From rheometry to rheology

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Abstract

Using a variety of examples from the recent literature on extensional flow of polymer solutions, this paper shows that simple constitutive equations are unable to capture the diversity of chain conformations in such flows. Such diversity is a feature of extensional flows and arises because deformation leads to significant chain extension. Substantial local extension appears even at low strains and the behaviour of these stretched out portions influences the dynamics of the chain and makes a dominant contribution to the stress. Both the distribution function and the chain conformation appear to follow different paths during stretching and relaxation. As a result the second moment of the distribution function does not contain enough information to correctly predict the dynamics. Resolution of this deficiency in simple constitutive models is one of the challenges for rheology.

1. Introduction

The last decade has witnessed some major strides in polymer solution rheology. The advent of several new techniques has yielded a profound understanding of the nexus between deformation, chain conformation and stress. This new knowledge has brought out certain deficiencies in our ability to model flow properties. The resolution of these difficulties is shaping to be a major goal of rheology in the new millennium. Here we present a personal perspective on this subject. While we recognise that significant advances have also been made in the flow of polymer melts, this paper is concerned only with solutions. It is worth recalling that much of the current thinking in rheology has been influenced by the behaviour of polymer chains in shear. However, it is well known that the extent of deformation and chain stretching in such flows is, at best, moderate. The situation is far more interesting and complex when flows involving a significant extensional deformation are encountered. This paper focuses on extensional deformation.

The advances noted above have been brought about by several concurrent developments. On the experimental front the two major achievements have been the development of the filament stretching rheometer and the development of fluorescence microscopy. In the theoretical arena, improved computing resources has enabled stochastic simulations to be performed revealing a wealth of detail on the chain structure.

In this paper we present several examples from the recent literature on extensional flows. We show how information gleamed from these advances permits a better appreciation of the dynamics of polymer chains. The emerging theme is that simple constitutive equations are unable to capture the conformational details to a sufficient degree to enable the stress in complex flows to be predicted with any degree of confidence. This is particularly the case where significant chain stretching is encountered. Severely stretched out portions of a chain appear even at low strains and these dominate the dynamics due to the nonlinear force law. There is an urgent need for a simplification, which allows the main concepts to be preserved in a tractable form so that flow simulations can be efficiently carried out.

2. Background

The filament stretching rheometer has permitted us to subject polymer liquids to an extensional flow. In its current form, it represents the culmination of nearly 40 years of research for the development of a suitable extensional rheometer. During this period several ingenious designs such as the Fano flow, the fibre spinning, the opposed jets have been proposed. Reviews discussing the advantages and disadvantages of these techniques are available (Gupta and Sridhar, 1988; Petrie, 1995). The filament stretching rheometer (Sridhar *et al.*, 1991; Tirtaatmadja and Sridhar 1993) has given a major fillip to the study of stretching flows of polymeric fluids as witnessed by the large numbers of papers, conferences and workshops devoted to this topic. Many research groups (Spiegelberg *et al.*, 1996, Solomon and Muller, 1996; Van Nieuwkoop and Muller Von Czernicki, 1996; Anna *et al.*, 1999) are using versions of this device. This instrument has also motivated several

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theoretical and numerical studies (Sizaire and Legat, 1997; Kolte *et al.*, 1997; Yao and McKinley, 1998) to examine the complex time dependent profiles of the free surface so that a better understanding of the spatial and temporal variations of the local deformation in the filament can be obtained. The consensus emerging from these studies is that the mid-filament plane undergoes a predominantly extensional deformation. Anna *et al.* (1999) have shown good agreement in the results from three different laboratories using this instrument. The contrast with the disappointing results obtained in the M1 exercise (Sridhar 1990) shows the significant progress in this field. Hence the filament stretching rheometer has proved to be a convenient and powerful tool to probe the dynamics of polymer chains. As a result we now have a significant body of new knowledge that is proving a serious challenge to contemporary ideas on constitutive equations.

Rheological measurements represent an ensemble average of events taking place within the fluid. Several structural measurements have been devised to complement this information (Larson 1999). Among such structural probes, the application of fluorescent microscopy to study the conformation of DNA molecules by Perkins *et al.* (1997) has created much excitement. Using optical traps to pin one end of the DNA molecule tethered to a polystyrene bead, these authors were able to image the conformation of the DNA under the influence of a uniform solvent velocity. Smith *et al.* (1998) used a cross-slot flow field and imaged DNA molecules at the stagnation point of a planar extensional flow field. This work has revealed the amazing diversity of molecular conformations that can arise during deformation. These conformations have been labelled dumbbells, half dumbbells, and folded coils. Fig. 1 shows a cartoon of these conformations. In a given flow field, the rate of chain unravelling is quite different for the different conformations. The configurations in Fig. 1 intuitively suggest that the dumbbell molecule would stretch faster than the folded molecule and this is bourne out by experiments. The fact that these various types of conformations
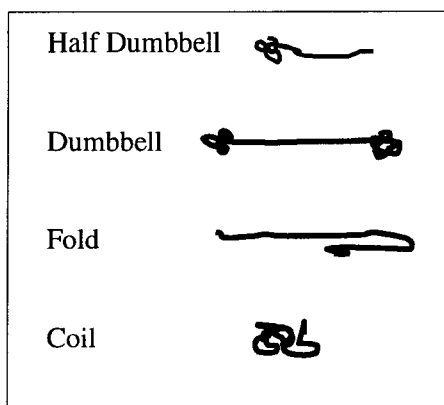

Fig. 1. Cartoon of the various configurations.

can emerge from seemingly similar initial conditions, has led de Genne (1999) to remark that these conformations represent a distorted picture of what the chain looked like prior to deformation. Capturing the dynamics of such tortured chains in a tractable manner is clearly a major challenge.

On the theoretical front, the development of the kinetic theory for polymers has been one of the outstanding intellectual achievements in rheology. It provides a rational basis for analysing the behaviour of a polymer chain in complex flows and thereby illustrates the mechanisms by which large stresses are developed even in dilute polymer solutions. A stunning array of constitutive equations have been developed either by coarse graining the configuration of a polymer chain or by incorporating increasingly sophisticated physics to describe the motion of a chain. In addition, a variety of mathematical approximations have been implemented and this has permitted several closed form constitutive equations to be generated. The choice of a constitutive equation with an appropriate level of sophistication for a particular problem requires a balance between mathematical complexity, the number of additional parameters and the need to describe specific properties of the polymer molecule. An exhaustive treatment of such models can be found in Bird *et al* (1987), Larson (1988) .

In an actual polymer molecule, the bond lengths and angles are restricted to quite narrow ranges (Flory, 1969). A polymer chain can thus be represented as a set of beads joined by mass less rods, where each bead represents a centre of mass corresponding to a monomer unit and the length of each rod connecting successive beads corresponds to the carbon-carbon bond length between monomers. The bead-rod model can be considerably simplified by replacing a portion of the chain consisting of several monomers with a single hookean spring describing the forces required to separate the chain. This bead-spring model allows the configurational dynamics of a polymer chain to be investigated without the computational difficulties associated with the fixed bond-length of the bead-rod model.

The bead-spring chains are able to capture some of the essential features of real polymer molecules, such as orientability and stretchability plus many internal degrees of freedom. Two different types of model have been developed. The first is the Rouse Bead-Spring Chain model. In this model, excluded volume and polymer-solvent interactions are neglected and the coil is assumed to have a Gaussian equilibrium distribution of configurations. The influence of neighbouring beads on the ambient velocity around a given bead is also neglected (Larson, 1988) leading to a free draining model. The second model considered here is the Zimm bead-spring model. The underlying assumptions for this model are identical to the Rouse model with the notable exception that the influence of neighbouring beads on the ambient velocity around a given

bead is included through the equilibrium averaged Oseen tensor (Larson, 1988). The resulting equations of motion are identical to those of the Rouse model with the exception that the relaxation times of each mode are different. The Rouse and Zimm models represent two limiting situations depending on the magnitude of the hydrodynamic interaction between beads.

These models can however be simplified further by replacing all of the individual monomers by a single spring with all the mass concentrated at each end, resulting in the elastic dumbbell model. Depending on the choice of force law chosen for the spring it is possible to derive constitutive equations and hence the model can be a useful tool to describe rheological phenomenon. Starting with the hookean elastic dumbbell model rheologists have constructed a variety of constitutive equations. Each of these equations introduces additional features and complexity into the basic dumbbell model (Larson 1988).

