Conformational relaxation time in polymer solutions by elongational flow experiments: 1. Determination of extensional relaxation time and its molecular weight dependence

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The nature of chain extension of high-molecular weight atactic polystyrene in an elongational flow field was investigated. In particular, we studied the sudden onset of high extension which, according to theory, is governed by the expression $\dot{\varepsilon}_c\tau = 1$. The molecular weight dependence of $\dot{\varepsilon}_c$ (the critical strain rate at which high extension occurs) was examined, and the corresponding relaxation time, τ, which would be relevant to the above expression was considered. The experimental measurements of absolute values and the functional dependence on molecular weight of the relaxation times demonstrates that it is the relaxation time associated with the Zimm non-free-draining model which is appropriate to this coil–stretch transition.

INTRODUCTION

This paper is a continuation of past studies in this laboratory of the chain-extending effect of extensional flow in polymer solutions. It also incorporates some results of a preceding paper[4] which the present work has brought to conclusion. To recall, these studies are based on the creation[1–4] of hydrodynamically-characterized extensional flow fields and on the *in situ* observation and measurement of the birefringence arising owing to chain extension*. It emerged that in solutions of $M_w = 2 \times 10^6$ of dilution less than 1% such chain-extension is always confined to sharply localized regions of the flow field where the residence time of the fluid element is long enough for the required extension to be achieved. Within these regions practically complete chain-extension can be attained provided both the strain rate ($\dot{\varepsilon}$) and the molecular weight (M_w) and through the latter the configurational relaxation time (τ), are sufficiently large. There has been extensive theoretical work concerned with the nature of chain extension in an elongational flow field, but relatively little experimental evidence has been reported. The initial aim of the work reported here was to compare the observed extension of the polymer molecules in the elongational flow field with the predictions of theory, in particular, the predicted sudden onset of high extension[5–7] at a critical strain rate, $\dot{\varepsilon}_c$, given by:

$$\dot{\varepsilon}_c\tau = 1 \tag{1}$$

where τ is the longest relaxation time of the isolated molecule, such that, below $\dot{\varepsilon}_c$, the chains are hardly affected, and above it complete extension is attained.

The aim of the present experiments was to test this critical strain rate criterion and to obtain values for τ as a function of molecular weight.

EXPERIMENTAL

Sufficiently high and quantitatively-defined strain rates were realized using two opposed jets operating in suction along lines previously described[4]. To obtain a unique relaxation time highly monodisperse polymer is required with sufficiently high molecular weight to become extended under the realizable strain rates. Special polystyrene fractions with M_w ranging from 2×10^6 to 2×10^7 satisfied these requirements. These were used in xylene solutions at concentrations ranging from 0.03 to 2%.

The solutions were sucked through the immersed double jets with increasing velocities, the strain rates themselves being calculated from the flow velocity and the geometry of the system. The effect of the flow field between the jet orifices was observed between crossed polars, oriented at 45° to the axis of the jets, using a telescope. The apparatus used is essentially as described previously[4] with the exception that the opposing faces of the glass-capillary jets were cut flat and parallel instead of the flame-polished ends used previously. This permits a more reliable measurement of jet separation.

RESULTS AND DISCUSSION

With increasing strain rate the field of view remained dark up to a critical value at which a sharp, negatively birefringent line appeared (*Figure* 1). *Figure* 2 shows the retardation as a function of $\dot{\varepsilon}$ for two concentrations. In spite of long error bars, it displays the principal features: (1) a sudden onset of birefringence; (2) a plateau region, the value of which has a broad proportionality to the concentration. The sudden onset of high extension reflected by these retardation measurements was predicted by theory, but we believe not previously observed. In the

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* Ref 4 contains some typographical errors in the symbols. Ambiguities arising there should become clear in the light of this paper.

