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# Polymer solutions under elongational flow: 2. An evaluation of models of polymer dynamics for transient and stagnation point flows

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Models for the dynamics of dilute polymer solutions under elongational flow have been examined in the light of new experimental data. In particular birefringence measurements on the polystyrene-decalin and poly(ethylene oxide)-water systems in both stagnation point and transient elongational flows are the most revealing as to the nature of polymer chain uncoiling and fracture. Both the deformation and fracture behaviour have been observed to depend on the type of elongational flow (transient, stagnation point) and the chemistry of the polymer chain. The data on the critical strain rate for chain fracture along with observations of precise midchain scission (as estimated from size exclusion chromatography), a limited overall chain deformation, and the role of accumulated energy (strain) in mechanochemical degradation, tend to imply that a hybrid model of polymer dynamics in elongational flows may be realistic. One such model, a 'multi-stranded yo-yo with surface energy dissipation and solid like stress response' has been developed as a general hypothesis to account for the deformation, stretching and fracture behaviour of polymer chains in both transient and stagnation point elongation flows. This modified yo-yo is found to be an energetically favourable alternative to an affinely deforming chain over certain degrees of elongation. It has been shown to qualitatively explain the apparent difference in behaviour of polymer chains in both stagnation point and transient elongational flows. The viscous coupling between the solvent and the polymer chain is also used as a qualitative parameter to account for the deformation and fracture behaviour of polymer chains under transient and stagnation point elongation flows. Based on these analyses, a set of recommendations as to future experiments are presented. Copyright © 1996 Elsevier Science Ltd.

**(Keywords: elongational flow; polymer dynamics; birefringence; multi-stranded yo-yo)**

## INTRODUCTION

Recent experimental results on the birefringence characterization of dilute polymer solutions under elongational flow[1] have indicated that the chain deformation and fracture behaviour are dependent on, among other variables, the nature of the flow (transient, stagnation point) and the polymer chemistry. In light of this and other recent data, we intend to re-evaluate the models for polymer dynamics. In particular we will use the viscous coupling of the bulk fluid with the polymer chain and its side groups, as a qualitative variable to explain a deformation mechamism for polystyrene and poly(ethylene oxide) in both stagnation point and transient elongation flows.

Dilute polymer solutions have historically been modelled as a freely jointed bead-rod or pearl necklace[2,3], a dumbbell[4-6] or a multi bead-spring/Gaussian subchain[7,8]. In summarizing the general consensus on the pioneering models of polymer dynamics in dilute solutions (*Table 1*) the bead-spring approaches of Rouse-Zimm are unable to predict the behaviour of polymers in strong flows since they are based on Gaussian springs which are inadequate at high elongations. The nonlinear elastic dumbbell approach[9,10] is usually advanced as a basic model for the fluid dynamics of polymer solutions. However, it has been argued that since these are based on equilibrium concepts (entropic spring) they should be valid only if the time constant for chain relaxation is much less than the time constant of the process. However, this is not satisfied in strong flows. Such flows also limit the number of thermodynamic configurations or render some configurations less probable than others. This further weakens the thermodynamic concept of entropic elasticity. Rabin[11] has also noted that the dumbbell models cannot predict the structure of polymers in elongational flows. For example, FENE dumbbell models predict that

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**Table 1** Models of polymer dynamics

| Model | Author | Year |
|---|---|---|
| Freely-joined bead rod | Kramers | 1944 |
| Pearl necklace | Frenkel | 1944 |
| Multi-bead spring/ Gaussian subchain | Rouse and Zimm | 1953, 1956 |
| Dumbbell FENE spring | de Gennes | 1974 |
| Recent models of polymer dynamics in elongational flow | | |
| Frozen chain | King and James | 1983 |
| Yo-yo | Ryskin | 1987 |
| Kink dynamics | Larson | 1990 |
| Dynamic blob | Rabin and Ottinger, Pincus | 1977 |
| Hairpin/energy dissipation | Kausch | 1990 |

all individual links are stretched simultaneously before extensive chain unfolding. This seems improbable given the evidence of precise midchain fracture[12] and centre uncoiling[13]. Such limitations and the lack of coincidence with experimental data, particularly in fast transient flows, has spurned several advanced models specific for elongational flow over the past two decades. These are listed in the second section of *Table 1*. It should be noted, however, that most of these models have been developed to fit a limited set of experimental data and have some restrictions in terms of applicability as will be discussed.

### *Overview of models for polymer dynamics in elongational flow*

The recent history of modelling of polymer chain dynamics in elongational flows can be summarized as follows. In 1980 James and Sarringer[14] used pressure drop measurements to infer the contribution of polymer stress to the flow field and found that this greatly exceeded predictions of dumbbell models and multi-bead spring models. In 1983 King and James[15] explained this phenomenon by suggesting that in transient flows chains 'freeze' in a partially extended form, i.e. after an initial degree of elongation, due to intramolecular 'knots' or entanglements (*Figure 1a*). These frozen chains are essentially rigid objects which generate large internal stresses with the solvent free to flow around them. In 1987 Ryskin developed a model based on Frenkel's prediction of a polymer chain's conformation in a supercritical elongational flow[3]. He assumed that a polymer chain possesses a straightened or stretched central portion in the direction of flow, with two coiled-up regions at the extremes[13]. Ryskin named this a 'yo-yo' model since the undeformed coils store elastic energy and the chain can either stretch or relax depending on the magnitude of the extensional flow, much in the way a child's toy behaves (*Figure 1b*). Rabin[11] has supported this idea of centre uncoiling. Larson and Magda[16] have also lent credibility to the idea through a multi-bead spring calculation which predicts that a chain is much more extended in the centre than at the ends for flows near the critical value. Chain fracture results in stagnation point[17] and transient[12,18] elongational flows have shown markedly non-random chain scission, with the fracture distribution having a very low polydispersity. Since the fracture distribution reflects the stress distribution on the chain prior to rupture then the scission data also support a model which features centre uncoiling and a taut portion where very large stresses are stored.

