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MOLECULAR DEGRADATION OF POLYMER SOLUTIONS IN A FAST TRANSIENT EXTENSIONAL FLOW

DISsertATION

Presented in Partial Fulfillment of the Requirements for
the Degree Doctor of Philosophy in the Graduate
School of The Ohio State University

by

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ABSTRACT

The extensional degradation of polymer solutions in a fast transient flow is studied. Extensional flows are prevalent in many polymer processing operations, such as film stretching, fiber spinning, and blow molding, but their effect on polymer degradation is not well understood. Degradation in this type of flow field is much more extensive than in a pure shear flow due to the lack of vorticity. This research extends solution degradation studies to the semidilute and concentrated regimes, where entanglements are expected to affect chain scission. The effect of scission on samples with different polydispersities and the effect of solvent viscosity on chain scission is also studied. Polystyrene solutions are degraded in an opposed pistons, multipass extensional flow apparatus. This device cycles the solution across a sharp contraction, exposing the coils to a high extension rate in a very short time period. The centerline strain rate is varied over a two decade range (5 \times 10^3 \text{ to } 5 \times 10^5 \text{ s}^{-1}) by changing the piston speed and the contraction ratio.

Degradation is quantified by changes in the molecular weight distribution (MWD). Chains are broken near the center, a phenomenon explained by the mechanism of coil unraveling in a strong flow. For a polydisperse sample, the high molecular weight species are preferentially ruptured. There is a critical molecular weight ($M_c$) above which all chains are broken, but low molecular weight chains are not fractured. Multiple passes through the high extension rate region increase chain scission, although degradation is the greatest in the first pass through the high extension rate region. For a monodisperse sample,
experiments in different concentration regimes point to a dual mechanism of chain scission. For isolated chains, intramolecular entanglements are responsible for scission. For interacting chains, both intra- and intermolecular entanglements result in bond rupture.

The flow field is modeled using POLYFLOW to determine the magnitude of important variables associated with the chain scission process. The centerline extension rate, energy dissipation rate, residence time in the high extension rate zone, the fluid strain, and the flow character are calculated and mapped onto the flow field.
Dedicated to my wife, Kristy
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1.1 Flow-induced bond scission

Extensibility is one of the most intrinsic properties of a chain molecule. A polymer chain can be extended due to its relative position in a flow field. Under certain conditions, chain extension can be quite dramatic. At very large deformations, the phenomena of conformational changes, disentanglement, and chain scission become important. Information on a chain's ability to stretch, on the method of extension, and on the fracture of extended chains is of fundamental importance.

It has been known for some time that mechanical stresses can cause bond scission in macromolecular solutions. Hydrodynamic forces can not only induce profound segmental rearrangement, but can impose forces which are significant enough to break carbon-carbon bonds. When a polymer solution is placed in a velocity gradient, there is asymmetry in the exchange of momentum between the flowing solvent and different parts of the chain. This imbalance of forces results in tensions on a molecular scale and stress concentration at a particular location. A polymer responds to the application of stress by chain orientation, disentanglement, and bond rupture (Figure 1.1). The relative importance of each of these mechanisms changes with the structure, the state of aggregation, and the molecular weight of the polymer.
Polymer degradation can be defined as the changes in physical properties caused by chemical reactions involving bond scission in the backbone of molecules (Schnabel, 1981). For linear polymers, degradation results in a decrease in chain length. It is useful to subdivide degradation into categories based on the mode of initiation. Some of the common modes of initiation include thermal, mechanical, photochemical, biological, chemical and radiation.

Chain scission is a chemical reaction. The chemical nature of the degradation has been monitored by the uptake of radioactive iodine as a free radical scavenger. The amount of radioactive iodine incorporated into polymers during shear degradation is approximately the amount expected based on the losses in molecular weight (Johnson and Price, 1960). This confirms that mechanical degradation ruptures chains to form free radicals, which are rapidly quenched with scavengers in the solution.

Degradation of polymers by mechanical action is a depolymerization reaction in which the activation energy is supplied by the mechanical action on the polymer. The field deals with the chemical stability of main chain valence bonds against chemical influences of the environment coupled with temperature. Mechanically induced chain scission is an activated process of breaking chemical bonds. Mechanical forces raise the energy levels of the bonds above the levels due to thermal factors alone, lowering the barrier to bond dissociation. The major difference between spontaneous chemical degradation and mechanically induced degradation is the distribution of bond sites activated to the level of breakage. In spontaneous chemical degradation, the activated bond sites are distributed uniformly, but in mechanically induced scission, the distribution of bond sites is non-uniform. The non-uniformity leads to regions with stress concentration.
1.2 Extensional flows

Polymer degradation experiments are studied in a fast transient extensional flow. Extensional flows are prevalent in many polymer processing applications (Figure 1.2). In these examples, polymer chains are exposed to a strong extensional flow for a short time. Although the chains are exposed to the strong flow for a short time, extensional flows are very effective in deforming the microstructure. Flow through a contraction is a good example of a fast transient extensional flow. Contraction flows are common in industry: extrusion, injection molding, and fiber spinning are some examples. Any abrupt change in geometry will generate a flow with an extensional component. The flow into a contraction is geometrically simple, but the flow is complex, with components of both shear and elongational flow. The strain rate is a function of radius, with a maximum at the centerline, and the flow is purely elongational only near the symmetry axis.

1.3 Experimental goals

There has been a great deal of research into the extensional degradation of dilute polymer solutions. This work extends the dilute solution studies into the concentrated regime, where entanglements are expected to result in increased chain scission. The impetus for studying the extensional degradation process is threefold. First, research has shown that extensional flows are much more effective than shear flows in deforming the microstructure. Second, entanglements in the concentrated regime are expected to change the scission behavior compared to dilute solutions. Finally, both the mechanical and rheological properties of a material are strongly affected by molecular degradation. Fundamental studies of the degradation process will lead to improvements which minimize processing degradation.

The contributions to extensional degradation are studied separately through a series of fundamental experiments. Polymer samples are exposed to controlled extensional flows.
and the degree of degradation is measured and correlated with the key flow parameters. The specific goals of the project are the following:

- degrade polymer solutions in a fast transient extensional flow
- quantify degradation by rheological measurements and changes in the molecular weight distribution
- model the flow field to determine key variables which are directly related to chain scission
- relate the results obtained with concentrated polymer solutions to the previous studies with dilute polymer solutions.

1.4 Outline of thesis

The report is grouped into the following main sections: Literature Review, Experimental Methods, Simulations, Results, and Conclusions. In the Literature Review, the effect of the flow field on microstructure deformation is noted. Two types of extensional flow are introduced. Results from dilute solution experiments are summarized. Techniques used for the experimental work are described in the Experimental Methods section. The techniques include an opposed-pistons extensional flow device designed and built by the authors and the use of rheological measurements and molecular weight distribution to quantify degradation. In the next chapter, the numerical simulations are summarized. A discussion of strong versus weak flows is provided. Important parameters linked to chain scission are quantified, including the flow field character, energy dissipation rate, and centerline strain rate. The Results chapters are presented next, with a confirmation of experimental methods. The results include extensional degradation studies with a polydisperse polystyrene polymer, a monodisperse polystyrene polymer, and a polystyrene Boger fluid. Degradation is quantified by several techniques and degradation characteristics are identified, including the drop in zero shear viscosity of the degraded
samples, the preferential degradation of high molecular weight chains, the existence of a
critical molecular weight, and a comparison to dilute solution results. The last two Results
chapters summarize two small parts of the research study: thermal degradation and the use
of the extensional flow technique and analysis in the cell culture field. Finally, the
Conclusions and Recommendations for Future Work recapitulate the results from the
experiments and list some areas of improvement.
Figure 1.1 Energy cascade in a polymer system after application of a stress. There are several modes by which a polymer chain can respond to external energy input.
Figure 1.2 Extensional flow in polymer processing operations.  
a) Film stretching: there is biaxial extensional flow when the film is stretched;  
b) Fiber spinning: the fiber is exposed to a uniaxial extensional flow due to the high speed take-up reel;  
c) Fountain flow in injection molding: a polymer chain is stretched at the melt front and freezes at the cool wall.
Chapter 2: Literature Review

2.1 Overview

The Literature Review serves two functions. First, it is an introduction and background on flow-induced polymer degradation. Second, it summarizes previous work in the field, providing a basis for interpretation and comparison of results. The Literature Review is divided into several sections, based on the following general topics. Flow-induced microstructure deformation is discussed, and the effectiveness of extensional flow is highlighted. Next, the two general types of extensional flow are introduced. Previous work on dilute solution polymer degradation is interpreted in terms of the different flow fields and the mechanism of chain unraveling. Finally, the effect of different concentration regimes on stress transmission and extensional flow-induced degradation is considered.

2.2 Flow field effect on polymer conformation

A polymer is a long chain of monomer units. In general, each monomer has some freedom of rotation, which allows the chain to kink randomly and take on a large number of conformations. Some internal rotations are limited by interactions with other monomers or chains. These limitations give the chain some resistance against bending or twisting. The interactions of the solvent with monomers and the long range interference of monomer units decidedly affect the number of conformations. Although a polystyrene chain is linear, the entropy is maximized when the chain occupies a spherical random coil shape.
With no external forces acting on them, polymer coils will approach and fluctuate around the most probable conformation accessible. The action of external forces causes a displacement of the chain from the most probable position and elicits retractive forces. A polymer chain in solution is distorted by a flow with a velocity gradient because there is a velocity difference between the two sides of a random walk. Brownian fluctuations in the chain configuration produce a relaxation of the conformation. This entropic desire to return to the most probable, symmetric coiled state is usually modeled by the elasticity of the spring.

The type of flow has a profound effect on chain conformation and stress transfer and thus also on the efficiency of degradation. In a shear flow, streamlines are parallel, but correspond to different material velocities. In an extensional flow, streamlines through a cross-section correspond to constant material velocities, but are not parallel. When a random coil is placed in a shear flow, the coil is slightly deformed and becomes aligned with the flow field. In a shear flow, the streamlines are perpendicular to the velocity gradient. As a result, once the molecules are aligned with the streamlines, they are convected with the fluid. In an extensional flow, the streamlines are parallel to the velocity gradient. Random coils are deformed to a much greater extent, and the velocity gradients along the length of the coil result in unbalanced stresses on the chain (Figure 2.1). As a result, degradation is much more effective in an extensional flow.

2.3 Flow-induced microstructure deformation

In many problems, the conformation of the microstructure is the most important feature of the system. Flow-induced changes in the microstructure can be dramatic and can directly result in changes in macroscopic properties of the system. For a polymer with a molecular weight of $10^6$, the length of a fully stretched out chain can be over two orders of magnitude larger than the characteristic dimension of a coil (Hinch, 1977). This dramatic
change in the linear dimensions of chains in two different conformations highlights the
effect of stretched chains on the rheological behavior of a solution. Significant rheological
changes will be observed even when the coils are partially uncoiled. The weight fraction is
an inappropriate measure of the possible effect of added polymer. A better measure is the
effective hydrodynamic volume fraction. This volume fraction is large if the polymers are
highly stretched.

It is important to understand the effect of the flow on the deformation of the
microstructure. The effect of the flow on the microstructure is determined by combinations
of the magnitude of the velocity gradient tensor, which represents the flow strength, and
the ratio of the strain rate to vorticity, which represents the flow type (Olbricht et al.,
1982). The type of flow has a profound effect on the stress transfer and microstructure
deformation. The relative orientation of the principal axes of strain with respect to a particle
plays a key role in determining whether there is significant deformation of the
microstructure. Lodge (1964) presents the description of stress and strain from a
mathematical perspective. In a uniform deformation, there are three material lines passing
through any particle which are mutually orthogonal in both states. These lines are the
principal axes of strain. A sphere of unit radius centered at the particle will become an
ellipsoid after any uniform deformation. The material lines coinciding with the main axes
of the ellipsoid are the principal axes of strain (Figure 2.2). The lengths of the main semi­
axes of the ellipsoid are the principal elongation ratios. Any uniform deformation can be
resolved into three components: rigid translation, rigid rotation, and a strain. In rigid
translation, the chosen particle is brought from its initial to final position. In rigid rotation,
the principal axes at the origin are rotated from their initial to their final orientation. For the
strain, three mutually perpendicular families of lines in the directions of the principal axes
are uniformly elongated by appropriate factors. For deformations involving more than two
states, as in the flow of a liquid, a given material line which is a principal axis for one state may or may not be a principal axis for the second state.

Simple shear differs from pure extensional flow by the rotation of the principal axes. In elongational flow, all three principal axes are constant in the material. In a steady shear flow, two of the principal axes correspond to different material lines for different pairs of states.

The orientation of the principal axes can be calculated given the stress on any point. It is always possible to take a cut through a point such that only a normal stress acts on the plane through the point. This is called a principal plane, and the stress acting on it is a principal stress. There are three principal planes and three principal stresses through a given point. The principal stresses can be pictured as a stress ellipsoid around a point (Macosko, 1994). The surface of the ellipsoid is formed by the locus of points at the end of the traction vector, \( t_n \), from the point when \( n \) takes all possible directions. The three axes of this ellipsoid are the principal stresses, \( \sigma_i \), and their directions are the principal directions, \( e_i \). When the coordinate system coincides with the three principal stresses, the only components in the stress tensor are the diagonal terms.

2.4 Taylor’s experiments on suspended drops

Taylor (1934) was the first to note the difference between shear and extensional flows on suspended materials, such as drops or polymer coils. Taylor studied the behavior of drops in controlled flows. The distortion produced by a given flow is of interest in understanding the rheological behavior of polymer solutions.

When one fluid is at rest in another fluid of the same density, it forms a spherical drop. Any movement of the outer fluid (other than pure rotation or translation) will distort the drop. The distorting force is due to traction on its surface from dynamic and viscous forces. Surface tension will tend to keep the drop spherical. There is a maximum size drop
which surface tension can hold together against the disruptive forces due to the viscous
drag of the surrounding fluid. Taylor used a four roll apparatus and an opposed bands
device to generate controlled flows (Figure 2.3). The flow in both flows can be
represented by simple mathematical equations:

\[ u = C x \quad \quad v = -C y \]  
\[ u' = \alpha y' \quad \quad v' = 0 \]  

By varying the speed of the devices, a variety of flows are possible. The two flow fields
are identical when the following conditions are met: the constant, C, in Equation 2.1 is set
to 0.5\( \alpha \); the axes of the parallel band coordinates are rotated with an angular velocity
0.5\( \alpha \); and these axes are instantaneously at a forty-five degree angle to the fixed axes. This
equivalence is important, since it can separate various effects on the drops. Effects which
depend only on the instantaneous distribution of velocity and are unaffected by a rotation of
the whole system will be identical when the two devices are operated at speeds such that C
= 0.5\( \alpha \). Effects which do not depend on the instantaneous distribution of velocity, but are
dependent on a sequence of such distributions are very different in the two experiments.

This similarity can be exploited to examine the effect of the type of flow on an
elongated symmetrical solid body. If the body is placed in the four roll mill, with its long
axis at an angle \( \theta \) to the axis of \( x \), its surface will be subjected to the same stresses that
would act on the body if it were in the parallel band apparatus, oriented with its long axis
\((45 + \theta)\) degrees to the axis of \( x' \). The type of flow will have a dramatic effect on the
subsequent motion of the body, though. In the extensional flow, the body will align itself
with the long axis parallel to the axis of \( x \). In the shear flow, the body will rotate about an
axis perpendicular to the plane \( x'y' \).

The behavior of drops is a strong function of the ratio of the strain rate to the vorticity.
At low flow strengths (ratio of strain rate to vorticity less than or equal to one), drops of all
viscosity ratios deform into prolate spheroids. The longest axis of the drop is aligned with
the principal axis of strain. When the drop viscosity is low compared to that of the suspending fluid, the shear rate required for burst becomes large. The drops attain a highly deformed state. When the ratio of drop viscosity to suspending fluid viscosity is large, drop behavior is qualitatively different in simple shear and irrotational flow fields. In extensional flow fields, where there is no rotation, the drops burst at low strain rates. In simple shear flows, where the vorticity equals the strain rate, viscous drops assume deformed shapes which are unaffected by further increases in the shear rate. Drop burst becomes impossible beyond a certain viscosity ratio.

Drop behavior differences in shear and extensional flows can be explained by the orientation of the drop with respect to the principal axes of the rate of strain. In the extensional flow, the lines of particles extending at the greatest rate are parallel to the x-axis. This line of particles remains in the direction of maximum stretch as long as the flow continues. The viscous drag of the moving fluid results in a stress on the deformed drop. When the viscous stress is larger than the surface tension forces, the drop bursts (Figure 2.4). In the shear flow, the direction of maximum rate of elongation is 45° to the bands. Lines of particles which are exposed to this maximum elongation are continually rotated away from that position towards a line parallel to the bands due to the nonzero vorticity. The molecule rotates with an angular velocity equal to half of the vorticity. In this orientation, the line of particles is neither elongated nor compressed. Further rotation brings the line of particles into an orientation where they are acted on by a compressive force. The drop attains a permanent deformed position, with the long axis parallel to the bands, with the internal fluid rotating. The line of particles is alternately exposed to elongational and compressive stresses. A macromolecule in a shear flow is exposed to forces which alternately extend and compress the molecule (Figure 2.5). The force is largest for \( \theta = 45^\circ \), zero for \( \theta = 0 \) and 90°, and is negative for \( \theta \) between 90° and 180°.
(Frenkel, 1944). A molecule rotating in a shear flow is exposed to an extension ($0 < \theta < 90^\circ$) and a compression ($90 < \theta < 180^\circ$).

Bentley and Leal (1986a,b) added to Taylor's work. The authors designed a computer controlled four roll mill to investigate particle and drop dynamics in two dimensional linear flows. The control objective is to keep the drop in the center of the rollers, at the stagnation point, while maintaining the shear rate and the ratio of vorticity to strain rate at fixed values. The four roll mill allows a systematic investigation of the effect of vorticity in strong flows, where the magnitude of the strain rate is greater than the magnitude of the vorticity. By varying the speed and direction of the rollers, the flow can be varied from pure rotation to pure strain. A key feature of particle or drop motion is that it is expected to depend critically upon the relative magnitudes of the vorticity and strain rates of the undisturbed motion.

In the four roll mill, there is a stagnation point located centrally between the rollers. A particle or drop located at this point will remain in this location, even if the flow is time dependent. The mill is capable of producing two dimensional flows with an arbitrary strain rate to vorticity ratio. This is accomplished by varying the ratio of the speeds of the crosswise pair of rollers. The velocity gradient tensor near the center of the device can be approximated by:

$$\nabla u = \frac{1}{2} \dot{\gamma} \begin{bmatrix} 1 + \alpha & 1 - \alpha & 0 \\ -1 + \alpha & -1 - \alpha & 0 \\ 0 & 0 & 0 \end{bmatrix}$$  \hspace{1cm} (2.3)$$

The flow parameter, $\alpha$, is a measure of the relative strength of the straining motion and vorticity in the flow. It ranges in value from -1 (purely rotational flow) to 1 (pure straining motion), and is equal to 0 for simple shear flow. The ratio of the magnitude of the rate of strain tensor to the vorticity tensor can be expressed in terms of $\alpha$:  

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The principal axes of the rate of strain tensor are at \( \theta = 0^\circ \) and \( \theta = 0.5\pi \), corresponding to the maxima in extension and compression, respectively. Strong flows are flows with a positive \( \alpha \). Bentley and Leal proved that strong flows are capable in producing appreciable deformation and burst of drops.

### 2.5 Shear degradation studies

Although most practical flows of polymers are concentrated solutions or melts, a majority of research on polymer degradation has been with dilute systems. Dilute systems have several experimental advantages over concentrated solutions and melts. A majority of studies with dilute systems use approximately monodisperse, nonentangled, high molecular weight polymer solutions. The stress on the macromolecule can be modeled using an appropriate mechanical model, such as the bead-spring model. Since the solutions are very dilute, the fluids are approximately Newtonian and the Navier-Stokes equations can be solved to provide details of the flow field. Also, changes in the polymer concentration change the degree of intermolecular interactions. Finally, the experiments can be performed at or near room temperature. In concentrated solutions and melts, the chains have both inter- and intra-molecular entanglements. The strain is partitioned between the individual molecules and the entanglements, making modeling difficult. Chain interaction leads to viscoelastic phenomena. There is a nonlinear relationship between the stress and the deformation which must be accounted for with a constitutive equation. Calculation of pertinent variables becomes quite cumbersome. Commercially available polymers also have a molecular weight distribution instead of a single molecular weight. Therefore, a statistical function or the appropriate average molecular weight must be used to correlate degradation with chain length. The higher viscosities and/or higher temperatures of
concentrated solutions and melts give rise to experimental difficulties not usually associated with dilute solutions.

Flow-induced chain scission was predicted as early as 1944 (Frenkel, 1944) and was first observed and verified in the 1960's. Some of the first studies utilized deoxyribonucleic acid (DNA) from microorganisms. DNA is ideal for studying macromolecule scission since it is a monodisperse, very high molecular weight polymer. Levinthal and Davison used $^{32}$P-labeled DNA to track the sedimentation coefficient of DNA before and after passage through a small diameter capillary (Levinthal and Davison, 1961). At low flow rates, there was no change in the sedimentation behavior of the material. As the flow rate was increased, degradation was detected by the presence of a small second peak of DNA settling more slowly than the intact DNA. High speed mixing of DNA solutions was found to cleave DNA fragments above a certain length (Rosenkranz and Bendich, 1960).

Previous research on the shear degradation of polymers in dilute solution must be subdivided into two categories: pure shear flows and flows with an extensional component. Much early work in polymer degradation in solution used small bore capillaries to achieve high shear rates. The degradation was often observed to be independent of capillary length (Cutler et al., 1975; Merrill and Leopairat, 1980). This indicates that the extensional component of the flow at the entrance to the small diameter capillary was probably responsible for chain scission. Table 2.1 lists some studies of the shear degradation of polymers in solution, including the geometry used to test the solutions.

Results from studies which utilized a Couette geometry to achieve a pure shear flow field showed that degradation is often not possible in a laminar flow. The solvent quality can have a dramatic effect on flow-induced scission, although there are some conflicting results (Ballauff and Wolf, 1988; Basedow et al., 1978; Zakin and Hunston, 1978;
Harrington and Zimm, 1965). The nature of solvent environment changes the conformation of the macromolecules in solution (Brochard and deGennes, 1977). The deterioration in solvent quality results in an increased number of contacts between the chains (Figure 2.6). Entanglements are a necessary prerequisite for the occurrence of chain scission under laminar conditions. Solutions of the same polymer at the same concentration in a good solvent do not exhibit chain scission compared to poor solvents which do show chain scission.

There are conflicting results concerning the effect of the solvent quality on flow-induced scission. The effect of solvent quality on the degradation in dilute solution fast transient extensional flow (FTF) has been examined (Nguyen and Kausch, 1990). Polystyrene solutions in two different solvents (decalin and 1-methyl-naphthalene) were tested at different temperatures to match solvent viscosity. Decalin is a poor solvent, while 1-methyl-naphthalene is a good solvent for polystyrene. It was expected that since coil dimensions and relaxation times would be larger in the good solvent, the coils would deform and break at a lower critical strain. However, experiments showed that the degradation curves were superimposable. Solvent quality appeared to have no influence on the degradation.

Several other studies have shown solvent quality to be a factor in chain scission. Zakin and Hunston (1978) degraded very dilute polystyrene solutions in a good solvent and in a mixed solvent that was close to theta conditions. The solutions were degraded in turbulent flow through a capillary and in high speed stirring. Mechanical degradation was observed in the poor solvent system, but not in the good solvent system under the same conditions. The researchers proposed that the threshold molecular weight for mechanical degradation is lower in a poor solvent system. Ballauf and Wolf (1988) studied the laminar flow degradation of semi-concentrated polystyrene solutions in a Couette device. The researchers found that moderately concentrated solutions do not degrade in a laminar shear
flow as long as the solvent quality is high. Basedow et al. (1978) reported similar results in a study of ultrasonic degradation in a mixed solvent system. The lack of degradation for a good solvent system is related to the entanglement behavior of the solution. The solvent power has a direct effect on the entanglement of chains in a solution. Contacts between different chains are favored upon deterioration of solvent power.

2.6 Extensional degradation

Studying polymer degradation in extensional flows is difficult, because it is experimentally impossible to isolate a pure extensional flow. The only recourse is to generate a flow with a high extensional component and interpret the data to capture this component in terms of the extensional viscosity and the strain rate. Experimentally, extensional flows can be divided into two categories: quasi-steady-state flows (QSSF) and fast transient flows (FTF). QSSF include four roll mills, crossed slots, and opposed nozzles. All QSSF have a stagnation point. FTF are characterized by finite spatial regions of high extension and short residence time. Flow through a contraction is the most common FTF (Figure 2.7).

A chain's conformation, the stress distribution, and the probability of chain scission are dependent on the state of coil extension, which in turn depends on the deformation of the surrounding fluid. In an extensional flow, the magnitude of the strain rate is the most important flow field variable that determines polymer conformation. The strain rate is the velocity gradient in the direction of flow. It is obtained from the diagonal components of the rate of deformation tensor.

A polymer in a rest state will adopt a random coil conformation, due to the relative freedom of rotation associated with the bonds. For extensional flows, the linear theory of distortions predicts a divergence when the product of the relaxation time and the extension rate is greater than a constant of order one. When the strain rate, \( \dot{\varepsilon} \), is equal to a critical
strain rate, $\dot{\varepsilon}$, there is an abrupt coil-stretch transition. The coil-stretch transition is a sudden and drastic conformational rearrangement which occurs when Brownian forces no longer balance drag forces. The transition from coil to stretched state is due to a hysteresis in the coil-stretch curve in a longitudinal gradient (deGennes, 1974). Hydrodynamic interactions between monomers decrease when the molecule is stretched. The inner monomers are more exposed to the velocity gradient, chain distortion increases, and more monomers are exposed. As the coil begins extending, there is a larger velocity gradient and increased drag forces, causing chain extension to accelerate. The polymer is almost fully extended after the coil-stretch transition. If the residence time in the extensional flow is long enough, the coil becomes fully stretched and aligned with the flow. The coil-stretch transition occurs over a narrow range of strain rates. Even when the coil unravels from the center out, the transition remains sharp.

Larson and Magda improved upon deGennes' predictions by replacing the dumbbell model with a bead-spring chain (Larson and Magda, 1989). The bead-spring chain still predicted an abrupt coil-stretch transition at a critical strain rate. Unlike the dumbbell model, it predicted that the coil-stretch transition is controlled by the extensional component of the flow for mixed shear and extensional flows, even if the shearing component is dominant over the extensional component of the velocity gradient. The deGennes dumbbell model does not correctly predict this behavior.

The critical strain rate required for chain extension is related to the longest relaxation time of the coil:

$$\dot{\varepsilon}_c \tau_z = A$$

(2.5)

where $A$ is an order unity constant and $\tau_z$ is the Zimm relaxation time. The Zimm relaxation time is defined:

$$\tau_z = 0.95\eta_s[\eta]M/RT$$

(2.6)
where \( \eta_s \) is the solvent viscosity, \( [\eta] \) is the intrinsic viscosity, \( M \) is the molecular weight. \( R \) is the gas constant, and \( T \) is the absolute temperature. Zimm behavior is appropriate, since extensional flows probe the dynamics of partially stretched coils (Odell et al., 1988). In extensional flow, coil unraveling is a prerequisite for chain scission.

2.6.1 Dilute solution degradation in quasi-steady-state flows

The impinging jets or opposed nozzle geometry has been used to demonstrate that flows free from rotation can extend random coils (Frank et al., 1971). In this geometry, fluid enters two nozzles, creating a stagnation point at the geometric center (Figure 2.8). This stagnation point experiment can effectively apply a controlled stress to polymer molecules. Birefringence associated with the localized alignment of the macromolecules was noted when polymer solutions flowed through an opposed nozzle apparatus. Odell and Keller have used an opposed nozzle apparatus to study the extensional degradation of polymer solutions (Odell and Keller, 1986). In a QSSF such as the opposed nozzle apparatus, chain scission occurs in a small portion of the solution. The large strains necessary to fully extend chains occur only on streamlines which pass close to the stagnation point. Since only a small percentage of the streamlines pass near the stagnation point, only a small percentage of chains are extended and a smaller fraction are cleaved. Cycling the solution through the apparatus multiple times will cause a larger number of chains to be broken. As \( \dot{\varepsilon} > \dot{\varepsilon}_c \), the stretched out chains become increasingly stressed until they rupture. There is no appreciable fracture until a critical fracture strain, \( \dot{\varepsilon}_f \), is reached.

If some chains are cleaved, recycling the solution through the device results in a new birefringence curve. The molecular weight distribution (MWD) is obtained by differentiating the birefringence intensity with respect to the strain rate. Birefringence curves of degraded solutions show a new peak at molecular weights exactly one half of the starting material, indicating central scission (Odell et al., 1990). The fracture strain rate is
proportional to the inverse square of the molecular weight. Both observations of QSSF
degradation indicate that the chain is fractured in a fully extended state. Stokes' Law is able
to accurately describe the frictional forces on the polymer coils after they have been
extended. Central scission and a fracture strain rate dependence on the inverse square of
the molecular weight are predicted from Stokes' Law. The flow field, which is
centrosymmetric with respect to the molecule, has a maximum in stress at the chain center.

2.6.1.1 Forces on a chain in a quasi-steady state flow

When a macromolecule is aligned with the extensional flow axis, the chain is under
tension, because of the sum of drag forces due to the velocity difference between the fluid
and the monomers. To calculate the tension in the chain, the polymer is usually represented
by a bead-spring model, where exposed monomers interact with the fluid. The
hydrodynamic forces are described by a linear relation between the drag resistance and the
relative bead velocity with respect to the fluid,

\[ f_i = \zeta_0 V_n \]  \hspace{1cm} (2.7)

where \( \zeta_0 \) is the bead-solvent friction coefficient, and \( V_n \) is the relative velocity between the
bead and solvent. The friction coefficient for a bead with radius \( a \) is often given explicitly
by Stokes' Law of drag resistance:

\[ \zeta_0 = 6\pi \eta a \]  \hspace{1cm} (2.8)

There is relative motion between the monomers and the fluid at all points except at the
midpoint. The relative velocity will increase towards the chain ends, as indicated in Figure
2.9. The relative velocity is a function of the strain rate (\( \dot{\epsilon} \)), the separation between the
beads (\( b \)), and the number of monomer units from the center (\( i \)):

\[ V_n = b_1 \dot{\epsilon} \]  \hspace{1cm} (2.9)
The chain as a whole is under tension, with a maximum in stress at the center because the sum of the drag on all segments connected from it and running in opposite directions. To find the force at the center of the molecule, the forces must be summed over all the beads from 1 to \( N/2 \), where \( N \) is the number of molecules in the chain. The sum is given by a series:

\[
F_c = \frac{6\pi}{8} \eta ab \beta N^2
\]  

(2.10)

The molecule will be fractured when the input energy is comparable to the bond dissociation energy for a carbon-carbon bond. In a fully stretched state, the stress on the chain is maximum at the center, resulting in centrosymmetric scission. Chain fracture does not occur until the strain rate is equal to a critical fracture strain rate, \( \epsilon_f \). The fracture strain is proportional to \( M^2 \) for fully stretched chains, as predicted by Stokes' Law. Therefore, shorter molecules require a higher extension rate to break in inverse square relation to their length. The fracture strain rate is a stronger function of the molecular weight than the coil-stretch strain rate. There can be a molecular weight above which the polymer fractures before it is fully stretched.

Using Stokes' Law and experimental results for polymer fracture, the magnitude of the tensile force can be compared to the carbon-carbon bond strength. For a polystyrene chain, the radius of the phenyl group can be used for estimates of the radius \( a = 2.0 \text{ Å} \) and bead separation \( b = 2.5 \text{ Å} \). With these parameters and experimental results for chain fracture as a function of molecular weight, Stokes' Law predicts frictional forces of 13.4 nN/chain (Odell and Keller, 1986).

This measured fracture stress can be compared to the bond strength by modeling bond scission due to stress as a unimolecular dissociation reaction. The applied tensile force is balanced by internal molecular forces. When these internal forces exceed the bond strength, the chain breaks. The bond strength can be calculated from the derivative of the
potential energy function. An applied tensile force modifies the potential energy function, reducing the bond rupture activation energy by an amount equal to the work performed by the force over the distance from the equilibrium position. Eyring’s transition state theory can be used to define a rate constant for the thermally activated fracture of polymers. For a carbon-carbon bond, the rate of chain scission is negligible unless the applied force is approximately 4-10 nN/chain (approximately $10^{-3}$ dyn/chain). Thus, the frictional forces in a persistently extensional flow can be comparable to the force required to rupture a C-C bond.

2.6.2 Dilute solution degradation in fast transient flows

Studies of FTF degradation have pointed out several differences in the degradation behavior in FTF versus QSSF. These differences are directly related to the different scission mechanism in the two types of flow. Merrill and Leopairat (1980) subjected dilute solutions of three polymers to transient, high elongational strain rates by passing the solutions through a sharp contraction, using a piston-cylinder apparatus. All of the solutions were at concentrations far below the critical value for entanglement. The MWD was measured by gel permeation chromatography (GPC) as a function of piston velocity. The GPC data indicated there was a critical orifice velocity for each polymer species, above which scission occurred. As mentioned earlier, FTF impose a high strain rate over a short period of time. The internal, self-entangled sections of the random coil cannot respond to this transient strain rate and are pulled and broken when the applied stress reaches a critical value.

The analysis of Armstrong et al. (1980) was used to calculate the strain rate at the centerline. This analysis assumes inviscid incompressible flow. The extensional strain rate was defined as:
\[ \varepsilon_{zz} = \frac{\partial v_z}{\partial z} \] (2.11) 

and was non-dimensionalized:

\[ \varepsilon_{zz}^* = \frac{R_0}{V_0} \varepsilon_{zz} \] (2.12)

where \( z \) is the flow direction, \( R_0 \) is the radius of the capillary, and \( V_0 \) is the volumetric average velocity in the orifice. The non-dimensional strain rate reaches a maximum (0.59) approximately 0.3 capillary radii before the orifice. The strain rate function is a spike, increasing from 0.1 to 0.59 in an axial distance of approximately one capillary diameter. This behavior is representative of FTF and contraction flows in general. The critical orifice velocity and the number of passes were the most important variables determining the degree of scission.

Nguyen and Kausch (1986) have studied the degradation of dilute solutions in a FTF. The experiments are performed with a piston-cylinder device which drives a solution across an orifice. A series of high molecular weight standards was degraded in a FTF and the fracture strain rate was proportional to \( M^{0.95} \) (1988). This is a much weaker dependence than in QSSF, where Stokes' Law and experimental results have shown the fracture strain rate proportional to the inverse square of the molecular weight.

Nguyen and Kausch also studied the effect of solvent viscosity on the degradation rate (Nguyen and Kausch, 1990). They used several solvents with a wide variation in viscosity and found that the fracture strain rate was weakly dependent on the solvent viscosity. The solvent viscosity is important in transferring kinetic energy from flow into the chain as elastic energy. The frictional coefficient between polymer segments and solvent molecules is directly proportional to the bulk viscosity of the solvent. Therefore, a chain in a more viscous solvent is more easily oriented and can be fractured at a lower critical strain rate. For stagnant flow, the fracture strain rate is inversely proportional to the solvent viscosity. However, Nguyen and Kausch found that for FTF, the fracture strain is much less
sensitive to the solvent viscosity ($\dot{\varepsilon}_f$ proportional to $\eta_s^{-0.25}$). This weak dependence on solvent viscosity points to a different mechanism for chain scission than in QSSF, since Stokes’ Law predicts the fracture strain rate inversely proportional to the solvent viscosity.

The effect of temperature on FTF scission was quantified by Nguyen and Kausch (Nguyen and Kausch, 1986). The overall degradation rate has a negative temperature coefficient, and there is a weak temperature dependence on degradation. The weak influence of temperature on the degradation is the result of two competing processes. An increase in temperature increases the rate constant for bond scission, but decreases the solvent viscosity. The decrease in solvent viscosity increases chain mobility and lowers the energy input to the chain. These two processes have opposite effects on chain degradation, thus lead to a weak temperature dependence.

One of the identifying features of FTF, the short residence time in the high strain rate region, has a profound effect on the polymer conformation and chain scission. In FTF, there is not sufficient time for the chain to stretch to full extension, even if the critical strain rate is exceeded. If coil deformation is affine with the surrounding fluid, the maximum strain that can be achieved is equal to the fluid strain ($\dot{\varepsilon}_t$). Since the residence time in the high extension rate region is very short, there is not enough time to accumulate strains large enough for full extension. Therefore, chains are fractured in a partially uncoiled state.

Rabin (1988) commented on experimental results for stretching and fracture of isolated polymers in extensional flow. The discrepancies between theoretical predictions and experimental results arise from the assumption of an abrupt transition from a uniformly deformed coil to a fully stretched state. The theoretical stress models are based on steady state conditions. In QSSF, the polymer molecules have a residence time which is much greater than the longest relaxation time for the molecule and a steady state analysis is valid. Experimental results using a QSSF show the fracture strain rate proportional to $M^2$ and scission occurring primarily at the center of the polymer chains. Full chain extension is
contingent on several points. Full extension occurs if the flow is persistently elongational. the strain rate is greater than the critical strain rate for uncoiling, and the residence time is greater than the longest chain relaxation time. Contraction flow, and FTF in general, do not satisfy any of these three requirements. Due to the short period in the high strain rate zone, the coils don't have time to stretch, even if \( \dot{\varepsilon}_s \) is exceeded. Therefore, FTF scission occurs at a higher strain rate than QSSF. Increasing the flow rate increases \( \dot{\varepsilon} \), but decreases the residence time. This results in a different scaling factor for the critical fracture strain. Bond scission in FTF takes place in a predominantly coiled state. Rabin showed that for FTF, \( \dot{\varepsilon}_f \) should vary with \( M^{(1.20)} \) with the exponent determined by the quality of the solvent. In addition, non-central scission is possible in FTF. As a result, the distribution of fracture products will be greater for FTF than for QSSF. The molecular weight dependence and distribution of fracture products in FTF have been verified experimentally (Nguyen and Kausch, 1992) and in molecular dynamics simulations (Knudsen et al., 1996).

2.6.2.1 Forces on chain in a fast transient flow

Comparisons of the frictional force in FTF and the bond rupture force confirm that chains are not ruptured in a fully uncoiled state. Models which assume full extension to calculate the tensile force are grossly in error for FTF. Merrill and Leopairat (1980) studied FTF degradation of dilute polystyrene solutions and modeled the system to predict the frictional forces. A Hookean dumbbell and Rouse model were used to calculate the tensile forces on a polymer chain in a FTF. Both models assume that the chain is a set of connectors which is fully extended before breaking. The calculated forces were three orders of magnitude smaller than the carbon-carbon bond strength. This discrepancy is a direct result of the false assumption of complete chain extension. Unlike QSSF, a coil in a FTF will be fractured in a partially uncoiled state. The short residence time does not give
parts of the chain time to disentangle from inter- and intra-molecular entanglements. At these points, the monomers are essentially fixed in place. These temporary entanglements lead to chain scission in FTF.

Forces achieved in a FTF can be compared to the breaking strength of a carbon-carbon bond. Instead of assuming a fully aligned chain, a statistical mechanics analysis can predict the magnitude of the tensile force on the chain. The theory of tension in a random-walk chain as a function of chain end separation can be used to analyze the problem (James and Guth, 1943). For a chain with neither valence nor rotation angle restrictions, the tensile force on a segment of the chain is a function of the distance of separation of the segment ends ($\delta$), the number of bonds in the chain segment ($n$), and the length per bond ($l$):

$$F_\delta = \left(\frac{kT}{l}\right) \Gamma^{-1}\left(\frac{\delta}{nl}\right)$$  \hspace{1cm} (2.13)

where $F_\delta$ is the tensile force, $k$ is the Boltzmann constant, $T$ is the absolute temperature, and $\Gamma^{-1}$ is the inverse Langevin function. The Langevin function is defined:

$$\Gamma(z) = \coth(z) - \frac{1}{z}$$  \hspace{1cm} (2.14)

The tensile force is a function of the argument in the inverse Langevin function, the separation distance divided by the straight chain length. The tensile force is very low until a significant extension is achieved, as a direct result of the behavior of the inverse Langevin function. For the tensile force to be comparable to the C-C bond strength (approximately $10^{-3}$ dyn), the separation must be over 99.7% of the straight chain length (Figure 2.10). As noted above, the coils do not have sufficient time in the high strain rate region to achieve this strain in a FTF. However, there is no restriction on the number of bonds in this equation for the tensile force, provided the two monomers are separated by a distance large enough to satisfy some numerical approximations in the derivation. The only parameter of interest is the distance between two monomers divided by the straight chain distance.
Therefore, it is not necessary for the entire isolated macromolecule to extend to greater than 99% of its straight chain length. If there is a segment of the chain which is stretched to over 99% of its straight chain length, the tensile force will be large enough to fracture that part of the chain. Temporary junctions, formed from intermolecular and intramolecular entanglements, hinder polymer extension and relaxation in an extensional flow field and provide the necessary restrictions to enable partial chain extension (Figure 2.11). This analysis clarifies the discrepancy between the calculated tensile force and the bond strength. In a FTF, the coils are fractured in a partially uncoiled state. Table 2.2 summarizes the main features of QSS and FTF extensional degradation.

2.7 Chain unraveling in a strong flow

Experimental results on FTF scission indicate that the polymer chains are still broken near the center of the chain, as in QSSF (Levinthal and Davison, 1961; Nguyen and Kausch, 1992). This indicates that tensile stresses can be transmitted through a chain backbone even when portions of the chain are looped and kinked. The approximate central scission in FTF can be explained by analyzing how the macromolecule unravels when placed in the strong flow field. The exact mechanism of coil extension in an extensional flow field is not known. The instantaneous conformation of a coil is determined by the relative magnitudes of the drag force, the spring-like elastic bond force, and Brownian motion. There are several models which have been proposed to explain the available experimental results.

James and Saringer (1980) measured the pressure drop of dilute polymer solutions in radial flow toward a point (sink flow). The pressure drop was much higher than for pure solvent. The additional stress due to the polymer molecules was very high; comparable to Newtonian stresses. High molecular weight polymer solutions exhibit pronounced non-Newtonian behavior when subjected to flows with an important extensional component.
The flow through a contraction is a mixed flow, with an important extensional component near the entrance. For polymer solutions, stress is strongly dependent on molecular strain. At conditions close to equilibrium, flexible polymers behave as independent coils. At low extension rates, molecules are only slightly deformed, and the polymer contribution to stress is negligible compared to the solvent contribution. As the extension rate is increased, molecules unravel due to the hydrodynamic pull of the solvent. As the molecules uncoil, elastic stresses are generated due to chain resistance to stretching. At still higher extension rates, the chains may be significantly stretched. Strong hydrodynamic interactions among chains may take place, further increasing the polymer contribution to the stress. Each mechanism leads to distinct macroscopic behavior. The pressure drop scales with flow rate differently in each regime (Cartalos and Piau, 1992).

James and Saringer proved that flexible necklace-type models such as the Rouse or Zimm models were incapable of generating the measured non-Newtonian stresses. Both models are based on linear Gaussian springs, which do not accurately describe the behavior in strong flows. Finite extension models also predicted deviatoric stresses which were much lower than experimentally measured. Different mechanistic models for chain extension have been proposed to explain the results of James and Saringer. Three proposed models for coil extension are the frozen necklace model, the kink model, and the yo-yo model (Figure 2.12).

