Synthesis and extensional rheology of linear and branched polymer melts

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Preface

This thesis presents the results of my Ph.D. project carried out at the Danish Polymer Centre, Department of Chemical Engineering, Technical University of Denmark (DTU) under the supervision of Professor Ole Hassager, Head of Department Kristoffer Almdal at Risø National Laboratory and Research Professor Kell Mortensen at Risø. The work was performed during the period from February 2004 to January 2007, and was made possible through a grant financed one third from the Technical University of Denmark, one third from the Graduate School of Polymer Science and one third from Risø National Laboratory.

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In many polymer-processing operations the polymer molecules experience a significant amount of orientation and chain stretching. These effects can sometimes be of benefit to the product, for example in a polymer fiber, when alignment of the molecules gives favorable characteristics for the finished product. On the other hand, the effect sometimes gives undesirable effects, for example thermal form instability that may result in warpage of the product. Chain stretching and orientation also has a significant effect on the processing of the product. Processing is often limited by sample breaks that are induced by the rheology of the polymer. Thus, knowledge of the chain orientation and stretch is of interest for not only scientists who are interested in polymer dynamics, but also for product engineers.

The conventional way of measuring the rheology of a given material is by using a shear rheometer. This method is good at inducing chain orientation in the sample, and a large amount of data in this area has insured very reliable models of chain orientation and its effect on rheology. However, because of the rotational nature of the shear flow, the chains are given a chance to relax before a significant amount of chain stretching is observed. Hence, shear rheology is not usable for probing chain stretch. The consequence of this lack of data is poor modes available for estimating the effects of chain stretching on the rheology and as a result, poor model predictions of processes at high deformation rates.

One good way of inducing chain stretch is by elongational rheology experiments. The purpose of this thesis is to investigate the elongational properties of well characterized polymers, with different molecular architecture, and provide reliable data that can be used to test polymer flow models.

The living anionic polymerization-technique is used to synthesize polystyrenes with known molecular weight and narrow molecular mass distribution. Different samples of polystyrenes with linear architecture are synthesized, which is relatively simple, and also polystyrene with star structure and double-star (dumbbell) structure are made, which is more challenging.

The elongational properties are measured in a filament stretching rheometer where a sample is placed between two parallel discs that are separated at a given speed, and the elongational force is measured on one of the discs. It is found that stress-strain behavior of binary blends of linear polystyrene can be described by a differential constitutive model that includes effects of finite chain length and anisotropic drag. It is furthermore found that the behavior of the double-star polystyrene in many ways resemble the behavior observed for a commercial low density polyethylene, know to have a random and unknown degree of branching.
I mange polymer processering enhedsoperationer vil de enkelte polymermolekyler blive udsat for betydelig orientering og kædestræk. Disse effekter er nogle gange fordelagtige for produktet, for eksempel i polymerfibre, hvor orientering af molekylerne i axial retning vil give favorable egenskaber i det endelige produkt. På den anden side kan orientering og kædestræk også give uønskede egenskaber i produktet, for eksempel termisk forminstabilitet, som kan resultere i skrævvrirdning af produktet. Kædestræk og orientering har også en betydelig effekt på processeringen af produktet. Processeringen er ofte begrænset af brud på prøven som er induceret af polymeerreologien. Derfor er kendskab til kædeorientering og stræk af interesse for både forskere som er interesserede i polymerdynamik men også for produktingeniører.

Den konventionelle måde at måle reologiske egenskaber for et givent materiale er ved hjælp af et forskydningsreometer. Denne metode er god til at inducere kædeorientering i en prøve og en stor mængde data inden for forskydningsreologi har givet udslag i meget pålidelige modeller inden for kædeorientering og effekten heraf på reologien. Men fordi forskydningsstrømning er en "roterende" strømning får polymerkæderne mulighed for at relaksere før en signifikant mængde kædestræk kan observeres. Derfor er forskydningsreologi ikke en brugbar metode til at undersøge kædestræk. Konsekvensen af den manglende mængde af data inden for dette område er at modeller til at estimere kædestræk er dårlige, og som et resultat heraf giver de fleste polymerstrømningsmodeller dårlige forudsigelser af processer med høje deformations hastigheder.

En god måde at inducere kædestræk er ved brug af forlængelsesreologi. Formålet med denne afhandling er at undersøge kædeorientering og forlængelsesegenskaberne for velkarakteriserede polymerer med forskellige molekylære arkitekturner, og frembringe pålidelige data som kan bruges til at teste polymerstrømningsmodeller.

Levende anionisk polymerisations-teknikken bliver brugt til at syntetisere polystyrene med kendt molekylvægt og snæver molekylvægtsfordeling. Forskellige prøver af polystyren med lineær arkitektur syntetiseres, hvilket er relativt simpelt, og polystyren med stjerne struktur og dobbeltstjerne, håndvægtsformet, struktur fremstilles, hvilket viser sig at være mere udfordrende.

Forlængelsesegenskaberne måles ved hjælp af en filament stræk reometer hvor en prøve placeres mellem to parallele plader, som derefter trækkes fra hinanden med en bestemt hastighed. Vi finder at spændings-tøjnings opførslen for binære blandinger af lineært polystyren kan beskrives ved hjælp af en differentiel konstitutiv model som inkluderer effekter af endelig
kædelængde og anisotropisk modstand. Desuden bestemmes at forlængelsesopførslen for dobbeltstjernen på mange måder minder om opførslen observeret for en kommerciel lav densitet polyethylen, som er kendt for at have en tilfældig og ukendt grad af forgrening.
1 Introduction

1.1 Polymer models and background

The flow behavior polymeric melts is of interest to both theoreticians who work on the basic understanding of rheology, and to engineers in the polymeric processing industry who deal with e.g. injection moulding or extrusion. The macromolecular character of polymers gives rise to phenomena such as shear thinning and extensional hardening that cannot be described by constitutive models developed for low molecular weight fluids with rate independent viscosities.

Most of the conceptual understanding of the dynamics of concentrated polymer solutions and polymer melts originate on the work by Doi and Edwards (1986) (DE), where the polymer chain, on a molecular level, is described as a chain constrained inside a tube, that consists of other chains. In this model the stresses arising from a deformation originated only from an orientation disturbance of the chain, that is, the DE assumes a non-stretchable chain. Furthermore the model only described the motion of the chain to happen in a repeating manner along its longitudinal direction, which explains why the model is often referred to as the "reptation model".

In the original DE model the fluctuating motion of the chain onto its own tube at the chain ends were neglected and gave account the scaling of the zero shear viscosity with the cube of the molecular weight, $\eta_0 \sim M_w^3$. This scaling was found to be true for monodisperse polymers melts with more than approximately 200 entanglements, $Z$. Entanglements are topological molecular restrictions resulting from the fact that the chains cannot pass through each other. The number of entanglements are often used as a measure of relative polymer length.

The most common polymers used commercially and for conceptual studies have however far fewer than 200 entanglements, and in 1998 Milner and McLeish proposed a addition to the DE model where the effect of chain-end fluctuations was included. This correction to the reptation model resulted in a prediction of the zero shear viscosity, $\eta_0 \sim M_w^{3.4}$ for polymers with $Z<200$, which agreed with experimental observations.

A number of corrections to the reptation model have throughout the two last decades been proposed. These include effects of constrain release mechanisms, and also chain stretch, Marrucci and Grizzutti (1988). The
combination of these different effects has refined the original reptation model, and enabled the understanding and prediction of not only linear chain dynamics, but also dynamics of branched polymers, such as stars and pompoms, (Ruymbeke et al. 2005, McLeish and Larson 1998). Furthermore steps into the more industrially important polydisperse polymers have been taken using double reptation, Des Cloizeaux (1988).

The validation of the different promising tube reptation models has however been mainly based on experimental measurements in the linear viscoelastic regime, such as loss and storage moduli results obtained by using commercial rotational rheometers. Other kinds of non-linear viscoelastic behavior can also be measured on rotational rheometers, such as stress response after a sudden shearing displacement, or the stress after transient shear start-up, but nevertheless, these measurements are limited to shear flow.

### 1.2 Elongational rheological studies

Shear rheology is the cornerstone in the experimental study of polymeric flow, and hence most theoretical models have for many years been compared with shear rheology-results, as is seen in textbooks such as Bird et al. (1986) and Larson (1999). Non-shear flows are however encountered in a number of polymer processing operations, such as fiber spinning and blow moulding where the extensional properties are totally dominating, but also in extrusion and injection moulding where a combination of shear-and non-shear occurs.

Besides from its industrial relevance, experimental data on non-shearing flows, e.g. elongational flow, is of interest in the development of molecular based constitutive model, such as tube-based models, because elongational flow in a sense is much stronger and simpler than shear flow. Shear flow is a "rotational" flow and for a constant shear rate the fluid elements are separated linearly in time, whereas elongational flow is irrotational, and the fluid element separation happens exponentially in time. This means that the deformation of the individual polymer chain in elongation can be much larger than in shear flow, and effects of chain stretch and orientation will be much more profoundly seen, and constitutive models can be challenged in a more extreme manner than in shear.

The studies of the behavior of polymers in elongational flow has for a long time been scarce which was due to experimental problems of constructing a rheometer that was able to generate a well-defined uniaxial extensional flow. Recently several experimental setups have been made to measure the elongational properties of polymers and since a 1994 Rheometric Scientific has sold the "Polymer melt elongational rheometer" (RME), which has been the most commonly used polymer melt rheometer to measure on elongational flow for a long time, described by Meissner and Hostettler 1994. The RME uses two belts, oppositely rotating, where a long
rod shaped polymer sample is stretched between the melts. One of the limitations of the RME is that the elongational deformation is merely imposed, and the strain is usually not visually confirmed. Schultze et al. (2001) compared the performance of several RME-rheometers placed in scientific laboratories around the world, and video recorded the samples during elongation to determine the true elongational rate. It was found that at high elongational rates, the difference between the imposed and the true elongational rate was up to 20%, and this difference was also polymer type dependent, the difference for PMMA being higher than for LLDPE. Another problem by the RME-type rheometer is the necking phenomena, which occurs if the elongated sample for instance contains small surface defects, and is often observed if the polymer does not exhibit elongational stain hardening. Because of the length of the polymer sample, the location of the necking cannot be predicted. The RME-type rheometer was able to measure the elongational properties of high viscous melts, but not the properties for low viscous melt or solutions. For this purpose an alternative type of extensional rheometer was developed, where a drop of polymer solution could be stretched as a filament, which gave birth to the science of filament stretching rheometry.

1.3 Filament stretching

The challenges arising in performing filament stretching rheometry have received much attention in the last two decades, and I will here give an overviews of some of the challenges and how different scientist have solved them. A thorough review of filaments stretching rheometry has been written by McKinley and Sridhar (2002). In filament stretching the test sample is placed between two parallel plates, usually circular plates, the plates are then separated with a given speed, and the force needed for the separation is measured at one of the endplates. A sketch of a filament is shown in figure 1.1. The test sample adheres to the plates, which gives rise to a no slip boundary condition, that inevitably will prevent an event stretch in the vertical plane. The different fluid elements of the filament close the endplates will be stretched less than the fluid at the center of the filament. Furthermore, the stress of the stretched filament was different in the vertical plane, since the diameter, and thereby the square section vary with height.

This gave rise to the need of visual strain measurements of the filament, and Sridhar et. al (1991) suggested that the filament diameter could be measured at the center of the filament during stretching, thereby calculating the stress as elongational force divided with square section area.

Another consequence of the no-slip boundary condition is that the kinematic deformation for a non-Newtonian fluid will not only depend on the separation of the endplates, but also on the speed of which the endplates are separated.
In order to have uniaxial stretch, the length of a cylindrically shaped fluid element has to increase exponentially, and assuming constant volume, the filament radius will decrease exponentially. In filament stretching this will however not happened: the center radius will decrease more than ideal cylinder, because much of the sample is places at the endplates.

To solve this problem Orr and Sridhar (1999) used an iterative approach, which relate the distance between the end plates and the radius of the filament. Using this approach the development in radius converges towards the desired profile after about four iterative experiments. Different groups have constructed rheometers that are able to reproduce elongational results using the same fluid, Anna et al. (2001). Most emphasis has been on testing polymer solutions at room temperature where the iterative approach of separating the endplates have shown to work successfully.

However for polymer melts, that exhibit much less strain hardening than polymer solutions, the filament kinematics is fundamentally different and the relationship between plate separation and mid-filament diameter is less obvious. This motivated the development of a filament stretching rheometer in which diameter measurements during filament stretching is used to control the position of the top-plate by closed loop control, Anna et al. (1999). Anna et. al however never successfully implemented the closed loop control what showed to be dynamically unstable.

1.4 Filament stretching Rheometer at DTU, Lyngby

The filament stretching rheometer situated at the Technical University of Denmark has implemented the feed back control of the endplates, and the sample is surrounded by a vertical oven, which has enabled it to measure on high temperature melts. With this rheometer the elongational properties of two well-characterized, narrow molecular-mass distributed polystyrene melts was measured over a broad range of elongational rates,
and the steady elongational viscosity was found, Bach et al. (2003).

The steady elongational viscosity is of little interest in industrial polymer processing operations, but has often been used to validate constitutive models. Bhattacharjee et al. (2003) did determine the steady state viscosity for narrow molecular distribution (NMMD), monodisperse polystyrene in a solution, but Bach et al. (2003) were the first to find it for a NMMD polymer melt. One reason of the success of the filament stretching rheometer (FSR) at DTU is the effort that is put into the construction of the surrounding oven to ensure constant temperature and eliminate temperature gradients. The implementation of the closed loop control of the deformation means that fewer experiments has to be performed to cover the elongational properties over a range of elongational rates, which is an important property, since melt rheology is very time consuming and requires patience in every step.

1.5 Material functions in rheology

The purpose of a shear rheometer is to measure the relation between applied deformation, strain, and the applied force needed for the deformation, \( F \). In an ideal case a fluid is placed between two parallel plates with a distance \( b \), and the displacement of the upper plate with a velocity \( V \) will create a velocity in the \( x \)-direction, \( v_x(y) \) where the velocity varies linearly in the \( x \)-direction. The steady shear rate denoted as \( \dot{\gamma} \) is defined as:

\[
\dot{\gamma} = \frac{V}{b} \quad (1.1)
\]

and the shear after a given time \( t \) is

\[
\gamma = \frac{V}{b} t \quad (1.2)
\]

![Figure 1.2. Oscillatory shear between two parallel plates.](image)

The shear stress is defined by:

\[
\sigma_{xy} = \frac{F}{A} \quad (1.3)
\]
where $A$ is the cross section area of the upper plate, and $F$ is the exerted force. Polymer liquids have viscoelastic properties, which means that they exhibit both viscous and elastic behavior. For very slow shear rates, a polymer shows properties that are viscous and conversely for large shear rates, elastic properties are measured.

The purpose of a small amplitude oscillatory shear experiment, as oppose to a steady strain rate experiment, is to quantify the viscous and elastic properties. The strain and stress will vary with time as:

$$\gamma(t) = \gamma_0 \sin(\omega t) \quad \text{and} \quad \sigma_{xy}(t) = \sigma_{xy,0} \sin(\omega t + \phi(\omega)). \quad (1.4)$$

The stress is out of phase with the strain and $\phi(\omega)$ is the phase shift between strain and stress. The stress can be decomposed into a component that is in-phase with the strain, and a component what is $90^\circ$ out of phase with the strain. The total stress is expressed as:

$$\sigma_{xy}(t, \omega) = \gamma_0 G'(\omega) \sin(\omega t) + \gamma_0 G''(\omega) \cos(\omega t). \quad (1.5)$$

The in-phase component, $G'$ is called the storage modulus, and captures the elastic properties, and the out-of-phase component, $G''$, is the loss modulus, that is a measure of the loss of energy by viscous dissipation, in other words the viscous character of the polymer liquid. The magnitude of the loss- and storage moduli depend on the frequency $\omega$, however for sufficiently small values of the strain amplitude $\gamma_0$, $G'(\omega)$ and $G''(\omega)$ are independent of $\gamma_0$, and are referred to as linear viscoelastic moduli. The pure solid- and liquid properties are given as:

$$\begin{align*}
\text{Solid:} & \quad G' = G \quad , \quad G'' = 0 \\
\text{Liquid:} & \quad G' = 0 \quad , \quad G'' = \mu \omega 
\end{align*} \quad (1.6)$$

where $G$ is the elastic modulus and $\mu$ is the newtonian viscosity.

The linear viscoelastic shear stress of the polymeric liquid is often described by using a integral method such that:

$$\sigma_{xy}(t, \omega) = \int_{-\infty}^{t} G(t - t') \gamma_{xy}(t')dt' = -\int_{-\infty}^{t} M(t - t') \gamma_{xy}(t')dt' \quad (1.7)$$

where $G(t - t')$ is the relaxation modulus, which is decreasing with time, and $M(t - t') = -\frac{dG(t - t')}{dt}$ is the memory modulus. If the strain is oscillatory, as given in equation 1.4, the loss and storage moduli are found as:

$$G'(\omega) = \omega \int_{0}^{\infty} G(t - t') \cos(\omega t')dt' \quad (1.8)$$

and
\[ G''(\omega) = \omega \int_0^\infty G(t - t') \sin(\omega t') dt' \quad (1.9) \]

The linear viscoelastic stress can be modeled by the generalized Maxwell model, which is a combination of Newtonian liquid and a elastic material following Hook’s law. The relaxation modulus is given as

\[ G(t) = \sum_{i} \frac{\eta_i}{\lambda_i} e^{t'/\lambda_i} \quad (1.10) \]

where \( \eta_i \) is the viscosity and \( \lambda_i \) is the time constant of each Maxwell elements.

If we consider uni-axial elongational flow, the rate of strain compounds are given as:

\[ \dot{\gamma}_{xx} = \dot{\gamma}_{yy} = -\dot{\epsilon} \quad \text{and} \quad \dot{\gamma}_{zz} = 2\dot{\epsilon} \quad (1.11) \]

The uniaxial elongational viscosity is defined as:

\[ \bar{\eta}^+ = \frac{\sigma_{zz} - \sigma_{xx}}{\dot{\epsilon}} \quad (1.12) \]

Assuming constant, time-independent elongational rate, the uniaxial viscosity is given by the generalized Maxwell model as:

\[ \bar{\eta}^+ = \frac{\sigma_{zz} - \sigma_{xx}}{\dot{\epsilon}} = 1 \int_{-\infty}^t \left[ \sum_{i} \frac{\eta_i}{\lambda_i} e^{t'/\lambda_i} \right] (2\dot{\epsilon} - (-\dot{\epsilon})) dt' = 3 \sum_{i} \eta_i (1 - e^{t/\lambda_i}) \quad (1.13) \]

which gives the linear viscoelastic prediction of the elongational viscosity, which is independent of the elongational rate. The limiting value of the viscosity for infinite time is given as:

\[ \bar{\eta}^+ \to 3\eta_0 \quad \text{for} \quad t \to \infty \quad (1.14) \]

The ratio between the elongational viscosity, \( \bar{\eta}^+ \) and the zero shear viscosity \( \eta_0 \) is called the Trouton ratio, and has a limiting value of 3.

If we considers a cylinder that is stretched with constant elongational rate, the length and diameter of will vary vary with time, \( t \) in the following way:

\[ L(t) = L_0 e^{\dot{\epsilon}t} \quad \text{and} \quad D(t) = D_0 e^{-1/2\dot{\epsilon}t} \quad (1.15) \]

where \( D_0 \) and \( L_0 \) and the is the initial diameter and length of the cylinder.

The strain measure for elongational is the logarithmic strain, called the Hencky strain which in terms of time, diameter, and length is given as:

\[ \epsilon = \dot{\epsilon} t = \ln(L/L_0) = -2 \ln(D/D_0) \quad (1.16) \]
1.6 Thesis Outline

The aim of this PhD project is to study the flow behavior of well characterized polymers in uniaxial flow, which are expected to display physical phenomena that are not detectable in shear flow. Furthermore the first the step into understanding polydisperse polymers are taken by studying bidisperse systems of polystyrenes. Another object is to understand the elongational properties of branched polymers, and for this purpose model branched polystyrenes are synthesized using anionic polymerization, that is the preferred technique for making model NMMD polymers. In chapter 2 the elongational properties for two commercially available low-density polyethylenes with different molecular weight are presented. The existence of the overshoot in transient start-up viscosity and the following steady elongational viscosity is showed, and the reason for this is discussed and is explained as a collapse of branches. Chapter 3 deals with the elongational properties of two NMMD linear polystyrenes, and the effect of blending these polymers with higher molecular mass polystyrenes to make bidisperse melts. The different behavior of the monodisperse compared to the bidisperse melt is discussed and theoretically explained in terms of a simple differential constitutive model, the Wiest model, that includes effects of the difference in anisotropy for a elongated melt whether it is mono- or bidisperse. In chapter 4 a method to synthesize branched polystyrenes is presented. The elongational properties for a NMMD pompom and a NMMD asymmetric star polystyrene are measured, and by separating time and strain for the transient elongational stresses, it is found that the pompom can be described by a single elongational-rate independent strain function, whereas this is not the case for the asymmetric star. Chapter 5 presents a new method for measuring the stress relaxation at cession of flow after an elongational start-up experiment of polystyrene. This involves a modification of closed loop control mechanism, extending it to the stress relaxation part of the elongational experiment. Chapter 6 extents the work from chapter 5, stress relaxation, to also involve measuring stress for a reversing elongational experiment, that is a biaxial flow, following uniaxial start-up. This is possible by forcing the endplates back together in the filament stretching rheometer when a certain extension is reached. In chapter 7 rheological properties of a highly entangled NMMD linear polyisoprene are analyzed and interpreted. The elongational behaviour is measured using two novel kinds of commercial extensional rheometers, which are compared with the homemade filament stretching rheometer. The elongational properties of the linear polyisoprene, with approximately 300 entanglements, are compared with the elongational properties of linear polystyrenes with less than 35 entanglements.

Chapter 2-7 have been written in the format of scientific articles, containing separate abstracts, theory section, conclusion and bibliographies to rationalize the process of publishing in scientific journals.
Bibliography


2

Viscosity overshoot in the start-up of uni-axial elongation of LDPE melts

The transient uni-axial elongational viscosity of DOW BASF Lupolen 1840D and 3020D melts have been measured on a Filament Stretch Rheometer (FSR) up to Hencky strains of 6 to 7. The elongational viscosity of both melts was measured at 130°C within a broad range of elongational rates. At high elongation rates an overshoot or maximum in the transient elongational viscosity followed by a steady viscosity was observed. The steady elongation viscosity was about 40%-50% less than the maximum at high strain rates. The steady elongational viscosity as a function of the elongation rate, \( \dot{\varepsilon} \), decreases approximately as \( \dot{\varepsilon}^{-0.6} \) in both melts at high strain rates. The transient elongational viscosity, measured at a specific elongation rate at 170°C on the DOW BASF Lupolen 3020D melt, did not follow the time temperature superposition principle based on linear viscoelasticity, during the decrease in the transient elongational viscosity toward the steady state. 

2.1 Introduction

Interest in the measurement of elongational viscosity of polymer melts started to grow about 40 years ago (R. T. Tanner et al. (1998)). Measurements are most frequently reported as either steady elongational viscosity as function of elongational rate or as transient elongational viscosity as function of time for a fixed elongational rate. Generally it seems to be assumed that the transient elongational viscosity (as opposed to the transient shear viscosity) is an monotone increasing function of time. The first measurement, concerning the possible existence of an overshoot in the transient uni-axial elongational viscosity of a polymer melt, were presented by Raible et al. (1979) for a low density polyethylene (LDPE). More recent measurements of elongational viscosity of LDPE (Wagner et al. 2000, Bach et al. 2003b) do not indicate the existence of an maximum

\[ 1 \] This part of the work has been published in J. Rheology., 49, 369-381 (2005).
in the transient elongational viscosity. The experimental observation of a maximum in the transient elongational viscosity would have important implications for the constitutive modeling of polymer melts.

In the recent suggested constitutive equations for branched polymer melts, the Pom-Pom model (McLeish and Larson (1998)) and the L-MSF model (Wagner et al. (2001)), a monotone increase in the transient elongational viscosity is found. However, some of the previous suggested constitutive equations were able to predict an overshoot followed by a steady viscosity (see for instance Wagner et al. (1979)). Hence, the question of whether or not a constitutive equation for branched polymer melts should be able to predict a maximum (followed by a steady state) or a monotone increase in the transient elongational viscosity to the steady viscosity is therefore of importance.

We have measured the transient uni-axial elongational viscosity of two BASF low-density polyethylene (LDPE) melts, DOW BASF Lupolen 1840D and 3020D using the FSR. In all measurements a steady-state viscosity was kept for 1-2.5 Hencky strain units.

2.2 Material

The Lupolen 3020D LDPE melt used here have previously been characterized in shear and uniaxial elongation. Bastian (2001) measured the transient uniaxial elongation viscosities at 170°C using the Rheometrics Melt Extensiometer (RME). Details of the RME rheometer design and experimental procedure are given in Bastian (2001). In this work uniaxial elongation measurements were performed at 130°C for the Lupolen 1840D and at 130°C and 170°C for the Lupolen 3020D LDPE melt. Note, that our measurements on the Lupolen 3020D are on the same grade as Bastian (2001), but not the same batch. Still, our small-amplitude oscillatory shear (using a plate-plate geometry on a TA Instruments, AR2000) are in agreement with Bastian (2001) and the elongation measurements are in reasonable agreement with Bastian (2001). The properties of the melts are listed in table 2.1. Note, that we have listed the linear viscoelastic properties from Bastian (2001) for the Lupolen 3020D melt. The linear viscoelastic memory function, \( M(s) \), and relaxation modulus, \( G(s) \), is described as a sum of exponential function. Thus

\[
M(s) = \sum_{i=1}^{N} \frac{g_i}{\tau_i} \exp(-s/\tau_i) \tag{2.1}
\]

and

\[
G(s) = \sum_{i=1}^{N} g_i \exp(-s/\tau_i) \tag{2.2}
\]

where the moduli \( g_i \) and relaxation times \( \tau_i \) are given in table 2.1.
### Table 2.1. Characterization of the DOW BASF Lupolen 1840D and 3020D polymer melts. Linear viscoelastic spectrum from Bastian (2001) for the Lupolen 3020D.