In 1988 Rallison and Hinch[19] developed a multi-bead link model and found that after the onset of a strong elongational flow the chain exhibits a highly folded or 'kinked' state. Reese and Zimm[20] have recently used a bead-spring approach to model biopolymers with ultra-high molecular weights and monodisperse molecular weight distributions. They found that when the flow had progressed almost to the point of chain fracture the springs were virtually parallel to the stretch axis, but contained many folds. *Figures 1c* and *d* show representations of kinked and folded chains proposed by Rallison and Hinch, and Reese and Zimm respectively.

In 1990 Larson[16] modelled quasi-stationary state flows in the supercritical strain rate region. He found that since the residence time in the strong flow region was very small, the drag force greatly exceeded the Brownian force. Larson also showed that a 'kinked state' was generated at high values of the Hencky strain ($\dot{\epsilon}t$) through a contraction of the chain in the $y$ and $z$ directions in favour of a one-dimensional like object oriented along the flow or $x$-axis. Larson also postulated that there may be essentially complete uncoiling with the exception of the kinks where chain reverses direction. The effect of strain on the development of kinks is shown in *Figure 1e*. It is interesting to note that Larson found that the predicted unravelling was very sensitive to the initial kinked state. This would correspond physically to the orientation of the chain with respect to the flow axis prior to encountering the high strain region. It is reasonable to assume a distribution of initial configurations all of which would uncoil over different time scales. Reese and Zimm have also found, through simulation, that the final state of the chain is very sensitive to its initial configuration[20].

It is perhaps non-coincidental that all the models for chain dynamics in elongational flow proposed over the last decade incorporate one form or another of intramolecular interaction which hinder elongation. Even Ryskin in his development of the yo-yo scheme conceded that a representation as a single taut string is oversimplified and in the initial supercritical stages a yo-yo actually likely possesses a bundle of coil–string–coil systems. This can be visualized as a chain very similar to the dynamic blob described by Pincus[21] and Rabin and Ottinger[22] or a yo-yo with multiple taut central strands (*Figures 1f,g*).

Nguyen and Kausch[23] have recently used scaling arguments to treat a macromolecule as a microscopic reactor, uncoupled from the surrounding fluid apart from the input of deformation energy. The latter assumption enables one to explain the $-1$ order dependence of the critical strain rate for fracture on the polymer molecular weight without recourse to slender body hydrodynamics which have severe restrictions for fast transient flows. Nguyen and Kausch proposed that an elongated molecular coil is continually subjected to frictional forces at its 'surface'. To the first approximation the total (elastic) energy incorporated, that is the accumulated strain, scales with the surface of the volume element containing a coil. This reflects a series of experimental data which shows that fast transient flows do not follow the classical model of chain loading through strain-rate dependent friction. Rather, friction is related not to the strain-rate on the polymer but the total accumulated *strain*[18].

Nguyen and Kausch showed that the rate of energy dissipation was inversely proportional to the polymer molecular weight:

$$\text{rate of energy dissipation} \propto M^{-1} \qquad (1)$$

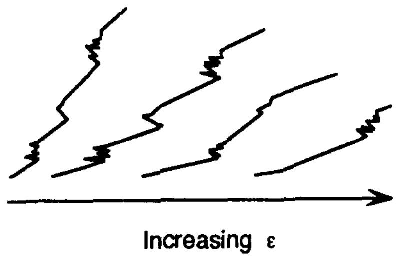
It is therefore reasonable to assume that a critical energy level such as the critical strain rate for fracture $\dot{\epsilon}_f$ will also scale with molecular weight to a $-1$ order dependence as is found experimentally[12]. The correlation between chain fracture and stress is similar to a phenomenon occurring in solid polymer materials where Kausch and Nguyen[24] have shown that the pullout of a chain depends on the rate of displacement ($\epsilon$ or velocity) and *not* the rate of deformation($\dot{\epsilon}$). The reciprocal dependence of fracture on molecular weight is also in agreement with theoretical

(a) 'knots'

(b)'yo-yo'

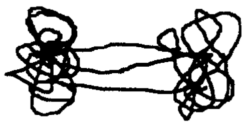
(c) 'kinked' chain

(d) 'folded' chain

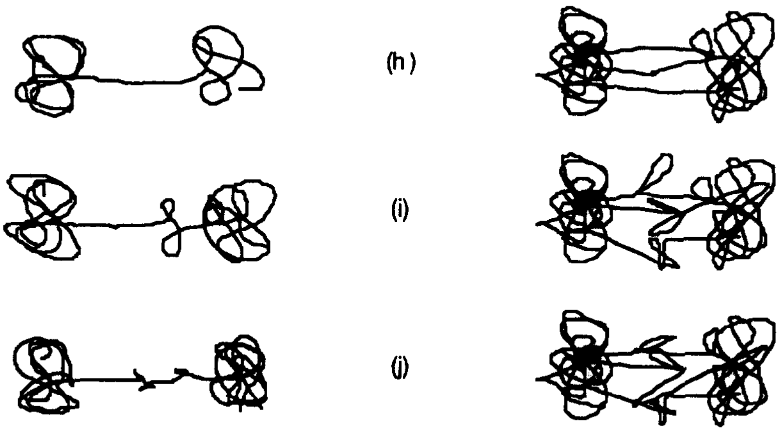


(e) Evolution of Larson's 'kinked' state [7]

(f) 'dynamic blob'



(g) 'multi-stranded yo-yo'



single strand

multi-strand

**Figure 1** Schematic representations of polymer chains under the influence of elongational flow fields. The first four sketches (a–d) show various interpretations of intramolecular interactions: (a) 'Knots' proposed by King and James[15], (b) Ryskin's 'yo-yo'[13], (c) Larson's 'kinked chain'[33], and Zimm's 'folded chain[20]. The fifth sketch (e) shows a schematic representation of the evolution of the 'kinked' state with the strain rate (from Larson[33]). The sixth and seventh sketches compare a 'dynamic blob' model (f)[21,22] with the 'multi-stranded yo-yo' (g). The eighth through tenth sketches (h, i, j) show representations of intramolecular interactions in single strand and multi-stranded yo-yos: (h) no intramolecular interations, (i) intramolecular knots, (j) intramolecular kinks predictions for the yo-yo model which indicate a −1.1 scaling law dependence[25].