Flexible necklace models are incapable of generating large non-Newtonian stresses in extensional flow. In a flexible chain, the macromolecule is easily deformed by the flow. There is a low relative velocity at each bead, resulting in a small overall drag. Larger drag forces are possible if the relative velocities between solvent and bead are much higher. This is possible if the monomers are constrained once the molecule is partially extended in an extensional flow. King and James (1983) proposed the frozen necklace model in an attempt to explain the large non-Newtonian stresses due to polymer molecules. In a
converging flow, the molecule initially deforms as a Rouse molecule, but the configuration is frozen after a certain amount of extension. Freezing of the configuration is due to entanglements. The constrained beads have higher relative velocities compared to the flowing solvent, resulting in higher drag. These frozen chains become rigid objects that generate large stresses as the solvent is forced to flow around them. The entanglements prevent further deformation, and the molecule is convected in its frozen configuration. The frozen necklace model predicts non-Newtonian stresses which are two orders of magnitude larger than a Rouse model.

Another mechanism for coil extension is the kink model proposed by Rallison and Hinch and modified by Larson. Rallison and Hinch (1988) used a nonlinear, inverse Langevin spring to extend the bead spring model to large extensions. Unlike simple Hookean springs, the finite extensibility springs limit the extensional viscosity to a finite value at high extension rates. In a strong flow, dumbbells are unable to stretch as fast as the fluid. Additional viscous stress are generated as a result of this nonaffine motion of part of the chain. A numerical simulation with the nonlinear spring model in a strong flow was performed, and nonaffine stretching due to kinks in the chain was observed. The kinks can slow the unraveling of the chain and produce a large drag because of the velocity gradient between the solvent and the chain. Rallison and Hinch’s model assumes that kinks, rather than self entanglements cause freezing of chain segments. Larson (1990) modified the analysis of Rallison and Hinch by slightly changing the onset of nonaffine deformation.

Ryskin (1987) proposed a sequence of events, called the yo-yo model, for chain unraveling in a strong extensional flow. The impetus behind the yo-yo model was the work of Frenkel (1944) concerning the equilibrium conformation of a macromolecule stretched by a strong flow. Ryskin noted that Frenkel’s unraveling mechanism is also valid during a transient process. The distribution of chains in a strong flow is analogous to the
alignment of electrically anisotropic molecules in a strong electric field. At very small strain rates, the chain preserves its undisturbed, random coil conformation. As the strain rate is increased, the entropic restoring force balances the increased viscous pull of the extensional flow, and the coil becomes partially elongated. When the strain rate reaches a critical value, the Brownian forces are no longer sufficient to balance the viscous drag, and the stretching becomes a runaway process. Frenkel predicted this process to occur when the velocity gradient exceeded a limiting value. For an extensional flow symmetric about the z-axis, the velocity components and the critical velocity gradient are:

\[ v_x = -\frac{1}{2} \dot{\varepsilon} x \quad v_y = -\frac{1}{2} \dot{\varepsilon} y \quad v_z = \dot{\varepsilon} z \]  
\[ \dot{\varepsilon}_c = \frac{3kT}{\zeta_0(Nl)^2} \]  

where \( N \) is the number of monomers, \( k \) is Boltzmann's constant, \( T \) is the absolute temperature, \( \zeta_0 \) is the friction coefficient, and \( l \) is the length per bond. Unlike other models, which assume that the polymer deformation at the onset of this runaway regime is affine with the surrounding fluid, Frenkel proposed that the central portion is straightened out along the direction of flow as soon as the critical velocity gradient was achieved, but the two ends remain curled as in the random coil conformation. The actual length of the straightened section can be estimated by the following formula:

\[ s = \frac{N}{2} + \sqrt{\left(\frac{N}{2}\right)^2 - \left(\frac{kT}{\zeta_0 \dot{\varepsilon} l^2}\right)} \]  

By Frenkel's convention, \( s \) is the number of links from the central molecule to the coil. The actual straightened section would then have \( 2s \) links.

The proposed unraveling mechanism is caused by the parabolic distribution of stresses in an extensional flow. The central portion is straightened out first, remains taut, and
grows in length at the expense of the two coiled ends. The two end portions move apart in a symmetrical manner, simultaneously decreasing in length. If the imposed flow field is removed, the polymer curls back into the unperturbed conformation. Ryskin noted that each half of the chain thus unravels like the string in a yo-yo. After the unraveling process begins, the central portion can be modeled as a rigid rod in terms of the additional stress generated in the pure straining motion. The additional stress due to the polymer molecules is a function of the extension of the molecules. Batchelor's formula for the stress in a suspension of rigid rods can be used to calculate the additional deviatoric stress due to the polymer molecules (Batchelor, 1971).

The three coil unraveling models are distinguished by the end-end separation compared to the deformation of the surrounding fluid elements. The frozen necklace model of King and James predicts the slowest and most non-affine end-end separation. The kink models predict an end-end separation intermediate between the nonaffine motion of the frozen necklace model and the nearly affine response of the yo-yo model. The Rallison-Hinch kink model predicts an affine end-end response until the chain is stretched to approximately five times the equilibrium length. For extensions past this point, the chains stretch at approximately one third the rate of the fluid elements. Larson's modified kink model is similar, but the onset of non-affine motion is delayed. Nonaffine motion begins when the chain is a critical degree from total stretch. Larson's modification to Rallison and Hinch's model would result in a different response for large chains. The yo-yo model of Frenkel and Ryskin predicts nearly affine motion of the chain ends until nearly complete extension.

2.8 Stress transfer in different concentration regimes

There are different mechanisms of stress transfer, depending on the polymer and the degree of interaction between polymer molecules. In highly dilute systems, where each macromolecule is isolated, the stress is transferred by viscous friction between the solvent
and monomeric segments. Self-entanglement is the only factor hindering polymer reorientation when a stress is imposed. For concentrated solutions and melts, there are interactions between polymer molecules with molecular weights larger than the critical molecular weight for entanglement. Entanglements form physical cross-links which act as load-bearing units. With the application of a stress, the entanglements can prevent a polymer chain from reorienting and possibly cause chain scission.

2.8.1 Concentration regimes

A polymer's conformation and size in solution depends on the molecular weight, temperature, concentration, and interactions between the chain and the solvent. There are different concentration regimes for a polymer solvent system (Figure 2.13). The boundaries between the regimes are a function of the molecular weight, concentration, and solvent-polymer interactions.

One model for a polymer chain is the random flight chain. In a random flight chain, the flexible polymer is modeled as a hypothetical chain made up of rigid thin rods of equal length connected linearly by universal joints. The random flight chain model gives no information about the primary chemical structure and local interactions of actual monomers, but it is useful for formulating global behavior of chains.

Thermal rotation of the chain segments leads to a vast number of possible conformations, but the chain must avoid conformations which result in bond overlap. When monomer units approach one another, they each exert a repulsive force which keeps the units apart. The strength of the force depends on the separation between the beads, the chemistry of the beads, the temperature, and the pressure. This repulsive force is known as the excluded volume effect. In general, the excluded volume effect is any effect arising from intrachain or interchain segment-segment interactions. In dilute polymer solutions,
excluded volume repulsion between monomers or segments is the major determining factor for both static and dynamic properties.

A polymer in a solvent may be pictured as a dilute solution of random flight chains. Each bond can interact with both solvent molecules and other beads. The force between beads is the sum of the repulsive force and a solvent-bead interaction force. The solvent-bead interaction force depends on the quality of the solvent. In a good solvent, the bead-solvent interaction is favored over bead-bead contact. The force tries to pull beads apart and prevent them from approaching. The net result of this interaction is an additional repulsive force between beads or an increase in the net excluded volume. Polymer coils in good solvents are expanded beyond their unperturbed values. In a poor solvent, bead-bead contact is favored over bead-solvent interactions. Therefore, the interaction force is attractive. With the proper solvent and at the right temperature (theta conditions), the magnitude of this force is equal to the vacuum repulsive force, the net force is zero and the chains act like Gaussian chains. Coil dimensions are minimum at the theta condition. The difference in coil size between a polymer in a good solvent and one in a theta solvent is given by the expansion factor, $\alpha$. The expansion factor is a function of solvent power and temperature.

2.8.1.1 Dilute regime

In sufficiently dilute systems, islands of polymer coils are scattered in a sea of liquid solvent. The polymer coils behave similar to impenetrable spheres, and the viscosity behavior resembles a suspension of discrete rigid particles. The islands occasionally impinge and interpenetrate. The spatial distribution of chain segments is heterogeneous and undergoes appreciable fluctuations with time. The dilute region is defined by the range of concentrations where chain dimensions are unaffected by neighboring chains.
2.8.1.2 Semidilute regime

The semidilute regime is defined by the concentrations where chain dimensions decrease because of the overlap of coils. The dimensions of random coil polymers in solution depend on both the solvent and the polymer concentration. In a theta solvent system, the coil dimension does not change, but retains its unperturbed value at all concentrations. For a dilute solution of a polymer in a good solvent, the coils are expanded by the excluded volume effect. As the concentration is increased, the coils contract due to screening of the segments in the same chain by neighboring segments. Random coils must overlap and interpenetrate extensively. Coils overlap when the Simha parameter, c[η], is approximately equal to one. For typical polystyrene molecular weights in good solvents, coil overlap begins between 1 and 2% concentration (Moore, 1989). Above the overlap concentration, the coil radius shrinks with the -1/4 power of the concentration (Figure 2.14). The semidilute region extends to a concentration on the order of 10 g/dl. At this concentration, the chain dimensions are the same as the melt (Moore, 1989). Coil dimensions do not change with increasing concentration once in the concentrated regime.

2.9 Extensional degradation with interacting chains

An isolated flexible chain molecule will undergo a coil-stretch transition at a critical extension rate. In dilute solutions, the transition can be monitored using flow birefringence. For quasi-steady state flows, the birefringent line is confined to a small portion of the flow domain near the stagnation point. If the strain rate is large enough, chains are broken at the midpoint. For mutually interacting chains, the birefringent zone becomes delocalized in a specific manner and chain scission is not as selective.

2.9.1 Semidilute solution degradation
There are two distinct stages in the development of birefringence with increasing strain rate for semidilute solutions (Chow et al., 1988). First, a birefringent line appears which is indistinguishable from the zone in dilute solutions. This corresponds to the extension of individual chains beyond a critical strain rate. For higher concentrations and at a higher strain rate, highly delocalized birefringence is observed. The birefringent region becomes much larger and fluctuates rapidly with time. This condition has been termed flare. This phenomenon is due to mechanically effective molecular entanglements. The short time scale in which the chains pass near the high extension rate zone is insufficient for the chains to disentangle before extending. The solution responds as a transient network and long-range orientation occurs. The lower concentration limit for the flare effect is lower by a factor of ten to fifty than the calculated concentration for the transition between dilute and semidilute regimes. The elongational flow-induced extension is much more sensitive to a lower degree of chain overlap than the conventional $c^*$ criterion (Chow et al., 1988). The use of a single parameter, such as the radius of gyration used to define $c^*$, is inadequate for defining conditions for interchain contact. Entanglement effects that show up on a macroscopic time scale are characterized by a high degree of interaction, but at short times, the degree of interaction necessary for connectivity is reduced since even peripheral contacts cannot disentangle fast enough.

2.9.2 Extensional degradation in polymer melts

LaMantia and Nocilla (1985) measured the molecular weight of polymers after passage through a capillary rheometer. The researchers varied the length of the capillary and orifice diameter (L/D ratio) and the number of passes and measured $M_w$ and $M_n$. They concluded that the molecular weight decreased with the number of passes, with the largest reduction in the first pass. The change in molecular weight also increased with increasing L/D ratios in the capillary. To eliminate shear flow in the capillary, the researchers removed the capillary
die, extruding the polymer through a sharp contraction (L/D close to 0). The researchers also tested samples that weren't extruded to quantify thermal degradation. Degradation was the largest in the shear-free (extensional) experiment. Therefore, the researchers concluded that elongational flow is primarily responsible for the mechanical degradation in converging flow. The entrance flow field extends the molecules in the flow direction and imposes a stress on the backbone. When this stress exceeds the C-C bond strength, there is scission and a decrease in the molecular weight.
**Figure 2.1** Polymer coils in shear and extensional flows. Extensional flows have the capability of inducing profound coil unraveling, leading to the possibility of chain scission.

**Figure 2.2** Principal stresses and directions before and after a deformation. If the stress tensor is symmetric, the three principal directions are mutually orthogonal. With a coordinate system defined by the three principal directions, the diagonal terms are the only non-zero terms in the stress tensor.
Figure 2.3 Taylor's experiments on suspended drops utilized a four roll mill and a parallel band apparatus. The two devices generate controlled flows and allow a systematic study of the effect of flow strength on microstructure deformation.
Figure 2.4 Volume element in an extensional flow field is highly deformed, since it cannot rotate away from the principal straining direction.
$t = 0 \quad t > 0$

Laboratory coordinates

Principal straining directions

Material rotates with angular velocity equal to one half the vorticity

Maximum stretching

Stress is relaxed

Maximum contraction

**Figure 2.5** Volume element in a shear flow field is only slightly deformed. The nonzero vorticity allows a material line to rotate away from the principal straining direction.
Figure 2.6  Intrasegmental contact is favored in a poor solvent compared to a good solvent. The difference in intramolecular entanglements can lead to increased chain scission in a poor solvent.

Figure 2.7  Two different types of extensional flows: quasi-steady-state-flow and fast transient flow. QSSF are characterized by the presence of a stagnation point. FTF have a small spatial region of high extension and a short residence time in the high extension rate zone.
Figure 2.8 Opposed nozzles device, used to generate a quasi-steady state extensional flow.

Figure 2.9 Coil extension in a strong extensional flow field. There is relative motion between the beads and fluid at all points except the midpoint. The relative velocity increases toward the chain ends.
Figure 2.10 Tensile force as a function of segment extension. The tensile force is comparable to the bond strength only when the segment separation is more than 99% of the straight chain length (Merrill and Leopairat, 1980).
Figure 2.11 Inter- and intra-molecular entanglements in a coil provide restrictions that can result in chain scission in FTF.

Figure 2.12 Coil unraveling mechanisms: a) frozen string model; b) kink model; c) yo-yo model.
Figure 2.13 Concentration-molecular weight diagram of viscoelastic regimes for polystyrene in a good solvent (Graessley, 1980).
Figure 2.14 Variation in coil size with concentration for a good solvent system. In the dilute and concentrated regimes, coil size is independent of concentration. In the semi-dilute regime, the coil size shrinks with increasing concentration (Graessley, 1980).
Table 2.1 Shear degradation studies in which extensional flow at the entrance to a small diameter capillary causes chain scission.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Material</th>
<th>Geometry</th>
<th>Dimensions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Harrington and Zimm</td>
<td>Polystyrene and DNA</td>
<td>Entrance to small diameter capillary</td>
<td>47.3 μm radius capillary</td>
</tr>
<tr>
<td>Levinthal and Davison</td>
<td>DNA</td>
<td>Entrance to small diameter capillary</td>
<td>125 μm radius capillary</td>
</tr>
<tr>
<td>Bestul (1956)</td>
<td>Polyisobutylene (PIB) in cetane</td>
<td>Entrance to small diameter capillary</td>
<td>191 μm radius capillary</td>
</tr>
<tr>
<td>McKee (1951)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Culter et al. (1975)</td>
<td>PIB, polyisoprene, polybutadiene</td>
<td>Entrance to small diameter capillary</td>
<td>254 μm radius capillary</td>
</tr>
</tbody>
</table>

Table 2.2 Summary of the degradation behavior in the two types of extensional flow. The state of coil extension at rupture is vastly different in the two different flow fields.

<table>
<thead>
<tr>
<th>Quasi-steady-state flow (QSSF)</th>
<th>Fast transient flow (FTF)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Highly stretched chains are broken</td>
<td>Scission before complete uncoiling</td>
</tr>
<tr>
<td>Frictional forces comparable to bond strength</td>
<td>Bonds ruptured due to entanglement-induced stresses</td>
</tr>
<tr>
<td>Only chains close to stagnation point are degraded</td>
<td>Larger percentage of chains ruptured compared to QSSF</td>
</tr>
<tr>
<td>Fracture strain rate proportional to M^2</td>
<td>Fracture strain rate proportional to M^{4(1/2)}</td>
</tr>
</tbody>
</table>
CHAPTER 3

EXPERIMENTAL METHODS

3.1 Opposed pistons apparatus

An opposed pistons apparatus designed and built in the laboratory is used to subject polymer solutions to a fast transient extensional flow. The opposed pistons apparatus is composed of four main parts: the hydraulic pumping system, two hydraulic cylinders, the stainless steel tubes and orifice, and the displacement measurement system. The hydraulic system is powered by a 5 horsepower, 1800 rpm, TEFC Lincoln motor. The pump is a variable volume, pressure compensated control pump manufactured by Oilgear. A Dynex dual flow control valve, a Denison lever-operated directional valve, and a LHA 50 micron return filter are the other main parts of the hydraulic system. The entire hydraulic system is mounted on a 15 gallon oil reservoir. The hydraulic pumping system drives two Miller J-Series hydraulic cylinders. The cylinders have a 3.81 cm bore diameter, a 1.5875 cm rod diameter, a 30.48 cm stroke, and a 2000 psi operating pressure limit. The front ports of the cylinders are connected in order to synchronize the movement of the cylinders. One cylinder is fully extended when the other cylinder is fully retracted. Stainless steel pistons (High Pressure Equipment Company) are connected to the cylinders by couplings. Each piston is 35.56 cm long, with a 1.262 cm OD and two glands for Viton O-rings. The pistons reciprocate inside two stainless steel tubes (1.27 cm ID, 1.905 cm OD), which are
connected by a removable orifice insert. The tubes have a 16 surface finish to facilitate the repeated cycling of the pistons. Three different inserts are available, with diameters of 1.27, 0.127, and 0.0635 cm (contraction ratios of 1:1, 10:1, and 20:1). The width of the orifice is 0.159 cm. The system is designed to allow piston velocities to vary from an arbitrarily low value to 34.29 cm/s. The volumetric flowrate is varied from 3.22 to 43.44 cm$^3$/s. By varying the speed and orifice insert, approximately two decades of strain rate are reached (Newtonian centerline maximum strain rates from $4.67 \times 10^3$ to $5.01 \times 10^5$ s$^{-1}$). Experiments are performed at a constant extension rate and different number of passes across the orifice. A schematic of the extensional apparatus is shown in Figure 3.1.

3.1.1 Velocity calibration

The position and velocity of the pistons are monitored by the voltage from a ten-turn potentiometer. A coupling connects one of the cylinders to a chain and pulley system. The ten-turn potentiometer is hooked to one of the pulleys, and the voltage varies with position. A static calibration procedure is used to calibrate voltage as a function of position. Velocity measurements are obtained by monitoring the changing voltage with an analog to digital converter (ADC-1, Remote Measurement Systems). Voltage is converted to position, and position is converted to velocity using a differencing technique. The velocity is adjusted by turning a set screw on the side of the hand valve. This procedure is repeated until the velocity is within one percent of the desired set point. A sample calibration curve for the potentiometer voltage versus position is shown in Figure 3.2.

3.1.2 Experimental procedure

To run an experiment, approximately 38.6 ml of solution is loaded into one of the stainless steel tubes. The hydraulic cylinders are cycled so that one piston is exactly 30.5 cm from the edge of the orifice. Therefore, the entire sample is loaded into one tube. The
pistons slide into the tubes to seal the system and are then attached to the hydraulic cylinders via couplings. Trapped air is removed from the sample upon threading the stainless steel tubes into the orifice insert through bleed holes in the orifice insert. The tubes rest in the bottom half of stainless steel blocks. After sample loading, the top of the blocks are bolted on top of the tubes to provide rigidity and aid in alignment. The hydraulic system is powered up, and a hand valve is used to direct the piston motion. The system is switched off after the desired number of passes. The experimental conditions are listed in Table 3.1.

3.2 Rheological characterization

Rheological properties are measured at various temperatures using a Rheometrics RFS-II and RMS-800. Both dynamic oscillatory and steady shear tests are used to characterize the material. Three different geometries are used for testing purposes: 50 mm parallel plate (Figure 3.3), 50 mm cone and plate, and a Couette cup and bob.

3.2.1 Temperature shifting

The viscosity of the different samples is first tested at several different temperatures to obtain the temperature sensitivity of the solutions. The zero shear viscosity is fitted to an Arrhenius equation.

\[
\ln(\eta_0) = m_{\text{Arr}} \left( \frac{1}{T} \right) + b_{\text{Arr}}
\]  

With the Arrhenius parameters, the viscosity can be calculated for subsequent tests at an arbitrary temperature. There is an additional benefit to testing at different temperatures. Tests at multiple temperatures are necessary to obtain data for a wide range of shear rates and frequencies. For example, high steady shear rate data is difficult to obtain, because the sample extrudes from the gap. However, by testing at a lower temperature and shifting the data, high steady shear rate data is obtained. Varying the temperature changes the torque...
and normal force at a given frequency or rate. Therefore, the testing range is varied for each temperature to ensure measurements are within the transducer limits. The data is reduced to a single temperature (25°C) using a time-temperature superposition procedure which assumes all relaxation modes have the same temperature dependence (Quinzani et al., 1990). The shift factor, $a_T$, is defined as the ratio of the zero-shear viscosity at temperature, $T$, to the value at a reference temperature, $T_o$. The rheological variables are shifted as follows:

$$ a_T(T) = \frac{\eta_o(T)}{\eta_o(T_o)} $$

$$ \omega(T_o) = a_T \omega(T) \quad \dot{\gamma}(T_o) = a_T \dot{\gamma}(T) $$

$$ G'(T_o) = G'(T) \quad G''(T_o) = G''(T) $$

$$ \eta'(T_o) = \eta'(T)/a_T \quad \eta''(T_o) = \eta''(T)/a_T $$

$$ \eta(T) = \eta(T)/a_T \quad \Psi_1(T_o) = \Psi_1(T)/a_T^2 $$

(3.2)

The temperature variation of the shift factor is represented with an Arrhenius-type expression:

$$ \ln(a_T) = m_{Arr} \left( \frac{1}{T} - \frac{1}{T_o} \right) + b_{Shift} $$

(3.4)

Tables 3.2 and 3.3 list the Arrhenius and shift factor parameters for the solvents and solutions. The zero shear viscosity at 25°C is also listed in the tables. Master rheological curves for three of the solutions are shown in Figures 3.4-3.7. Viscosity comparisons for similar solutions are shown in Figures 3.8-3.10.

3.2.2 Extensional rheology characterization

The extensional viscosity of the 40% Styron in 1-methyl-naphthalene solution is characterized by two different techniques: opposed nozzles geometry and filament
stretching. This information is essential, since the extensional viscosity of fluids determines the entry flow behavior. The opposed nozzles instrument measures the torque on a lever arm as fluid is sucked into two mutually opposed nozzles. The extensional viscosity is calculated from the magnitude of the torque. The extensional viscosity behavior is shown in Figure 3.11, which plots the Trouton ratio versus extension rate. For a Newtonian solution, the Trouton ratio is always equal to three. For non-Newtonian solutions, the Trouton ratio can attain values several orders of magnitude greater than this (Jain, 1997).

The extensional viscosity is also measured using a filament stretching device (Shackleford, 1996). In this experiment, a small cylinder of fluid is pulled at a constant stretching rate by two end plates. The force on one of the plates is measured with a force transducer, and the diameter is measured with a laser. The extensional viscosity is calculated from the force, and the stretching rate is calculated from the diameter. The measured extensional viscosity for the 40% Styron in 1-methyl-naphthalene is shown in Figure 3.12. The Trouton ratio is plotted versus Hencky strain in Figure 3.13.

The filament stretching rheometer is used to characterize two other solutions. Figure 3.14 plots the transient Trouton ratio versus Hencky strain for the 25% monodisperse polystyrene in 1-methyl-naphthalene. A similar plot for the 0.25% monodisperse polystyrene in polystyrene oligomer (Boger fluid) is shown in Figure 3.15.

3.2.3 Model parameters

The rheological behavior of the solutions must be accurately modeled in order to simulate the flow field. The extension rates, stresses, flow field character, and other important variables are dependent on the rheological properties of the fluids. When selecting a constitutive model to represent the behavior of a fluid, it is important to assess the relative importance of the information to be obtained from the model. The ideal
constitutive model would accurately predict the viscosity as a function of shear rate, viscoelastic phenomena, and the extensional viscosity behavior. The extensional viscosity behavior is key to the behavior of a fluid in an entrance flow. The selection of a rheological constitutive model is an optimization between the accuracy of the model and two discrete difficulties. Experimentally, there is a challenge in obtaining accurate shear and extensional data. Shear viscosity measurements of viscous fluids, especially at high shear rates, are difficult to obtain. Extensional viscosity measurements are perhaps even more challenging (Gauri, 1996; Shackleford, 1996). Numerically, complex constitutive relations can lead to problems with numerical stability and solution convergence. The nonlinear terms in complex constitutive equations are especially unstable in flows with large velocity gradients, as in flow through a sharp contraction.

The viscosity of the solutions is represented by different constitutive models for numerical simulations. For the dilute solutions, the viscosity is independent of shear rate and a Newtonian model is sufficient to characterize the rheological behavior. As the concentration increases, the rheological behavior is more complex. Shear thinning and viscoelastic effects are observed in rheological measurements. The more concentrated polymer solutions are modeled as both a Newtonian and Generalized Newtonian Fluid (GNF) Cross model fluid. The Cross model is capable of capturing the shear dependent viscosity of the solutions, although it does not predict any viscoelastic behavior. The Cross model is defined (Macosko, 1994):

\[
\eta = \frac{\eta_0}{1 + (\lambda \dot{\gamma})^m}
\]  

(3.5)

The concentrated solutions are also modeled with the Giesekus constitutive equation. The Giesekus model is based on the concept of a deformation-dependent tensorial mobility of dissolved molecules.

\[
\tau = \tau_i + \tau_p
\]  

(3.6)
\[ \tau_s = -\eta_s 2D \]  

\[ \tau_p + \lambda_1 \tau_{p(t)} - \alpha \frac{\lambda_1}{\eta_p} \{ \tau_p \cdot \tau_p \} = -\eta_p 2D \]  

The nonlinear term (dot product of polymer stress tensor) allows simple qualitative descriptions of some of the characteristic properties of viscoelastic fluids, including shear thinning, non-zero second normal stress differences, and stress overshoot in transient flows. The parameter, alpha in the equations is called the mobility factor. When the mobility factor is equal to zero, the model reduces to the Oldroyd-B rheological model. The mobility factor accounts for anisotropic hydrodynamic drag on the polymer molecules. The Giesekus model is able to accurately reflect the effects of the presence of a strong flow on the physics. The parameters for the Giesekus model are fit to experimental data using an optimization procedure, minimizing the difference between the measured data and the predictions for the material functions. The material functions for the Giesekus model are given below (Bird et al., 1987).  

\[ \frac{\eta}{\eta_0} = \frac{\lambda_2}{\lambda_1} + \left( 1 - \frac{\lambda_2}{\lambda_1} \right) \frac{(1 - f)^2}{1 + (1 - 2\alpha) f} \]  

\[ \frac{\psi_1}{2 \eta_0 (\lambda_1 - \lambda_2)} = \frac{f (1 - \alpha f)}{(\lambda_1 \dot{\gamma})^2 \alpha (1 - f)} \]  

\[ f = \frac{1 - \chi}{1 + (1 - 2\alpha) \chi} \]  

\[ \chi^2 = \frac{(1 + 16 \alpha (1 - \alpha) (\lambda_1 \dot{\gamma})^2)^{\nu^2} - 1}{8 \alpha (1 - \alpha) (\lambda_1 \dot{\gamma})^2} \]  

\[ \frac{\eta'}{\eta_0} = \frac{1 + \lambda_1 \lambda_2 \omega^2}{1 + \lambda_1^2 \omega^2} \]  

\[ \frac{\eta''}{\eta_0 \omega} = \frac{(\lambda_1 - \lambda_2)}{1 + \lambda_1^2 \omega^2} \]  

55
Tables 3.4 and 3.5 list the Cross and Giesekus model parameters for the solutions used in this study. Experimental rheological data and predictions from the constitutive equations for several solutions are shown in Figures 3.16-3.18.

3.3 Measurement of the molecular weight distribution

The molecular weight distribution will be used as a measure of the extent of degradation in this study. In order to understand its significance on the properties of polymers, it is necessary to present some background on this topic. Polymeric materials do not consist of identical molecules. Instead, they are mixtures of many species, each with a different molecular weight (M). Since there is no single molecular weight for polymeric materials, average molecular weights are used. Some common averages are the number average (Mn), the weight average (Mw), the Z average (Mz), and the viscosity average (Mv). The number average molecular weight is obtained by dividing the mass of the polymer by the number of moles. Every molecule is counted the same way, regardless of mass. Conversely, heavy molecules contribute more to Mw than light ones. Mw is always greater than or equal to Mn. The ratio of Mw to Mn is the polydispersity. The average molecular weights are calculated from the distribution of molecular weights via the following equations, where ni is the number of moles and Mi is the molecular weight.

\[
\begin{align*}
\overline{M_n} &= \frac{\sum n_i \times M_i}{\sum n_i} \quad (3.15) \\
\overline{M_w} &= \frac{\sum n_i \times M_i^2}{\sum n_i \times M_i} \quad (3.16) \\
\overline{M_z} &= \frac{\sum n_i \times M_i^3}{\sum n_i \times M_i^2} \quad (3.17)
\end{align*}
\]

The existence of a distribution of molecular weights results from the statistical nature of polymerization reactions. The molecular weight distribution (MWD) is the frequency of
species plotted against the molecular weight. A narrow MWD indicates a more homogeneous sample. The polydispersity ($M_w/M_n$) is a measure of the breadth of the MWD. The shape of the MWD affects the average molecular weight values. The presence of high or low molecular weight tails can dramatically change $M_n$ or $M_w$.

Changes in the molecular weight distribution are one way to track polymer degradation. The MWD can be measured by a variety of experimental techniques. The most common method of measuring the MWD is gel permeation chromatography, also known as size exclusion chromatography. Gel permeation chromatography (GPC) segregates molecules based on differences in their size in solution. Columns are packed with porous particles (crosslinked styrene divinylbenzene gel packing). Pores in the packing are on the same order as the size of molecules in the sample. Large molecules cannot penetrate into the pores and are eluted first. Smaller particles are distributed in the pores as well as voids between gel particles and emerge later. The total volume in the columns is made up of three parts: the solid volume occupied by the packing, the void volume between the packing, and the pore volume. Not all of the pore volume is accessible to particles in a given molecular weight class. The fraction of the pore accessible to molecules in class $i$ is represented by $K_i$. $K_i$ is equal to zero for large molecules and is equal to one for very small particles. The retention volume for a molecular weight fraction is the sum of the void volume and $K_i$ times the pore volume.

$$V_r = V_v + K_j V_p$$  \hspace{1cm} (3.18)

The retention volume is converted to molecular weight via calibration with a solute of known molecular weight. A plot of $\log(M)$ vs. $V_r$ is linear over several orders of magnitude in molecular weight. The solute, solvent, packing, and operating conditions all affect the calibration curve. The relationship between retention volume and molecular weight is shown in Figure 3.19.
3.3.1 Conversion to molecular weight distribution

The conversion of GPC data to a molecular weight distribution is based on measuring at each elution volume the molecular weight and a concentration-sensitive signal. The molecular weight vs. retention volume is used to construct a calibration curve. An unknown sample is then injected into the system. The output signal, h(V), is proportional to the mass of sample in the elution volume V to V+dV. F(V) is the weight fraction of sample eluted up to retention volume V. Therefore, for each dV, h(V)dV is proportional to dF(V). When h(V) is normalized, these two quantities are equal (Shortt, 1993).

\[ \frac{\int h(V)dV}{dF(V)} = \frac{dF(V)}{dV} \]  \quad (3.19)

The cumulative weight fraction, W(M), is defined as the weight fraction of molecules in the sample having a molecular weight less than M. W(M) equals the mass of sample having molecular weight less than M divided by the total sample mass. The differential weight fraction distribution, w(M) is the derivative of W(M) with respect to M. The quantity w(M)dM is the weight fraction of sample having a molecular weight between M and M+dM. F(V) is related to the cumulative weight fraction and differential weight fraction as follows:

\[ F(V) = 1 - W(M) \]  \quad (3.20)

\[ w(M) = -\frac{dF(V)}{dM} \]  \quad (3.21)

According to equation (3.21), the weight differential distribution is the negative rate of change of the weight fraction of sample with respect to the molecular weight. This quantity cannot be evaluated, since V and M have not yet been related. These two variables are linked by the calibration curve. To convert, use the chain rule:

\[ w(M) = -\frac{dF(V)}{dV} \frac{dV}{d(\log_{10} M)} \frac{d(\log_{10} M)}{dM} \]  \quad (3.22)
Note that \( \frac{dV}{d\log_{10}M} \) is the slope of the calibration curve. Over the linear portion of the calibration curve, this value is a constant. The weight differential distribution can thus be obtained from the output and calibration curve. The weight differential distribution is plotted versus the molecular weight on a linear scale. For samples with a broad MWD, where the molecular weight can extend over several decades, it is much easier to use the differential log MWD instead. The differential log MWD, \( x(M) \), can be obtained by a similar analysis. The differential log MWD is often used for samples which contain fractions of very different molecular weight, since a logarithmic scale is used. In the linear region of the calibration curve, \( x(M) \) is just a rescaled version of the elution curve \( h(V) \). The two different MWD are related by a simple expression:

\[
x(M) = \frac{M}{\log_{10} e} w(M)
\]

(3.23)

3.3.2 Correction for axial dispersion

In gel permeation chromatography, axial dispersion occurs due to the separation process and the no-slip boundary condition at the walls. The chromatogram of an ideal monodisperse compound would not appear as a zero-width impulse, but as a bell-shaped Gaussian curve. The position of the peak depends on the molecular weight, the area under the curve is proportional to the weight or concentration, and the width of the curve is a measure of the resolution of the chromatographic system. For a polydisperse sample, the chromatogram is the composite of the Gaussian curves of all components (Figure 3.20). The height at a particular retention volume depends not only on the abundance of a particular species, but also on the abundance of its neighboring components. At the two extremities of the chromatogram, there are curve portions representing high and low molecular weight species not present in the sample. The correction of axial dispersion is more important for narrow molecular weight samples than broad molecular weight.
samples, but the chromatogram must be corrected for axial dispersion to obtain the true molecular weight and molecular weight distribution.

The amount of each species must be extracted from the chromatogram in order to obtain the distribution. The experimental chromatogram is the summation of individual species chromatograms weighted by a Gaussian function (Tung, 1966),

\[ F(V) = \int_{-\infty}^{\infty} W(y)G(v,y)dy \]  

(3.24)

where \( F(V) \) is the chromatogram, \( W(y) \) is the chromatogram corrected for axial dispersion, and \( G(v,y) \) is the instrument spreading function. \( G(v,y) \) can be interpreted as the response for a unit input of a monodisperse polymer sample. The variables \( v \) and \( y \) are both used to represent the eluent volume, with \( y \) used to denote the volume as a variable under the integral sign. The spreading function can be approximated by a Gaussian distribution (Tung, 1969).

\[ G(v,y) = \left( \frac{h}{\pi} \right)^{0.5} \exp\left\{-h(v-y)^2\right\} \]  

(3.25)

The resolution factor, \( h \), is an empirical parameter describing the resolution of the system. Higher values of the resolution factor decrease the axial dispersion correction. For infinitely large resolution, \( h \) goes to infinity.

### 3.3.3 Gel permeation chromatography system

The gel permeation chromatography (GPC) system consists of a Waters 6000A pump, a Rheodyne 7012 loop filler port with a six-port 7012 injector valve, a Waters 410 Differential Refractometer, three styrene divinylbenzene separation columns, and a temperature controlled chamber for the columns. The columns are 30 cm long, 7.8 mm ID Ultrastyragel columns arranged in series \((10^3, 10^4, 10^5 \text{ Å})\). The temperature is set at 35.0°C, and the sensitivity and scale factor of the Waters 410 are set at 256 and 40.
respectively. These settings give the optimum chromatogram with a maximum signal-noise ratio. The GPC system is shown in Figure 3.21.

Stabilized tetrahydrofuran (THF, Mallinkrodt) is continually passed through the columns and detector at a low flowrate (0.1 ml/min) and recycled back to the reservoir. The reference cell is purged daily. Before tests are performed, the flowrate is slowly increased to 1.0 ml/min. This flowrate is maintained for approximately two hours in order to obtain a stable baseline. Samples are prepared several days before a test. Polystyrene standards are prepared as 0.10 w/v% (1 mg/ml) solutions in THF. Other samples are prepared as 0.25 w/v% samples. A twisted pair cable is attached from the refractive index detector to an analog-to-digital converter (ADC-1, Remote Measurement Systems). A data logging file is set up to read the output at one second intervals, and the plot window is changed to display one point every five seconds, in order that the whole chromatogram can be seen on the screen. After the baseline stabilizes, the injector is moved to the load position, and 0.10 ml of the dilute solution is injected with a tuberculin syringe. The data logging is started, and the sample is injected five seconds later. The eluent is collected in a graduated cylinder to accurately measure the volumetric flow rate. After the sample has passed completely through the system (detectable by the end of the peak and the beginning of a negative peak representative of dissolved air), the data logging is terminated and the eluent collection is stopped. The syringe and injection port are both flushed with excess THF to prepare for the next sample.

The samples tested in the opposed pistons apparatus are dissolved in 1-methyl-naphthalene or decalin. For GPC characterization, the samples must be dissolved in THF. After testing in the extensional flow device, a small amount (0.5 ml) of the solution is placed in a separate aluminum pan, and the solvent is evaporated under a mild vacuum. The temperature is kept below 100°C to eliminate thermal degradation. The dried polymer sample is then dissolved in tetrahydrofuran in preparation for GPC characterization.
3.3.4 Data analysis

The GPC data is analyzed using a series of FORTRAN programs written by the author to convert the raw data to a molecular weight distribution. The data file from the ADC contains the millivolt output from the 410 as a function of tics (1/60 second). The flowrate and delay time are input to the first program, GPC, which converts the data to time (seconds), output (mV), and volume (ml). The second program, SPRED, corrects for axial dispersion. The output from SPRED is the normalized output, the corrected normalized output, a data point counter, and the volume. The second iterative method developed by Ishige et al. (1971) is used to correct the chromatograms. The method is based on the observation that any GPC response F always has a broader distribution than the input distribution W. If a distribution F_i is broader than F, the input W_i must be sharpened to obtain the true F. Using the notation above, the (i+1)th guess is:

\[ W_{i+1} = \left( \frac{F}{F_i} \right) W_i \]  

The initial guess, W_1, is started from F itself. The calculated input distribution, W_{i+1} is normalized and the cycle is repeated. The iterations are terminated when the following convergence criteria cited by Ishige et al. is below 0.01 or reaches the first minimum.

\[ \Delta S = \int_0^\infty |F(v) - F_i(v)| dv \leq 0.01 \]  

The difference in area between the original chromatogram and the corrected chromatogram is also calculated. The Ishige correction procedure is illustrated in Figure 3.22.

The third program, NORMAL, standardizes the output with respect to volume, allowing direct data comparison at a given elution volume. The data from NORMAL is read into POLY, which performs the molecular weight calculations. Figure 3.23
summarizes the data analysis. The programs used in the data analysis are printed in the Appendix.