<table>
<thead>
<tr>
<th>Polymer melt</th>
<th>LDPE</th>
<th>LDPE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Product</td>
<td>Lupolen 3020D</td>
<td>Lupolen 1840D</td>
</tr>
<tr>
<td>Producer</td>
<td>DOW BASF</td>
<td>DOW BASF</td>
</tr>
<tr>
<td>$M_W$ [g/Mol]</td>
<td>300000</td>
<td>490000</td>
</tr>
<tr>
<td>$M_n$ [g/Mol]</td>
<td>37500</td>
<td>16000</td>
</tr>
<tr>
<td>$M_W/M_n$</td>
<td>8</td>
<td>30.6</td>
</tr>
<tr>
<td>$T_m$ [ºC]</td>
<td>114</td>
<td>110</td>
</tr>
<tr>
<td>$T$ [ºC]</td>
<td>170</td>
<td>130</td>
</tr>
<tr>
<td>$g_i$ [Pa]</td>
<td>1.117·10^2</td>
<td>6.07·10^2</td>
</tr>
<tr>
<td>$\tau_i$ [s]</td>
<td>3.278·10^2</td>
<td>1.0·10^3</td>
</tr>
<tr>
<td>$g_i$ [Pa]</td>
<td>1.081·10^3</td>
<td>5.141·10^1</td>
</tr>
<tr>
<td>$\tau_i$ [s]</td>
<td>9.052·10^3</td>
<td>5.0·10^2</td>
</tr>
<tr>
<td>$g_i$ [Pa]</td>
<td>3.904·10^3</td>
<td>3.25·10^3</td>
</tr>
<tr>
<td>$\tau_i$ [s]</td>
<td>1.626·10^0</td>
<td>1.0·10^2</td>
</tr>
<tr>
<td>$g_i$ [Pa]</td>
<td>1.008·10^4</td>
<td>1.11·10^4</td>
</tr>
<tr>
<td>$\tau_i$ [s]</td>
<td>4.06·10^2</td>
<td>5.0·10^0</td>
</tr>
<tr>
<td>$g_i$ [Pa]</td>
<td>2.220·10^4</td>
<td>1.95·10^4</td>
</tr>
<tr>
<td>$\tau_i$ [s]</td>
<td>2.855·10^−1</td>
<td>1.0·10^0</td>
</tr>
<tr>
<td>$g_i$ [Pa]</td>
<td>3.686·10^4</td>
<td>2.36·10^4</td>
</tr>
<tr>
<td>$\tau_i$ [s]</td>
<td>4.997·10^−2</td>
<td>5.0·10^−1</td>
</tr>
<tr>
<td>$g_i$ [Pa]</td>
<td>5.886·10^4</td>
<td>5.0·10^4</td>
</tr>
<tr>
<td>$\tau_i$ [s]</td>
<td>9.580·10^−3</td>
<td>1.0·10^5</td>
</tr>
<tr>
<td>$g_i$ [Pa]</td>
<td>1.542·10^5</td>
<td>1.472·10^−3</td>
</tr>
<tr>
<td>$\tau_i$ [s]</td>
<td>1.008·10^4</td>
<td>1.472·10^−3</td>
</tr>
</tbody>
</table>

The moduli and relaxation times, from Bastian (2001), for the Lupolen 3020D melt are listed at 170ºC in table 2.1. As our elongation measurements mainly are performed at 130ºC the linear viscoelastic time-temperature shift factor, $a_T$, from 130ºC to 170ºC was measured. This value, $a_T = 6.4$, was calculated as the ratio between the angular frequencies, $\omega$, at the cross over point for the two temperatures. The cross over point is defined as the angular frequency where the storage modulus are equal to the loss modulus; $G'(\omega) = G''(\omega)$. The storage modulus and loss modulus was measured in small amplitude oscillatory shear flow where a plate-plate geometry on an AR2000 rheometer from TA Instruments was used.

We have not been able to measure the largest relaxation times, and thereby the zero-shear viscosity, for the Lupolen 1840D melt, as the linear viscoelastic measurements are affected by cross-linking at the time needed to characterize at angular frequencies lower than $5 \cdot 10^{-4}$ s$^{-1}$ at 130ºC.

### 2.3 The filament stretching rheometer

An extensive review of elongational rheometry with particular emphasis on the filament stretch rheometer (FSR) has been given by Mckinley and Sridhar (2002). The apparatus used here is a vertical filament stretching rheometer, surrounded by a thermostated environment, where the bottom plate is stationary and the upper plate is pulled. In basic a cylindrical
sample is placed between two parallel plates and at times, \( t \geq 0 \), the upper plate is pulled at such a rate that the mid-radius in the sample, \( R(t) \), decreases exponentially. This applies a constant elongation rate, \( \dot{\epsilon}_0 \), at the centre of the sample from \( t = 0 \). At \( t < 0 \) the strain rate is 0. A laser is used to measure the mid diameter of the filament during an experiment. From the measurement of radius (e.g. diameter), the average strain rate, \( \dot{\epsilon}_0 \), could be calculated by fitting an exponential function \( R(t) = R_0 \exp(-\dot{\epsilon}_0 t/2) \) where \( R_0 \) is the initial sample radius and \( R(t) \) the actual sample radius. Generally the relative deviation between measurements and fit was never above 4%. Though at elongation rates lower than 0.1\( s^{-1} \) the deviation between measurements and fit was never above 2% and was usually within 1%.

The FSR has the advantage compared to conventional techniques for elongation rheometry that the location of the symmetry plane (the necking) of the sample can be predicted. This critical region can then be monitored and the distance between the end-plates adjusted online in such a way as to obtain a constant stretch rate at the neck. A recent improvement (Bach et al. 2003a) on the FSR rheometer, using a closed loop proportional regulator scheme to control the deformation of the sample, replacing the iterative Orr-Sridhar method (Bach et al. (2003b)), has allowed measurements at considerably higher strain values than presented before.

During an experiment both the sample radius \( R(t) \) and axial force \( F(t) \) in the filament were measured as a function of time. The axial force is measured on the fixed bottom end plate, which is mounted on a weight cell placed outside the thermostated environment.

When the average strain rate had been established, the transient elongational viscosity \( \bar{\eta}^+(t) \) was calculated using

\[
\bar{\eta}^+(t) = \frac{F(t) - m_1 g}{\pi R(t)^2 \dot{\epsilon}_0}
\]

where the measured force, \( F \), has been corrected by the weight of lower half of the polymer filament, \( m_1 \) and the gravitational acceleration \( g \) (Szabo 1997). This weight is measured by forcing the filament to break in the symmetry plane after the end of an experiment.

Here we present measurements of transient elongational viscosity of up to a Hencky strains of 7. The Hencky strain is defined as \( \epsilon(t) = -2 \ln \left( \frac{R(t)}{R_0} \right) \) where \( R_0 \) is the initial sample radius and \( R(t) \) the actual sample radius, measured at the symmetry plane of the filament, as a function of the time.

### 2.4 LDPE test sample

The two LDPE polymers, supplied in pellets, were pressed into cylindrical test specimens, by a Carver hydraulic press at 130°C, with radius \( R_0 = 4.5 \)
Figure 2.1. The uncorrected transient elongation viscosities $\dot{\eta}^+$ of Lupolen 3020D measured at 130°C, using equation (3.3), shown as a function of the Hencky strain, $\epsilon$. $\dot{\eta}^+$ are measured at five different elongational rates $\dot{\epsilon}$ as shown in the figure.

mm and lengths, $L_0=2.5$ mm, giving an aspect ratio $\Lambda_0 = L_0/R_0=0.56$. Measuring on LDPE melt at high elongation rates in the FSR requires a low initial aspect ratio. At low aspect ratio the location of the neck in the circular sample, during the extension, is predictable. Namely in the middle of the filament, creating the symmetry plane, where the laser sheet is located. By contrast, with a high aspect ration, an unexpected neck located closer to one of the end plates typically occurs. As a consequence the filament will break asymmetrically and the symmetry plane at the mid filament is lost. The procedure to apply the cylindrical sample to the cylindrical shaped stainless steel end plates is described in detail in Bach et al. (2003b).

At small strains there is an extra force contribution from the shear components in the deformation field during start-up, especially at small aspect ratios. The extra shear component originates from the no slip condition at the rigid end plates. For Newtonian fluids this reverse squeeze flow problem can be modelled analytically so the effect of the shear may eliminated by a correction factor (Spiegelberg and McKinley (1996)).

$$\dot{\eta}_{corr}^+ = \dot{\eta}^+ \left(1 + \frac{\exp(-7\epsilon/3)}{3\Lambda_0^2}\right)^{-1}$$

(2.4)

where $\dot{\eta}_{corr}^+$ is the corrected transient uni-axial elongation viscosity.

This correction is analytically correct for very small strains (e.g. basically $\epsilon = 0$) for all type of fluids. Though, the corrections are less
2.5 Elongational Viscosity Measurements

appropriate at increasing strains where the effect of the correction fortunately vanishes. In this work we have chosen to present the data both uncorrected and corrected in the presentation of the elongation measurements, as we also prefer to present the raw data. For the aspect radius used here, this extra force contribution is negligible after about one strain unit. This was also demonstrated theoretically in Kolte et al. (1997) and experimentally in Bach et al. (2003b) for polymer melts.

2.5 Elongational Viscosity Measurements

During extension the molten polymer filament is surrounded by nitrogen. Hence, there is a lower limit on the extension rate at which sagging of the filament can be neglected during an experiment. A relevant measure of the magnitude of gravitational forces relative to the viscous forces is the ratio of the Reynolds number to the Froude number, $L_0 \exp(\epsilon) \rho g/(2\dot{\epsilon}_0 \bar{\eta}^+)$, where $\rho$ is the density of the polymer melt. From this we estimate that sagging of the polymer melt can be neglected, as this number is less than 0.2 in all performed experiments.

The effect of the surface tension can be neglected as the surface elasticity number (Spiegelberg and McKinley (1996); Rasmussen and Hassager (2001)) do have values of the order $10^{-5}$ for the two polymer melts. The surface elasticity number is calculated as the ratio of stresses due to surface tension relative to the elastic modulus.

We have measured the transient uni-axial elongational viscosity of the two low-density polyethylene (LDPE) melts, BASF Lupolen 1840D and 3020D. We present our complete data series, measured at 130°C, for the LDPE melts in the figures 2.1, 2.2, 2.3, and 2.4. In figure 2.1 and 2.3 the uncorrected transient elongation viscosities, using equation (3.3), are shown as a function of the Hencky strain. Keep in mind, that our data should not be used without correction for Hencky strains less than unity. In the figures 2.2 and 2.4 these measurements are shown corrected, using equation (6.1), as a function of the time. Note, the theory of linear viscoelasticity (the line in figure 2.2 and 2.4) may be used to predict the corrected transient elongational viscosity at (very) small strains from the relaxation modulus. The experiments show good agreement with the predictions from linear viscoelasticity. In order to illustrate the reproducibility some of the measurements have been repeated two or three times. As the strain or elongation rates of the repeated experiments are within 1%, the measurements are not labelled individually. Overall the experiments show differences of about 10% to 20%. We notice that the elongational viscosity reaches a steady state in all experiments. The plateau values of elongational viscosity are constant within about 10% and the steady state has been measured during at least one strain unit for both melts. The only exception is at the highest strain rate. At the highest elongation velocity, it has not been possible to adjust the plate motion to avoid sample failure.
2.6 Discussion

The measurements below elongation rates of $0.3\,s^{-1}$ reach Hencky strains of 6-7, and they all show a convincing steady plateau at high strain. This plateau is reached after going through a significant maximum in the tran-

![Figure 2.2.](image)

Figure 2.2. The corrected transient elongation viscosities $\overline{\eta}^+$ of Lupolen 3020D
at $130^\circ$C, using equation (6.1), shown as a function of the time, $t$. The measurements are the same as in figure 2.1. The line are the linear viscoelastic prediction of the transient elongational viscosity.

This is due to the strong non-linear elastic behaviour of the LDPE melts. Note, the small fluctuations in the steady-state values are correlated with small changes in the instantaneous strain rate.

The elongation measurements on the BASF Lupolen 3020D were also performed at the elevated temperature $170^\circ$C, to examine the effects of time-temperature superposition. In figure 2.6 we plot the extensional stress $(\sigma_{zz} - \sigma_{rr} = \overline{\eta}^+(t)\dot{\epsilon}_0)$ divided with the absolute temperature as a function of the Hencky strain. Notice $\sigma_{zz}$ and $\sigma_{rr}$ are the axial and radial stress components respectively. The three measurement at strain rate $0.03\,s^{-1}$ from figure 2.1 (at $130^\circ$C) and three measurements performed at $170^\circ$C at an elongation rate of $a_T \cdot 0.03\,s^{-1} = 0.192\,s^{-1}$ are shown.

To test whether or not the elongation measurements at $170^\circ$C are affected by cross-linking during the thermo-stating of the LDPE sample, measurements was performed decreasing the time of the thermo-stating period of about a factor of two. All measurements were within the experimental accuracy.

2.6 Discussion

The measurements below elongation rates of $0.3\,s^{-1}$ reach Hencky strains of 6-7, and they all show a convincing steady plateau at high strain. This plateau is reached after going through a significant maximum in the tran-
2.6. Discussion

\[ \dot{\epsilon} = 0.03 \text{s}^{-1} \]
\[ \dot{\epsilon} = 0.01 \text{s}^{-1} \]
\[ \dot{\epsilon} = 0.003 \text{s}^{-1} \]

\[ \bar{\eta} + \eta^\text{corr} \] [MPa·s]

**Figure 2.3.** The uncorrected transient elongation viscosities $\bar{\eta}^+$ of Lupolen 1840D measured at 130°C, using equation (3.3), shown as a function of the Hencky strain, $\dot{\epsilon}$. $\bar{\eta}^+$ are measured at three different elongational rates $\dot{\epsilon}$ as shown in the figure.

\[ t \] [s]

**Figure 2.4.** The corrected transient elongation viscosities $\bar{\eta}^+$ of Lupolen 1840D at 130°C, using equation (6.1), shown as a function of the time, $t$. The measurements are the same as in figure 2.3. The line are the linear viscoelastic prediction of the transient elongational viscosity.
2.6. Discussion

Figure 2.5. The steady elongation viscosities $\eta$ of Lupolen 1840D ($\circ$) and Lupolen 3020D ($x$), measured at 130°C, shown as a function of the elongation rate $\dot{\varepsilon}$.

sient elongational viscosity at high strain rates. Depending on the elongational rate, the steady elongational viscosities are reduced by factors in the range $1.0 - 1.9$ for both melts. A monotone increase in the transient elongational viscosity to its steady viscosity are measured at low elongation rates, and we have to note that the area with the maximum, at high strain rates, can erroneously be interpreted as a steady viscosity, as the transient viscosity do not change more than 10% within one Hencky strain units. However, the steady viscosity is reached about one strain unit later than the area with the maximum. In the terminology of the Pom-Pom model (McLeish and Larson (1998)) we interpret the relatively steep drop in the transient elongational viscosity as a result of a sudden retraction of side chains from the backbone of the branched polyethylene molecule, into the tube occupied by the backbone. We should mention that the above maximum in the transient elongation viscosity is only related to branched polymer melt. Linear melts do show a monotone increase in the transient elongational viscosity to its steady viscosity (Bach et al. (2003a) and (2003b)).

On figure 2.6 we compare measurements performed at 130°C with measurements performed at 170°C but shifted to 130°C by the shift factor obtained in linear viscoelastic measurements. It is seen until a Hencky strain somewhat below 3, that practically all the data collapse on a single curve. Hence, the measurements follow the time temperature superposition principle based on linear viscoelasticity. Above a Hencky strain value of 3 the deviations between the measurements at 170°C and 130°C, as
2.6. Discussion

\[ \dot{\varepsilon} = 0.3 \text{s}^{-1}, \quad T = 130\degree C \]
\[ \dot{\varepsilon} = 0.192 \text{s}^{-1}, \quad T = 170\degree C \]

\[ \sigma_{zz} - \sigma_{rr} = \bar{\eta} + (t)\varepsilon_0, \]

\[ \frac{(\sigma_{zz} - \sigma_{rr}) \cdot 403K/T}{[KPa]} \]

Figure 2.6. The uncorrected extensional stress, \( \sigma_{zz} - \sigma_{rr} = \bar{\eta} + (t)\varepsilon_0 \), divided with the absolute temperature, T, as a function of the Hencky strain, \( \varepsilon \) of Lupolen 3020D melt. \( \sigma_{zz} - \sigma_{rr} \) or \( \bar{\eta} + (t) \) are measured at 130\degree C and \( \dot{\varepsilon} = 0.03 \text{s}^{-1} \) (The measurements are the same as in figure 2.1) and at 170\degree C and \( \dot{\varepsilon} = 0.192 \text{s}^{-1} \).

Presented in the figure, are up until 40% as the decrease in transient elongational viscosity at 170\degree C happens about one strain unit later than the measurements at 130\degree C. Though, as the steady state is reached, all the measurements in figure 2.6 match, within the relative large experimental scattering. The delay of the decrease in the transient elongational viscosity emphasize that the time constant in the underlying dynamics, which we expect is the sudden retraction of side chain, do scale differently than the overall dynamics of the polymer.

In figure 2.5 we show the steady elongational viscosity, \( \bar{\eta} \), as a function of the elongation rate, for the Lupolen 1840D and 3020D melt. At high elongation rates the viscosity decreases approximately as \( \dot{\varepsilon}^{-0.6} \) in both melts. The same slope, within the experimental accuracy, have been observed by Bach et al. (2003a), measuring on mono-disperse (linear) polystyrene melts and by Guptal at al. (2000), measuring the elongational viscosity on polystyrene solutions. This phenomenon has also been observed by Bach et al. (2003b) on LLDPE melts.

Though, the observation that the steady viscosity decreases with the same slope as linear melts and follows the time temperature superposition principle indicate that all side chain in fact retract, leaving only one effective chain that is expected to behave similar to a linear polymer. We take this as an indication, that the LDPE arms are indeed collapsed into the tube occupied by the backbone so the LDPE behaves in the steady state effectively as a linear polymer. The asymptotic behaviour of elongational
Acknowledgments

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Appendix

In this paper we have reported and discussed experimental observations of time dependent uni-axial elongation viscosities of LDPE melts. One of the classical theoretical discussions in the literature is whether or not a constitutive equation for branched polymeric melt should be separable in time and strain. See Wagner et al. (2001) for more details. A constitutive model as the Pom-Pom model is not separable in time and strain whereas the MSF model is. In this appendix we will apply the assumption of time and strain separability on our Lupolen 3020D elongation data as a contribution to the ongoing discussion. In start-up of uni-axial elongation

\[
\dot{\epsilon} = \frac{3}{s-1} \\
\dot{\epsilon} = \frac{1}{s-1} \\
\dot{\epsilon} = \frac{0.03}{s-1} \\
\dot{\epsilon} = \frac{0.01}{s-1} \\
\dot{\epsilon} = \frac{0.003}{s-1}
\]

Figure 2.7. The strain function, \( S(\epsilon) \) defined in equation (2.5), as a function of the Hencky strain, \( \epsilon \). The viscosity measurements, of Lupolen 3020D measured at 130°C, used to calculate \( S(\epsilon) \), from equation (2.6), are from figure 2.1.
flow the time and strain separability requires that the stress or viscosity can be written as (see Wagner et al. (1978)):

\[
\bar{\eta}^+ = \frac{G(t)S(\dot{\epsilon}_0 t)}{\dot{\epsilon}_0} + \frac{1}{\dot{\epsilon}_0} \int_0^t M(t - t')S(\dot{\epsilon}_0(t - t'))dt'
\] (2.5)

where \(S(\epsilon)\) is a strain dependent function, \(t\) the present time, \(G(t)\) and \(M(t-t')\) is the linear viscoelastic relaxation modulus and memory function respectively. The memory function and relaxation modulus are defined in equation (2.1) and (2.2) respectively.

Using equation (2.5) the strain function can be calculated from the viscosity data as

\[
S(\epsilon) = \frac{\bar{\eta}^+}{G(\epsilon/\dot{\epsilon}_0)} - \int_0^\epsilon \frac{\bar{\eta}^+}{G(\epsilon'/\dot{\epsilon}_0)} \frac{M(\epsilon'/\dot{\epsilon}_0)}{G(\epsilon'/\dot{\epsilon}_0)^2} d\epsilon'
\] (2.6)

from Wagner (1978).

Note that we use the corrected viscosity from equation (6.1) in this formula. As mentioned before is this correction analytically correct for very small strains (e.g. basically \(\epsilon = 0\)) for all type of fluids. Though, the correction is less appropriate at increasing strains where the effect of the correction fortunately vanishes. The strain function \(S(\epsilon)\), based on the assumption of time and strain separability, is written as a function of the Hencky strain in figure 2.7, using the measurements from figure 2.2. As seen is the time strain separability an excellent assumption until a Hencky strain value of 3 where this assumption is no longer valid. Though, notice that we can not preclude, on the basis of our performed experiment, that the principle of time strain separability may be valid at higher strain rates than shown in figure 2.7.
Bibliography


Elongational viscosity of monodisperse and bidisperse polystyrene melts

The startup and steady uniaxial elongational viscosity have been measured for two monodisperse polystyrene melts with molecular weights of 52 kg/mole and 103 kg/mole, and for three bidisperse polystyrene melts. The monodisperse melts show a maximum in the steady elongational viscosity vs. the elongational rate, $\dot{\varepsilon}$, of about two times $3\eta_0$ whereas the bidisperse melts have a maximum of up to a factor of seven times the Trouton limit of $3\eta_0$. The Wiest model which incorporates anisotropic drag and finite extensibility may be used to interpret the results in molecular terms.  

3.1 Introduction

The scaling of linear viscoelastic properties such as the zero shear viscosity, $\eta_0$, and the characteristic reptation time, $\tau_d$, for the Doi-Edwards model (Doi and Edwards, 1986) have been investigated thoroughly both theoretically and experimentally in the literature for monodisperse polymer melts. It is commonly accepted that the zero shear viscosity and the reptation time both scale with the molecular weight as $\eta_0 \sim M^{3.4}$ and $\tau_d \sim M^{3.4}$ for monodisperse polymers with molecular weights substantially above the entanglement molecular weight, $M > (2-4)M_e$. Elongational flow properties have however not been analyzed as intensely. Thorough investigation of the elongational viscosity for very diluted solutions of monodisperse (and bidisperse) polystyrene have been made and analyzed by Gupta et al. (2000) and Ye et al. (2003). Wagner et al. (2005) have recently published elongational results for bidisperse blends of small amounts of ultra high, narrow molecular weight polystyrene, $M_w = 3220$ kg/mole and $M_w = 15400$ kg/mole in lower molecular weight polydisperse polystyrene, $M_w = 423$ kg/mole. Steady state was never reached, but the authors found that the blends were more strain hardening than the monodisperse melts, and that maximum amount of strain hardening increased with increasing

\footnote{This part of the work has been published in \textit{J. Rheology}. 50, 453-476 (2006).}
content of ultra high molecular weight polystyrene. To our knowledge the only published steady elongational viscosities for monodisperse melts are those of Bach et al. (2003a) and Luap et al. (2005). Neither the Doi-Edwards model nor other reptation-based models (Marrucci and Grizzutti (1988), Mead et al. (1998), Fang et al. (2000), Ianniruberto and Marrucci (2001), Schieber et al. (2003)) have effectively been able to predict the flow behaviour of especially high Deborah-number flows, i.e. fast elongational flows with \( \dot{\varepsilon} \geq 1/\tau_d \). Indeed, the major limitation to progress in the understanding of the nonlinear properties in elongational flow seems to be the scarcity of data for well-characterized narrow molecular weight linear polymer melts.

There have been a number of recent efforts at extending the basic reptation picture to incorporate additional physical mechanisms that modify the evolution in the polymeric stress in strong stretching flows. These include incorporating the role of ’intrachain pressure’ within a differential framework (Marrucci et al. 2004) and within the integral molecular stress function formulation (Wagner et al. 2005) or through detailed analysis of the rate of creation and destruction of ’slip links’ (Likhtman 2005). The key change that each of these models seek to incorporate is a modification in the scaling of the steady elongational steady stress with the elongational rate, \( \sigma_{zz} - \sigma_{rr} \sim \dot{\varepsilon}^n \). The bare reptation model of Doi and Edwards predicts a saturation in the stress, \( n = 0 \) (corresponding to thinning in the elongational viscosity). Incorporation of chain stretching results in unbounded stress growth, which can be truncated through considering the finite extensibility of the chains resulting ultimately in \( n = 1 \) (Fang et al. 2000) corresponding to finite limiting value of the elongational viscosity. The proposed models by Marrucci and Ianniruberto (2004) and Wagner et al. (2005) both find that \( n = 0.5 \). In the present work we use the simple model proposed by Wiest (1989) which models the effects of the surroundings chains as an anisotropic drag acting on a finitely-extensible dumbbell that represents a single segment of the orienting and elongating chain. This computationally simple model gives \( n = 0.5 \) and we show below that it is able to capture many of the important features that we observe in the steady elongational viscosity.

Bach et al. (2003a) measured the elongational viscosity of two narrow molar mass distribution polystyrene melts, with \( M_w = 200 \text{ kg/mole} \), PS200K, and \( M_w = 390 \text{ kg/mole} \), PS390K. The main conclusions drawn from this work were: 1) The steady elongational viscosity for Deborah numbers, defined as \( De = \dot{\varepsilon} \tau_d \) greater than unity scales as \( \bar{\eta} \sim \dot{\varepsilon}^{-0.5} \). 2) The steady elongational viscosity scales linearly with the molecular weight for \( De > 1 \), i.e. \( \bar{\eta} \sim M_w \dot{\varepsilon}^{-0.5} \) and finally 3) the steady elongational viscosity is a monotone decreasing function of the elongational rate. That is, \( \bar{\eta} \) does not exceed \( 3\eta_0 \) for any elongational rate accessed experimentally.

The authors did point out, that their conclusions with regard to molecular mass scaling were based on merely two samples. Based on the scaling
properties of $\eta_0$ and $\tau_d$ with the molecular weight it is however realized that these conclusions cannot be true if one extends them to elongational measurements of lower molecular weights. There are simply too many constraints. Marrucci and Ianniruberto (2004) have treated this problem theoretically and suggested that melts with fewer entanglements may show a maximum in $\bar{\eta}$ as function of $\dot{\varepsilon}$.

The first purpose of this work is to investigate how two polystyrene melts with $M_w = 103 \, kg/mole$, PS100K, and $M_w = 52 \, kg/mole$, PS50K, behave in a uniaxial elongational flow at $130^\circ C$. Polystyrene has an entanglement molecular weight of $M_e = 13.3^{3s/mol}$ (Fetters et al., 1994), giving the melts respectively 7.7 and 3.9 entanglements. With these fluids it is possible to analyze what happens to $\bar{\eta}$ in the transition going from low to high Deborah numbers, i.e. from the linear to the non-linearly dominated regime. The elongational measurements can give an indication of which of the constraints noted above must be relaxed.

<table>
<thead>
<tr>
<th>Blend 1</th>
<th>Blend 2</th>
<th>Blend 3</th>
<th>Ye et al.</th>
<th>Wagner I</th>
<th>Wagner II</th>
</tr>
</thead>
<tbody>
<tr>
<td>w/w% PS50K</td>
<td>95.98</td>
<td>85.63</td>
<td>0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>w/w% PS100K</td>
<td>0</td>
<td>0</td>
<td>85.98</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>w/w% PS390K</td>
<td>4.02</td>
<td>14.37</td>
<td>14.02</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>cPS390K/c*</td>
<td>2.5</td>
<td>10</td>
<td>10</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$M_w[kg/mol]$</td>
<td>65.3</td>
<td>100.3</td>
<td>143.1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$G_r$</td>
<td>0.499</td>
<td>0.499</td>
<td>0.064</td>
<td>0.0192</td>
<td>0.0075</td>
</tr>
</tbody>
</table>

The reptation time for PS100K is $\tau_d \approx 100$ s at $130^\circ C$. The range over which the elongational rates can be measured by the filament stretching rheometer (FSR) to avoid dissipative heating in the sample is $\dot{\varepsilon} \leq 0.3s^{-1}$ (Bach et al. 2003a), making it possible to transition from low to high Deborah numbers for PS100K. The lower molecular weight PS50K sample is expected mostly to provide information about the linear region, since $\tau_d \approx 10s$.