Many of these constitutive equations can been solved for the stress without requiring the distribution function to be worked out. The hookean spring model does not impose any restriction on the extension of the spring and this deficiency has been overcome by the development of non-linear spring models that impose a certain maximum permissible extension Q_0. However, this renders it impossible to derive a closed form constitutive equation from the diffusion equation for the configuration distribution function Ψ (Q,t) where Q is the vector connecting the beads. Mathematically, there are three different approaches that can be exploited to calculate the stress (see for example Keunings, 1997). One can numerically solve the diffusion equation for the evolution of Ψ with the stress being calculated from the Kramers expression. More recently, the stochastic differential equation for the chain trajectory has been solved and the stress calculated by appropriate averaging (Ottinger 1995). Both these techniques are difficult to apply for complex flow calculations. A variety of closure approximations have also been developed and these lead to a closed form constitutive equation for the stress without having to solve for the distribution function. The best known among such models is the FENE-P model.

The effect of these approximations and numerical schemes are only now being understood and this continues to be an area of research (Van den Brule, 1993; Liliens et al., 1998). Stochastic simulations of FENE dumbbells (where the actual dumbbell distribution is calculated) have shown that the FENE-P models predict identical steady state behaviour in uniaxial extension to the FENE model although significant differences are observed for transient flows (Keunings, 1997; Doyle and Shaqfeh, 1998). These differences appear to be a result of the inability of the pre-averaging process to capture the true distribution of FENE dumbbell lengths, which are not well approximated by a

Gaussian distribution. In particular, only the average extension of the FENE-P dumbbells is limited to Q_0. Hence some dumbbells will actually exceed this limiting value. Any differences between the individual distribution functions are not adequately captured by the second moment of the distribution Ψ (Larson, 1988).

In a seminal paper, Acierno et al. (1974) compared the stress growth obtained from bead-rod simulations to a dumbbell model with an inverse Langevin spring connector. These simulations showed that the elastic dumbbell model consistently under-predicted the bead-rod stress. The authors observed that segments of the bead-rod chain folded over one another during extensional flow tending to increase the resistance of the chain to affine deformation. The effect of folded sections on the ability of the chain to distort with the flow was likened to the internal viscosity model. In this model, internal barriers to free-range movement result in an additional dissipative stress term in addition to the elastic restoring force due to chain extension. Brownian simulations of bead-spring models with a non-linear spring law have reached a level of maturity. Larson et al. (1999) have shown that many of the unusual conformations observed by Smith and Chu (1998) can be adequately modelled by stochastic simulations using bead-spring models. A recent review of these techniques is found in the book by Ottinger (1995).

In summary, these theoretical models have attained a level of sophistication but at the cost of complexity. The major advantage of these models is that the internal structure of the model is exposed. This permits a better understanding of the data from the experimental techniques mentioned earlier. In the following examples, we show that simple constitutive equations fail in extensional flow and the brownian simulations suggest reasons for this and allow at least a qualitative understanding of the impact of the flow field on the chain structure.

3. Example 1: Stress growth at constant strain-rates

The availability of the filament stretching rheometer permits a systematic investigation of the effect of concentration (c) and molecular weight (M_w) on the extensional stresses. Gupta et al. (1999) present a comprehensive set of data on polystyrene solutions. The concentration range from 69 ppm to 777 ppm and the molecular weight from 1.95 M to 20 M. The shear data (see Fig. 2) for such solutions can be adequately described by the bead spring model with a pre-averaged non-linear spring (FENE-PM) along with a Zimm relaxation spectra (McKinley, 1998). The largest relaxation time (λ_z) shows the expected dependence on molecular weight $(\lambda_z \sim M_w^{1.5})$, while the polymer viscosity scales with the square root of the molecular weight. Note that Fig. 2 shows that the free
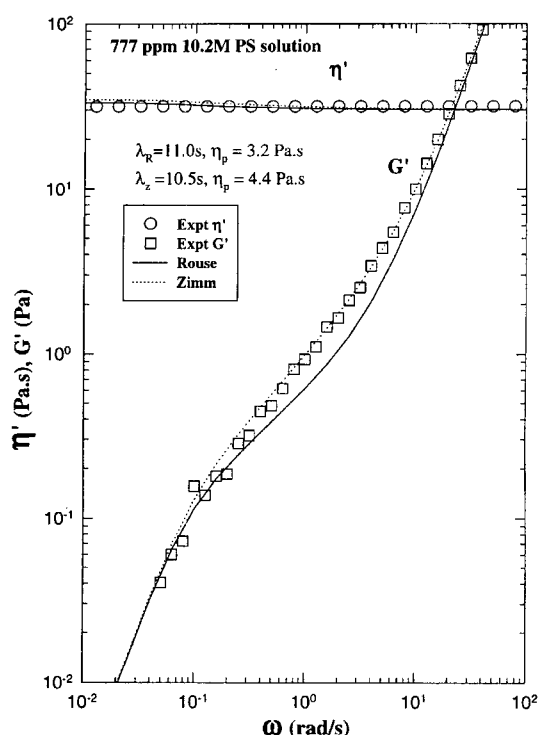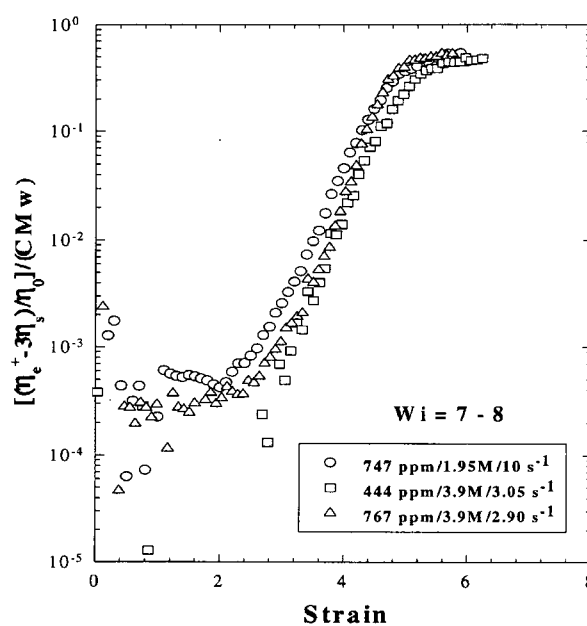
Fig. 2. Dynamic viscosity and storage modulus for a polystyrene solution. The predictions of the Zimm and Rouse models are shown (Gupta, 1998).
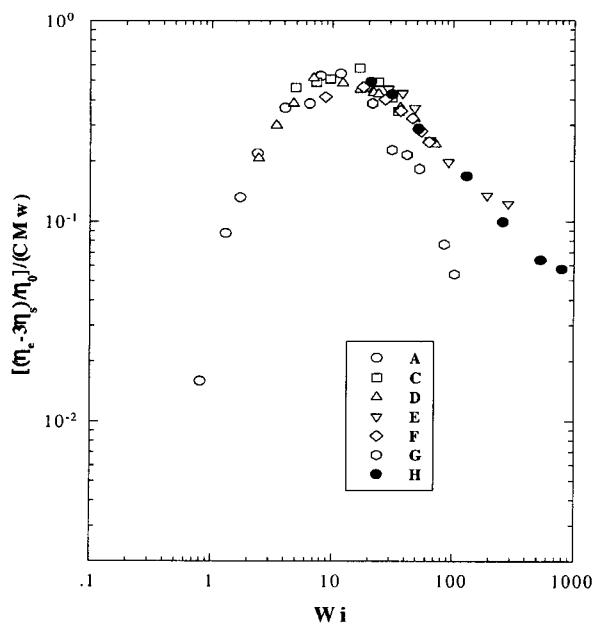

Fig. 3. The polymer contribution to the transient Trouton ratio at a constant Weissenberg number. Data shows that the polymer contribution is proportional to c and M_W.

Fig. 4. The effect of Weissenberg number on the steady state Trouton ratio.

draining Rouse model does not predict the storage modulus as well as the Zimm model. Hence under these conditions, the polymer chain is a compact coil and hydrodynamic interaction is predominant.