### 3.3.5 Column calibration

The system is calibrated with eleven polystyrene standards (Waters and Polymer Laboratories). The peak molecular weight of each standard is supplied with the sample. The standards are run through the columns twice, and the volume at peak maximum is measured and the peak volume for the two runs is averaged. A calibration curve is plotted from this data. The calibration curve is shown in Figure 3.24. A third order polynomial is fit to the data. The calibration curve is linear over the majority of the molecular weight range. The spreading coefficient for each molecular weight fraction is obtained from the width of the calibration standards' peaks. Tangents to the peaks are extended to the baseline, and the spreading coefficient is related to the width where the tangents intersect the baseline (W):

\[ h = \frac{8}{W^2} \]  

(3.28)

The variation of \( h \) with retention volume is plotted and a piece-wise fit is used in the axial dispersion correction (Figure 3.25). Table 3.6 shows the standards used to calibrate the system and the retention volumes and spreading coefficients.
Figure 3.1 Opposed pistons, multi-pass extensional flow apparatus used to generate a fast transient flow (FTF). The hydraulic system cycles the pistons, pushing the polymer solution across an abrupt contraction. The piston speed is measured with a computer. Three contraction ratios are used. By varying the speed and contraction ratio, the Newtonian centerline extension rate is varied from $4.67 \times 10^3$ to $5.01 \times 10^3$ s$^{-1}$. 
Figure 3.2 Piston position is linearly related to the output voltage from a ten-turn potentiometer. The measurement of the potentiometer voltage allows calibration of the piston speed.
Figure 3.3 Parallel plate geometry used to measure rheological properties of the polymer solutions. The bottom tool rotates or oscillates and a transducer in the top tool measures the torque and normal force generated.
Figure 3.4 Master rheological curves for 40% Styron 666D in 1-methyl-naphthalene. The data is reduced to a single reference temperature (25°C) by time-temperature superposition.
Figure 3.5 Master rheological curves for 25% monodisperse polystyrene in 1-methyl-naphthalene. The data is reduced to a single reference temperature (25°C) by time-temperature superposition.
Figure 3.6 Master rheological curves for polystyrene oligomer. The data is reduced to a single reference temperature (25°C) by time-temperature superposition.
Figure 3.7 Master rheological curves for 0.25% monodisperse polystyrene in polystyrene oligomer. The data is reduced to a single reference temperature (25°C) by time-temperature superposition. The intermediate plateau in the first normal stress coefficient is characteristic of Boger fluids.
Figure 3.8 Comparison of the viscosities of the Styron solutions. Three solutions are shown for comparison: 40% Styron in 1-methyl-naphthalene (40%N); 40% Styron in decalin (40%D); and 20% Styron in 1-methyl-naphthalene (20%N). The data is reduced to a single reference temperature (25°C) by time-temperature superposition.
Figure 3.9 Comparison of viscosities for the three monodisperse solutions in 1-methylnaphthalene. The data is reduced to a single reference temperature (25°C) by time-temperature superposition.
Figure 3.10 Comparison of viscosity of polystyrene oligomer and Boger fluid. The data is reduced to a single reference temperature (25°C) by time-temperature superposition.
Figure 3.11  Trouton ratio versus extension rate for the 40% Styron in 1-methyl-naphthalene solution. The solution is tested in the Rheometrics RFX opposed nozzles geometry.
Figure 3.12 Trouton ratio versus time for the 40% Styron in 1-methyl-naphthalene solution. The solution is tested in a filament stretching device (Shackleford, 1996) at an average extension rate of 1.0 s$^{-1}$. 
Figure 3.13 Transient Trouton ratio versus Hencky strain for the 40% Styron in 1-methyl-naphthalene solution. The solution is tested in a filament stretching device (Shackleford, 1996) at an average extension rate of 1.0 s⁻¹.
Figure 3.14 Transient Trouton ratio versus Hencky strain for the 25% monodisperse polystyrene in 1-methyl-naphthalene solution. The solution is tested in a filament stretching device (Shackleford, 1996) at average extension rates of 4.49 s⁻¹ (Run 1) and 3.99 s⁻¹ (Run 2).
Figure 3.15 Transient Trouton ratio versus Hencky strain for the 0.25% monodisperse polystyrene in polystyrene oligomer. The solution is tested in a filament stretching device (Shackleford, 1996) at average extension rates of 1.68 s⁻¹ (Run 1) and 1.88 s⁻¹ (Run 2).
Figure 3.16 Viscosity versus shear rate behavior for the 40% Styron in 1-methylnaphthalene solution with predictions from the Generalized Newtonian Fluid Cross model.
Figure 3.17 Rheological data for the 25% monodisperse polystyrene in 1-methyl-naphthalene solution with predictions from the Giesekus model. The model predictions are given by the lines.
Figure 3.18  Viscosity versus shear rate for the 25% monodisperse polystyrene in 1-methyl-naphthalene solution with predictions from the Cross model.
Figure 3.19 GPC output to molecular weight conversion. The principal behind the conversion is the construction of a calibration curve, relating elution volume to molecular weight. Different molecular weight species are separated based on their size in solution.
Figure 3.20 Overlapping curves in gpc. The output is the composite of two overlapping individual peaks.
Figure 3.21 Gel permeation chromatography system. The system consists of three main parts: a) Waters 6000A pump with a six-way Rheodyne injection port system; b) styrene divinylbenzene separation columns; c) differential refractometer.

\[ F = G \{ W_i \} \]

Figure 3.22 Ishige's technique for the correction for axial dispersion. The output from an ideal peak is broader than the input due to instrument effects and the parabolic velocity profile. The correction procedure is based on measuring an empirical spreading coefficient as a function of elution volume.
Raw data from GPC (Output (mV), Tics (1/60 s))

**INPUTS**
- Flowrate, Delay time
- Baseline and peak limits, Spreading coefficient
- Baseline and peak limits, δV for normalization
- Baseline and peak limits, Calibration equation

**OUTPUTS**
- Time (s), Output (mV), Data counter, Volume (ml)
- Normalized output, Output corrected for axial dispersion, Data counter, Volume (ml)
- SPRED.FOR output standardized with respect to elution volume
- Molecular weight averages and distributions

**Figure 3.23** Algorithm for gpc data analysis. A series of FORTRAN programs developed by the authors are used to convert the raw data into a molecular weight distribution.
Figure 3.24 Calibration curve for gpc system. Eleven standards were used to construct the calibration curve. The log of the molecular weight is directly proportional to the elution volume over a wide range of the curve.
Figure 3.25 Empirical spreading coefficient as a function of elution volume. The spreading coefficient is obtained by measuring the width of output curves from very narrow molecular weight samples.
<table>
<thead>
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<th>Contraction</th>
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<th>Average orifice velocity (m/s)</th>
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<td>10:1</td>
<td>43.4</td>
<td>34.3</td>
</tr>
<tr>
<td>2.54</td>
<td>20:1</td>
<td>3.22</td>
<td>10.2</td>
</tr>
<tr>
<td>8.89</td>
<td>20:1</td>
<td>11.3</td>
<td>35.6</td>
</tr>
<tr>
<td>15.2</td>
<td>20:1</td>
<td>19.3</td>
<td>61.0</td>
</tr>
<tr>
<td>22.9</td>
<td>20:1</td>
<td>29.0</td>
<td>91.4</td>
</tr>
<tr>
<td>26.7</td>
<td>20:1</td>
<td>33.8</td>
<td>107</td>
</tr>
<tr>
<td>30.5</td>
<td>20:1</td>
<td>38.6</td>
<td>122</td>
</tr>
<tr>
<td>34.3</td>
<td>20:1</td>
<td>43.4</td>
<td>137</td>
</tr>
</tbody>
</table>

**Table 3.1** Experimental conditions for experiments with the opposed pistons apparatus. The average orifice velocity is varied by changing the contraction ratio and the piston speed.
Table 3.2 Solvent rheological parameters. The temperature sensitivity of the zero shear viscosity is modeled with an Arrhenius expression (Equation 3.1). The reference temperature is 25°C.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$m_{\text{Arr}}$</th>
<th>$b_{\text{Arr}}$</th>
<th>$\eta_0$ (P)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-methyl-naphthalene</td>
<td>2285</td>
<td>-11.11</td>
<td>0.032</td>
</tr>
<tr>
<td>Decalin</td>
<td>1540</td>
<td>-8.93</td>
<td>0.023</td>
</tr>
<tr>
<td>Polystyrene oligomer</td>
<td>19220</td>
<td>-58.94</td>
<td>251</td>
</tr>
</tbody>
</table>

Table 3.3 Solution Arrhenius and shift factor parameters. The temperature sensitivity of the zero shear viscosity is modeled with an Arrhenius expression (Equation 3.1). The temperature variation of the shift factor is given by Equation 3.4. The reference temperature is 25°C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Solvent</th>
<th>Conc (w/v %)</th>
<th>$m_{\text{Arr}}$</th>
<th>$b_{\text{Arr}}$</th>
<th>$b_{\text{Shift}}$</th>
<th>$\eta_0$ (P)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Styron 666D</td>
<td>1-me-n</td>
<td>20</td>
<td>3566</td>
<td>-9.71</td>
<td>-1.520 x 10^3</td>
<td>9.5</td>
</tr>
<tr>
<td>Styron 666D</td>
<td>1-me-n</td>
<td>40</td>
<td>4969</td>
<td>-11.69</td>
<td>-1.827 x 10^4</td>
<td>145.4</td>
</tr>
<tr>
<td>Styron 666D</td>
<td>Decalin</td>
<td>40</td>
<td>6643</td>
<td>-16.99</td>
<td>1.473 x 10^4</td>
<td>199.0</td>
</tr>
<tr>
<td>Monodisperse PS</td>
<td>1-me-n</td>
<td>0.25</td>
<td>1870</td>
<td>-9.197</td>
<td>7.028 x 10^{-4}</td>
<td>0.054</td>
</tr>
<tr>
<td>Monodisperse PS</td>
<td>1-me-n</td>
<td>2.5</td>
<td>2098</td>
<td>-7.313</td>
<td>-1.309 x 10^5</td>
<td>0.758</td>
</tr>
<tr>
<td>Monodisperse PS</td>
<td>1-me-n</td>
<td>25</td>
<td>4314</td>
<td>-6.481</td>
<td>9.160 x 10^{-6}</td>
<td>2950</td>
</tr>
<tr>
<td>Monodisperse PS</td>
<td>Oligomer</td>
<td>0.25</td>
<td>20010</td>
<td>-60.38</td>
<td>2.172 x 10^{-5}</td>
<td>833.4</td>
</tr>
</tbody>
</table>
Table 3.4 Model parameters for the Generalized Newtonian Fluid Cross model (Equation 3.5).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Solvent</th>
<th>Conc (w/v %)</th>
<th>( \eta_0 ) (P)</th>
<th>( \lambda ) (s)</th>
<th>m</th>
</tr>
</thead>
<tbody>
<tr>
<td>Styron 666D</td>
<td>1-me-n</td>
<td>40</td>
<td>146</td>
<td>0.0030</td>
<td>0.675</td>
</tr>
<tr>
<td>Monodisperse PS</td>
<td>1-me-n</td>
<td>2.5</td>
<td>0.761</td>
<td>2.2 x 10^4</td>
<td>1.23</td>
</tr>
<tr>
<td>Monodisperse PS</td>
<td>1-me-n</td>
<td>25</td>
<td>2980</td>
<td>0.082</td>
<td>0.992</td>
</tr>
</tbody>
</table>

Table 3.5 Model parameters for the differential viscoelastic Giesekus model (Equation 3.6).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Solvent</th>
<th>Conc (w/v %)</th>
<th>( \eta_0 ) (P)</th>
<th>( \lambda_1 ) (s)</th>
<th>( \lambda_2 ) (s)</th>
<th>( \alpha )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Styron 666D</td>
<td>1-me-n</td>
<td>40</td>
<td>146</td>
<td>0.0125</td>
<td>0.0023</td>
<td>0.35</td>
</tr>
<tr>
<td>Monodisperse PS</td>
<td>1-me-n</td>
<td>25</td>
<td>2910</td>
<td>0.130</td>
<td>0.0091</td>
<td>0.46</td>
</tr>
</tbody>
</table>
Table 3.6 GPC calibration standards. The average peak volume is used to construct the calibration curve and the average spreading factor is used in the axial dispersion correction.
CHAPTER 4

SIMULATIONS

4.1 Flow field modeling

The goal of the numerical simulations is to extract a quantity from the flow field that can be related to chain scission. For simulations, the flow field is modeled as a two-dimensional, axisymmetric flow through a small diameter capillary. The flow field is inhomogeneous, with pure extensional flow only along the centerline.

4.2 Problem definition

4.2.1 Contraction flow field

The flow into a contraction is geometrically simple, but the flow is mixed, with components of both shear and elongation. The flow field usually consists of a central core and vortex region, but the exact shape of the flow field is determined by the volumetric flow rate and the rheological properties of the fluid. The elongational properties of the rheological model play an important role in determining the way the fluid responds to the accelerating forces as it approaches the corner. For Newtonian fluids in laminar flow, the streamlines flow radially inward. This simple flow pattern results in a relatively small
pressure drop. The entrance flow pattern for polymer melts and solutions can be more complex. Melts and solutions behave like Newtonian liquids at low flow rates, but as the flow rate is increased, elastic effects can change the flow field. In the entrance region, the melt is forced into a converging flow pattern and undergoes a large axial acceleration. As the flow rate is increased, the axial acceleration increases, and the melt or solution becomes more elastic. Vortices are formed for most elastic fluids. The occurrence of vortices is a mechanism for the relief of large tensile stresses induced by the elongational flow in the converging region. Vortices occur to maintain extension rates at relatively low levels.

Vortex formation can drastically change the flow field. The polymer entering the orifice forms a wine glass pattern, with an entrance angle, $\alpha$, that is a function of the viscosity and the first normal stress coefficient. As the flowrate is increased, the vortex size can increase: a situation known as vortex enhancement. Vortex enhancement is determined by the extensional stress growth behavior of a fluid (White and Baird, 1986). There is a significant excess pressure drop associated with vortex enhancement for elastic liquids that is not seen for Newtonian or nonelastic liquids. The entrance flow geometry and the phenomenon of vortex enhancement is shown in Figure 4.1.

The entrance angle is a variable which is directly related to the upstream vortex size and determines the extension rate distribution. The magnitude of the entrance angle and its variation with flowrate can be used to track the formation and expansion of the upstream vortex. As the entrance angle becomes smaller, the maximum extension rate along the centerline becomes smaller, and the onset of fluid acceleration occurs further upstream (Figure 4.2). Ballenger and White (1971) performed visualization studies of molten polystyrene in a capillary extrusion rheometer. The observed flow field was a function of the flow rate through the orifice. At low flow rates, there was essentially radial flow into the entrance of the capillary. As the flow rate increased, the entrance angle decreased from 180° and formed a funnel-shaped entrance flow. A wine glass velocity field was observed,
with secondary vortices on either side of the contraction. As the volumetric flow rate increased, the entrance angle decreased from 142 to 115°. Newtonian fluids flowing into a sharp contraction have a constant reattachment length and thus a constant entrance angle (Boger, 1981). The entrance angle is approximately 137° for a contraction ratio of four or greater.

4.2.2 Governing equations

The geometry of the entry flow problem is shown in Figure 4.3. A cylindrical coordinate system is used, with z in the axial direction and r in the radial direction. Symmetry about the centerline is used to reduce the simulation domain. The ratio of the upstream diameter to the orifice diameter is set at either 10:1 or 20:1. The flow field is governed by a set of conservation and constitutive equations. The nonlinear system of equations consisting of the momentum equation, continuity equation, and the rheological constitutive equation are solved numerically. The continuity equation and the momentum balance equations are given below. Since the conservation equations are independent of flow geometry, the boundary conditions alone distinguish the specific flow problem. The boundary conditions for the entry flow problem are standard: no-slip along the walls, fully developed profile away from the contraction, and symmetry at the centerline. The solution is assumed to be a continuum for modeling purposes. A suspension of small particles can be treated as a continuum as long as the particles are smaller than the smallest length scale of the flow. A randomly coiled polymer is sufficiently small to satisfy this hypothesis, since it is typically one hundredth the size of the smallest eddy (Hinch, 1977). Although the Reynolds number is very low for most of the flow field, the inertial terms are included in the momentum equation.

\[
\frac{\partial \rho}{\partial t} + \frac{1}{r} \frac{\partial}{\partial r} (r \rho v_r) + \frac{1}{r} \frac{\partial}{\partial \theta} (\rho v_\theta) + \frac{\partial}{\partial z} (\rho v_z) = 0
\]  

(4.1)
The rheological constitutive equation is the other relation necessary to solve this system of equations. The choice of the constitutive equation will dictate the behavior of the specific fluid studied. The choice of the constitutive relation is not straightforward. The constitutive model should be able to predict simple shear and extensional properties. Three different constitutive equations are used in the simulations: Newtonian, Generalized Newtonian Fluid Cross model, and the differential viscoelastic Giesekus model. The relative merits of the three constitutive relationships have been summarized in the Experimental chapter. Based on filament stretching results, the only fluid likely to exhibit vortex enhancement is the Boger fluid. Therefore, for all other fluids, the predictions from the Newtonian and Cross models are expected to be in reasonable agreement with the actual flow field.

4.2.3 POLYFLOW specifications

Polyflow is a computational fluid dynamics package used to obtain information on the flow field. POLYFLOW uses mathematical models derived from continuum mechanics and the most recent finite element methods to simulate fluid flows. POLYFLOW outputs velocities, stream function, components of the rate of deformation tensor and the vorticity tensor, and other variables. Polyflow outputs most of the necessary variables from the simulation, including the following: values of the stream function, velocities, pressures, residence times, and components of the rate of deformation tensor. The results from a simulation are used to calculate variables which determine chain scission in a fast transient extensional flow.

The sharp contraction geometry used in this study leads to large gradients. These gradients can result in numerical convergence problems. The loss of solution may be
caused by the full set of differential equations or by the discretized algebraic forms of the equations. Failure can result from bifurcation points, where the solution becomes multivalued and the method cannot choose the correct branch, and limit points, beyond which no solution exists for the given equations. Severe oscillations occur which are caused by numerical artifact. The oscillations are caused by the large gradients of the stresses generated at the corner point.

The mesh is an important variable in determining the limit of convergence. A very fine mesh does not increase the convergence limit, perhaps in part due to the fact that a finer mesh will decrease the smoothing effect of the discretization (White et al., 1987). The flow is predominately extensional very close to the orifice, but the simulation domain is defined with long entry and exit sections. The mesh used for the simulations is shown in Figure 4.4. Different meshes are tested to verify that the solution was not a function of the mesh density. The mesh is concentrated near the entrance and exit of the contraction, where the gradients are the largest.

POLYFLOW can model steady and time dependent laminar flows of both Newtonian and non-Newtonian fluids at low Reynolds numbers. The program is useful for simulating polymer processing applications since it has a wide variety of rheological models and is able to solve problems with strong non-linearities. Simulations are performed for Newtonian and Cross model fluids. A Newton-Raphson iterative technique is used for the Newtonian simulations, and a Picard iterative scheme is used for the Cross model simulations. An evolution on the relaxation time is used to aid in the convergence for the Cross model simulations.

4.3 Results from Generalized Newtonian simulations

POLYFLOW results are obtained with the Newtonian and Cross models for all experimental conditions. The solution is verified by checking the shear rate and velocity
profile in the upstream simple shear flow region with predictions from the Hagen-Poiseuille equation. The strain rate at the centerline is obtained from the diagonal of the rate of deformation tensor. The flow field predicted from the two Generalized Newtonian Fluid (GNF) models did not differ a great deal. The results will be presented in terms of dimensionless variables to encompass the different experimental conditions. Differences between the Newtonian and Cross model predictions are noted.

The streamlines for the 10:1 and 20:1 contractions are shown in Figure 4.5. The wineglass entry flow pattern is visible with both contractions. There is a small recirculating vortex upstream of the entrance to the sharp contraction. Both GNF constitutive equations predict an entrance angle which does not change with flowrate. The Newtonian model predicts an entrance angle of approximately 137°, in accordance with experimental observations. The flow is nearly symmetric around the small diameter capillary for the Newtonian predictions. The downstream vortex is constant in size and is nearly the same size as the upstream vortex. The Cross model predicts a slightly smaller upstream vortex and an entrance angle of approximately 155°. The Cross model predicts a downstream vortex that expands with an increase in flowrate. The expanding vortex results from inertia and the extensive shear thinning in the orifice.

Profiles of axial velocities in the contraction are shown in Figure 4.6. The curves are obtained by defining a cross section perpendicular to the flow at an axial position midway through the small diameter capillary. The Reynolds number is low enough for a fully developed profile to be formed with the Newtonian constitutive equation. For the Cross model, flow through the contraction is more plug flow in nature. Figure 4.7 is a plot of the velocity vectors near the entrance to the orifice. Due to conservation of mass, there is a rapid acceleration of the fluid close to the entrance.
4.4 Parameters related to chain scission

There are several parameters which could cause flow-induced polymer degradation. Several possible flow field variables which can lead to chain scission are calculated. It is the goal of this simulation work to quantify the important flow variables in a control volume representative of the experimental flow field. The values of each of the variables are calculated along streamlines through the flow field. Since particles follow streamlines, this provides an indication of the type and magnitude of the forces to which a polymer coil is exposed when flowing through the opposed pistons device. The importance of the rate of energy input, total energy input, and flow character are related to polymer degradation in the opposed pistons device.

4.4.1 Centerline extension rate

As noted in the Literature Review, the extension rate is the most important variable determining polymer conformation in an extensional flow. The stress in an extensional flow field is related to the extension rate by the viscosity. Large stresses on polymer coils can result in chain scission. Although the flow field is inhomogeneous, there is pure extensional flow along the centerline. The centerline extension rate is calculated from the diagonal of the rate of deformation tensor, 2D:

\[ 2D = \nabla U + (\nabla U)^T \quad (4.3) \]

The rate of deformation tensor for a two-dimensional, axisymmetric flow is:

\[
2D = \begin{bmatrix}
2 \frac{\partial v_r}{\partial r} & \left( \frac{\partial v_r}{\partial z} + \frac{\partial v_z}{\partial r} \right) & 0 \\
\left( \frac{\partial v_r}{\partial z} + \frac{\partial v_z}{\partial r} \right) & 2 \frac{\partial v_z}{\partial z} & 0 \\
0 & 0 & 2 \frac{v_r}{r}
\end{bmatrix}
\quad (4.4)
\]
Extensional flow is restricted to a small portion of the flow domain. Most of the fluid acceleration occurs approximately one orifice radius upstream of the orifice. Figure 4.8 shows a plot of the axial velocity in the vicinity of the orifice. Close to the entrance, the velocity is proportional to the inverse square of the distance from the orifice. This rapid change in the velocity results in an impulse jump in the strain rate. The stretching rate is a stronger function of distance than the velocity. The extension rate is proportional to the inverse cube of the distance from the orifice. For streamlines off of the centerline, there is mixed flow. For a sink flow, the velocity along a streamline is not a function of the angle, but depends only on the distance from the orifice (Feigl and Ottinger, 1994). The dependence of the centerline strain rate on different volumetric flowrates and contraction ratios can be examined by non-dimensionalizing the strain rate and axial position. The dimensionless strain rate is defined below, with \( v_0 \) and \( r_o \) the average orifice velocity and radius, respectively.

\[
\tilde{\varepsilon} = \tilde{\varepsilon} \left( \frac{r_o}{v_o} \right)
\]  

(4.5)

All Newtonian simulations collapse onto a single curve after non-dimensionalizing the strain rate and axial position (Figure 4.9). The axial coordinate origin (\( z = 0 \)) is defined at the leading edge of the orifice. Therefore, negative dimensionless axial coordinates refer to positions upstream of the capillary. The dimensionless centerline strain rate reaches a maximum approximately 0.4 orifice radii before the leading lip of the orifice. At this point, the coils are subjected to a severe uniaxial extension. The constant of proportionality between the maximum dimensionless centerline strain rate and the ratio of the axial distance and the orifice radius is 1.19.

Shear thinning reduces the maximum centerline strain rate, even for this moderately shear thinning fluid. Due to the high shear rates in the orifice, there is plug flow through the contraction. The centerline velocity is lower for the Cross model simulations and the
strain rate is reduced. The results from the Cross model simulations form a family of curves, depending on the average velocity and contraction. The constant of proportionality between the maximum dimensionless centerline strain rate and the ratio of the axial distance and the orifice radius ranges from 1.0 to 0.89 as the average orifice velocity increases. The two curves which bracket all Cross model simulations are plotted in Figure 4.9 with the master curve from the Newtonian simulations. The Cross model also predicts an expanding downstream vortex as the strain rate is increased. Although the Cross model can correctly predict shear thinning, it also predicts extension thinning along the centerline. Table 4.1 lists the centerline extension rates for both Newtonian and Cross models. The centerline extension rate for the Newtonian model as a function of the average orifice velocity is shown in Figure 4.10. For a given flow rate, there is no dependence of the strain rate on the radial position of the streamline. The maximum strain rate is similar along all streamlines (Feigl and Ottinger, 1994).

As the molecules exit the orifice, they are subjected to a biaxial extension, and the strain rate is negative (Figure 4.11). The flow field is not homogeneous. There is purely extensional flow only along the central streamline. The vorticity increases as the radius increases, resulting in pure shear flow at the wall.

The high strain rate region is very small, and the transit time through this region is very short. The molecules are exposed to this extension on the order of microseconds to milliseconds. Table 4.2 lists the centerline residence time in the high extension rate zone and in the small diameter capillary. The centerline residence time is calculated as the transit time from a dimensionless extension rate of 0.1 to the maximum extension rate. The residence times are taken from Newtonian simulations. Cross model predictions are very close to these values. The residence time in the high strain rate region is plotted in Figure 4.12. The high extension rate zone residence time is defined based on the value of the
dimensionless centerline strain rate. The residence time is defined as the transit time from a value of the dimensionless strain rate equal to 0.1 to the maximum.

### 4.4.2 Rate of energy input

Another important variable which may determine chain scission is the rate of energy input to the coil. The rate of energy input is calculated from the viscous dissipation in the fluid. It is assumed that the energy input to a fluid element is passed to a polymer coil that is in the control volume of the element. The rate at which work is done on a fluid element can be extracted from the rate of deformation tensor. The rate of deformation tensor is a logical choice to compare degradation in different flow fields, since chains will be ruptured when the imposed deformation results in stresses which exceed the bond strength. For an incompressible fluid, the rate at which work is done on a fluid element is given by:

\[
\Phi = \mu \left[ \nabla U + (\nabla U)^T \right] : \nabla U \tag{4.6}
\]

This quantity is called the dissipation function. It is uniquely defined at a given time and position. The cgs units of the dissipation function are erg/cm³s. When the dissipation function is multiplied by a representative control volume, the rate of energy dissipation in erg/s is obtained. The dissipation function can be related to velocity gradients and the components of the rate of deformation tensor for a two-dimensional, axisymmetric flow.

\[
\Phi = \mu \left[ 2 \left( \frac{\partial v_r}{\partial r} \right)^2 + 2 \left( \frac{\partial v_z}{\partial z} \right)^2 + 2 \left( \frac{v_r}{r} \right)^2 + \left( \frac{\partial v_r}{\partial z} + \frac{\partial v_z}{\partial r} \right)^2 \right] \tag{4.7}
\]

\[
\Phi = \mu \left( 2D_{11}^2 + 2D_{22}^2 + 2D_{33}^2 + D_{12}^2 \right) \tag{4.8}
\]

For the Newtonian simulations, the flow field is similar for all flow rates. For a given fluid, regardless of the solution viscosity, the components of the rate of deformation tensor will be constant for a given flowrate through a given orifice. Therefore, the behavior of the
dissipation function can be expressed for different fluids on the same curve by dividing by the viscosity. Figure 4.13 plots the energy dissipation divided by the viscosity versus the average orifice velocity. These values are listed in Table 4.3. The energy dissipation refers to the change in internal energy as a result of conversion from kinetic energy. To analyze whether the energy input rate is sufficient to cause chain scission, this value must be compared to the amount of energy in a backbone bond. If the energy input rate is multiplied by the pervaded volume of a coil, the energy to which a coil is exposed can be calculated. The size of a linear polymer can be expressed using various parameters (Bueche, 1962). A polymer chain is constantly vibrating and changing its configuration due to thermal motion. Therefore, any quantification of polymer size is an average value. One measure of the polymer size is the mean square end-to-end distance, \( R^2 \). For polystyrene in a theta solvent at 25°C, the experimentally measured mean square end-to-end length is related to the molecular weight (Flory, 1953).

\[
\left( \frac{R^2}{M} \right)^{0.5} = 0.735
\]  

(4.9)

Using the end-to-end length as an estimate of the effective radius of a sphere, the volume pervaded by a polymer coil can be calculated. The volume for chains with molecular weights of \( 1.0 \times 10^6 \) is \( 1.66 \times 10^{-21} \) m\(^3\).

The energy required to break a C-C bond is \( 6.0 \times 10^{-18} \) J (Wolf, 1987). This value can be compared to the product of the polymer volume and the energy input rates in Table 4.3. For the concentrated Styron solution, the viscosity is 145.4 P. For the flow through the 10:1 contraction at an average orifice velocity of 2.54 m/s, the energy input to a chain with a molecular weight of \( 1.0 \times 10^6 \) in the high extension rate zone is \( 2.83 \times 10^{-15} \) J. The energy dissipated in the volume pervaded by a coil is clearly much larger than the bond strength and would result in scission of all chains in a short time. However, the energy stored is lower than the energy dissipated and is on the same order as the C-C bond.
strength (Wolf, 1987). In order to break a C-C bond, the energy stored in a chain must be greater than the bond strength. The energy input from the flow field is temporarily stored in the bonds, causing portions of the chain to move (Bestul, 1956).

To break bonds, the stored energy must be concentrated in a few sites on the chain. The number of sites in which energy is stored can be calculated if it is assumed that the sites of stored energy are equivalent to physical entanglements. Graessley's theory of entanglement formation and destruction allows the calculation of the number of entanglements as a function of the imposed deformation rate (Graessley, 1974). The number of entanglements in a chain can be calculated from the molecular weight of the chain, the entanglement molecular weight, and the volume fraction of the polymer in the solution. For polystyrene, the entanglement molecular weight is 18,100 (Graessley, 1974).

\[
\varepsilon = \varepsilon_0 g(\theta) = \left( \frac{M}{M_e} \right) \Phi g(\theta) \quad (4.10)
\]

When there is a deformation imposed on a polymer solution, the entanglement density can change. Graessley provided an expression for a function, \( g(\theta) \), which accounts for the disentanglement processes leading to a reduction in the number of entanglements.

\[
g(\theta) = \left( \frac{2}{\pi} \right) \left[ \arccot(\theta) + \left( \frac{\theta}{1 + \theta^2} \right) \right] \quad (4.11)
\]

\[
\theta = \frac{\eta - \eta_{\text{fic}}}{\eta_0 - \eta_{\text{fic}}} \dot{\gamma} \tau_0 \left( \frac{1}{2} \right) \quad (4.12)
\]

\[
h(\theta) = \frac{2}{\pi} \left[ \arccot(\theta) + \frac{\theta (1 - \theta^2)}{(1 + \theta^2)^2} \right] \quad (4.13)
\]

\[
\eta = \eta_{\text{fic}} + \eta_{\text{ext}} \quad (4.14)
\]
In this theory, the viscosity is divided into two parts: a frictional contribution which is independent of shear and an entanglement contribution which decreases with increasing shear (Ballauff et al., 1983).

The number of entanglements is calculated for the 25% monodisperse polystyrene solution in 1-methyl-naphthalene. The viscosity behavior is input to an Excel worksheet and the Graessley parameters are obtained by a minimization of the square of the difference between the experimental data and the model predictions. For this solution, the following parameters are obtained: $\eta_e = 2800 \text{ Pa s}$, $\tau_e = 0.245 \text{ s}$, $\eta_{\text{tie}} = 36.5 \text{ Pa}$. At this concentration, the solution has approximately thirteen entanglements per weight average chain in a quiescent solution. When polymer coils are exposed to a velocity gradient, there is some energy stored in the chain. The stored energy is distributed between the entanglements in a chain. The change in entanglement density with increasing deformation rate is shown in Figure 4.14. It can be seen that the number of entanglements decreases with increasing deformation rate. The variable quantifying the disentanglement process, $g(\theta)$, does not change appreciably at large values of $\theta$. Therefore, when the chain has disentangled and there are only one to two grip points, changes in the deformation rate have negligible effects. As the chain disentangles, the stored energy becomes concentrated in the reduced number of grip points. The chain can rupture if the stored energy is large enough and the number of entanglements is low enough to have the stored energy distributed among one to two grip points. The difference in the initial number of entanglements for good versus poor solvents explains the experimentally observed phenomenon that chains often rupture in poor solvents at lower deformation rates than in good solvents. In poor solvents, the coil is more compact and there are fewer entanglements with neighboring chains. The stored energy is distributed among a smaller number of grip points and the energy becomes greater than the C-C bond energy at lower deformation rates.
Figure 4.15 shows contour plots of the maximum dissipation for the GNF models. In these figures, the dissipation function contours are plotted as a percentage of the maximum dissipation rate. For the Newtonian simulations, these values are directly applicable to all simulations. The dissipation function has a maximum at the edge of the small diameter capillary, where the shear rate is the highest. The function decays in value rapidly with increasing distance from the contraction. The dissipation function cannot distinguish between the type of flow and thus provides no information on the efficiency of microstructure deformation. The flow at the walls of the capillary is simple shear in nature and may be ineffective in deforming the coiled chains. Along the centerline, the flow is purely elongational. The dissipation rate along the centerline is lower than at the capillary walls, but the coils may be deformed to a greater extent since this type of flow is more efficient at deforming the microstructure.

4.4.3 Strain

A minute quantity of high molecular weight polymer can have a profound effect on certain types of flows if the flow is strong enough to produce a transition from a coil conformation to a highly stretched state. The strains necessary to substantially stretch high molecular weight polymers are typically on the order of 100. This is equivalent to a Hencky strain of 4.6. The relaxation time of flexible macromolecules can change when they are substantially deformed (Dyakonova et al., 1996). In some flows, polymer molecules can accumulate strain as they move through the flow field, with incomplete relaxation in between stretches. The deformed molecules do not have enough time to collapse back to their initial conformations and thus accumulate strain with repeated passes through the high strain rate region.

There have been numerous studies in extensional rheology highlighting the need to include the strain history and strain along with the strain rate when reporting extensional
rheological data (Keiller, 1992; Hudson and Jones, 1993). Molecular behavior cannot be extracted from macroscopic flow measurements alone without local probing of strain history. To fully characterize the transient extensional flow in the entrance region, both the extension rate and the strain are required. In the vicinity of the contraction, the extensional flow can impart significant strains on the sample. The extensional strain and the strain rate increase rapidly as the fluid approaches the die entrance.

Total strain is one of the determining factors in the response of a polymer molecule to an extensional flow. Measurements of the extensional viscosity using a filament stretching device have shown that the rise of extensional viscosity is only a function of strain (Shackleford, 1996). Quantifying the effect of different contraction ratios and different flowrates on the total strain is essential to understand the deformation and degradation of the polymers in solution.

The importance of the total strain and the extensional viscosity in entrance flow were illustrated in a study of LDPE melts tested in a commercial capillary rheometer (Padmanabhan and Macosko, 1997). The entrance pressure was measured in a 12:1 contraction. The uniaxial extensional viscosity was calculated from the entrance pressure drop. Due to the transient nature of entrance flows, the extensional viscosity is also a function of the strain. The extensional viscosity from the entrance pressure drop measurements was compared to the transient extensional viscosity obtained from fiber spinning measurements. The transient extensional viscosity at a Hencky strain of three is close to the extensional viscosity obtained from the entrance pressure method. The fluid Hencky strain in the 12:1 contraction is 4.97, which is larger than the Hencky strain at which there was agreement between the two techniques. The authors ascribed this difference to the nonaffine deformation of the polymer chains.

The strain experienced by the coils as they flow through the contraction is approximated as the strain on a volume element as it travels along a streamline. If polymer deformation is
affine with the surrounding medium, this will be equal to the strain for the chain. However, polymer deformation can be non-affine (Carrington et al., 1997). This analysis can still provide some information as to the maximum possible strain experienced by polymer chains.

4.4.3.1 Fluid strain

The fluid strain is calculated based on the change in cross sectional area as the fluid moves through the sharp contraction. An approximate method to calculate the fluid strain along streamlines is by considering the stretch of a cylindrical fluid element in the large diameter tube upstream of the capillary. As the fluid accelerates to move through the small diameter capillary, the cylinder is extended (Figure 4.16). The relative stretch ratio in the direction of flow between times $t'$ and $t$, where $t' \leq t$, is only a function of the relative velocities (Winter, 1982).

$$\lambda (t, t') = \frac{l(t)}{l(t')} = \frac{|u(t)|}{|u(t')|}$$

(4.15)

The maximum value of the stretch ratio for all streamlines is directly related to the change in cross sectional area. Assuming the fluid is incompressible, the maximum Hencky strain is given by the natural log of the ratio of cross sectional areas in the tube and the contraction. With an incompressible fluid in an entrance flow, this is equivalent to stating that the fluid strain is a function only of the contraction ratio.

$$\varepsilon_{\text{max}} = \ln \left( \frac{A_t}{A_c} \right) = \ln \left[ \left( \frac{r_t}{r_c} \right)^2 \right]$$

(4.16)

The fluid strain is not a function of the streamline or the strain rate. Figures 4.17 and 4.18 show the fluid stretch ratio as a function of residence time for different streamlines in the flow for the two different contraction ratios. The time origin is defined for all curves at the
point where the streamline enters the small diameter orifice. The different streamlines reach a maximum in fluid strain just after the entrance to the capillary. The fluid stretch ratio increases at a faster rate along particle paths closer to the centerline (Feigl and Ottinger, 1994).

4.4.3.2 Material strain

The polymer chains will not have strains equal to the fluid strain for two reasons. First, there is nonzero vorticity for all streamlines other than the central streamline. The polymer chain will rotate due to the vorticity and thus will not be exposed to the maximum stretch for the entire transit time. The chain may even be in a conformation in which it is compressed instead of stretched. Second, coil deformation may not be affine with the fluid deformation. There may be relative slip between the surrounding fluid and the chain. Individual chain segments in a deforming matrix do not generally deform in an affine manner. Local deformation can be non-affine, due to segmental mobility and the dispersed nature of the applied forces (Kausch and Plummer, 1994). Chain segments can be oriented efficiently if they can be tightly gripped. Entanglements could provide the gripping points necessary to efficiently orient chain segments. If there is non-affine deformation, the fluid strain must be larger than the strain needed to extend chains. At a high Deborah number, there is almost quantitative agreement between the fluid strain and the molecular strain along any streamline (Chow et al., 1988; Carrington and Odell, 1996).

An approximate analysis is used to obtain an estimate of the material strain. Rotation due to the nonzero vorticity is taken into account, but slip between the polymer chain and the surrounding fluid is not. Chain relaxation and Brownian motion are also neglected in the analysis. In the model, a material line in a volume element is used to represent the polymer chain. A material line has both length and direction. A given material line changes length (is stretched or compressed) due to its orientation with the principal straining axes.
and the length of time it is exposed to the principal straining axes. The same material line rotates due to nonzero vorticity. To calculate the strain on a material line in a volume element, motion along a streamline is discretized between nodes. The residence time and coordinates along a streamline are obtained from the simulations. This data is input to a FORTRAN program, along with the coordinates, velocities, components of the rate of deformation tensor, and components of the vorticity tensor at each node. The principal directions and strain rates are obtained at the streamline data points. To obtain the strain rates along the principal directions, a transformation from a fixed to a rotating coordinate system is required. In a coordinate system attached to the principal axes, there are no off-diagonal components of stress tensor.

\[ T^p = \begin{bmatrix} \sigma_1 & 0 & 0 \\ 0 & \sigma_2 & 0 \\ 0 & 0 & \sigma_3 \end{bmatrix} \]  

(4.17)

By incompressibility, the sum of the diagonal components of the stress tensor is equal to zero.

The angle between the material line and the principal straining direction is calculated and the sign of the stretching rate is adjusted, if necessary. Figure 4.19 shows the effect of the relative orientation of a material line with the stretching axis. The incremental strain between nodes is approximated as the product of the stretching rate and the residence time between nodes (Macosko, 1994). The material line changes length due to this incremental strain. Before moving to the next set of data points along the streamline, the material line is rotated due to the nonzero vorticity. The calculation then shifts along the streamline and the procedure is repeated. The program calculates the strain for different initial material line orientations and outputs the strain along a streamline for the initial orientation which results in the largest strain. Figures 4.20 and 4.21 show the calculated material strain for four streamlines. The material strain is lower than the fluid strain and decreases for streamlines.
closer to the wall. The increased vorticity for the streamlines near the wall rotates the material lines. This prevents a material line from accumulating significant strain.

4.4.4 Flow field character

The final variable important to polymer degradation in a flow field is the type of flow to which the polymer coil is exposed. The response to flow depends on the type of flow field. The behavior of viscoelastic fluids is often markedly different in steady shearing flows and in flows where an extensional motion predominates. The extensional flow has greater power to reorganize the fluid microstructure.

Flows can be divided into several categories. Viscometric flows, extensional flows, and solid body rotation are three types of flows that differ widely in their impact on the microstructure. Purely extensional flows result in severe stresses in elastic liquids, while rigid body motions do not generate any extra stress in a fluid. Although some experiments can be performed in each of these different flow regimes, real flows are much more complicated and are composed of superpositions of each of these general flow categories. It would be advantageous to calculate a scalar invariant which identifies the flow regime for any given flow pattern.

In many problems, the conformation of the microstructure is the most important feature of the system. Flow-induced changes in the microstructure can be dramatic and can directly result in changes in macroscopic properties of the system as a whole. It is important to understand the effect of the flow on the deformation of the microstructure. The experimental observations of Taylor prompted quantification of the type of flow. Most real flows are a mixture of shear and extension. It would be advantageous to calculate a scalar parameter which represents the flow character at any point. There have been several attempts to develop flow classification schemes. A unifying theme has been the requirement that the model be able to predict the ability of the flow to deform the
microstructure. Flows which are capable of producing a large deformation in a finite time are called strong. All other flows are classified as weak. Numerically, a strong flow has one or more positive, real eigenvalues of the velocity gradient tensor. The effect of the flow on the microstructure is determined by combinations of the magnitude of the velocity gradient tensor, which represents the flow strength, and the ratio of the strain rate to vorticity, which represents the flow type (Olbricht et al., 1982).

Giesekus (1962) investigated the behavior of solid particles of a general dumbbell nature in a homogeneous flow field. Giesekus proposed a scalar flow classification parameter that depends on the second invariants of the rate of deformation tensor and the vorticity tensor. These variables were chosen based on the observation that microstructure deformation is determined by the relative values of both the rate of deformation and the vorticity. The direct relationship between molecular orientation and the ratio of the vorticity and the rate of deformation has been studied by several researchers (Taylor, 1934; Hakim and Schowalter, 1980; Bentley and Leal, 1986; Bedford and Burghardt, 1996)

\[ \varepsilon = \sqrt{-\Pi_D} \]  
\[ \Pi_D = D_{11}D_{22} + D_{11}D_{33} + D_{22}D_{33} - D_{12}^2 \]  
\[ \Omega = \frac{1}{2}[(\nabla u)^T - \nabla u] \]  
\[ \omega = \sqrt{\Pi_\Omega} \]  
\[ \Pi_\Omega = -\Omega_{12}\Omega_{21} \]  
\[ R = \frac{\varepsilon - \omega}{\varepsilon + \omega} \]

where \( \Pi_D \) and \( \Pi_\Omega \) are the second invariants of the rate of deformation tensor and the vorticity tensor, respectively. A scalar parameter, \( R \), is defined in terms of these variables.
The flow classification parameter, $R$, equals -1 for solid body rotation ($\omega \gg \epsilon$), 0 for simple shear flow ($\omega = \epsilon$), and 1 for pure extensional flow ($\omega = 0$).

Tanner and Huilgol (1975) and Tanner (1976) extended Giesekus’ work. The Tanner flow criteria allows particles to change conformations as they flow. Motions with constant stress history are obtained from steady, homogenous velocity fields. Tanner defined a flow to be strong if the strain history contains a component which grows sufficiently fast exponentially in time. Such flows may then give rise to unbounded stresses. A flow is weak if it does not contain any exponentially growing strain terms. The proposed flow classification scheme contains only two categories: strong and weak. A shear flow is a weak flow, while an extensional flow is a strong flow. A strong flow has positive real eigenvalues of the velocity gradient matrix.

Hinch provided a mathematical definition of strong and weak flows (Hinch, 1977). Flows are classified as strong or weak, depending on the magnitude of the largest real eigenvector of the rate of deformation tensor. If the largest eigenvector is smaller than the spring restoring force, the flow is insufficient to cause a large distortion (weak flow). If the largest eigenvector is larger than the spring restoring force, the distortion increases in time (strong flow). Strong flows are expected to result in dramatic rheological changes, since they result in extended polymer chains and an increase in the hydrodynamic volume fraction.

4.4.4.1 Astarita's flow parameter

Astarita listed the required properties for any proposed scalar flow classification (Astarita, 1979). First, the parameter should be local, instead of global. In many flows, there is a dramatic difference in the flow type between two separate regions. The scalar parameter should also be invariant under a change of reference frame. This requirement is necessary for the parameter to be useful for comparison between two different geometries.
and for its inclusion in a constitutive equation. The final restriction is that the parameter be generally applicable. Calculation should be possible for any type of flow field.

The essential character of the flow field's effect on a material is the rate of rotation with respect to the direction of maximum stretch. The rate of rotation is defined in terms of the co-rotational derivative. The direction of maximum stretch is set by the principal axes of the rate of deformation tensor. If the largest rate of stretching is applied to the same material line, an elastic liquid can accumulate stresses due to progressive strains. The accumulation of stress will depend on the rate of stress relaxation. If a material rotates, a given material line is not always exposed to the highest rate of stretch. Therefore, the stress accumulation is much less severe.

The rate of rotation of a material locally with respect to the rate of strain field at the same location distinguishes shear and extensional flows. Simple shear flows are one half extension and one half rotation. Coils placed in an shear flow align and tumble in the flow. As a result, a material line is not exposed to the same strain direction. Purely extensional flows have zero vorticity, meaning materials do not rotate locally compared to the primary straining directions. Since a material line is exposed to a given strain, the molecule uncoils and is aligned with the flow.

The local flow character is quantified by a scalar parameter, first described by Astarita (1979) and subsequently used by Schunk and Scriven (1990). The derivation of the parameter assumes that the response of a material to deformation at the submicroscopic scale depends on the relative rates of molecular deformation versus molecular rotation and relaxation. The scalar flow parameter that is calculated for the flow field is the rate at which the principal straining axes turn with respect to the fluid itself. This relative rotation rate is frame independent. It equals zero for pure extensional flow and is infinite for solid body rotation.
4.4.4.2 Calculation of the flow parameter

The flow character scalar parameter can be obtained from the numerical simulation with some modifications to the code. The variables necessary for the calculation are the vorticity tensor and the principal stresses at each node. The principal stress directions can be obtained from the invariants of the stress tensor. The principal stresses are the roots of the following cubic equation, with the coefficients given by the invariants of the stress tensor.

\[ \sigma^3 - \eta \sigma^2 + \Pi_\eta \sigma - \Pi_{\eta} = 0 \]  \hspace{1cm} (4.24)

\[ I_\eta = \text{tr}(T) \]  \hspace{1cm} (4.25)

\[ \Pi_\eta = \frac{1}{2} \left[ I_\eta^2 - \text{tr}(T^2) \right] \]  \hspace{1cm} (4.26)

\[ \Pi_{\eta} = \det(T) \]  \hspace{1cm} (4.27)

The invariants of the stress tensor can be evaluated for a two-dimensional, axisymmetric flow in terms of the components of the rate of deformation tensor.

\[ I_\eta = 2\mu \left( D_{11} + D_{22} + D_{33} \right) \]  \hspace{1cm} (4.28)

\[ \Pi_\eta = \mu^2 \left( 4D_{11}D_{22} + 4D_{11}D_{33} + 4D_{22}D_{33} - D_{12}^2 \right) \]  \hspace{1cm} (4.29)

\[ \Pi_{\eta} = \mu^3 \left( 8D_{11}D_{22}D_{33} - 2D_{12}D_{23}D_{31} \right) \]  \hspace{1cm} (4.30)

Since the components of this tensor are available from the simulation, the invariants can be evaluated, and the cubic equation solved to obtain the principal stresses. A cubic solution algorithm (Perry et al., 1984) is used to solve for the principal stresses. Due to the axisymmetric nature of the flow field, there are two types of solutions: three unequal real roots or three real roots, of which two of the roots are equal.