The lack of a maximum in $\bar{\eta}$ vs. $\dot{\varepsilon}$ for PS200K and PS390K is believed to be related to the monodisperse character of the melts, and it has therefore been decided to make three bidisperse melts, in which each of the individual polymers in the blend are expected not to display a maximum in $\bar{\eta}$ vs. $\dot{\varepsilon}$ when studied in isolation. We have decided to mix PS390K with PS50K in two different concentrations in order to investigate the effect of diluting PS390K with PS50K. Secondly we have made a mixture of PS390K with PS100K, where PS390K has the same mass-concentration as one of the PS390K+PS50K-blends.

The composition of the three blends used in the work is shown in table 3.1. In this table we also show the concentration of PS390K relative to the overlap concentration, c*, of PS390K in a dilute solution under theta
3.2 Experimental section

3.2.1 Synthesis and Chromatography

The two polystyrene samples PS50K and PS100K were synthesized by anionic polymerisation (Ndoni et al. 1995). The molecular weights were determined by size exclusion chromatography (SEC) with toluene as the eluent using a Viscotec 200 instrument equipped with a PLguard and two PLgel mixed D columns in series (from Polymer Laboratories) using a RI detector. On the basis of calibration with narrow molecular weight polystyrene standards, the values of \(M_w\) and \(M_w/M_n\) were measured for the monodisperse samples. The results are given in table 3.3.

<table>
<thead>
<tr>
<th>Name</th>
<th>PS50K</th>
<th>PS100K</th>
<th>PS200K</th>
<th>PS390K</th>
<th>Blend 1</th>
<th>Blend 2</th>
<th>Blend 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>(M_w) [kg/mol]</td>
<td>51.7</td>
<td>102.8</td>
<td>200.0</td>
<td>390.0</td>
<td>65.3</td>
<td>100.3</td>
<td>143.1</td>
</tr>
<tr>
<td>(M_w/M_n)</td>
<td>1.026</td>
<td>1.022</td>
<td>1.040</td>
<td>1.060</td>
<td>1.218</td>
<td>1.683</td>
<td>1.248</td>
</tr>
</tbody>
</table>

Table 3.2. Molecular weights \(M_w\) and polydispersities \(M_w/M_n\) of the pure and blended polystyrene melts

3.2.2 Mechanical Spectroscopy

The viscoelastic properties of the polystyrene melts were obtained from small amplitude oscillatory shear flow measurements on an AR2000 rheometer from TA instruments using a plate-plate geometry (see figure 3.1 and 3.2). The measurements were performed at 130\(^\circ\)C for the PS50K, PS100K and blends, and at 150\(^\circ\)C for the blends. The measured data at 150\(^\circ\)C was shifted to 130\(^\circ\)C using the time temperature superposition shift factor \(a_T\) found from the WLF-equation (Bach et al. 2003a):

\[
\log_{10}(a_T) = \frac{-c_1^0(T - T_0)}{c_2^0 + (T - T_0)}
\]

(3.1)

where \(c_1^0 = 8.86\), \(c_2^0 = 101.6^\circ C\), \(T_0 = 136.5^\circ C\) and \(T\) is the sample temperature in \(^\circ C\).
3.2. Experimental section

Figure 3.1. Results of linear viscoelastic measurements of $G'$ as a function of the angular frequency $\omega$. The measurements on the polystyrene melts were performed at 130, 150, and 170°C. The data are all time-temperature shifted to a reference temperature of $T_0 = 130$ °C.

Figure 3.2. Results of linear viscoelastic measurements of $G''$ as a function of the angular frequency $\omega$. The measurements on the polystyrene melts were performed at 130, 150, and 170 °C. The data are all time-temperature shifted to a reference temperature of $T_0 = 130$ °C.
3.2.3 Transient elongational viscosity measurements

The transient elongational viscosity was measured using a filament stretching rheometer which is described in detail elsewhere (Bach et al. 2003b). The polystyrene melts were dried according to the protocol of Schausberger and Schindlauer (1985), and moulded into cylindrical-shaped samples, with radius of \( R_i = 4.5 \text{mm} \) and height of \( L_i = 2.5 \text{mm} \) using a Carver hydraulic press. The PS50K and PS100K-samples were pressed at 150\(^\circ\)C and annealed at this temperature for 2 minutes. The bidisperse blends were pressed and annealed for 2 minutes at 170\(^\circ\)C. The temperatures were chosen to ensure that the polymer chains were completely relaxed and still did not degrade; this was confirmed using SEC after the elongational experiment was performed. The moulded pellets were placed between two parallel plates inside the filament stretching rheometer, and the temperature was raised to 130\(^\circ\)C. To ensure adhesion between the end plates and polymer melt, the end plates were coated with a solution of polystyrene in tetrahydrofuran as described in Bach et al. (2003a). In most of the experiments performed the sample was pre-stretched in order to reduce the transmitted force in the vertical plane to avoid the sample being ripped of the end plates. All samples were pre-stretched by variable amounts, thus the initial radius for experiments with PS100K at \( \dot{\varepsilon} = 0.3 \text{s}^{-1} \) was \( R_0 = 1.5 \text{mm} \), whereas the initial radius for Blend 3 was \( R_0 = 4.3 \text{mm} \) at \( \dot{\varepsilon} = 0.00015 \text{s}^{-1} \). The pre-stretch was performed with stretch rates considerably lower than the inverse of the longest relaxational time. The melt is allowed to relax before every elongational experiment is started. We wait until all residual orientation in the polymer has disappeared, which is the case when no residual forces are present as indicated by the load cell. This equilibration time is at least ten times the longest relaxation time of the melt.

During a stretching experiment a laser micrometer samples the central diameter of the elongating filament while a load cell measures the force at the end plate. The diameter data is sent directly to a controller that produces a signal to the motor pulling the end plates apart. This control method ensures that the radius decreases exponentially with time as \( R(t) = R_0 e^{-\dot{\varepsilon}t/2} \). The Hencky strain is defined as \( \varepsilon = -2 \ln(R(t)/R_0) \). After an elongational experiment is complete, the measured radius \( R(t) \) and force \( F(t) \) are used to calculate the tensile stress

\[
\sigma_{zz} - \sigma_{rr} = \frac{F(t) - m_1 g}{\pi R(t)^2}
\]  
(3.2)

and the transient elongational viscosity as:

\[
\bar{\eta}^+(t) = \frac{\sigma_{zz} - \sigma_{rr}}{\dot{\varepsilon}}
\]  
(3.3)

where the measured force, \( F \), is corrected by the weight of lower half of the polymer filament, \( m_1 \) and the gravitational acceleration \( g \) (Szabo 1997).
3.2. Experimental section

\[ \dot{\eta} = 0.3 \text{s}^{-1} \]

\[ \dot{\eta}_c = 0.1 \text{s}^{-1} \]

\[ \dot{\eta}_c = 0.003 \text{s}^{-1} \]

Figure 3.3. Corrected (equation 6.1) transient extensional viscosity of PS50K and PS100K measured at different strain rates. Measurements were performed at 130 °C.

This weight is measured by forcing the filament to break at the symmetry plane after the end of an experiment.

At small strains there is an extra force contribution from the shear components in the deformation field during start-up. The shear component originates from the no slip condition at the rigid end plates and is especially important at small aspect ratios. For Newtonian fluids this reverse squeeze flow problem can be modelled analytically and the effect of the additional shear may be eliminated by a correction factor (Spiegelberg and McKinley (1996)).

\[ \eta_{corr}^+ = \eta^+ \left( 1 + \frac{\exp(-7\epsilon + \epsilon_0)/3}{3\Lambda_i^2} \right)^{-1} \]

where \( \Lambda_i = L_i/R_i \) is the initial aspect ratio, \( \epsilon_0 \) is the pre stretched Hencky strain, defined as \( \epsilon_0 = -2\ln(R_0/R_i) \) and \( \eta_{corr}^+ \) is the corrected transient uni-axial elongation viscosity.

This correction is analytically correct for very small strains (\( \epsilon \rightarrow 0 \)) for all types of fluids. However, the correction is less accurate at increasing strains where the effect of the correction fortunately vanishes.

In this work we have chosen to present the elongation measurements in both uncorrected and corrected form, as we also prefer to present the raw data. For the aspect ratio used here, the extra force contribution is negligible after about one additional strain unit. This was demonstrated experimentally in Bach et al. (2003b), and theoretically in Kolte et. al. (1997) for polymer melts.
3.3. Linear Viscoelastic Measurements

Eriksson and Rasmussen (2005) suggest that the relevant non-dimensional measure of the surface tension in viscoelastic flow is the ratio of the surface tension stresses to the complex modulus \(G^*(\omega) = \sqrt{G'(\omega)^2 + G''(\omega)^2}\), i.e. \(V_c = \sigma/\left(RG^*(\dot{\varepsilon})\right)\), where the angular frequency, \(\omega\), has been replaced with the characteristic deformation rate, \(\dot{\varepsilon}\). This Viscoelastic Capillary number resembles the surface elasticity number, (Spiegelberg and McKinley (1996) and Rasmussen and Hassager (2001)) at high deformation rates and the inverse of the classical Capillary number at low deformation rates. As \(V_c\) stays below 0.03 in all experiments, the effect of surface tension is negligible.

The effect of gravitational sagging can be evaluated using a relevant measure of the magnitude of gravitational forces relative to the viscous forces. Here we use the ratio \(L_i \exp(\dot{\varepsilon}_i + \dot{\varepsilon}_0) \rho g/(2\dot{\varepsilon}\eta^*)\) as in Rasmussen et al. (2005) where \(\rho\) is the density of the polymer melt. The duration of the elongational experiments in this work were considerably below the sagging time, as this number is less than 0.1 in all the performed experiments.

See Szabo and McKinley (2003) for additional discussion of similar correction factors.

3.3 Linear Viscoelastic Measurements

A linear viscoelastic (LVE) analysis provides us with an estimate of the elongational behaviour in the limit \(De \to 0\) and provides a verification of the reliability of the elongational experiments especially at short times and small strains. If the verifications of the experiments were the sole purpose of doing LVE-experiments a simple Maxwell-fit to the data would be sufficient. But we also seek to determine the characteristic time constants of the individual polymeric species in the melt, and for this the Baumgaertel, Schausberger and Winter (BSW) model is used (Baumgaertel et al. 1990). Each polymer contributes a distinct spectrum with a characteristic time constant. We analyse the LVE-data with a theoretical approach suggested by Jackson and Winter (1995) which handles mono- and bidisperse melts. This is not to be confused with a blend rule, since the LVE-properties of the blends cannot be predicted from the composition of long- and short polymers by this procedure. The LVE properties of monodisperse linear polymers (Milner and McLeish, 1998) and mixing rules for blends of monodisperse species (des Cloizeaux (1988)) have been studied in detail. In terms of physical insight the BSW-approach is not far from a simple Maxwell-fit, with few exceptions as described later.

The relaxation modulus \(G(t)\) is found from the continuous-spectrum \(H(\lambda)\), which for the bidisperse blends is composed of two individual spectra:
\[ G(t) = G_1(t) + G_2(t) \]

\[ G_i(t) = \int_0^\infty \frac{H_i(\lambda)}{\lambda} \exp(-t/\lambda) d\lambda, \quad i = 1, 2 \]

\[ H_i(\lambda) = n_e G_{N,i}^0 \left[ \left( \frac{\lambda}{\lambda_{\text{max},i}} \right)^{n_e} + \left( \frac{\lambda}{\lambda_c} \right)^{-n_g} \right] h(1 - \lambda/\lambda_{\text{max},i}) \]

Here \( h(x) \) is the Heaviside step function, \( n_e \) is the slope of the \((\log(\omega), \log G')\) curve at intermediate frequencies \( \omega \), \( n_g \) is the slope of \((\log(\omega), \log G'')\) for \( \omega \to \infty \), and \( \lambda_c \) is called the crossover relaxation time. We constrain the individual contributions to the modulus in a way such that \( G_0^0 = G_{N,1}^0 + G_{N,2}^0 \) is constant.

When least-squares fitting (Rasmussen et al. 2000) the BSW model to the LVE data, \( n_e, n_g \) (both independent of temperature), \( \lambda_c \) and \( G_0^0 \) are treated as fixed values. The cross over time \( \lambda_c \) depends on temperature as any other relaxation time. \( n_e = 0.23, n_g = 0.67 \) and \( \lambda_c = 0.4s \) (at 130°C) as obtained by Jackson and Winter (1995). The value of \( G_0^0 \) was found by Bach et al. (2003a) to be 250 kPa at 130°C, and we have decided to use this value as a fixed parameter. This means, that the only remaining adjustable parameters to model the LVE data are the two largest relaxation times, \( \lambda_{\text{max},1} \) and \( \lambda_{\text{max},2} \) as seen in Table 3.3.

<table>
<thead>
<tr>
<th>Name</th>
<th>PS50K</th>
<th>PS100K</th>
<th>PS200K</th>
<th>PS390K</th>
<th>Blend 1</th>
<th>Blend 2</th>
<th>Blend 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \eta_{0,1} [MPas] )</td>
<td>0.82</td>
<td>7.88</td>
<td>82.9</td>
<td>724</td>
<td>0.78</td>
<td>1.02</td>
<td>5.97</td>
</tr>
<tr>
<td>( \eta_{0,2} [MPas] )</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.59</td>
<td>4.64</td>
<td>8.58</td>
</tr>
<tr>
<td>( \eta_0 [MPas] )</td>
<td>0.82</td>
<td>7.88</td>
<td>82.9</td>
<td>724</td>
<td>1.37</td>
<td>5.66</td>
<td>14.6</td>
</tr>
<tr>
<td>( \lambda_{\text{max},1} [s] )</td>
<td>12.8</td>
<td>158</td>
<td>1749</td>
<td>15441</td>
<td>12.2</td>
<td>17.4</td>
<td>122.1</td>
</tr>
<tr>
<td>( \lambda_{\text{max},2} [s] )</td>
<td>2186</td>
<td>3182</td>
<td>5572</td>
<td>-</td>
<td>5.66</td>
<td>14.6</td>
<td>122.1</td>
</tr>
<tr>
<td>( \lambda_{a,1} [s] )</td>
<td>7.05</td>
<td>87.02</td>
<td>965</td>
<td>8517</td>
<td>6.73</td>
<td>9.60</td>
<td>67.4</td>
</tr>
<tr>
<td>( \lambda_{a,2} [s] )</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1206</td>
<td>1755</td>
<td>3074</td>
</tr>
<tr>
<td>( G_{N,1}^0 [kPa] )</td>
<td>250</td>
<td>250</td>
<td>250</td>
<td>250</td>
<td>249</td>
<td>242</td>
<td>242</td>
</tr>
<tr>
<td>( G_{N,2}^0 [kPa] )</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.43</td>
<td>7.73</td>
<td>8.18</td>
</tr>
<tr>
<td>( G_N kPa )</td>
<td>250</td>
<td>250</td>
<td>250</td>
<td>250</td>
<td>250</td>
<td>250</td>
<td>250</td>
</tr>
</tbody>
</table>

**Table 3.3.** Linear viscoelastic properties of the pure and blended melts at 130°C. The constants in the BSW model are: \( n_e = 0.23, n_g = 0.67 \) and \( \lambda_c = 0.4s \) as obtained from Jackson and Winter (1995) plus \( G_N^0 = 250kPa \).
The experimental results for $G'$ and $G''$ are shown in figures 3.1 and 3.2 together with the best fit of the BSW-model. The zero shear viscosities are calculated as:

$$
\eta_{0,i} = \int_0^\infty G_i(s)ds = n_e G_{N,i}^0 \lambda_{max,i} \left( 1 + n_e \frac{\lambda_{max,i}}{1 - n_g} \right)^{-n_g}
$$

(3.8)

For the monodisperse melts $i = 1$. For the bidisperse melts $i = 1, 2$, and the individual $\eta_{0,i}$ can be added to find the actual, measured value of $\eta_0 = \eta_{0,1} + \eta_{0,2}$.

Fitting $\eta_0$ for the monodisperse melts PS50K, PS100K, PS200K and PS390K with the molecular weight as a power law, the exponent is found to be 3.38 as generally observed for these moderately entangled systems.

The average reptation time is calculated as:

$$
\lambda_{a,i} = \frac{\int_0^\infty G_i(s)ds}{\int_0^\infty G_i(s)ds} \approx \lambda_{max,i} \left( 1 + n_e \frac{2}{1 + n_e} \right)
$$

(3.9)

This expression applied to the Doi Edwards relaxation modulus gives a value that is within 2% of the commonly denoted reptation time, $\tau_d$. This time is found to scale with molecular weight as $\lambda_d \sim M^{3.52}$ for our monodisperse melts.

The characteristic time constants for the bidisperse systems found in table 3.3 show that the smaller time constant in the blend is more or less unchanged compared to the time constant for the undiluted small molecular weight melt. This is in agreement with the expectation (Doi et al. 1987) that there will be no tube dilation for the short chains. By contrast the longest relaxation time in the blend has been significantly reduced compared to the longest relaxation time for an undiluted melt of long chains which is attributed to the effect of tube dilation, Doi et al. (1987).

Struglinski and Graessley (1985) have predicted that when the molar masses in a binary blend of short ($M_s$) and long ($M_l$) chains are far apart, the reptation time for the longest molecules should not depend on the blend composition. The relevant constraint release parameter is defined as $G_r = M_l M_s^2 / M_l^3$ with the prediction that the reptation time of the longer chains should be unchanged provided $G_r < 0.1$. More recent investigations (Lee et al. 2005 and Park et al. 2004), however, suggest that the critical condition is somewhat lower with $G_{rc} \approx 0.064$ such that the non-dilation regime is limited to $G_r < G_{rc}$. The constraint release parameters for our blends (shown in table 3.1) are indeed all larger than $G_{rc}$ indicating that tube dilation takes place and that relaxation of the stress carried by the long chains is the result of constraint release due to reptation of the short chains. This is reflected in the values of $\lambda_{a,2}$ for the blends.
3.3. Linear Viscoelastic Measurements

compared to the value $\lambda_{a,1}$ for the pure long chains (PS390K) in table 3.3. By contrast the short relaxation time of blend ($\lambda_{a,1}$) is substantially unchanged compared to that of the pure short chains indicating that the short chains are reptating in an essentially frozen network of long chains. Moreover according to the revised Struglinski and Graessley criterion our blend 3 should be the least affected by tube dilation also in agreement with observations.

Struglinski and Graessley also conclude that the zero shear viscosity $\eta_0$ for bidisperse melts depends on the weight average molecular weights as the monodisperse melts where $\eta_0 \sim M_w^{1.34}$. This prediction deviates less than 40 percent from our measured zero shear viscosities.

Ye et al. (2003) used two monodisperse polystyrene samples of molar masses $M_s = 2890 \text{ kg/mole}$ and $M_l = 8420 \text{ kg/mole}$ to prepare a series of bidisperse solutions spanning the range from pure short chains to long chains. All blends were dissolved in tricresyl phosphate with an overall polymer volume fraction of 7%. These blends, all in the semidilute regime, were subsequently characterized in uniaxial extensional flow using a filament stretching devise and successfully compared to the predictions of a simplified reptation model designed to investigate the effects of polydispersity. A characteristic feature of the steady elongational viscosity measured for all investigated solutions, including the monodisperse ones, was a transition to strain hardening which was interpreted as a signature of chain stretching. In other words there was no qualitative difference between the measured elongational viscosity of the entangled monodisperse and bidisperse polystyrene solutions. The results obtained by Ye et al. are thus expected to differ from our study for at least two reasons. Firstly, in table 3.1 we show the values of the Struglinski-Graessley parameter $G_r$ for the

![Blind 1](image)

**Figure 3.4.** Corrected transient extensional viscosity (equation 6.1) of Blend 1 measured at different strain rates. Measurements were performed at 130 °C.
blends studied by Ye et al. The widely disparate values of the reptation times for the two species lead to $G_{rc} << 1$ and indicate that, in contrast to our experiments, the dynamics of the longer chain should remain unchanged regardless of the presence of the shorter species. Secondly, the materials studied by Ye et al. are semi-dilute entangled solutions rather than melts. Even though the number of entanglements is comparable, the higher molecular weight of each entangled segment when diluted by a solvent results in a greater number of Kuhn steps in each segment and consequently a larger molecular extensibility (Appendix 8.2). For completeness, we have also included the Graessley parameters for Wagner et al.’s (2005) bidisperse melts in table 3.1.

### 3.4 Elongational Viscosity Measurements

#### 3.4.1 Startup of elongational flow

Figures 3.3, 3.7 and 3.9 show the corrected transient elongational viscosity (equation 6.1) for PS50K, PS100K, Blend 1 and Blend 3 together with the LVE-prediction, all measured at 130°C. The elongational measurements for all melts show good agreement with the LVE prediction at small strains. The deviation between the transient elongational data and LVE measurements is less than 15% in all measurements. Figures 3.4, 3.5, 3.8 and 3.10 show the same measurements as in the Figures 3.3, 3.7 and 3.9, with uncorrected tensile stress differences (equation 3.3) plotted against strain. It is seen, that the steady elongational viscosity is obtained for all elongational rates. As the elongational rate increases, the plateau region is maintained for fewer strain units compared to smaller rates.

![Figure 3.5](image-url)

**Figure 3.5.** Corrected transient extensional viscosity (equation 6.1) of Blend 3 measured at different strain rates. Measurements were performed at 130 °C.
is due to a larger pre-stretch, $\epsilon_0$, for the high stretch rate experiments. The reason for increasing the pre-stretch in the faster experiments is two-fold. Firstly, it minimizes the magnitude of the correction for reverse squeeze flow at high rates (see eq.(4)). Secondly it helps reduce the tendency for deadhesion of the sample from the endplate. The adhesive force holding the sample to the end plate has a maximum value; by pre-stretching the sample to induce a neck at the midplane, higher tensile stresses (and hence higher maximum stretching rates) can then be tolerated in the middle of the filament for a given force of adhesion at the end-plates.

### 3.4.2 Steady viscosity scaling at intermediate Deborah numbers

#### 3.4.2.1 Monodisperse melts

We first turn our attention to the results for the monodisperse melts in order to compare with the results from Bachs et al. (2003a). We see from figure 3.3 and 3.13 that the steady viscosity for PS100K reaches a value very close to $3\eta_0$ for the lowest elongational rate. The time dependent transient viscosity, $\bar{\eta}^+$, for the lowest rate follows the LVE-prediction. At intermediate Deborah numbers, i.e. $1 < De < 10$, the steady elongational viscosity, $\bar{\eta}$, rises above $3\eta_0$. For PS100K $\bar{\eta}$ is about 50% above $3\eta_0$, and the $\bar{\eta}$-maximum is stretched over two decades of $\dot{\epsilon}$. The maximum for PS50K is measured to be at least 100% above $3\eta_0$. It is possibly higher than $6\eta_0$, since the highest measured elongational rate also gives the highest $\bar{\eta}$-value. The rate at which the maximum occurs corresponds to a Deborah number around $De \approx 3$ for both melts (assuming that $\bar{\eta}$ reaches its maximum at a elongational rate somewhat higher than $\dot{\epsilon} = 0.3s^{-1}$ for

![Figure 3.6. Same data as in figure 3.3 for PS50K but plotted as uncorrected transient extensional stress (equation 3.3) against Hencky strain $\epsilon$.](image-url)
3.4. Elongational Viscosity Measurements

PS50K).

The elongational viscosity measurements for PS100K and PS50K in the
nonlinear regime, i.e $De > 3$ are very limited because of the restriction due
to dissipative heating limiting the measurements to $\dot{\varepsilon} \leq 0.3 s^{-1}$. There
are only two measurements in the nonlinear regime available for PS100K,
and none for PS50K. This makes it difficult to compare with the scaling
behaviour proposed by Bach et al. (2003a).

Bach et al. (2003a) claimed that the steady elongational stress scaled
linearly with the molecular weight at high Deborah numbers. This scaling
can be illustrated by interpreting data according to recently published
theory by Marrucci and Ianniruberto (2004). Figure 3.6 shows steady
values of $(\sigma_{zz} - \sigma_{rr})/G_N^0$ vs. $\dot{\varepsilon}\tau_p$ for all of the monodisperse melts. Here $\tau_p$
represents the relaxation time of the squeezing pressure effect as defined
by Marrucci and Ianniruberto (2004). Marrucci and Ianniruberto report
$\tau_p$ for PS200 to be $\tau_p = 1000s$, and the scaling is $\tau_p \sim M_w^2$. This is
used to calculate $\tau_p$ for the other monodisperse melts, which then become:
$\tau_p = 66.8s$ for PS50K, $\tau_p = 264.2s$ for PS100K and $\tau_p = 3802.5s$ for
PS390K. It is seen in figure 3.6, that the scaled values for PS50K and
PS100K lie on the same line as the data for PS200K and PS390K steady
state stresses, hereby showing that the linear scaling of steady stress with
molecular weight at high Deborah-numbers is valid.

Another conclusion from the work of Bach et al. (2003a) was that the
steady elongational viscosity scales with about $\dot{\varepsilon}^{-0.5}$ for large Deborah
numbers. By examining the raw-data from Bach et al. (2003a) more
closely and performing a linear regression it is however concluded that
the exponent is $-0.42 \pm 0.03$ within a 95% confidence interval. In the
present study there are only two measurements of $\bar{\eta}$ for PS100K that
could confirm this power law behaviour, and none for PS50K. Figure 3.13

![Figure 3.7](image)

**Figure 3.7.** Same data as in figure 3.3 for PS100K but plotted as uncorrected
transient extensional stress (equation 3.3) against Hencky strain $\varepsilon$. 
3.4. Elongational Viscosity Measurements

\[ \dot{\epsilon} = 0.3 \text{s}^{-1} \]
\[ \dot{\epsilon} = 0.1 \text{s}^{-1} \]
\[ \dot{\epsilon} = 0.03 \text{s}^{-1} \]
\[ \dot{\epsilon} = 0.01 \text{s}^{-1} \]
\[ \dot{\epsilon} = 0.003 \text{s}^{-1} \]
\[ \dot{\epsilon} = 0.001 \text{s}^{-1} \]
\[ \dot{\epsilon} = 0.0003 \text{s}^{-1} \]
\[ \dot{\epsilon} = 0.00015 \text{s}^{-1} \]

Figure 3.8. Same data as in figure 3.7 for Blend 1 but plotted as uncorrected transient extensional stress (equation 3.3) against Hencky strain \( \dot{\epsilon} \).

Figure 3.9. Same data as in figure 3.9 for Blend 3 but plotted as the uncorrected transient extensional stress (equation 3.3) against Hencky strain \( \dot{\epsilon} \).
shows the steady elongational viscosity of PS100K, and it appears to show the expected asymptotic behaviour.

### 3.4.2.2 Bidisperse melts

Figure 3.7 and 3.9 show the corrected transient elongational viscosity for the blends denoted Blend 1 and Blend 3, see table 3.1. It can be seen from both plots, that there is good agreement between the elongational measurements and the LVE prediction for small strains. The steady viscosity lie substantially above $3\eta_0$ for all measurements, except for Blend 3 at $\dot{\varepsilon} = 0.3 s^{-1}$.