Fig. 3 shows some typical data on extensional stress growth at a constant strain rate $\dot{\varepsilon}$. The strain rate is chosen so that comparison between the different solutions is made under conditions of constant Weissenberg number (Wi = $\lambda_z \dot{\varepsilon}$). Fig. 3 shows that at a given strain, the extensional viscosity is proportional to concentration and molecular weight. Fig. 4 shows the steady state extensional viscosity as a function of the Weissenberg number (Wi). Again the extensional viscosity is directly proportional to c and M_W. For Wi < 4, the steady state extensional viscosity is an increasing function of the strain rate. For 4 < Wi < 10, the steady state extensional viscosity is independent of the strain rate. Surprisingly, for Wi > 10, the steady state extensional viscosity decreases with increasing strain rate.

Predictions of the FENE-P model are compared to the extensional viscosity in Fig. 5. Following the methodology of Spiegelberg and McKinley (1996) and Doyle et al. (1998), the extensibility parameter b was calculated from molecular parameters, which yields a value of 39000 for this fluid. Referring to Fig. 5, predictions using this value of b is observed to significantly over-predict the steady state extensional viscosity observed experimentally. Therefore, following the methodology of Remmelgas et al.

(1998), b was chosen to match the steady state extensional viscosity yielding a value of 20000. The FENE-P simulations, with such a value of b, significantly under-predict the extensional growth observed experimentally. Even smaller values of the extensibility parameters (b = 1000) are required to capture the dramatic increase in stresses at low strains. Small values of the extensibility parameter bring the nonlinear spring into play even at low strains and
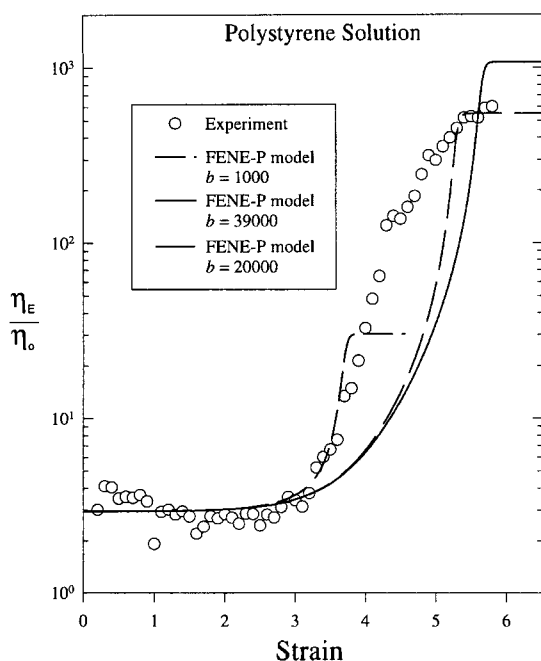
Fig. 5. Comparison of FENE-P predictions with transient viscosity using different extensibility parameters.

perhaps mimic the development of stretched segments. However, at low strains the effect of pre-averaging results in differences between the FENE-P model and the FENE model.

In order to bring out the effect of multiple relaxation times this dependency on c and M_w can also be examined in terms of the Zimm and Rouse models. The Zimm model would predict a scaling with c and $M_w^{0.5}$ for the transient viscosity and scaling with c and $M_w^{1.5}$ for the steady state viscosity. On the other hand, the Rouse model predicts a scaling with c and M_w (for transient extensional viscosity) and with c and M_w^2 (for steady state extensional viscosity). Hence the data appears to follow a Rouse-like behaviour for the transient viscosity. This implies that as the polymer chain is extended, the hydrodynamic interaction between chain segments is reduced leading to the Rouse model. The ratio of the Rouse to Zimm relaxation time can be calculated by modelling the changes in the drag on the polymer chain as a result of deformation. If the fully extended chain is represented by a cylinder, then the ratio of the drag coefficients is (Larson 1999)

$$\frac{\varsigma_{rod}}{\varsigma_{coil}} = \sqrt{\frac{n}{C_\infty}}/\ln(L/d)$$

where d is the molecular diameter ($\sim10A^0$) and L is the contour length. Since the relaxation time is proportional to the drag, we can estimate the ratio of relaxation times as:

$$\frac{\lambda_R}{\lambda_z} = \sqrt{\frac{n}{C_\infty}}/\ln(L/d) = \frac{0.04\sqrt{M_w}}{\ln(M_w/200)}$$

Hence using the Zimm relaxation time evaluated from shear data, one can estimate the Rouse relaxation time. Note that this is an upper bound on the Rouse relaxation time, since the contour length is used to estimate the drag on the chain even though the chain is not fully extended. The predictions of a FENE PM model using a Rouse and Zimm relaxation spectra are compared with experimental data in Fig. 6. Even with multiple relaxation modes the Zimm model fails to predict the data. While the Rouse relaxation spectrum, at least qualitatively, predicts the transient viscosity, it does over estimate the steady state viscosity. This is effectively a one-parameter model with all parameters being calculated, except the Zimm relaxation time, which in any case is measured independently. The only constitutive physics that can predict a decrease of extensional viscosity with Wi is the concept of anisotropic drag (Wiest, 1989). This idea postulates that the drag along the chain is less than that in the transverse direction. Gupta *et al.* (1999) show that such a model can predict these data and their predictions is also shown on Fig. 6.

In order to bring out the effect of pre-averaging, we turn to Brownian dynamics (BD) simulations of this data to illustrate other possible complications. Li *et al.* (1999) show that parameters extracted from the Zimm theory can be combined with molecular properties of the polystyrene solutions accurately predict the steady shear viscosity and normal stresses. The prediction of the extensional data is shown in Fig. 7. The Zimm relaxation time is unable to predict the extensional data and changes in hydrodynamics need to be incorporated. One advantage of the BD simulations is that it yields the conformation of individual chains as they slowly unravel under the influence of the hydrodynamic forces. Fig. 8 shows a sample of the configurations at a strain of $\varepsilon = 4.2$. At these strains the stress is an order of magnitude lower than the steady state stress and hence one does not expect significant overall stretching of the molecule. Surprisingly a large proportion of the chains exhibit taut segments and the proportion of folded and dumbbell shaped molecules is very high. As much as 40-50% of the entire population of chains is in the folded state. The folded and the dumbbell molecules have stretched out positions and contribute a large stress while the coiled molecules do not contribute much. Of the molecules that contribute 90% of the stress of 75% are classified as taut with a fully extended central position. Typically, the dumbbell shaped molecule at a strain of 4.2 contributes 100 times as much stress as a coiled molecule. These folds unravel rather slowly (Perkins *et al.*, 1999), and can take as much as 9 strain units to fully unravel. The stress during the latter phase of unravelling is also expected to change slowly.

Considering these results it is not surprising that the simple dumbbell model is only able to predict the correct magnitude of the stress is by using very low extensibility
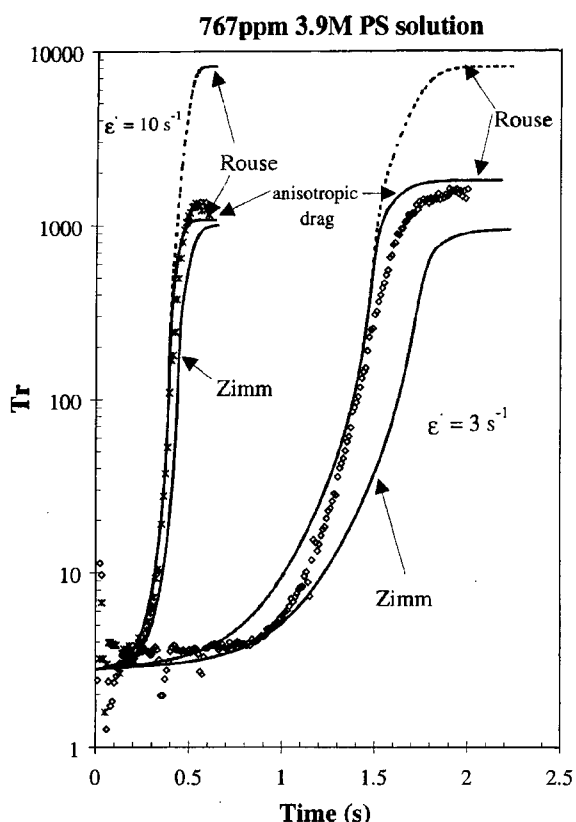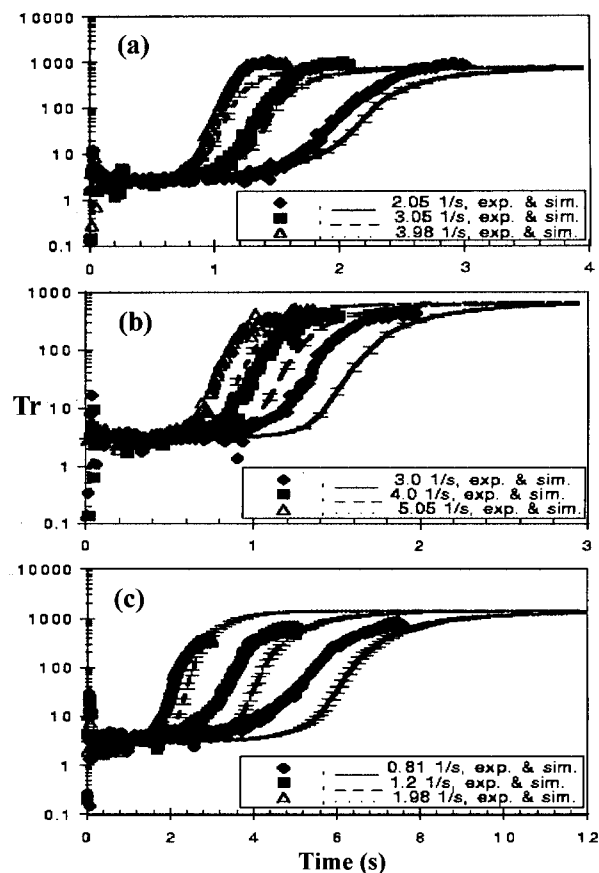
Fig. 6. Predictions of the Rouse and Zimm models for transient extensional viscosity. The middle line represents the model with a Rouse relaxation spectrum along with anisotropic drag.