The flow parameter is calculated as follows. First, the principal directions are calculated from the components of the rate of deformation tensor (Macosko, 1994). The principal axes of the rate of deformation tensor, the principal directions, are given by the
unit eigenvectors, \( e_1, e_2, \) and \( e_3 \). On the principal plane, the traction vector and unit normal to the plane are in the same direction. This enables the calculation of the principal directions from the principal stresses:

\[
e_i \cdot T = \sigma_i e_i \quad (4.31)
\]

Expanding Equation (4.31) gives the following system of equations for the principal stresses:

\[
T_{11}e_{11} + T_{12}e_{12} = \sigma_1 e_{11} \quad (4.32)
\]

\[
T_{21}e_{11} + T_{22}e_{12} = \sigma_1 e_{12} \quad (4.33)
\]

\[
T_{33}e_{13} = \sigma_1 e_{13} \quad (4.34)
\]

For the axisymmetric case, the third principal stress is always equal to the 33 component of the stress tensor. This stress lies along the theta axis. For \( i=1 \) and \( 2 \) (\( r \) and \( z \)), \( e_{33} = 0 \). For \( i=3 \), \( e_{31} = e_{32} = 0 \). For the vectors in the \( r-z \) plane, the system of equations can be solved by assuming \( e_{12} = 1 \) and solving for \( e_{11} \):

\[
e_{11} = \left( \frac{T_{12}}{\sigma_1 - T_{11}} \right) \quad (4.35)
\]

To obtain a unit vector, \( e_{11} \) and \( e_{12} \) are divided by the magnitude:

\[
\text{Magnitude} = \sqrt{1 + |e_{11}|} \quad (4.36)
\]

Since the stress tensor is symmetric, the eigenvectors are mutually orthogonal, and the principal stresses form a rigid triad. Therefore, the rotation rate of one of the vectors is equal to the rotation rate of the triad. In a reference frame, \( F \), the angular velocity of this triad that follows a microscopic volume element of liquid is:

\[
w = e_i \times \frac{D_p e_i}{Dt} = e_i \times \left( \frac{\partial_p e_i}{\partial t} + U \cdot \nabla e_i \right) \quad (4.37)
\]

where \( U \) is the volume element's velocity. Hamoy (1976) was the first to define the derivative with respect to a coordinate system attached to the principal axes of the rate of
strain tensor. Since the key is the relative rotation rate of the principal axes with respect to the fluid, the angular velocity of the flowing liquid must be taken into account. The local angular velocity of a flowing liquid is one half of the vorticity in the same frame (Debye, 1946). The vorticity is defined:

\[
\omega = \nabla \times \mathbf{U}
\]  

(4.38)

Therefore, the rotation rate of the rate of strain tensor relative to the flowing liquid is:

\[
W_{rel} = \mathbf{w} - \frac{\omega}{2} = e_i \times \left( \frac{\partial e_i}{\partial t} + \mathbf{U} \cdot \nabla e_i \right) - \frac{1}{2} \left( \nabla \times \mathbf{U} \right)
\]  

(4.39)

After expansion, this equation reduces to the following:

\[
W_{rel} = v_r v_z \frac{\partial e_r}{\partial z} + v_r v_z \frac{\partial e_z}{\partial z} - e_z v_r \frac{\partial e_r}{\partial r} - e_z v_r \frac{\partial e_z}{\partial r} - \frac{1}{2} \frac{\partial v_z}{\partial r} + \frac{1}{2} \frac{\partial v_r}{\partial z}
\]  

(4.40)

\(W_{rel}\) is a vector in the theta direction. The reciprocal of the magnitude of this vector, \(1/W_{rel}\), is the time scale of rotation. The time scale of liquid deformation is given by the square root of the inverse of the second invariant of the rate of deformation tensor:

\[
\frac{1}{S} = \frac{1}{\sqrt{\text{tr}(D^2)}}
\]  

(4.41)

The dimensionless ratio \(W_{rel}/S\) thus represents the ratio of the time scale of liquid deformation to the time scale of rotation. The dimensionless ratio is zero for pure extensional flow, unity for simple shear, and becomes very large for solid body rotation. A small quantity, \(\varepsilon\), is introduced to keep the dimensionless function defined when the flow tends to solid body rotation. This variable is small enough not to affect the limits of the parameter, but is large enough to keep it well defined as \(S\) goes to zero. To use the flow parameter as a normalizing variable, the function is set equal to one for all ratios greater than one. Only a small portion of the flow domain has flows approaching solid body rotation, so this truncation will not adversely affect the mapping of the flow field. The dimensionless flow parameter is defined:
\[
W = \begin{cases} 
\frac{W_{rel}}{S + \varepsilon} & \frac{W_{rel}}{S} < 1 \\
1 & \frac{W_{rel}}{S} \geq 1 
\end{cases}
\tag{4.42}
\]

To evaluate \(W_{rel}\), the principal directions must be calculated at each node and derivatives of the principal directions with respect to the coordinates must be evaluated. The principal directions at each node are evaluated from the components of the rate of deformation tensor. Derivatives with respect to coordinates are evaluated by defining four pseudo-data points around each node using an interpolation scheme and using a finite difference scheme. This technique is necessary since node spacing varies throughout the domain and nodes are not aligned at constant radial or axial positions. The distance between a node and all other nodes is first calculated, and the minimum separation distance is identified. For interpolation purposes, a radius of inclusion is defined as four times the minimum separation distance. For the mesh, this results in the use of between eight and fifty neighboring data points in the interpolation scheme. The pseudo-data points are aligned with the coordinate axes and are separated from the node by a distance equal to one half of the minimum separation distance (Figure 4.22). The values of the principal directions at each pseudo-node are defined using an Adaptive Gaussian Window (AGW) interpolation technique (Spedding and Rignot, 1993). The value of the interpolation function, \(F\), is computed from the weighted sum of the known data points, \(f_k\).

\[
F(r,z) = \frac{\sum_{k=1}^{n} w_k(r,z) f_k}{\sum_{k=1}^{n} w_k(r,z)}
\tag{4.43}
\]

\[
w_k = \exp\left[-\frac{d_k^2}{\sigma^2}\right]
\tag{4.44}
\]

\[
d_k = \sqrt{(r - r_k)^2 + (z - z_k)^2}
\tag{4.45}
\]
In the above equations, $w_k$ is the weighting function. It has a exponentially decaying form, dependent on the distance, $d_k$, and the width of the Gaussian function, $\sigma$. The width of the Gaussian function is set at 1.4 times the mean distance between the interpolated data point and the other interpolating data points (Agui and Jimenez, 1987).

4.4.3 Results from flow parameter

Figure 4.23 shows a shaded contour plot of the Astarita flow parameter for the sharp contraction flow. The flow field is inhomogeneous, with pure extensional flow only along the centerline. As the radius increases, the vorticity increases, and the flow is more shear in nature. The dimensionless flow parameter is able to accurately describe the flow field character. The parameter is zero at the centerline (pure extensional flow) and is one near the walls (simple shear flow). The flow field is predominately simple shear until approximately one centimeter before the entrance to the orifice. This corresponds to approximately 0.8 tube diameters. At this point, the flow field becomes a mixed flow, with an increasing proportion of extensional-type flow. Line contour plots of the dimensionless flow character are shown in Figure 4.24 for the region close to the small diameter capillary.

The local flow field character, which describes the mechanism of fluid deformation, is analogous to an effectiveness factor for energy input. Extensional flow fields, with zero vorticity, are highly effective in channeling hydrodynamic energy to the polymer chains. Streamlines near the wall, with high shear rates, will have a high dissipation function, but the simple shear flow is not efficient at transferring energy to the polymer chains. To include the effectiveness of the energy input, the values were normalized with the flow parameter, $(1-W)$. When the dimensionless flow parameter is used to normalize the dissipation function, the region just before the entrance to the orifice has the maximum effective energy input. Contour plots of the effective dissipation function, normalized with the maximum value are shown in Figure 4.25.
4.5 Viscoelastic simulations

The flow of a polymer solution through an abrupt contraction can be viscoelastic in nature, depending on the relaxation time of the solution, the contraction ratio, and the volumetric flow rate. Viscoelastic effects can change the flow field when the Deborah number is greater than one. In these situations, a Generalized Newtonian Fluid constitutive equation is insufficient to accurately model the flow field. Viscoelastic simulations are performed to highlight the differences between the GNF predictions and the predictions of a potentially more accurate constitutive equation. POLYFLOW results are obtained for a viscoelastic simulation only for very low flow rates. Comparison and contrast with the predictions of the Generalized Newtonian constitutive equations are made below.

4.5.1 Difficulties associated with viscoelastic modeling

Contraction flows of viscoelastic fluids are important in fundamental flow property measurements and are also important in many industrial applications involving molding and extrusion of polymer melts and solutions. There have been a large number of numerical studies on this topic (White et al., 1987).

The theoretical prediction of entry flow for non-Newtonian fluids remains a difficult problem. The major complication that exists in the numerical simulation of viscoelastic flows is that the set of equations to be solved is far too complicated to be solved analytically. The constitutive equations of non-Newtonian fluids are non-linear, making the set of differential equations nonlinear, even for very low Reynolds number. An iterative technique is required which will linearize the problem at each iteration by updating the solution using the values of the previous iteration and then recalculate the new solution.
until the difference between successive iterations is small. One of the primary difficulties is the presence of a geometrical singularity at the re-entrant corner.

One technique used in the simulation of viscoelastic models is a decoupled approach to the solution of the governing equations. The stress and momentum equations are decoupled and solved separately for the stress or velocity field with the other kept constant. Decoupled approaches reduce the full problem to repeatedly solving two simpler problems. However, decoupled schemes have poorer convergence properties. Picard-type iterations are generally used, with the polymer stress obtained from the solution of the stress equation, using the old velocity field, providing a body force in the solution of a Newtonian-like problem for the new velocity field. A major problem for coupled and decoupled techniques is the failure to obtain solutions for a wide variety of problems for a Weissenberg number much greater than one. The Weissenberg number (We) is a dimensionless group defined as the product of the characteristic time of the fluid ($\lambda$) and the characteristic shear rate or strain rate ($\kappa$) (Bird et al., 1987).

$$\text{We} = \lambda \kappa$$

In many problems, the inverse of the characteristic shear rate or strain rate is used as the time scale of flow and We is equal to the Deborah number. For entry flow, the Weissenberg number is often defined in terms of rheological properties (relaxation time) and geometric or flow properties (characteristic shear rate or strain rate). Care must be taken when using We, since some researchers define We using different variables (Keunings and Crochet, 1983; Debbaut and Crochet, 1986; Keiller, 1993).

The underlying equations are mixed hyperbolic-elliptic type in the absence of a Newtonian stress term. The stress equation is hyperbolic. The stress equations can be solved everywhere simultaneously by the solution of a global set of equations or the stresses at individual points in the flow field can be calculated by separate integrations of the stress equation. Calculating the stress at individual points in the flow field uses
potentially more accurate streamline integration techniques. Along streamlines, the stress equations becomes ordinary differential equations. They can be solved by standard numerical techniques. Stability is improved since information is only propagated forward along the streamline.

Global upwinding techniques may result in poor accuracy where there are large velocity gradients. Streamline integration produces much smoother and more accurate results. Streamline integration techniques eliminate the problem of cross-stream diffusion of stress. Since stress is dependent on flow history and neighboring fluid elements can have disparate histories, stress boundary layers can develop. As We is increased, the fluid remembers more of its history, so the boundary layers become more severe. By treating individual grid points separately, the stress is less affected by the stress boundary layers. The main downside to streamline integration techniques is that they can be computationally intensive.

For viscoelastic simulations, the choice of finite elements and the interpolations for pressure, velocity, and stress are of paramount importance. Although there are no optimal choices, it is generally advisable that the pressure, velocity, and stress variables for a non-Newtonian simulation should collapse onto their Newtonian values when the stress is purely Newtonian. Hermitian elements and $4 \times 4$ sub-elements have been used successfully to satisfy this requirement. To obtain convergence at higher Weissenberg numbers, a coarser grid may be helpful (Azaiez et al., 1996).

A major problem in the simulation of contraction flows is the stress singularity at the lip of the contraction. This singularity can have a significant effect on the onset of numerical instability. In a study on the effect of the mesh on solution convergence, three different meshes were used (Keunings and Crochet, 1984). They differed in the number of nodes and, more importantly, in the size of the corner element. The numerical simulation failed to converge beyond a critical value of We. The critical upper We is related to the size of the reentrant corner element. The mesh with the smallest number of elements, but with the
smallest corner element area converged up to a We of 1.75. The three meshes produced essentially the same results up to their lack of convergence. The upstream vortex size was quantified by the ratio of the reattachment length of the cell to the diameter of the upstream tube. The dimensionless vortex size varied from 0.18 at a We value of 0 to 0.46 for We=1.75. The limit points have a numerical origin. Their location depends on the coarseness of the mesh (Debbaut and Crochet, 1986).

One possible solution for the avoidance of problems at the reentrant corner is to use a rounded corner. Without the singularity, the numerical method possesses second order convergence everywhere. The rounding of the corner should be gradual, with a maximum radius of curvature approximately 0.75 times the downstream radius. Experiments have shown that vortex enhancement may also be observed in flows with rounded corners. Rounding the corner may move the onset of non-Newtonian effects to higher We than would be required for sharp corners (Keiller, 1993).

4.5.2 Viscoelastic results

A viscoelastic simulation using the Giesekus model is converged for the 10:1 contraction and a flow rate of 0.042 cm$^3$/s. The rheological properties from a concentrated monodisperse polystyrene solution are used as input to POLYFLOW. This flow rate is well below the lowest level used in the experiments, but the predictions from the simulation are useful in a comparison and contrast with the predictions from the Generalized Newtonian models. Evolution on the flowrate is used to enable solution convergence. A new mesh is defined with fewer nodes and a smaller element adjacent to the sharp corner. Due to the large number of unknowns, a buffer is activated to store intermediate variables.

A flow rate of 0.042 cm$^3$/s with the concentrated monodisperse polystyrene solution corresponds to a We greater than one as defined by several researchers. Therefore, viscoelastic phenomena should be evident from the simulation results. The We definitions
are shown below, with references. In these equations, $\lambda$ is the relaxation time of the fluid. $v_o$ is the average orifice velocity, $d_o$ is the orifice diameter, $r_o$ is the orifice radius, and $(\dot{\gamma}_w)_o$ is the wall shear rate in the orifice for fully developed flow.

\[
\text{We} = \frac{\lambda v_o}{d_o} = 3.38 \quad (\text{Keunings and Crochet, 1984}) \quad (4.47)
\]

\[
\text{We} = \frac{\lambda v_o}{r_o} = 6.77 \quad (\text{Debbaut and Crochet, 1986}) \quad (4.48)
\]

\[
\text{We} = \lambda (\dot{\gamma}_w)_o = 27.1 \quad (\text{Keiller, 1993}) \quad (4.49)
\]

### 4.5.2.1 Streamlines and entrance angle

The streamlines for the viscoelastic simulation are shown in Figure 4.26. There is negligible difference in the streamline behavior. However, the entrance angle differs from the GNF predictions. The entrance angle predicted from the Giesekus model simulation is $117.7^\circ$. The vortex reattachment length is equal to $0.302d_i$, where $d_i$ is the tube diameter. The Newtonian constitutive equation predicts an entrance angle of $137^\circ$ and a vortex reattachment length of $0.18d_i$. At very low flowrates, the Giesekus model predictions coincide with the Newtonian predictions. Therefore, increased vortex reattachment length and smaller entrance angle indicate that the Giesekus model does predict slight vortex enhancement.

### 4.5.2.2 Centerline strain rate

The dimensionless centerline strain rate is shown in Figure 4.27 for the Giesekus model and the two GNF models. Since the Giesekus model predicts a larger upstream vortex, the centerline strain rate distribution differs from the GNF predictions. The Giesekus model predicts the rise in the centerline strain rate to begin further upstream and the peak strain rate to be slightly smaller than for the GNF models. The proportionality
constant between the maximum centerline strain rate and the ratio of the orifice radius to the average orifice velocity is 0.903 for the Giesekus model, compared to 1.18 for the Newtonian model and from 0.89 to 1.0 for the Cross model. The Cross model predictions are for simulations with higher flow rates than the Giesekus simulation. With the lower flowrate, shear thinning would be reduced and the Cross model predictions would be similar to the Newtonian value.

The Giesekus model can predict extension thickening. The zz-components of the stress tensor for a Newtonian model and the Giesekus prediction are shown in Figure 4.28. The Giesekus model predicts a higher axial stress than the Newtonian model due to extension thickening. The increase in the axial stress is not large for the low flowrate, but a deviation from the Newtonian model is observed. It should be noted that this increase is present in spite of the fact that the zz-component of the rate of deformation tensor for the Giesekus model is smaller in magnitude than for the Newtonian model, since the entrance angle is smaller for the Giesekus model. For the same magnitude of $D_{zz}$, the Giesekus model would predict a value 1.58 times that predicted by the Newtonian constitutive equation.

The normal stress difference, $\tau_{zz} - \tau_n$, is shown in Figure 5.29. This quantity is zero for the Newtonian simulation, but is nonzero near the orifice in the Giesekus predictions. The normal stress difference is directly related to the molecular orientation tensor.

4.5.2.3 Flow field character

The dimensionless flow character for the Giesekus model is shown in Figures 4.30 and 4.31. As for the GNF models, the flow field is primarily simple shear until regions close to the orifice.
Figure 4.1 Vortex enhancement. At low flowrates ($v_1$), there is essentially radial flow into the capillary. For many fluids, an increase in the average velocity ($v_2 > v_1$) will result in a growth of recirculating vortices in the corners. This phenomenon is a function of the extensional properties of a fluid.
Figure 4.2 Effect of different entrance angles on the centerline strain rate distribution. The lower entrance angle with the 14° conical inlet results in a broadening of the strain rate distribution and a reduction in the peak centerline strain rate.
Figure 4.3 Simulation geometry. The symmetry about the centerline is used to simplify the flow domain. Long entrance and exit sections are used to obtain fully developed profiles before and after the entrance to the capillary.
Figure 4.4 Mesh used for flow field simulations. The mesh was created using the program POLYMESH. Symmetry about the centerline is used to simplify the simulation domain. The mesh is concentrated near the entrance and exit of the orifice, where gradients are the largest.
Figure 4.5 Streamlines for the entrance flow in a) 10:1 and b) 20:1 contraction. The streamline patterns are calculated from the Newtonian simulations.
Figure 4.6 Velocity profiles in the orifice for the Newtonian and Cross models. The Reynolds number is low enough for a fully developed profile to be obtained in the orifice for the Newtonian simulations. The shear thinning in the Cross model results in a velocity profile which is more plug flow in nature.
Figure 4.7 Velocity vectors near the entrance to the orifice. The flow profile exactly matches the Hagen-Poiseuille Law until a point very close to the orifice. There is a rapid acceleration as the streamlines contract to pass through the orifice.
Figure 4.8 Centerline axial velocity in the vicinity of the orifice. The velocity is non-dimensionalized with the centerline velocity in the large diameter upstream tube. The axial coordinate is nondimensionalized with the orifice radius. The apparent shift in the 20:1 curve is due to the smaller orifice radius.
Figure 4.9  Nondimensional strain rate versus nondimensional axial position for the Newtonian simulation and Cross simulation. The leading edge of the orifice is defined as $z = 0$. The Newtonian curves collapse onto a single curve. The Cross model curves lie within an envelope given by the two curves for different centerline strain rates.
Figure 4.10 Maximum centerline strain rate for the two GNF models and the two contraction ratios. The centerline strain rate is varied over a two decade range in the experiments.
Figure 4.11 Centerline strain rate in the vicinity of the contraction. There is a uniaxial extensional flow before the entrance to the orifice and a biaxial extensional flow after the fluid exits the contraction. The Newtonian simulations are symmetric about the contraction.
Figure 4.12 Residence times in the high extension rate zone and in the capillary for the two contraction ratios. The residence times range from milliseconds down to microseconds.
Figure 4.13 Specific dissipation rates for the two contractions. Two values are given: the maximum centerline dissipation rate, which occurs just before the entrance to the capillary and the maximum dissipation rate at the wall, which occurs at the front lip of the small diameter capillary.
Figure 4.14 Reduction in entanglement density as a function of deformation rate. The calculations are based on the concentrated monodisperse polystyrene solution in 1-methyl-napthalene. This solution has an average of approximately fourteen entanglements per weight average molecule in a quiescent solution.
Figure 4.15 Dissipation function contour plots for a) 10:1 contraction and b) 20:1 contraction. The contour lines refer to a fraction of the maximum dissipation rate. The maximum dissipation rate occurs in a small region near the front lip of the orifice.
Figure 4.16 Fluid strain calculations. The stretch in the streamline direction, $l_1$, changes the cross sectional area of the stream tube around the path line.
Figure 4.17 Fluid strain for three streamlines (10:1 contraction). All of the streamlines reach values on the order of one hundred, or the square of the contraction ratio. The streamline near the wall has an earlier onset and reaches a higher peak. The other two streamlines nearly coincide. The time axis is defined with $t = 0$ at the entrance to the orifice.
Figure 4.18 Fluid strain for three streamlines (20:1 contraction). All of the streamlines reach values on the order of four hundred, or the square of the contraction ratio. The streamline near the wall has an earlier onset and reaches a higher peak. The other two streamlines nearly coincide. The time axis is defined with $t = 0$ at the entrance to the orifice.
Figure 4.19 Evaluation of material strain. The length and orientation of a material line in a volume element is tracked as the volume element travels along a streamline. The length of the material line changes based on the relative orientation of a material line to the principal stretching axes. The orientation of a material line changes based on the rotation due to vorticity.
Figure 4.20 Material strain for three different streamlines (10:1 contraction). The material strain is lower than the fluid strain due to rotation. The material strain increases closer to the centerline, nearing the fluid strain at the centerline. The high vorticity near the wall prevents material lines flowing along these streamlines from achieving high strains.
Figure 4.21 Material strain for three different streamlines (20:1 contraction). The material strain is lower than the fluid strain due to rotation. The material strain increases closer to the centerline. The material strain increases closer to the centerline, nearing the fluid strain at the centerline. The high vorticity near the wall prevents material lines flowing along these streamlines from achieving high strains.
Node at which derivative is to be determined

Pseudo-node created to evaluate derivative as difference

Figure 4.22 Procedure used to calculate Astarita flow parameter. Pseudo-nodes are created around each node. The values of variables at the pseudo-nodes are calculated using an Adaptive Gaussian Window Interpolation scheme. Derivatives are approximated as finite differences.
Figure 4.23 Contour plot of Astarita's dimensionless flow parameter, $W$. The parameter quantifies the relative rotation rate of the rate of strain axes with respect to the fluid itself. It has a value of one in simple shear flow and zero in a pure extensional flow.
Figure 4.24 Contour plot of Astarita's dimensionless flow parameter near the sharp contraction. The tube flow upstream is simple shear, but the flow is mixed near the entrance to the orifice. On the centerline, there is pure extensional flow.
Figure 4.25 Effective energy dissipation contour plot near the sharp contraction for a) 10:1 contraction and b) 20:1 contraction. The Astarita flow parameter is used as a normalization factor for the dissipation rate, since extensional flows are more effective in channeling energy to coils. The contour lines refer to a fraction of the maximum effective energy dissipation.
Figure 4.26 Streamlines predicted by the Giesekus differential viscoelastic model. Even at low flowrates, the Giesekus model is able to predict slight vortex enhancement upstream of the capillary.
Figure 4.27 Dimensionless centerline strain rate predicted by the Giesekus model. The Newtonian curve is also presented for comparison. Due to the reduced entrance angle, the Giesekus model predicts a lower centerline strain rate for a given flowrate.
Figure 4.28  $\tau_{zz}$ component of the stress tensor along the centerline streamline. For the same volumetric flow rate, the Giesekus model predicts a higher axial stress. The two curves are based on the concentrated monodisperse solution.
Figure 4.29 Normal stress difference along the centerline streamline as predicted by the Giesekus model. The normal stress difference is related to the molecular orientation tensor.
Figure 4.30 Giesekus dimensionless flow parameter for the differential viscoelastic simulation. The Giesekus flow parameter is equal to 1.0 in a pure extensional flow and 0.0 in a simple shear flow.
Figure 4.31 Line contour plot of Giesekus dimensionless flow parameter for the differential viscoelastic simulation. The Giesekus flow parameter is equal to 1.0 in a pure extensional flow and 0.0 in a simple shear flow.
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*Table 4.1* Centerline extension rates predicted by the Newtonian and Cross models. All Newtonian predictions superimpose when nondimensionalized with the orifice radius and average orifice velocity. The Cross model predictions are slightly lower due to shear thinning in the orifice.
Table 4.2 Residence times in the high extension rate zone and in the small diameter capillary. The residence time in the high extension rate zone is defined based on the value of the non-dimensional centerline strain rate. The transit time is defined between the times when the dimensionless variable is equal to 0.1 up to the maximum value.
<table>
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<th>Piston speed (cm/s)</th>
<th>Contraction</th>
<th>Average orifice velocity (m/s)</th>
<th>Centerline energy dissipation (s^2)</th>
<th>Maximum energy dissipation (s^2)</th>
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Table 4.3 Energy dissipation rates for the experimental conditions as predicted by the Newtonian model. Since the components of the rate of deformation tensor are independent of viscosity for a given flow rate, the energy dissipation rates divided by the viscosity are presented above. The maximum energy dissipation rate is obtained by multiplying the above values by the solution viscosity.
CHAPTER 5
EXTENSIONAL DEGRADATION OF STYRON 666D

5.1 Extensional flow degradation (Styron 666D)

Commercially available polystyrene (Dow Styron 666D) is used in different solvents and at different concentrations to examine the extensional degradation of polymer solutions. The molecular weight distribution of Styron 666D is shown in Figure 5.1. The sample has a weight average molecular weight of $2.28 \times 10^5$, a polydispersity of 2.1, and a z-average molecular weight of $3.90 \times 10^5$.

At room temperature, 1-methyl-naphthalene is a good solvent for polystyrene. For Styron 666D in a good solvent, the static overlap concentration is approximately 1 g/dl (1 w/v%) (Graessley, 1980). The 40 w/v% solution is in the concentrated entangled regime, with a coil size similar to a melt. The entanglement molecular weight, or the molecular weight between coupling junctions, is approximately $4.6 \times 10^4$ (Graessley, 1974). Each weight average molecule has between four and five entanglements. The solvent has a high boiling point to reduce solvent evaporation at room temperature. However, the boiling point is low enough to allow vacuum evaporation at low temperatures. The solvent must be boiled off to allow GPC characterization in tetrahydrofuran.

Flow-induced degradation is quantified by rheological measurements and changes in the molecular weight distribution. The experimental results are divided into four parts: a) concentrated Styron in 1-methyl-naphthalene, one pass results; b) concentrated Styron in 1-
methyl-naphthalene, multipass results; c) effect of different solvents on extensional degradation (decalin and 1-methyl-naphthalene); d) effect of concentration on extensional degradation. Results will be presented in terms of the average orifice velocity and number of passes through the high extension rate zone. Since flow visualization was not performed, the details of the flow field at the entrance to the capillary are unknown. A constitutive equation is necessary to obtain stresses, extension rates, and other flow field parameters. Since the details of the flow field are not directly measured, the results are presented in terms of the average orifice velocity. The average orifice velocity is constant for a given piston velocity and contraction ratio and thus is independent of the exact flow field details.

5.2 One pass results

5.2.1 Viscosity drop due to degradation

The drop in the zero shear viscosity is an indirect measure of chain scission. For polystyrene, as chains are broken, the average molecular weight declines. The reduction in molecular weight reduces the viscosity of the solution. The reduction in viscosity is tracked by measuring the viscosity of solutions after passing across the sharp contraction in the opposed pistons device. The ratio of the zero shear viscosity of the degraded samples to the undegraded solution is defined as the viscosity ratio. The viscosity ratio is plotted versus the average orifice velocity in Figure 5.2. There is a small reduction in the viscosity for orifice velocities below 20 m/s. The slope of the curve changes and the drop becomes more substantial for orifice velocities between 20 and 90 m/s. There is a plateau for orifice velocities above 90 m/s. At the highest speeds, there is a 30-35% reduction in the zero shear viscosity after one pass across the contraction.
5.2.2 Changes in the molecular weight distribution

Measuring changes in the molecular weight distribution (MWD) of the degraded samples provides much more insight into the degradation process. The normalized chromatograms of the degraded samples are compared to the undegraded chromatogram to quantify degradation. By measuring the MWD, the reduction in average molecular weights can be tracked. In addition, analysis of the chromatograms can yield information on the scission mechanism. The molecular weight region where chains are broken and the new chains are formed can be determined from the chromatograms.

To verify that chain scission occurs only near the contraction, a test is performed with the highest piston speed and the 1:1 orifice insert, generating pure shear flow. The molecular weight distribution of this sample does not significantly deviate from the undegraded sample. Based on this control test, it is hypothesized that all chain scission results from the extensional flow region near the orifice. The exact geometry of the sharp contraction does not seem to affect polymer scission (Merrill and Leopairat, 1980; Nguyen and Kausch, 1991). Degradation takes place in the high strain rate, extensional flow region before the contraction, not in the orifice or the exit.

For samples exposed to extensional flows, no significant degradation is observed for average orifice velocities below 15 m/s. The GNF Cross model maximum centerline strain rate at this average velocity is approximately $2.1 \times 10^4$ s$^{-1}$. For isolated chains, this strain rate corresponds to a coil-stretch transition for chains with molecular weights above approximately $1.05 \times 10^6$ (Nguyen and Kausch, 1992; Chow et al., 1988; Menasveta and Hoagland, 1992). The coil-stretch transition for isolated chains cannot be extrapolated into the entangled regime, but the value provides a rough estimate of the range of molecular weights undergoing this transition. All chains shorter than this will not be extended, but will remain in a coiled conformation. This is at the high end of the polystyrene distribution.
used in this study, so most chains are not extended at these low strain rates. As the
centerline strain rate is increased, a larger percentage of the chains undergo the coil-stretch
transition and are extended to a conformation where entanglements cause chain rupture.
Other studies have noted a critical strain rate or molecular weight, below which no chains
are broken (Merrill and Leopairat, 1980; Bestul, 1956; Culter et al., 1975). For average
orifice velocities above 30 m/s, deviations in the MWD are more obvious. It is noted that
chain scission is not random. The chromatograms differ principally at the high molecular
weight end of the distribution. The curves are very similar to the undegraded MWD for \( M < 6.0 \times 10^4 \). Chromatograms of samples degraded in a 10:1 contraction and a 20:1
contraction are shown in Figures 5.3 and 5.4.

5.2.3 Average molecular weight reduction

Average molecular weights for the degraded samples are calculated from the MWD.
Table 5.1 lists the average molecular weights for the one pass experiments. As noted in the
discussion of the chromatograms, degradation results in changes at the high molecular
weight end of the MWD. The preferential scission of the longest chains is highlighted by
further analyzing the chromatograms. Figure 5.5 shows the drop in the normalized \( z \)-
average molecular weight as a function of average orifice velocity. \( M_z \) is used, since it is
more sensitive to the longest chains in the distribution. \( M_z \) drops sharply, especially for
average orifice velocities above 40 m/s. The reduction in \( M_z \) slows at high orifice
velocities, but still results in a 30-35% reduction compared to the undegraded sample.
Figure 5.5 is quite similar to the plot of viscosity drop (Figure 5.2), since the viscosity is a
strong function of the longest chains in the distribution.
5.2.4 Differential gel permeation chromatography (DGPC)

When comparing the MWD of polydisperse polymers, changes are usually not seen as an increase or decrease in the number of peaks, but as a shift in the distribution. These shifts are difficult to discern from the complete chromatogram, but can be detected by subtracting chromatograms. To compare chromatograms of degraded samples to the virgin, the data is normalized and standardized with respect to elution volume, and the virgin chromatogram is subtracted from each test chromatogram. A positive deviation indicates an excess of sample in the given molecular weight range. Similarly, a value less than zero means the sample has a deficit compared to the virgin polymer in the given molecular weight range. This technique is known as differential gel permeation chromatography (DGPC) (Billiani and Fleischmann, 1990; Hassell et al., 1979). DGPC plots are ideal for examining degradation, since they can highlight the molecular weight region where fracture occurred.

Comparison of chromatograms is limited by the accuracy and reproducibility of the gpc system. To quantify the repeatability and set limits on the applicability of DGPC, a series of tests are performed on the virgin polymer sample. Twenty chromatograms are analyzed to determine the standard deviation. DGPC traces greater than this standard deviation indicate changes which are significant when compared to experimental scatter. Within the standard deviation limits, the system is capable of resolving molecular weight changes of three percent or less. The standard deviation as a function of molecular weight is given in Figure 5.1 with the undegraded chromatogram.

DGPC traces for three extensionally degraded samples at different orifice velocities and a 10:1 contraction are shown in Figure 5.6. At the lowest average orifice velocity (2.54 m/s), there is no scission detectable outside of the experimental noise. As the centerline strain rate increases, the deviation from the undegraded sample becomes larger. There is preferential scission of the high molecular weight end of the distribution.
Figure 5.6 plots DGPC traces for four samples degraded in the 20:1 contraction. It should be noted that the y-axis limits are different than Figure 5.7. Scission is much more extensive with the higher orifice velocities attained in the 20:1 contraction. The preferential scission of the high molecular weight chains is more obvious than for the 10:1 experiments. As the average orifice velocity increases, the negative deviation increases, meaning more chains are broken.

The DGPC traces deviate from the undegraded sample primarily at high molecular weights. This is important for two reasons. First, this indicates that extensional degradation is non-random and preferentially degrades the longer, higher molecular weight chains. Preferential degradation of high molecular weight chains has been noted in other FTF studies (Culter et al., 1975; Doulah, 1978; Yu, 1977). Second, the high molecular weight chains are ruptured near the center, resulting in two chains which still have high molecular weights. The ratio of the molecular weight at the lowest and highest points of the curves in Figure 5.7 has a value between 2.6 and 3.0. If scission were exactly central, this ratio would be two by definition. Exact central scission is not expected due to the short residence time in the high strain rate region and entanglements in the solution. Although the chains unravel from the center out, they may not be constrained in a symmetrical configuration.

Extensional flow induced scission is similar to thermal degradation with respect to reaction kinetics. The major difference between the two types of scission is the distribution of bond sites that become activated to the level of breakage. In thermal degradation, the distribution is uniform. All bond sites have an equal probability of becoming activated to a level which will cause scission. By contrast, in extensional flow induced degradation, there is a nonrandom distribution of activated bond sites caused by the concentration of stress at specific locations.
5.2.5 Percentage of chains broken

The ratio of the gpc outputs of the degraded and undegraded samples is used to calculate the percentage of chains broken at discrete molecular weights. Figure 5.8 shows the percentage of chains cleaved versus molecular weight for five average orifice velocities and one pass across the orifice. The molecular weight range is restricted to the high end of the distribution to highlight the preferential scission of high molecular weight chains. The exact limits of the plot are determined by experimental difficulties. At higher molecular weights, the chromatogram output is low and noise introduces significant error. At lower molecular weights, the formation of new chains after a long chain is broken interferes with the interpretation of the data.

The percentage of chains ruptured increases with increasing molecular weight. For some molecular weights, there exists a critical molecular weight, above which all chains are cleaved. For one pass through the contraction and an average orifice velocity of 137 m/s, all chains with molecular weights above $8.2 \times 10^3$ are ruptured. Some smaller chains are also ruptured, with the percentage of chains cleaved decreasing with decreasing molecular weight. All chains with a coil-stretch strain rate below the maximum centerline strain rate have a probability of rupture. However, all extended chains are not cleaved due to the variation in the number of entanglements and the inhomogeneity of the flow field. With lower strain rates, a smaller percentage of chains are ruptured. At the lowest orifice velocity, there is negligible chain scission.

5.2.6 Critical molecular weight

For the extensionally degraded samples, there is a critical molecular weight ($M_c$), above which all chains are completely broken. The critical molecular weight after one pass through the high strain rate zone is plotted versus the average orifice velocity in Figure 5.9. The drop in $M_c$ mirrors the decline in the viscosity ratio and $M_c$. At low orifice velocities,
\( M_g \) is near the highest molecular weight in the undegraded sample. For average orifice velocities below 15 m/s, there is no detectable \( M_g \). The detector noise at the onset of the chromatogram limits the accuracy of \( M_g \) determinations for molecular weights above 1.3 \( \times 10^6 \). As the average orifice velocity increases, more chains are broken. The onset of the chromatograms for the degraded samples is shifted to lower molecular weights. Due to the shape of the MWD at the highest molecular weights, it is necessary to break more chains in order to result in a lower \( M_g \).

Preferential cleavage of high molecular weight chains could be expected based on the mechanism of chain scission. Longer chains have a coil-stretch transition at lower strain rates and also have more entanglements than shorter chains. When long chains pass through the high strain rate region, they are stretched and broken. For a given average velocity, chains with a coil-stretch transition below the maximum extension rate will be stretched to some extent. Coil extension is a prerequisite for chain scission in FTF. Lower molecular weight chains may not be long enough to undergo the coil-stretch transition or may not have the necessary entanglement concentration to cause chain scission.

**5.3 Effect of multiple passes on chain scission**

The opposed pistons apparatus is designed to allow multiple passes across the contraction. Therefore, degradation can be monitored as a function of repeated passes through the high strain rate region.

**5.3.1 Viscosity drop due to degradation**

The viscosity drop for multiple passes through the high strain rate zone is shown in Figure 5.10. The general shape of the curves for multiple passes is similar to the one pass curve. There is a small drop for average orifice velocities below 25 m/s. The rate of
change in the zero shear viscosity increases with orifice velocities between 25 and 90 m/s. The viscosity levels off for velocities above 90 m/s. The viscosity drop per pass is the most severe after the first pass through the high strain rate region. Additional passes cause a further reduction, but the incremental drop is less than for the first pass.

5.3.2 Changes in the molecular weight distribution

Figures 5.11 and 5.12 show the molecular weight distributions for samples degraded at two different average orifice velocities and different number of passes across the contraction. In Figure 5.11, the average orifice velocity is 15.2 m/s. There is a detectable deviation from the undegraded chromatogram, although changes are relatively small. The average orifice velocity for the samples in Figure 5.12 is 122 m/s. There is an obvious reduction at the high molecular weight end of the distribution. Multiple passes cause increased chain scission and a reduction in the molecular weight at the onset of the chromatogram. The molecular weight distributions are very similar for molecular weights below $8.0 \times 10^4$.

5.3.3 Average molecular weight reduction

Average molecular weights for the degraded samples are calculated from the MWD. Tables 5.2 and 5.3 list the average molecular weights for the multi-pass experiments. The normalized z-average molecular weight ($M_z$) is plotted versus the number of passes in Figure 5.13 for six different average orifice velocities. $M_z$ is used, because it is sensitive to changes in the high molecular weight tail of the distribution. The most extensive degradation occurs in the first pass across the orifice. Additional passes cause additional chain scission and reduce $M_z$, although the drop is much less severe than the first pass. This diminishing returns phenomenon has been noted in previous fast transient flow degradation studies (Merrill and Leopairat, 1980; Bestul, 1956; Culter et al., 1975).
Multiple passes through a high strain rate region can result in increased chain scission, with the largest number of chains broken in the first pass. There is an observable difference between samples degraded in the 10:1 contraction compared to samples degraded in the 20:1 contraction. The higher average orifice velocity obtained in the 20:1 contraction results in increased chain scission.

### 5.3.4 Differential gel permeation chromatography (DGPC)

The degraded chromatograms are subtracted from the undegraded chromatogram to highlight changes in the molecular weight distributions (MWD). Figure 5.14 shows differential gel permeation chromatograms (DGPC) for samples degraded in the 10:1 contraction geometry at an average orifice velocity of 15.2 m/s. The DGPC trace provides insight into the scission process, in contrast to Figure 5.11, where differences in the MWD are difficult to discern. As in the one pass results, there is preferential degradation of the high molecular weight chains and production of new chains with molecular weights near one half of the starting chain. Multiple passes increase the deviation from the undegraded MWD. The MWD after twenty passes is very similar to the MWD after five passes.

The DGPC traces for samples degraded in the 20:1 contraction geometry and an average orifice velocity of 122 m/s are shown in Figure 5.15. At the higher orifice velocity, there are many more chains broken compared to Figure 5.14.

### 5.3.5 Percentage of chains broken

The effect of multiple passes through the high strain rate region is illustrated in Figures 5.16 and 5.17, which plot the percentage of chains cleaved versus molecular weight for two different average orifice velocities. Multiple passes through the high strain rate region result in a larger percentage of chains ruptured at a given molecular weight. Some smaller chains are also ruptured, with the percentage of chains cleaved decreasing with decreasing
molecular weight. With multiple passes, there is a greater chance of passing through the orifice near the centerline streamline, where chain extensions are the greatest. All chains with a coil-stretch strain rate below the maximum centerline strain rate have a probability of rupture. However, all extended chains are not cleaved due to the variation in the number of entanglements and the inhomogeneity of the flow field. The highest molecular weight chain present in the sample decreases with increasing passes through the high strain rate region. After twenty passes at an average orifice velocity of 122 m/s, all chains with molecular weights above $5.8 \times 10^5$ are ruptured, equivalent to 5.5% of the sample. Some chains in the original sample must be broken multiple times in order to have a critical molecular weight this low.

5.3.6 Critical molecular weight

The molecular weight above which all chains are broken is calculated from the MWD. Average molecular weights for the degraded samples are calculated from the MWD. The critical molecular weights for multiple passes and different orifice velocities are shown in Figure 5.18. The $M_c$ behavior is very similar to the reduction in $M_c$, with a majority of the drop occurring in the first pass. Multiple passes further reduce $M_c$, with a small reduction per pass for most samples.

5.3.7 Very large passes

As noted above, there is a diminishing scission per pass phenomenon observed up to twenty passes. To see if this trend continues, samples are degraded in the opposed pistons apparatus for up to two hundred passes. To minimize viscous dissipation for these long experiments, there is a twenty second delay time between passes. The drop in the normalized $z$-average molecular weight for two different average orifice velocities is shown in Figure 5.19. The values tend to level off after the first few passes, indicating that most
of the chains which can be broken in the flow field are ruptured in the initial stages of the experiment.

5.4 Effect of solvent on FTF degradation

Characteristic dimensions of a random coil (including mean end-to-end distance and radius of gyration) are controlled by both local structure and long-range interactions. Local structure includes variables such as the bond angle and steric restrictions. Long-range interactions deal with the excluded volume effect. In a melt, a $2.0 \times 10^5$ molecular weight chain has an effective average diameter of 20 nanometers (Moore, 1989). In dilute solutions with good solvents, the coils are expanded. For the same $2.0 \times 10^5$ molecular weight chain, the effective average diameter would be 40 nanometers.

Solvent quality determines the size of a polymer coil in solution. Solvent quality may effect the entanglement concentration and change the degradation behavior in a fast transient flow (FTF). As noted in the Literature Review, there are conflicting results on the effect of solvent quality on degradation in dilute solution FTF (Nguyen and Kausch, 1990; Zakin and Hunston, 1978; Ballauff and Wolf, 1988).

A 40% solution is prepared in decalin, a poor solvent for polystyrene, and degraded in the opposed pistons device. The effect of solvent power on chain scission is tested based on results from experiments at the same conditions. The mechanism for FTF scission in concentrated solutions is based on entanglement-induced fracture. Therefore, changes in the solvent power are expected to change the scission products. A complicating factor is the different solution viscosity for the decalin and 1-methyl-naphthalene solutions. All experiments are performed at room temperature. For a true measure of the effect of solvent quality on the degradation process, the temperature should be adjusted to match solvent viscosities. The results from the decalin experiments are shown in Table 5.4.
5.4.1 Average molecular weight reduction

The reduction in $M_\text{c}$ with increasing passes for the two solvents is shown in Figure 5.20. There is some scatter in the data, but $M_\text{c}$ is generally lower for the decalin solution compared to the 1-methyl-naphthalene solution at the same average orifice velocity. The solution viscosity is higher for the decalin solution, resulting in higher extensional stresses and energy dissipation values.