The complex interdependence of the transient extensional rheology of the entangled blends on stretching rate, molecular weight and concentration is illustrated in figure 3.11 for the PS50K/PS390K blends. For a pure PS50K melt at a strain rate of $\dot{\varepsilon} = 0.1 s^{-1}$ the transient extensional response closely follows the linear viscoelastic envelope. The addition of a small concentration of high molecular weight to the blend (Blend 1; $c/c^* = 2.5$) results in a substantial transient strain-hardening and also a steady extensional viscosity that is substantially above $3\eta_0$ for the blend. That this additional stress is contributed by the higher molecular species can be easily demonstrated by examining the tensile stress contribution associated with a single mode Upper Convected Maxwell, (UCM) model (with modulus and relaxation time determined from table 3.3). This is shown by the dashed line in Figure 3.11. As the concentration of higher molecular weight species is increased to 14% (Blend 2) the magnitude of the extensional viscosity climbs further. Once again we show the contribution of the high molecular weight species to the transient stress growth by

![Figure 3.10](image.png)

**Figure 3.10.** Steady elongational viscosity as a function of the elongational rate for PS50K, PS100K, PS200K and PS390K. All measurements performed at 130$^\circ$C. The solid lines are the predictions of the Wiest model.
3.5. Constitutive Modelling of the Steady Elongational Viscosity

The mathematical inconsistency mentioned in the introduction is solved by acknowledging that the steady elongational viscosity for moderately entangled melts can have a maximum that exceeds \(3\eta_0\); the magnitude

plotting the response of an UCM model (solid line). The increase in the relaxation time of blend 2 also results in an increase in the Deborah number \((De_{\text{blend}2} = 1755 \cdot 0.1s^{-1} = 176)\) and consequently the chains are fully elongated during the course of the experiment. This is illustrated by the horizontal dotted line in Figure 3.11 which corresponds to cutting off the stress growth for Blend 2 at a Hencky strain of \(\epsilon_{\text{max}} = \frac{1}{2}\ln(N_{K,seg}) = 1.55\), see appendix 8.2. Although the ultimate steady elongational viscosity shows some increase over 3 times the steady state shear viscosity for this blend, the Trouton ratio is clearly reduced substantially compared to Blend 1. Finally we also show in Figure 3.11 the transient response of the pure PS390K material at the same imposed stretch rate of \(0.1s^{-1}\), together with the UCM model (dashed dot line). The material shows an initial linear viscoelastic response, followed by strain-hardening but a steady elongational viscosity that is substantially less than \(3\eta_0\). Plotting the steady elongational viscosity against elongational rate in figure 3.14, 3.15 and 3.16, it is seen that the maximum in elongational viscosity is about 90% above \(3\eta_0\) for Blend 3, and about 700% above for Blend 2.

Figure 3.11. The steady stress divided with the plateau modulus against the Marrucci-Deborah number \(\epsilon_Tp\) for PS50K, PS100K, PS200K and PS390K.

3.5 Constitutive Modelling of the Steady Elongational Viscosity

The mathematical inconsistency mentioned in the introduction is solved by acknowledging that the steady elongational viscosity for moderately entangled melts can have a maximum that exceeds \(3\eta_0\); the magnitude
3.5. Constitutive Modelling of the Steady Elongational Viscosity

The constitutive model in terms of integral average of the connector

![Figure 3.12](image)

**Figure 3.12.** Corrected transient extensional viscosities (equation 6.1) of Blend 1, Blend 2, PS50K and PS390K at \( \dot{\epsilon} = 0.1 \text{s}^{-1} \). The broken line is the Upper Convected Maxwell (UCM) prediction for Blend 1, \( De = \lambda_{a,2,blend1} \cdot 0.1 \text{s}^{-1} = 121 \), the solid line is the UCM prediction for Blend 2 \( De = \lambda_{a,2,blend2} \cdot 0.1 \text{s}^{-1} = 176 \), the dashed dot line is the UCM prediction for PS390K \( De = \lambda_{a,1,PS390K} \cdot 0.1 \text{s}^{-1} = 1544 \). The dotted line is the neo-Hookean model with \( G = 250 \text{ kPa} \), cut off at \( \dot{\epsilon}_{\text{max}} \). The values of three times the zero shear viscosity for each melt is shown on the right with punctured lines.

The behaviour of the elongational viscosity for dilute solutions for high Deborah numbers has been studied by Gupta et al. (2000) who found that \( \bar{\eta} \sim \dot{\epsilon}^{-0.5} \) for very diluted solutions of narrow molar mass distribution polystyrene. This result can be modeled theoretically by including finite extensibility into the Giesekus (1982) anisotropic friction dumbbell model to account in an average fashion for the orientation of the surrounding molecules (Wiest 1989). The asymptotic analysis is performed in details in the Appendix. Marrucci and Ianniruberto (2004) quantitatively predict the experimentally found asymptotic stress behaviour by incorporating chain squeeze into their model. This will essentially give rise to anisotropic friction too, and the Wiest model is a simple way of describing this.

The behaviour of the elongational viscosity for dilute solutions for high Deborah numbers has been studied by Gupta et al. (2000) who found that \( \bar{\eta} \sim \dot{\epsilon}^{-0.4} \) for large Deborah numbers, but where Bach et al. (2003a) claimed that this behaviour starts at \( De > 1 \), the results from PS100K show that this occurs at much higher Deborah numbers, \( De > 10 \), and for PS50K even higher. It is thus clear that the shape of the steady elongational viscosity curve \( \bar{\eta} \) is molecular weight dependent. The results from the blends show, that the magnitude of the steady viscosity maximum becomes greater as the difference between the chain lengths in the blend increase.

The value of the maximum depending on the molecular weight. The viscosity was found to scale with \( \dot{\epsilon}^{-0.4} \) for large Deborah numbers, but where Bach et al. (2003a) claimed that this behaviour starts at \( De > 1 \), the results from PS100K show that this occurs at much higher Deborah numbers, \( De > 10 \), and for PS50K even higher. It is thus clear that the shape of the steady elongational viscosity curve \( \bar{\eta} \) is molecular weight dependent. The results from the blends show, that the magnitude of the steady viscosity maximum becomes greater as the difference between the chain lengths in the blend increase.

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The constitutive model in terms of integral average of the connector
3.5. Constitutive Modelling of the Steady Elongational Viscosity

Figure 3.13. Steady elongational viscosity against the elongational rate for Blend 3. All measurements performed at 130°C. The solid line is the overall prediction of the Wiest model, and the dashed lines are the individual contributions from the two individual polymer species.

Figure 3.14. Steady elongational viscosity against the elongational rate for Blend 2. All measurements performed at 130°C. The solid line is the overall prediction of the Wiest model, and the dashed lines are the individual contributions from the two individual polymer species.
3.5. Constitutive Modelling of the Steady
Elongational Viscosity

The dyad $\langle QQ \rangle$ is:

$$\langle QQ \rangle_{(1)} = -\frac{4H}{\zeta^{-1}} \left( f\langle QQ \rangle - \frac{kT}{H} I \right)$$

$$= 4kT\zeta^{-1} - 4H\langle QQ \rangle f\zeta^{-1}$$

(3.10)

(3.11)

where the Giesekus mobility tensor is:

$$\zeta^{-1} = \frac{1}{\zeta} \left( \delta - \frac{a}{nkT} \tau_p \right)$$

(3.12)

and $f$ describes the nonlinearity of the Warner spring in the FENE-P dumbbell model:

$$f = \left[ 1 - \frac{\langle Q^2 \rangle}{Q_0^2} \right]^{-1}$$

(3.13)

where $\langle Q^2 \rangle = tr(QQ)$. Here $H$ is a spring constant, $n$ is the number density of dumbbells, $k$ is Boltzmann’s constant, $T$ the absolute temperature, $I$ is the unit tensor, and $Q_0$ is the maximum length of the dumbbell. The stress tensor for the polymer is given by eq. (13.7-5) of Bird et al (1987):

$$\tau_p = -nHf\langle QQ \rangle + nkT\delta$$

(3.14)

By elimination of $\langle QQ \rangle$ a constitutive equation in terms of the polymeric stress, $\tau_p$, may be obtained in the form:

![Figure 3.15](image_url)

**Figure 3.15.** Steady elongational viscosity against the elongational rate for Blend 1. All measurements performed at 130°C. The solid line is the overall prediction of the Wiest model, and the dashed lines are the individual contributions from the two polymers.
3.5. Constitutive Modelling of the Steady
Elongational Viscosity

\[
(Z - \lambda_H \frac{DlnZ}{Dt}) \tau_p + \lambda_H \tau_{p,(1)} - \frac{aZ}{nkT} (\tau_p \tau_p) = -nkT \lambda_H \left( \dot{\gamma} + \frac{DlnZ}{Dt} \delta \right)
\]

(3.15)

Where

\[
Z = \frac{1}{b} \left( b + 3 - \frac{\delta \tau_p}{nkT} \right)
\]

(3.16)

\( \dot{\gamma} \) is the strain rate tensor and \( b \) is the finite extensibility parameter for the entanglement segment found as: \( b = H_{seg} Q_k^2 / (kT) \) and \( \lambda_H \) is the single time constant of the model \( \lambda_H = \zeta / (4 H_{seg}) \). The zero shear viscosity is found (Wiest, 1989) to be \( \eta_0 = nkT \lambda_H b / (b + 3) \).

This model has three free parameters, \( a, b \) and \( \lambda_H \), where \( a \) is a dimensionless scalar between 0 and 1 describing the degree of anisotropy in the hydrodynamic drag in the melt; when \( a = 0 \) the drag is completely isotropic while \( a = 1 \) corresponds to maximum anisotropy. The model describes the dynamics of one entangled segment. The finite extensibility parameter \( b \) is expected to be independent of molecular weight, see appendix 8.2 and equal to three times the number of Kuhn steps in a entanglement segment, \( N_{k,seg} \), and \( \lambda_H \) is a characteristic time constant. By solving the constitutive equation for uniaxial elongational flow one sees, that by changing the \( a \)-parameter from 0 to 1 at fixed values of \( b \) and \( \lambda_H \), the steady elongational viscosity \( \bar{\eta} \) has a maximum above \( 3 \eta_0 \), whose magnitude increases as \( a \to 0 \), and decreases, and almost disappears as \( a \to 1 \).

Relating the maximum in \( \bar{\eta} \) with drag anisotropy for monodisperse melts may help rationalize why the local maximum is almost absent for high molecular weight melts, such as PS390K, and becomes increasingly larger with lower molecular weights. If the size of \( a \) is interpreted as a potential for anisotropy, one would intuitively assume that for a 100% stretched and aligned polymer melt, which would be the case at infinite elongational rate at steady state, the anisotropy inside the melt would be largest in the limit of long chains. A melt of shorter, but still stretched and aligned chains, would have a higher density of free ends thereby reducing anisotropy.

The same arguments can be used for bidisperse melts. Blend 1 and 2 contain the same polymers, but the long chains are more diluted by short chains in Blend 1 and we would expect the \( a \)-parameter for Blend 2 to be larger than for Blend 1, since the potential for anisotropic drag is lowest when the longer chains are surrounded by fewer long chains. Blend 2 and 3 have the same mass fraction of PS390K, but are mixed with PS50K and PS100K chains, respectively. Again we expect the anisotropic parameter \( a \) to be smallest for Blend 2, which is the case as shown later. This effect is more pronounced compared to the difference between Blend 1 and 2.

The question is now whether or not the model is able to explain the data quantitatively. If the model is fitted to results of the monodisperse melts,
ideally only two parameters should be fitted, $a$ and $\lambda_H$, since $b$ is related to the number of Kuhn steps in an entanglement segment which is known. It is not expected that a single mode version of the model will describe the complete transient elongational viscosity because the initial transient growth in the stress is related to the LVE behaviour, and the Wiest model is basically a single time constant model with inclusion of anisotropy and a FENE-P spring between the dumbbells. A multi mode version would be needed to quantitatively describe the LVE behaviour. Since we are concerned primarily with the steady elongational viscosity only one mode is used in this analysis.

PS100K is the melt with the most elongational measurements above and below $\epsilon = 1/\tau_d$, i.e. at intermediate Deborah numbers, which in this work is the most interesting area. To obtain an idea of the relative magnitude of the different constitutive parameters, a fit to the elongational viscosity data for PS100K is made by changing both $a$, $b$ and $\lambda_H$, and a separate fit where $b$ is kept constant at $3N_{k,seg}$ and only $a$ and $\lambda_H$ are allowed to change. Bach et al. (2003a) reported the number of Kuhn steps between entanglement segments as $N_{k,seg} = 22$, which makes $b = 66$. The result is shown in figure 3.12, and the fitted values are shown in the caption. Both fits give reasonable agreement with the experimental data. The time constant $\lambda_H$ is in both fits of about the order of the expected reptation time in both fits, around 100 seconds, and $a$ is in the expected interval between 0 and 1. In contrast to the limiting case of the Giesekus model ($b \to \infty$), the Wiest model does not predict unphysical degree of shear-thinning in the steady shear viscosity for $a > 0.5$, Wiest (1989). Instead, it is found that the shear stress plateaus at high shear rates, corresponding to the steady shear viscosity decreasing as $\dot{\gamma}^{-1}$.

The least square fitted value of $b$ corresponds to very little extensibility which appears unphysical. Since we find no consistency in the magnitude of $b$, this parameter is allowed to float in the following fits of the experimental data to the model.

<table>
<thead>
<tr>
<th>Name</th>
<th>PS50K</th>
<th>PS100K</th>
<th>PS200K</th>
<th>PS390K</th>
<th>Blend 1</th>
<th>Blend 2</th>
<th>Blend 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>w% PS50K</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>95.98</td>
<td>85.63</td>
<td>0</td>
</tr>
<tr>
<td>w% PS100K</td>
<td>0.1372</td>
<td>0.2182</td>
<td>0.7033</td>
<td>1.000</td>
<td>1.9 · 10^{-4}</td>
<td>5.65 · 10^{-4}</td>
<td>0.1982</td>
</tr>
<tr>
<td>w% PS390K</td>
<td>4.02</td>
<td>14.37</td>
<td>14.02</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\bar{\eta}_{max}/(3\eta_0)$</td>
<td>2.56</td>
<td>1.54</td>
<td>1.17</td>
<td>1</td>
<td>7.40</td>
<td>5.06</td>
<td>1.95</td>
</tr>
</tbody>
</table>

Table 3.4. The least square fitted of the Wiest model parameters $a$ and $b$ for the different melts together with dimensionless maximum in the steady elongational viscosity $\bar{\eta}_{max}/(3\eta_0)$

The value of $\lambda_H$ does seem to resemble the reptation time, and in the following fits the value of $\lambda_H$ is held fixed on $\lambda_a$. The experimental data
3.6 Conclusion

The steady elongational viscosity of two moderately entangled monodisperse polystyrene melts, with molecular weights of 52 kg/mole and 103 kg/mole, have been found for elongational deformation rates ranging from $\dot{\varepsilon} = 0.003 \text{s}^{-1}$ to $\dot{\varepsilon} = 0.3 \text{s}^{-1}$. It is observed, that the steady elongational viscosity vs. elongational rate goes through a maximum, and followed by a decrease where the elongational rate scales as $\tilde{\eta} \sim M_w \dot{\varepsilon}^{0.4}$ for large elongational rates. The maximum is the result of fewer entanglements in these melts, in agreement with the predictions of Marrucci and Ianniruberto (2004).

The steady elongational viscosity has also been measured for bidisperse blends of a high and a low molecular weight monodisperse polystyrene.
Here we also observe a maximum in the steady elongational viscosity vs. elongational rate. This maximum, relative to three times the zero shear viscosity, increase as the concentration of high molecular weight chains decrease. This observation is contrary to that reported by Wagner et al. (2005), who found that the strain hardening increased with increasing concentration of ultra high molecular weight polystyrene. The molar masses in their studies are, however, well above $365 \text{kg/mol}$ which may be argued to be the upper limit for the application of the Wiest model, see appendix (3.8.3). Conversely the maximum in steady elongational viscosity against elongational rate increases with reduced molecular weight of the low molecular weight chains.

The maximum found for bidisperse polymer blends indicates a qualitative difference between monodisperse and bidisperse melts. This is different from the corresponding situation between monodisperse and bidisperse solutions (Ye et al. 2003) with Graessley parameters $G_r << G_{rc}$.

The fact that the steady elongational viscosity of a blend of long (390 kg/mol) and short polystyrene chains exhibits a maximum as function of elongation rate while the melt of pure long chains does not, may be interpreted in terms of the Wiest dumbbell model which combines the Giesekus anisotropic friction concept with finite extensibility. Indeed the pure melt of long chains has a large potential for anisotropic drag corresponding to the Giesekus parameter $a = 1$. Conversely in blends with a significantly lower molar mass or even entangled solutions, the long chains will encounter an environment with less potential for anisotropy. Basically the long chains undergo stretching at extensional rates at which the shorter chains are not oriented thereby providing an isotropic drag environment.

![Figure 3.16](image-url)

**Figure 3.16.** Steady extensional viscosity measurements of PS100K (○) measured at 130 °C. The solid line is the Wiest fit where $a=0.1805$, $b=4.44$ and $\lambda_H = 66.85s$. The dotted line is the Wiest fit where $a=0.4055$, $b=66$ and $\lambda_H = 105.7725s$. 
3.7 Acknowledgments

The authors gratefully acknowledge financial support to the Graduate School of Polymer Science from Danish Research Training Council and the Danish Technical Research Council to the Danish Polymer Centre.

3.8 Appendix

3.8.1 Behaviour of the Wiest-model for $\dot{\epsilon} \to \infty$

The constitutive equation for homogeneous steady flow of the Wiest model is:

$$Z\tau_p + \lambda_H\tau_{p(1)} - \frac{aZ}{nkT}(\tau_p\tau_p) = -nkT\lambda_H\dot{\gamma} \quad (3.17)$$

In strong uniaxial elongation, steady flows, the only stress contribution to the forces in the melt is $\tau_{zz}$. To solve $\tau_{p,zz}$ the variable substitution $y = -\tau_{p,zz}/(nkT)$, and $x = \lambda_H\dot{\epsilon}$ is introduced. The stress in the zz-direction then becomes:

$$-\frac{ay^3}{b} + \frac{y^2}{b} + 2xy + 2x = 0 \quad (3.18)$$

Since $\tau_{zz}$ in stretching is negative, $y > 0$ for all values of $x$. It is assumed that for large elongational rates, the viscosity, and thereby also $y$ behaves as a power law-function i.e.: $y \sim Ax^\alpha$ for $x \to \infty$. Substituting this into equation (3.18) we get:

$$-\frac{aA^3x^{3\alpha}}{b} + \frac{A^2x^{2\alpha}}{b} + 2Ax^{1+\alpha} + 2x = 0 \quad (3.19)$$

Since the absolute value of the stress, $|\tau_{zz}|$, and therefore $y$, increase for increasing elongational rates $\alpha$ must be larger than zero. The largest terms in equation (3.19) are $2Ax^{1+\alpha}$ and $-aA^3x^{3\alpha}/b$ which have to balance as $x \to \infty$, whereby we obtain $\alpha = 1/2$.

The pre-exponential terms also have to balance, for $x \to \infty$ so the parameter $A$ becomes:

$$2A = \frac{a}{b}A^3 \Rightarrow A = \sqrt{\frac{2b}{a}} \quad (3.20)$$

The final asymptotic result is that:

$$\frac{\tilde{\eta}}{nkT\lambda_H} = \sqrt{\frac{2b}{a}} (\lambda_H\dot{\epsilon})^{-1/2} \quad \text{for} \quad \dot{\epsilon} \to \infty \quad (3.21)$$

The modified Giesekus model thereby gives a physical explanation for the fact, that $\tilde{\eta} \sim \dot{\epsilon}^{-1/2}$ for high elongational rates whereas the simple Giesekus model predicted $\tilde{\eta}$ as having a finite limit for infinite $\dot{\epsilon}$. 
3.8.2 Molecular interpretation of the finite extensibility $b$-parameter

We apply the Wiest model to a representative single entangled tube segment of the melt. The chain in the tube segment is modeled as a FENE spring with maximum length $Q_0$ and spring constant $H_{seg}$ given by:

$$Q_0 = N_{k,seg} L_k$$  \hspace{1cm} (3.22)

and

$$H_{seg} = \frac{3kT}{N_{k,seg} L_k^2}$$  \hspace{1cm} (3.23)

where $N_{k,seg}$ is the number of Kuhn steps in entanglement segment, and $L_k$ is the length of each Kuhn step. From these equations the constant $b$ is defined, which yields a simpler expression:

$$b \equiv \frac{H_{seg} Q_0^2}{kT} = 3N_{k,seg}$$  \hspace{1cm} (3.24)

The finite strain extensibility of an entanglement segment is given by $\exp(\epsilon_{max}) = \sqrt{N_{k,seg}}$, Fang (2000), which means that in the affine limit, that is at infinite elongational rate, the segment has reached its maximum stretch at a strain of

$$\epsilon_{max} = \frac{1}{2} \ln N_{k,seg} = \frac{1}{2} \ln \left( \frac{1}{3} b \right)$$  \hspace{1cm} (3.25)

3.8.3 Scaling of steady state stress with $M_w$ in the Wiest model

For an entangled polymer melt, the pre factor scale for stress is independent of molecular weight: $ nkT \equiv G_N^0 = \rho RT/M_c $. With respect to the time constant $\lambda_H$, the relevant times to consider would be either the reptation time, which is the characteristic time of the entire chain in the constrained tube taken from the Doi-Edwards interpretation of a polymer melt, or the Rouse time, which is a time constant for the stretching of the entangled chain. It makes sense in the Wiest model to choose a Rouse scaling for $\lambda_H$ since it describes stretching which would make $\lambda_H \sim M_w^2$. However, fitting showed that $\lambda_H \simeq \lambda_a$ which suggests that $\lambda_H$ scales as the Doi-Edwards reptation time i.e. $\lambda_H \sim M_w^2$. Of course, such apparent inconsistencies are inevitable with a dumbbell-based segment-level model. More detailed constitutive models for monodisperse melts (Marucci and Ianniruberto 2004) recognize that the time-scales for orientation
and chain-stretching scale differently with molecular weight. This is beyond the scope of the present discussion. We seek simply to show that a simple model with anisotropic drag such as the Wiest model is capable of describing the experimental observations in pure melts and in blends. As we have noted above the extensibility $b$ only a function of the length of an entangled segment and is therefore independent of $M_w$.

The steady stress scaling then become:

$$
(\sigma_{zz} - \sigma_{xx}) = \dot{\eta} \dot{\varepsilon} = G_N^0 \cdot \lambda_H^{1/2} \cdot b^{1/2} \cdot a^{-1/2} \dot{\varepsilon}^{1/2} \sqrt{2}
\sim (M_w^0) \cdot (M_w^3)^{1/2} \cdot (M_w^1)^{1/2} \cdot (M_w^x)^{-1/2}
$$

Assuming that the stress scales as $(\sigma_{zz} - \sigma_{xx}) \sim M_w \dot{\varepsilon}^{1/2}$ an expression for molecular weight scaling-factor $x$ of $a$ is found using equation (3.26) to be $a \sim M_w^1$. This is only valid as long as $a \leq 1$.

Figure 3.17 below shows the fitted values of $a$ as function of the molecular weight $M_w$. The solid line is the best linear fit against molecular weight, i.e. $a = A M_w^1$.

It is not possible to validate the molecular weight scaling of $a$ from the plot, since only three data points are available. But the plot does indicate that the Wiest model cannot be applied as a constitutive equation of polystyrenes with molecular weights more than around 365 $\text{kg/mole}$ and this also explain why the fit for the steady elongational viscosity for PS390K was so poor. The drag anisotropy appears to saturate for entangled polystyrene melts with molecular weights above 365 $\text{kg/mole}$.

![Figure 3.17. Least square fitted parameter of $a$ against $M_w$. Solid line is a linear fit, $a = A(M_w)^1$.](image-url)
Bibliography


Two branched polystyrene melts with narrow molar mass distribution have been synthesized: A multiarm \( A_n - C - C - A_n \) pom-pom polystyrene and an \( A_n - C \) asymmetric star polystyrene where \( n \) is the number of arms. The pom-pom and the asymmetric star have molar masses of \( M_w = 300 \) kg/mol and \( M_w = 275 \) kg/mol, respectively. The pom-pom was estimated to have 2.5 arms on average, while the estimate is 3.3 for the asymmetric star. The molar mass of each arm is about 27 kg/mol. The melts were characterized in the linear viscoelastic regime and by elongational rheometry in the non-linear regime. For asymmetric star polystyrene, the measured transient elongational viscosity is not consistent with a rheological constitutive equation that is separable in time and strain. Contrary to this situation however for pom-pom polystyrene, the transient elongational viscosity may be described by a time-strain separable constitutive equation for elongation rates larger than the inverse reptation time. Up to a Hencky strains of 2.6, the corresponding stress tensor component for the pom-pom is closely approximated by a model that assumes the arms to be fully relaxed while the cross-bar is part of an unrelaxed entanglement network model. At Hencky strains above 2.6 a saturation of stress occurs that we interpret as withdrawal of the arms into the cross-bar tube. The observed strain associated with arm withdrawal is significantly larger than that predicted from an equilibrium force balance on the branch points while it corresponds well with an estimate of the maximum stretchability of the cross-bar. At the highest elongation rate investigated, the transient elongational viscosity for pom-pom went through a reproducible maximum as function of time.  

\[^1\text{This part of the work has been published in Macromolecules, 39 8844-8853 (2006).}\]
4.1 Introduction

Well defined branched polymer melts have proven valuable as model materials useful to gain insight into the complex physics of long chain branched (LCB) polymer melts. In one model architecture, often denoted pom-pom polymer, two branch points are connected by a polymer backbone denoted the cross-bar. A number of arms emanate from the branch-points. We refer to the pom-pom as $A_n - C - C - A_n$ and to the asymmetric star as $A_n - C$. Note that all blocks in the polymers are consisting of homo polymers. Figure 4.1 shows a schematic drawing of a pom-pom polystyrene molecule with three arms.

In a comprehensive investigation of model branched melts, McLeish and coworkers (1) have reported theory, rheology and scattering of 4 isoprene H-shaped polymers (pom-pom polymer with two arms). Archer and Juliani (2) have reported on the dynamics of multiarm $A_n - C - C - A_n$ 1,4 polybutadiene melts. According to the H-polymer theory (1; 3) relaxation in branched systems occurs in a hierarchical fashion: arms relax on a shorter timescale than the cross-bar. The cross-bar does not begin to relax before the arms are completely relaxed, whereby a separation of time scales occurs. Qualitative agreement is generally observed between theory and experiments in the linear viscoelastic regime (1; 2; 4).

In the nonlinear range, the additional phenomenon of branch-point withdrawal is believed to occur for large deformations. Once the cross-bar reaches a critical extension, the tension in the cross-bar is sufficient to pull the arms into the cross-bar tube (5). A force balance on the branch point leads to the prediction (5) that the resulting arm retraction should occur when the relative stretch of the crossbar equals the number of arms. In non-linear step strain the predicted critical magnitude of strain (6) is approximately $\gamma = \sqrt{3(q^2 - 1)}$ where $q$ is the number of arms. Archer and Juliani (2) used 3-arm polybutadiene melts (2) to test this prediction

Figure 4.1. A schematic drawing of a pom-pom molecule with 3 branches linked to the crossbar. The chemical formula for the polymer is: $(St_m)_n - (St_k) - (St_k) - (St_m)_n$ where $St$ is styrene, $n$ is the number of arms, $m$ is the number of monomers in the arms, and $k$ is half the number of monomers in the cross bar. We simplify the nomenclature so that the arm is: $A \equiv St_m$ and crossbar is $C \equiv St_k$. The pom-pom is refereed to as $A_n - C - C - A_n$ and the asymmetric star as $A_n - C$. 
up to shear strain magnitudes of 12. They do indeed find a transition at about the predicted critical shear magnitude. However the measured stress is less than predicted by the theory especially below the transition point where the material is predicted to behave as an elastomeric network.