Kausch and Nguyen later added a 'hairpin' model to their surface energy dissipation postulate[24]. This approach assumed that the stresses acting on any two legs of the hairpin combine and are transferred through the *stiff* chain to the adjoined segments and toward the centre. This assumption of increased stress transfer is similar to the models for internal stiffness due to hindered rotation[26–28], internal viscosity[13,29,30], or large loop intramolecular contacts[13,30]. An alternative explanation of scission as a cooperative process involving several mainchain bonds was also forwarded by Kausch and explained in terms of coupled vibrations along the chain[31].

The dynamic blob model[13,21] describes a stretched polymer as a chain of tensile blobs. Rabin and Ottinger's[13] interpretation assumes that viscous dissipation is only through small scale intraparticle motions which evolve on a $\dot{\epsilon}^{-1}$ time scale and unfold into shear or dynamic blobs each with a given equal radius.

## DISCUSSION

### *Hybrid models of polymer dynamics*

It is further possible to postulate the existence of several hybrid polymer dynamic models. While the combinations are certainly more than can be reasonably listed in this paper we shall examine those combinations with Ryskin's yo-yo model. The yo-yo model has been chosen as a basis since recent calculations for both Langevin models of free-draining ideal chains[11] and bead-spring chains[32] have indicated that the centre portion of the molecule is the most stretched-out portion of the chain.

The central portion of a multi-stranded yo-yo constitutes virtually the entire effective hydrodynamic length of the polymer chain. This region of the chain also accumulates all the stresses which are generated via a dissipative mechanism. It is therefore not difficult to imagine why such a configuration would lead to a precise midchain halving. However, experimental results in fast transient flows indicate that the fracture distribution is

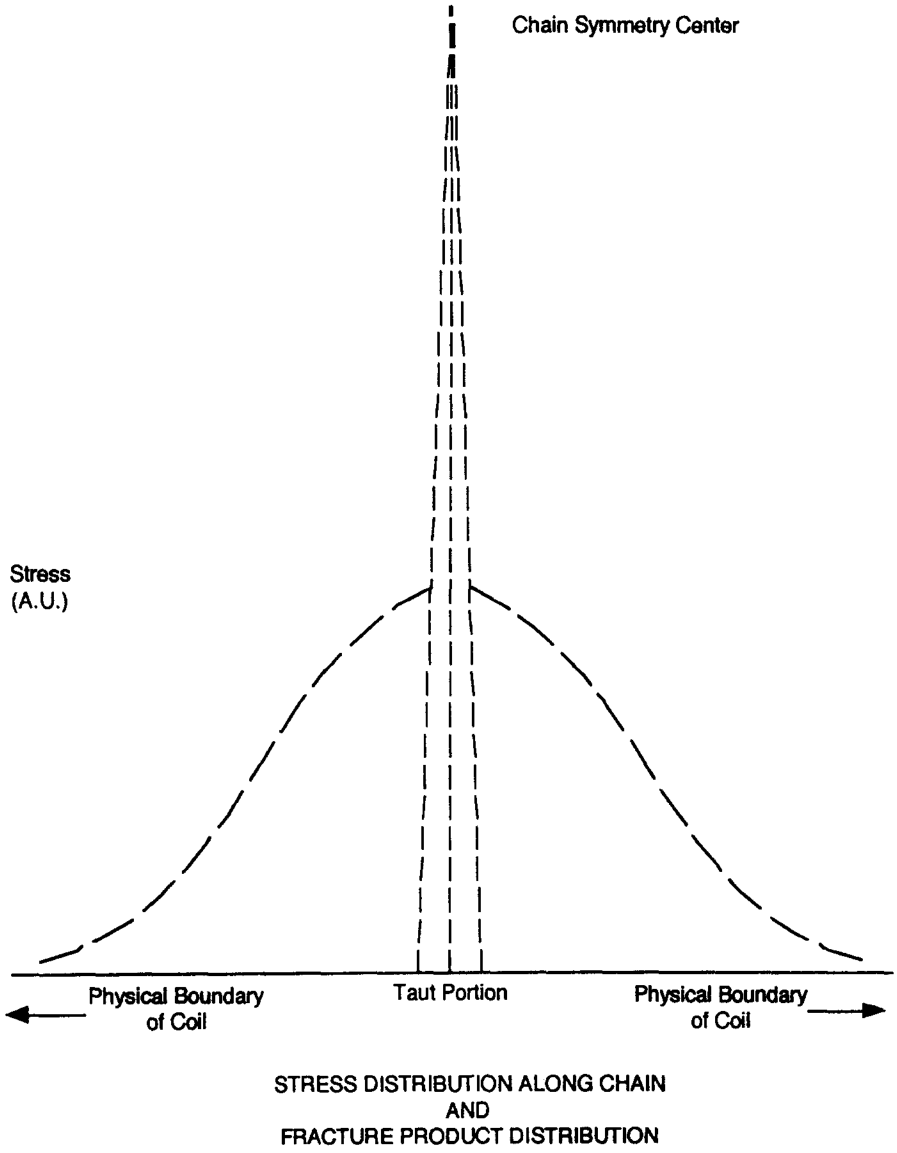


**Figure 2** A schematic representation of the stress distribution along a chain (bell-shaped curve) and the corresponding fracture product distribution (sharp peak) for two polymer configurations: highly elongated coils, and deformed chains with a taut central portion and two highly coiled extremes. In the 'yo-yo' configuration the stress is transmitted to the central taut portion of the chain through a solid like response mechanism where it accumulates. Such a model can explain the highly precise nature of chain fracture in transient elongational flows where deformation is only modest

approximately Gaussian with a standard deviation of only 4–7%[12]. This is slightly dependent on the thermodynamic quality of the solvent[23]. The spread in the fracture distribution can be explained by an entangled multi-segmental yo-yo where the fracture would be randomized within the taut portion of a single strand. This would lead to a spread in the fracture product distribution in relation to the stress on the central portion, which could be imagined as parabolic. The standard deviation of this distribution would be a function of the length of the central portion relative to the length of the chain if fully extended. Since the taut portion will be a small percentage of the total length, and the total polymer mass, at any given $\dot{\epsilon}$, the fracture distribution will possess a very small, but non-zero, standard deviation. This is to say the standard deviation of the fracture distribution is related to the percentage of the polymer chain which exists as the taut portion of the yo-yo (*Figure 2*).