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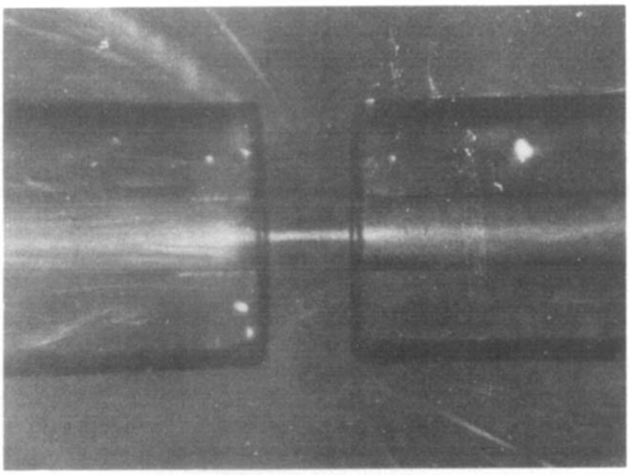

Figure 1 Birefringent line between jets for a 0.1% solution of polystyrene observed with monochromatic light and crossed polarizer and analyser at 45° to jet axis

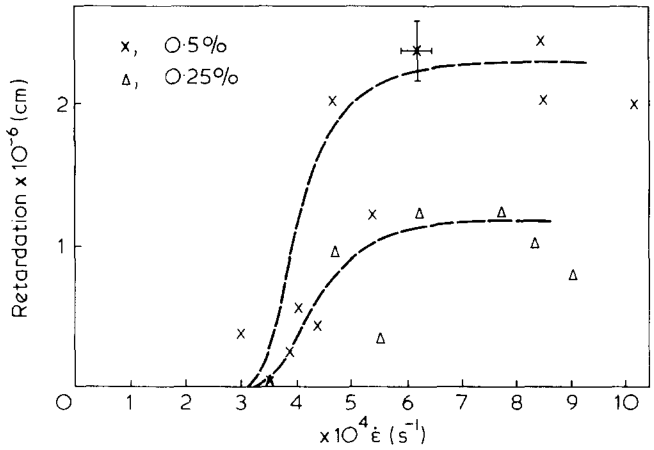

Figure 2 Retardation plotted as a function of strain rate, $\dot{\varepsilon}$, for concentrations of 0.5 and 0.25%. Error bars, shown for one point only, are representative of the rest

range of concentrations 0.03 to 0.5%, birefringence normalized to 100% concentration gave essentially the same value of about 0.06 which is in the range of birefringence (0.1) due to fully-oriented chains as calculated from values of bond polarizabilities. The observed behaviour was the same down to the lowest concentrations at which observations could be made, indicating we are working in the dilute solution regime, observing the behaviour of an assembly of essentially independent molecules. At concentrations greater than 1%, the birefringence between the jets became broad and unstable. So far we have not investigated this effect further, but it should be mentioned that this region of concentration corresponds roughly to the calculated value of de Gennes' c^*[8] of about 1.5%; the concentration at which molecular overlap first occurs[4].

Having established that the nature of the extension of isolated molecules in an elongational flow field corresponds to that which has been predicted by theory, the question arises as to the value of the relaxation time under the condition $\dot{\varepsilon}_c\tau = 1$. Here, theory provides two possible limiting values for the configurational relaxation time of an isolated molecule in solution. One relaxation time, associated with Rouse[9], corresponds to the free-draining molecule, that is, to the case when solvent streams through the molecule almost unperturbed by it. The second relaxation time, associated with Zimm[10] corresponds to the non-free-draining molecule, where solvent in the interior of the molecule moves with the molecule, leading to the concept of the equivalent hydrodynamic sphere impenetrable to flowing solvent. These models predict different frictional coefficients and damping, and thus lead to different relaxation times. The two relaxation times are given by:

$$\tau_{fd} = \frac{\pi\eta_0 b^3 \cot^2 \frac{1}{2}\alpha}{2kT} N^2 \tag{2}$$

$$\tau_{nfd} = \frac{2\pi\eta_0 b^3 \cot^{5/2} \frac{1}{2}\alpha}{kT} N^{3/2} \tag{3}$$