Fig. 7. Bead spring simulation of the extensional viscosity with a Zimm spectrum for three different MW polystyrene solution (Li *et al.* 1999).

parameter. It is unable to mimic folds. The large number of slowly changing folded chains also raises the question whether the steady states shown earlier represent full extension. Unfortunately experimental difficulties make it difficult to reach stains of 9 and 10 to enable this question to be answered with any confidence.

4. Example 2: Stress relaxation

A refinement to the Rouse model attempts to capture the barriers to small-scale distortions that make the chain somewhat rigid. In terms of modelling, this is incorporated in the bead-spring model through the addition of a dashpot. This has been termed internal viscosity and has remained a somewhat nebulous concept. However, its consequences are clear, and it results in an additional stress which is strain-rate dependent and appears purely viscous in nature. Over the years, several experimental observations have been interpreted in terms of a viscous stress and are discussed by Orr and Sridhar (1996), Spiegelberg and McKinley (1996) and Orr (1998). Stress decay during relaxation was, after extensional deformation, soon identified as one way of studying this phenomenon. Any viscous stress would decay rapidly permitting the stress at any strain to be

partitioned into its viscous and elastic components. Fig. 9 shows a family of curves corresponding to the stress growth and subsequent relaxation at a strain rate of $2s^{-1}$ for a range of strain. The stresses initially relax rapidly followed by a slower relaxation. The initial stress decay was labelled a viscous stress.

The concept of a viscous stress has been controversial and several theoretical papers have examined it (Hinch, 1994; Rallison, 1997; Remmelgas *et al.*, 1998; Doyle *et al.* 1998). Rallison (1997) concludes that the viscous stress may be a pragmatic way of including the effects of the shortest relaxation times. Remmelgas *et al.* (1998) use the Chilcott-Rallison version of the FENE model with the dumbbell extensibility parameter obtained from data on stress growth in uniaxial extension. Such an approach adequately models the experimental data of Orr and Sridhar (1996), hence suggesting that the fast relaxation is due to the non-linear spring law, which manifests as a decrease in the effective relaxation time. There are some obvious problems with invoking non-linear spring laws for explaining rapid relaxation. Such an explanation is available only at large strain, whereas the experimental data exhibits fast relaxation even when the chain is unlikely to
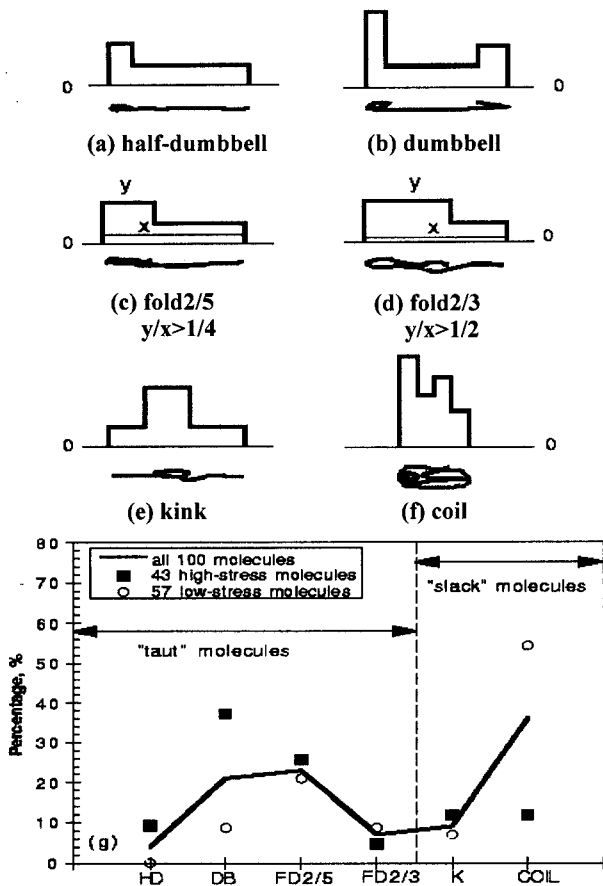
Fig. 8. Typical configuratoins at a strain of 4.2 for 100 molecules using Brownian bead-spring simulations (Ki *et al.* 1999) Schematic of the various configurations is shown above the figure.

Fig. 9. Stress relaxation after various strains for a polystyrene solution (Orr, 1998).

be fully extended.

The stress relaxation is not described by the single exponential function predicted by the FENE-P model in the linear regime. The absence of any strain dependence suggests that within the limitations of the experiments, the rate of stress relaxation over the range of strain 4 to steady state (~5.85) is not very different. FENE-P simulations for a strain rate of $2s^{-1}$ and strain, prior to cessation of flow, equal to 4 are shown on figure 10a. The extensibility parameter b is independently chosen so as to match the initial stress before relaxation. This procedure yielded a value of b equal to 1000. Two important observations can be made from the results of this simulation. Firstly, compared to the theoretical value of b (=39000), a very small value is required to predict the relaxation data. Secondly, the simulation shows that a steady state has been attained by a strain of 4 for b = 1000 implying that the rate of stress relaxation exhibits characteristics normally associated with a fully stretched molecule. Included on Fig. 10a are FENE-P predictions for relaxation after a strain of 5.84 with b = 20000. Note that although this simulation is unable to
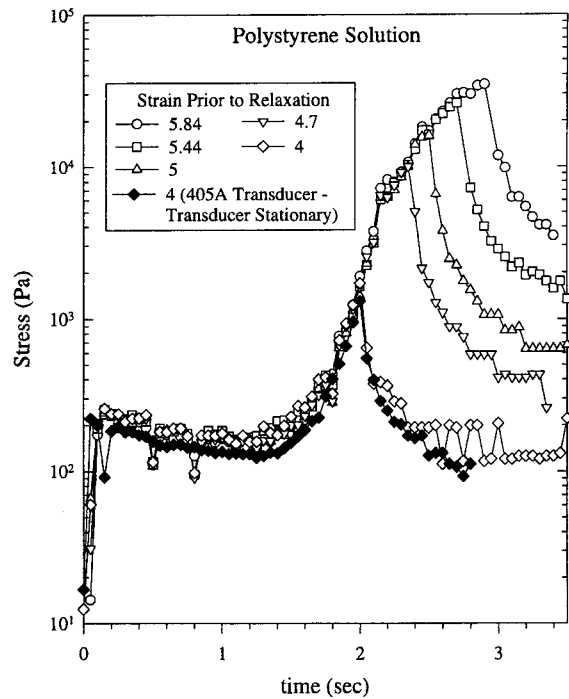
predict the rate of stress growth observed experimentally, the model is able to quantitatively describe the rate of stress relaxation from steady state.

To further illustrate the concept that non-linear stresses normally associated with highly extended molecules are also observed at lower strains, the FENE-P prediction from steady state is compared to normalised relaxation data for a range of strain in Fig. 10b. Quantitative agreement between the FENE-P predictions and experimental data is obtained, further suggesting that the polymer solution exhibits behaviour associated with highly-extended segments even at strains lower than required for a steady state to be achieved.