The intramolecular interactions within the central portion of the yo-yo which lead to multistrands could be due to knots, as proposed by King and James[15], kinks[19,33], hairpins[24] or other effects such as internal viscosity. The configurations of such hybrid partially uncoiled yo-yos may be represented schematically as in *Figures 1h, i, j*.

*Evaluation of the yo-yo model for transient elongational flows*

Larson[33] made an excellent evaluation of the models of polymer dynamics in transient elongational flow in 1990. The results of his Table 1 are largely used in the following discussion.

Recent publications from two independent groups measuring birefringence and light scattering have shown that for several polymer–solvent systems in solvents of varying thermodynamic quality and viscosity, the local extent of orientation (birefringence) is not saturated[34] and the overall deformed length indicates only moderate extension[15,35]. The lack of saturation in transient elongational flows, reported herein, has been observed on near monodisperse polystyrene as well as poly(ethylene oxide)s with large polydispersities. This indicates, at least for the polystyrene data, that the lack of saturation cannot be attributed to polydispersity effects. Furthermore, light scattering results in stagnation point flows[35] indicate that the radius of gyration measured under elongational flow ($h$) divided by the radius under quiescent conditions ($h_0$) is only on the order of approximately two, which roughly agrees with Smith and Merrill's data of several years ago in a transient apparatus[36] ($h/h_0 \approx 4$) both of which imply only a modest deformation. Therefore, the precise midchain scission reported over the last several years in fast *transient* flows[12,18] can be reconciled with this work and the data of Menasveta and Hoagland[35] and Smith and Merrill[36] only by employing a model which contains all of the following features:

1. The polymer coil deforms but is not fully extended (birefringence less than saturation) for all physically obtainable values of $\dot{\epsilon}$.
2. The overall deformed length is relatively small, indicating some intramolecular hindrance to full extension. Through these intersegmental interactions stress is transmitted from the surface to the centre of the coil where energy is accumulated[23].
3. The deformed coil collects and accumulates energy as strain from the deforming fluid element[18] with the polymer coil statically loaded from the surface of the circumscribed volume element.
4. The central portion of the polymer chain is elongated to a much greater extent than the remainder of the 'coil' and effectively represents the entire hydrodynamic volume of the chain. The taut portion accumulates stress and fractures in a precise midchain manner with a small distribution of fracture products[12].

Such a scenario is consistent with a multi-stranded yo-yo model which contains intramolecular hindrances with energy accumulation in proportion to the external surface area and stored as some form of deformation energy*. All three features are important. The multistrand hypothesis is a macroscopic representation of the intramolecular contacts. This was mentioned by Ryskin[13,37] although without any predictions as to birefringence. The surface energy accumulation is used to predict the $-1$ order scaling law of the critical strain rate for fracture on molecular weight, and the energy storage to reflect the observation that strain, and not strain rate, is the driving force behind chain scission[18]. We have speculated as to several potential causes of the intramolecular restrictions, all of which tend to imply that the central portion of the chain acts in a solid-like manner with respect to stress transmission. Further, it is unlikely that with any experimental tools presently available (birefringence for measuring local orientation, light scattering for estimating global deformation, g.p.c. for measuring the molecular weight distribution of fracture products and inferring the stress distribution along the chain prior to fracture, and mechanical techniques to measure the polymer contribution to the stress tensor) that we could distinguish between the various models for intramolecular interactions described in *Figure 1*. It is also of relatively minimal importance as we are really only interested in the number of such contacts or entanglements or the relative molecular weight of the 'multi-stranded' region compared to that of the whole chain. This information can be inferred from the standard deviation of the fracture product distribution to some adequate precision.

The 'multi-stranded yo-yo with surface energy dissipation and solid-like stress response' ($\mathrm{MSY}_{\mathrm{SED,SSR}}$) may also be a precursor to a fully stretched chain observed in some quasi-stationary state flows. Certainly the birefringence results presented herein for stagnation point elongational flows would not be incorrectly interpreted with the above hybrid yo-yo model.

*Transient* versus *stagnation point elongational flows*

*Table 2* compares the behaviour of polystyrene solutions in transient and stagnation point elongational

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*Other models of polymer dynamics can also certainly be developed which predict the desired properties of chains in elongation flow fields. However, at this point the multi-stranded yo-yo model with intramolecular hindrances and surface energy accumulation is consistent with the data from various authors and can represent the transient and stagnant elongational flow behaviour of several polymer–solvent systems

**Table 2** A comparison of the behaviour of polystyrene solutions in transient and stagnation point elongational flows

| | Transient | Stagnation point |
|---|---|---|
| $\epsilon_{c\text{-}s}$ ($4 \times 10^6$ daltons) | $2 \times 10^{-4}$ s | $2 \times 10^{-4}$ s |
| $\tau_{c\text{-}s}$ | $\propto M^{-1.81}$<br>PEO/$H_2O$ (good solvent) | $\propto M^{-1.5}$ $\theta$-solvent<br>$\propto M^{-1.767}$ good solvent |
| Time in strong flow ($\dot{\epsilon} = 3.9 \times 10^{-4}$ s) | ~ 150 $\mu$s | ~ 10 $\mu$s[a] |
| Time in strong flow/Zimm relaxation time of molecule | 0 (10) | 0 (1) |
| $\dot{\epsilon}t$ (4 is the critical value for sudden chain extension[47]) | 7.5 | ~ 1.1 |
| Birefringence profile | Tube-like, extending several mm away from jet | Birefringent line, localized to region between jets |
| Degradation/pass | >80% | <0.5% |
| $\epsilon_f \propto M^{-a}$ | 1[b] | 2[c] |

[a] The second jet interferes with the development of the flow profile
[b] This agrees with Rabin's prediction[25], $\epsilon_f \propto M^{-1}$ in a $\theta$-solvent and $\epsilon_f \propto M^{-1.2}$ in a good solvent for transient elongational flows with centre uncoiling
[c] The complete experimental data are listed in *Table 5*

flows. The data are limited to experiments where both transient and stagnation point measurements were made under identical conditions. This corresponds to polymers of the same molecular weight and polydispersity, the same solvent and temperature and the same flow geometry. The latter requires that an opposed jet apparatus be employed with a removable jet so that both stagnation point and transient conditions could be monitored respectively. From *Table 2* the following conclusions are evident:

1. Dilute solutions of polymer chains in transient and stagnation point elongational flows show an initial deformation at the same critical strain rate $(\dot{\epsilon})_{\text{C-DC}}$. That is, the coil–deformed coil transition occurs at the same strain rate in transient and stagnation point elongational flows.
2. Deformation occurs over the entire cross-sectional volume of the orifice in transient flows (tube-like birefringence profile) whereas it is limited to a highly localized birefringent line in stagnation point flows.
3. Degradation is over two orders of magnitude larger in transient flows than in stagnation point flows at the same strain rate.
4. The time in the strong flow is larger by approximately one order of magnitude in transient flows relative to stagnation point flows (birefringence signals were observed several mm from the orifice in transient elongational flows at concentrations far below the overlap concentration). This is contrary to the general theoretical interpretation which assumes that material in the fluid element on the streamline passing through a true 'stagnation' point will have no velocity and essentially an infinite residence time. In contrast particles in transient flows have an inherently much smaller residence time. The results indicate that, while this postulate is true for molecules on streamlines at or near the stagnation point, this corresponds to a very small fraction of the chains, or fluid elements, passing through the orifice. For the remainder of the fluid elements on streamlines not extremely close to the stagnation point, their residence time is much less ($\dot{\epsilon}t = 1.1$) than in a transient elongational flow ($\dot{\epsilon}t = 7.6$). This is due to the development of transient elongational flow fields which begin several orifice diameters away from the jet entrance[1]. In contrast, an opposed jet apparatus largely interferes with this flow development and blocks a large volume. Consequently, with the exception of polymer chains travelling along the centre streamline, the fluid elements in stagnation point elongational flows have a small uniaxial distance in which to accelerate.

The coincidence of the higher residence time and larger degradation yields in transient flows is likely an important indicator as to the mechanism of polymer behaviour in elongational flows. If we combine this with an $\dot{\epsilon}_f \propto M^{-1}$ dependence in transient flows, which indicates that energy is accumulated in proportion to the surface area of the deformed polymer molecule (static loading of the surface), then the following conclusions can be made. In transient elongational flows the high residence time in the strong flow region leads to large molecular deformations which ultimately can lead to fracture. As was discussed in the preceding section, such observations along with the precise midchain scission can be represented by a 'multi-segmental yo-yo model with surface energy dissipation and a solid like stress response' of $\text{MSY}_{\text{SED,SSR}}$. This model is the only one presently elucidated which is consistent with experimental birefringence (lack of saturation), light scattering (deformation and not full extension) and degradation results (the inverse scaling of the strain rate for fracture and the polymer molecular weight, the importance of strain and no-strain rate in the fracture mechanism, and the narrow but non-zero dispersity of the fracture product distribution). Additionally, it offers a plausible answer to the long-standing question: 'If a polymer chain is only partially uncoiled then how does it know its centre of mass?'

### *Dependence of chain fracture on molecular weight*

*Figure 3* shows the dependence of the critical strain rate for fracture for polystyrene in decalin in both transient and stagnation point elongational flows. It is unfortunate that the molecular weight range where both types of flows have been measured is minimal. This is due to experimental limitations in the quasi-stationary state

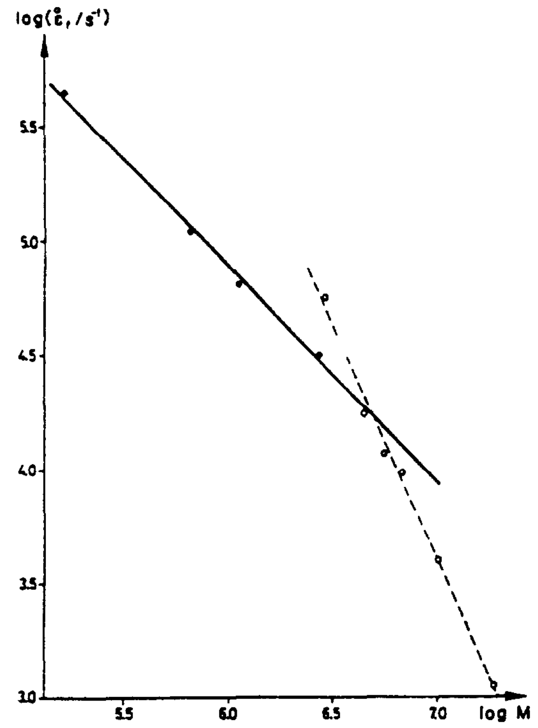

**Figure 3** Dependence of the critical strain rate for chain scission ($\dot{\epsilon}_f$) on the polymer molecular weight for polystyrene in decalin. Transient elongational flow (——) and stagnation point elongational flow (- - -) results are given

flow apparatus which place a low molecular weight boundary on polymers which can be measured[17] and the lack of availability of ultra-high molecular weight fractions with narrow polydispersities. The only molecular weight which has been measured in both flows ($4 \times 10^6$) certainly does not fracture at the same strain rate in transient and stagnation point apparatus. Furthermore, the data demarcate a transition between a $-1$ order dependence of the fracture strain rate on molecular weight for low molecular weight polymers in transient flows and a $-2$ order dependence for high molecular weight species in stagnation point flows. This can be due to either a molecular weight effect or flow type effect and the resolution of this requires further experimentation. It is worthwhile to note, however, that all the data can be fitted to an empirical fracture model of the form $\dot{\epsilon}_f = A/M + B/M^2$. Such a fit would imply the superimposition of two fracture mechanisms, each with a different molecular weight dependence.

The folowing categorizations can be made:

1. For low molecular weight polymers in transient flows, the polymer coil behaves like an impermeable ellipsoid[25] with surface energy dissipation, solid-like stress response and centre uncoiling.
2. For high molecular weight polymers in stagnation point flows, the polymer chain is highly and perhaps even fully extended. The chain can no longer be characterized as an ellipsoid. The TABS theory (Thermally Activated Barrier to chain Scission[38]) describes the fracture behaviour of a fully extended chain.