where η_0 = solvent viscosity; b = bond length; k = Boltzmann's constant; T = absolute temperature; N = number of monomers. Substituting suitable values for the case of a 2×10^6 molecular weight polystyrene molecule gives:

$$\tau_{fd} = 3.5 \times 10^{-3}\ \text{s}$$

$$\tau_{nfd} = 2.5 \times 10^{-5}\ \text{s}$$

The experimental value obtained from $\dot{\varepsilon}_c$ measurements is:

$$\tau_{exp} = 2.23 \times 10^{-5}\ \text{s}$$

Clearly, the experimental value is in good agreement with the non-free-draining or Zimm relaxation time.

A further experimental check can be made by investigating the molecular weight dependence of the relaxation time. The free-draining model predicts a quadratic dependence (see equation 2) on molecular weight, whereas the non-free-draining model predicts a 1.5 power law dependence (see equation 3). Critical strain rates for

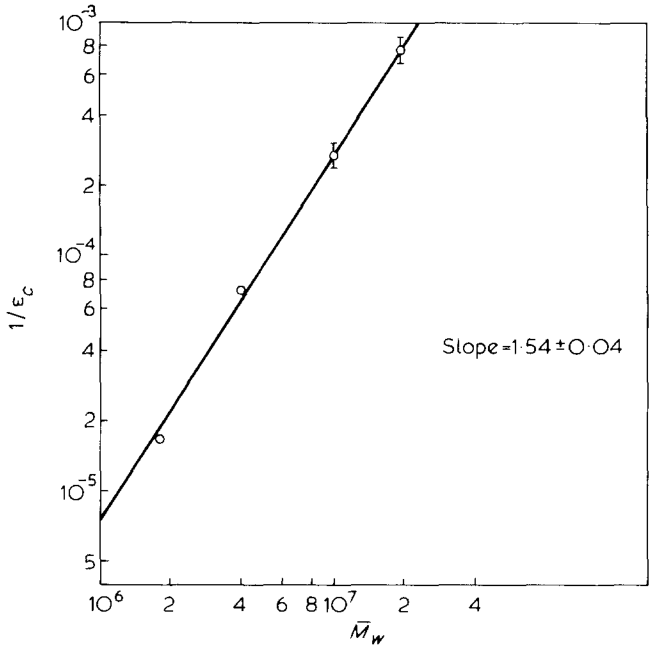

Figure 3 Log τ (or $1/\dot{\varepsilon}_c$) as a function of log $\bar{M}_w$, showing a straight-line relationship. For $\bar{M}_w = 2 \times 10^6$: $\tau_{exp} = 2.23 \times 10^{-5}$ s and $\tau_{Zimm} = 2.5 \times 10^{-5}$ s

four monodisperse polystyrenes from 2 to 20×10^6 molecular weight were determined and the corresponding relaxation times are plotted against molecular weight on log–log scales in *Figure* 3. The value of slope now gives the exponent of molecular weight, and the value of 1.54 obtained, disregarding the last decimal, which is just at the error limit, is in remarkable agreement with the Zimm non-free-draining model. Strictly, this power law dependence shows that the relaxation time relevant to the coil–stretch transition occurring at the critical strain rate depends on the end-to-end distance of the coil in the unperturbed state. Both the functional and absolute value agreement strongly support the Zimm model.

Further noteworthy observations include a reversal of sign at extremely low birefringences, which we attribute to the influence of form birefringence due to coil distortion competing with chain alignment preceding the sudden chain stretching, an effect which together with several other associated, intriguing observations is currently receiving attention.

In conclusion the sudden onset of chain alignment resulting in complete, or near complete, chain extension at a critical elongational strain rate has been directly observed, leading to a configurational relaxation time which was found to be very close to that expected from a non-free-draining coil (Zimm relaxation time) both with respect to its absolute value and its molecular weight dependence in the molecular weight range of 2×10^6–2×10^7.

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