5.4.2 Percentage of chains broken

The distribution of chains broken is examined for the two solutions in Figure 5.21, which plots the percentage of chains ruptured at discrete molecular weights. The results are for twenty passes through the high strain rate region. The samples degraded in decalin have more chains ruptured than samples degraded in 1-methyl-naphthalene for the two lower average orifice velocities. At the highest average orifice velocity, the two samples have very similar behavior in the molecular weight region of interest.

5.4.3 Critical molecular weight

The critical molecular weights for decalin and 1-methyl-naphthalene solutions are shown in Figure 5.22. The decalin solutions have lower $M_\text{c}$ values at the same average orifice velocity, indicating increased chain scission. Entanglements determine scission in a fast transient extensional flow. The increased scission in the decalin solution may be due to the fact that the entanglement contribution to the viscosity (Equation 4.14) is larger in the decalin solution compared to the 1-methyl-naphthalene solution. The entanglement viscosity for the decalin solution is 154 Pa, compared to 143 for the 1-methyl-naphthalene solution.
5.5 Effect of concentration on fast transient flow degradation

To test the effect of concentration on fast transient flow degradation, two additional samples are prepared. A 5% sample is in the semidilute regime and a 20% sample is near the border between the semidilute and concentrated regimes. The samples are tested at similar conditions to the 40% concentrated solution and the results are compared.

5.5.1 Semidilute solution degradation (5%)

It is anticipated that the semidilute solution would have detectable degradation only at the highest average orifice velocities. Therefore, the sample is tested at the highest piston speed. There was no critical molecular weight observed, even for one pass through the high strain rate zone at an average orifice velocity of 137 m/s. The z-average molecular weight decreased to 91% of its undegraded value after one pass, compared to a reduction to 70.5% in the concentrated solution. Figure 5.23 plots the reduction in the z-average molecular weight for the 5% solution. For fast transient flow, chain interaction is required to achieve tensile forces large enough to break C-C bonds. Entanglements in the concentrated regime clearly increase chain scission compared to the semidilute unentangled solution, where only intramolecular entanglements are present.

5.5.2 Semidilute solution degradation (20%)

To investigate the effect of a different concentration on extensional flow-induced degradation, experiments are performed with a 20% Styron in 1-methyl-naphthalene solution. This solution is near the border between the entangled and unentangled regimes and between the semidilute and concentrated regimes. For a given molecular weight, a coil in the 20% solution will have a lower number of entanglements compared to the 40% solution. The results are presented in Table 5.5.
5.5.2.1 Average molecular weight reduction

The semidilute solution was tested at the highest range of average orifice velocities. The reduction in $M_w$ for one pass through the high strain rate region and different average orifice velocities is shown in Figure 5.24. The drop in $M_w$ is strikingly similar for the two solutions. This is somewhat unexpected, since the solution viscosity and entanglement density are much higher in the 40% concentrated solution. It is believed that two factors result in the similarity between the different solutions. First, the samples are exposed to the high strain rate for a very short time. There is not sufficient time for reptation to result in disentanglement. Chain segments which are part of an entanglement junction will be ruptured. Once a chain is broken once, a much higher strain rate is required to break it again. Therefore, whether chains are in the concentrated or semidilute regime, any entanglements can cause chain scission. The density is not as important as the simple presence of entanglements. The second reason for the similarity between the solutions is the fact that entanglement effects in extensional flow are manifested at lower concentrations than in shear flow. The concentration where entanglements modify the flow behavior is different in an extensional flow compared to a shear flow. The overlap concentration for QSSF is much lower than the concentration predicted from shear measurements (Muller et al., 1988). This is due to the short time scales in extensional flows. At short time intervals, the degree of chain interaction required for connectivity is reduced. Any tenuous peripheral entanglements cannot disentangle quickly enough. The limits determining the concentration regime are applicable for shear flow, but may not be representative in extensional flows.
5.5.2.2 Percent chains ruptured

The percent chains ruptured for one pass with the 40% and 20% samples is shown in Figure 5.25. Again, there is no apparent dependence on concentration. The two solutions have essentially identical behavior. At high average orifice velocities, a significant number of long chains are stretched when passing through the high strain rate region. Uncoiling is required for chains to break in extensional flows. Even though the 20% solution has a lower entanglement density, scission is very similar to the 40% solution.

5.5.2.3 Critical molecular weight

The critical molecular weights for one pass with the 40% and 20% solutions are shown in Figure 5.26. Note that the x-axis is truncated, with the upper range of orifice velocities presented. There is no critical molecular weight for one pass and an average orifice velocity of 34.3 m/s. For higher average orifice velocities, the more concentrated solution has a lower critical molecular weight, with some scatter in the data.

5.5.2.4 Average molecular weight reduction

The drop in $M_c$ for semidilute solutions is compared to concentrated solution experiments in Figure 5.27. With some experimental scatter in the data, the semidilute solution exhibits similar behavior to the concentrated solution. The largest reduction occurs in the first pass, with little change after five passes.

5.5.2.5 Critical molecular weight

The critical molecular weight reduction with increasing passes is shown in Figure 5.28. As in the above results, $M_c$ is a function of the average orifice velocity and the number of passes only and not of the concentration.
5.6 Conclusions

In this experiment, polystyrene solutions are degraded in a transient extensional flow. An opposed piston apparatus cycles the polymer solution across a sharp contraction, imposing a high strain rate over a short spatial distance. The drop in the zero shear viscosity and changes in the molecular weight distribution are used to quantify the degradation. The results of the experiment are similar to earlier results on dilute systems: onset of scission after a critical average orifice velocity, preferential scission of high molecular weight chains and increased degradation with increasing average orifice velocity after the onset of degradation. The increased number of entanglements in the chains results in more extensive degradation compared to a dilute system. Increased chain scission is measured for multiple passes across the orifice, with the most extensive scission in the first pass.

The concentration and polydispersity of the sample complicate the degradation mechanism. The entanglements modify the solution response to stress. Chow et al. (1988) hypothesized that the extension of chains in the entangled state is different than for isolated chains. Degradation in a polydisperse, concentrated solution in an extensional flow could result from a combination of two mechanisms: isolated chain fracture and entanglement induced fracture. For a polydisperse sample, molecules can be selectively broken from the distribution individually, starting with the longest chains. However, this is not always true since the behavior of a polydisperse sample in an elongational flow is not a simple additive function of its monodisperse components (Muller et al., 1988).

Studies of the extensional degradation of polymer solutions are important, since there is a strong extensional flow component in many flows, and extensional flows are much more efficient than shear flows in causing polymer scission. Chain scission can dramatically alter the physical properties of the polymer as a whole. FTF processes are often
encountered in polymer processing and other operations. Some examples include entrance flows, ultrasonic fields, and turbulent drag reduction. Degradation studies in transient flow are useful for modeling polymer scission under real conditions where the short deformation time scale does not permit full chain extension.
Figure 5.1 Styron 666D molecular weight distribution. The standard deviation curve is used to quantify the repeatability of the GPC apparatus and is calculated from twenty chromatograms.
Figure 5.2 Viscosity drop as a function of average orifice velocity. The viscosity ratio is defined as the ratio of the zero shear viscosity of the degraded solution divided by the zero shear viscosity of the undegraded solution.
Figure 5.3 Molecular weight distributions of undegraded Styron 666D and three samples degraded at different average velocities (10:1 contraction). The degraded chromatograms differ slightly from the undegraded trace.
Figure 5.4 Molecular weight distributions of undegraded Styron 666D and four samples degraded at different average velocities (20:1 contraction). The degraded chromatograms differ from the undegraded trace primarily at the high molecular weight end of the distribution.
Figure 5.5 Reduction in z-average molecular weight versus average orifice velocity. The z-average molecular weight highlights the scission of high molecular weight chains.
Figure 5.6 Differential gel permeation chromatography (DGPC) traces for three extensionally degraded samples (10:1 contraction). The dark band delineates one standard deviation. Differences outside of this band are considered statistically significant. There is minimal degradation at low average velocities, but scission increases as the velocity increases. There is preferential scission of the high molecular weight compounds.
Figure 5.7 Differential gel permeation chromatography (DGPC) traces for four extensionally degraded samples (20:1 contraction). The dark band delineates one standard deviation. Differences outside of this band are considered statistically significant. Chain scission is much larger than for the 10:1 contraction. Again, scission increases as the velocity increases. There is preferential scission of the high molecular weight compounds.
Figure 5.8 Percentage of chains cleaved at discrete molecular weights for five average orifice velocities (five different centerline strain rates). Data is presented for one pass through the high strain rate region. The data is obtained by comparing the output from the gel permeation chromatogram for the degraded samples to the undegraded samples at discrete molecular weights. Increasing average orifice velocity (or strain rate) results in increased chain scission.
Figure 5.9  Critical molecular weight versus average orifice velocity. The critical molecular weight is defined as the molecular weight above which all chains are ruptured. The plot follows a trend similar to the viscosity drop, again highlighting the preferential scission of high molecular weight compounds and the increased scission with increasing average velocity.
Figure 5.10 Viscosity drop versus average orifice velocity for different number passes through the high strain rate zone. There is little viscosity drop for low average velocities and a linear decline over much of the test range. Much of the viscosity drop is in the first pass through the high strain rate region.
Figure 5.11 Molecular weight distributions of extensionally degraded samples (10:1 contraction). The samples were degraded at a constant average orifice velocity and varying number of passes. The samples are degraded at an average orifice velocity of 15.2 m/s.
Figure 5.12 Molecular weight distributions of extensionally degraded samples (20:1 contraction). The samples were degraded at a constant average orifice velocity and varying number of passes. The samples are degraded at an average orifice velocity of 122 m/s.
Figure 5.13 Reduction in z-average molecular weight versus average orifice velocity. The z-average molecular weight highlights the scission of high molecular weight chains. Most of the drop in $M_z$ occurs in the first pass through the high strain rate region.
Figure 5.14 Differential gel permeation chromatography (DGPC) traces for four extensionally degraded samples (10:1 contraction). The dark band delineates one standard deviation. Differences outside of this band are considered statistically significant. There is preferential scission of the high molecular weight compounds.
Figure 5.15 Differential gel permeation chromatography (DGPC) traces for four extensionally degraded samples (20:1 contraction). The dark band delineates one standard deviation. Differences outside of this band are considered statistically significant. There is preferential scission of the high molecular weight compounds.
Figure 5.16 Percentage of chains cleaved at discrete molecular weights for a given average orifice velocity (or centerline strain rate) and multiple passes through the high strain rate region. The data is obtained by comparing the output from the gel permeation chromatogram for the degraded samples to the undegraded samples at discrete molecular weights. Increasing passes increase scission, although most of the degradation occurs in the first pass.
Figure 5.17 Percentage of chains cleaved at discrete molecular weights for a given average orifice velocity (or centerline strain rate) and multiple passes through the high strain rate region. The data is obtained by comparing the output from the gel permeation chromatogram for the degraded samples to the undegraded samples at discrete molecular weights. Increasing passes increase scission, although most of the degradation occurs in the first pass.
Figure 5.18 Critical molecular weight versus number of passes for different average orifice velocities in multipass experiments. The critical molecular weight is defined as the molecular weight above which all chains are ruptured. The plot follows a trend similar to the reduction in $M_\alpha$, with the majority of the drop in $M_\alpha$ occurring in the first pass through the high strain rate region. There is preferential scission of high molecular weight compounds and the increased scission with increasing average velocity.
Figure 5.19 Drop in $M_e$ for a large number of passes. The trend evident in the results for one to twenty passes extends out to a much larger number of passes. Most of the chain scission occurs in the first few passes through the high extension rate zone.
Figure 5.20 Drop in z-average molecular weight for concentrated solutions in decalin (D) and 1-methyl-naphthalene (N). The drop in $M_z$ for a given number of passes is greater in the poor solvent (decalin) compared to the good solvent (1-methyl-naphthalene).
Figure 5.21 Percent chains broken as a function of molecular weight for the two concentrated solutions. There are more chains broken in the decalin solution compared to the 1-methyl-naphthalene solution at the same average orifice velocity. All data is obtained from experiments with twenty passes through the high strain rate zone.
Figure 5.22 Critical molecular weight for concentrated solutions in decalin (D) and 1-methyl-naphthalene (N). The drop in $M_c$ for a given number of passes is greater in the poor solvent (decalin) compared to the good solvent (1-methyl-naphthalene).
Figure 5.23 Drop in the normalized z-average molecular weight for two solutions of Styron in 1-methyl-naphthalene. The 5% solution is in the semidilute unentangled regime. The 40% solution is in the concentrated entangled regime. There is significantly more chain scission in the concentrated solution compared to the semidilute solution.
Figure 5.24 Drop in $M_2$ for 20% and 40% Styron in 1-methyl-naphthalene. The 20% solution is in the semidilute regime, and the 40% solution is in the concentrated regime. The drop in $M_2$ is strikingly similar for the two solutions.
Figure 5.25  Percentage of chains cleaved at discrete molecular weights for a given average orifice velocity (or centerline strain rate) and one pass through the high extension rate zone. The data is obtained by comparing the output from the gel permeation chromatogram for the degraded samples to the undegraded samples at discrete molecular weights.
Figure 5.26 Critical molecular weight for 20% and 40% Styron in 1-methyl-naphthalene after one pass through the high strain rate region.
Figure 5.27 Reduction in the $z$-average molecular weight for two Styron solutions. Although the 20% solution has fewer entanglements than the 40% solution, the drop in $M_z$ is similar.
Figure 5.28 The critical molecular weight, above which all chains are ruptured for the 20% and 40% Styron solutions. There is a slightly larger drop in $M_c$ for the 40% solution, although the 20% solution exhibits significant degradation.
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Table 5.1 Results from one pass experiments with 40% Styron in 1-methyl-naphthalene. The viscosity ratio is the ratio of the zero shear viscosities of the degraded and undegraded samples. The critical molecular weight is the molecular weight above which all chains are ruptured. N/A = not available; - = none detectable.
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Table 5.2  Results for multiple pass experiments, 10:1 contraction, 40% Styron in 1-methyl-naphthalene. N/A = not available; - = none detectable.
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Table 5.3 Results for multiple pass experiments, 20:1 contraction, 40% Styron in 1-methyl-naphthalene. N/A = not available; - = none detectable.
Table 5.4 Results for experiments with 40% Styron in decalin. Decalin is a poor solvent for polystyrene, unlike 1-methyl-naphthalene, which is a good solvent for polystyrene. N/A = not available; - = none detectable.
Table 5.5 Results for experiments with 20% Styron in 1-methyl-naphthalene. The 20% solution is near the border of entanglement. N/A = not available; - = none detectable.
CHAPTER 6

EXTENSIONAL DEGRADATION OF MONODISPERSE POLYSTYRENE SOLUTIONS

6.1 Introduction

Chapter 5 summarized experiments with a polydisperse, commercially available polystyrene sample (Styron 666D). Concentrated solutions were degraded in a fast transient flow using an opposed pistons apparatus. Analysis of the degradation products revealed that the extensional flow resulted in a preferential scission of the longest chains in the distribution. These chains are degraded near the central monomer, producing two new chains with relatively high molecular weights. In this chapter, solutions of a different polymer are degraded in the fast transient extensional flow. The polymer sample used for this phase of the experiments is a high molecular weight, very narrow molecular weight distribution sample produced by Polymer Source specifically for this work. The polystyrene was prepared by an anionic polymerization of styrene using s-butyl lithium as an initiator. After the polymerization, the polymer was precipitated into methanol and dried under vacuum. This sample has none of the additives present in the Styron sample. The chains are similar in length and will have relaxation times which are close in magnitude to one another. The high molecular weight of the sample will allow degradation to be...
observed at lower concentrations and lower average orifice velocities since the fracture
strain rate is relatively low.

The experimental goals for this phase of the experimental study are threefold. First, the
extensional degradation of a narrow molecular weight distribution sample is compared to
the behavior observed with the Styron, a polydisperse sample. Second, the effect of
different concentrations on the extensional degradation of polymer solutions is investigated.
Samples are prepared in the dilute, semidilute, and concentrated regimes. These solutions
are degraded in the opposed pistons apparatus, and the degradation behavior is related to
the polymer conformation and coil size. Finally, the effect of the solvent viscosity on the
degradation of dilute solutions is studied by quantifying the degradation in two different
solvents. Dilute solutions in 1-methyl-naphthalene and a polystyrene oligomer are
degraded and the scission is measured.

6.2 Monodisperse polystyrene sample

The molecular weight distribution of the high molecular weight sample is shown in
Figure 6.1. The average molecular weights of the sample are the following: $M_w = 1.065 \times
10^6$, $M_n = 1.035 \times 10^6$, $M_w/M_n = 1.029$, and $M_c = 1.094 \times 10^6$. For brevity, this sample
will hereafter be referred to as the monodisperse polystyrene sample. A perfect
monodisperse polymer is obtainable only with certain systems and under special
conditions. Some examples include DNA and some star polymers. Even with a
polydispersity of 1.029, the sample still has chains from $1.7 \times 10^6$ to $6.6 \times 10^5$ at a level of
one percent of the maximum output. This is equivalent to a difference of contour lengths of
2.6. The low polydispersity of this sample is contrasted with the Styron sample, which
has a polydispersity of 2.2. The molecular weight distributions of the two samples are
compared in Figure 6.2. In the figure, the maximum output is standardized at a value of
one to allow comparison between the samples.
6.2.1 Solution properties

Four different solutions are prepared with the monodisperse polystyrene sample. Three samples are dissolved in 1-methylnaphthalene at concentrations of 25, 2.5, and 0.25 w/v\% (g/dl). These concentrations are selected to have solutions in the concentrated, semidilute, and dilute regimes. Experiments with these solutions will allow investigation of the effect of concentration on fast transient extensional flow degradation. A final solution is prepared with polystyrene oligomer as the solvent. The polystyrene oligomer (Piccolastic A5, Hercules Chemical) has a molecular weight of 430. The Piccolastic oligomer is polydisperse, but does not have components with molecular weights greater than $5.0 \times 10^3$. The dilute solution in the oligomer is a Boger fluid (Boger, 1977). Boger fluids exhibit negligible shear thinning, but have elastic behavior. They are routinely used in fluid mechanics experiments to isolate elastic behavior from shear thinning. There has been some concern about flow induced degradation of the Boger fluids during these experiments.

The 25 w/v\% solution is in the concentrated, entangled regime. The entanglement molecular weight in solution is obtained from the entanglement molecular weight for the undiluted polymer and the volume fraction of polymer in solution (Graessley, 1974).

$$ (M_e)_{\text{solution}} = \frac{M_e}{\phi} \quad (6.1) $$

The entanglement molecular weight for polystyrene is $1.95 \times 10^4$ (Davidson et al., 1993). The concentrated solution, with a concentration of 25 w/v\%, has a volume fraction of 0.271, assuming no volume change on mixing. The solution has an entanglement molecular weight of approximately $7.19 \times 10^4$. Therefore, the concentrated solution has approximately fifteen entanglements per weight average molecule.

The 2.5 w/v\% solution is in the semidilute, unentangled regime. The coil size is larger than in the concentrated solution, but smaller than the expanded coil in the dilute solution.
In the semidilute regime, the coils begin to see other coils and decrease in size due to excluded volume effects. The coils do not interpenetrate and entanglement effects are not observed in shear measurements.

The 0.25 w/v% solutions are in the dilute regime. Since 1-methyl-naphthalene is a good solvent for polystyrene, the coil in this solvent will have a larger size compared to the theta condition. Coils are treated as independent and do not interact with other chains. The dilute solution in the polystyrene oligomer is prepared in two steps, since the diffusivity in the viscous solvent is very small. First, the monodisperse polymer is added to the stoichiometric amount of oligomer and a smaller amount of tetrahydrofuran (THF). After the polymer is completely dissolved, the THF is evaporated off in a vacuum oven. The sample is tested in the opposed pistons apparatus when the solution mass asymptotes to a constant value. The polystyrene oligomer solvent is expected to be a good solvent for the monodisperse polymer, since the two species are chemically identical. Static light scattering experiments for a mixed solvent system indicated that an increasing fraction of polystyrene oligomer in the solvent improved the solvent quality (Solomon and Muller, 1996). Figure 6.3 shows the location of the three concentrations on a concentration-molecular weight diagram for polystyrene in a good solvent.

6.3 Effect of concentration on extensional flow degradation

Samples are degraded in the opposed pistons apparatus and the degradation is quantified by analyzing the molecular weight distributions using gel permeation chromatography. Degradation is related to the drop in the molecular weight averages and the percentage of chains which are degraded.
6.3.1 Scission yield as a function of average orifice velocity

The percentage of chains in the undegraded sample which are cleaved is obtained by calculating the relative area of the degraded chromatogram for molecular weights less than \(7.0 \times 10^5\). There is some chain overlap at the lower molecular weights, but since the solution has such a low polydispersity, this contribution is small. To completely eliminate chain overlap, the sample would have to be refractionated to obtain a sample with an even lower polydispersity. The area of the degraded chromatograms for molecular weights below \(7.0 \times 10^5\) is defined as the scission yield. There is no observable degradation at the lowest average orifice velocity (2.54 m/s). For isolated chains, this corresponds to a coil-stretch transition for chains with molecular weights above approximately \(2.35 \times 10^6\) (Nguyen and Kausch, 1992; Chow et al., 1988; Menasveta and Hoagland, 1992). Although the coil-stretch transition cannot be extrapolated into the entangled regime, this value provides a rough estimate of the range of molecular weights which will undergo the coil-stretch transition. All chains shorter than this will not be extended, but will remain in a coiled conformation. Since there are no chains in the distribution with molecular weights in this range, the extension necessary to rupture chains is not achieved.

The scission yield as a function of the average orifice velocity for the three solutions is shown in Figure 6.4. All three solutions have a sigmoidal shape, with the onset of the rise occurring at different average orifice velocities for the different solutions. The scission yield for the concentrated solution increases rapidly from zero, and asymptotes to a scission yield of 58% for average orifice velocities above 50 m/s. The high molecular weight of the monodisperse polystyrene solution means that the chains will undergo a coil-stretch transition at low extension rates. When the chains begin to stretch, they are hindered by entanglements. The stress rises and bonds are broken.

The scission yield curves for the semidilute and dilute solutions also have a sigmoidal shape, with the rise in the semidilute solution occurring at an average orifice velocity of
approximately 80 m/s, and the rise in the dilute solution at approximately 110 m/s. Scission in the dilute solution is due solely to intramolecular entanglements, since the chains do not interact. There is a measurable difference in scission yield between the dilute and the semidilute solutions for average orifice velocities above 80 m/s. As discussed above, the 2.5 w/v% solution is in the unentangled regime. It must be noted that this designation is based on shear measurements. It has been proposed that the entanglement limit in extensional flow is lower than in shear flow (Chow et al., 1988). This drop in the entanglement concentration in extensional flow is due to the effectiveness of coil interactions on the periphery of the coils. Peripheral entanglements, which do not have time to disentangle in the short residence time in the high extension rate zone, make the semidilute solution behave similar to the concentrated solution at higher average orifice velocities. These chain contacts can disentangle in a shear flow measurement and thus classical entanglement behavior is not observed in these flows.

6.3.2 Drop in average molecular weight

The drop in the number average molecular weight for the three solutions in 1-methyl-naphthalene versus the average orifice velocity is shown in Figure 6.5. $M_n$ is directly related to the number of broken bonds and is independent of the degradation mechanisms. As expected, the reduction in $M_n$ is the greatest in the concentrated solution. The reduction in $M_n$ for the concentrated solution has a logarithmic dependence on the average orifice velocity (Figure 6.6). The dilute solution exhibits a negligible reduction in $M_n$ for average orifice velocities below approximately 80 m/s. For average orifice velocities greater than 100 m/s, $M_n$ drops sharply. The reduction of $M_n$ in the semidilute solution is slower than the drop in the concentrated solution for low average orifice velocities, but it approaches the concentrated solution values for average orifice velocities greater than 80 m/s.
Unlike $M_n$, the higher moments of the molecular weight distribution are sensitive to the position of the broken bond. The change in the $z$-average molecular weight is shown in Figure 6.7. The drop in $M_z$ is very similar to drop in $M_n$. The dilute solution $M_z$ decreases sharply for average orifice velocities greater than 100 m/s. The semidilute solution has $M_z$ intermediate between the concentrated and dilute solutions. The drop in $M_z$ for the concentrated solution is again logarithmically related to the average orifice velocity. The $z$-average molecular weights drops as much as 27.5% after one pass through the high extension rate zone.

6.3.3 Scission index

The reduction in the number-average molecular weight is directly related to the number of broken bonds. The scission index, $s$, is defined as the number of broken bonds per initial chain, with subscript $o$ indicating the initial number-average molecular weight (Merrill and Leopairat, 1980).

$$s = \frac{\langle M_n \rangle_o}{M_n} - 1$$ (6.2)

The scission index for the three solutions is shown as a function of the average orifice velocity in Figure 6.8. The scission index behavior is remarkably similar to the scission yield for all three solutions. Bonds are broken in the concentrated solution from the lowest average orifice velocities. The scission index rises to a value of 0.76 bonds broken per initial macromolecule. In the dilute regime, the scission index does not rise until average orifice velocities are above 100 m/s. The semidilute solution again shows behavior which changes, depending on the average orifice velocity. The scission index for the semidilute solution is low, similar to the dilute solution, for average orifice velocities less than 80 m/s. The scission index rapidly rises for average orifice velocities greater than 80 m/s and approaches the values in the concentrated regime.
The localization of bond scission is of utmost importance in determining the scission mechanism. The scission index is independent of the degradation mechanism. However, information on the randomness of the degradation process can be obtained by plotting the relative change of one of the higher moments of the molecular weight distribution with respect to $M_n$ as a function of the scission index. The change in the polydispersity versus the scission index is shown in Figure 6.9. The two solid curves are from a modeling study of the degradation process for a sample with a low initial polydispersity (Nguyen, 1997). In this work, the degradation reaction proceeds with different rate constant dependencies. For a random degradation, $M_c/M_n$ changes more rapidly than for degradation in which chain scission is centered around the center of the chains. The parameter $R$ in the model reflects the standard deviation of the Gaussian rate constant curve which is centered about the midpoint of the chains. The change in $M_c/M_n$ versus the scission index is shown in Figure 6.10.

6.3.4 Changes in the molecular weight distribution

The analysis of the entire molecular weight distribution provides additional information about the scission process. A chromatogram after degradation in dilute solution is shown in Figure 6.11. The sample is degraded at an average orifice velocity of 132 m/s. After correction for axial dispersion, the chromatogram is resolved into two different peaks: a high molecular weight peak which is the undegraded starting material and a second peak generated as a result of the degradation process. The new peak is centered around a molecular weight approximately one half of the peak molecular weight of the undegraded monodisperse polystyrene. In Figure 6.11, Gaussian curves have been fitted to the two peaks to illustrate that the complete chromatogram is actually the summation of two different peaks. As noted in the Literature Review, near central scission occurs in dilute solution fast transient extensional flow. The chains are broken near the central monomer,
even though they are unable to completely uncoil. The most probable coil unraveling mechanisms have the chain straighten from the center out, thus leading to near central scission. The dilute solution chromatograms all have the larger curve with a peak at approximately the same molecular weight. The second, lower molecular weight peak increases in size as the average orifice velocity increases.

The second, low molecular weight peak is present in the chromatograms for dilute solution samples degraded at an average orifice velocity greater than 10.2 m/s. To account for experimental noise in the chromatograms, the defined onset of degradation is slightly higher than this value. Nguyen and Kausch (1992) use a scission yield of 7% as the definition of the onset of chain scission. This limit is set to avoid error at low scission yields where the onset of the sigmoidal curve can lead to uncertainty in the determination of the exact extension rate. The 7% scission yield occurs at an average orifice velocity between 61.0 and 71.1 m/s. The onset of degradation can be compared to previous dilute solution studies. Merrill and Leopairat (1980) noted that the scission index was linearly related to the average orifice velocity above a critical orifice velocity. The measured critical orifice velocity for a dilute solution of polystyrene ($M_w = 8.0 \times 10^2$, $M_w/M_n = 1.10$) in toluene was approximately 66 m/s. The sample and the contraction ratio are different for this study compared to the present work, but the two variables counteract one another. The molecular weight used in this study is higher, which would result in a reduction in the critical orifice velocity. However, the contraction used by Merrill and Leopairat was 37.5:1, moving the onset to a lower orifice velocity. Nguyen and Kausch (1992) measured the scission yield for a series of very narrow MWD polystyrene samples and proposed a functional relationship between the scission yield and the average orifice velocity. For the monodisperse polystyrene sample, the 7% scission yield limit is predicted to occur at an average orifice velocity of 39.6 m/s. The difference in the predictions of Nguyen and Kausch and the experimentally measured valued may be due to the higher polydispersity of
the samples used in this study. The samples used by Nguyen and Kausch had a polydispersity of 1.017. A numerical kinetic analysis of the scission process has shown that the MWD affects the scission yield curve. The scission yield versus average orifice velocity sigmoidal curve has a lower slope with a more polydisperse sample (Nguyen and Kausch, 1989).

Chromatograms of the undegraded monodisperse polystyrene and four semidilute solution samples degraded at different average orifice velocities are shown in Figure 6.12. The peak molecular weight is shifted to lower molecular weights compared to the undegraded sample, even at low average orifice velocities. There is a depletion of the highest molecular weight chains, but it is not large enough to consider the scission a critical phenomena which breaks all chains above a certain length. In contrast to the polydisperse Styron sample, there is no critical molecular weight as the chains are degraded. For the polydisperse system, the critical molecular weight, above which all chains are degraded, decreased with increasing average orifice velocity. For the monodisperse sample, this is not the case. The reason this does not occur is that the relaxation times for the chains are similar and thus all chains stretch in a narrowly defined range of extension rates. The wide range of relaxation times in the polydisperse sample resulted in the longest chains stretching first and rupturing before the smaller chains had a chance to uncoil. The narrow molecular weight distribution of the monodisperse sample does not allow a critical molecular weight to be defined. A second, lower molecular weight peak is generated as the samples degrade, but this peak is not as sharply defined as in the dilute samples.

The differential gel permeation chromatograms (DGPC) of the semidilute samples are shown in Figure 6.13. An interesting observation can be made based on the shape of the curves as a function of the average orifice velocity. For low average orifice velocities, the DGPC traces indicate that chains are ruptured for molecular weights above approximately $9.5 \times 10^5$. The DGPC traces are positive, indicating more chains than in the undegraded
sample for molecular weights between $6.0 \times 10^5$ and $9.5 \times 10^5$. The shape of the curves changes as the average orifice velocity increases above 100 m/s. There is a generation of more chains at lower molecular weights, giving a nonzero DGPC signal to molecular weights as low as $3.0 \times 10^5$. This limit between the different degradation behavior, $v_o > 100$ m/s, is also the point at which the dilute solution began to exhibit significant degradation. It is hypothesized that extensional degradation in the semidilute solution occurs by two different processes. At low average orifice velocities, chain motion is hindered by peripheral entanglements. These intermolecular entanglements provide the necessary grip points to cause chain scission. Since the entanglement density is lower than in the concentrated regime, chain scission is also lower for the semidilute solutions. As the average orifice velocity increases, two things occur. First, the effective intermolecular entanglement density increases, since more chain segments cannot disentangle from different chains in the decreasing residence time. Second, the velocity gradient reaches a level where independent chains can be broken. The mechanism for independent chain scission is exactly the same as in dilute solution. It is caused by intramolecular entanglements. Therefore, for the highest average orifice velocities, chain scission occurs by both intra- and intermolecular entanglement mechanisms.

The chromatograms of concentrated solutions degraded in the fast transient flow are shown in Figure 6.14. Again, there is no critical molecular weight due to the low polydispersity of the sample. The peak molecular weight shifts to progressively lower values as the centerline strain rate increases. With the increasing number of chains broken in the concentrated system, there is an overlap between chains which are broken and chains which are undegraded. In addition, there is the possibility of some chains being broken twice as they pass through the high extension rate zone. After a polymer chain is broken once, a considerably higher strain rate is necessary to break the fragments a second time. This explains the lack of a GPC peak at one quarter the molecular weight of the degraded
chains. Only chains which have a sufficiently low fracture strain rate will have the possibility of being fractured twice. The small residence time through the high extension rate zone also prevents more than two scission events from taking place (Nguyen and Kausch, 1988). Chain overlap and the possibility of multiple scission complicates the interpretation of the chromatograms. The differential chromatograms for the concentrated solution are shown in Figure 6.15. The presence of new chains at molecular weights as low as $3.0 \times 10^5$ indicates that there are multiple scission events taking place for some of the larger chains in the distribution.

6.3.5 Degradation of a Boger fluid in a fast transient extensional flow

A dilute solution of the monodisperse polystyrene in polystyrene oligomer is tested to analyze the effect of solvent viscosity on fast transient flow degradation. The effect of solvent viscosity on dilute solution FTF degradation was quantified for several organic solvents (Nguyen and Kausch, 1990). The study used solvents with viscosities from 0.329 to 10.46 cP. For these dilute solutions, the fracture strain rate was found to be proportional to the $-0.25$ power of the solvent viscosity. This weak dependence on the solvent viscosity proves that the degradation mechanism in a FTF is not controlled by viscous drag alone. The purpose of these experiments is to see if the experimental scaling extends over a much wider range of solvent viscosity. The solvent in the Boger fluid is polystyrene oligomer, which has a shear viscosity of 251 P. This is over 7800 times larger than the shear viscosity of 1-methyl-naphthalene. Based on the scaling for the lower viscosity solvents and the dilute solution results in 1-methyl-naphthalene, the fracture strain rate in the oligomer would be predicted to occur at a fracture strain rate which is 10.6% of the fracture strain rate in the 1-methyl-naphthalene. Since the average orifice velocity is directly proportional to the strain rate, the critical average orifice velocity for the onset of degradation is also predicted to be 10.6% of the original critical velocity (71.1 m/s).
Several experiments are performed over the range of average orifice velocities used for the 1-methyl-naphthalene solutions. The scission yield curves for the Boger fluid is shown in Figures 6.16 and 6.17, with the data points from the dilute solution in 1-methyl-naphthalene also included for reference. It is obvious that the Boger fluid has an onset of degradation much earlier than predicted by the previously determined scaling law.

The large amount of scission seen in the Boger fluid solution is illustrated in a plot of the scission index versus the average orifice velocity (Figure 6.18). The scission index is a measure of the number of bonds broken per initial chain. While the highest level achieved with the 1-methyl-naphthalene solutions is approximately 0.75 in the concentrated solution, the scission index for the Boger fluid is greater than one for low average orifice velocities \( (v_o > 0.4 \text{ m/s}) \). On average, more than one bond is broken for each chain in the distribution. The scission index reaches a maximum of 16.25 for an average orifice velocity of 50.8 m/s.

The molecular weight distributions of the degraded Boger solutions show that a large proportion of the initial distribution has been degraded and a series of low molecular weight peaks have been formed. Figure 6.19 shows a chromatogram for the Boger solution degraded at an average orifice velocity of 2.54 m/s. The lines correspond to individual peaks and occur at the following molecular weights: a) \( 1.30 \times 10^6 \); b) \( 6.92 \times 10^5 \); c) \( 3.99 \times 10^5 \); d) \( 1.44 \times 10^5 \); e) \( 7.40 \times 10^4 \). In dilute solution, nearly central scission is expected. These molecular weights roughly correspond to the peak values which would be obtained by an integer number of breaks for a chain with the peak molecular weight. The monodisperse chromatogram has a peak molecular weight of \( 1.03 \times 10^6 \). Repeated exact central scission would result in molecular weights of \( 5.15 \times 10^5 \) (1 scission event); \( 2.57 \times 10^5 \) (2 scission events); \( 1.29 \times 10^5 \) (3 scission events; and \( 6.43 \times 10^4 \) (4 scission events). The differences between the values on the Boger fluid chromatogram and the values predicted from the undegraded monodisperse sample result from two factors. First, the
sample is not perfectly monodisperse, and some broadening is expected since there are some chains cleaved which have molecular weights above or below the peak molecular weight. Second, the conversion of GPC output to molecular weight for the Boger fluid is not as exact as for the 1-methyl-naphthalene samples. The output from the GPC directly depends on the coil size in solution. With the 1-methyl-naphthalene solutions, the solvent is evaporated off in a vacuum oven. The solid polymer sample is then dissolved in THF and the MWD is measured. This procedure is impossible with the Boger fluid, since the vapor pressure of the oligomer is so high. Instead, the Boger fluid is diluted with THF in a 4:1 ratio. The polystyrene coil size will be modified by the presence of the two solvents. The addition of the oligomer will improve the solvent quality and increase the coil size in solution (Solomon and Muller, 1996). With an increased coil size in solution, the measured molecular weight will be slightly greater than the calibrated molecular weight.
Figure 6.1 Chromatogram of monodisperse polystyrene. The output before and after correction for axial dispersion is shown above. The sample has the following molecular weight averages: $M_w = 1.065 \times 10^6$, $M_n = 1.035 \times 10^6$, $M_w/M_n = 1.029$, $M_z = 1.094 \times 10^6$. 
Figure 6.2 Comparison of chromatograms for Styron 666D and the monodisperse polystyrene sample. The outputs from the chromatograms are modified such that the peak maximum for both curves is 1.0.
Figure 6.3 Location of monodisperse polystyrene solutions on a concentration-molecular weight diagram of viscoelastic regimes for polystyrene in a good solvent (Graessley, 1980).
Figure 6.4 Scission yield versus average orifice velocity. The scission yield is defined as the percentage of the degraded chromatogram which is at molecular weights lower than those present in the undegraded chromatogram.
Figure 6.5 Drop in $M_n$ for the three solutions as a function of the average orifice velocity. The reduction in $M_n$ is directly related to the number of bonds broken. The entanglements in the concentrated solution cause increased chain scission compared to the dilute and semidilute solutions.
Figure 6.6 Drop in $M_n$ for the concentrated monodisperse polystyrene solution. The reduction in $M_n$ versus the average orifice velocity follows a logarithmic dependence.
Figure 6.7 Change in the $z$-average molecular weight as a function of average orifice velocity. $M_z$ drops as much as 27.5% after one pass through the high extension rate zone.
Figure 6.8 Scission index versus average orifice velocity. The scission index is defined as the number of bonds broken per initial chain. The scission index is calculated from the change in the number-average molecular weight. The change in the scission index as a function of the average orifice velocity is different for the three different solutions.
Figure 6.9 Change in the polydispersity as a function of the scission index. The number-average molecular weight is independent of the degradation mechanism, but the weight-average molecular weight is sensitive to the position of the broken bond. The relative change in the polydispersity versus the scission index allows inferences about the randomness of the degradation process. All three solutions are cleaved preferentially near the center of the chain. The lines are predictions for a similar system (Nguyen, 1997).
Figure 6.10 Relative change of $M/M_n$ with scission index. The number-average molecular weight is independent of the degradation mechanism, but the $z$-average molecular weight is sensitive to the position of the broken bond.
Figure 6.11 Chromatogram of sample degraded in dilute solution in the fast transient extensional flow. Even though the chain does not completely uncoil, it is still cleaved near the center of the chain. The ratio of the peak molecular weights for the two curves is 1.97. The two peaks are fit with Gaussian peaks. The experimental curve is the composite of the two Gaussian curves.
Figure 6.12 Chromatograms of samples degraded in semidilute solutions in the fast transient extensional flow. As the average orifice velocity is increased, there are an increasing number of chains broken. A new peak, with a molecular weight approximately one half of the starting material grows in area as the degradation proceeds.
Figure 6.13 Differential gel permeation chromatography (DGPC) of samples degraded in semidilute solutions in the fast transient extensional flow. New chains are generated with high molecular weights, indicating that chains are ruptured near the center. With an average orifice velocity greater than 71.1 m/s, there are two scissions per chain for the longest chains and a new peak is generated at lower molecular weights.
Figure 6.14 Chromatograms of samples degraded in concentrated solutions in the fast transient extensional flow. As the average orifice velocity is increased, there are an increasing number of chains broken. The peak progressively shifts to lower molecular weights.
Figure 6.15 Differential gel permeation chromatography (DGPC) of samples degraded in concentrated solutions in the fast transient extensional flow. New chains are generated with high molecular weights, indicating that chains are ruptured near the center. With an average orifice velocity greater than 71.1 m/s, there are two scissions per chain for the longest chains and a new peak is generated at lower molecular weights.
Figure 6.16 Scission yield for the two dilute solutions. There is significantly more degradation in the Boger fluid compared to the 1-methyl-naphthalene solution. The x-axis is logarithmic, since the average velocity varies over a wide range.
Figure 6.17 Scission yield for the Boger fluid versus centerline strain rate. The predicted onset is calculated from the previous scaling law (Nguyen and Kausch, 1990).
Figure 6.18 Scission index for the Boger fluid versus average orifice velocity. A logarithmic x-axis is used, since the average velocity varies over a wide range. The dilute solution in 1-methyl-naphthalene is included for reference. Even at the lowest average velocities, there is more than one bond broken per initial macromolecule.
Figure 6.19 Chromatogram of the Boger fluid after degradation at an average orifice velocity of 2.54 m/s. The lines correspond to individual peaks and occur at the following molecular weights: a) $1.30 \times 10^6$; b) $6.92 \times 10^5$; c) $3.99 \times 10^5$; d) $1.44 \times 10^5$; e) $7.40 \times 10^4$. The monodisperse chromatogram has a peak molecular weight of $1.03 \times 10^6$. Repeated exact central scission would result in molecular weights of $5.15 \times 10^5$ (1 scission event); $2.57 \times 10^5$ (2 scission events); $1.29 \times 10^5$ (3 scission events); and $6.43 \times 10^4$ (4 scission events).
CHAPTER 7

THERMAL DEGRADATION

7.1 Background on thermal degradation

As noted in the Introduction, flow-induced degradation is a depolymerization reaction in which the activation energy is supplied by mechanical action on the polymer. Due to the stress distribution, extensional flow-induced degradation results in preferential scission of the longest chains in the distribution and scission near the center of the chain. To contrast flow-induced degradation with other degradation mechanisms, experiments are performed to analyze the thermal degradation of Styron 666D.

During processing, polymers are exposed to elevated temperatures in order to melt the solid pellets and reduce the viscosity to aid in processing. Vinyl polymers, such as polystyrene, are susceptible to thermal degradation. The temperature and residence time are the key parameters which determine the amount of degradation.

The thermal degradation of polystyrene proceeds by a free-radical chain mechanism. The rate of degradation depends on the method of synthesis, but after about 10% weight loss, all polystyrene degrades at the same rate. Most commercial polystyrene is synthesized in a free-radical polymerization. There are various temperature regimes for polystyrene degradation. The effect of thermal degradation on the molecular weight is evident at temperatures above 290°C. The molecular weight drops abruptly during the first
few percent loss of weight to approximately $8.0 \times 10^5$. Below this, the molecular weight decrease is gradual (Madorsky, 1964).

Polystyrene undergoes a slight decrease in the number average molecular weight, $M_n$, between 180 and 220°C. This drop is due to random scissions from weak links in the chain. After the initial chain cleavages, no further degradation occurs at temperatures below 250°C. Random chain scissions occur at approximately 1:10,000 structural units below 250°C (Guaita, 1986).

Little volatilization occurs at temperatures below 300°C. Between 280 and 300°C, free radicals are generated by random chain scissions. The free radicals can combine (no molecular weight reduction) or undergo disproportionation to produce a double bond on a chain end. There is no depolymerization (unzipping) below 300°C (Guyot, 1986). The C-C bond β to the double bond is weaker than normal polystyrene linkages and is the primary initiation site for thermal degradation above 300°C.

At temperatures greater than 330°C, volatile species evolve from all polystyrene samples. The three major components of the volatile mixture are the monomer, trimer, and dimer (Guaita et al., 1985). Between 330 and 450°C, the primary sites for radical generation become chain ends, not random chain scissions. Initiation at the chain ends results in a tolyl radical and a polystyryl radical. There are three different propagation reactions that lead to the formation of the monomer, dimer, and trimer from the polystyryl radical. Figure 7.1 sums up the temperature regimes for polystyrene degradation.