The preceding discussion can be represented in *Figure 4*. The diagnonal elements, which are designated by question marks, indicate that insufficient experimental information exists to make conclusions on the behaviour of polymer solutions in these two domains. Such data are likely to be important to developing or refining models of polymer dynamics and should be given a deserved priority in future research.

### *Resolving the differences between transient and stagnation point flows*

*Chain deformation and fracture.* Although the mechanism of chain deformation, stretching and fracture in elongational flows remains indeterminate, experimental data does indicate a difference in behaviour between stagnation point and transient elongational flows with respect to the size of the birefringence zone and the magnitude of chain extension. Furthermore, the data from various groups indicate that in transient elongational flows chains deform but are not completely extended whereas in stagnation point elongational flows the polymer chains may fully stretch. A stretched chain certainly accumulates strain in a different manner than a deformed coil, the former according to Stokes drag[17], and the latter by frictional forces at the surface of the molecular coil[23,24]. Since the fracture of polymers has been shown to depend on the total strain accumulated by the isolated coil then it is not unreasonable that two different flow types (transient and stagnation point) which show different birefringence and elongation also possess different strain accumulation

| | | | |
|---|---|---|---|
| **Flow type** | **Stagnant** | ? | Elongated Chain<br>$\varepsilon_f$ α $M^{-2}$ |
| | **Transient** | multi-stranded yo-yo with surface energy dissipation and solid-like stress response<br>$\varepsilon_f$ α $M^{-1}$ | ? |
| | | **low** | **high** |

**4·10$^6$**

**Figure 4** Categorization of polymer dynamics as a function of the type of elongational flow (transient or stagnation point) and the molecular weight. Four domains are observed. The diagnoal elements are represented by question marks to indicate a lack of experimental data in these regions mechanisms, and uncoiling and fracture characteristics, as is experimentally observed.

*The chemical and physical effects of side chain groups on the polymer backbone.* The magnitude of birefringence and the extent of polymer chain deformation were shown to differ markedly for polystyrene and poly(ethylene oxide) in stagnation point flows, whereas the two polymers behaved in a similar manner in transient flows. Chain elongation is therefore a function of the applied strain, temperature, solvent type and viscosity, polymer molecular weight, the chemical composition of the polymer, and the type of elongational flow (stagnation point or transient). Consider the following three examples:

1. Polystyrene has a bulky phenyl side chain group which generates a large amount of viscous coupling with the bulk fluid. It is also observed that the extent of elongation or deformation in stagnation point flows exceeds that in transient flows. This indicates that a bidirectional flow can elongate a chain to a higher degree in a short time than a unidirectional or transient flow can in a much larger residence time in the strong flow region (refer to data in *Table 2*).
2. Poly(ethylene oxide) has a relatively sleek profile perpendicular to the polymer backbone and the elongation is approximately identical in stagnation point and transient flows. Both unidirectional (transient) and bidirectional (stagnation point) elongation flows are therefore equally effective in disentangling the polymer–solvent system, at least in this instance when the viscous coupling is weak.
3. Atkins has recently investigated the elongational flow of biopolymers and concluded that pullulan, a six-membered ring polysaccharide with methoxy side groups and a high viscous coupling, behaves analogously to polystyrene and provides a sharp birefringence line[39].

This shows that the role of the polymer composition is predominantly to influence the viscous coupling between the side group of the polymer and the fluid. *Table 3* summarizes the experimental observations. The following conclusions can be made:

1. The viscous coupling between a polymer chain and the solvent is an increasing function of the thermodynamic quality of the solvent (increase in $R_G$) and polymer concentration (intermolecular entanglement) and a decreasing function of temperature (increase in $\eta_s$).
2. As the extent of elongation increases the viscous coupling also rises, with all other conditions constant[11].
3. For a given polymer–solvent pair, polymer molecular weight, temperature and strain rate, both the segmental orientation and global chain deformation increase as the viscous coupling betweeen the fluid and polymer coil increase.
4. As the molecular weight of a polymer increases, for a given solvent, temperature and strain rate, the chain is more likely to fracture prior to full extension.
5. According to theoretical predictions the extent of viscous coupling scales with the viscosity of the solvent to the first power. This dependency has been verified experimentally in stagnation point flows ($\dot{\epsilon} \propto \eta^{-0.86}$)[39]. However, in transient flows the dependence is much lower ($\dot{\epsilon} \propto \eta^{-0.25}$)[23]. This deviation of a dynamic scaling law from that under static conditions is certainly not uncommon[40,41] and this could reflect the lack of validity of a continuum viscosity on the molecular level, or more likely the dependence of 'internal viscosity' on the velocity gradient, which has been shown to occur in simple shear flow[42] elongational flows[43]. The discrepancy between a continuum viscosity and a local or dynamic viscosity would likely be larger for uncoiled chains since most of the monomer segments are shielded from the flow. The extended chain would be more exposed to the bulk fluid and in the limit of full stretching (stagnation point flow) a continuum viscosity may be a very reasonable approximation of the molecular parameter.

*General qualitative framework for chain deformation and fracture under elongational flows.* The conclusions in the preceding section can be used to construct a general framework for explaining the deformation and fracture of a polymer coil in an elongational flow. *Figure 5* shows plots of the viscous coupling as a function of the strain rate. The following characteristics are evident:

1. $\dot{\epsilon}_{\text{c-s}}$ and $\dot{\epsilon}_{\text{f}}$ are less for poly(ethylene oxide)–water than for polystyrene–decalin, which is derived from experimental results and rationalized in terms of viscous coupling.
2. As the coupling decreases to zero the strain rates required for deformation, stretching, and fracture increase, again in concordance with experimental results.
3. The difference in the critical strain rate for the coil–deformed coil and deformed coil–stretch transitions represents the spread in the strain rate observed in transforming an unperturbed coil to a fully stretched chain, provided the molecular weight is monodisperse. For heterogeneous molecular weight distributions the molecular weight effect and