Experimental information on well characterized model LCB melts in nonlinear elongation is more limited (1). Arm retraction has been predicted (6) to cause failure of polymer filaments in extension. Consequently steady stress will not be observed unless special precautions are made (7).

In an early development on the rheology of LCB melts, Wagner (8) demonstrated that it is possible to separate time and strain effects in start-up of elongational flow of low density polyethylene (LDPE) melts. From the resulting strain information it is then possible to obtain information on the nonlinear strain behavior including arm-retraction in elongation. We intend here to use this methodology to investigate the non-linear rheology of well characterized model LCB melts in elongational flow. In particular we study long-chain branched $A_n - C - C - A_n$, pom-pom, and $A_n - C$, asymmetric star, polystyrene melts. With a glass transition temperature around 100°C polystyrene has proven to be a suitable model melt. In the temperature range 130°C-170°C we can adjust the time constants of the melt to suit the operating conditions for the rheometer. Time-temperature shifting may then be applied to check consistency of the measurements.

Knauss and Huang (9) developed a method for preparation of $A_n - C - C - A_n$ polystyrenes by anionic polymerisation. The number of arms is not a fixed value but rather a distribution with an average value $N_n$ given by the stoichiometry (11). In the work by Knauss and Huang and in the more recent work by Ryu et al. (11) all arms are below one entanglement length however. To be able to compare with H-polymer theory, we have synthesized an $A_n - C - C - A_n$ with about 2 entanglements in each arm. With this length of the arms the final step in the pom-pom synthesis, the reaction between two asymmetric stars, appeared to be a difficult task. However we used an alternative coupler (12), 2,2-dimethyl-1,3-ditosylene-propane (DMDSP), that did enable a high yield of the desired $A_n - C - C - A_n$ pom-pom polystyrene. Important for the success of the pom-pom synthesis was also the determination of the rate constant for the anionic polymerization in the presence of THF whereby the optimal time for addition of the coupler could be computed.

In the elongational flow rheology we use a filament stretching rheometer (13) modified with a thermostat for polymer melts (14). While elongational rheometers normally require large quantities of the polymer, this instrument operates with samples of about 0.1-0.2g for a single measurement.
4.2 Experimental Section

4.2.1 Materials

Styrene (from Aldrich with purity larger than 99%) was firstly filtered through a column of aluminum oxide (Aldrich) to remove stabilizer and water. The styrene was vacuum distilled twice from dibutylmagnesium immediately before use. Living styryl anion was generated in the solvent, cyclohexane (Fisher Scientific, HPLC grade with purity larger than 99.8%) by adding styrene and sec-buthyllithium (Aldrich, 1.6 M in hexane). Following reflux under argon the cyclohexane was distilled into the reactor. Tetrahydrofurane (THF) (purity larger than 99.5%) from Fisher Scientific was purified by passage through aluminum oxide before it was refluxed under argon in the presence of sodium (Aldrich, 30-35wt % dispersion in paraffin). 4-(chlorodimethylsilyl)styrene (CDMSS) was synthesized as reported in Knauss and Huang (9) from p-chlorostyrene (Aldrich, purity larger than 97%) and dichlorodimethylsilane (Aldrich) in a Grignard reaction and purified by vacuum distillation prior to use.

4.2.2 Coupling- and kinetics experiments

Linear styryl anions were polymerized in a solvent consisting of 97 wt % cyclohexane and 3 wt % THF to a length of about 50kg/mole at 8°C. The stoichiometric amount of the bi-functional coupler, dichlorodimethylsilane, was then titrated into the reaction mixture over approximately 60 minutes at which point the mixture changed color from yellow to colorless, indicating that all anions had reacted.

A similar experiment was performed with an alternative bi-functional coupler, DMDSP. The coupling reaction is shown in Figure 4.2. The coupling reaction with DMDSP was considerably slower than using dichlorodimethylsilane, and the change in color from yellow to colorless took about 24 hours. To compare the two coupling agents both polymers were analyzed by Size Exclusion Chromatography (SEC) as shown in Figure 4.3.

We observed that the styryl anions in the 97% cyclohexane/ 3% THF solvent even at reduced temperature were less stable than in a 100% cyclohexane solution at room temperature and in fact deactivate after about three hours, leaving almost no chemically active 'asymmetric star' molecules.

To estimate the optimal time and temperature for introduction of the DMDSP coupler further, two model experiments were conducted. Anionic polymerization of linear polystyrene were performed according to the protocol given by Ndoni et al. (10), substituting the 100% cyclohexane solvent with a 97% cyclohexane/3% THF solvent. In the two experiments we initiated styrene with sec-butyllithium at 3°C and 8°C, respectively. During the polymerization a series of exactly 1.00 ml sample was transferred from the reaction mixture to vials containing toluene/methanol-mixture,
Figure 4.2. Bi-functional coupling using 2,2-dimethyl-1,3-ditosylene-propane (DMDSP).

Figure 4.3. Comparison of SEC output for model linear polystyrene obtained from coupling styryl anions with DMDSP and dichlorodimethylsilane respectively.
where methanol act as a terminating agent for the polymerization. The conversion was determined by measuring the polymer mass concentration (proportional to the integrated Differential Refractive Index (DRI)-signal) in these samples. The amounts of chemicals used in the two experiments along with the temperatures used are listed in Table 4.1.

<table>
<thead>
<tr>
<th>Temp.</th>
<th>conc. BuLi</th>
<th>vol. styrene</th>
<th>vol. cyclohexane</th>
<th>vol. THF</th>
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<tr>
<td>Exp. 1</td>
<td>3°C</td>
<td>0.92·10^{-3} mole/L</td>
<td>11.21 mL</td>
<td>201.40 mL</td>
</tr>
<tr>
<td>Exp. 2</td>
<td>8°C</td>
<td>1.76·10^{-3} mole/L</td>
<td>27.97 mL</td>
<td>251.00 mL</td>
</tr>
</tbody>
</table>

Table 4.1. Experimental conditions for determination of rate constants for anionic polymerization

### 4.2.3 Synthesis of the Asymmetric star

All polymerizations were performed in a round bottom flask with five necks, thermostated in a water bath. The anionic polymerizations were done in an argon atmosphere under a slight overpressure of 0.2 Bar. The first step was to synthesize the linear polystyrene for the arms of the stars. Styrene was dissolved, 5-10wt %, in cyclohexane, and a stoichiometric amount of sec-butyllithium was added using a gas tight syringe. This mixture was left overnight at room temperature under stirring.

In the second step, the temperature was lowered to 8°C and purified THF was added by cannula to reach 3 wt % THF. The stoichiometric amount of CDMSS was then added using a gas tight syringe, all at once, and the coupling reaction was left for one to two hours.

In the third step more styrene monomer was added to make the long arm in the asymmetric star. To terminate the living anion in the ‘asymmetric star’ formation, degassed methanol was added after a reaction time of about 100 min. This reaction time is estimated from an independent kinetics investigation as explained in section 4.3.2. The dissolved polymer solutions was then precipitated in iso-propanol and washed with HPLC-grade methanol before being filtered. The reaction mixture was fractionated to remove low molecular byproducts. We used toluene/methanol as solvent/non-solvent pair for fractional precipitation of the highest molar mass polystyrene component.

### 4.2.4 Synthesis of the Pom Pom

The synthesis of the Pom-pom followed the same protocol as for the asymmetric star, except instead of terminating with methanol, a fourth step was added after the 100 min. In this step, 2/3 of the stoichiometric amount
of DMDSP was added and the reaction was left overnight. Then more bi-
functional coupler was added slowly until the yellow color from the styryl
anion disappeared. The expected coupling scheme is shown in Figure 4.2.

4.2.5 Chromatography

The molar mass was determined by size exclusion chromatography (SEC)
with THF as the eluent and employing a column set consisting of a 5 \( \mu \)m
guard column and two 300×8 mm\(^2\) columns (PLgel Mixed C and Mixed
D). The system is equipped with a triple detector system, a combined
Viscotek model 200 differential diffractive index (DRI) and differential
viscosity detector plus a Viscotek model LD 600 right angle laser light
scattering detector (RALLS).

The column is calibrated with a number of narrow molar mass distribu-
tion linear polystyrene standards. The application of this calibration
to the branched pom-pom and Asymmetric star may underestimate the
molar mass to some extent, depending on the amount of branching. To
check the molar mass of the branched polymers we use a method that is
independent of the measured retention time, but employs both the DRI
and RALLS signals as follows:

\[
DRI = k_1 \cdot c \frac{\partial n}{\partial c} \quad (4.1)
\]

\[
RALLS = k_2 \cdot c \cdot M \left( \frac{\partial n}{\partial c} \right)^2 \quad (4.2)
\]

Here \( k_1 \) and \( k_2 \) are proportionality constants, \( c \) the mass concentra-
tion and \( \partial n/\partial c \) the refractive index increment. These equations may be used
to obtain,

\[
M = \frac{RALLS \cdot k_1/k_2}{DRI \cdot \partial n/\partial c} \quad (4.3)
\]

This relation is used to compute \( M \) from the two signals and a knowledge
of \( (k_2/k_1)\partial n/\partial c \). Since the relation is independent of branching, the quan-
tity \( (k_1/k_2)\partial n/\partial c \) is determined from the SEC-signals of anarrow MMD
linear polystyrene standard. We evaluate the signals at the peak value
of the RALLS signal to obtain a measurement of the mass average molar
mass, \( M_w \) of the pom-pom molecule independent of the column calibra-
tion (Table 4.2).

4.2.6 Mechanical Spectroscopy

We performed small amplitude oscillatory shear to obtain an accurate
determination of the linear viscoelastic properties (LVE) of the polystyrene
melts. We used a plate-plate geometry on an AR2000 rheometer from TA
4.2. Experimental Section

<table>
<thead>
<tr>
<th></th>
<th>pom-pom</th>
<th>Assymetric Star</th>
<th>Linear</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N_n$</td>
<td>2.5</td>
<td>3.3</td>
<td>-</td>
</tr>
<tr>
<td>$M_w$ (Eq. 4.3)</td>
<td>300 kg/mol</td>
<td>not measured</td>
<td>not measured</td>
</tr>
<tr>
<td>$M_w$ (linear)</td>
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<td>275 kg/mol</td>
<td>390 kg/mol</td>
</tr>
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<td>$M_w/M_n$</td>
<td>1.08</td>
<td>1.08</td>
<td>1.06</td>
</tr>
<tr>
<td>$M_{n,A}$</td>
<td>28 kg/mol</td>
<td>25 kg/mol</td>
<td>-</td>
</tr>
<tr>
<td>$M_{n,A}/M_{n,A}$</td>
<td>1.06</td>
<td>1.05</td>
<td>-</td>
</tr>
<tr>
<td>$M_{n,B}$</td>
<td>140 kg/mol</td>
<td>170 kg/mol</td>
<td>-</td>
</tr>
<tr>
<td>$n_e$</td>
<td>0.10</td>
<td>0.10</td>
<td>0.16</td>
</tr>
<tr>
<td>$n_g$</td>
<td>0.67</td>
<td>0.67</td>
<td>0.7</td>
</tr>
<tr>
<td>$\lambda_c$</td>
<td>0.4 s</td>
<td>0.4 s</td>
<td>0.4 s</td>
</tr>
<tr>
<td>$G_0^N$</td>
<td>480 kPa</td>
<td>540 kPa</td>
<td>257 kPa</td>
</tr>
<tr>
<td>$G_{N,1}^0$</td>
<td>120 kPa</td>
<td>250 kPa</td>
<td>257 kPa</td>
</tr>
<tr>
<td>$G_{N,2}^0$</td>
<td>360 kPa</td>
<td>290 kPa</td>
<td>-</td>
</tr>
<tr>
<td>$\lambda_{max,1}$</td>
<td>11000 s</td>
<td>14000 s</td>
<td>21000 s</td>
</tr>
<tr>
<td>$\lambda_{max,2}$</td>
<td>70 s</td>
<td>56 s</td>
<td>-</td>
</tr>
<tr>
<td>$\lambda_{a,1}$</td>
<td>5760 s</td>
<td>7330 s</td>
<td>11270 s</td>
</tr>
<tr>
<td>$\lambda_{a,2}$</td>
<td>37 s</td>
<td>29 s</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 4.2. Chemical and physical (130°C) properties of model polymers. The third column contain data for a narrow MMD linear polystyrene melt Bach et al. (16). $N_n$ indicates the number of arms (pom-pom and asymmetric star). $M_w$ (linear) is obtained from a column calibrated with linear standards; $M_w$ (Eq. 4.3) is obtained by a technique independent of column calibration (pom-pom only).

Instruments. The measurements were performed at 130°C and 150°C for both melts and at 140°C and 170°C for the pom-pom molecule. The measured data was time temperature shifted to master curves at 130°C using the time-temperature superposition shift factor $a_T$ (15) found from the WLF equation (16):

$$\log_{10}(a_T) = \frac{-c_1^0(T - T_0)}{c_2^0 + (T - T_0)}$$

where the reference temperature $T_0 = 136.5°C$, and the parameters $c_1^0 = 8.86$ and $c_2^0 = 101.6°C$, respectively. $T$ is the sample temperature in °C.

4.2.7 Filament Stretching Rheometer

We used a filament stretching rheometer in which the sample is surrounded by a thermostated environment. This chamber contains a nitrogen gas atmosphere during the extension of the polystyrene samples.

The procedure designed to prepare the cylindrical polystyrene sample, with radius of $R_i = 4.5$mm and height of $L_i = 2.0$mm, and apply these to the cylindrical shaped stainless steel end plates is described in detail in
4.2. Experimental Section

Bach et al. (14). In all of the experiments the sample was pre-stretched (at 150°C) to reduce the transmitted force in the vertical plane during a measurement to ensure the adhesion between end plates and polymer melt.

The pre-stretch was performed at stretch rates considerably below the inverse of the maximum relaxation time. Subsequently the samples were allowed to relax until all measurable residual stresses in the polymer had disappeared. SEC was applied on all samples after an elongational experiment, to check that no degradation of the polystyrene had occurred during the experiment.

In start-up of elongational flow, the sample is at rest for $t < 0$, while a constant elongation rate $\dot{\varepsilon}_0$ is applied for $t > 0$. To monitor the elongation rate, a Keyence LS7500 laser is used to measure the mid diameter of the filament during an experiment. The average strain rate, $\dot{\varepsilon}_0$, is calculated from the measurement of the diameter by fitting an exponential function $R(t) = R_0 \exp(-\dot{\varepsilon}_0 t/2)$ where $R_0$ is the sample radius, at $t = 0$, and $R(t)$ the measured sample radius at time $t$. Generally, the relative deviation between measurements and fit never exceeded 0.6%. The only exception is elongation at the highest elongation rates of $0.1 \text{s}^{-1}$. Here the deviation was within 2.6%. Hencky strain is defined and calculated as $\varepsilon(t) = -2 \ln(R(t)/R_0)$.

The axial force, $F(t)$, is measured using a weight cell mounted on the bottom end plate. This allows the calculation of the transient elongational viscosity $\tilde{\eta}^+(t)$ as

$$\tilde{\eta}^+(t) = \frac{\sigma_{zz} - \sigma_{rr}}{\dot{\varepsilon}_0} = \frac{F(t) - m_f g/2}{\pi R(t)^2 \dot{\varepsilon}_0}$$

(4.5)

where $g$ is the gravitational acceleration, $m_f$ is the weight of the polymer filament (17) and $\sigma_{zz} - \sigma_{rr}$ are the stress difference between the axial and radial component of the stress tensor.

At small strains there are an extra force contribution from the shear components in the deformation field during start-up. For Newtonian fluids this reverse squeeze flow problem can be modeled analytically and the effect of the additional shear may be eliminated by a correction factor (18) to yield for the corrected transient uniaxial elongation viscosity and $\tilde{\eta}^+$:

$$\tilde{\eta}_{\text{corr}}^+ = \tilde{\eta}^+ \cdot \left( 1 + \frac{\exp(-7 \cdot (\epsilon + \epsilon_0)/3)}{3 \Lambda_i^2} \right)^{-1}$$

(4.6)

Here $\Lambda_i = L_i/R_i$ is the aspect ratio computed from the initial sample length $L_i$ and radius $R_i$ prior to pre-stretching while $\epsilon_0 = 2 \ln(R_i/R_0)$ is the Hencky strain of the pre-stretched configuration. This correction is analytically correct for very small strains for all types of fluids. However, the correction is less accurate at increasing strains where the effect of the correction fortunately vanishes (19). In the following we show both uncorrected and corrected data. For the aspect ratios used here, the extra
force contribution is negligible (less than 10 percent) after less than 0.7
strain units of $\varepsilon$.

Surface tension has a negligible effect since the viscoelastic surface elastic-
ticity number (20) $\sigma/(RG(\dot{\varepsilon}_0))$ stays below 0.04 in all experiments. Here $\sigma$
is the coefficient of surface tension, $R$ the radius and $G^* = \sqrt{G'^2 + G''^2}$, the
complex moduli being evaluated at experimental elongation rates. Likewise gravity is found to be negligible as the sag time (13) is much longer
than the duration of the experiments.

4.3 Results

4.3.1 Comparison bi-functional couplers

The results of the two model experiments in which we couple living linear styryl anions with respectively dichlorodimethylsilane and DMDSP are
shown in Figure 4.3. Both DRI signals in the figure have been normalized,
so that the area under the graphs are unity, and the DRI signal for the
DMDSP-coupling has been shifted upwards with one unit to better dis-
tinguish the results. The length of styryl anions just prior to coupling are
57.8 kg/mole in the dichlorodimethylsilane experienmt, and 48.7 kg/mole
in the DMDSP experiment, explaining the slight horizontal shift of the
peaks for the two experiments.

From the magnitude of the high molecular peak compared to the low
molecular peak, we estimate that the coupling with dichlorodimethylsilane
gives a yield of about 40 %, whereas the yield using DMDSP is 60 %. Hence we use DMDSP as coupler for the pom-pom synthesis.

4.3.2 Kinetics experiment

Figure 4.4 shows the styrene monomer concentration at 3°C and 8°C as
a function of the time in a 3 wt % THF solution in cyclohexane. The
measurements confirm that the reaction is first order in the concentration
of styrene monomer $[St](t)$, so the concentration decreases according to
$[St](t)/[St](t = 0) = \exp(-k(T) \cdot t)$. Moreover from the kinetics we expect
the temperature dependent rate constant $k(T) \propto \sqrt{[BuLi]}$ where $[BuLi]$ is
the initial concentration of sec-butyllithium.

The presence of THF increases the reaction rate considerably. The val-
ues of $k(T)$ at 3°C and 8°C is 0.0040 min$^{-1}$ and 0.031 min$^{-1}$ respectively.
At the temperature of 8 °C the reaction rate turned out to be similar
to ordinary anionic polymerization of linear polystyrenes in pure cyclo-
hexane performed at room temperature. Therefore the polymerizations
of the pom-pom and asymmetric star were performed at 8°C. The esti-
mated reaction time for 95% conversion of the styrene at 8°C becomes
$-\ln(0.05)/(0.031 \text{ min}^{-1}) \approx 100$ min. We use this estimate to determine
the optimal time for addition of DMDSP (coupling for pom-pom synthe-
4.3. Results

Figure 4.4. The relative styrene concentration, $\frac{[St](t)}{[St](t=0)}$, at temperatures $T=3^\circ C$ and $T=8^\circ C$, as a function of the time, $t$, in a 3% THF-solution.

4.3.3 Molecular Structure

The relation between the Retention Volume, $RV$, in the SEC measurements and molar mass, $M$, is based on calibration with linear polystyrene. In the range of molar masses investigated the calibration curve is given to sufficient accuracy by the relation $\log M(RV) = a_0 + a_1 RV$, where $a_0$ and $a_1$ are constants ($a_1 < 0$) independent of $M$. Moreover let the molar mass change from $M$ to $M + dM$ when the retention volume changes from $RV$ to $RV + dRV$. Since the DRI signal is proportional to the mass concentration we then have,

$$P(M)dM = k \cdot DRI(RV)dRV \quad (4.7)$$

where $P(M)$ is the molar mass distribution function and $k$ is a constant independent of molar mass. It follows that

$$P(M) = k \frac{DRI(RV)}{M} \frac{dRV}{dM} = \tilde{k} \frac{DRI(RV)}{M^2} \quad (4.8)$$

The above equation also allows the inverse calculation from the distribution function to a DRI signal.

While anionic polymerization under ideal conditions would result in a Poisson distribution of very narrow MMD (21), nonideal conditions will inevitably result in broader MMD than predicted by the Poisson distribution. To model the data we choose a Schultz-Zimm distribution (22; 23; 24) in the form:

$$P_n(M) = \frac{M^\mu \exp(-M/\alpha)}{\Gamma(n\mu)\alpha^{n\mu}} \quad (4.9)$$
Here $\Gamma$ is the Gamma function and $n \geq 1$ denotes the number of arms in the stars, with $n = 1$ corresponding to the initial chains. The molar mass distribution for the initial arms is described by $n = 1$. The distribution in Eq. 4.9 then gives $M_{n,A} = \alpha \mu$ and $M_{w,A}/M_{n,A} - 1 = 1/\mu$. The two free parameters $\alpha$ and $\mu$ are therefore determined from the SEC data for the initial chains (A) by substituting the measured number and weight average molar mass into these relations with the results in Table 4.2. The SEC output for the initial chains appears together with the resulting Schultz-Zimm distribution (recalculated to a DRI signal) in figure 4.5. Note the small peak of about twice the molar mass. This is the result of termination of living anions due to the presence of oxygen in the syringe used for sample takeout.

Based on the assumption of an ideal reaction kinetics in the linking of the chains (A), the distribution function, $P_n$, of the n-armed stars may be computed from successive convolution integrals (11). The distribution in Eq. 4.9 is adjusted so the convolution is performed simply by adding indices,

$$P_{n+m}(M) = \int_0^M P_n(M_1)P_m(M - M_1)dM_1 \quad (4.10)$$

Figure 4.5. SEC chromatograms for the individual steps in the 'pom-pom' synthesis. The Refractive Index (DRI) signals are normalized with the area beneath the curve and subsequently multiplied by the total amount of added mole styrene in the reaction mixture. The dashed (---), dotted/dashed (--·--·--), and solid (——) lines are the reaction bath after the first, second and fourth step as described in sections 2.3 and 2.4. (A) initial chain (arms); (B) dimers; (C) stars; (D) star-block-linear or 'Asymmetric star'; (E) 'pom-pom' molecule. The dotted line is the Schultz-Zimm distribution in Eq. 4.9 with $n = 1$, $M_{n,A} = 28 \text{ kg/mol}$ and $M_{w,A}/M_{n,A} - 1 = 0.06$ recalculated to a DRI signal.
where $P_{n+m}(M)$ is given again by Eq. 4.9. The predicted number and mass average molar mass of the a star is then given by $M_{n, A_n} = n \alpha \mu$ and $M_{w, A_n}/M_{n, A_n} - 1 = 1/(n \mu)$, respectively.

It remains to determine the distribution of arms in the stars. While ideal reaction kinetics may suggest a Poisson distribution we choose to determine the relative amounts from the SEC data. In so doing we make use of the observation (25) that retention volume of polystyrene stars with up to 4 arms is approximated by that of linear polystyrene of the same molar mass. Moreover we use an overall distribution function of

$$P(M) = \sum_{n=1}^{4} p_n \cdot P_n(M)$$

where the $p_n$ are free parameters. Figure 4.6 shows the DRI signal for the intermediate star ($A_n$) molecules (solid line) in the pom-pom synthesis.

The measured DRI signal is shown together with the overall $P(M)$ (dotted line) and individual distribution functions $p_n \cdot P_n(M)$, $n = 1, 2, 3$ and $4$ (dashed lines) for the parameter combination $(p_1, p_2, p_3, p_4) = (0.220, 0.445, 0.276, 0.059)$ obtained from a least squares fitting. However not all stars are chemically active. In particular it may be seen from Figure 4.5 that a fraction of the single arms do not react further. If we assume that all single arms are inactive the number average $N_n = 2.5$. We point

**Figure 4.6.** SEC chromatogram for the intermediate stars ($A_n$). The solid line (—) shows the measured DRI-signal for the intermediate star ($A_n$) molecules in the 'pom-pom' synthesis. This correspond to the dotted/dashed line in figure 4.5. The measured DRI signal is shown together with a least square fitting based of the overall $P(M)$ (dotted line, ···) and individual distribution functions $P_n(M)$, $n = 1, 2, 3$ and $4$ from equation 4.11 (dashed lines, −−−). All molar masses are recalculated to a DRI signal based on calibration with linear polystyrene.
out, that a Poisson distribution
\[ n_i = (N_n - 1)^{i-1} \exp(1 - N_n)/(i - 1)! \] (4.12)
with number average \( N_n = 2.5 \) would give \((n_1, n_2, n_3, n_4, \cdots) =
\((0.223, 0.335, 0.251, 0.126, \cdots)\), which is in fact a somewhat broader distribution than that found by least squares fitting. In the 'asymmetric star' synthesis we obtained a number average arm number of about \( N_n = 3.3 \). In both cases the stoichiometry was adjusted so we expected \( N_n = 3 \).

Figure 4.7 shows the distribution function, \( P(M) \), as a function of the molecular weight, \( M \), calculated using equation 4.8 (based on the calibration with linear polystyrenes), of the final reaction mixture of the pom-pom molecule after five fraction steps. The final value of \( M_w/M_n \) was estimated to be 1.08 for both the pom-pom and asymmetric star. These polydispersities were based on the SEC calibration with linear polystyrenes. The fractioned pom-pom mixture contains almost no fractions of linear arms and stars and only a minor fraction of 'asymmetric stars'. The amount of low molecular byproducts left, mainly 'asymmetric stars' molecules, can be estimated to be about 7 wt % using the distribution function in figure 4.7. The fractionation of the 'asymmetric stars' molecule required only three fractionation steps, to obtain a final value of \( M_w/M_n \) of 1.08.

The \( M_w \) obtained from the calibration curve with linear standards (280 kg/mol) is about 7% smaller than that obtained from Equation 4.3 (300 kg/mol). While this is qualitatively in agreement with expectations for branched polymers, the difference is in fact within experimental error. This may be due to the relatively low degree of branching in the mole-

**Figure 4.7.** Molecular weight distribution after four fractionation steps in the pom-pom reaction batch. The calculated distribution function, \( P(M) \), is shown as a function of the molecular weight, \( M \), using equation 4.8 based on the calibration with linear polystyrenes. The (D) corresponds to \( M_n \) of the starblock-linear or 'Asymmetric star' and (E) the \( M_n \) of the 'pom-pom' molecule.
cules (25). Based on number averages, the molar mass in the cross-bar is obtained by subtracting the arms from the total mass.