The atmosphere can have a profound effect on the rate and extent of polystyrene thermal degradation. Polymers heated in a vacuum exhibit less degradation than polymers heated in a gaseous atmosphere (even if neutral). When an atmosphere is present, diffusion of volatile products formed in the interior of the sample is retarded. These products can undergo secondary reactions before escaping the sample. The type of atmosphere also plays a role in the degradation mechanism. Polymers heated in an oxygen
atmosphere degrade faster than polymers in a neutral atmosphere. The activation energy for thermal degradation in O₂ at temperatures above 350°C is less than half of the activation energy in N₂. The polystyryl radical generated thermally reacts with O₂ 10⁶ times faster than with the polystyrene molecule. This reaction produces a peroxy radical, which rapidly attacks a 3° hydrogen on the polymer chain, forming a polystyrene hydroperoxide. The thermal decomposition of the hydroperoxide yields a variety of oxygenated species.

7.2 Thermal degradation experiments

To quantify the thermal degradation of polystyrene, small samples of Styron 666D (Dow) pellets are placed in a preheated oven. Small samples (approximately 3.5 g) are used to minimize thermal gradients. The samples form a layer approximately one pellet deep in an aluminum weighing dish. Four different tests are performed to identify the effect of temperature and atmosphere on the degradation of the polymer. The temperature setpoint is 200 or 250°C, and the atmosphere in the oven is air or nitrogen. Five samples are placed in the oven for each test. At the specified time (15, 30, 60, 120, or 180 minutes), a sample is removed from the oven. The oven atmosphere is purged after each sample is removed. The molecular weight distribution of the degraded samples is measured in the GPC, and the viscosity is measured with a rheometer.

7.3 Results from thermal degradation experiments

7.3.1 Molecular weight distributions

There are four sets of data from the thermal degradation study: 200°C and 250°C in both air and nitrogen atmospheres. The data is presented separately for each of these four categories. The GPC chromatograms for the tests are shown in Figures 7.2-7.5. The legends indicate the temperature, atmosphere, and time (minutes). There is a slight shift to
lower molecular weight with time for all samples. This shift is more pronounced for the higher temperature samples compared to the 200°C samples. The air samples have a greater shift than the nitrogen samples.

7.3.2 Differential gel permeation chromatography

It is difficult to compare chromatograms when there are slight differences, as in these plots. Therefore, the data is standardized with respect to elution volume, and the virgin chromatogram is subtracted from each test chromatogram. The differential chromatograms are shown in Figures 7.6-7.9. Differential GPC makes data comparison much easier. A value greater than zero indicates an excess of sample in the given molecular weight range. Similarly, a value less than zero means the sample has a deficit compared to the virgin polymer in the given molecular weight range. The standard deviation included in the plots is from a series of tests with the undegraded Styron samples. DGPC traces above this standard deviation indicate changes which are significant when compared to experimental scatter. For samples which are heated at a constant temperature and in a given atmosphere, increased time in the oven results in a shift to lower molecular weight as the residence time increases.

Figure 7.10 is a plot of the differential chromatograms from all four categories after 180 minutes in the oven. This plot allows comparisons between the different temperatures and the different atmospheres. Degradation, as measured by a shift in the chromatogram, is more pronounced at the higher temperature and is also greater in air as compared to nitrogen. The increase in temperature leads to a generation of a larger number of small chains, especially at the longest times. The increased scission in air compared to nitrogen is due to the lower activation energy and the increased reactivity of the peroxy radical. This plot is representative of all time intervals, although the differences at shorter time intervals are smaller.
7.3.3 Molecular weight decline

The average molecular weights of the samples are calculated from the chromatograms and are compared to the virgin polymer in Table 7.1 and Figure 7.11. The numbers are consistent with the chromatograms. The general trend of the data is a drop in molecular weight with time and minor differences between samples at the same time intervals. The decline in the weight average molecular weight is quite large. For both 250°C samples and the 200°C sample in air, $M_w$ drops more than fifty percent in the first fifteen minutes. After three hours in the oxidative environment, $M_w$ is as low as $1.6 \times 10^4$. The drop in the weight average molecular weight is not as large compared to the number average molecular weight. Therefore, the polydispersity increases with increasing degradation.

7.3.4 Viscosity decline

Figure 7.12 shows the zero shear viscosity of the samples. The viscosity is measured at 190°C using the Rheometrics RFS-II. After the initial drop from the virgin zero-shear viscosity, there is only a slight decrease in the viscosity. The approximate order of magnitude decrease in the zero shear viscosity after thirty minutes is probably due more to the volatilization of very low molecular weight plasticizers than to the reduction in the average molecular weight. There is no appreciable difference in the zero shear viscosity drop for the four experiments.

7.4 Conclusions

The results from the thermal degradation study are consistent with the above discussion of temperature regimes. At 200 and 250°C, the thermal degradation of polystyrene is random and no unzipping occurs. There is essentially no production of volatiles and the
average molecular weight declines. The reduction in the weight average molecular weight is relatively small. There is a greater reduction in the number average molecular weight, thus increasing the polydispersity. Since thermal degradation of polystyrene is random with respect to bond location, there are a large number of small chains generated. This is best noted from the positive deviations at low molecular weights in the DGPC traces.

The thermal degradation of polystyrene occurs by a vastly different mechanism than extensional flow-induced degradation. In the extensional flow experiments, there is preferential scission of the high molecular weight chains. These chains are broken near the center, even when entanglements are present. The nonrandom scission observed in extensional flow is in sharp contrast to a thermally degraded sample (Figure 7.13). The thermally degraded sample exhibits deviations from the undegraded sample over most of the distribution. Thermal degradation is a random process and results in the creation of various length chains. Extensional flow induced scission is similar to thermal degradation with respect to the kinetic treatment. The major difference between the two types of scission is the distribution of bond sites that become activated to the level of breakage. In thermal degradation, the distribution is uniform. All bond sites have an equal probability of becoming activated to a level which will cause scission. By contrast, in extensional flow induced degradation, there is a nonrandom distribution of activated bond sites caused by the concentration of stress at specific locations.

The DGPC traces provide insight into the degradation process. The maximum deviations in the DGPC traces of the thermally degraded samples are on the same order as for the extensionally degraded samples. However, the shape of the DGPC trace for the two samples are quite different. For the extensionally degraded samples, there is a negative deviation, thus chains broken, on the DGPC trace for molecular weights above $2.3 \times 10^3$. Extensional flow results in a preferential scission of the longest chains in the distribution. For some conditions, there is a critical molecular weight, above which all chains are
ruptured. In addition, chains are broken at or near the center, generating two new chains with relatively large molecular weights. The chromatograms for the extensionally degraded samples matches the undegraded chromatogram for molecular weights below $2-3 \times 10^4$ and sometimes up to much higher molecular weights. $M_w$ is more sensitive to changes in the molecular weight distribution, and changes more than $M_n$. As a result of the distribution of chains broken, the polydispersity of the degraded samples is lower compared to the undegraded sample.

The DGPC traces for the thermally degraded samples have a negative deviation, indicating chains broken, which is centered at molecular weights of $2-3 \times 10^5$. This molecular weight range is significant, because it is the region with the highest frequency of chains in the undegraded sample. Since the thermo-oxidative degradation of polystyrene is a random process, the molecular weight range with the largest number of chains is expected to have the largest deviation from the undegraded sample. There is no preferential scission of the longest chains in the distribution and no critical molecular weight. New chains are generated as a result of the degradation process. The molecular weight of the new chains is not restricted to high molecular weights, as for the extensionally degraded samples. For some samples, the DGPC trace is positive for molecular weights below the resolving power of the columns. Chains can break at any bond in the chain, including bonds near the ends of chains. There is a generation of very small chains due to the thermal degradation. $M_n$ is dramatically reduced compared to $M_w$, and the polydispersity attains large values.
Figure 7.1 Temperature regimes for polystyrene degradation. The molding temperature is 190°C for Styron 666D. There is a dramatic shift in the mechanism between 300 and 350°C.
Figure 7.2 Differential log MWD of thermally degraded polystyrene samples. The samples were placed in a 200°C oven with an air atmosphere for various times (minutes). The virgin chromatogram is included for comparison.
Figure 7.3 Differential log MWD of thermally degraded polystyrene samples. The samples were placed in a 200°C oven with a nitrogen atmosphere for various times (minutes). The virgin chromatogram is included for comparison.
Figure 7.4 Differential log MWD of thermally degraded polystyrene samples. The samples were placed in a 250°C oven with an air atmosphere for various times (minutes). The virgin chromatogram is included for comparison.
Figure 7.5 Differential log MWD of thermally degraded polystyrene samples. The samples were placed in a 250°C oven with a nitrogen atmosphere for various times (minutes). The virgin chromatogram is included for comparison.
Figure 7.6 Differential chromatogram of thermally degraded polystyrene samples. The samples are placed in a 200°C oven with an air atmosphere for various times (minutes). The virgin chromatogram is subtracted from the individual chromatograms to highlight differences.
Figure 7.7 Differential chromatogram of thermally degraded polystyrene samples. The samples are placed in a 200°C oven with a nitrogen atmosphere for various times (minutes). The virgin chromatogram is subtracted from the individual chromatograms to highlight differences.
Figure 7.8 Differential chromatogram of thermally degraded polystyrene samples. The samples are placed in a 250°C oven with an air atmosphere for various times (minutes). The virgin chromatogram is subtracted from the individual chromatograms to highlight differences.
Figure 7.9 Differential chromatogram of thermally degraded polystyrene samples. The samples are placed in a 250°C oven with a nitrogen atmosphere for various times (minutes). The virgin chromatogram is subtracted from the individual chromatograms to highlight differences.
Figure 7.10 Differential chromatograms of 180 minute samples. Samples were at 200 and 250°C in air and nitrogen atmospheres. The virgin chromatogram is subtracted from the individual chromatograms to highlight the differences.
Figure 7.11 $M_w$ and $M_n$ for thermally degraded polystyrene as a function of heating time. The molecular weight decline is minimal and there is little difference between the individual samples.
Figure 7.12 Zero-shear viscosity for thermally degraded polystyrene as a function of heating time. After an initial drop, the viscosity does not change appreciably.
Figure 7.13 Differential chromatograms of Styron after thermal degradation and after extensional degradation. The preferential scission of the high molecular weight chains in the extensional flow is contrasted with the random mechanism of thermal degradation.
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Table 7.1 Average molecular weights for thermally degraded polystyrene. The weight average molecular weight declines slightly from the initial value, but the number-average molecular weight has a sharp decline. This increases the polydispersity of the degraded samples.
8.1 Background

The final results chapter focuses on a different application for the opposed pistons device. The system is used to analyze the effect of extensional flow on cell damage in a biological culture. Solutions are passed through the abrupt contraction and cell damage is quantified by a cellular-based assay. This chapter highlights the versatility of the experimental design. Similar techniques and analysis are used for a problem in a field completely separate from polymer science.

8.1.1 Scale up in stirred tank reactors

The scale-up of stirred tank reactors is as much an art as a science. The use of large scale microcarrier cultures has been limited, due in part to the lack of scale-up data. Successful scale-up to high density, large volume cultures requires an understanding on the hydrodynamics in the reactor. The hydrodynamics directly determine the overall performance of a cell culture. The flow field determines characteristics such as the circulation pattern, distribution of kinetic energy, and its rate of dissipation (Kresta and Wood, 1993). The optimum stirred tank culture would provide adequate mass transfer without damaging cells. There is a need for experiments with well-defined flow systems.
which can quantify the relationships between the flow field variables and cell damage (Merchuk, 1991).

Cell cultures as a rule are turbulent. Turbulence is necessary to provide a uniform mixing environment. Although the flow field in a turbulent stirred tank is quite complex, some well-defined structures are present. On the largest scales of length and time, overall circulation patterns can be identified. On a shorter time scale, the circulation pattern varies with time. The flow field variations can be broken down into a periodic component that is related to the rotation rate of the turbine and a second component that is related to the turbulent variations from the mean velocity (Rao and Brodkey, 1971).

Traditionally, scale-up has been based on correlations of overall average vessel parameters. These approaches do not provide any insight on the local mixing phenomena. Mapping of the flow field in a stirred tank proved that the energy input from the impeller is not uniformly distributed. In a stirred tank, the impeller is the channel for the introduction of power into a system. At the edge of the impeller blades, high velocity gradients exist which result in efficient mixing. These gradients can also result in cell damage. Van't Riet and Smith (1975) identified a trailing vortex pair in a turbine-stirred vessel. Calabrese and Stoots (1989) used laser Doppler anemometry to accurately map the flow field immediately adjacent to the blades. There are high velocity gradients and a high dissipation of energy in this region due to the vortices. Wu and Patterson (1989) performed an energy balance around the impeller and showed that approximately sixty percent of the energy is dissipated in the impeller region and stream, although this volume was only nine percent of the total volume. Therefore, the energy dissipation rate in this region is fifteen times higher than in the bulk. Venkat et al. (1996) used particle tracking velocimetry to characterize the flow field in the impeller region of cell culture vessels. Isolated flow regions were identified which had local energy dissipation rates which exceeded values based on impeller power
draw per unit mass by an order of magnitude. The nonhomogeneity of the flow field requires that these factors be considered when scale-up calculations are performed.

8.1.2 Cell damage as a function of deformation type

Cell damage in microcarrier culture has been studied by numerous researchers (O'Connor and Papoutsakis, 1992; Mufti and Shuler, 1995; Cherry and Papoutsakis, 1988; Lakhota and Papoutsakis, 1992). It has been proven that excessive agitation causes cell damage. These studies have been performed in spinner vessels. Cell damage is extensive when the smallest eddy size is comparable to the microcarrier beads. Croughan and Wang (1989) investigated hydrodynamic effects on cells in microcarrier cultures. At mild agitation levels, there was no change in net cell growth. At high agitation rates, there was extensive removal of the cells from the microcarriers. Removal of the cells was noted to be irreversible and lethal. The removal of cells increased with the level of agitation, indicating removal was due to hydrodynamic forces. However, cell removal was random and was not a function of mitotic index. Since mitotic cells are more rounded, they experience a higher torque than a flattened interphase cell when exposed to a shearing force. If cell removal was caused by shear stresses, cell removal would be preferential for mitotic cells. Since cell removal was random, Croughan and Wang hypothesized that it occurred primarily through normal forces. The importance of extensional flow was also noted in studies on suspended cell hydrodynamic damage (McQueen et al., 1987; McQueen and Bailey, 1989). Garcia-Briones and Chalmers (1994) also studied the flow field in the bubble rupture process. The region just below the collapsing bubble was observed to have a high extensional character.
8.2 Application of opposed pistons apparatus to cell culture experiments

This work tests the hypothesis that there are two important parameters which determine cell detachment caused by hydrodynamic forces. The first important variable is the rate of energy input to the microcarrier. The final parameter is the type of flow to which the cells are exposed. Microcarrier solutions are cycled through an opposed piston, sharp contraction flow. The viability of the cells are assessed after testing under controlled conditions. It is the goal of this simulation work to quantify the important flow variables in a control volume representative of the experimental flow field. The values of the two variables are calculated along streamlines through the flow field. Since particles follow streamlines, this provides an indication of the type and magnitude of the forces to which a microcarrier is exposed when flowing through the opposed pistons device. These forces are related to the cell viability and predictions of microcarrier detachment forces.

8.3 Experimental

8.3.1 Extensional flow experiments

Chinese hamster ovary (CHO) cells are used as a representative cell line. CHO cells are ideal as a model system, since they are robust and are widely used to produce recombinant proteins. Details of the CHO cell culture are given in the thesis of Gregoriades (1997). Typically, one to three cells are expected to attach to each microcarrier. The cells then multiply and completely cover the surface of the microcarrier. Flow experiments are performed when the microcarrier culture is at least 90% confluent.

Cell cultures are exposed to an extensional flow in an opposed pistons, contraction flow apparatus. The apparatus consists of two mutually opposed pistons which are cycled in phase by a hydraulic system. The pistons force the culture through high pressure tubing (1.27 cm diameter, 35.56 cm long) and across a short capillary, subjecting the cells to an
impulse jump in strain rate. There are two contraction ratios available: 10:1 and 20:1. By varying the speed and orifice insert, approximately two decades of strain rates are reached (centerline maximum strain rates from $3.48 \times 10^2$ to $1.18 \times 10^5$ s$^{-1}$). The experimental parameters are listed in Tables 8.1 and 8.2. Experiments indicate that delay time has a dramatic effect on the absorbance readings. The pH in the solution changes rapidly when the media is not oxygenated. Therefore, samples are removed from the spinner flasks just before the experiments are performed, and the cells are spun down directly after the experiments are completed.

8.3.2 Quantification of cell damage

To quantify cell damage, a lactate dehydrogenase (LDH) based assay (Sigma) is used. This assay measures the amount of cytoplasmic LDH that is leaked into solution after a cell membrane is damaged. LDH readings are measured on a spectrophotometer with a 490 nm light source. A standard curve relating absorbance to cell concentration is constructed (Gregoriades, 1997). The absorbance is directly proportional to the cell concentration for absorbances less than 1.4 (Figure 8.1). After experiments are performed in the opposed pistons device, the samples are collected and a small portion is tested using the LDH assay. The samples are diluted as necessary to ensure that the absorbance readings are below 1.2. Since there is some free LDH in the medium in a healthy culture, this background must be subtracted to obtain the increase in LDH due to cell damage. To compensate for the increase in medium LDH with culture age and density, two reference samples are set aside before each set of experiments. The first sample is centrifuged coincident with the first experiment and the supernatant is separated from the cells. This sample sets the baseline LDH at the beginning of the experiments. The second sample is tested after all experiments have been performed and sets the baseline at the end of the experiments. A linear relationship between the background LDH is subtracted from the experimental samples.
Therefore, the increase in LDH occurs only due to hydrodynamic-induced damage. An additional sample is sonicated so that all cell membranes are ruptured. The LDH level of this sample represents complete lysis.

8.3.3 High shear rate experiments

Experiments are performed in a Couette geometry to test the hypothesis that simple shear flow, even at high shear rates, is ineffective in damaging microcarrier cultures. Samples are placed in a Couette cell on a Rheometrics RMS-800 (Figure 8.2). The bottom cup is kept in motion at a shear rate of 45 s\(^{-1}\) during the addition of the culture to minimize microcarrier settling. The dimensions of the Couette cell are the following: bob diameter = 32.0 mm; cup diameter = 34.0 mm; bob length = 32.0 mm. When properly loaded, the volume in the gap is approximately 3.32 ml. To maximize the amount of sample in this region, which will see the highest shear rates, only 7.0 ml is added to the cup. Thus, approximately 50% of the sample is in the high shear rate region. The bottom of the bob is recessed, and the bob traps an air bubble when it is lowered into the sample. The material at the bottom of the cup experiences a lower shear rate than the material between the cup and bob. Tests are performed at a constant shear rate for different times. The shear rates tested in the Couette cell were at 1750 s\(^{-1}\). Times ranged from 1 s to 60 s.

To achieve higher shear rates, samples are also tested in a 50 mm parallel plate geometry. The advantage of the parallel plate geometry is that the shear rate can be varied by one of two means: changing the rotation rate of the bottom tool or decreasing the gap. Shear rates up to 8350 s\(^{-1}\) are possible in this geometry (gap = 0.299 mm). The gap separation is limited by the size of the microcarriers. At the smallest gap separation, microscopic analysis after the experiment did not identify any damage to the microcarriers. The Reynolds number, based on the cup and bob radii and the rotation rate, is calculated to
verify that there was no turbulence during the experiments. The LDH assay is used to quantify the percentage of cell damage resulting from the high shear rate tests.

8.4 Flow field modeling

The flow field on a local level determines the type of flow to which cells are exposed. The mechanism of fluid deformation is vital and determines the intensity of cell culture damage as a function of the hydrodynamic forces. The response to flow depends on the type of flow field.

There are two parameters which are hypothesized to be directly related to flow-induced cell damage. The first important variable is the rate of energy input to a microcarrier. It is assumed that the energy input to a fluid element is passed to a microcarrier that is in the control volume of the element. Augenstein et al. (1971) noted a correlation between cell death and the energy input rate. The rate of energy input is not sufficient to impose deformation and result in cell damage. The second parameter is a measure of the effectiveness of the input energy, as expressed by the type of flow. A FORTRAN program is used to calculate the effective rate of energy input along a streamline in the flow field. The effective energy input rate is calculated from two variables: the dissipation function and a normalized scalar which quantifies the effectiveness of energy input.

8.4.1 Entry flow analysis

The flow in the inlet of a pipe is a subject which has been extensively studied. Langhaar (1942) provided an approximate solution for the flow in the inlet of a pipe. The Navier-Stokes equations are solved with the aid of a linearizing approximation for the case of steady flow in the transition length of a pipe. A family of velocity profiles is expressed in terms of Bessel functions. For a constant inlet velocity ($U_0$), the velocity at any downstream position ($U_x$) is given by the following:
\[
\frac{U_x}{U_o} = \frac{I_0(\gamma) - I_0(\gamma r/r_o)}{I_2(\gamma)}
\]  

(8.1)

where \( \gamma \) is a dimensionless parameter, \( r \) is the radius, and \( I_0 \) and \( I_2 \) are Bessel functions of the first kind, of order zero and two, respectively. When a uniform flow enters a pipe, there is some distance required for the flow to assume its fully developed velocity profile. This distance is termed the entrance length (Figure 8.3).

Langhaar's solution for the developing velocity profile is input into an Excel spreadsheet and the normalized velocity at four different axial positions is obtained, using twenty data points for each velocity. The dimensionless velocity profile is the same for all contractions. Profiles for piston velocities of 0.254 cm/s and 10.2 cm/s runs are shown below in Figures 8.4 and 8.5. The volumetric flow rate for these two piston speeds is 0.322 and 12.9 cm/s, respectively. The transient velocity profiles show that the short orifice length (0.159 cm) is insufficient for the development of a steady state velocity profile. Instead, most of the flow passes through the orifice in a plug, with a high shear rate zone near the walls. As the flowrate is increased, the profile becomes more plug-like in nature.

In the inlet flow problem, the initial plug flow velocity profile at the entrance is transformed into a parabolic profile as described by the Hagen-Poiseuille equation. Viscous friction at the walls will cause a boundary layer to be formed at the walls. The effect of viscous shear force from the wall propagates toward the center of the pipe, increasing the boundary layer thickness and changing the velocity profile. A cross section of the pipe shows a velocity profile which consists of two growing boundary layers at the walls joined by a central, constant velocity region. Downstream, the boundary layers merge into one another and the velocity profile is parabolic. At the entrance length, the flow is fully developed and the velocity profile does not change. Before this point, the flow can be divided into two portions: the boundary layer and the unsheared core region.
The maximum boundary layer thickness occurs at the back edge of the orifice. The velocity profile at this location was analyzed to determine the percentage of cells which pass through the orifice in the unsheared core region. The radius at which the velocity dropped to ninety-nine percent of its centerline value was chosen as the limit for the unsheared core region. The percentage of cells in the unsheared core region was calculated by the following formula:

\[
\text{% cells in unsheared core} = \left( \frac{r}{R} \right)^2 \times 100\%
\]  

(8.2)

Figure 8.6 plots the percentage of cells in the unsheared core region versus the average upstream velocity. As expected, the amount of cells in the plug flow region increases with increasing velocity.

The shear rates for the different experiments as a function of radius are calculated from the derivative of the dimensionless flow profiles:

\[
\frac{d}{dr} \left( \frac{U}{U_0} \right) = \frac{r_0}{U_0} \frac{dU}{dr} = \frac{r_0}{U_0} \dot{\gamma}
\]

(8.3)

The shear rate for a fully developed flow is linear with respect to radius. The shear rate is zero only at the centerline. For the transient velocity profiles, the shear rate is zero in the entire core region. For radii greater than the plug flow region, the shear rate is nonlinear with radius and is fit with a cubic equation.

\[
\frac{r_0}{U_0} \dot{\gamma} = M_0 + M_1 \left( \frac{r}{r_0} \right) + M_2 \left( \frac{r}{r_0} \right)^2 + M_3 \left( \frac{r}{r_0} \right)^3
\]

(8.4)

The cubic parameters and the limiting radius for different average velocities are listed in Table 8.3. Shear rates at selected radii are listed in Table 8.4. Shear rate profiles for two average velocities are shown in Figure 8.7.
8.4.2 Verification of laminar flow in orifice

In fully developed pipe flow, the flow is either laminar or turbulent throughout the length of the pipe, depending on the Reynolds number. In the entrance to a pipe, there is a length necessary to obtain a fully developed flow profile. In a boundary layer, the upstream flow is always laminar, but depending on the Reynolds number, an increasing portion of the downstream flow is turbulent. For pipe flow, at small distances from the inlet, the boundary layer will grow in the same way as it does along a flat plate at zero incidence (Schlichting, 1955). The development of the boundary layer on a flat plate illustrates the transition from laminar to turbulent flow. At a sufficiently high Reynolds number, the boundary layer becomes turbulent at the trailing edge of the plate. As the Reynolds number is further increased, the boundary layer becomes turbulent further upstream (Figure 8.8). The Reynolds number based on the plate at which boundary layer turbulence first appears at the trailing edge is the critical Reynolds number. The critical Reynolds number depends on the surface roughness and external disturbances, but a value of 5x10^5 is reasonable (Mironer, 1979).

\[ N_{Re,z} = \frac{z U_o \rho}{\mu} \]  \hspace{1cm} (8.5)

The Reynolds number is calculated at the trailing edge of the orifice for all of the experimental runs. The Reynolds number at the trailing edge of the orifice for the highest piston velocity (10.2 cm/s) is 1.34x10^4 and 5.38x10^4 for the 10:1 and 20:1 contractions, respectively. Since these values are well below the critical Reynolds number at which the boundary layer undergoes the laminar to turbulent transition, all experiments are performed solely in the laminar regime.
8.5 Results

8.5.1 Simulation results

Extensional flow is restricted to a small portion of the flow domain. Most of the fluid acceleration occurs approximately one orifice diameter upstream of the contraction. This rapid change in the velocity results in an impulse jump in the strain rate. The dependence of the centerline strain rate on volumetric flow rate and contraction ratio can be examined by defining dimensionless strain rate and axial position. The dimensionless strain rate is defined below, with \( \bar{v} \) and \( r_o \) the average orifice velocity and radius, respectively.

\[
\overline{e} = \frac{r_o}{v_o} \left( \frac{v^*}{v_o} \right)
\]

The dimensionless strain rate increases from approximately zero at an axial position approximately two orifice radii from the front edge of the orifice to a maximum just before the entrance to the orifice. At this point, the fluid elements are in a strong, uniaxial extensional flow. The simulation results for different runs collapsed onto a master curve after a dimensionless strain rate and axial coordinate were defined (Figure 8.9). The constant of proportionality varied depending on the contraction, but was constant for a given contraction ratio (10:1 = 0.87; 20:1 = 0.93). The axial coordinate origin (z = 0) is defined at the leading edge of the orifice. The high velocity gradients near the entrance to the orifice also makes this the region with the largest values for the dissipation function. The centerline strain rates and the centerline dissipation rates are given in Table 8.5.

8.5.2 Qualitative cell damage from microscopy analysis

The microcarriers are examined under a microscope before and after experiments to analyze the confluence of the culture. As the piston speed increases, more microcarriers are
bare and there is an increase in cell debris. Pictures of four cultures are shown in Figures 8.10 and 8.11.

8.5.3 Cell damage from absorbance assay

A qualitative measure of cell damage is obtained from the LDH assay. Since the absorbance is directly proportional to the cell concentration, direct comparison can be made. Results from the LDH assay are shown in Figures 8.12-8.14. Similar to the results with the polymer solutions, the 20:1 contraction results in significantly more damage compared to the 10:1 contraction.

The percentage of cells removed was calculated from the absorbances based on the following formula:

\[
\% \text{ cells damaged} = \frac{\text{Abs}_{\text{exp}} - \text{Abs}_{\text{bl}}}{\text{Abs}_{\text{cl}} - \text{Abs}_{\text{pl}}} \tag{8.7}
\]

where the subscripts refer to the following: exp = cells degraded in opposed pistons experiment; bl = baseline; cl = complete lysis. Differences in the scaling between experiments performed on different days are probably due to differences in cell confluence, different delay times between experiments and the LDH assay, and nonlinearities for samples with high absorbances. Table 8.6 summarizes the results from the experiments.

8.5.3.1 Cell damage related to effective energy dissipation

The dissipation function is the rate of energy input to a volume element. The flow character is the effectiveness of the input energy. The effectiveness of energy input is defined as follows:

\[
E = (1 - W) \tag{8.8}
\]

Therefore, a pure extensional flow is one hundred percent effective in channeling energy to a microcarrier (W = 0), while a simple shear flow is ineffective in channeling energy to a microcarrier (W = 1). When the effectiveness of energy input is combined with the rate of
energy input, the maximum energy input rate occurs at the centerline, just before the entrance to the orifice. The dissipation function maximum along the center streamline can be obtained from the maximum strain rate and the viscosity. For a pure extensional flow,

\[ \dot{\varepsilon} = D_{22} = -2D_{11} = -2D_{33} \]  
\[ D_{12} = 0 \]

(8.9)  
(8.10)

With these substitutions, the dissipation function simplifies to:

\[ \Phi_{el} = 3\mu\dot{\varepsilon}^2 \]  
(8.11)

The percent cells damaged as a function of the maximum effective rate of energy input is shown in Figure 8.15.

8.5.4 Cell damage from high shear rate experiments

The percentage of cells damaged in the high shear rate experiments is shown in Figures 8.16 and 8.17. There is a low percentage of cell damage from the high shear rate experiments. Due to experimental limitations, the shear rates obtained with the RMS-800 cannot reach the values to which the cells are exposed as they flow through the opposed pistons device. However, the flow field developed in the Couette gap exposes all cells to a constant shear rate, as contrasted with the entry flow problem in which a small percentage of cells are exposed to the high shear rates. In addition, the high shear rate experiments expose cells to high shear rates for much longer times than in the opposed pistons device. If shear forces were as effective as extensional forces in causing cell damage, there would be a significantly higher level of cell damage due to the increased residence time in the Couette geometry.

8.6 Conclusions

This work attempts to highlight the importance of the local hydrodynamics on microcarrier culture damage. Improved flow field mapping techniques have identified
regions in a stirred tank where the local rate of energy dissipation is much higher than the overall average. It is hypothesized that it is these regions of high gradients and a strong extensional flow character that result in hydrodynamic damage. Scale-up based on overall averages does not accurately reflect the local nature of the flow field. Controlled experiments which can measure cell damage as a function of these local flow field parameters may be able to provide new insights on the damaging effects of agitation and enable improved scale-up approaches.

In this experiment, microcarrier cultures of Chinese hamster ovary cells are subjected to a fast transient extensional flow in an opposed pistons apparatus. Cell cultures are pumped across a sharp contraction, imposing a high strain rate over a short spatial distance. This flow field is used since previous research has indicated that extensional flows are responsible for causing damage in microcarrier cultures. Flow field simulations are performed to relate the hydrodynamic conditions to cell damage. The rate of energy input and the effectiveness of the energy input (as represented by a scalar flow parameter) are calculated throughout the flow field. Cell damage is quantified by a lactate dehydrogenase enzyme assay and is related to the imposed flow conditions.

The flow across the sharp contraction attempts to mimic the flow near the impeller region in a stirred tank reactor. As in the commercial reactor, there is an unequal dissipation of kinetic energy. There is a small region with very high velocity gradients and a large energy dissipation. In addition, the flow near the entrance to the contraction has a high extensional character. Without the freedom to rotate away from high forces, cells are ripped off of the surface of the microcarriers. There is a small amount of damage for low energy input rates, but the culture damage rises sharply when the centerline rate of energy input becomes greater than $5 \times 10^7$ erg/cm$^3$s. This value corresponds to a power input of 500 W/l. This value is representative of the centerline streamline. Off of the centerline, the flow has an increasing shear character and the effective dissipation function is lower.
Therefore, cell damage probably occurs at an onset value approximately one order of magnitude lower. The microcarriers have an average diameter of 170 μm. Assuming the microcarriers do not alter the radius appreciably, the volume of a microcarrier covered with cells is $2.57 \times 10^{-6}$ cm$^3$. Based on an energy input rate of $5 \times 10^7$ erg/cm$^3$s, a microcarrier has approximately 130 erg/s input from the flow field.
Figure 8.1 Calibration curve relating absorbance to cell concentration. Cell membrane rupture is quantified by a lactate dehydrogenase-based assay. The cell concentration is independently measured with a hemocytometer (Gregoriades, 1997).
Figure 8.2 Couette geometry used for high shear rate tests. Cells are tested in the Couette geometry to quantify the effect of simple shear flow on cell damage.
Figure 8.3 Boundary layer formation at the entrance to a pipe. The entry length is a function of the Reynolds number.
Figure 8.4 Transient velocity profiles for 0.254 cm/s experiments. A fully developed velocity profile has a centerline velocity equal to twice the average velocity. Profiles are shown for three different positions in the capillary. $z$ represents the axial position and $l$ the length of the capillary. The short length of the capillary is not sufficient to produce a fully developed velocity profile.
Figure 8.5 Transient velocity profiles for 10.2 cm/s experiments. A fully developed velocity profile has a centerline velocity equal to twice the average velocity. Profiles are shown for three different positions in the capillary. $z$ represents the axial position and $l$ the length of the capillary. At this piston velocity, a large majority of the material is in the unsheared core region and is not exposed to high shear rates.
Figure 8.6 Percentage of flow in unsheared core region, as calculated from the transient velocity profile at the back edge of the orifice. The plug flow region increases with increasing average velocity.
Figure 8.7 Dimensionless shear rate profiles for two different average velocities. The shear rate profiles are calculated from the derivatives of the transient velocity profiles.
**Figure 8.8** Transition from laminar to turbulent flow in the boundary layer. The transition from a laminar to a turbulent boundary layer depends on the plate Reynolds number.
Figure 8.9 Dimensionless centerline strain rate for 10:1 and 20:1 simulations. The simulations for different flowrates converge onto a master curve after dimensionless strain rate and axial position are defined.
Figure 8.10 Qualitative cell damage is seen in pictures of the cell culture after experiments. Cell damage is noted by an increase in cellular debris and a larger proportion of microcarriers that are not confluent.
Figure 8.11  Qualitative cell damage is seen in pictures of the cell culture after experiments. Cell damage is noted by an increase in cellular debris and a larger proportion of microcarriers that are not confluent.
Figures 8.12 Quantitative cell damage is measured by an LDH-based assay. The amount of LDH in the medium is directly proportional to the concentration of cells which have damaged membranes. To subtract background LDH, control cultures are tested before and after the experiments. An additional sample is sonicated to rupture all cell membranes, generating a complete lysis reference. The experiments are with a 10:1 contraction.
Figures 8.13 Quantitative cell damage is measured by an LDH-based assay. The amount of LDH in the medium is directly proportional to the concentration of cells which have damaged membranes. To subtract background LDH, control cultures are tested before and after the experiments. An additional sample is sonicated to rupture all cell membranes, generating a complete lysis reference. The experiments are with a 10:1 contraction.
Figures 8.14 Quantitative cell damage is measured by an LDH-based assay. The amount of LDH in the medium is directly proportional to the concentration of cells which have damaged membranes. To subtract background LDH, control cultures are tested before and after the experiments. An additional sample is sonicated to rupture all cell membranes, generating a complete lysis reference. The experiments are with a 10:1 and 20:1 contraction.
Figures 8.15 Cell damage related to the maximum effective rate of energy input. The percentage of cells damaged in the fast transient extensional flow is calculated from an LDH-based assay. The maximum effective rate of energy input is calculated from the extension rate at the centerline. There is a sharp rise in the percentage of cells damaged when the maximum effective rate of energy input is greater than $10^7$ erg/cm$^3$·s.
Figures 8.16 Cell damage as a function of shear rate for the Couette studies. Cells are subjected to a high shear rate for one second. Due to instrument parameters, approximately fifty percent of the material is between the concentric cylinders, while the remainder is in the bottom of the cup in a lower shear rate zone.
Figures 8.17  Cell damage as a function of time for the Couette studies. Cells are subjected to a shear rate of $1750 \text{ s}^{-1}$ for varying times. Due to instrument parameters, approximately fifty percent of the material is between the concentric cylinders, while the remainder is in the bottom of the cup in a lower shear rate zone.
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CHAPTER 9

CONCLUSIONS AND RECOMMENDATIONS

9.1 Summary of experimental work

Flow-induced macromolecular scission is a chemical depolymerization in which the activation energy is supplied by mechanical forces. When a polymer solution is placed in a velocity gradient, there is asymmetry in the exchange of momentum between the flowing solvent and different parts of the chain. This imbalance of forces results in tensions on a molecular scale and stress concentration at a particular location. A polymer responds to the application of stress by chain orientation, disentanglement, and bond rupture. The relative importance of each of these mechanisms changes with the structure, the state of aggregation, and the molecular weight of the polymer.

The type of flow has a profound effect on the stress transfer and efficiency of degradation. Polymer conformation and flow induced degradation are very different in shear and extensional flows. Random coils are deformed to a much greater extent in extensional flows, due to the lack of vorticity. Extensional flows are prevalent in polymer processing operations, but their effect on polymer degradation is not well understood. The critical parameters that affect degradation in solution include the strain rate, the initial molecular weight, and the concentration.
In many problems, the conformation of the microstructure is the most important feature of the system. Flow-induced changes in the microstructure can be dramatic and can directly result in changes in macroscopic properties of the system. It is important to understand the effect of the flow on the deformation of the microstructure. The effect of the flow on the microstructure is determined by combinations of the magnitude of the velocity gradient tensor, which represents the flow strength, and the ratio of the strain rate to vorticity, which represents the flow type.

The impetus for studying the degradation process is threefold. First, both mechanical and rheological properties are strongly affected by molecular degradation. Second, studying the variables that influence degradation will aid in improving designs to reduce degradation. Finally, if the amount of degradation and the residual properties can be predicted given the processing conditions, the use of the recycled material could be optimized.

Polymer degradation in an extensional flow is studied by subjecting polymer solutions to a fast transient extensional flow (FTF), using an opposed pistons apparatus. One of the identifying features of FTF, the short residence time in the high strain rate region, has a profound effect on the polymer conformation and chain scission. There is not enough time to accumulate strains large enough for full extension. Therefore, chains are fractured in a partially uncoiled state. Temporary junctions, formed from intermolecular and intramolecular entanglements, hinder polymer mobility in an extensional flow field and provide the necessary restrictions to cause chain scission.

9.2 Conclusions from fast transient flow studies

1. Chain entanglements and coil extension are prerequisites for molecular degradation of a polymer chain in a fast transient flow. Chain scission in a fast transient extensional flow results directly from the increase in stress as a constrained chain attempts to change its
conformation. The entanglements on a particular chain can be with other segments of the same chain (intramolecular) or with segments of other chains (intermolecular). Chain entanglements are not sufficient to cause chain scission in an extensional flow. Some of the chains must be extended in order to generate the forces required to break C-C bonds. There is no extensional flow-induced degradation for polymer solutions below a critical average orifice velocity. This extension rate at this velocity is below the coil-stretch limit for the chains in the distribution. All polymer chains pass through the sharp contraction without significant extension and without chain rupture. As the velocity gradient is increased, the chains begin to undergo the coil-stretch transition. This transition, beginning with the longest chains, leads to hindered chain relaxation, an increase in stress, and bond rupture.

2. The scission process in a fast transient extensional flow can result from intra- or intermolecular entanglements. The controlling mechanism depends on the concentration, chain length, the maximum extension rate in the high strain extension rate region, and the relaxation time of the chains. These last two properties can be combined to define a Deborah number (De) representative of the chains and the flow field. In a dilute solution, where chains are isolated, intermolecular entanglements are the only mechanism for chain rupture. When the velocity gradient in a fast transient extensional flow exceeds a critical limit, chains stretch and may break if they are constrained by entanglements. In a concentrated solution, there are both intra- and intermolecular entanglements. As a result, chain scission is greater in a concentrated solution compared to a dilute solution in the same flow field.

For a semidilute solution, fast transient extensional flow causes entanglements to be manifested at lower concentrations compared to conventional shear concentration limits. Peripheral coil contacts, which cannot disentangle in the short residence time of the high
extension rate zone act as effective entanglements. In the semidilute regime, the controlling mechanism for chain scission depends on concentration and the Deborah number (product of the maximum centerline extension rate and the relaxation time of chain). Chain scission at low De in a semidilute solution occurs by an intramolecular entanglement mechanism. Chain scission occurs at lower average orifice velocities compared to the dilute solution in part because the coil size is reduced in the semidilute regime. The scission mechanism changes when the velocity gradient reaches the critical limit where peripheral coil contacts do not have time to disentangle from one another. For the monodisperse semidilute solution, this transition is reached at an average orifice velocity of 81.2 m/s and a Deborah number of 1200. For higher average orifice velocities, chain scission in a semidilute solution occurs by a combination of intra- and intermolecular entanglements. The effective entanglements at the edge of the coils cause chain rupture. Since the semidilute solution has a reduced number of grip points compared to a concentrated solution, the scission yield is also reduced. With a smaller number of entanglements, a slightly higher strain rate is needed to degrade the polymer coils. The proposed mechanism of chain scission in entangled systems, in which chain segments cannot disentangle quickly enough to avoid scission, is in agreement with these results. At high De, the scission yield in a semidilute solution is similar to that in a concentrated solution.

3. The energy stored in a polymer chain is responsible for chain scission in a fast transient extensional flow. The energy input to the coil is far larger than the amount of energy required to cause bond breakage. However, only part of this energy is stored in a chain. This energy is distributed among several grip points. The combination of a high velocity gradient and a flow with a high extensional character causes disentanglement, reducing the number of grip points and increasing the load at each grip point. As the chain disentangles, the segments are exposed to an increasing velocity gradient and separate at a
faster rate. The remaining entanglements hinder chain relaxation and result in bond scission.

4. Extensional flow is highly effective in causing microstructure deformation and chain scission. The essential character of the flow field's effect on a material is the rate of rotation with respect to the direction of maximum stretch. The direction of maximum stretch is set by the principal axes of the rate of deformation tensor. If the largest rate of stretching is applied to the same material line, the microstructure can be significantly deformed. Purely extensional flows have zero vorticity, meaning materials do not rotate locally compared to the primary straining directions. Since a material line is aligned with the principal straining axes, the molecule uncoils and is aligned with the flow. The flow field character is described by a scalar parameter which quantifies the rotation rate of the rate of strain axes with respect to the fluid. This scalar parameter is mapped onto the flow field. There is pure extensional flow along the centerline in the flow through a contraction. The flow character is mixed for streamlines off of the centerline, with a high extensional flow character near the entrance to the small diameter capillary.

Studies of the extensional degradation of polymer solutions are important, since there is a strong extensional flow component in many flows, and extensional flows are much more efficient than shear flows in causing polymer scission. Chain scission can dramatically alter the physical properties of the polymer as a whole. FTF processes are often encountered in polymer processing and other operations. Some examples include entrance flows, ultrasonic fields, and turbulent drag reduction. Degradation studies in transient flow are useful for modeling polymer scission under real conditions where the short deformation time scale does not permit full chain extension.
5. The analysis of the entire molecular weight distribution after chain scission is an excellent technique for analyzing the chains which are ruptured and the products of chain scission. This information provides much more insight into the degradation mechanism compared to an analysis of the drop in the molecular weight averages. The shifts in the molecular weight distribution as a result of degradation can be difficult to discern from the complete chromatogram, but can be detected by subtracting chromatograms. This technique, known as differential gel permeation chromatography (DGPC), is ideal for examining degradation, since it can highlight the molecular weight region where fracture occurred.