Brownian dynamic simulations using bead-rod models is able to throw further light on the chain configurations during stretching and relaxation (Doyle *et al.*, 1998). Even at low strains the chain configuration is significantly open with an extended middle section flanked by folds (or backloops) at the ends. As the strain increases, the backloops gradually unfold until the fully extended configuration is attained. What is surprising is that the process of relaxation of the chains from an extended to a coiled configuration follows an entirely different path (see Fig. 11). When the flow stops the chain develops modulations along its backbone, which is able to rapidly relieve the stresses. Further relaxation of the chain takes place from the ends. Hence it appears that the rapid decay of stresses in the experiments of Orr and Sridhar (1996) are a result of these modulations.
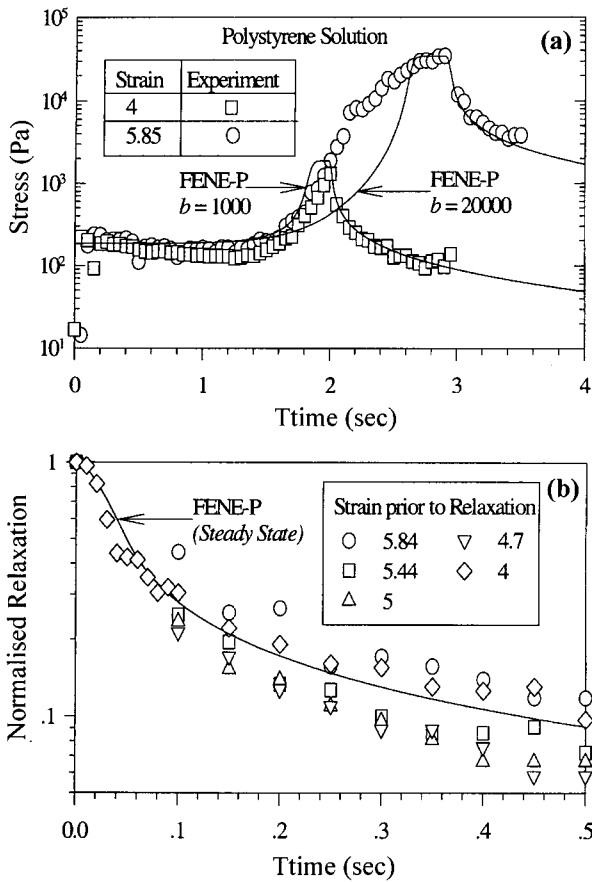
Fig. 10. (a) FENE-P model predictions for the stress relaxation : effect of varying the extensibility parameter. (b) Steady state FENE-P predictions for the normalised stress relaxation, compared with data from all strains.
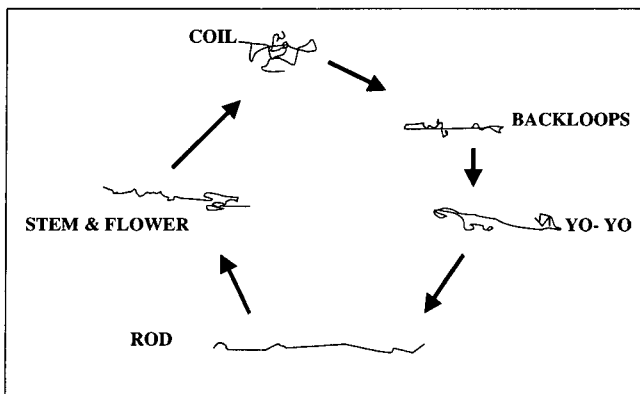
Fig. 11. Schematic of the chain conformations during stretching and relaxation (Doyle *et al*, 1998).

Doyle *et al.* (1998) show that the experimental relaxation data is similar to the Universal Relaxation Curve based on the relaxation of an initially straight bead-rod chain (see also Grassia and Hinch, 1996). Perkins *et al.* (1994) examined the relaxation of fully extended single DNA molecules by optical microscopy. Rapid recoil of the free end to

about 70% of the full length followed by a slower relaxation is observed in agreement with the data presented earlier.

In summary, these data appear consistent with the presence of highly extended portions and folded sections in the population of chains. Due to the nonlinearity of the spring force, these segments make the predominant contribution to the stress. As a result, it is their dynamics that is measured in a relaxation experiment. Again simple models are not capable of portraying such diversity unless abnormal values of the parameters are used.

5. Example 3: Step-change in strain rate during uniaxial extension

In the previous sections, non-linear behaviour was observed during stress relaxation, which persisted to low levels of strain. It is intuitively obvious that the response of a chain to imposed deformation is determined by its configuration. Rigid segments are expected to respond more rapidly than coiled chains. To further investigate the nature of stresses developed during extensional flow, Orr and Sridhar (1999) have investigated the effect of a step-change in strain rate. Fig. 12 shows the stress for a step-change in strain rate at strains of (a) 2.8, (b) 3.6 and (c) 4.4 plotted against strain. Also included on these plots is the stress growth corresponding to experiments conducted at constant strain rates of $2s^{-1}$ and $4s^{-1}$. Prior to the step-change the stress follows the curve described by a strain rate of $2s^{-1}$. At the instant that the step-change is imposed (shown by the arrow on these figures), the stress exhibits a jump to the value associated with a strain rate of $4s^{-1}$. This suggests that following a step-change in strain rate, the polymer solution responds almost instantaneously to the new strain rate.

We now turn to the response of the purely elastic FENE-P model to such a strain rate history. As noted in example 1, the FENE-P model significantly under-predicts the level of stress observed experimentally at the levels of strain that is of interest in this section. Thus for the purposes of comparison, the behaviour of the FENE-P model was investigated at a similar level of stress to that observed experimentally for a strain of 4.4 at a strain rate of $2s^{-1}$. The corresponding level of strain required for the FENE-P model to attain this level of stress was 5.3, and the predicted behaviour for a step-change in rate from $2s^{-1}$ to $4s^{-1}$ is shown in Fig. 13. Note that this implies that the comparisons shown in this figure are at the same stress level and not at the same strain as in the experiment. Also included on this figure are predictions for constant strain rates of $2s^{-1}$ and $4s^{-1}$ respectively. In contrast to the experimental results, the FENE-P model exhibits no noticeable jump and continues to grow monotonically with strain albeit at the faster rate dictated by the post-step strain rate. The stress following the step-change is parallel to the curve
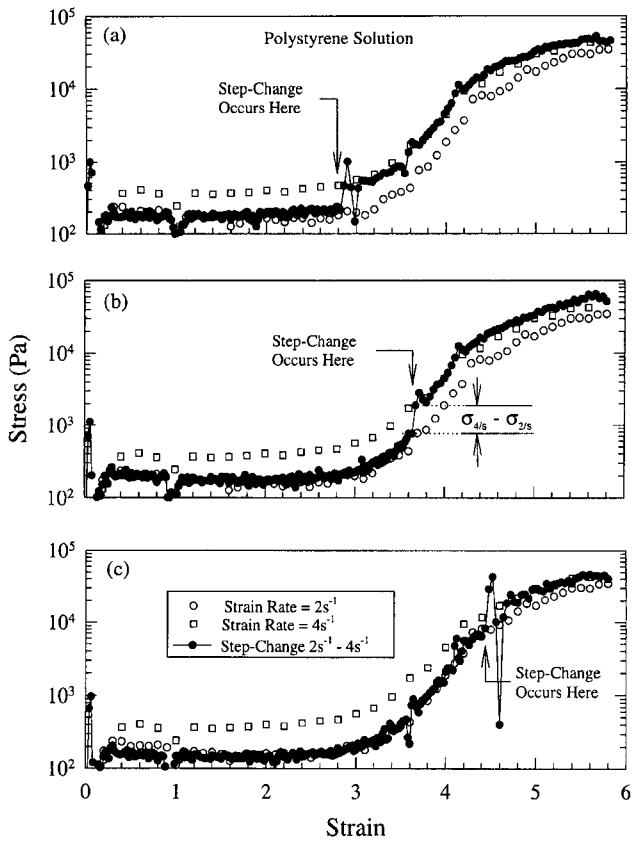
Fig. 12. Response of a polystyrene fluid to a step jump in strain rate at different strains (Orr and Sridhar, 1999)
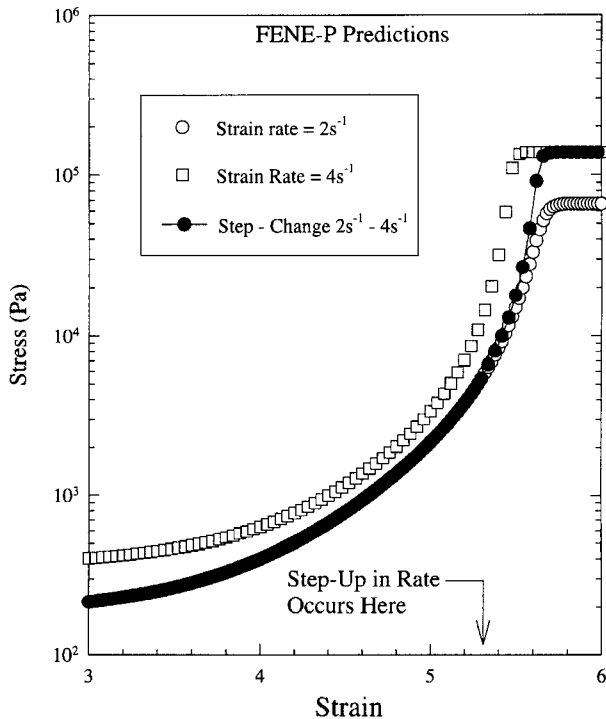