**Table 3** A comparison of transient and stagnation point elongation flows

<table>
<tr><th>Viscous coupling (A.U.)</th><th>Transient</th><th>Stagnation point</th></tr>
<tr><td>High</td><td>Chains deform to less than the full extent<br>Tube-like birefringence behaviour with high percent fracture<br>Precise midchain scission</td><td>Full chain stretching possible<br>Narrow birefringent lines observed with low percent fracture<br>Precise midchain scission</td></tr>
<tr><td>Low</td><td colspan="2">Chain deforms to less than full extent<br>Tube-like birefringence behaviour with high percent fracture<br>Precise midchain fracture distribution has not been measured</td></tr>
</table>

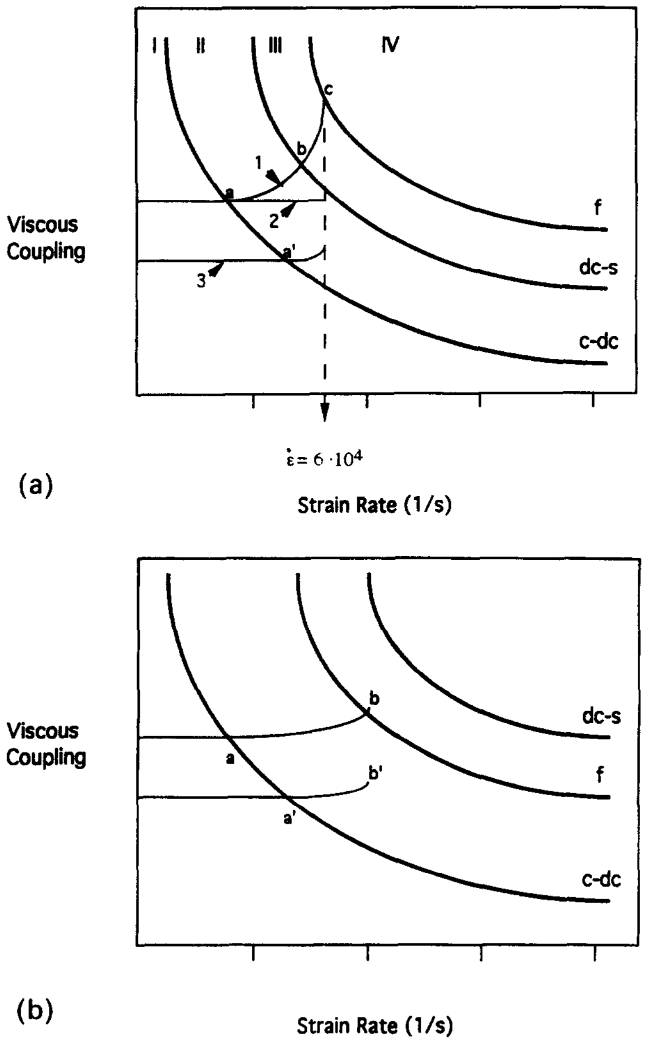

**Figure 5** The conformation of a polymer chain under elongational flow is represented as a function of the applied strain rate and the extent of viscous coupling. Four states are identified: I, undeformed; II, deformation less than the fully stretched limit; III, fully stretched; IV, degraded. Line 1: stagnation point elongational flow of a polystyrene of $1 \times 10^6$ daltons in decalin. a, Critical strain rate for the coil-to-deformed coil transition ($\dot{\epsilon}_{c\text{-dc}}$); b, critical strain rate for the deformed coil-to-stretch transition ($\dot{\epsilon}_{dc\text{-s}}$); c, critical strain rate for fracture ($\dot{\epsilon}_f$). Line 2: transient elongational flow of a polystyrene of $1 \times 10^6$ daltons in decalin. Line 3: transient elongational flow behaviour of a poly(ethylene oxide) chain of $1 \times 10^6$ daltons in water. a', ($\dot{\epsilon}_{c\text{-dc}}$). (b) Line 1: transient elongational flow of a polystyrene of $1 \times 10^7$ daltons in decalin. Line 2: transient elongational flow behaviour of a poly(ethylene oxide) chain of $1 \times 10^7$ daltons in water

deformation–stretch transition must be deconvoluted if the intensity signal is to be accurately interpreted. An example of the transition is illustrated in the work of Odell and Keller[17]*.

*Figure 5a* can be used as a semi-quantitative visual aid to explain the experimental results for polystyrene and poly(ethylene oxide) in both stagnation point and transient flows. The three parallel exponential curves are used to qualitatively indicate the transitions between regions where undeformed, deformed, stretched and fractured chains exist. The exponential nature of these transitions is necessary to accommodate the intuitive reciprocal relationship between the extent of the solvent–chain coupling and the strain rate required for a transition, such as coil–deformed coil ($\dot{\epsilon}_{\text{C-DC}} \propto 1/$viscous coupling). As the strain rate increases the polymer chain remains undeformed (region I) until a critical value ($\dot{\epsilon}_{\text{C-DC}}$) is reached (point a) at which point the chain begins to deform. The extent of deformation increases as the chain proceeds through region II. At a sufficiently high strain rate the coil fully stretches (point b) and eventually at much higher strain rates fracture occurs (point c). The fully stretched and fracture domains are represented by regions III and IV respectively. This description can be used to represent the stagnation point flow of polystyrene of $10^6$ daltons and is designated by curve 1 on *Figure 5a*.

In transient flows the deformation and fracture behaviour is quite different, as might be expected based on the preceding discussion and experimental data[1]. For strain rates prior to deformation transient and stagnation point flows behave identically and have the same viscous coupling. However, as the chains begin to deform the mechanism of stretching differs between stagnation point and transient flows, as was discussed in Section 2 of this paper. In stagnation point flows as the chain expands the coupling increases significantly. However, in transient flows the molecular deformation is non-affine and a centre uncoiling proceeds. Such a yo-yo-like chain remains essentially highly coiled at the extremes and the coupling therefore does not increase to the extent observed in stagnation point flow, as has been observed in the birefringence and light scattering data. The strain imparted in transient elongational flow can, therefore, be thought of as a stretching or deformation inefficiency relative to the strain in stagnation point elongational flows. More friction is dissipated rather than transferred into energy to uncoil the chain. This can equivalently be viewed as a lower extent of viscous coupling and can be described by curve 2 on *Figure 5a*. Therefore, for a given value of the strain rate ($\dot{\epsilon} = 6 \times 10^4$), a polymer in a transient elongational flow field is less likely to reach a fully stretched state than one in a stagnation point elongational flow. The declining exponential structure of *Figure 5a* allows us to indicate that the spread between the coil-to-deformed coil and deformed coil-to-stretch transition will be small for stagnation point flows and larger for transient flows, in agreement with experimental data[17,29].

