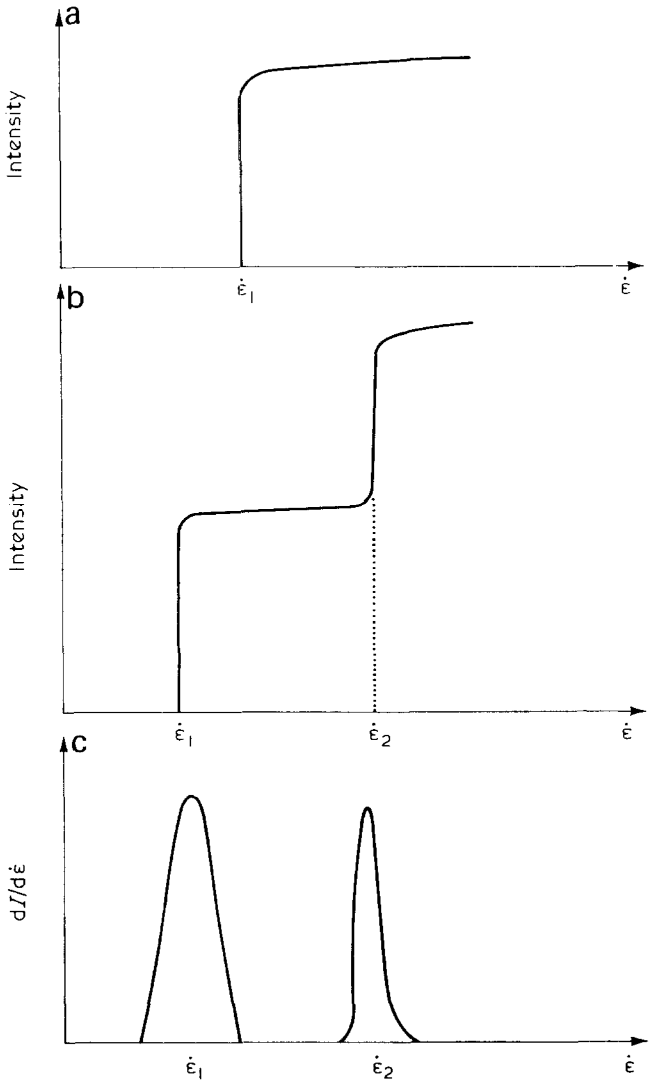

Figure 4 (a) Expected plot of intensity, I, against strain rate, $\dot{\varepsilon}$, for a solution containing single monodisperse fraction; (b) plot of I against $\dot{\varepsilon}$ expected for two monodisperse fractions where the molecules act independently in solution; (c) plot (b) differentiated with respect to the strain rate, showing peaks corresponding to the two fractions

direct determination of flow velocities at the actual localities where the birefringence is being observed. The experiment for such a determination is currently being designed. Until such information becomes available the above interpretation of molecular behaviour must remain tentative. However, this qualification should not obscure the fact that extension and retraction of molecules, encompassing full chain extension, can now be studied in a direct and surprisingly simple manner, which is the message we have endeavoured to convey by reporting these preliminary observations.

IDENTIFICATION OF MOLECULAR WEIGHT FRACTIONS IN A MIXTURE

In Part 1 we established a relationship between molecular weight and the extensional relaxation time of molecules, or, rather, between molecular weight and the strain rate, $\dot{\varepsilon}_c$, at which birefringence suddenly set in for a solution containing a narrow molecular-weight fraction. Theory predicts[7-9] that in the region of $\dot{\varepsilon}_c$, extremely rapid extension of the molecule occurs from the coiled state to full extension for a small increase in $\dot{\varepsilon}$, and our observations in Part 1 come close to this prediciton. For our present experimental development this prediction and observation can be approximated by:

$$\dot{\varepsilon} < \dot{\varepsilon}_c \qquad \varepsilon = 0$$

$$\dot{\varepsilon} > \dot{\varepsilon}_c \qquad \varepsilon = \varepsilon_{max}$$

where ε_{max} is the strain of the completely extended molecule compared with the unperturbed random coil.

The optical retardation is now proportional to the mass of molecules extended, that is, the mass of the molecules with $\dot{\varepsilon}$ less than the current value of strain rate. If there is a range of M_w, progressively shorter chains will extend with increasing $\dot{\varepsilon}$ and the retardation will increase accordingly. For small retardations (here, typically $<\lambda/10$) the intensity of the birefringence observed between crossed polars can be taken as being approximately proportional to the retardation.

Figure 4a illustrates diagrammatically the expected plot of intensity, I, against strain rate, $\dot{\varepsilon}$, for a dilute solution containing one narrow molecular weight fraction. *Figure 4b* is what might be expected for a dilute solution containing two narrow molecular weight fractions. It assumes that the molecules behave independently, resulting in the sum of two displaced 'step functions'.