### 4.3.4 Linear rheology

We analyze the LVE data with a theoretical approach suggested by Jackson and Winter (26) which handles mono and bidisperse linear polymer melts, using the BSW model (27). Given the separation of time scales into arm dynamics and cross-bar dynamics we propose to model the relaxation modulus by a double mode BSW model. In terms of the continuous relaxation spectrum $H_i(\lambda)$ (15), we then use:

$$G(t) = \sum_{i=1}^{2} G_i(t)$$

$$G_i(t) = \int_{0}^{\infty} \frac{H_i(\lambda)}{\lambda} \exp\left(-\frac{t}{\lambda}\right)d\lambda, \quad i = 1, 2$$

$$H_i(\lambda) = n_e G_{N,i}^{0} \left[ \left( \frac{\lambda}{\lambda_{\text{max},i}} \right)^{n_e} + \left( \frac{\lambda}{\lambda_{c}} \right)^{-n_g} \right] h(1 - \lambda/\lambda_{\text{max},i}), \quad i = 1, 2$$

Here $h(x)$ is the Heaviside step function. In the absence of glassy modes the parameter $n_e$ is the absolute value of the slope of $\log(G'')$ as a function of $\log(\omega)$ for both contributions to $G''$, while $n_g$ is the slope of $\log(G'')$ as a function of $\log(\omega)$ the glassy region for high $\omega$. The parameter $\lambda_c$, called the crossover relaxation time depends on temperature as any other relaxation time while $n_e$ and $n_g$ are independent of temperature. The plateau modulus, obtained as $G_0^0 = G_{N,1}^{0} + G_{N,2}^{0}$ corresponds to $G(0)$ where the glassy part of the spectrum has been excluded. This definition of the plateau modulus is then the elastic modulus in fast deformation of the hypothetical material in which the glassy behavior is neglected. Our expression is in agreement with the integral involving the loss modulus given in (15), the two expressions being related by a Fourier transformation. However, in practice, the methods differ in the way the glassy behavior is filtered out.

The constants $n_g = 0.67$ and $\lambda_c = 0.4s$ (at $T = 130^\circ\text{C}$), as obtained from Jackson and Winter (26). The remaining parameters have been adjusted by least square fitting to $G'$ and $G''$ data (28), see figure 4.8 and 4.9.

The resulting parameters are given in Table 4.2. Also included in the table are the LVE properties of a linear polystyrene of molar mass 390 kg/mol (14).

Based on the parameters in Table 4.2 we define Deborah numbers as

$$De_i = \dot{\epsilon}_0 \cdot \lambda_{a,i} \approx \dot{\epsilon}_0 \cdot \lambda_{\text{max},i} \frac{1 + n_e}{2 + n_e}$$  (4.16)
4.3. Results

Figure 4.8. Linear viscoelastic data for the pom-pom polystyrene melt. The measurements were performed at 130, 140, 150, and 170°C. The data are all time-temperature shifted to 130°C. Open circles (○) are the loss modulus ($G''$) and bullets (●) the storage modulus ($G'$), both as a function of the angular frequency, $\omega$. The solid lines (—) are the least-squares fitting to the BSW model in equation 4.13-4.15. The dashed lines (−−−) and dotted lines (···) are the first and second rubbery mode in the fitted BSW model.

Figure 4.9. Linear viscoelastic data for the 'asymmetric star' polystyrene melt. The measurements were performed at 130 and 150°C. The data are all time-temperature shifted to 130°C. Open circles (○) are the loss modulus ($G''$) and bullets (●) the storage modulus ($G'$), both as a function of the angular frequency, $\omega$. The solid lines (—) are the least-squares fitting to the BSW model in equation 4.13-4.15. The dashed lines (−−−) and dotted lines (···) are the first and second rubbery mode in the fitted BSW model.
where \( \lambda_{a,i} \) is defined as:

\[
\lambda_{a,i} = \frac{\int_{0}^{\infty} G_{i}(s) s ds}{\int_{0}^{\infty} G_{i}(s) ds}
\]  

(4.17)

For the pom-pom polystyrene, \( D_{e1} \) is a Deborah number for cross-bar relaxation, while \( D_{e2} \) is a Deborah number for arm relaxation. The rationale behind the definition in Eq. 4.17 is that for a linear polymer this definition gives a value that is within a few percent of the Doi Edwards reptation time, \( \tau_{d} \).

### 4.3.5 Start-Up of Elongational Flow

Figures 4.10 and 4.11 show the measured corrected transient elongational viscosity \( \bar{\eta}_{corr}^{+}(t) \) for the pom-pom and asymmetric star molecule along with predictions from LVE at 130°C. The elongational viscosity measurements rates were performed at 130°C except for the two lowest elongational rates for the pom-pom molecule. They were measured at 150°C and then subsequent time-temperature superposition shifted to 130°C. The LVE predictions were based on the parameters in table 4.2. In both plots there is agreement between measurements and LVE predictions up to a certain level of strain. It is seen that the transient elongational viscosity

![Figure 4.10](image-url)

**Figure 4.10.** The corrected transient elongation viscosities \( \bar{\eta}_{corr}^{+} \) of the pom-pom melt at 130°C, using equation 4.6, shown as a function of the time, \( t \). The line is the linear viscoelastic prediction of the transient elongational viscosity. \( \bar{\eta}_{corr}^{+} \) was measured at seven different elongational rates \( \dot{\epsilon} \) (shifted to 130°C) of 0.1s\(^{-1}\), 0.03s\(^{-1}\), 0.01s\(^{-1}\), 0.003s\(^{-1}\), 0.001s\(^{-1}\), 0.0003s\(^{-1}\) and 0.00003s\(^{-1}\) as shown in the figure.
4.3. Results

Figure 4.11. The corrected transient elongation viscosities $\bar{\eta}^+_{\text{corr}}$ of the 'asymmetric star' melt at $130^\circ C$, using equation 4.6, shown as a function of the time, $t$. The line is the linear viscoelastic prediction of the transient elongational viscosity. $\bar{\eta}^+_{\text{corr}}$ was measured at three different elongational rates $\dot{\varepsilon}$ of $0.1s^{-1}$, $0.03s^{-1}$ and $0.003s^{-1}$ as shown in the figure.

The elongation viscosity for the pom-pom melt exhibits a maximum as function of time for $\dot{\varepsilon} = 0.1s^{-1}$. Such a maximum has been observed previously in branched polymer melts (low density polyethylene) (29; 7) but to our knowledge not in a well characterized material. We show a second independent experiment in figure 4.12 where we use a linear scale for the stress difference, that also shows the maximum. Generally all data points in figure 4.10 and 4.11 have been reproduced within a 15% scattering. The maximum appears when the arm Deborah number $De_2 > 1$, whereas $\bar{\eta}^+(t)$ is monotone increasing for $De_2 < 1$. While a simple explanation for the maximum has been proposed elsewhere (7) we do not pursue mechanism further here.

As an alternative representation, we plot the same data as uncorrected stress versus strain in figures 4.13 and 4.14. In this representation the duration of the steady-state elongational viscosity is more apparent. The elongational viscosity for the pom-pom molecule reaches a steady state in all series except at the highest elongational rate. Here the elongational viscosity does not reach a steady plateau at high strain, but is going through a significant maximum in the transient elongational viscosity. Apart from this experiment, the plateau values of stress are constant within 10% for (at least) one strain units, except at the fastest ($0.1s^{-1}$) measurement on the 'asymmetric star' molecule where the deviation is 20%. The fluctuations in the steady-state value are correlated with small changes in the
4.3. Results

\[ \varepsilon = 0.1, a \]
\[ \varepsilon = 0.1, b \]

Figure 4.12. The uncorrected stress difference \( \sigma_{zz} - \sigma_{rr} \) (equation 4.5) relative to the elastic modulus \( G_N^0 \), as function of the Hencky strain, \( \varepsilon \), for the pom-pom melt for two experiments at \( \dot{\varepsilon} = 0.1 \text{s}^{-1} \) measured at 130\(^\circ\)C. The stress goes through a reproducible maximum whereafter it decays about 30%. No steady stress is observed.

Figure 4.13. The uncorrected transient stress difference \( \sigma_{zz} - \sigma_{rr} \) relative to the elastic modulus \( G_N^0 \), of the pom-pom melt using equation 4.5, shown as a function of the Hencky strain, \( \varepsilon \). The stress differences were measured at 130\(^\circ\)C and at 150\(^\circ\)C for the two lowest elongational rates. The measurements at 150\(^\circ\)C were time-temperature superposition shifted to 130\(^\circ\)C.
4.4 Discussion

A key issue in the constitutive modelling of polymeric liquids is the factorization of the kernel functions in integral models into a product of time-dependent and strain-dependent factors (30; 31). While such a factorization is assumed in the theory of linear viscoelasticity and almost universally observed for small deformations, the situation is more open for large deformations. By way of examples, the now classical pom-pom model (5) for branched polymer melts is not separable in time and strain, whereas the Molecular Stress Function (MSF) (32) model is. Moreover, whereas the strain and time contribution to stress are straightforward to uncouple in step strain experiments, the two contributions are convoluted in start-up of flow. However in an early investigation on branched polyethylene, Wagner (8) devised a method to de-convolute the contributions. Following that method we consider a generic time-strain separable integral constitutive for which the stress in elongational flow is given by

\[ \sigma(t) = \sigma_{zz} - \sigma_{xx} = \int_{t'=-\infty}^{t} M(t - t') S(\epsilon(t, t')) dt' \]  

(4.18)

Here \( M(s) \) is the time-dependent memory function and \( \sigma_{zz} \) and \( \sigma_{xx} \) are respectively the axial and transverse components of stress tensor. Likewise \( S \) is the difference between the \( zz \) and \( xx \) component of the nonlinear

\[ \varepsilon(\sigma_{zz} - \sigma_{rr})/G_0 \]

Figure 4.14. The uncorrected transient stress difference \( \sigma_{zz} - \sigma_{rr} \) relative to the elastic modulus \( G_0 \), of the ‘asymmetric star’ melt measured at 130°C, using equation 4.5, and shown as a function of the Hencky strain, \( \epsilon \).

instantaneous strain rate.
strain measure which again is a function of the Hencky strain:

\[
\epsilon(t, t') = \begin{cases} 
\dot{\epsilon}_0 t, & t' < 0 \\
\dot{\epsilon}_0 (t - t'), & t' > 0
\end{cases}
\] (4.19)

Hence

\[
\sigma(t) = G(t)S(\dot{\epsilon}_0 t) + \int_{s=0}^{t} M(s)S(\dot{\epsilon}_0 t) ds
\] (4.20)

This equation may be solved for \( S \) to yield

\[
\frac{d}{dt} S(\dot{\epsilon}_0 t) = \frac{1}{G(t)} \frac{d\sigma}{dt}
\] (4.21)

where \( G(t) \) is the relaxation modulus related to the memory function by \( M(s) = -dG(s)/ds \). An integration by parts then yields the Wagner (8) expression for the strain measure:

\[
S(\epsilon) = \frac{\sigma(t)}{G(t)} - \int_0^t \frac{M(t')}{(G(t'))^2} \sigma(t') dt'
\] (4.22)

where \( \epsilon = \dot{\epsilon}_0 t \). In other words, if the assumption of time-strain factorability holds, then the above expression should give a unique function \( S(\epsilon) \) independent of the applied strain rate \( \dot{\epsilon}_0 \).

In the application of this formula we use the corrected stress values from equation 4.6. As mentioned, this correction is analytically correct for very small strains, but less accurate and tending to zero at increasing strains. The result of Eq. 4.22 for \( S(\epsilon) \) is shown in figures 4.15 and 4.16, using the measurements from figure 4.10 and 4.11, respectively.

We also include a figure with the elongational based strain function for a narrow MMD linear polystyrene with a molar mass of 390 kg/mol in figure 4.17. That strain function is calculated using the LVE and elongational measurements from Bach et al. (16). The transient and steady elongational viscosity, measured on linear monodisperse polystyrenes ranging from a molecular weight of 51 kg/mole to 390 kg/mole (16; 33), has been discussed and predicted theoretically recently (34; 35).

We note first of all, that for linear polystyrene and for the asymmetric star polystyrene the result of Eq. 4.22 is not a function of strain only. This means that the data for linear and asymmetric star polymers melts do not observe time-strain separability in the window of strain-rates investigated. Consequently we must conclude, that neither the asymmetric star nor the linear polystyrene melt may be described by a constitutive equation of the generic form in Eq. 4.18. On the other hand for the pom-pom melt, the time-strain separability turns out to be an excellent assumption for almost all investigated rates. Practically all data collapse on a single curve. However at time scales larger than the reptation time the strain function is significantly lower. This agrees with the observation in Archer and Juliani (2004), measuring the non-linear step shear on a \( A_n – C – C – A_n \) pom-pom
Figure 4.15. The strain function, $S(\epsilon)$ defined in equation 4.18, as computed from Eq. 4.22 for pom-pom polystyrene. The figure is based on the (corrected) viscosity measurements in figure 4.10 measured at 130°C. Except for $D_{e1} = 1.7$ the data do show a unique function $S(\epsilon)$. The full line is the prediction of H-polymer theory (Eq. 4.33) with $\phi_a = 0.50$, $\phi_b = 0.50$. The dashed-dotted line is Eq. 29. The lower dashed and dotted lines are Eqs. 4.34 and 4.32 respectively.

Figure 4.16. Attempt to compute the strain function, $S(\epsilon)$, defined in equation 4.18, from equation 4.22 for asymmetric star polystyrene. The data do not show a unique $S(\epsilon)$. The figure is based on the (corrected) viscosity measurements in figure 4.11 measured at 130°C. The dashed-dotted line is Eq. 4.31. The lower dashed and dotted curves are Eqs. 4.34 and 4.32 respectively.
Figure 4.17. Attempt to compute the strain function, $S(\epsilon)$, defined in equation 4.18, from equation 4.22 for narrow molar mass distribution linear polystyrene melt with a molar mass of 390 kg/mol. The data do not show a unique $S(\epsilon)$. The figure is based on the time-dependent elongational viscosity measurements of Bach et al. (16)) (Figure 4.6). The dashed-dotted line is Eq. 4.31. The lower dashed and dotted curves are Eqs. 4.34 and 4.32 respectively.
4.4. Discussion

1,4-polybutadiene melt, as they observe a transition in the strain curve at the reptation time.

Time-strain separability appears to be connected to the existence of at least two branch points, as neither the 'asymmetric star' (figure 15), containing one branch point, nor the linear molecule (figure 16) shows any separability. We therefore expect that the separability occurs due to the stretching of the cross-bar between the two branch points.

It is of interest to compare the experimentally observed strain measure with those obtained from the molecular theories for entangled polymer networks without relaxation. We consider a fast deformation in which a given particle with coordinates $(x'_1, x'_2, x'_3)$ in the stress free reference state (time $t'$) is displaced to coordinates $(x_1, x_2, x_3)$ in the current state (time $t$). Then the components macroscopic displacement gradient tensor is given by

$$E_{ij}(x, t, t') = \frac{\partial x_i}{\partial x'_j}, \quad i = 1, 2, 3 \text{ and } j = 1, 2, 3 \quad (4.23)$$

A tube segment of unit length and orientation given by the unit vector $\mathbf{u}$ in the stress free state is deformed into $\mathbf{E} \cdot \mathbf{u}$ in the current state. The tube model for an entangled network (36) then gives the following expression for the free energy in the deformed state:

$$A(E) = \frac{3}{2} n_c k_B T Z \frac{a^2}{Nb^2} \langle |\mathbf{E} \cdot \mathbf{u}|^2 \rangle$$

$$= \frac{3}{2} n_c k_B T Z \langle |\mathbf{E} \cdot \mathbf{u}|^2 \rangle \quad (4.24)$$

Here $n_c$ is the number density of chains, $k_B$ Boltzmann’s constant, $T$ the absolute temperature, $N$ the number of Kuhn steps in the chain, $b$ is the Kuhn step length, $a$ is the tube diameter, $Z$ the number of entanglements per chain and we have used that $Za^2 = Nb^2$. The angular brackets denote an average over a unit sphere:

$$\langle \ldots \rangle = \frac{1}{4\pi} \int_{|\mathbf{u}|=1} \ldots d\mathbf{u} \quad (4.25)$$

Basically $|\mathbf{E} \cdot \mathbf{u}|$ is the stretch factor for a tube segment. The corresponding stress tensor may be found by computing the time derivative of $A$,

$$\frac{d}{dt} A = \frac{\partial A}{\partial E_{jn}} E_{jn} \frac{\partial E_{jn}}{\partial t} = \frac{\partial A}{\partial E_{jn}} E_{in} (\nabla v)_{ij} \quad (4.26)$$

where $(\nabla v)_{ij}$ the components of the velocity gradient. By comparing this result with the rate of doing work, it follows that apart from an additive isotropic pressure the stress tensor components must be given by:

$$\sigma_{ij} = \frac{\partial A}{\partial E_{jn}} E_{in} \quad (4.28)$$
4.4. Discussion

In particular for the expression in Eq. 4.24

$$\sigma_{ij} = 3n_c k_B T Z \left\langle \frac{E_{iu_n} E_{jm} u_m}{|E \cdot u|} \right\rangle$$

(4.29)

$$\sigma_{ij} = n_c k_B T Z \left( \delta_{ij} + \frac{4}{5} (\alpha_{ij} + \alpha_{ji}) + \ldots \right)$$

(4.30)

In the second line we have specialized to small deformation in which $E_{ij} = \delta_{ij} + \alpha_{ij}$ where $\delta_{ij}$ is Kronecker's delta and $\alpha_{ij}$ is the infinitesimal deformation gradient. Hence the factor in front of the infinitesimal strain tensor must be the elastic modulus of the network, $G = (4/5)n_c k_B T Z = (4/5) \rho RT / M_e$ where $\rho$ is the density and $M_e$ the molar mass between entanglements. With this definition of $G$, Eq. 4.29 may be written in the form:

$$\sigma_{ij}^{NET} / G = \frac{15}{4} \left\langle \frac{|E \cdot u|}{|E \cdot u|} \right\rangle \left\langle \frac{E_{iu_n} E_{jm} u_m}{|E \cdot u|} \right\rangle$$

(4.31)

The decoration $NET$ has been added to indicate an entanglement network without chain retraction. The corresponding strain measure is therefore the expression on the right of Eq. 4.31. Conversely the Doi-Edwards strain measure for an entanglement network with instantaneous chain retraction becomes

$$\sigma_{ij}^{DE} / G = \frac{15}{4} \left\langle \frac{|E \cdot u|}{|E \cdot u|} \right\rangle \left\langle \frac{E_{iu_n} E_{jm} u_m}{|E \cdot u|} \right\rangle$$

(4.32)

We are now in a position to test the assumption that the pom-pom cross-bar is unrelaxed while the arms are fully relaxed. The corresponding stress would then be

$$\sigma_{ij}^H = \phi_b \sigma_{ij}^{NET} + \phi_a \sigma_{ij}^{DE}$$

(4.33)

as predicted by H-polymer theory (1). Here the $\phi_b$ and $\phi_a$ are the volume fractions of cross-bar and arms respectively. The expression is expected to hold until branch point withdrawal occurs.

For completeness we give the corresponding expression for the Doi-Edwards model (37; 38) with the independent alignment approximation included:

$$\sigma_{ij}^{IIA} / G = 5 \left\langle \frac{E_{iu_n} E_{jm} u_m}{|E \cdot u|^2} \right\rangle$$

(4.34)

All of the above strain measures have the property of simplifying to the infinitesimal strain tensor for small deformations.

We have included a number of the above predictions in figures 4.15, 4.16 and 4.17 although the comparison is meaningful for the pom-pom melt only.

For the pom-pom melt, where we do get a unique function $S(\epsilon)$, it appears that the data are well described by the H-polymer model in Eq. 4.33 up to a total Hencky strain of about 2.6. In other words, the data support an interpretation that there is no relaxation in the cross-bar tube while the arms are fully retracted to their equilibrium length in their short tubes of merely two entanglements.
4.5 Conclusion

The critical Hencky strain that we interpret as arm retraction into the cross-bar tube, however is much larger than the value ($\epsilon_c \approx \ln(\sqrt{3}q) \approx 1.5$) predicted from the force balance argument in H-polymer theory with $q = 2.5$. As an alternative we estimate the Hencky strain at which the cross-bar on average becomes fully extended. For this purpose we model the cross-bar as a Kramers chain composed of $n_K$ freely jointed Kuhn steps of length $l_K$. The equilibrium dimension of the chain is then given by $n_K l_K^2 = C_\infty n \cdot l^2$ where $n$ is the number of C-C bonds of length $l$ and $C_\infty = 9.6$ for polystyrene (39). The maximum chain length is $n_K l_K = 0.83 n \cdot l$ where the factor 0.83 is included to take account of the bond angles (40). We then estimate $n_K = (0.83)^2 n / C_\infty \approx 210$. Hence the Hencky strain for maximum extension of the cross-bar becomes $\ln(n_K) \approx 2.7$ which corresponds well with the observed transition to steady stress.

4.5 Conclusion

We have synthesized two well characterized model materials for branched polymer melts. One with a single branch point (an asymmetric star) and one with two branch points (a pom-pom). The use of a novel coupler was instrumental in the synthesis.

A filament stretching apparatus was used to measure transient elongational viscosity of the two model branched polymer melts. The transient elongational viscosity for polymer melts without a branch point or with a single branch point is not separable in time and strain. On the other hand the transient elongational viscosity for the pom-pom melt (two branch points) is separable in time and strain for times less than the reptation time. We therefore link the separability to the stretching of the cross-bar between two branched points. Moreover the resulting strain function is well described by a model in which the deformation of the cross-bar is assumed to follow an entanglement network, while the arms are relaxed as in the H-polymer theory (1). At Hencky strains of about 2.6 a stress saturation occurs that we interpret as withdrawal of the arms into the cross-bar tube. The observed strain associated with arm withdrawal, however, is significantly larger than that predicted from an equilibrium force balance on the branch points while it corresponds well with an estimate of the maximum stretchability of the cross-bar.

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Bibliography


The stress in startup of uniaxial elongational flow until steady state, followed by stress relaxation has been measured for a narrow molar mass distribution polystyrene melt with a molecular weight of 145 kg/mole. The experiments are conducted on a filament stretching rheometer, where a closed loop control of the mid-filament diameter ensures controlled uni-axial extension. The closed loop control algorithm is extended to apply to the stress relaxation part of the experiment. It ensures a constant mid-filament diameter, by controlling the motion of the end-plates. By dividing the measured stress with the theoretically predicted stress from the Doi and Edwards model during relaxation, the stretch factor is found. These stretch factors converge to a unique envelope and eventually converge to unity for long times for all measured elongational rates. It is found that the stretch contribution to the stress relaxes faster than the orientation contribution.  

5.1 Introduction

The progress in understanding of the nonlinear properties of polymer melts in elongational flow seems to be limited by the scarcity of data for well-characterized narrow molar mass distribution (NMMD) polymer melts. Bach et al. (2003a), Luap et al. (2005) and Nielsen et al. (2006a) have presented transient and steady elongational viscosity of NMMD linear polystyrene melts. Nielsen et al. (2006b) have presented data on branched melts in the form of a multiarm $A_n - C - C - A_n$ pom-pom polystyrene and an $A_n - C$ asymmetric star polystyrene where $n$ is the average number of arms.

None of the reptation-based models developed prior to the publishing of

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1This part of the work has been submitted to J. Rheology. (November 2006).
these data were effectively able to predict the extensional flow behaviour of these polymers melts. They include the Pom-Pom model (McLeish and Larson, 1998) for branched polymers and an immense variety of concepts for linear polymers, such as Doi and Edwards (1979), Marrucci and Grizzutti (1988), Pearson et al. (1989), Mead et al. (1998), Fang et al. (2000), Ianniruberto and Marrucci (2001), and Schieber et al. (2003). Recently Marrucci and Ianniruberto (2004) introduced the idea of 'intrachain pressure' and Likhtman et al. (2005) creation and destruction of 'slip links' into the basic reptation picture for linear melts. The 'intrachain pressure' concept agrees well with experimental findings and was adopted by Wagner et al. (2005) within an integral molecular stress function formulation.

Here we will present a new technique for direct measurements of the stress relaxation following steady uni-axial extensional flow in a NMMD linear polystyrene melt, in order to gain further insight into the dynamics of polymer melts.

To our knowledge the only published results for highly nonlinear stress relaxation after extension of polymer melts are those of Sentmanat et al. (2005). They presented the uni-axial elongational startup data, for broadly distributed low density polyethylene, followed by stress relaxation performed on a new extensional rheometer, the Sentmanat Extensional Rheometer (SER). On this kind of rheometer the polymer sample is placed between two cylindrical drums that are rotated in opposite directions, and thereby stretch the sample generating an elongation flow. The drums are stopped, and the stress is measured in the following relaxation. This technique is limited at high strains, by the appearing of a progressive thinning of the sample ending with a ductile necking.

The first controlled filament stretching rheometer (FSR) was developed by Sridhar et al. (1991). Since then the FSR has been used to examine the stress relaxation following uni-axial extension on polymer solutions (Spiegelberg and McKinley, 1996a), Orr and Sridhar (1996), van Nieuwkoop and von Czernicki (1996), Doyle et al. (1998), Bhattacharjee et al. (2003) and Shaqfeh et al. (2004)). In these experiments a cylindrical polymer sample is placed between two cylindrical end-plates that are moved apart. The velocity of the moving end-plates can be arrested and the flow stops followed by a stress relaxation. Applying this method on polymer melts, results in a progressive thinning of the sample.

The use of laser microscopy in the FSR has enabled online strain confirmation, and subsequently closed loop control of the filament diameter by actively controlling the end plate separation. This was initiated by Anna et al. (1999). In our paper we present a new method of measuring the stress relaxation after startup of uniaxial elongational flow, that uses a closed loop control of the end plates in the filament stretching rheometer to ensure true cessation of the flow, corresponding to no change in the mid filament diameter during stress relaxation.
5.2 Material

The polystyrene used in this work has been synthesized by anionic polymerization in an argon atmosphere according to the procedure suggested by Ndoni et al. (1995). The synthesis is performed with cyclohexane as solvent and styrene is initiated by sec-butyl lithium at room temperature. When the styrene has reacted fully we added de-gassed methanol to terminate the reaction. The polystyrene was precipitated in isopropanol, filtered and vacuum dried according to the protocol described in Schausberger et al. (1985) before rheological use.

The molar mass was determined by size exclusion chromatography (SEC) with tetrahydrofuran (THF) as eluent and employing a column of a 5µm guard column 300x8 mm² column (PLgel Mixel C and Mixed D). The system is equipped with a differential refractive index detector. Based on calibrations with narrow molecular weight polystyrene standards the values of \( M_w \) and \( M_w / M_n \) were determined to be respectively 145 kg/mole and 1.03.

5.2.1 Mechanical Spectroscopy and Linear Viscoelasticity

The linear viscoelastic properties were obtained using small amplitude oscillatory shear measurements on an AR2000 rheometer from TA Instruments. We used a 25mm plate-plate geometry and measured the loss and storage moduli, \( G' \) and \( G'' \) at temperatures ranging from 120°C to 150°C. The data were converted to 120°C using time-temperature superpositioning with a shift factor \( a_T = 23 \) between 120°C and 130°C and \( a_T = 44 \) between 130°C and 150°C.