For a sleek polymer such as poly(ethylene oxide), the viscous coupling will also be lower from the onset (low strain rates) and the polymer coil will not fully stretch at a strain rate which is sufficient to stretch a polystyrene. This is represented by curve 3 on *Figure 5a*. It is evident from *Figure 5a* that poly(ethylene oxide) requires a much larger strain rate for deformation or fracture than polystyrene, in agreement with experimental data. Thus the use of viscous coupling as a general, although at this point qualitative parameter, helps us explain an apparent disparity in the experimental observations from several laboratories.

*Figure 5a* has been scaled to fit the coil–deformed coil, coil–stretch and fracture strain rates for a polystyrene of one million daltons in decalin (*Table 4*). At higher molecular weights Odell and Keller have noted that even in stagnation point flows it is not

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* Although a sudden coil-to-stretch transition was predicted by de Gennes[4] experimental data have shown a more gradual transition. This may be due to the heterogeneous molecular weight distributions of the measured polymers of a more complicated deformation mechanism

**Table 4** Summary of the critical strain rate data for fracture and the coil-to-stretch transition

| Polymer | Solvent | Type of elongational flow | MW range | 'a' in $\dot{\epsilon}_f \propto M^{-a}$ | Reference |
|---|---|---|---|---|---|
| Styrene | Decalin | Stagnation point | $2 \times 10^6$–$2 \times 10^7$ | 1.98 | 44 |
| Styrene | Toluene | Stagnation point | $2 \times 10^6$–$2 \times 10^7$ | 2.3 | 44 |
| Styrene | Decalin | Transient | $4.3 \times 10^5$–$2.9 \times 10^6$ | 0.95 | 12 |
| Styrene | Dimethylphthalate | Transient | $1.03 \times 10^6$–$2.8 \times 10^6$ | 1.3 | 18 |

| Polymer | Solvent | Type of elongational flow | MW range | 'a' in $\dot{\epsilon}_{c\text{-}s} \propto M^{-a}$ | Reference |
|---|---|---|---|---|---|
| Ethylene oxide | Water | Stagnation point | $6.8 \times 10^5$–$1.4 \times 10^6$ | 1.47 | 17 |
| Styrene | Decalin | Stagnation point | $2 \times 10^6$–$2 \times 10^7$ | 1.50 | 44 |
| Styrene | Dioctylphthalate($\theta$)<br>tricresylphosphate | Stagnation point | $2.96 \times 10^6$–$7.7 \times 10^6$ | 1.50 | 46 |
| Pullulan | Water | Stagnation point | $1.86 \times 10^5$–$8.53 \times 10^5$ | $1.85 \pm 0.06$ | 39 |
| Ethylene oxide | Water | Transient | $2 \times 10^6$–$7 \times 10^6$ | 1.81 | 1 |

possible to fully extend chains[44]. Polystyrene and poly(ethylene oxide) chains of $10^7$ daltons are schematized in *Figure 5b*. Since $\dot{\epsilon}_f \propto M^{-2}$ and $\dot{\epsilon}_{c\text{-}s} \propto M^{-1.5}$, then the critical strain rates for the coil–stretch and fracture transitions shift toward each other at high molecular weights. This is also seen in *Figure 3*. Therefore, when the polymer has a sufficiently high molecular weight, a chain can fracture prior to full extension. The behaviour shown in *Figures 5a* and *b* is obviously very sensitive to the polymer molecular weight. At low molecular weights tremendous energy is required to deform, stretch or fracture a chain. As the molecular weight increases these critical strain rates, for deformation, stretching and fracture, decrease in a non-equal fashion with the result being that very high molecular weight polymers can fracture prior to full extension, as is known from experimental results.

*Figure 5a* can also explain the fracture temperature dependence if we recognize that the critical strain-rate for chain scission shifts to lower values as the temperature is increased[38]. This implies that the application of polymers in elongational flow systems will be more restricted at higher temperatures since there will be a small 'window' between the deformation and fracture strain rates.

## CONCLUSIONS

The complicated nature of the interactions between elongational flows and the deformation and fracture of dilute polymer solutions remains fundamentally challenging. With several important applications of dilute polymer solutions, such as in drag reduction, research is not likely to stagnate. However, improving our understanding of polymer dynamics may require expanding our frame of reference to analogies of the behaviour of chains in macroscopic systems such as pulp fibre suspensions in paper making or even the deformation, fracture and pullout of trees in strong winds. Other analogies to elongational flows include chains grafted onto inert polar surfaces, where coil-to-stretch transitions have been observed[45], and ultrasonic degradation, in which a reciprocal relation exists between the applied energy (stress) required to fracture a polymer and the molecular weight, as is also found for transient elongational flows. Understanding elongational flows in these and other systems, will require many additional carefully defined and controlled experiments. These might include, but are not limited to:

1. Measurements of the critical strain rate for the coil-to-deformed coil transition and chain fracture should be performed on a variety of polymer–solvent systems. Highly-fractionated polymers should be evaluated at different molecular weights in both transient and stagnation point flows created on the same apparatus. The equivalence of all molecular and geometric parameters will permit the elucidation of the anomalous fracture behaviour as either a molecular weight or flow type property. The current lack of data from such experiments hinders the further development of the dynamics of polymer chains and blurs the distinction between transient and stagnation point flows.
2. Experimental measurements of the segmental orientation (birefringence) should be coupled with observations of the overall deformation length (light scattering), particularly in transient flows where the behaviour of polymers at different vertical and horizontal positions within the flow field is unknown.
3. In stagnation point flows light-scattering measurements should be performed at all positions with the flow field.
4. The separation of the orifice in an opposed jet apparatus should be varied to observe the transition between stagnation point and transient flows. This might be particularly interesting in the polystyrene–decalin system where the transformation between a birefringent 'line' and 'tube' could be monitored and correlated with flow and molecular properties.

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