If the molecules in a small molecular weight range have critical strain rates in the range $\dot{\varepsilon}$ to $\dot{\varepsilon} + \delta\dot{\varepsilon}$ and the mass in this range is $m(\dot{\varepsilon})\delta\dot{\varepsilon}$, the orientation of these molecules in the elongational flow field contributes δI to the total intenstiy, where:

$$\delta I \propto m(\dot{\varepsilon})\delta\dot{\varepsilon}$$

and, in the limit as $\delta\dot{\varepsilon} \rightarrow 0$

$$\frac{dI}{d\dot{\varepsilon}} \propto m(\dot{\varepsilon})$$

that is, in the case of two molecular weight fractions in a dilute solution, a plot of $dI/d\dot{\varepsilon}$ against $\dot{\varepsilon}$ would contain two peaks (*Figure 4c*) corresponding to the two molecular weights, if the molecules behave independently.

In Part 1 the sudden onset of high extension at $\dot{\varepsilon}_c$ was observed through the rapid increase in optical retardation with strain rate, at $\dot{\varepsilon}_c$. Using the photodetector, the equivalent direct plot of intensity against strain rate in *Figure 5*

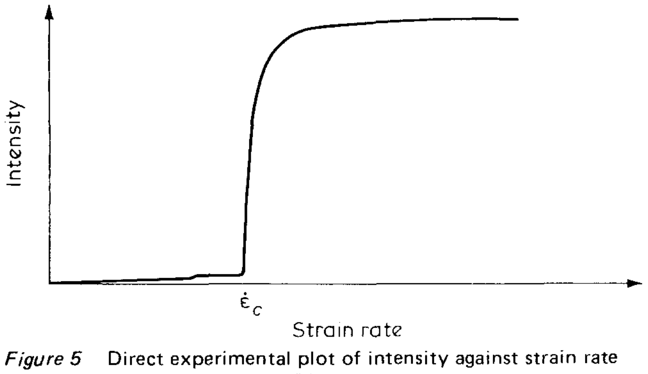

Figure 5 Direct experimental plot of intensity against strain rate for a monodisperse fraction of PS in dilute solution

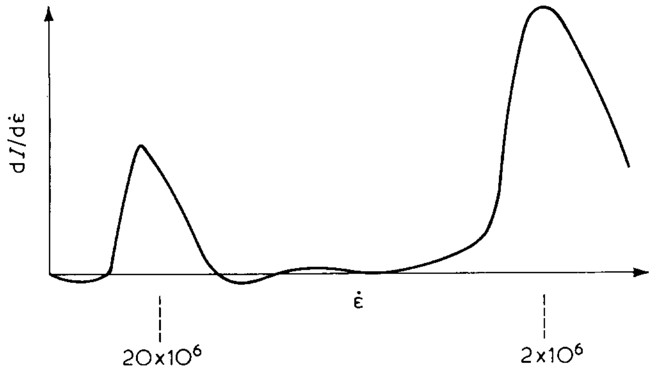

Figure 6 Differentiated plot of intensity against strain rate for a solution containing a mixture of two monodisperse fractions. An instrumental broadening (estimated at about 50% for this slot) due to non-uniformity in slot dimensions has been introduced into this plot

shows the same features. In order to test for the independence of molecular behaviour in a solution containing a mixture of $M_w = 2 \times 10^6$ and $M_w = 2 \times 10^7$ ($M_w/M_n = 1.2$), the photodetector set-up was used and the differentiated plot is shown in *Figure* 6. At the solution concentration used (0.1%), the molecular weight species appear to have behaved independently, resulting in increased intensity at two distinct strain rates rather than some average value of the two critical strain rates.

In the first place the above behaviour indicates that the extension of a portion of the molecules does not have a significant enough effect on the flow itself to reduce its orienting ability as regards the rest of the molecules which are still unextended.

More significantly for the present purpose, the observation in question suggests that such a system could be used to identify molecular weight fractions in a mixture. Indeed, this system is potentially a method for molecular weight distribution measurements, particularly well-suited for high molecular weights where other methods, such as gel permeation chromatography, become unreliable. However, so far it has not proved possible to assess this potential experimentally, as the strain rates realizable in the present apparatus limit measurement to high molecular weights for which accurate distribution data are not available from other sources.

CONCLUSIONS

In Part 1 the relaxation time associated with the extension of the molecule from the random coil state was found to correspond to the Zimm non-free-draining model and displayed the molecular weight dependence appropriate to this model. In Part 2, it has been found that the relaxation time associated with the retraction from full extension takes much longer and is closer to that expected for the Rouse or free-draining model. Thus, extension and retraction involve a fast and slow process, resulting in a hysteresis in the deformation of an isolated molecule in solution, and further, experiments indicate that the retraction itself consists of two components, an initial slow one (referred to above) followed by a more rapid one completing the retraction.

A possible method for distinguishing molecular weights in a mixture by exploiting the critical strain rate–molecular weight relationship was demonstrated.

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