The measurements for the loss modulus \( G'' \) and the storage modulus \( G' \) shown in figure 5.1 as function of the angular frequency, \( \omega \) in the oscillation. The linear viscoelastic (LVE) data are fitted with a continuous BSW relaxation spectrum, given by Baumgaertel et al. (1990).

\[
G(t) = \int_0^\infty \frac{H(\tau)}{\tau} e^{-t/\tau} d\tau, \tag{5.1}
\]

\[
H(\tau) = n_e G^0 \left[ \left( \frac{\tau}{\tau_{\text{max}}} \right)^{n_e} + \left( \frac{\tau_c}{\tau_c} \right)^{-n_\eta} \right] h(1 - \tau / \tau_{\text{max}}) \tag{5.2}
\]

where \( h(x) \) is the Heaviside step function, \( n_e \) is the slope of the \((\log(\omega), \log G')\) curve at intermediate frequencies \( \omega \); \( n_\eta \) is the slope of \((\log(\omega), \log G'')\) for \( \omega \to \infty \), and \( \tau_c \) is the crossover relaxation time.

The experimental results for \( G' \) and \( G'' \) are shown in figure 5.1 together with the best fit (Rasmussen et al. 2000) of the BSW-model. The obtained parameters are given in table 6.1.
5.2. Material

![Graph](image)

**Figure 5.1.** Measured loss, $G''$ (open circles; ◦) and storage moduli, $G'$ (bullets; •) both as a function of the angular frequency, $\omega$. The data are obtained from small angle oscillatory shear rheometry. The experiments have been performed at $120^\circ C$, $130^\circ C$ and $150^\circ C$, and shifted to a reference temperature of $T_0 = 120^\circ C$. The solid lines (——) are the least-squares fitting to the BSW model in equation 6.3.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M_w$ [kg/mol]</td>
<td>145 kg/mole</td>
</tr>
<tr>
<td>$M_w/M_n$</td>
<td>1.03</td>
</tr>
<tr>
<td>$G_N^0$ [kPa]</td>
<td>244 kPa</td>
</tr>
<tr>
<td>$n_e$</td>
<td>0.23</td>
</tr>
<tr>
<td>$n_g$</td>
<td>0.67</td>
</tr>
<tr>
<td>$\tau_{max}$ [s]</td>
<td>14000</td>
</tr>
<tr>
<td>$\tau_c$ [s]</td>
<td>12</td>
</tr>
<tr>
<td>$\tau_a$ [s]</td>
<td>7700</td>
</tr>
</tbody>
</table>

**Table 5.1.** Linear viscoelastic and molecular weight properties of the NMMD polystyrene melts at $120^\circ C$. The $n_e$, $n_g$ and $\tau_c$ constants in the BSW model are obtained from Jackson and Winter (1995) and $G_N^0 = 244 kPa$ from Bach et al. (2003a)

We define a characteristic relaxation time:

$$
\tau_a = \frac{\int_0^\infty G(s)sd\sigma}{\int_0^\infty G(s)ds} \approx \tau_{max} \left(\frac{1 + n_g}{2 + n_e}\right)
$$

(5.3)

which is also given in Table 6.1. We use the relaxation time $\tau_a$ to define a Deborah number for the elongational flow, $De = \dot{\epsilon} \cdot \tau_a$, since it is given that $\tau_a$ is within 5% is equal to the Doi-Edwards relaxation time $\tau_d$. 

5.3 Elongational technique

The elongational experiments were performed using a filament stretching rheometer surrounded by a thermostated environment as described by Bach et al. (2003b). The polystyrene samples were molded into cylindrically formed pellets with height \(L_i\) of 2 mm and diameter of \((2R_i)\) of 9 mm. The pellet is placed in the rheometer between two parallel steel cylinders having the same diameter as the pellet.

All polystyrene samples are pre-stretched to a radius of \(R_0\) (and length \(L_0\)) at approximately 150°C prior to the elongational experiments. The rate at which we pre-stretch correspond to a Deborah number much less than unity. After pre-stretching the temperature inside the rheometer is decreased to 120°C, at which temperature all the elongational experiments are run, except for one. Before starting the experiments the polystyrene samples are relaxed until all residual forces are gone. This is verified by measuring the vertical force, \(F\), on the load cell.

The advantage of the FSR compared to conventional techniques for elongation rheometry is the ability to predict the location of the mid-filament or symmetry plane (the necking) of the sample. Subsequently this critical region can be monitored, and the distance between the end-plates adjusted online obtaining a predefined stretch rate at the neck. Here the closed loop proportional regulator scheme from Bach et al. (2003b) has been extended to control the fixed mid-filament diameter during the stress relaxation.

The elongational stress, the stress difference between the axial and radial component of the stress tensor, is calculated as

\[
\sigma_{zz} - \sigma_{rr} = \frac{F(t) - m_f g / 2}{\pi R(t)^2} \tag{5.4}
\]

where \(R(t)\) is the radius of the filament and \(F(t)\) the axial force, \(g\) the gravitational acceleration and \(m_f\) the weight of the polymer filament (Szabo, 1997). Hencky strain is defined and calculated as \(\epsilon(t) = -2 \ln(R(t)/R_0)\). The surface tension, \(\sigma\), has a negligible effect since the surface tension relative to the measured stress \(R(t)(\sigma_{zz} - \sigma_{rr})/\sigma\) stays below 0.02 in all presented data. Likewise gravitational sagging is found to be negligible as the sag time is much longer than the duration of the experiments, (McKinley and Sridhar, 2002).

In the start-up of elongational flow, the sample is at rest for \(t < 0\), and is applied a constant elongation rate, \(\dot{\epsilon}\), for \(t > 0\). This is followed by no change in the mid filament radius during the stress relaxation starting at a Hencky strain of \(\epsilon_0\). Generally, the relative deviation between measurement and expected radius never exceeded 3 %. The average strain rate, \(\dot{\epsilon}\), is calculated from the measurement of the diameter by fitting an exponential function \(R(t) = R_0 e^{-t/2}\).
The viscosities during startup and stress relaxation are defined as
\[ \tilde{\eta}^+ = \frac{\sigma_{zz} - \sigma_{rr}}{\dot{\epsilon}} \quad \text{and} \quad \tilde{\eta}^- = \frac{\sigma_{zz} - \sigma_{rr}}{\dot{\epsilon}} \] (5.5)
respectively. The viscosity during the stress relaxation is defined using the elongational rate from the preceding flow.

Due to the small aspect ratios used in the stretching experiments, an extra shear contribution adds to the measured elongational force during the startup of the extension flow. This shear contribution is negligible during the stress relaxation. This reverse squeeze flow originates from the no-slip boundary condition at the steel end plates, and is especially important at small Hencky strains. The effect of the additional shear may be eliminated by a correction factor (Spiegelberg and McKinley, 1996b) to yield for the corrected transient uniaxial elongation viscosity:
\[ \tilde{\eta}^+_{corr} = \tilde{\eta}^+ \left( 1 + \frac{e^{-7(\epsilon + \epsilon_{pre})/3}}{3\Lambda_i^2} \right)^{-1} \] (5.6)

Here \( \epsilon_{pre} = 2 \ln(R_i/R_0) \) is the Hencky strain of the pre-stretched configuration while \( \Lambda_i = L_i/R_i \) is the aspect ratio computed from the initial sample prior to pre-stretching, fixed at a value of \( \Lambda_i = 0.444 \) in all experiments. This correction is analytically correct for very small strains for all types of fluids. However, the correction is less accurate at increasing strains where the effect of the correction fortunately vanishes (Kolte et al. 1997). The values of \( \epsilon_{pre} \) in the presented data, are given in table 6.2 together with the initial value of the viscosity correction (eq. 6.1).

<table>
<thead>
<tr>
<th>( \dot{\epsilon} [s^{-1}] )</th>
<th>1.1 \times 10^{-5}</th>
<th>0.0003</th>
<th>0.001</th>
<th>0.003</th>
<th>0.01</th>
<th>0.03</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \epsilon_{pre} )</td>
<td>0.57</td>
<td>0.84</td>
<td>1.27</td>
<td>1.28</td>
<td>1.71</td>
<td>1.97</td>
</tr>
<tr>
<td>( \tilde{\eta}^+_{corr}(0)/\tilde{\eta}^+(0) )</td>
<td>0.6914</td>
<td>0.81</td>
<td>0.92</td>
<td>0.92</td>
<td>0.97</td>
<td>0.98</td>
</tr>
</tbody>
</table>

Table 5.2. at 120°C. Pre stretch values

One of the characteristics of elongational flow in a filament stretching apparatus is, that the extension is not uniform in the vertical direction of the fluid. Because of the no-slip boundary condition in the radial direction at the end-plates, the elongation is highest in the middle of the filament, and smallest close to the end-plates. When stopping the motion of the end-plates the polymer will start to relax, but due to the uneven stretch and therefore stress along the vertical direction, the different fluid elements will relax differently and not necessarily without flow, as illustrated in the following.

We performed a stretching experiment with a rate of \( \dot{\epsilon} = 0.03 s^{-1} \). At a Hencky strain of \( \epsilon_0 = 3 \) the motion of the end-plates \( L(t) \) was stopped. It is seen in figure 5.2 that the filament diameter continues to decrease after 100 seconds, and finally at about 150 seconds the sample ruptures. The
5.3. Elongational technique

Figure 5.2. Evolution of filament diameter, $2R(t)$ and plate separation, $L(t)$, for an elongational rate of $\dot{\varepsilon} = 0.03 \text{s}^{-1}$ at $120^\circ C$, stretched for 100 s and then relaxed. During the relaxation, the diameter is kept constant by the closed loop controller in the experiment in the left figure, and the distance between the end plates is kept constant in the experiment in the figure to the right.

same type of filament thinning for less viscous solutions is seen and utilized in the capillary breakup extensional rheometer (CaBER) to measure the extensional properties of liquids, Rodd et al. (2005). We however wish to avoid this, and therefore the concept of closed loop control of the diameter is used to stop the elongation, simply by moving the end-plates back together, as illustrated in figure 5.2 and 5.3. Figure 5.3 shows quenched samples. We performed stretching and relaxation experiments with the same elongational rate of $\dot{\varepsilon} = 0.03 \text{s}^{-1}$ until a strain of $\varepsilon_0 = 3$. This was followed by a quench of the polystyrene samples at several times after cessation of the flow. Note in figure 5.3, that the diameter at the thinnest place, located at the mid-filament plane, is the same for all seven filaments.

The elongational stress for the controlled and uncontrolled stress relaxation is showed in figure 5.4. In both cases we calculate the true stress based on the measured diameter, $\sigma_{zz} - \sigma_{rr}$. The measured stress from the uncontrolled relaxation experiment is almost constant for about 40 seconds after stopping the end-plates, and finally increases rapidly. The stress in the controlled relaxation experiments decreases immediately after cessation of flow. The importance of having a direct strain verification provided by the laser micrometer is illustrated in Figure 5.4. It includes stress curves calculated with the assumption of a constant mid-filament diameter during the relaxation as $\sigma_{zz} - \sigma_{rr} = (F(t) - m_t g/2)/(\pi R_0^2 e^{\varepsilon_0})$. It is exactly the true stress in a controlled relaxation experiment but not in an uncontrolled relaxation experiment. The difference between the stresses calculated this way, and the real stress for the uncontrolled experiments is significant.

While the feedback control is crucially needed to follow the stress relaxation after large strain states (as seen in figure 5.2, 5.3 and 5.4) it is
Figure 5.3. Quenched polystyrene filaments after cessation of flow. The elongational rate at startup is $\dot{\epsilon} = 0.03 \text{s}^{-1}$, the strain at relaxation is $\epsilon_0 = 3$ and the temperature $120^\circ\text{C}$ in all performed experiments. The samples are relaxed respectively [0s 7s 47s 126s 350s 3000s 7000s] before the quenching. The ruler to the right shows the length in millimeters.

It is of interest to compare the experimental observations with predictions from reptation based constitutive theories, since these have monodisperse polymers as the model molecule.

The first reptation based model was introduced by Doi and Edwards (1979). To explain the disagreements between mainly elongational flow Doi and Edwards (1986) incorporated a stretch factor in this model. Based on a strain measure for an entanglement network with instantaneous chain
5.4. Reptation based constitutive models

\[ \sigma_{zz} - \sigma_{rr} = F(t) \frac{\pi R(t)^2}{\pi R_0 e^{-\varepsilon_0}} \]
\[ \text{No control, } (\sigma_{zz} - \sigma_{rr})_{\text{relax}} = F(t) \frac{\pi R(t)^2}{\pi R_0 e^{-\varepsilon_0}} \]
\[ \text{No control, } \sigma_{zz} - \sigma_{rr} = F(t) \frac{\pi R(t)^2}{\pi R_0 e^{-\varepsilon_0}} \]

\[ \text{Control, } \sigma_{zz} - \sigma_{rr} = F(t) \frac{\pi R(t)^2}{\pi R_0 e^{-\varepsilon_0}} \]

\[ t \text{ [s]} \]
\[ \sigma_{zz} - \sigma_{rr} \text{ [kPa]} \]

Figure 5.4. Measured stress (at 120°C) as a function of time at startup \((\dot{\varepsilon} = 0.03 s^{-1})\) and relaxation \((\varepsilon_0 = 3)\) of elongational flow, as in figure 5.2. The diameter is kept constant by the closed loop controller in one of the experiments (+). In the two other curves is the plate separation, \(L(t)\), stopped at \(t=100\) s. The boxes (■) are the calculation of the true stress \(\sigma_{rr} - \sigma_{zz}\), where the open circles (○) curve are calculated with the assumption of a constant mid-filament diameter during the relaxation as \((F(t) - m f g/2)/\pi R_0^2 e^{-\varepsilon_0})\).

The stress tensor is

\[ \sigma_{D,ij} = \lambda_D(t)^2 \sigma_{DE,ij}(t) \equiv \lambda_D(t)^2 \int_{-\infty}^{t} M(t-t') \frac{15}{4} \left( \left< \frac{E_{im} u_m E_{jm} u_n}{|E \cdot u|} \right> \right) dt' \]

(5.7)

where the stretch of the tube segments, \(\lambda\), is an explicit function of the present time \(t\). The decoration \(D\) has been added to clarify that this is based on the Doi Edwards (DE) strain tensor without the independent alignment approximation. The memory function \(M(t - t')\) is related to the relaxation modulus as \(M(t - t') = dG(t - t')/dt'\). The angular brackets denote an average over a unit sphere \(\langle \ldots \rangle = 1/(4\pi) \int_{|u|=1} \ldots du\) where a tube segment of unit length and orientation given by the unit vector \(u\).

The vector \(u\) in the stress free state is deformed into \(E \cdot u\) in the current state. Here the components of the macroscopic displacement gradient tensor is given by \(E_{ij}(x, t, t') = \frac{\partial x_i}{\partial x_j}, i = 1, 2, 3\) and \(j = 1, 2, 3\). \((x'_1, x'_2, x'_3)\) is the coordinates of a given particle in the stress free reference state (time \(t'\)), displaced to coordinates \((x_1, x_2, x_3)\) in the current state (time \(t\)). The term \(\sigma_{DE}(t)\) is the integral stress term, without the independent alignment approximation and \(\lambda_D\) is the corresponding stretch factor.
5.4. Reptation based constitutive models

Figure 5.5. Figure a shows the measured startup and relaxation viscosity performed at an elongational rate of $\dot{\epsilon} = 0.03s^{-1}$. In one experiment the filament is stretched for 100 s and then relaxed (plusses, +), and in the other experiment the filament is stretched for 6.6 s and then relaxed, (boxes, □). The two dotted lines (- - -) are the linear viscoelastic prediction for startup and relaxation after 6.6 s. Figure b) is the evolution of filament diameter, $2R(t)$ and plate separation, $L(t)$, for the experiment with elongational rate of $\dot{\epsilon} = 0.03s^{-1}$ at $120^\circ C$, stretched for 6.6 s and then relaxed. The diameter is kept constant by the closed loop controller in this experiment.

An alternative representation of the strain tensor, is the use of the independent alignment approximation (I) introduced in the original work by Doi and Edwards (1979):

$$\sigma_{I,ij} = \lambda_I(t)^2 \sigma_{DE,IAA,ij}(t) \equiv \lambda_I(t)^2 \int_{-\infty}^{t} M(t-t')5 \left\langle \frac{E_{in}u_n E_{jm}u_m}{|E \cdot u|^2} \right\rangle dt'$$

(5.8)

These equations needs a stretch evolution equation, and a immense variety of concepts have been published (Doi (1980), Marrucci and Grizzutti (1988), Pearson et al. 1989, McLeish and Larson (1998); Mead et al. 1998 etc.). None of these models have effectively been able to predict the extensional flow behavior of mono-disperse polymer melts, although the stretch factor in the Doi-Edwards model is in principle expected to be capable of doing this.

Wagner et al. (2005) recently adopted the 'intrachain pressure' concept introduced by Marrucci and Ianniruberto (2004) into an integral molecular stress function (MSF) formulation (Wagner and Schaeffer, 1992):

$$\sigma_{ij}^{MSF} = \int_{-\infty}^{t} M(t-t')f(t,t')5 \left\langle \frac{E_{in}u_n E_{jm}u_m}{|E \cdot u|^2} \right\rangle dt'$$

(5.9)
where

$$\frac{\partial}{\partial t} f(t, t') = f(t, t') \left[ \frac{\partial}{\partial t} \langle \ln |\mathbf{E} \cdot \mathbf{u}| \rangle - \frac{1}{\tau_{\text{dia}}} f(t, t') \left( f(t, t')^3 - 1 \right) \right]. \quad (5.10)$$

$\tau_{\text{dia}}$ is called the tube diameter relaxation time. The Doi-Edward's model operates with an averaged orientation factor and stretch; whereas the molecular stress function formulation considers a stretch for all deformed segments. The MSF model from equation (6.5) and (6.6) agrees well with measured startup and steady uniaxial elongational flow of mono disperse polystyrenes with molar masses in the range of 50 kg/mole to 390 kg/mole, Wagner et al. (2005).

### 5.5 Elongational measurements

Figure 5.6 show the measured corrected transient elongational viscosity, $\bar{\eta}_{\text{corr}}(t)$ followed by the viscosity $\bar{\eta}^{-}(t)$ during the stress relaxation for the NMMD polystyrene with predictions from LVE. The elongational viscosity measurements were performed at 120°C except for the lowest elongational rates. That was measured at 150°C and then subsequent time-temperature superposition shifted to 120°C. The LVE predictions were based on the parameters in table 6.1. In both plots there is agreement between measurements and LVE predictions up to a certain level of strain. It is seen that the transient elongational viscosity rises above LVE at intermediate strains.

From Wagner et al., 2005 we have obtained a value of the $\tau_{\text{dia}} = 7000s$ at 120°C for the tube diameter relaxation time, so that $\tau_{\text{dia}}/\tau_a = 0.9$. It appears that the startup and steady elongational data in figure 5.6 are well described by the model as expected.

As an alternative representation, we plot the measured steady state elongational stresses as $(\sigma_{zz} - \sigma_{rr})/G_N^0$ vs. $\dot{\epsilon}_p$. $\tau_p$ is the tube diameter relaxation time, which is defined by Marrucci and Ianniruberto (2004). Marrucci and Ianniruberto report $\tau_p$ at 130°C for PS200 to be $\tau_p = 1000s$, i.e. $\tau_p = 23000s$ at 120°C, and the scaling is $\tau_p \sim M_w^2$. This is used to calculate $\tau_p$ for the other molecular weights. Together with the data for our $M_w = 145$ kg/mole polystyrene we have included the steady state values measured by Bach et al. (2003a) and Nielsen et al. (2006a). It is seen in figure 5.7, that the scaled values for all measurements collapse onto one single curve.

### 5.6 Stress Relaxation

The stretch factor $f(t, t')$ in the MSF model, eq. 9, depends both on the time of creation ($t'$) of segments and the present time ($t$). Consequently, at any time, $t$, it is not possible to assign a single value to the polymer...
Figure 5.6. The measured corrected startup and relaxation viscosity performed at rates of $\dot{\epsilon} = [0.03 \ 0.01 \ 0.003 \ 0.001 \ 0.0003 \ 0.0001] \text{s}^{-1}$ at 120$^\circ$C. In all cases the flow is stopped at an extension of $\epsilon_0 = 3$ and allowed to relax for 4 hours, 14400 seconds. The solid lines (-----) are the Doi Edwards predictions of the transient elongational viscosity, eq 6.4 with $\lambda(t) = 1$. The dashed lines (- - - -) are the MSF model-prediction from equation 6.6 with a tube diameter relaxation time of $\tau_{\text{dia}} = 7000 \text{s}$. stretch. If however one uses the constitutive integral form from equation 5.7 and 6.4, where the stretch factor $\lambda^2$ is placed in front of the integral it is possible to compute a single stretch-factor that applies for every startup and relaxation experiment. It is of interest to compare the experimentally observed stresses during the relaxation with those obtained from the Doi-Edward approach in this alternative representation. Following that method an experimentally expression for the stretch factor can be obtained independent of the stretch evolution equation as:

$$\lambda_D(t)^2 = \frac{\sigma_{zz} - \sigma_{rr}}{\sigma_{zz,DE} - \sigma_{rr,DE}}$$

or

$$\lambda_I(t)^2 = \frac{\sigma_{zz} - \sigma_{rr}}{\sigma_{zz,DE,IAA} - \sigma_{rr,DE,IAA}}$$  \hspace{1cm} (5.11)$$

where $\sigma_{zz} - \sigma_{rr}$ is the experimentally measured stress from equation 5.4. $\sigma_{DE}(t)$ and $\sigma_{DE,IAA}(t)$ are given in equation 5.7 and 6.4, respectively. The experimentally determined stretch factor are shown as a function of the non-dimensional time in figure 5.9 and 5.10, with the strain based on a the strain measure for an entanglement network with instantaneous chain.
retraction ($\lambda_2^2$), and of the independent alignment approximation ($\lambda_{2I}$) respectively. We note first of all that at long times the experimental stretch values, $\lambda_2^2$ and $\lambda_{2D}$, approach unity, but the experimental accuracy seems to decrease somewhat with time. Therefore we cannot experimentally distinguish between the two different strain tensors in the Doi-Edwards model.

Pearson et al. (1989) suggested the stretch factor to follow a first order differential equation in the present time $t$. For completeness we give the analytical solution of the stretch during stress relaxation, by Pearson et al. (1989):

$$\lambda(t) = 1 + (\lambda(\epsilon_0/\dot{\epsilon}) - 1)e^{(\epsilon_0/\dot{\epsilon} - 4)/\tau_s}.$$  

$\tau_s$ is a material dependent constant and $\lambda(\epsilon_0/\dot{\epsilon})$ is the value of the stretch where the flow stops. This model, as many others are not consistent with the experimentally observed stretch.

Adopting the 'intrachain pressure' concept within the Doi-Edwards model we can gain more insight into the stretch mechanism. Marrucci and Laniruberto (2004) derived an equation for the tube diameter, $a$, in an uniaxial elongational flow, based on the 'intrachain pressure' concept. The tube diameter $a$ follows the expression:

Figure 5.7. The steady stress divided with the plateau modulus against the Marrucci-Deborah number $\epsilon_\tau_p$ for PS50K, PS100K, PS145, PS200K and PS390K at 120°C. The value of $\tau_p,PS_{200K}$ is 43.5 s at 120°C. $\eta_0$ is the zero-shear viscosity.
\[
\dot{\epsilon} = 0.03 \text{s}^{-1} + \\
\dot{\epsilon} = 0.01 \text{s}^{-1} \\
\dot{\epsilon} = 0.003 \text{s}^{-1} \\
\dot{\epsilon} = 0.001 \text{s}^{-1} \\
\dot{\epsilon} = 0.0003 \text{s}^{-1}
\]

\[
t - \frac{\epsilon_0}{\dot{\epsilon}} \quad [\text{s}]
\]

**Figure 5.8.** The measured relaxation viscosity at 120\(^{\circ}\)C from figure 5.6 as a function of the time, from the start of the stress relaxation. The solid lines (-----) are the MSF model in equation 6.6 with a tube diameter relaxation time of \(\tau_p = 7000\)s. The dotted lines (- - - -) are the Marrucci model predictions with finite extensibility, using the theoretical stretch factors from figure 10 and calculated from equation 8.

\[
\frac{\delta a}{\delta t} = -\dot{\epsilon} a + \frac{a_0}{\tau_p} \left( c^2 \frac{a_0}{a^3} - 1 \right)
\]  

(5.12)

where \(\tau_p\) is a tube diameter relaxation time, \(a_0\) the initial diameter and \(c\) a nonlinear spring coefficient represented by a relative Pade approximation (Cohen 1991). Marrucci and Ianniruberto (2004) did not include finite extensibility and therefore assumed \(c = 1\). Rolon-Garrido et al. (2005) later replaced the stretch factor with the inverse tube diameter, \(\lambda = a_0/a\) and introduced finite extensibility in equation 5.12, obtaining an expression for the stretch:

\[
\frac{\delta \lambda}{\delta t} = \dot{\epsilon} \lambda - \frac{\lambda^2}{\tau_p} \left( c(\lambda)^2 \lambda^3 - 1 \right).
\]

(5.13)

The relative Pade inverse Langevin function (Ye and Sridhar, 2005) is

\[
c(\lambda) = \frac{(3 - \lambda^2/\lambda_{max}^2)(1 - 1/\lambda_{max}^2)}{(3 - 1/\lambda_{max}^2)(1 - \lambda/\lambda_{max}^2)}
\]

(5.14)
where $\lambda_{\text{max}}$ is the stretch of the fully extended molecule. An estimate of the extension at which the molecule on average becomes fully extended is needed. For this purpose we model the chain as a Kramers chain composed of $n_K$ freely jointed Kuhn steps. Based on this assumption we estimate $n_K \approx 220$ as described in details in Nielsen et al. (2006b). The maximal tube length of a fully extended molecule is then estimated as $\lambda_{\text{max}}^2 \approx \sqrt{n_K} = 15$.

In stress relaxation where $\dot{\varepsilon} = 0$ in the present time we obtain

$$\frac{\delta \lambda}{\delta t} = -\frac{\lambda^2}{\tau_p} (c(\lambda)^2 \lambda^3 - 1). \quad (5.15)$$

Using an tube diameter in the steady elongational ($\frac{\delta \lambda}{\delta t} = 0$) as initial value, the value of the stretch where the flow stops is calculated through the steady state solution equation $c(\lambda(\dot{\varepsilon_0}/\dot{\varepsilon}))^2 \lambda(\dot{\varepsilon_0}/\dot{\varepsilon})^4 - \lambda(\dot{\varepsilon_0}/\dot{\varepsilon}) - \tau_p \dot{\varepsilon} = 0$.

![Figure 5.9](image_url)

**Figure 5.9.** The stretch, $\lambda_D^2$, calculated using the measured relaxation viscosity at 120°C in figure 5.6, as a function of the time, from the start of the stress relaxation. The stretch is based on an entanglement network with instantaneous chain retraction, equation 5.7. The solid lines (---) are the stretch calculated using equation 5.15 with a tube diameter relaxation time of $\tau_p = 14000s$.

It appears that the maximal values of the stretch data are well described by the 'intrachain pressure' model in equation 5.15. By fitting the tube
Figure 5.10. The stretch, $\lambda^2_I$, calculated using the measured relaxation viscosity at 120°C in figure 5.6, as a function of the time, from the start of the stress relaxation. The stretch is found using equation 5.11 is based on the independent alignment approximation, equation 6.4. The solid lines (——) are the stretch calculated using equation 5.15 with a tube diameter relaxation time of $\tau_p = 7000$ s.