The analysis of the MWD is performed using a series of programs written by the authors. This approach provides the needed flexibility to extract the maximum amount of information from the measurements. The programs convert the raw signal from the gel permeation chromatography apparatus into a MWD in a series of steps. The output is corrected for axial dispersion, and the volume is converted to molecular weight via a calibration curve. For DGPC analysis, the MWD are standardized and normalized with respect to volume and subtracted. For all samples, there is an average velocity and an extension rate below which there is no chain scission. After the onset of chain scission, it is noted that chain scission is not random. Chains are broken near the central monomer, producing two new chains with approximately equal molecular weights.

6. Extensional flow-induced chain scission in a polymer solution with a polydisperse polystyrene sample (Styron 666D) results in preferential degradation of the longest chains in the distribution. This phenomenon, combined with the wide range of chain lengths, complicates the interpretation of the degradation mechanism. Chains which are broken overlap with existing undegraded chains. In addition, only a small percentage of the sample is degraded in the fast transient extensional flow. The study of the extensional
degradation of this material is of relevance to polymer processors, since this is a commercially available resin.

The preferential scission of long chains is highlighted in the DGPC plots. As the centerline strain rate increases, the deviation from the undegraded sample becomes larger. The DGPC traces only vary from the undegraded sample at the high molecular weight end of the distribution. This is important for two reasons. First, this indicates that extensional degradation is non-random and preferentially degrades the longer, higher molecular weight chains. Second, the high molecular weight chains are ruptured near the center, resulting in two chains which still have high molecular weights. Exact central scission is not expected due to the short residence time in the high strain rate region and entanglements in the solution. Although the chains unravel from the center out, they may not be constrained in a symmetrical configuration. There is a critical molecular weight ($M_J$), above which all chains are completely broken.

Preferential cleavage of high molecular weight chains could be expected based on the mechanism of chain scission. Longer chains have a coil-stretch transition at lower strain rates and also have more entanglements than shorter chains. When long chains pass through the high strain rate region, they are stretched and broken. Lower molecular weight chains may not be long enough to undergo the coil-stretch transition or may not have the necessary entanglement concentration to cause chain scission. The cleavage of the long chains in the distribution and the near central scission result in a reduction in the polydispersity of the sample.

The initial molecular weight influences the flow-induced degradation in two ways. First, the molecular mobility decreases with increasing chain length. A larger coil can be deformed at a lower strain rate. Second, a larger macromolecule can store more elastic energy and accumulate more strain. The result of these two factors is an increase in the susceptibility of bond scission with increasing chain length. With increasing molecular
weight, there is an increase in the effectiveness of entanglements for localizing mechanically applied energy as temporarily stored potential energy due to the increased number of chain entanglements.

The design of the opposed pistons apparatus allows the effect of multiple passes on chains scission to be investigated. Styron solutions are repeatedly passed through the high strain rate region, and chain scission is quantified after a set number of passes. There is increased chain scission measured for multiple passes across the orifice, with the most extensive scission in the first pass. Experiments are performed for up to two hundred passes to verify this observation.

7. Studies of flow-induced scission of a monodisperse polymer in solution allow for a systematic analysis of the degradation process. The high molecular weight of the undegraded sample results in polymer degradation at lower velocities compared to the lower molecular weight Styron sample. The low polydispersity minimizes overlap of degraded and undegraded chains. Changes in the molecular weight distribution and the drop in the average molecular weights are easier to detect due to the small polydispersity. Experiments with the monodisperse sample in different concentration regimes permits the elucidation of the two different FTF scission mechanisms noted in the above discussion.

In contrast to the polydisperse results, there is no critical molecular weight for the degraded monodisperse solutions. The critical molecular weight phenomena in the polydisperse solution is due to the longest chains undergoing a coil-stretch transition before the smaller chains in the distribution. In the monodisperse sample, there is little differentiation in the onset of the coil-stretch transition, since all chains are similar in length and thus have similar relaxation times.
8. A small set of experiments on the degradation of a Boger fluid resulted in significantly more chain scission than observed in the less viscous 1-methyl-naphthalene solutions. The scission in the Boger fluid is much higher than predicted based on previous dilute FTF degradation studies which showed the viscosity to be weakly related to the fracture extension rate. Based on these studies, the onset of Boger fluid scission is expected to occur at an average orifice velocity of approximately 20.3 m/s. Instead, there is an average of approximately eight bonds broken per weight average chain for an average velocity of 10.2 m/s. The onset of scission in the Boger fluid occurs at an average orifice velocity of approximately 0.4 m/s. The severe deviation points to a possible change in the scission mechanism in highly viscous solvents.

9. Preliminary thermal degradation studies highlight the difference between flow-induced chain scission and a random degradation process. Extensional flow-induced chain scission is analogous to thermal degradation with respect to a kinetic analysis, but the two processes differ in the distribution of bond sites that become activated to the level of breakage. Thermal degradation is a random process, and all bond sites have an equal probability of rupture. Therefore, there is no degradation preference based on chain size and many small chains are generated. In extensional-flow induced chain scission, there is a nonrandom distribution of activated bond sites caused by the concentration of stress at a particular location.

10. The techniques and tools used in the polymer degradation studies also find application in different fields. The opposed pistons apparatus is useful for studying the effect of imposing a fast transient extensional flow on animal cell microcarrier cultures. Controlled studies of cell damage due to hydrodynamic forces are important in the scale up of bench scale reactors to production scale vessels. Experiments with a microcarrier culture
indicate that cell damage is related to the centerline dissipation rate, with a dramatic increase in cell damage for a dissipation rate greater than $5.0 \times 10^7$ erg/cm^3s.

9.3 Recommendations for future work

1. One of the main challenges in this study is the linkage between the experimental degradation measurements and the simulation of the flow field. Flows with viscoelastic fluids in a large velocity gradient present significant simulation difficulties. As noted in the Experimental chapter, the choice of a constitutive equation for the rheological behavior of the fluid sets constraints on the results from the flow field simulations. One possibility to overcome this limitation is to perform flow field visualization. This would provide information on the flow field without the assumption of a constitutive equation. This would be of great usefulness for two reasons. First, it would allow a direct comparison of the details of the flow field to the degradation process. Also, it would allow for a comparison with numerical results and the possibility of selecting a constitutive equation which most accurately describes the fluid response in the flow in question. The use of flow field visualization is not a panacea, however. Experimental difficulties and interpolation error would lead to some uncertainty in the results.

2. Instead of focusing on macroscopic flow field modeling, some attention should be drawn to performing molecular scale modeling. The goal of this type of modeling would be to predict the orientation and elongation of a chain molecule as it flows through a fast transient flow. There is a continuing dilemma regarding the gap between continuum mechanics and molecular scale modeling. With improvements in computer capability and increased knowledge of the response of chains to extensional flows, this is one area in which a significant contribution could be made.
3. Both the extension rate and strain history are important in the response of a polymer to an extensional flow. The incorporation of birefringence measurements would permit an estimation of the molecular strain. This technique has been used with success in quasi-steady-state extensional flows (Carrington et al., 1997). The molecular strain, combined with extensional rheology measurements and numerical estimates of the fluid strain, would provide insight into how the extensional response of chains modifies the stretching behavior in a strong flow.

4. The advances in the extensional rheology characterization of polymer samples have pointed out the importance of the extensional properties in a flow with a high extensional component. Better extensional characterization of the fluids used in degradation experiments will allow for improved modeling of the response in fast transient extensional flows. The characterization of a fluid's behavior with respect to different extension rates and with different strain histories will broaden the understanding of the flow of complex fluids in extensional flows.

5. Improved measurements of the viscosity at very high shear rates would improve the current study in two ways. First, analysis of samples after exposure to a pure shear flow at high shear rates would quantify the effect of shear flow on polymer degradation. Based on previous results with entrance flows, it has been noted that the extensional flow before the orifice controls scission behavior. The solutions used in this study are subjected to a high shear rate as they pass through the small diameter capillary. Tests at very high shear rates in a controlled shear flow would verify that shear flow is much less effective in causing bond scission. The second reason for testing the viscosity at high shear rates is to improve the constants in the constitutive equation. Instrument limitations prevent measuring the viscosity at the shear rates to which the fluids are exposed in the capillary. The addition of
a transducer which can measure higher torques would permit high shear rate measurements of the viscous solutions at higher shear rates. Care would have to be taken with the lower viscosity solutions to avoid turbulence and instabilities at the high shear rates.

6. The effect of a fast transient extensional flow on the degradation of polymer chains should be extended to a study of polymer melts. The study of melts presents several experimental difficulties, but is possible with some modifications to the drive system of the single-screw and the twin-screw extruders. The entanglements in the concentrated solutions make these solutions an analog for melts, but the use of melts would be of much more interest to polymer processors.

7. Additional information on chain rupture could be obtained by performing a kinetic analysis of the degradation process. A detailed kinetic analysis would solve for the individual rate constants for each bond in each chain (Basedow et al., 1978; Ballauff and Wolf, 1981; Nguyen and Kausch, 1989; Nguyen, 1997; Nguyen et al., 1997). The solution of this large set of equations would yield a predicted molecular weight distribution (MWD). The model MWD could be compared to the measured MWD to optimize the rate constants. The DGPC analysis and the change in the higher moments of the MWD allowed some preliminary assumptions on the non-randomness of extensional flow-induced degradation, but a detailed kinetic analysis is required to completely characterize the selectivity of the scission process.

8. The early results from the Boger fluid experiments warrant further study to identify the onset of chain scission and the scaling with solvent viscosities higher than typical organic solvents. The scission in the Boger fluid is more extensive for a given average orifice velocity than in a concentrated solution. Additional studies with this unusual
solution can provide insight into the scission mechanism in dilute solution FTF. Changing the concentration of the polymer in the oligomer and using oligomer solvents with different degrees of polymerization will permit experiments at solution viscosities between the current experimental value and the lower viscosity organic solvents.
BIBLIOGRAPHY


APPENDIX

FORTRAN PROGRAMS USED IN STUDY

GFC,FOR
PROGRAM TO READ DATA FROM ADC BOARD

INTEGER I,J,N,TICS(5000),J,K,FLAG
REAL *8 FLOW,SAMPINT,VOLTS(5000),SEC(5000),ZERO,VOL(5000)
CHARACTER *40 FILENAME,OUTPUT

ENTER FILENAMES OF DATA FILE AND OUTPUT FILE

WRITE(6,1)
1 FORMAT(1X,'ENTER NAME OF DATA FILE')
READ(5,2) FILENAME
2 FORMAT(A40)
WRITE(6,3)
3 FORMAT(1X,'ENTER NAME OF OUTPUT FILE')
READ(5,4) OUTPUT
OPEN(44,FILE=FILENAME,STATUS='OLD')
OPEN(45,FILE=OUTPUT,STATUS='NEW')

ENTER SOLVENT FLOW RATE

WRITE(6,4)
4 FORMAT(1X,'ENTER SOLVENT FLOW RATE (ML/MIN)')
READ(5,5) FLOW

RESET TIME TO ZERO AND WRITE TO OUTPUT FILE

WRITE(6,5)
5 FORMAT(1X,'ENTER DELAY TIME (S)')
READ(5,5) DELAY

N=0
FLAG=0
DO 1=1,5000
IF(FLAG.LE.1) THEN
   READ(44,*,END=1000) TICS(I),VOLTS(I)
   N=N+1
   ZERO=TICS(DELAY)
   SEC(I)=TICS(I)/60.0
   SEC(I)=SEC(I)-ZERO/60.0
   VOL(I)=FLOW/60.0*SEC(I)
   VOL(I)=VOL(I)+0.05
   IF(VOL(I).LE.0.00000001) THEN
      FLAG=FLAG+1
   ENDIF
1 CONTINUE
WRITE TO DATA FILE
K=0
DO J=DELAY,N-1

328
PROGRAM TO CORRECT FOR AXIAL DISPERSION IN GPC ANALYSIS

WRITTEN BY JOHN CLAY 2/95

VARIABLE FUNCTIONS

INTEGER BLB, BLE, DATA(5000), PAB, PAE, DP, J, K
REAL*8 TIME(5000), VOLTS(5000), VOL(5000), VOLBB, VOLBE, BLSL
REAL*8 BLINT, BL(5000), VOLPB, VOLPE, RAW, RAWSA, F(5000)
REAL*8 W(5000), WFA, WFSA, NORM, WN(5000), FSUM, MP(5000)
REAL*8 FSA, FA, FN(5000), WA, WSA, CONV(5000), MAREA, MAREA, CONVS
REAL*8 DIFF(5000), WXG(5000), WXGSUM, PJH(5000), MFA, MFSA
CHARACTER*20 FILENAME, OUTPUT

READ IN DATA FILE

THIS IS LINE 25

WRITE (6, 1)
FORMAT (1X, ENTER FILENAME WITH RAW DATA)
READ(5, 2) FILENAME
2 FORMAT (A20)
WRITE (6, 3)
FORMAT (1X, ENTER NAME OF OUTPUT FILE)
READ (5, 4) OUTPUT
OPEN (UNIT=44, FILE=FILENAME, STATUS='OLD')
OPEN (UNIT=45, FILE=OUTPUT, STATUS='NEW')
DO 1 = 1, 5000
READ(44, *.END=1000) TIME(I), VOLTS(I), DATA(I), VOL(I)
ENDDO
CONTINUE

SET BASELINE

THIS IS LINE 45

WRITE (6, 20)
FORMAT (1X, ENTER VOLUME AT BASE LINE BEGINNING)
READ(5, 2) VOLBB
DO 1 = 1, 5000
IF (VOL(I) .GE. VOLBB) THEN
BLB = I
GOTO 2000
ENDIF
ENDDO
ENDDO
CONTINUE

WRITE (6, 21)
FORMAT (1X, ENTER VOLUME AT BASE LINE END)
READ(5, 2) VOLBE
DO 1 = 1, 5000
IF (VOL(I) .GE. VOLBE) THEN
BLE = I
GOTO 3000
ENDIF
ENDDO
ENDDO
CONTINUE

WRITE (6, 23) VOL(BLB), VOL(BLE)
23 FORMAT (1X, F8.4, 5X, F8.4)
BLSL = VOLTS(BLE) - VOLTS(BLB) / VOL(BLE) - VOL(BLB)
BLINT = VOLTS(BLB) - BLSL * VOL(BLB)
WRITE (6, 22) BLSL, BLINT
22 FORMAT (1X, THE SLOPE IS:, 1X, F8.3, 1X, THE INT IS:, 1X, F8.3)
DO I=BLB,BLE
    BL(I)=BLSL*VOL(I)+BLINT
ENDDO

* ***************
* SET LIMITS ON PEAK
* ****************** THIS IS LINE 85
* 
WRITE(6,30)
30 FORMAT(1X,'ENTER VOLUME AT BEGINNING OF PEAK')
READ(5,*) VOLPB
DO I=1,1500
    IF(VOL(I).GE.VOLPB) THEN
        PAB=I
        GOTO 4000
    ENDIF
ENDDO
4000 CONTINUE

WRITE(6,31)
31 FORMAT(1X,'ENTER VOLUME AT END OF PEAK')
READ(5,*) VOLPE
DO I=1,5000
    IF(VOL(I).GE.VOLPE) THEN
        PAE=I
        GOTO 5000
    ENDIF
ENDDO
5000 CONTINUE

DP=PAE-PAB+1
WRITE(6,32) DP
32 FORMAT(1X,'NUMBER OF DATA POINTS IN RANGE:')
FORMAT(1X,14)

* ***************
* AREA OF OUTPUT VS. VOLUME CURVE
* ******************* THIS IS LINE 115
* 
ARAW=0.0
DO I=BLB,(BLE-I)
    RAWSA=0.5*(VOLTS(I)+VOLTS(I+1)-BL(I)-BL(I+1))
    (VOL(I+1)+VOL(I))
    RAWA=ARAW+RAWSA
ENDDO
WRITE(6,76)
76 FORMAT(1X,'AREA CALCULATED')

* DO I=BLB,BLE
    MF(I)=VOLTS(I)-BL(I)/ARAW
    IF(MF(I).LT.0.0001) THEN
        MF(I)=0.0
    ENDIF
    W(I)=MF(I)
    WN(I)=W(I)
    IF(VOL(I),.LE.17.8) THEN
        H(I)=4.0
    ELSEIF(VOL(I),.GE.25.85) THEN
        H(I)=1.75
        ELSE
            H(I)=-102.28445469+10.273841117*VOL(I)-0.24166677254
                *VOL(I)**2
    ENDIF
ENDDO
WRITE(6,77)
77 FORMAT(1X,'H CALCULATED')

* ***************
* LOOP TO CORRECT FOR BAND SPREADING
* ****************** THIS IS LINE 143
* 
PI=3.141592654
DO K=1,20
    DO I=BLB,BLE
        WXG(I)=WN(I)*(H(I)/PI)**0.5*EXP(-H(I)***(VOL(I)-
                VOL(I)**2))
    ENDDO
F(I)=0.0
DO J=PAB,(PAE-1)
   WXGSUM=0.5*(WXG(I)+WXG(I+1))*(VOL(I+1)-VOL(I))
   F(J)=F(J)+WXGSUM
ENDDO

FA=0.0
MFA=0.0
DO J=BLB,(BLE-1)
   MFS A=0.5*(MF(J)+MF(J+1))*(VOL(J+1)-VOL(J))
   MFA=MFA+MFS A
   FSA=0.5*(F(J)+F(J+1))*(VOL(J+1)-VOL(J))
   FA=FA+FSA
ENDDO

DO J=BLB,BLE
   FN(J)=F(J)/FA
   W(J)=(MF(J)/F(J))*WN(J)
ENDDO

WA=0.0
DO J=BLB,(BLE-1)
   WSA=0.5*(W(J)+W(J+1))*(VOL(J+1)-VOL(J))
   WA=WA+WSA
ENDDO

DO J=BLB,BLE
   WN(J)=W(J)/WA
   DIFF(J)=MF(J)-FN(J)
ENDDO

CONVS=ABS(FA-MFA)/MFA
CONV(K)=0.0
DO J=BLB,(BLE-1)
   CONVSA=0.5*(ABS(DIFF(J))+ABS(DIFF(J+1)))*
          *(VOL(J+1)-VOL(J))
   CONV(K)=CONV(K)+CONVSA
ENDDO

WRITE(6,78) K,CONV(K),CONVS
78 FORMAT(1X,ITERATION,' ',J4,3X,CONV=,' ',F15.9,3X,CONV=,' ',F15.9)

IF(K.GT.1) THEN
   IF(CONV(K),GT,CONV(K-1)) THEN
      WRITE(6,99) CONV(K-1),K
   FORMAT(1X,'MIN CONV=',F10.6,3X,ITER+1:', ',14)
   GOTO 7000
ENDIF

PC=MOD(K,20)
IF(PC.EQ.0) THEN
   DO J=BLB,BLE
      WRITE(45,60) MF(J),WN(J),FN(J),VOL(J)
   ENDDO
ENDIF

IF(CONV(K),LE,0.010) THEN
   WRITE(6,52) CONV(K),K
   FORMAT(1X,'CONVERGENCE! CONV=',F10.6,3X,ITER=', ',14)
   GOTO 7000
ENDIF

ENDDO

7000 CONTINUE

WRITE OUTPUT TO DATA FILE

DO J=BLB,BLE
   WRITE(45,60) MF(J),WN(J),FN(J),VOL(J)
60 FORMAT(1X,F12.9,3X,F12.9,3X,F12.9,3X,F12.8)
ENDDO

CLOSE(44)
CLOSE(45)

END
NORMAL FOR
PROGRAM TO NORMALIZE GPC DATA AND CONVERT TO STANDARD VOLUMES
WRITTEN BY JOHN CLAY 4/95

***************
VARIABLE FUNCTIONS
***************

INTEGER LB,LB,DATA(5000),PB,PAB,PJ,KB,NE
REAL*8 TIME(5000),VOLTS(5000),VOL(5000),VOLPB,VOLBE,BLSL
REAL*8 BLINT,BL(5000),VOLPB,VOLPE,RAW,RAWSA
REAL*8 NOUT(5000),VOLNB,VOLNE,DELVOL,NVOL(5000),NSEC(5000)
REAL*8 SOUT(5000),SEC(5000)
CHARACTER*20 FILENAME,OUTPUT,SANS

READ IN DATA FILE

WRITE (6,1)
FORMAT(1X,'ENTER FILENAME WITH RAW DATA')
READ(5,2)FILENAME
FORMAT(A20)
WRITE(6,3)
FORMAT(1X,'ENTER NAME OF OUTPUT FILE')
READ(5,2)OUTPUT
OPEN(UNIT=44,FILE=FILENAME,STATUS='OLD')
OPEN(UNIT=45,FILE=OUTPUT,STATUS='NEW')
N=0
DO I=1,5000
READ(44,*,END=1000)SEC(I),VOLTS(I),DATA(I),VOL(I)
N=N+1
ENDDO
CONTINUE

SET BASELINE

WRITE(6,20)
FORMAT(1X,'ENTER VOLUME AT BASE LINE BEGINNING')
READ(5,3)VOLBB
DO I=1,5000
IF(VOL(I).GE.VOLBB) THEN
BLB=I
GOTO 2000
ENDIF
ENDDO
CONTINUE

WRITE(6,30)
FORMAT(1X,'ENTER VOLUME AT END OF PEAK')
READ(5,30)VOLBE
DO I=1,5000
IF(VOL(I).GE.VOLBE) THEN
BLE=I
GOTO 3000
ENDIF
ENDDO
CONTINUE

WRITE(6,23)VOL(BLB),VOL(BLE)
FORMAT(1X,'THE SLOPE IS:',F8.3,'THE INT IS:',F8.3)
DO I=BLB,BLE
BLSL=(VOLTS(BLE)-VOLTS(BLB))/(VOL(BLE)-VOL(BLB))
BLINT=VOLTS(BLB)-BLSL*VOL(BLB)
WRITE(6,22)BLSL,BLINT
ENDDO

SET LIMITS ON PEAK

WRITE(6.30)
FORMAT(1X,'ENTER VOLUME AT BEGINNING OF PEAK')
READ(5,*) VOLPB
DO I=1,5000
  IF(VOL(I).GE.VOLPB) THEN
    PAB=I
    GOTO 4000
  ENDIF
ENDDO
CONTINUE
4000 CONTINUE
WRITE(6,31)
31 FORMAT(1X,ENTER VOLUME AT END OF PEAK')
READ(5,*) VOLPE
DO I=1,5000
  IF(VOL(I).GE.VOLPE) THEN
    PAE=I
    GOTO 5000
  ENDIF
ENDDO
CONTINUE
5000 CONTINUE
DP=PAE-PAB+1
WRITE(6,32) DP
32 FORMAT(1X.NUMBER OF DATA POINTS IN RANGE: ,1X,I4)

* *************** AREA OF OUTPUT VS. VOLUME CURVE ***********************
* THIS IS LINE 111
* ARAW=0.0
DO I=PAB,PAE-1
  RAWSA=0.5*(VOLTS(I)+VOLTS(I+1)-BL(I)-BL(I+1))*(VOL(I+1)-VOL(I))
  ARAW=ARAW+RAWSA
ENDDO
DO I=PAB,PAE
  NOUT(I)=(VOLTS(I)-BL(I))/ARAW
ENDDO
6000 CONTINUE
* *************** CONVERT TO STANDARD VOLUME ***********************
* THIS IS LINE 128
WRITE(6,40)
40 FORMAT(1X.DO YOU WISH TO STANDARDIZE WRT VOLUME? (Y OR N)')
READ(5,41) SANS
41 FORMAT(A1)
IF(SANS.EQ.'Y' OR SANS.EQ.'Y') THEN
  WRITE(6,42)
42 FORMAT(1X.ENTER VOLUME AT BEGINNING (ML)')
READ(5,43) VOLNB
WRITE(6,43)
43 FORMAT(1X.ENTER VOLUME AT END (ML)')
READ(5,44) VOLENE
WRITE(6,44)
44 FORMAT(1X.ENTER VOLUME INTERVAL (ML)')
READ(5,*) DELVOL
DO I=1,5000
  IF(I.EQ.1) THEN
    NB=I
    NVOL(I)=VOLNB
  ELSE
    NVOL(I)=NVOL(I-1)+DELVOL
  IF(NVOL(I).GE.VOLENE) THEN
    NE=I
    GOTO 7000
  ENDIF
ENDIF
ENDDO
CONTINUE
7000 CONTINUE
* DO NB,NE
* WRITE(6,45) I,NVOL(I)
45 FORMAT(1X.I,'',I4.3X,NVOL(I),'F8.3)
ENDDO
PROGRAM TO CALCULATE AREA OF GPC PEAKS

WRITTEN BY JOHN CLAY 10/94


***********************
VARIABLE FUNCTIONS
***********************

AA: AREA ARRAY (ROWS=PEAK#; COLUMNS=SEGMENT AREAS)
A: AREA OF SEGMENT
AC: AREA COUNTER (COUNTS DATA POINTS WITHIN SEGMENTS)
ATOT: TOTAL AREA FOR PEAK (SUM OF SEGMENT AREAS)
BL: BASELINE OUTPUT
BLB: VOLUME AT BEGINNING OF BASELINE

END
WRITE(6,1)
1 FORMAT(1X,'ENTER FILENAME WITH RAW DATA')
READ(5,2) FILENAME
WRITE(6,3)
3 FORMAT(1X,'ENTER NAME OF OUTPUT FILE')
READ(5,2) OUTPUT
WRITE(6,4)
4  THIS IS LINE 107
FORMAT('ENTER NAME OF FILE TO SEND KALEIDA DATA')
READ(3,2) KALEIDA
OPEN(UNIT=44,FILE=FILENAME,STATUS='OLD')
OPEN(UNIT=45,FILE=OUTPUT,STATUS='NEW')
OPEN(UNIT=46,FILE=KALEIDA,STATUS='NEW')
DO 1=1,5000
READ(44,*).END=1000) TIME(I),VOLTS(I),DATA(I),VOL(I)
1 CONTINUE

****************
* MOLECULAR WEIGHT CALIBRATION
**************** THIS IS LINE 130

CAL=0
WRITE(6,20)
20 FORMAT('DO YOU WANT TO CONVERT DATA TO MW? (Y OR N)')
READ(5,21) CANS
21 FORMAT(A1)
IF(CANS.EQ.'Y'.OR.CANS.EQ.'Y') THEN
   CAL=1
   WRITE(6,22)
   *22 FORMAT('FORM OF CALIBRATION IS LOG(MW)=CUBIC')
   WRITE(6,23)
   *23 FORMAT('INPUT CONSTANT IN CUBIC')
   READ(5,*) COC
   WRITE(6,24)
   *24 FORMAT('INPUT 2ND COEFFICIENT (X VOL^1)')
   READ(5,*) CSC
   WRITE(6,25)
   *25 FORMAT('INPUT 3RD COEFFICIENT (X VOL^2)')
   READ(5,*) CTC
   WRITE(6,26)
   *26 FORMAT('INPUT 4TH COEFFICIENT (X VOL^3)')
   READ(5,*) CFC
   COC=15.441538605
   CSC=-1.0035223865
   CTC=0.035619626458
   CFC=-0.00052559303641

2000 CONTINUE
MHS=0
WRITE(6,29)
29 FORMAT('DO YOU WISH TO CALCULATE MV? (Y OR N)')
READ(5,21) MVANS
30 IF(MVANS.EQ.'Y'.OR.MVANS.EQ.'Y') THEN
   MHS=1
   WRITE(6,30)
   30 FORMAT('MHS EQUATION HAS THE FORM: [N]=(K)*(MW)^a')
   WRITE(6,31)
   31 FORMAT('INPUT a')
   READ(5,*) MHSA
   ELSEIF(MVANS.EQ.'N'.OR.MVANS.EQ.'N') THEN
   GOTO 3000
   ELSE
   GOTO 1000
   ENDIF
3000 CONTINUE

***************************
* INITIALIZE VARIABLES AND MATRICES
*************************** THIS IS LINE 182

RUNA=0.0
CPA=0.0
DO RIC=U 0
   DO CIC=U 0
      AA(RIC,CIC)=0.0
   ENDDO
ENDDO

336
INPUT NUMBER OF PEAKS

WRITE(6,40)
FORMAT(1X,'ENTER NUMBER OF PEAKS TO BE ANALYZED')
READ(5,*) J
WRITE(6,41) J
FORMAT(1X,'THE NUMBER OF PEAKS IS:',1X,J)

BEGIN LOOP FOR EACH PEAK: CALCULATE AREA

DO K=1,J

SET BASELINE

WRITE(6,50)
FORMAT(1X,'ENTER VOLUME AT BASE LINE BEGINNING')
READ(5,*) VOLBB
DO I=1,5000
IF(VOL(I).GE.VOLBB) THEN
   BLB=I
   GOTO 4000
ENDIF
ENDDO
CONTINUE
WRITE(6,51) VOLBB,VOL(BLB)
FORMAT(1X,'INPUT:'.1X,E8.4.5X.'VOLBB:'.1X,E8.4)

WRITE(6,52)
FORMAT(1X,'ENTER VOLUME AT BASE LINE END')
READ(5,*) VOLBE
DO I=1,5000
IF(VOL(I).GE.VOLBE) THEN
   BLE=I
   GOTO 5000
ENDIF
ENDDO
CONTINUE
WRITE(6,53) VOLBE,VOL(BLE)
FORMAT(1X,'INPUT:'.1X,E8.4.5X.'VOLBE:'.1X,E8.4)
WRITE(6,54) VOLBB,VOL(BLB)
WRITE(6,55) SL,INT
FORMAT(1X,'THE SLOPE IS:'.1X,E8.3.1X,'THE INT IS:'.1X,E8.3)
DO I=BLB,BLE
   BL(I)=SL*VOL(I)+INT
ENDDO

SET LIMITS ON PEAKS AND FIND MAXIMUM

WRITE(6,60)
FORMAT(1X,'ENTER VOLUME AT BEGINNING OF PEAK')
READ(5,*) VOLPB
DO I=1,5000
IF(VOLPB.LE.VOL(I)) THEN
   PAB=I
   GOTO 6000
ENDIF
ENDDO
CONTINUE
WRITE(6,61) VOLPB,VOL(PAB)
FORMAT(1X,'INPUT:'.1X,E8.4.5X,'VOLPB:'.1X,E8.4)

WRITE(6,62)
FORMAT(1X,'ENTER VOLUME AT END OF PEAK')
READ(5,*) VOLPE
DO I=1,5000
IF(VOLPE.LE.VOL(I)) THEN
   PAE=I
   GOTO 7000
ENDIF
ENDDO
CONTINUE
WRITE(6,63) VOLPE,VOL(PAE)
FORMAT(1X,'INPUT:'.1X,E8.4.5X,'VOLPE:'.1X,E8.4)
ENDIF
ENDDO
7000 CONTINUE
WRITE(6,63) VOLPE, VOL(PAE)
63 FORMAT(1X, 'INPUT: MXj=8.4^VOL;MXJ^.4)
* 
DP=PAE-PAB+1
WRITE(6,64) DP
64 FORMAT(IX, 'NUMBER OF DATA POINTS IN RANGE: ', IX, 14)
* 
VMAX=VOLTS(PAB)
VOLMAX=VOL(PAB)
DO MC=PAB, PAE
IF(VOLTS(MC).GT.VMAX) THEN
VMAX=VOLTS(MC)
VOLMAX=VOL(MC)
ENDIF
ENDIF
ENDDO
70 
8000 CONTINUE
* 
* DIVIDE PEAK INTO SECTIONS
* ****************** THIS IS LINE 296
* 
WRITE(6,70)
FORMAT(IX, 'ENTER NUMBER OF DATA POINTS PER SEGMENT)
READ(*,*) PPS
DO SCD=1,300
IF(SC.EQ.1) THEN
SC=PB+PPS
ELSE
SC=SC+1)+PPS
ENDIF
IF(S(C),GE.PAE) THEN
SC=PAE
GO TO 8000
ENDIF
ENDDO
* 
* USE TRAPEZOIDAL RULE TO CALCULATE AREA PER SEGMENT
* ****************** THIS IS 317
* 
ATOT(K)=0.0
DO OAC=1,SC
IF(OAC.EQ.1) THEN
A(OAC)=0.0
DO AC=PB,(S(OAC)-1)
SA=0.5*(VOLTS(AC)+VOLTS(AC+1)-BL(AC)-BL(AC+1))
+ (VOL(AC)+1)-VOL(AC))
A(OAC)=A(OAC)+SA
ENDDO
ENDIF
IF(CAL.EQ.1) THEN
MWB=10**((COC+CSC*VOL(PAB)+CTC*VOL(PAB)**2
+ CFC*VOL(PAB)**3)
MWE=10**((COC+CSC*VOL(S(OAC))+CTC*VOL(S(OAC))**2
+ CFC*VOL(S(OAC))**3)
DEL.MW(OAC)=MWB-MWE
LDEL.MW(OAC)=LOG(MWB)-LOG(MWE)
MWVOL=MWB+VOL(PAB)+VOL(S(OAC))/2
MW(OAC)=10**((COC+CSC*MWVOL+CTC*MWVOL**2+CFC*MWVOL**3)
CSL(OAC)=CSC+2*CTC*MWVOL+3*CFC*MWVOL**2
VAVG(OAC)=VOLTS(PAB)+VOLTS(S(OAC))
+ -BL(PAB)-BL(S(OAC))/2
ENDDO
ELSE
A(OAC)=0.0
DO AC=(S(OAC)-1), (S(OAC)-1)
SA=0.5*(VOLTS(AC)+VOLTS(AC+1)-BL(AC)-BL(AC+1))
+ (VOL(AC)+1)-VOL(AC))
A(OAC)=A(OAC)+SA
ENDDO
ENDIF
IF(CAL.EQ.1) THEN
MWB=10**((COC+CSC*VOL(S(OAC)-1)+CTC*VOL(S(OAC)-1))**2
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```plaintext
+ CFC*VOL(S(OAC-1))**3)
+ MWE=10***(COC+CS*VOL(S(OAC))+CTC*VOL(S(OAC)**2
+ CFC*VOL(S(OAC)**3)
DELMW(OAC)=MWB-MWE
LDELMW(OAC)=LOG(MWB)-LOG(MWE)
MWVOL=VOL(S(OAC-1))+VOL(S(OAC))**2
MW(OAO)=10**(COC+CS*MWVOL+CTC*MWVOL**2+CFC*MVOL**3)
CSL(OAO)=CS+2*CTC*MWVOL+3*CFC*MWVOL**2
VAVG(OAO)=(VOLTS(S(OAC-1))+VOLTS(S(OAC))
  -BL(S(OAC-1)))/BL(S(OAC))**2
ENDIF
ENDIF
ATOT(K)=ATOT(K)+A(OAC)
WRITE(6,80) OACA(OAC)
FORMAT(IX,' SEGMENT;M4.1X.-AREA:MXJ=8J)

STORE SEGMENT AREAS IN ARRAY

Molecular Weight Calculations

IF(CALCQ.I) THEN
WMWN=0.0
NMWD=0.0
ZMWN=0.0
VMWN=0.0
DO OAC=1,SC
WN=A(OAC)*MW(OAC)
WMWN=WMWN+WN
WMW=WMWN/ATOT(K)
WRITE(6,89) A(OAC),MW(OAC),ATOT(K)
FORMAT(IX,' ;A(OAC);:F10.5,5X;MW(OAC);:F12.3,5X;ATOT;F10.5)
ND=A(OAC)/MW(OAC)
NMWD=NMWD+ND
ZN=A(OAC)*MW(OAC)**2
ZMWN=ZMWN+ZN
IF(MHS.EQ.1) THEN
IF(A(OAC).GE.0.0) THEN
VN=A(OAC)*MW(OAC)*MHSA
VMWN=VMWN+VN
VMW=(VMWN/ATOT(K)**(1/MHSA))
ENDIF
ENDIF
ENDIF
NDDO
NMW=ATOT(K)/NMWD
PD=WMW/NMW
ZMW=ZMWN/NMW
ENDIF