Fig. 13. FENE-P predictions for a step jump in strain rate at a strain of 5.4 (Orr and Sridhar, 1999).

for the constant strain rate of $4s^{-1}$, and hence the model prediction is similar to the solution of an initial value problem.

Referring to example 2, the stress behaviour normally attributed to highly extended molecules has been observed which the FENE-P model was only able to describe when the elastic dumbbell was close to its maximum extension. Following this line of thought, the response of the FENE-P model to a step-change in strain rate at steady state is investigated for a step-change in strain rate from $2s^{-1}$ to $4s^{-1}$ and vice versa in Fig. 14. The purely elastic dumbbell model is able to describe the jump in stress observed experimentally when the dumbbell extension is in the highly non-linear region.

Based on this observation, a possible explanation for the experimental behaviour is that for strains much less than required for steady state, the polymer solution contains molecules that have experienced a large degree of stretch. These molecules will then contribute a highly non-linear response to a step-change in strain rate.

Li *et al.* (1999) have successfully used bead rod models to simulate the stress after a step in the strain rate. By following the dynamics of different classes of configurations they show that a dumbbell shaped chain reacts far more rapidly than a coiled molecule. We have earlier remarked on the diversity of configurations obtained during extensional flow. A large number of folded and dumbbell molecules, which are taut, are present. The number of strain units required by a chain to react to the step change is inversely related to the stress contributed by the molecule. Hence highly extended molecules which contribute most of the stress require very little time (strain) to react to the step change. In many ways they behave like rigid objects.

6. Example 4: Stress and birefringence in extension

The previous examples have suggested that stretched out segments of a chain can have a significant impact on the evolution of the stress. Optical birefringence is sensitive to local orientation of the polymer chain. The polymer stress, however, responds to the overall deformed length of the polymer chain. The stress optical law provides a convenient relationship between birefringence and stress. Significant improvements in the measurement of optical birefringence (Fuller 1995) now enable even transient flows to be conveniently studied. The noninvasive nature of the measurement has resulted in a vast literature on the use of birefringence to examine flow problems. While the stress optic rule has been verified in shear flows, there is some evidence that in strong flows the anticipated chain extension may lead to a break down of this rule.

Simultaneous measurements of extensional stresses and birefringence are rare, especially for polymer solutions in
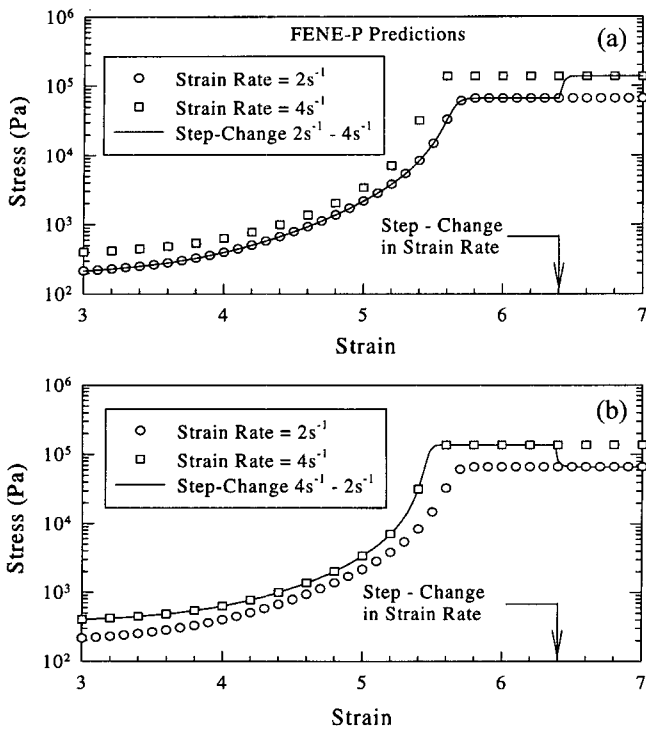
Fig. 14. FENE-P predictions for a step jump in strain rate at steady state (Orr and Sridhar, 1999)

Fig. 15. Growth of birefringence and stress at a constant strain rate (Sridhar et al., 1999).

extension and an example of such a measurement is that due to Spiegelberg and McKinley (Doyle et al. 1998). This work reported a unique example of stress-birefringence hysteresis. Sridhar et al. (1999) report similar measurements using the filament stretching rheometer and a phase modulated birefringence system. This work was able to reach higher strains and we discuss below some of the main findings.

Fig. 15 shows the transient growth of birefringence and stress at a constant strain rate. At small time the stress and birefringence are dominated by the solvent contribution. At 0.4 seconds corresponding to a strain of 2 units, the polymer chain begins to orient with the flow and unravel and as a consequence both the stress and birefringence increase. Two identical experiments are shown in Fig. 15 demonstrating good reproducibility. Fig. 16 shows the polymer contribution to the birefringence as a function of the strain. Surprisingly, the strain rate has a minor influence on the growth of the birefringence. The Trouton ratio is also independent of strain rate and is predominantly dependent on strain (Tirtaatmadja and Sridhar 1993). Hence this suggests a relationship between Trouton ratio and polymer birefringence. This directly contradicts the stress optical rule, which postulates a relationship between birefringence and stress. The saturation birefringence agrees with the calculated birefringence for a fully extended polymer chain (Peterlin 1961). However, estimates of the saturation value of the extensional viscosity using Batchelors formula
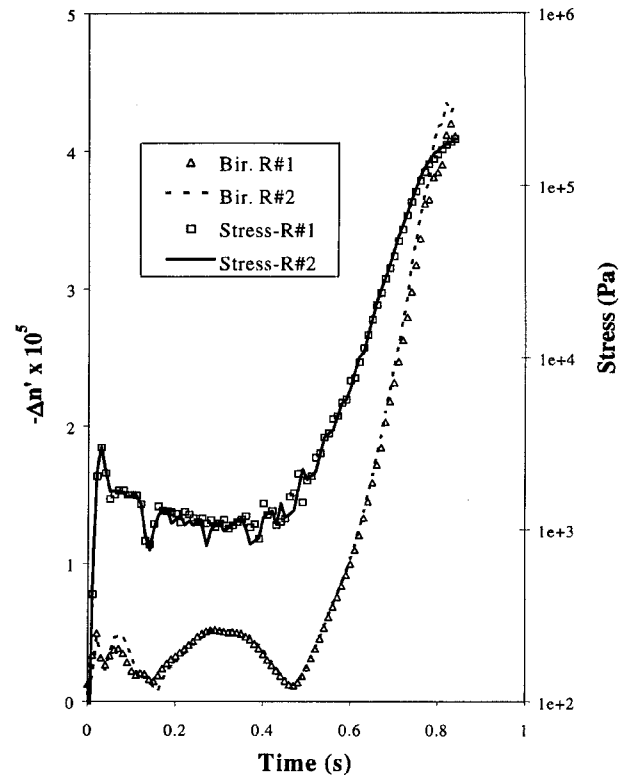
for suspensions of elongated fibres are much higher than observed. The Trouton ratio saturates at about 50% of the expected value for a fully extended chain.

We have commented on the large number of folded structures formed during stretching. Larson et al. (1999) show that folded configurations appear to hesitate at about 50% extension before extending further. These folded configurations can require 8 to 9 strain units before reaching full extension. On a extensional viscosity versus strain plot this translates into a plateau corresponding to a strain of about 5 units and a slow growth from there up to a steady state corresponding to full extension. Measurements at such high strains are dogged by experimental difficulties. The most important issue is filament breakage and the difficulty of maintaining a constant strain rate. However, for some fluids these difficulties can be overcome and Sridhar et al. (1999) present data up to a strain of 7.8. Fig. 17 shows that the Trouton ratio increases rapidly up to a plateau of around 800 before increasing slowly up to a value of 1500. This shows similarity with the behaviour of the folded structure discussed above and the final steady state is also consistent with the estimates of the Batchelor theory. Birefringence depends on the orientation at the Kuhn length scale and is not expected to be able to differentiate between folded and fully extended structures. The saturation of birefringence under these conditions is therefore not surprising.
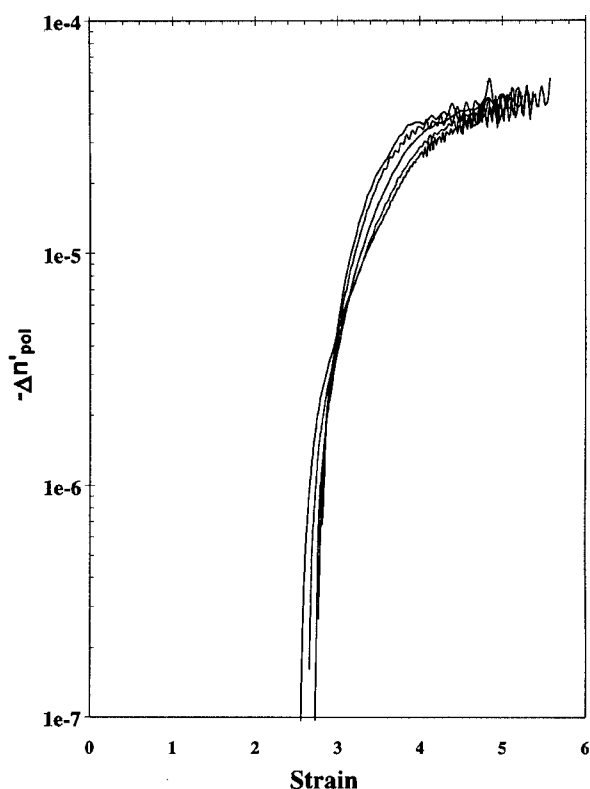
48

Fig. 16. Polymer contribution to the birefringence as a function of strain at different strain rates (Sridhar *et al.*, 1999).
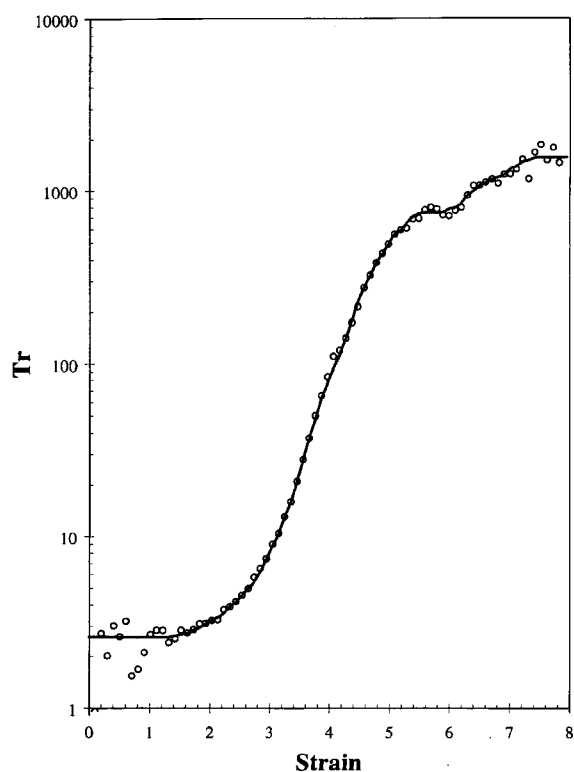

Fig. 17. Stress growth at high strains. Note that the stress reaches a second plateau at high strains (Sridhar *et al.*, 1999).

From the simultaneous measurements of stress and birefringence, the stress optic coefficient can be calculated. Fig. 18 shows that the stress optical coefficient decreases rapidly with increasing strain. This dramatic breakdown of the stress optic rule is consistent with the bead rod simulations of Doyle *et al.* (1998). Fig. 18 also shows the simulations of Doyle *et al.* (1998) for two different values of N, the number of links in the chain. While the values of N used do not correspond to the polymer used in this work, the agreement is qualitatively good. The stress optic law is premised on a linear force law for the spring. The fact that the stress optic coefficient breaks down at even low strains suggests that, even under these conditions, the stress arises predominantly from portions of the chain that are extended beyond the linear region.

The filament stretching rheometer also makes it possible to study relaxation of stress and birefringence. Doyle *et al.* (1998) suggest that a plot of stress versus birefringence is a convenient way of displaying the difference in way the relaxation of stress and birefringence. Fig. 19 shows a plot of stress versus birefringence for two different strain rates and demonstrates a pronounced hysteresis. The stress is much larger, for a given deformation, during start-up than during relaxation. Doyle *et al.* (1998) first documented such a hysteresis and their data is also shown in Fig. 19. Fig. 19 also includes the predictions of Doyle *et al.* (1998) for a FENE model with configuration-dependent drag coefficient. The qualitative agreement between these results is encouraging. Fig. 19 shows that the stress-birefringence relationship during stretching depends on strain rate. During relaxation, the stress drops rapidly whereas the birefringence changes slowly. After this initial period, the stress birefringence profile is independent of strain rate. The relaxation data for birefringence in shear and extension are in qualitative agreement with the bead-rod simulations of Doyle *et al.* (1998). The simulations also demonstrate that the evolution of stress and birefringence during start-up and relaxation exhibits a pronounced hysteresis. This hysteresis arises due to the skewed distribution of dumbbell lengths in a FENE model. The stress results predominantly from dumbbells near their full extension due to the highly non-linear restoring force. On the other hand, the contribution to birefringence scales linearly with length. The bead-rod model simulations show that the chain configuration during start-up and relaxation is significantly different. During relaxation, the chain essentially relaxes from the free ends. The simulations of Doyle *et al.* (1998) and the earlier study of Grassia and Hinch (1996) suggests an universal curve for a fully extended chain onto which can be superimposed the relaxation of all other chains by a shift in time (as shown in example 2). The process of relaxation of these chains is similar, in that they all relax from the chain ends in the so-called stem and flower configuration. As a result, a universal curve for
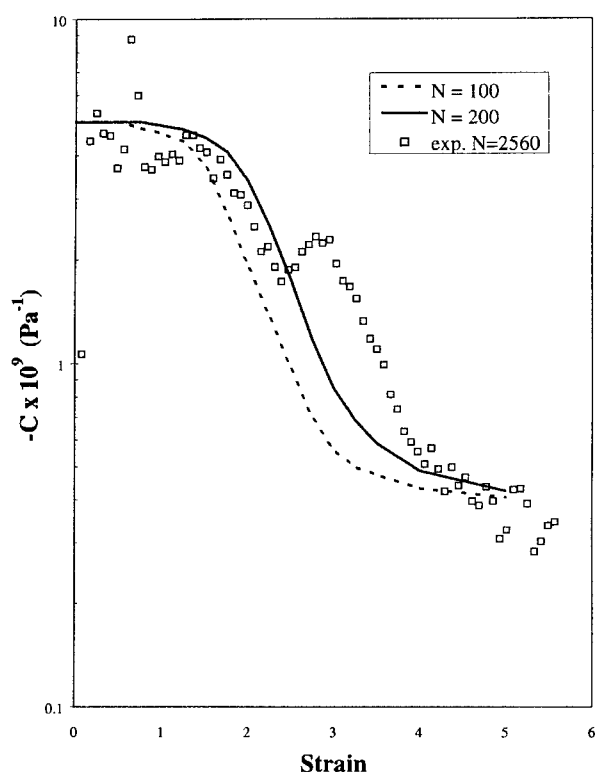
Fig. 18. Stress optical coefficient as a function of strain. The lines are the predictions of the bead rod model from Doyle *et al.* (1998).