WRITE TO DATA FILE

WRITE(45,90)
FORMAT(IX,'OUTPUT FROM RUN)
WRITE(45,91) K
FORMAT(IX,'PEAK #:I4)
WRITE(45,92) PAB,PAE
FORMAT(IX,'BEGINNING POINT::I1X,14.5X,END POINT::I1X,14.5)
WRITE(45,93) VMAX,YOXLMAX
FORMAT(IX,'MAXIMUM OUTPUT::I1X,F20.5,5X,VOL AT MAX::I1X,F15.9)
IF(CALCQ.EQ.1) THEN
WRITE(45,94) MWMAX
FORMAT(IX,'MAXغالORATE AT MAX::I1X,F15.3)
WRITE(45,95) WMW,NMW
FORMAT(IX,'WEIGHT AVG MW ::I1X,F15.3,5X,NUM AVG MW ::I1X,
  F15.3)
WRITE(45,96) PD,ZMW
FORMAT(IX,'POLYDISPERSITY ::I1X,F12.4,5X,Z AVG MW ::I1X,
  F15.3)
IF(MHS.EQ.1) THEN
```
WRITE(45.97) VMW
ENDIF
FORMAT(1X,VISCOSITY AVG MW=1X,F15.3)
ENDIF
WRITE(45.98) SC
ENDIF
FORMAT(1X,NUMBER OF SECTIONS=1X,I4)
CWD=0.0
CWDD=0.0
LCMWD=0.0
WRITE(45.99)
FORMAT(1X,SEGMENT,5X,AREA,12X,MW,10X,w(M),10X,
'SUM w(M)*dMMW')
DO OC=1,SC
  FRAC=A0CVRUNA
  CWD=CWD+FRAC
  IF(ICALÆQ.1) THEN
    FRAC=A0CVRUNA
    WDD=(-0.434294481/(MW(OC)*CSL(OC)))*(VAVG(OC)/ATOT(K))
    CWDD=CWDD+WDD+DELMW(OC)
    LCMWD=LCMWD+DELMW(OC)
  WRITE(45.100) OC,A0CVRUNA,MW(OC)
ENDIF
ENDDO
WRITE(45,103) ATOT(K)
FORMAT(1X,TOTAL AREA FOR PEAK=1X,F16.3)
ENDDO
WRITE(45.104) RUNA
FORMAT(1X,TOTAL AREA FOR RUN=1X,F18.3)
DO K=1,J
  DO PAC=1,SCA(K)
    SPA=AA(K,PACVRUNA*100
    CPA=CPA+SPA
    WRITE(45,105) K
    WRITE(45,106) PAC
  ENDIF
ENDDO
FORMAT(1X,PEAK #=1X,F14)
FORMAT(1X,SECTION #=1X,F14)
FORMAT(1X,PERCENT AREA=1X,F10.5)
FORMAT(1X,CUMULATIVE PERCENT AREA=1X,F10.5)
ENDDO
CLOSE(44)
CLOSE(45)
CLOSE(46)
END

AFLOW
WRITTEN BY JOHN CLAY. 2/97

THIS PROGRAM CALCULATES ASTARITA'S FLOW PARAMETER FROM
DATA GENERATED IN THE SIMULATION PACKAGE, POLYFLOW.
THE RESULT FILE FROM A SIMULATION IS EDITED TO ISOLATE THE
COORDINATES, VELOCITIES, COMPONENTS OF THE RATE OF
DEFORMATION TENSOR, VISCOSITY, AND THE VORTICITY TENSOR.
THE NUMBER OF NODES IS INPUT AND THE PROGRAM READS THE
DATA AND Assigns VALUES TO EACH NODE. THE INVARIANTS ARE
CALCULATED, THE CUBIC CHARACTERISTIC EQUATION IS SOLVED
FOR THE PRINCIPAL STRESSES, AND THE PRINCIPAL DIRECTIONS
ARE OBTAINED. TO OBTAIN DERIVATIVES OF THE PRINCIPAL
DIRECTIONS AT EACH NODE, PSEUDO DATA POINTS ARE ASSIGNED
AROUND EACH NODE, SPACED ONE HALF THE MINIMUM DISTANCE
TO THE NEAREST ADJACENT NODE. AN ADAPTIVE GAUSSIAN
WINDOW TECHNIQUE IS USED FOR INTERPOLATION. THE ASTARITA
FLOW PARAMETER IS CALCULATED AND USED TO NORMALIZE THE
DISSIPATION FUNCTION AND NORMAL STRESS DIFFERENCE.
THE PROGRAM WRITES THESE VALUES TO FILES WHICH ARE THEN
PLACED IN THE RESULT FILE FOR A POLYFLOW SIMULATION IN
PLACE OF THE PRESSURE. THE DATA FILE IS RUN WITH THIS

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MODIFIED RESULT FILE AND ZERO ITERATIONS. GENERATING NEW P2M AND P2R FILES. WITH THESE FILES, POLYPLOT CAN DISPLAY THE CALCULATED PARAMETERS.

VARIABLE FUNCTIONS THIS IS LINE 29

I: INTEGER COUNTER
J: INTEGER COUNTER
K: INTEGER COUNTER
L: INTEGER COUNTER
NODES-NODES4: INTEGER COUNTERS FOR NODES
ROW: INTEGER COUNTER FOR ROWS IN RAW DATA SETS
COL: INTEGER COUNTER FOR COLUMNS IN RAW DATA SETS
TENROWS: INTEGER COUNTER FOR ROWS IN 2D DATA SET
RZROWS: INTEGER COUNTER FOR ROWS IN COORD DATA
VORROWS: INTEGER COUNTER FOR ROWS IN VORTICITY DATA
DATA: NUMBER OF DATA POINTS IN AGW INTERPOLATION
POS: R AND Z COORDINATES
R: RADIAL COORDINATE
Z: AXIAL COORDINATE
DII-D33: COMPONENTS OF RATE OF DEFORMATION TENSOR
VIN1-V22: 11 COMPONENTS OF VORTICITY TENSOR
DIN1-DIN3: INVARIANTS OF RATE OF DEFORMATION TENSOR
VIN2: SECOND INVARIANT OF VORTICITY TENSOR
CUBR: VARIABLE WHICH DETERMINES TYPES OF ROOTS IN CUBIC A.
PHIARG: INTERMEDIATE VARIABLE IN SOLUTION OF CUBIC
PHI: INTERMEDIATE VARIABLE IN SOLUTION OF CUBIC
SIGMA1-SIGMA3: THREE PRINCIPAL STRESSES
E1: PRINCIPAL DIRECTION UNIT VECTOR
E2: PRINCIPAL DIRECTION UNIT VECTOR
MAG: MAGNITUDE OF DIRECTION VECTOR
PI: RATIO OF CIRCUMFERENCE TO DIAMETER
VISC: VISCOSITY
DISS: DISSIPATION FUNCTION
GIESR: GIESEKUS FLOW PARAMETER
EPS: ROOT OF SECOND INARIANT OF R OF D TENSOR
OMEGA: ROOT OF SECOND INARIANT OF VORTICITY TENSOR
STR1-STR33: COMPONENTS OF STRESS TENSOR
NDISS: DISSIPATION FXN NORMALIZED WITH ASTARITA PARAM
RHO: RATIO OF EPS TO OMEGA
NSD: NORMAL STRESS DIFFERENCE (T22-T11)
NNSD: NORMAL STRESS DIFFERENCE NORMALIZED WITH AFP
W: ASTARITA FLOW PARAMETER
MDIST: MINIMUM DISTANCE FROM NODE TO ADJACENT NODE
MEAND: MEAN DISTANCE FROM NODE TO OTHERS IN RADIUS
WKSUM: SUM OF WEIGHTING FUNCTION
CUB0: INTERMEDIATE PARAMETER IN SOLUTION OF CUBIC
ABS CUBR: ABSOLUTE VALUE OF INT IN SOLUTION OF CUBIC
WKE1-WKE2: WEIGHTING FXN TIMES PRINCIPAL DIRECTIONS
RADIUS: RADIUS OF INCLUSION FOR AGW INTERPOLATION
NEWZ: Z COORDINATE FOR PSEUDO DATA POINT
NEWZ: Z COORDINATE FOR PSEUDO DATA POINT
PDIST: DISTANCE FROM PSEUDO DATA POINT TO OTHER NODES
SPHARRAY: SQUARE ROOT OF INTERMEDIATE IN CUBIC SOLUTION
MEAN DISTANCE FROM NODE TO OTHERS IN RADIUS
SIGMA: VALUE USED IN ADAPTIVE GAUSSIAN WINDOW INTERP
WK: WEIGHTING FUNCTION
DIST: DISTANCE FROM NODE TO OTHER NODES
V2: Z VELOCITY
VR: R VELOCITY
WK1: SUM OF WEIGHTING FXN TIMES 1 DIRECTION
WK2: SUM OF WEIGHTING FXN TIMES 1 DIRECTION
VELO: VELOCITY RAW DATA
PS1-PSE: PRINCIPAL DIRECTION AT PSEUDO DATA POINTS
WREL: ROTATION RATE OF 1 STRAINING DIRECTIONS WRT LIQUID
DE1DZ: DERIVATIVE OF R COMPONENT OF 1 AXIS WRT Z
DE1DR: DERIVATIVE OF R COMPONENT OF 1 AXIS WRT R
DE2DZ: DERIVATIVE OF Z COMPONENT OF 1 AXIS WRT Z
DE2DR: DERIVATIVE OF Z COMPONENT OF 1 AXIS WRT R
S: SQUARE ROOT OF NEGATIVE OF DIN2
EP: SMALL VALUE USED TO PREVENT DIVISION BY ZERO
COORD: DATA FILE WITH COORDINATES
DEFORM: DATA FILE WITH RATE OF DEFORMATION COMPS
VORTIC: DATA FILE WITH VORTICITY COMPONENTS
VELOC: DATA FILE WITH VELOCITIES

FLOFILE: NAME OF FILE TO WRITE FLOW PARAMETER

DISFILE: NAME OF FILE TO WRITE DISSIPATION FUNCTION

THIS IS LINE 107

INTEGER I, J, K, L, NODES, NODES2, NODES3, NODES4, ROW, COL
INTEGER TENROWS, RZROWS, VORROWS, IDATA(2500)
REAL*8 D1(2500), D2(2500), D3(2500), D4(2500), D5(2500), VISC
REAL*8 DATA(10000), POS(2500, 5), R(2500), Z(2500), ROD(2500, 5)
REAL*8 VOR(2500, 5), V1(2500), V2(2500), V3(2500), V4(2500), V5(2500)
REAL*8 DIN1(2500), DIN2(2500), DIN3(2500), DIN4(2500), DIN5(2500)
REAL*8 DISFILE, NAME OF FILE TO WRITE DISSIPATION FUNCTION

READ IN RAW DATA

WRITE(6, 1)
1 FORMAT(1X, 'ENTER FILENAME WITH COORDINATES')
READ(5, 2) COORD
2 FORMAT(A20)

WRITE(6, 3)
3 FORMAT(1X, 'ENTER FILENAME WITH COMPONENTS OF D')
READ(5, 2) DEFORM

WRITE(6, 4)
4 FORMAT(1X, 'ENTER FILENAME WITH COMPONENTS OF VORTICITY')
READ(5, 2) VORTIC

WRITE(6, 5)
5 FORMAT(1X, 'ENTER FILENAME WITH VELOCITIES')
READ(5, 2) VELOC

WRITE(6, 11)
11 FORMAT(1X, 'ENTER FILENAME TO WRITE ASTARITA FLOW PARAMETER')
READ(5, 2) FLOFILE

WRITE(6, 12)
12 FORMAT(1X, 'ENTER FILENAME TO WRITE DISSIPATION FXN')
READ(5, 2) DISFILE

WRITE(6, 18)
18 FORMAT(1X, 'ENTER NUMBER OF NODES')
READS(19) NODES

WRITE(6, 14)
14 FORMAT(1X, 'ENTER VISCOSITY IN POISE')

READ(5, *) VISC

OPEN(UNIT=44, FILE=COORD, STATUS=OLD)
OPEN(UNIT=45, FILE=DEFORM, STATUS=OLD)
OPEN(UNIT=46, FILE=VORTIC, STATUS=OLD)
OPEN(UNIT=47, FILE=VELOC, STATUS=OLD)
OPEN(UNIT=55, FILE=FLOFILE, STATUS=NEW)
OPEN(UNIT=66, FILE=DISFILE, STATUS=NEW)
OPEN(UNIT=77, FILE=DISFILE, STATUS=NEW)

READ IN FILES AND CONVERT TO VARIABLES

THIS IS LINE 18
**READ IN COORDINATES**

RZROWS=NODES2+1  
READ(44,*,END=100) ((POS(ROW,COL).COL=1,5).ROW=1,RZROWS)  
100 CONTINUE  

DO I=1,2500  
DO J=1,5  
K=5*(I-1)+J  
IF(K.LE.NODES) THEN  
R(K)=POS(LJ)  
ELSE  
L=K-NODES  
Z(L)=POS(LJ)  
ENDIF  
ENDDO  
ENDDO  

**READ IN COMPONENTS OF 2D**  
TENROWS=NODES4+1  
READ(45,*,END=200) ((ROD(ROW,COL).COL=1,5).ROW=1,TENROWS)  
200 CONTINUE  

DO I=1,2500  
DO J=1,5  
K=5*(I-1)+J  
IF(K.LE.NODES) THEN  
D11(K)=ROD(LJ)  
STR11(K)=2*VISC*D11(K)  
ELSEIF(K.LE.NODES2) THEN  
L=K-NODES  
D22(L)=ROD(LJ)  
STR22(L)=2*VISC*D22(L)  
ELSE  
L=K-NODES2  
D12(L)=ROD(LJ)  
STR12(L)=2*VISC*D12(L)  
ENDIF  
ENDDO  
ENDDO  

**READ IN COMPONENTS OF VORTICITY**  
VORROWS=NODES+1  
READ(46,*,END=300) ((VOR(ROW,COL).COL=1,5).ROW=1,VORROWS)  
300 CONTINUE  

DO I=1,2500  
DO J=1,5  
K=5*(I-1)+J  
IF(K.LE.NODES) THEN  
V21(K)=VOR(LJ)  
V12(K)=-VOR(LJ)  
ENDIF  
ENDDO  
ENDDO  

**READ IN VELOCITY COMPONENTS**  
READ(47,*,END=400) ((VELO(ROW,COL).COL=1,5).ROW=1,RZROWS)  
400 CONTINUE  

DO I=1,2500  
DO J=1,5  
K=5*(I-1)+J  
IF(K.LE.NODES) THEN  
VR(K)=VELO(LJ)  
VZ(K)=VELO(LJ)  
ENDIF  
ENDDO  
ENDDO

DO I=1,NODES
  DIN(I)=D11(I)+D22(I)+D33(I)
  DIN2(I)=D11(I)*D22(I)+D11(I)*D33(I)+D22(I)*D33(I)-D11(I)**2
  DIN3(I)=D11(I)**2*D22(I)+D33(I)**2-D11(I)**2
  TIN(I)=2*VISC*DIN(I)
  VIN2(I)=4*VISC**2*DIN2(I)
  TN3(I)=8*VISC**3*DIN3(I)
ENDDO

SOLVE CUBIC EQUATION FOR PRINCIPAL STRAINING DIRECTIONS

SOLUTION TO CUBIC FROM PERRY'S PAGE 2-15
ROOTS DEPEND ON SIGN AND MAGNITUDE OF VARIABLE CUBR
CUBR=0 GIVES 3 REAL ROOTS WITH AT LEAST 2 EQUAL
CUBR>0 GIVES 1 REAL AND 2 COMPLEX CONJUGATE ROOTS
CUBR<0 GIVES 3 UNEQUAL REAL ROOTS

PI=3.1415927

DO I=1,NODES
  CUBP(I)=(3*TIN2(I)-TINI(I)**2)/3
  CUBQ(I)=(-27*TIN3(I)+9*TINI(I)*TIN2(I)-2*TINI(I)**3)/27
  CUBR(I)=(CUBP(I)/3)**3+(CUBQ(I)/2)**2
  ABSCUBR(I)=ABS(CUBR(I))
  IF(ABSCUBR(I).EQ.0) THEN
    WRITE(6,31) I, R(I), Z(I), TIN2(I), TIN3(I), CUBR(I)
  ELSEIF(ABSCUBR(I).EQ.0) THEN
    A(I)=(-TIN2(I)**0.3333333)
    SIGMA1(I)=2*A(I)
    SIGMA2(I)=-A(I)
    SIGMA3(I)=-A(I)
  ELSE
    PHIARG(I)=(27**(CUBQ(I))**2/-4*CUBP(I)**3))
    SPHIARG(I)=SQRT(PHIARG(I))
    IF(PHIARG(I).LT.0) THEN
      WRITE(6,555) I, TIN2(I), TIN3(I)
  ELSE
    SIGMA1(I)=2*SQRT(-TIN2(I)/3)*COS(PHI(I)+4*PI/3)
    SIGMA2(I)=2*SQRT(-TIN2(I)/3)*COS(PHI(I)+2*PI/3)
    SIGMA3(I)=2*SQRT(-TIN2(I)/3)*COS(PHI(I)+3*PI)
  ENDIF
ENDDO

OBTAIN 1 DIRECTIONS FROM 1 STRESSES AND STRESS TENSOR

DO I=1,NODES
  IF(SIGMA1(I).EQ.STR11(I)) THEN
    E2(I)=0
    E3(I)=1
  ELSE
    E1(I)=STR12(I)*SIGMA1(I)-STR11(I)
  ENDIF
ENDDO
MAG(I) = \sqrt{1 + E(I)^2}
E(I) = E(I) / MAG(I)
E2(I) = 1 / MAG(I)
ENDIF
ENDDO

***************
CALCULATE ASTARITA FLOW CRITERIA
***************

ZERO COUNTERS

DO \( I = 1, NODGES \)
RADIUS(I) = 2.0
TOTDIST(LK) = 0.0
WKSUM(LK) = 0.0
WKEISUM(LK) = 0.0
WKE2SUM(LK) = 0.0
IDATA(I) = 0
ENDDO
ENDDO

DEFINE FOUR PSEUDO DATA POINTS AROUND NODE. THE DATA POINTS WILL IN A CHECKERBOARD PATTERN, WITH A SEPARATION OF ONE HALF OF THE MINIMUM SEPARATION.

DO \( I = 1, NODGES \)
DO \( J = 1, NODGES \)
DIST = (R(I) - R(J))^2 + (Z(I) - Z(J))^2
IF(DIST.GT.0.AND.DIST.LT.MDIST(I)) THEN
MDIST(I) = DIST
RADIUS(I) = 4 * MDIST(I)
NEWR(I, 1) = R(I) + (MDIST(I) / 2)
NEWZ(I, 1) = Z(I)
NEWR(I, 2) = R(I)
NEWZ(I, 2) = Z(I) + (MDIST(I) / 2)
NEWZ(I, 3) = Z(I)
NEWR(I, 4) = R(I)
NEWZ(I, 4) = Z(I) - (MDIST(I) / 2)
ENDIF
ENDDO
ENDDO
ENDDO
ENDDO

CALCULATE THE MEAN PARTICLE SEPARATION AND WIDTH OF GAUSSIAN FUNCTION FOR EACH PSEUDO DATA POINT.

DO \( I = 1, NODGES \)
DO \( K = 1, 4 \)
DO \( J = 1, NODGES \)
DIST = (R(I) - R(J))^2 + (Z(I) - Z(J))^2
IF(DIST.LE.RADIUS(I)) THEN
PDIST = (R(J) - NEWR(I, K))^2 + (Z(J) - NEWZ(I, K))^2
IDATA(I) = IDATA(I) + 1
TOTDIST(LK) = TOTDIST(LK) + PDIST
MEAND(LK) = TOTDIST(LK) / IDATA(I)
SIGMA(LK) = 1.24 * MEAND(LK)
ENDIF
ENDDO
ENDDO
ENDDO
ENDDO
ENDDO
ENDDO

USE AN ADAPTIVE GAUSSIAN WINDOW TO INTERPOLATE AT THE PSEUDO DATA POINTS

DO \( I = 1, NODGES \)
DO \( K = 1, 4 \)
DO \( J = 1, NODGES \)
DIST = (R(I) - R(J))^2 + (Z(I) - Z(J))^2
PDIST = (R(J) - NEWR(I, K))^2 + (Z(J) - NEWZ(I, K))^2
IF(DIST.LE.RADIUS(I)) THEN
WK(I, K) = EXP(-PDIST / SIGMA(LK)^2)
WKSUM(LK) = WKSUM(LK) + WK(I, K)
WKEISUM(LK) = WKEISUM(LK) + WK(I, K) * E(I)
WKE2SUM(LK) = WKE2SUM(LK) + WK(I, K) * E2(I)
ENDIF
ENDDO
ENDDO
ENDDO
ENDDO
ENDDO
ENDDO
ENDDO

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WKE2SUM(I.K)=WKE2SUM(LK)+WKE2(I.K)

PSE1(I.K)=WKE1SUM(I.K)/WKSUM(LK)
PSE2(I.K)=WKE2SUM(I.K)/WKSUM(LK)

ENDIF
ENDDO
ENDDO
ENDDO

USE DIFFERENCES BETWEEN PSEUDO DATA POINTS TO APPROXIMATE
DERIVATIVES 

DO I=1,NODES
DE1DR(I)=(PSE1(I1)-PSE1(I3))/MDIST(I)
DE2DR(I)=(PSE2(I1)-PSE2(I3))/MDIST(I)
DE1DZ(I)=(PSE1(I2)-PSE1(I4))/MDIST(I)
DE2DZ(I)=(PSE2(I2)-PSE2(I4))/MDIST(I)
ENDDO

***************
CALCULATE WEIGHTING FUNCTION

EP=0.0000001

DO 1=1,NODES
WREL(I)=E1(I)^VZ(I)^[(DE1DZ(I)/DE2DZ(I)]
+[-E2(I)^VR(I)^((DE1DR(I)+DE2DR(I)))/0.5^V12(I)]
WREL(I)=ABS(WREL(I))
S(I)=SQRT(DINI(I)^2-DIN2(I))
W(I)=WREL(I)/S(I)
IF(W(I)).GE.1.0 THEN
W(I)=1.0
ENDIF
ENDDO

ENDDO

*******NOTE: INSERTED FROM OTHER*********
CALCULATE GIESEKUS FLOW CRITERIA

DMAX=0.0

DO 1=1,NODES
DII(I)=VISC^2*(D11(I)^2+D22(I)^2+D33(I)^2+D12(I)^2+D13(I)^2+D23(I)^2)
NSD(I)=STR22(I)-STR11(I)
NNSD(I)=NSD(I)*(1-W(I))
IF(NNSD(I).GT.DMAX) THEN
DMAX=NDISS(I)
DMAXR=R(I)
DMAXZ=Z(I)
ENDIF
ENDDO

WRITE(6,424) DMXR, DMAXR, DMAXZ

424 FORMAT(1X,'DISS MAX. ',F8.3)

**********PROGRAM TO SAVE SPACE**********THIS IS LINE 257********

DO 1=1,NODES
EPS(I)=SQRT(-DIN2(I))
WRITE(6,123) D11(I),D12(I),D22(I),D33(I),DIN2(I)
123 FORMAT(1X,SE14.7)
OMEGA(I)=0.5^ABS(V12(I))
IF(ABS(OMEGA(I)).LE.0.0000001) THEN
OMEGA(I)=0.0
ENDIF
IF(EPS(I).EQ.0.0) THEN
WRITE(6,71) I
71 FORMAT(1X,'PROBLEM W/ EPS=0 AT I: ',I5)
ELSE
RHO(I)=OMEGA(I)/EPS(I)
GIESR(I)=(1-RHO(I))/W(I+EPS(I))
ENDIF
IF(GIESR(I).GT.1.2) THEN
WRITE(6.93) I, R(I), Z(I), EPS(I), OMEGA(I), GIESR(I)
FORMAT(1X,4,3X,5E14.7)
ENDIF
ENDDO

***************
WRITE INFORMATION TO FILES
***************  THIS IS LINE 468

DO I=1,NODES,5
WRITE(77.91) DISS(I), DISS(I+1), DISS(I+2), DISS(I+3), DISS(I+4)
WRITE(66.91) NDISS(I), NDISS(I+1), NDISS(I+2), NDISS(I+3), NDISS(I+4)
WRITE(55.91) W(I), W(I+1), W(I+2), W(I+3), W(I+4)
FORMAT(5E14.7)
ENDDO

CLOSE(44)
CLOSE(45)
CLOSE(46)
CLOSE(47)
CLOSE(55)
CLOSE(66)
CLOSE(77)

END

MSTRAIN.FOR
WRITTEN BY JOHN CLAY, 7/97

THIS PROGRAM CALCULATES THE TOTAL STRAIN ON A MATERIAL
LINE FROM DATA GENERATED IN THE SIMULATION PACKAGE,
POLYFLOW. THE FOLLOWING VARIABLES ARE INPUT ALONG A
GIVEN STREAMLINE: COORDINATES, COMPONENTS OF THE RATE
DEFORMATION AND VORTICITY TENSORS, AND RESIDENCE TIME.
THIS PROGRAM CALCULATES THE INVARIANTS, SOLVES THE CUBIC
CHARACTERISTIC EQUATION FOR THE PRINCIPAL STRESSES AND
SOLVES FOR THE PRINCIPAL DIRECTIONS AND PRINCIPAL
STRETCHING RATES. THE INCREMENTAL STRAIN ALONG A
STREAMLINE IS THEN CALCULATED BETWEEN ADJACENT NODES.
FIRST, THE AVERAGE STRETCHING RATE AND STRAINING
DIRECTION ARE CALCULATED BETWEEN NODES. NEXT, THE ANGLE
BETWEEN THE STRAINING AXIS AND THE MATERIAL LINE IS
CALCULATED. THE INCREMENTAL STRAIN BETWEEN TWO NODES IS
CALCULATED FROM THE STRAIN RATE AND RESIDENCE TIME.
AFTER THE MATERIAL LINE IS DEFORMED, IT IS ROTATED BASED
ON THE MAGNITUDE OF THE VORTICITY. THE CALCULATION THEN
MOVES TO THE NEXT NODE ALONG THE STREAMLINE

VARIABLE FUNCTIONS  THIS IS LINE 26

I: INTEGER COUNTER
J: INTEGER COUNTER
K: INTEGER COUNTER
L: INTEGER COUNTER
R: RADIAL COORDINATE
Z: AXIAL COORDINATE
ROD: RATE OF DEFORMATION TENSOR COMPONENTS
VOR: VORTICITY TENSOR COMPONENTS
V12-V21: COMPONENTS OF VORTICITY TENSOR
D11-D33: COMPONENTS OF RATE OF DEFORMATION TENSOR
D11-D13: INVARIANTS OF RATE OF DEFORMATION TENSOR
T11-T13: INVARIANTS OF RATE OF STRESS TENSOR
V12: SECOND IN Variant OF VORTICITY TENSOR
CUBR: VARIABLE WHICH DETERMINES TYPES OF ROOTS IN CUBIC
A: INTERMEDIATE VARIABLE IN SOLUTION OF CUBIC
PHIARG: INTERMEDIATE VARIABLE IN SOLUTION OF CUBIC
PHI: INTERMEDIATE VARIABLE IN SOLUTION OF CUBIC
SIGMA1-SIGMA3: THREE PRINCIPAL STRESSES
E1: PRINCIPAL DIRECTION UNIT VECTOR
E2: PRINCIPAL DIRECTION UNIT VECTOR
MAG: MAGNITUDE OF DIRECTION VECTOR
STREAM: NAME OF FILE WITH DATA ALONG A STREAMLINE
SFILE: NAME OF FILE TO WRITE TOTAL STRAIN
THIS IS LINE 52

INTEGER I, K, IDATA, TGTC, TLTC, SWCOUNT, MAXFLAG, MINFLAG
INTEGER PTCOUNT
REAL*8 D11(1000), D12(1000), D22(1000), D33(1000), VISC
REAL*8 R(1000), Z(1000), V12(1000), V21(1000), D11(1000)
REAL*8 D22(1000), D33(1000), T11(1000), T22(1000), TIN(1000);
REAL*8 VINC(1000), VISC, TIME(1000), AD11(1000), AD22(1000)
REAL*8 CUBR(2500), SIGMA1(1000), SIGMA2(1000), SIGMA3(1000)
REAL*8 PHIARG(1000), PHI(1000), E11(1000), MAC1(1000), E12(1000), P1
REAL*8 STR1(1000), STR2(1000), AD33(1000), AD12(1000)
REAL*8 STR12(1000), STR33(1000), ABS_CUBR(1000), SIGMA1(1000)
REAL*8 CUBQ(1000), SIGMA2(1000), TSTRAIN(1000), MATRX(1000)
REAL*8 SPHIARG(1000), MATRL, MATZL, EAVG(1000), ROTATE(1000)
REAL*8 ANGLE1(1000), COSARG(1000), NEWANG(1000)
REAL*8 SR11(1000), SR22(1000), SR33(1000), STMAX(1000), STRMIN(1000)
REAL*8 ZMAX(1000), LOGSTM(1000), LOGSTL(1000), STRMIN(1000)
REAL*8 Z11(1000), S11AVG(1000), SR22AVG(1000), E11AVG(1000)
REAL*8 E21(2500), E22(2500), E11AVG(2500), F11AVG(1000)
REAL*8 E11TEMP, E12TEMP, SITEMP, E22AVG(1000)
REAL*8 ANGL1ARG(1000), ANGL2ARG(1000), MATRMX(1000)
REAL*8 MATZM(1000), MATRMN(1000), MATZMN(1000)
REAL*8 AD11(1000), AD12(2000), AD33(1000)
CHARACTER*20 STREAM I, STREAMZ, SFILE, SFILE2, SFILE3
CHARACTER*20 SFILE4

READ IN RAW DATA

WRITE(6,1)
1 FORMAT (I10,' ENTER FILENAME WITH R. Z. TIME AND VORT)
READ(5,2) STREAM1

WRITE(6,3)
3 FORMAT (A20)

WRITE(6,11)
11 FORMAT (I10,' ENTER FILENAME TO WRITE STRAIN')
READ(5,5) SFILE

WRITE(6,12)
12 FORMAT (I10,' ENTER FILENAME TO WRITE MAX STRAIN')
READ(5,5) SFILE2

WRITE(6,13)
13 FORMAT (I10,' ENTER FILENAME TO WRITE MIN STRAIN')
READ(5,5) SFILE3

WRITE(6,14)
14 FORMAT (I10,' ENTER FILENAME TO WRITE SR')
READ(5,5) SFILE4

WRITE(6,21)
21 FORMAT (I10,' ENTER VISCOSITY IN POISE')
READ(5,*) VISC
VISC=VISC/10000

OPEN (UNIT=41, FILE=STREAM1, STATUS=OLD)
OPEN (UNIT=42, FILE=STREAM2, STATUS=OLD)
OPEN (UNIT=51, FILE=SFILE, STATUS=NEW)
OPEN (UNIT=52, FILE=SFILE2, STATUS=NEW)
OPEN (UNIT=53, FILE=SFILE3, STATUS=NEW)
OPEN (UNIT=54, FILE=SFILE4, STATUS=NEW)

READ IN FILES AND CONVERT TO VARIABLES

READ(5,9) IDATA

DO 1=1,1000
READ(41,* , END=100) R(I), Z(I), TIME(I), V21(I)
V12(I)=V21(I)
IDATA=IDATA+1
1 ENDDO

348
CONTINUE

DO I=1,1000
   READ(42,*) END=200 D11(I),D22(I),D33(I),D12(I)
ENDDO

CALCULATE INVARIANTS

THE INVARIANTS ARE CALCULATED BASED ON THE FORMULAS IN MACOSKO.
NOTE THAT THESE ARE DIFFERENT THAN THE INVARIANT DEFINITIONS IN
DYNAMICS OF POLYMERIC LIQUIDS. THE FIRST INVARIANT IS THE TRACE
OF THE TENSOR. THE SECOND INVARIANT IS ONE-HALF OF THE TRACE
SQUARED MINUS ONE-HALF OF THE TRACE OF THE TENSOR SQUARED. THE
THIRD INVARIANT IS THE DETERMINANT OF THE TENSOR.

SET TOLERANCES TO AVOID ROUND-OFF ERROR

DO I=1,DATA
   AD11(I)=ABS(D11(I))
   AD22(I)=ABS(D22(I))
   AD33(I)=ABS(D33(I))
   AD12(I)=ABS(D12(I))
   IF(AD11(I).LT.0.000001) THEN
      D11(I)=0.0
   ELSEIF(AD22(I).LT.0.000001) THEN
      D22(I)=0.0
   ELSEIF(AD33(I).LT.0.000001) THEN
      D33(I)=0.0
   ELSEIF(AD12(I).LT.0.000001) THEN
      D12(I)=0.0
   ENDIF
   STR1(I)=2*D11(I)*VISC
   STR22(I)=2*D22(I)*VISC
   STR33(I)=2*D33(I)*VISC
   STR12(I)=2*D12(I)*VISC
ENDDO

DO I=1,DATA
   DIN1(I)=D11(I)+D22(I)+D33(I)
   DIN2(I)=D11(I)*D22(I)+D11(I)*D33(I)+D22(I)*D33(I)-D12(I)**2
   DIN3(I)=D11(I)*D22(I)*D33(I)-D33(I)*D12(I)**2
   A1(I)=ABS(DIN1(I))
   A2(I)=ABS(DIN2(I))
   A3(I)=ABS(DIN3(I))
   IF(A1(I).LT.0.000001) THEN
      DIN1(I)=0.0
   ELSEIF(A2(I).LT.0.000001) THEN
      DIN2(I)=0.0
   ELSEIF(A3(I).LT.0.000001) THEN
      DIN3(I)=0.0
   ENDIF
   T1(I)=2*VISC*DI1(I)
   T22(I)=4*VISC**2*DI2(I)
   T33(I)=8*VISC**3*DI3(I)
   V12(I)=V12(I)*V21(I)
ENDDO

SOLVE CUBIC EQUATION FOR PRINCIPAL STRAINING DIRECTIONS

THE SOLUTION TO CUBIC FROM PERRY'S, PAGE 2-15
ROOTS DEPEND ON SIGN AND MAGNITUDE OF VARIABLE CUBR
CUBR=0 GIVES 3 REAL ROOTS WITH AT LEAST 2 EQUAL
CUBR>0 GIVES 1 REAL AND 2 COMPLEX CONJUGATE ROOTS
CUBR<0 GIVES 3 UNEQUAL REAL ROOTS
PI=3.1415927
TGTC=0
TLTC=0
SWCOUNT=0

DO I=1,JDATA
CUBP(I)=(3*DIN2(I)-DrNl(I)**2)/3
CUBQ(I)=(-27*DIN3(D+9*DINI(I)**2)/27
CUBR(D=(CUBP(I)**3+(CUBQ(I)**2
ABSCUBR(I)=ABS(CUBR(I))

IF(CUBR(I).GE.1.E-5) THEN
WRITE(6,31) I, R(I),Z(I),DIN2(I), DIN3(I), CUBR(I)
FORMAT(1X, 'COMPLEX', 4,1X, 5E15.7)
ELSEIF(ABSCUBR(I).EQ.0) THEN
A(I)=-DIN2(I)**2*(1.0/3.0)
SIGMA1(I)=2*A(I)
SIGMA2(I)=SIGMA1(I)*10000
SIGMA3(I)=A(I)
SIGMA1(I)=SIGMA3(I)*10000
SIGMA2(I)=SIGMA1(I)
SIGMA3(I)=SIGMA3(I)
SR11(I)=SIGMA1(I)
SR22(I)=SIGMA2(I)
SR33(I)=SIGMA3(I)
ELSE
PHIARG(I)=27*(1(CUBQ(I)**2)*4*CUBP(I)**3))
WRITE(6,378) PHIARG(I)
378 FORMAT(1X, 'LPHIARG',I)
SPHIARG(I)=SQRT(PHIARG(I))

IF(SPHIARG(I).GE.1.0.AND.SPHIARG(I).LE.1.01) THEN
SPHIARG(I)=1.0
ELSEIF(SPHIARG(I).LE.-1.0.AND.SPHIARG(I).GE.-1.01) THEN
SPHIARG(I)=-1.0
ENDIF

IF(PHIARG(I).LT.0) THEN
WRITE(6,555) I, DIN2(I), DIN3(I)
555 FORMAT(NEG SQRT,1X,4,1XE14.7,1XE14.7)
ENDIF
PHI(I)=ACOS(SPHIARG(I))
IF(DIN3(I).GT.0) THEN
IF(DIN2(I).GT.0) THEN
WRITE(6,279) I, D11(I), D22(I), D33(I), D12(I), DIN2(I)
279 FORMAT(1X, 'LPHI',I)
ENDIF
SIGMA1(I)=2*SQRT(DIN2(I)/3)*COS(PHI(I)/3)
SIGMA2(I)=SIGMA1(I)*10000
SIGMA3(I)=SIGMA2(I)*10000
SIGMA1(I)=SIGMA3(I)*2*SQRT(DIN2(I)/3)*COS(PHI(I)/3+2*PHI/3)
SIGMA2(I)=SIGMA3(I)*10000
SIGMA3(I)=SIGMA1(I)*2*SQRT(DIN2(I)/3)*COS(PHI(I)/3+4*PHI/3)
SR11(I)=SIGMA1(I)
SR22(I)=SIGMA2(I)
SR33(I)=SIGMA3(I)
TGTC=TTGTC+1
ELSE
IF(DIN2(I).GT.0) THEN
WRITE(6,279) I, D11(I), D22(I), D33(I), D12(I), DIN2(I)
ENDIF
SIGMA1(I)=2*SQRT(DIN2(I)/3)*COS(PHI(I)/3)
SIGMA2(I)=SIGMA1(I)*10000
SIGMA3(I)=SIGMA2(I)*10000
SIGMA1(I)=SIGMA3(I)*2*SQRT(DIN2(I)/3)*COS(PHI(I)/3+2*PHI/3)
SIGMA2(I)=SIGMA3(I)*10000
SIGMA3(I)=SIGMA1(I)*2*SQRT(DIN2(I)/3)*COS(PHI(I)/3+4*PHI/3)
SR11(I)=SIGMA1(I)
SR22(I)=SIGMA2(I)
SR33(I)=SIGMA3(I)
TLTC=TLTC+1
ENDIF
ENDIF
ENDDO

******************************************************************************
OBTAIN 1 DIRECTIONS FROM 1 STRESSES AND STRESS TENSOR
******************************************************************************
• SOLVE FOR SIGMA 1 DIRECTION

DO I=1,DATA
  IF(SIGMA1(I).EQ.D11(I)) THEN
    E13(I)=0.0
    E11(I)=1.0
  ELSE
    E11(I)=D12(I)/SIGMA1(I)-D11(I))
    MAG1(I)=SQRT(E11(I)**2+E12(I)**2)
    E12(I)=E11(I)/MAG1(I)
    E11MAG1(I)=SQRT(E11(I)**2+E12(I)**2)
  ENDIF
ENDDO

WRITE(6,599)
599 FORMAT(1X,'MADE IT TO SOLVING FOR SIGMA2 DIRECTION')

• SOLVE FOR DIRECTION FOR SIGMA2

DO I=1,DATA
  IF(SIGMA2(I).EQ.D11(I)) THEN
    E22(I)=0.0
    E21(I)=1.0
  ELSE
    E21(I)=D12(I)/SIGMA2(I)-D11(I))
    MAG2(I)=SQRT(E21(I)**2+E22(I)**2)
    E22(I)=E21(I)/MAG2(I)
    E22MAG2(I)=SQRT(E21(I)**2+E22(I)**2)
  ENDIF
ENDDO

WRITE(6,607)
607 FORMAT(1X,'MADE IT TO COMPARING PRINCIPAL DIRECTIONS')

• COMPARE PRINCIPAL DIRECTIONS TO ENSURE CONSISTENCY

CHECK THE ROTATION ANGLE FOR A PRINCIPAL AXIS BETWEEN
TWO ADJACENT NODES. IF THE ANGLE IS GREATER THAN A
SET TOLERANCE, VERIFY THAT THE OTHER AXIS IS WITHIN
THE TOLERANCE. IF SO, CHANGE SIGMA1 AND ITS
DIRECTIONS TO SIGMA2 AND ITS DIRECTIONS.

PTCOUNT=DATA-1
DO I=1,PTCOUNT
  ANG1ARG(I)=E11(I)*E11(I+1)+E12(I)*E12(I+1)
  ANG2ARG(I)=E11(I)*E21(I+1)+E12(I)*E22(I+1)
  IF(ANG1ARG(I).LE.-1.0.0R.ANG1ARG(I).GE.1.01) THEN
    WRITE(6,921) I,ANG1ARG(I)
  ENDIF
  IF(ANG2ARG(I).LT.-1.0.0R.ANG2ARG(I).GT.1.01) THEN
    WRITE(6,923) I,ANG2ARG(I)
  ENDIF
921 FORMAT(1X,'PROBS WITH ANGLE1.1X,I4,1X,E14.7)
923 FORMAT(1X,'PROBS WITH ANGLE2.1X,I4,1X,E14.7)
ELSEIF(ANG1ARG(I).LT.-1.0.0R.ANG1ARG(I).GT.1.01) THEN
  ANG1ARG(I)=1.0
ELSEIF(ANG1ARG(I).GT.1.0.0R.ANG1ARG(I).LT.-1.01) THEN
  ANG1ARG(I)=-1.0
ENDIF
921 FORMAT(1X,'PROBS WITH ANGLE1.1X,I4,1X,E14.7)
923 FORMAT(1X,'PROBS WITH ANGLE2.1X,I4,1X,E14.7)
ELSEIF(ANG2ARG(I).LT.-1.0.0R.ANG2ARG(I).GT.1.01) THEN
  ANG2ARG(I)=1.0
ELSEIF(ANG2ARG(I).GT.1.0.0R.ANG2ARG(I).LT.-1.0) THEN
  ANG2ARG(I)=-1.0
ENDIF
921 FORMAT(1X,'PROBS WITH ANGLE1.1X,I4,1X,E14.7)
923 FORMAT(1X,'PROBS WITH ANGLE2.1X,I4,1X,E14.7)
ELSEIF(S11ANG(I).LE.0.0 AND.S11ANG(I).GE.0.698) THEN
  SWCOUNT=SWCOUNT+1
  E1TEMP=E11(I)
  E12TEMP=E12(I)
  SITEMP=SIGMA1(I)
  SRITEMP=SR11(I)
  S11ANG(I)=ACOS(S11ANG(I))
S12ANG(I)=ACOS(S12ANG(I))
IF(S11ANG(I).GE.0.698.0R.S12ANG(I).LE.0.698) THEN
  SWCOUNT=SWCOUNT+1
ELSEIF(S11ANG(I).LE.0.0.0R.S11ANG(I).GE.0.698) THEN
  SWCOUNT=SWCOUNT+1
  E1TEMP=E11(I)
  E12TEMP=E12(I)
  SITEMP=SIGMA1(I)
  SRITEMP=SR11(I)
  S11ANG(I)=ACOS(S11ANG(I))
S12ANG(I)=ACOS(S12ANG(I))
IF(S11ANG(I).GE.0.698.0R.S12ANG(I).LE.0.698) THEN
  SWCOUNT=SWCOUNT+1
ENDIF

351
\( E_{12}(I) = E_{22}(I) \)
\( \sigma_{11}(I) = \sigma_{22}(I) \)

\[ \begin{align*}
E_{11}(I) &= E_{11} \quad \text{TEMP} \\
E_{22}(I) &= E_{22} \quad \text{TEMP} \\
\sigma_{12}(I) &= \sigma_{12} \quad \text{TEMP} \\
\sigma_{21}(I) &= \sigma_{21} \quad \text{TEMP} \\
\end{align*} \]

\[ \text{ELSEIF} (S_{11}(I). \geq 0.698 \text{ AND } S_{12}(I). \gt 0.698) \text{ THEN} \]
\[ \text{WRITE}(6,713) \]
\[ \text{FORMAT}(1X, \text{BIG PROBLEMS WITH E SWITCH}) \]

713 ENDIF
ENDDO

| **CALCULATE STRAIN FOR DIFFERENT MATERIAL LINE ORIENTATIONS** |
| **THIS IS LINE 316** |

| **DEFINE INITIAL STRAIN AND ORIENTATION** |
| **STRAIN(I) = 1.0** |
| **MATZ(I,I) = -1.0** |
| **MATR(I,I) = 0.0** |
| **STRMAX = 1.0** |
| **STRMIN = 1.0** |

**BIG LOOP CALCULATES STRAIN FOR 100 DIFFERENT ORIENTATIONS**

\[ \text{DO } K = 1, 100 \]

\[ \text{MAXFLAG} = 0 \]
\[ \text{MINFLAG} = 0 \]

\[ \text{DO } 1 = 1, \text{PCOUNT} \]
\[ \text{SR}_{11} \text{AVG}(I) = (\text{SR}_{11}(I) + \text{SR}_{11}(I+1))/2 \]
\[ \text{SR}_{22} \text{AVG}(I) = (\text{SR}_{22}(I) + \text{SR}_{22}(I+1))/2 \]
\[ \text{E}_{11} \text{AVG}(I) = (\text{E}_{11}(I) + \text{E}_{11}(I+1))/2 \]
\[ \text{E}_{22} \text{AVG}(I) = (\text{E}_{22}(I) + \text{E}_{22}(I+1))/2 \]
\[ \text{EMAG}(I) = \sqrt{(\text{E}_{11}\text{AVG}(I))^2 + (\text{E}_{22}\text{AVG}(I))^2} \]
\[ \text{E}_{11} \text{AVG}(I) = \text{E}_{11}\text{AVG}(I)/\text{EMAG}(I) \]
\[ \text{E}_{22} \text{AVG}(I) = \text{E}_{22}\text{AVG}(I)/\text{EMAG}(I) \]
\[ \text{VORAVG}(I) = (\text{V}_{12}(I) + \text{V}_{12}(I+1))/2 \]
\[ \text{DELT}(I) = \text{TIME}(I+1) - \text{TIME}(I) \]
\[ \text{COSARG}(I) = \text{MATR}(K,I) \cdot \text{E}_{11}(I) + \text{MATZ}(K,I) \cdot \text{E}_{12}(I) \]
\[ \text{IF}(\text{COSARG}(I). \leq -1.01 \text{ OR } \text{COSARG}(I). \geq 1.01) \text{ THEN} \]
\[ \text{WRITE}(6,63) \]
\[ \text{FORMAT}(1X,T,T,J4,1X,E14.7) \]
\[ \text{ELSEIF}(\text{COSARG}(I). \gt 10.0 \text{ AND } \text{COSARG}(I). \lt -1.01) \text{ THEN} \]
\[ \text{COSARG}(I) = 1.0 \]
\[ \text{ELSEIF}(\text{COSARG}(I). \lt -1.0 \text{ AND } \text{COSARG}(I). \gt -1.01) \text{ THEN} \]
\[ \text{COSARG}(I) = -1.0 \]

63 ENDIF

\[ \text{THETA}(I) = \text{ACOS}(\text{COSARG}(I)) \]
\[ \text{IF}(\text{THETA}(I). \geq \text{PI}/2) \text{ THEN} \]
\[ \text{THETA}(I) = \text{PI} - \text{THETA}(I) \]

ENDIF

**COMPARE STRAIN TO FIND MAXIMUM**

**THIS IS LINE 154**

\[ \text{IF}(\text{STRAIN}(I). \leq \text{STRAIN}(I). \text{AND} \text{STRAIN}(I). \lt \text{STRAIN}(I). \geq \text{STRAIN}(I). \gt \text{STRMIN}) \text{ THEN} \]
\[ \text{STRMAX} = \text{STRAIN}(I) \]
\[ \text{MATR} = \text{MATR}(K,I) \]
\[ \text{MATZ} = \text{MATZ}(K,I) \]
\[ \text{MAXFLAG} = 1 \]

ENDIF

\[ \text{IF}(\text{STRAIN}(I). \lt \text{STRAIN}(I). \text{AND} \text{STRAIN}(I). \leq \text{STRAIN}(I). \geq \text{STRAIN}(I). \gt \text{STRMIN}) \text{ THEN} \]
\[ \text{STRMIN} = \text{STRAIN}(I) \]
\[ \text{MATR} = \text{MATR}(K,I) \]
\[ \text{MATZ} = \text{MATZ}(K,I) \]
\[ \text{MINFLAG} = 1 \]

ENDIF

| **CALCULATE STRAIN FROM TIME AND STRETCHING RATE** |
| **THIS IS LINE 352** |

\[ \text{ERAVG}(I) = \text{SR}_{11}(I) \cdot \cos(\text{THETA}(I)) + \text{SR}_{22}(I) \cdot \sin(\text{THETA}(I)) \]
\[ \text{STRAIN}(I+1) = \text{STRAIN}(I) \cdot \exp(\text{ERAVG}(I) \cdot \text{DELT}(I)) \]
\[ \text{IF}(\text{EQ} \cdot 30) \text{ THEN} \]
WRITE(6,111) I, ERAVG(I), DELT(I), STRAIN(I)
111 FORMAT(1X,I4,1X,E14.7,1X,DT,E14.7, 1X,IN,E14.7)
ENDIF

* ROTATE MATERIAL LINE FROM VORTICITY CONTRIBUTION

ROTATE(I)=0.5*12(I)*DELT(I)
IF(MATZ(K,J).EQ.0) THEN
  ANGLE(I)=PI/2
ELSE
  ANGLE(I)=ATAN(MATR(K,J)/MATZ(K,J))
ENDIF
NEWANG(I)=ANGLE(I)+ROTATE(I)
MATZ(K+1,J)=COS(NEWANG(I))
MATR(K+1,J)=SIN(NEWANG(I))
ENDDO
MATZ(K+1,J)=MATZ(K,J)+0.02
MATR(K+1,J)=MATR(K,J)

* COMPARE STRAIN TO FIND MAXIMUM AND MINIMUM

IF(MAXFLAG.EQ.1) THEN
  DO 1=1,PTCOUNT
    STMAX(I)=STRAIN(I)
    RMAX(I)=R(I)
    ZMAX(I)=Z(I)
    LOGSTM(I)=LOG(STRAIN(I))
    MATRMX(I)=MATR(K,I)
    MATZMX(I)=MATZ(K,I)
  ENDDO
ENDIF

IF(MINFLAG.EQ.1) THEN
  DO 1=1,PTCOUNT
    STMIN(I)=STRAIN(I)
    RMIN(I)=R(I)
    ZMIN(I)=Z(I)
    LOGSTM(I)=LOG(STRAIN(I))
    MATRMN(I)=MATR(K,I)
    MATZMN(I)=MATZ(K,I)
  ENDDO
ENDIF
ENDDO

WRITE INFORMATION TO FILES
***************
WRITE(51,91) RMAX(I), ZMAX(I), STMAX(I), LOGSTM(I)
91  FORMAT(I4,1X,E15.8,1X,E15.8,1X,E15.8,1X,E15.8)
WRITE(52,92)ZMAX(I),MATRMX(I),MATZMX(I),ERAVG(I),STMAX(I)
92  FORMAT(I4,1X,E15.8,1X,E15.8,1X,E15.8,1X,E15.8)
WRITE(53,92)ZMIN(I),MATRMN(I),MATZMN(I),ERAVG(I),STMIN(I)
93  FORMAT(I4,1X,E15.8,1X,E15.8,1X,E15.8)
ENDDO
WRITE(6,727) TGTC, TLTC
727  FORMAT(I4,1X,E15.8,1X,E15.8,1X,E15.8)
WRITE(6,87) SWCOUNT
87  FORMAT(I4,1X,E15.8,1X,E15.8,1X,E15.8)
WRITE(6,88) STRMAX, MATRM, MATZM
88  FORMAT(I4,1X,E15.8,1X,E15.8,1X,E15.8)
WRITE(6,89) STRMIN, MATRL, MATZL
89  FORMAT(I4,1X,E15.8,1X,E15.8,1X,E15.8)
ENDDO
WRITE(6,353)
353  WRITE(5,41) CLOSE(41)
41  WRITE(5,42) CLOSE(42)
42  WRITE(5,31) CLOSE(31)
31  WRITE(5,32) CLOSE(32)
32  WRITE(5,33) CLOSE(33)
33  WRITE(5,34) CLOSE(34)
END