stress birefringence during relaxation is not surprising and relaxation of partially extended chains eventually follows this curve. Constitutive equations based on pre-averaged closure approximations such as the FENE-P model are unable to show such hysteresis (Sizaire *et al.*, 1999)

6. Example 5: Complex flows: Transitions in chain configuration.

Complex flows can be modelled as a sequence of stretching and relaxation. The bead rod simulations of Doyle *et al.* (1998) have recently suggested that the conformational dynamics of an initially straight chain during stress relaxation are significantly different than that observed for the same chain during extensional stress growth. The authors also observe that following a period of stress relaxation, a large amount of stress appears to be lost whilst the chain remains relatively extended. Hence if a polymer solution was to be deformed by a combination of extension and relaxation, each for different periods, then one could obtain fluid elements having the same stress but quite different chain configuration. If such a fluid is further subjected to an extensional deformation, its response will be determined by its starting configuration. Orr and Sridhar (1999) have subjected fluids to a sequence of stretching, relaxation and further stretching.
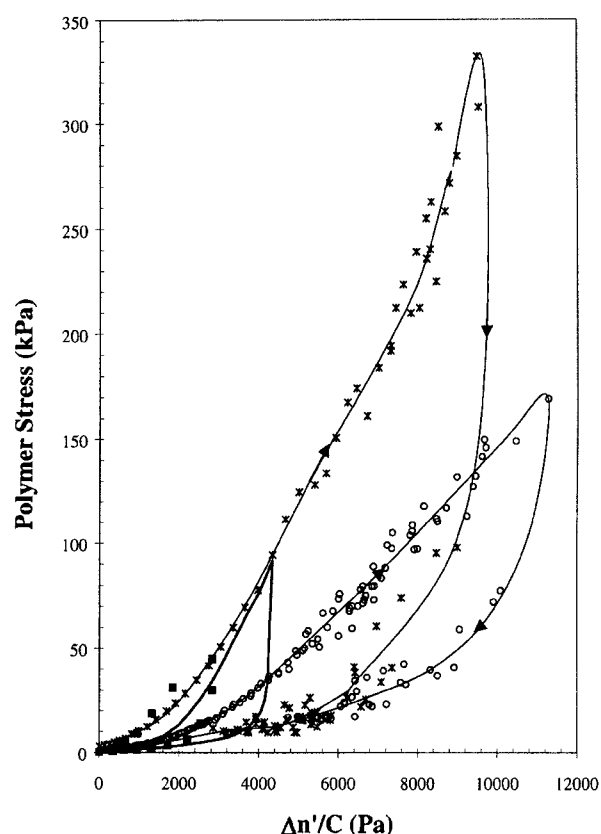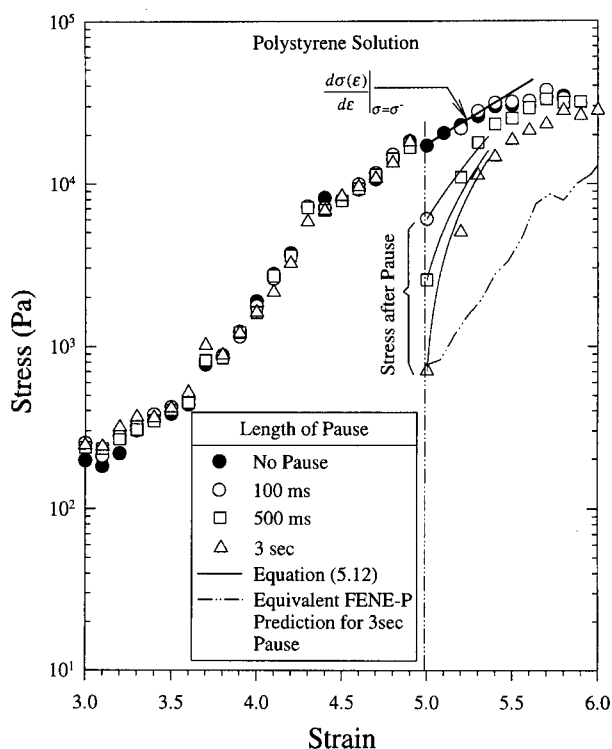

Fig. 19. Extensional flow start-up and subsequence relaxation for stress versus birefringence of a polystyrene solution (Sridhar *et al*, 1999); data points : asterisk : Wi = 41.7; circle : Wi = 16.8 ; square [Doyle *et al* 1998] : Wi = 2.84, line [Doyle et al 1998] : conformation dependent FENE model (Wi = 2.84).

Fig. 20 shows the stress growth history for these experiments plotted against strain. A pause of 100 ms, 500 ms and 3 seconds was introduced into a constant strain rate experiment at a strain of 5, after which flow was resumed. The strain rate prior and subsequent to the pause was $2s^{-1}$. Note that during the pause the accrued strain is equal to zero, and hence the flow stops and starts at the same strain. Note that the behaviour of the stress growth is significantly different for experiments that have experienced a pause in flow. The stress growth predicted by the FENE -P model depends only on the initial value of stress regardless of how that stress was obtained and is also sketched on figure 20. This result is in contrast to the experimental results.

One possible conclusion is that even though the fluids are at the same stress, the polymer chains in the different experiments have quite different configuration distributions. It is quite possible that these different distributions give rise to the same stress but yet contain within them some information of their previous deformation. The bead-rod simulations of Doyle *et al.* (1998) suggest that the chain configuration relax far slower than the stress. Hence

Fig. 20. Effect of stopping the deformation at a strain of 5 during a constant strain rate experiment. The dynamics on resumption of deformation is much faster than predicted by the FENE-P type models (Orr and Sridhar, 1999). The rate of stress growth after the pause is not different from the rate just before the pause.

tributions for the experiments of Orr and Sridhar. They show a hierarchy of configuration changes during the relaxation and subsequent stretching. For example during relaxation half dumbbells relax to form dumbbells whereas folds relax to form coils. The net result is that the conformation at the same strain can be quite different even though the stress is the same. The transitions in these configurations will determine the stress in complex time dependent flows. This is not captured by closed form constitutive equations due to the effect of pre-averaging the spring law.

In summary, the results indicate that the stress and configuration of a polymer chain appear to have different dynamics, which the simple elastic dumbbell model is unable to capture. The configuration distribution contains within it all the information about the deformation history and as distinct configuration distributions can lead to the same stress, the instantaneous polymer stress is by itself an inadequate measure of its ability to respond to deformation. This example clearly indicates that in order to mimic complex flows, the changes in chain conformation needs to be accurately portrayed as this has a dominant influence on the dynamics.

7. Summary

This paper presents a series of examples from the recent literature on extensional flows. As anticipated these strong flows cause a significant distortion of the chain. The dynamics of the polymer chain is influenced by the unusual conformations that the chain is able to achieve. In many situations these conformations reflect the initial conformation and orientation of the chain. Closed form constitutive equations are simple because they smear out these differences. They do not mimic either the diverse conformations or the distribution function for the chain extension. Attempts to derive better closure approximations may be able to solve only the latter problem (Liliens et al., 1998). Only detailed Brownian dynamics simulations are able to mimic the conformational peculiarities. Techniques such as the CONFFESIT program (Ottinger 1995) which couples finite element techniques with stochastic simulations are needed to incorporate these in flow calculations. There are several areas, which require further work. For example we still do not quite understand the role of molecular flexibility on chain dynamics. These unresolved issues will continue to attract the attention of rheologists in the new millenium.

each of the three experiments on Fig. 20 still retains some memory of its configuration prior to relaxation. One simple estimate of this configuration is arrived by assuming that during the relaxation process the configuration does not change. Following this assumption one could further assert that the stress response of the fluid would depend only on its configuration. That is a chain with a more open structure is able to respond more rapidly to imposed deformation than a compact chain. This then leads to an estimate of the stress growth at the re-inception of flow as the rate of stress growth at the time the flow stopped (in other words at the same configuration). The resulting stress growth is then given by

$$\sigma(\varepsilon) = \sigma_o + \left(\frac{d\sigma(\varepsilon)}{d\varepsilon}\bigg|_{\sigma=\sigma^-}\right)d\varepsilon$$

where σ_o is the stress where flow is resumed, σ^- is the level of stress attained immediately prior to the pause and ε is the strain. Predictions using the above equation are compared to the experimental data in Fig. 20. The evidence clearly points to the role of the configuration distribution as the prime determinant of stress response.

Li et al. (1999) have determined the configuration dis-

Acknowledgement

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