By using equation 8 the theoretical values of $\lambda^2_I(t)$ are used to compute the viscosities during relaxation. These predictions are shown in figure 5.8 with dotted lines, and represent the prediction by using finite extensibility in the Marrucci formulation of the stress relaxation, which gives a better prediction to the data than using MSF model, eq(9). Note that the value of $\tau_p$ is fitted from the relaxation data only.
5.7 Conclusion

A filament stretching apparatus was used to measure the uniaxial elongational viscosity followed by stress relaxation using a 145 kg/mole narrow molar mass distribution polystyrene melts. The closed loop control in the filament stretching apparatus was extended to handle the stress relaxation. Here the end plates in the filament stretching rheometer was controlled to ensure the no flow condition, corresponding to no change in the mid filament diameter. The main conclusions of this work are:

- Stress relaxation after the cessation of steady elongational flow may be used to measure the time dependency in the stretch factor under the assumption of separation of the stress tensor into a stretch part and an orientation part.

- The stretch factor curves from several initial conditions converge to a unique envelope corresponding (in our measurements) to the largest stretch curve measured.

- The stretch factors all converge to unity when the time after relaxation time becomes larger than the reptation time $\tau_a$, corresponding to Doi Edwards behaviour at large times. Thus it appears that the stretch contribution to the stress, relaxes faster than the orientation part as indeed expected from the Doi Edwards theory.

- The interchain pressure concept describes the data well, within 50%. Although the convergence of the stretch factor curves is not as clear as in the data.

5.8 Acknowledgment

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Bibliography


Reversed extension flow of monodisperse polystyrene

A filament stretching rheometer (FSR) was used for measuring the startup of uni-axial elongational flow followed by reversed bi-axial flow, both with a constant elongational rate. A narrow molecular mass distribution linear polystyrene with a molecular weight of 145 kg/mole was subjected to the start-up of elongation for three Hencky strain units and subsequently the reversed flow. The integral molecular stress function formulation within the 'intra-chain pressure' concept agrees with the experiments. In the experiments the Hencky strain at which the stress becomes zero (the recovery strain) in the reversed flow has been identified. The recovery strain is found to increase with elongational rate, and has a maximum value of approximately 1.45. The Doi Edwards model using any stretch evolution equation is not able to predict the correct level of the recovery strain.  

6.1 Introduction

Well defined narrow molar mass distribution (NMMD) polymer melts have proven valuable as model materials for gaining insight into the complex physics of polymer melts. The understanding of nonlinear flow properties of polymer melts requires reliable experimental stress measurements on well-characterized NMMD polymers. Recent experimental efforts include the characterization of linear and multiarm polymers in uni-axial extension (Bach et al. (2003a), Luap et al. (2005) and Nielsen et al. (2006a),(2006b),(2007)) and shear flow (Pearson et al. (1989), Archer and Juliani (2004)). The latter has been challenged by recent measurements in rate controlled shear fields on entangled NMMD polymer solutions (Tapadia and Wang (2004)), implying that a homogeneous flow field in NMMD melts may not necessarily develop in a shear rheometer.

Theoretically, reptation based constitutive theories do have the monodisperse polymer as the model molecule. None of the reptation-based models developed prior to the publishing of the uni-axial extension data have been

\footnote{This part of the work has been submitted to Physical Review E (January 2007).}
able to predict the measured extensional flow behaviour of these polymers melts effectively. These include the Pom-Pom model (McLeish and Larson, 1998) for branched polymers and an immense variety of concepts for linear polymers, such as Doi and Edwards (1979), Marrucci and Grizzutti (1988), Pearson et al. (1989), Mead et al. (1998), Fang et al. (2000), Ianniruberto and Marrucci (2001), and Schieber et al. (2003).

Recently, Marrucci and Ianniruberto (2004) introduced the idea of 'intrachain pressure' and Likhtman et al. (2005) proposed creation and destruction of 'slip links' in the basic reptation picture for linear melts. The 'intrachain pressure' concept agrees qualitatively with experimental findings and was adopted by Wagner et al. (2005) and Rolon-Garrido et al. (2006) within an integral molecular stress function formulation and by Nielsen et al. (2007) within a stretch evolution equation.

It is commonly accepted that stresses in polymers are of etropic nature. Reversing flow gives insight into the etropic state of the melt as it mount the work performed by the polymer. Reversed extension flow is an especially challenging task for any constitutive approach. In the early developments of constitutive theories Wagner (1978) demonstrated that it is possible to separate time and strain effects in start-up of elongational flow of a (broadly distributed) low density polyethylene (LDPE) melt. The separability seems to be a general phenomena in the start-up phase of elongational flow of long chain branched polymer melts (Nielsen et al. (2006a)), but it fails in the elastic recovery of the LDPE melt flow. The elastic recovery is the maximal recoverable Hencky strain in the reversed bi-axial flow following uni-axial elongation flow, measured without externally applied forces on the sample. Experimental techniques to measure well defined reversed elongational flow do to our knowledge not exist.

To gain insight into the flow physics of polymer melts, we will present a new method for direct measurements of the bi-axial reversed flow following (steady) uni-axial extensional flow, both presenting a constant elongational rate. For simplicity we apply the method on a NMMD linear polystyrene polymer as a model material, as the chemical structure of the material is exactly known, eliminating effects as polydispersity or branching.

### 6.2 Elongational technique

The first controlled filament stretching rheometer (FSR) was developed by Sridhar et al. (1991): A cylindrical shaped liquid sample is placed in between two parallel steel cylinders having the same diameter as the pellet. Separation of the plates will extend the sample. The advantage of the FSR compared to conventional techniques for elongation rheometry is the ability to predict the location of the necking (the mid-filament plane) of the extended sample. As in most polymer melts, the sagging effect of the gravitation is negligible (Nielsen et al. (2007)). Therefore the sample
stays symmetric across the mid-filament plane. Subsequently this critical region can be monitored using laser microscopy, and the distance between the end-plates adjusted, thus obtaining a predefined stretch rate at the neck.

The use of laser microscopy in the FSR has enabled online strain confirmation, and subsequently a closed loop control of the mid-filament diameter controlling the end plate separation. This was initiated by Anna et al. (1999). Our experiments are performed using currently the only existing filament stretching rheometer surrounded by a thermostated environment described by Bach et al. (2003b). This rheometer allows measurements on polymer melts at high temperatures. It maintains a constant extension rate, measuring the filament diameter at the thinnest place on the necking of the sample with a laser micrometer. Through a feedback mechanism, the separation of the endplates is controlled and the elongational rate is thereby kept constant. Modification of the closed loop mechanism has enabled us to measure the transient uniaxial stretching followed by biaxial squeezing. For simplicity both the uni-axial and the bi-axial elongational rates are kept constant through an experiments. The elongation experiments were performed using the protocol described in details in Bach et al. (2003a) and Nielsen et al. (2006b). The polymer is pressed into cylindrically formed pellets with diameter $D_i = 9$ mm, and length of $L_i = 2$ mm. The pellet is placed inside the FSR between the two cylindrically shaped endplates with diameters of 9 mm. To concentrate the stress at the centre of the sample, the pellets are pre-stretched to a mid-filament diameter of $D_0$ and annealed, until all detectably forces in the polymer are gone, at elevated temperatures of about 150°C. The extension rate during the pre stretch prior to the elongational experiments is considerably lower than the inverse of the largest relaxation time in the polymer. The temperature is lowered and thermostatted to 120°C or 130°C, the temperatures where all presented experiments are performed. All the measurements are subsequent time-temperature super-positioned to 120°C as the reference temperature.

During the extension of the polystyrene sample a weight cell measures the elongational force, $F(t)$, and a laser micrometer measures the filament diameter, $D(t)$, at the mid-filament plane. In elongation the relevant strain is the Hencky strain ($\epsilon$), which is defined as $\epsilon(t) = -2 \ln(D(t)/D_0)$ for filament stretching of cylindrically shaped samples. Initially, the sample is at rest for $t < 0$. In this paper we intend to perform transient uniaxial stretching up to a Hencky strain of $\epsilon_0$, followed by transient biaxial squeeze. We use a fixed value of $\epsilon_0 = 3$ in all the presented experiments. At this Hencky strain value, the elongational stress has reached a steady state. The elongational rate is $\dot{\epsilon} = d\epsilon/dt$. For uniaxial stretching we define the rate $\dot{\epsilon}^+ = \dot{\epsilon}$ and in biaxial squeeze the rate is defined as $\dot{\epsilon}^- = -\dot{\epsilon}$. Both $\dot{\epsilon}^+$ and $\dot{\epsilon}^-$ will stay positive and constant during extension. Figure 6.1 shows the evolution of the filament diameter and plate separation.
in an elongational experiment with an imposed uni-axial startup rate of \( \dot{\epsilon}^+ = 0.01 \text{s}^{-1} \) followed by a bi-axial squeeze after 300 s with a squeeze rate of \( \dot{\epsilon}^- = 0.01 \text{s}^{-1} \). Generally, the relative deviation between measured and expected diameter never exceeded 3\% in all experiments.

Due to the small aspect ratios used in our experiments, an extra shear contribution adds to the measured elongational force during the startup of the extension flow. This shear contribution is negligible during the reversed flow. The effect of the additional shear may be eliminated by a correction factor (Spiegelberg and McKinley, 1996b) to yield for the corrected transient uniaxial elongational stress. From the sampling of the force \( F(t) \) and diameter \( D(t) \) the elongational stress is calculated to be

\[
\sigma_{zz} - \sigma_{rr} = \frac{4F(t)}{\pi D(t)^2} \left( 1 + \frac{e^{-7(\epsilon + \epsilon_{pre})/3}}{3\Lambda_i^2} \right)^{-1} \quad (6.1)
\]

where \( \epsilon_{pre} = 2 \ln(D_i/D_0) \) is the Hencky strain of the pre-stretch while \( \Lambda_i = L_i/(D_i/2) \) is the aspect ratio of the initial sample prior to pre-stretching. It is fixed at a value of \( \Lambda_i = 0.444 \) in all experiments. The last term in the equation, inside the brackets, is the correction for the shear contribution at the end plates, and is negligible (less than 5\%) in the experiments after more than 0.6 Hencky strain units. This correction for the shear contribution is analytically correct for very small strains for all types of fluids. However, the correction is less accurate at increasing strains, where the effect of the correction fortunately vanishes (Kolte et al. 1997).

The elongational stress \( \sigma_{zz} - \sigma_{rr} \) calculated using equation (6.1), with an imposed rate of \( \dot{\epsilon}^- = \dot{\epsilon}^+ = 0.01 \text{s}^{-1} \) is shown in figure 6.1. An important quantity in a reversing flow experiment is the Hencky strain at which the stress in the filament changes sign from positive to negative stress, here referred to as the "strain recovery", \( \epsilon_R \). The magnitude of the strain recovery is expected to depend on the rate of the startup and reversing flow, and we will map \( \epsilon_R \) versus \( \dot{\epsilon} \) and compare with the theoretical prediction. \( t_R \) is the time at which the stress changes sign from positive to negative value. After this time the sample will bend due to the compression force and a reliable stress cannot be measured. We define the strain recovery as \( \epsilon_R = \epsilon_0 - \epsilon(t_R) \) where \( \sigma_{zz} - \sigma_{rr} = 0 \); which is the needed bi-axial strain to reach zero extensional stress.

### 6.3 Material Properties

The NMMD polystyrene used in this work is the same batch as used by Nielsen et al. (2007). The polydispersity of the material is \( M_w/M_n = 1.03 \) with a weight based average molecular weight \( M_w \) of 145 kg/mole. The linear viscoelastic properties were obtained using small amplitude oscillatory shear measurements and fitted with a continuous BSW relaxation
Figure 6.1. The left figure shows the measured mid filament diameter in an elongational startup and reversed experiment, stretched to a Hencky strain of $\varepsilon_0 = 3$, plotted against time. The imposed elongational rates are similar, $\dot{\varepsilon}^+ = \dot{\varepsilon}^- = 0.01 \text{s}^{-1}$ at $120^\circ \text{C}$. The right figure is the measured elongational stress in the same experiment. The arrow emphasizes the recovery time, $t_R$ where the stress changes sign from positive to negative.

Table 6.1. Linear viscoelastic and molecular weights of the NMMD polystyrene melts at $120^\circ \text{C}$ form Nielsen et al. (2007). $M_n$ and $M_w$ are weight and mole based average molar masses respectively. The $n_e$, $n_g$ and $\tau_c$ constants in the BSW model are obtained from Jackson and Winter (1995) and $G_N^0 = 244 kPa$ from Bach et al. (2003a)

\begin{tabular}{l|c}
\hline
$M_w [\text{kg/mol}]$ & 145 kg/mole \\
$M_w/M_n$ & 1.03 \\
$G_N^0$ & 244 kPa \\
n_e & 0.23 \\
n_g & 0.67 \\
$\tau_{\text{max}}$ & 14000 s \\
$\tau_c$ & 12 s \\
$\tau_{\text{dia}}$ & 7000 s \\
$\lambda_{\text{max}}^2$ & 15 \\
\hline
\end{tabular}

\section*{Material Properties}

\begin{align}
G(t) &= \int_0^\infty \frac{H(\tau)}{\tau} e^{(-t/\tau)} d\tau, \\
H(\tau) &= n_e G_N^0 \left[ \left( \frac{\tau}{\tau_{\text{max}}} \right)^{n_e} + \left( \frac{\tau}{\tau_c} \right)^{-n_g} \right] h(1 - \tau/\tau_{\text{max}})
\end{align}

where $h(x)$ is the Heaviside step function, $n_e$ is the slope of the $(\log(\omega), \log G')$ curve at intermediate frequencies $\omega$, $n_g$ is the slope of $(\log(\omega), \log G'')$ for
6.4. Reptation based constitutive models

It is of interest to compare the experimental observations with predictions from reptation based constitutive theories, since these have the monodisperse polymer as the model molecule.

The first reptation based model was introduced by Doi and Edwards (1979). To explain the disagreements between mainly elongational flow Doi and Edwards (1986) incorporated a stretch factor in the model. This was initiated by Marrucci and Cindio (1980). Based on the original strain measure, which is the independent alignment approximation (Doi and Edwards (1979)), the extensional stress is

\[
\sigma_{zz} - \sigma_{xx} = \lambda(t)^2 \int_{-\infty}^{t} M(t-t') 5 \left( \frac{E_{in} u_n E_{jm} u_m}{|\mathbf{E} \cdot \mathbf{u}|^2} \right)_{zz} - \left( \frac{E_{in} u_n E_{jm} u_m}{|\mathbf{E} \cdot \mathbf{u}|^2} \right)_{xx} dt'
\]

(6.4)

where the stretch of the tube segments, \( \lambda \), is an explicit function of the present time \( t \). The memory function \( M(t-t') \) is related to the relaxation modulus as \( M(t-t') = dG(t-t')/dt' \). The angular brackets \( \langle ... \rangle = 1/(4\pi) \int_{|u|=1} ... d\mathbf{u} \) (Wagner et al. (2005) and Rolon-Garrido et al. (2006) adopted the 'intrachain pressure' concept into an integral molecular stress function (MSF) formulation (Wagner and Schaeffer, 1992):

\[
\sigma_{zz} - \sigma_{xx} = \int_{-\infty}^{t} M(t-t') c(f)^2 5 \left( \frac{E_{in} u_n E_{jm} u_m}{|\mathbf{E} \cdot \mathbf{u}|^2} \right)_{zz} - \left( \frac{E_{in} u_n E_{jm} u_m}{|\mathbf{E} \cdot \mathbf{u}|^2} \right)_{xx} dt'
\]

(6.5)
where
\[
\frac{\partial}{\partial t} f(t, t') = f(t, t') \left[ \frac{\partial}{\partial t} \langle \ln |E\cdot u| \rangle - \frac{1}{\tau_{\text{dia}}} f(t, t') \left( c(f(t, t'))^2 f(t, t')^3 - 1 \right) \right].
\] (6.6)

with initial condition \( f(t', t') = 1 \). \( \tau_{\text{dia}} \) is referred to as the tube diameter relaxation time. The Doi-Edwards model operates with an averaged orientation factor and stretch, whereas the molecular stress function formulation considers a stretch for all deformed segments. In this formulation, the stretch factor is placed inside the integral, and it is not possible to construct one average, unique stretch function against time \( t \). Rather we have a new evolving stretch function for each segment developed at time \( t' \) and running in \( t \).

The MSF model from equation (6.5) and (6.6) agrees qualitatively with the measured startup and steady uniaxial elongational flow and subsequent stress relaxation of monodisperse polystyrenes with molar masses in the range of 50 kg/mole to 390 kg/mole. Here a nonlinear spring coefficient \((c)\) is represented by a relative Pade approximation (Cohen 1991):

\[
c(\lambda) = \frac{(3 - \lambda^2/\lambda_{\text{max}}^2)(1 - 1/\lambda_{\text{max}}^2)}{(3 - 1/\lambda_{\text{max}}^2)(1 - \lambda^2/\lambda_{\text{max}}^2)} \] (6.7)

where \( \lambda_{\text{max}}^2 \) is the stretch of the fully extended molecule, as estimated by Nielsen et al. (2007) to \( \lambda_{\text{max}}^2 \approx 15 \) for a 145 kg/mole monodisperse polystyrene. Marrucci and Ianniruberto (2004) and Wagner et al. (2005) did not consider finite extensibility and therefore assumed \( c = 1 \).

### 6.5 Results and Discussion

In figure 6.2 we show the measured recovery strain as a function of the elongational rate. Please notice that there are two measurements at the two highest extensional rates. The extensional rate of both the startup and reversed flow in each experiment are identical; \( \dot{\varepsilon}^+ = \dot{\varepsilon}^- \). We see that \( \varepsilon_R \) increase with \( \dot{\varepsilon} \) and reaches a maximum value of \( \varepsilon_R = 1.45 \) at \( \dot{\varepsilon} = 0.01 \text{s}^{-1} \). The recovery strain reaches a maximum as the character of the melt changes and becomes less elastic as it gradually moves from the rubbery region into the glassy region.

Figure 6.2 shows the prediction for the strain recovery \( \varepsilon_R \) found using the MSF model equation 6.5 with and without \((c = 1)\) the finite extensibility assumption. We have also included the prediction for the Doi and Edwards model equation 6.4. As given with the stretch factor in the Doi and Edwards model \( \lambda(t)^2 \geq 1 \), the solution to \( \sigma_{zz} - \sigma_{rr} = 0 \) for any given startup and reversing flow will be independent of the stretch evolution equation. The Doi and Edwards model is not able to predict the recovery
strain for any stretch evolution function as seen in figure 6.2, since the recovery strain, $\epsilon_R$ is independent of the stretch evolution function. As a more fundamental problem with the Doi and Edwards model, which is based on an average stretch factor (equation 6.4), the recovery strain ($\epsilon_R$) increases with increasing $\epsilon_0$ value for $\epsilon_0 \geq 3$, where steady state have been reached. That is, the model does not capture the concept of steady state in reversing flows. The MSF model agrees qualitatively both with and without the finite extensibility assumption, although the inclusion of a maximal extensibility shows a maximum in the recoverable strain which is in qualitative agreement with the measurements. As experimentally observed by Bach et al. (2003a), the maximal extensibility is responsible for the transition to steady elongational viscosity at high extension rates.

![Figure 6.2](image)

**Figure 6.2.** Recovery strain value, $\epsilon_R$, plotted against elongational rate (at $120^\circ$C). $\dot{\epsilon}^+ = \dot{\epsilon}^- = |\dot{\epsilon}|$ in all experiments. The dotted line (· · · · · ·) is the Doi and Edwards model equation 6.4, with any stretch evolution equation. The dashed line (− − − − − −) is the MSF model equation 6.5 without finite extensibility ($c = 1$). The solid line (——) is the MSF model equation 6.5 with finite extensibility as defined in equation 6.6.

Figure 6.3 shows the results of the transient startup and reversing flows where both the startup- and reversing rates in each experiment are identical, $(\dot{\epsilon}^+ = \dot{\epsilon}^-)$. Moreover, figure 6.4 shows the results of transient startup and reversing flow where $\dot{\epsilon}^+ = 0.03s^{-1}$ in all five experiments, whereas the reversing rate is $\dot{\epsilon}^- = [0.03, 0.01, 0.003, 0.001, 0.0003]s^{-1}$ respectively. A plot of the measured recovery strains is shown in the bottom left corner, $\epsilon_R$ for each of the reversing rates, $\dot{\epsilon}^-$. We see that $\epsilon_R$ decreases with $\dot{\epsilon}^-$ which is also intuitively expected.
Figure 6.3. Startup and reversing elongational experiments with $\dot{\varepsilon}^+ = \dot{\varepsilon}^- = |\dot{\varepsilon}|$. The measurements are done for the following elongational rates: $\dot{\varepsilon}^+ = 0.00003 s^{-1}$, 0.0001 $s^{-1}$, 0.0003 $s^{-1}$, 0.001 $s^{-1}$, 0.003 $s^{-1}$, 0.01 $s^{-1}$ and 0.03 $s^{-1}$. The lines (——) are the MSF model corresponding to the experiments; equation 6.5 with finite extensibility is defined in equation 6.6. The dashed line (---) is the MSF model at an elongational rate of $\dot{\varepsilon}^+ = 0.03 s^{-1}$.

Table 6.2. Recovery strain $\epsilon_R$ versus extension rate experiments at 120°C. The startup and reversing elongational rate $\dot{\varepsilon}^+ = \dot{\varepsilon}^- = |\dot{\varepsilon}|$ are identical.

<table>
<thead>
<tr>
<th>$\dot{\varepsilon} [s^{-1}]$</th>
<th>0.0001</th>
<th>0.0003</th>
<th>0.001</th>
<th>0.003</th>
<th>0.01</th>
<th>0.03</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\epsilon_R$</td>
<td>0.512</td>
<td>0.7965</td>
<td>1.07</td>
<td>1.29</td>
<td>1.45</td>
<td>1.32</td>
</tr>
</tbody>
</table>

Figure 6.3 and 6.4 shows the measured extensional stress as a function for the Hencky strain, including the MSF model (equation 6.5) with finite extensibility. Analyzing the observed stress in the reversed flow with the theoretical MSF approach, the measurements are in most cases somewhat larger than that predicted from the MSF model, in contradiction to the Doi Edwards model.

The MSF model is based on the 'interchange pressure' by Marrucci and
6.5. Results and Discussion

Figure 6.4. Startup and reversing elongational experiments with a fixed startup \(\dot{\varepsilon}^+ = 0.03 \text{s}^{-1}\). The reversed rate \(\dot{\varepsilon}^- = 0.0003 \text{s}^{-1}, 0.001 \text{s}^{-1}, 0.003 \text{s}^{-1}, 0.01 \text{s}^{-1}\) and 0.03 \(\text{s}^{-1}\). The lines (-----) are the MSF model corresponding to the experiments; equation 6.5 with finite extensibility as defined in equation 6.6. The dashed line (---) is the MSF model at an elongational rate of \(\dot{\varepsilon}^+ = \dot{\varepsilon}^- = 0.03 \text{s}^{-1}\).

Ianniruberto (2004). This model predicts the experimentally found asymptotic steady elongational stress behavior in monodisperse polystyrenes (Bach et al. (2003a)) at high rates by incorporation of chain squeeze: \(\sigma_{zz} - \sigma_{rr} \sim M_w \cdot \dot{\varepsilon}^{0.5}\). Essentially this will give rise to anisotropic friction. Bach et al. (2003a) observed experimentally that the steady elongational stress scaled about as \(\sigma_{zz} - \sigma_{rr} \sim M_w \cdot \dot{\varepsilon}^{0.5}\), based on two NMMD polystyrenes of 200\(\text{kg/mole}\) and 390\(\text{kg/mole}\). But, the observed agreement is qualitative. Nielsen et al. (2006b) concluded that the exponent in the elongational rate dependency was \(0.42 \pm 0.03\) within a 95% confidence interval and not 0.5. This was based on a more close inspection of the data from Bach et al. (2003a) as well as on steady elongational stress measurements on two NMMD polystyrenes of 50\(\text{kg/mole}\) and 100\(\text{kg/mole}\).

Therefore the 145\(\text{kg/mole}\) polystyrene material is more extensional strain hardening at low extensional rates and less at high extensional rates than
predicted by the MSF model. In the startup of the extension, the maximal deviations from the experimental values are about 30\%, where the measurements scatters within 15\% as seen in figure 6.4.

6.6 Conclusion

A filament stretching rheometer (FSR) was modified to measure reversed elongational flow. A narrow molecular mass distribution polystyrene with a molecular weight of $145\text{kg/mole}$ has been subjected to the start-up of uniaxial elongation for three Hencky strain units and subsequently to the reversed bi-axial flow at 120°C. Both flows are carried out with a constant elongational rate.

The integral molecular stress function formulation within the ‘intrachain pressure’ concept agrees qualitatively with the experiments. Although, discrepancy between a formulation with and without a maximal extensibility is not possible, based on the measurements. A Doi Edwards model using any stretch evolution formulations is not able to predict the correct level of the recovery strain, $\epsilon_R$.

6.7 Acknowledgment

The authors gratefully acknowledge financial support to the Graduate School of Polymer Science from the Danish Research Training Council and the Danish Technical Research Council to the Danish Polymer Centre.
Bibliography


Observation of chain stretch transition in a highly entangled polyisoprene melt using transient extensional rheometry

We measure the viscoelastic properties of a highly entangled narrow molecular weight polyisoprene melt with approximately 280 entanglements in steady and transient shear and elongational flows. The storage and loss moduli are found to be described well by the Milner and McLeish model. The relaxation modulus $G(t, \gamma)$ is measured using stress relaxation after a sudden shearing displacement and we experimentally determine the Rouse time, $\tau_R$, by observing strain-time separability $G(t) = G(t, \gamma)/h(\gamma)$ for $t > \tau_R$. The transient elongational properties have been measured using three distinct instruments; the SER universal testing platform from Xpansion Instruments, its counterpart the EVF from TA instruments, and a Filament Stretching Rheometer. The kinematics obtained in each device are sensitive to the aspect ratio of the sample and care must be taken to achieve homogeneous deformation conditions. We find that the initial growth in the tensile stress follows the prediction given by the Doi and Edwards reptational model, at Deborah numbers based on Rouse time, $De_R$ less than unity. The transient uniaxial elongational viscosity follows the linear viscoelastic envelope with very little strain hardening. Consequently the elastic sample ruptures at moderate Hencky strains well before steady elongation is reached. Measurements show that it fails close to the maximum in engineering stress, in agreement with the Consideré criterion. At $De_R > 1$ sample rupture is not encountered until much larger strains, and the tensile stress differences rise above the Doi Edwards prediction, exhibiting strain hardening. The transient elongational viscosity exceeds the linear viscoelastic envelope at Hencky strains greater than unity. We interpret this to be a clear signature of the onset of chain stretching in this very highly entangled polymer for elongational deformation rates faster than the inverse Rouse time. 

This part has been presented in an oral talk by Jens Kromann Nielsen at the 78th Annual Meeting of Society of Rheology in Portland, Maine (2006).
7.1 Introduction

Non-linear rheological phenomena are encountered in polymer processing with very large deformations gradients, and arise in both shear- and extension dominated flows. Reptational tube models identify two characteristic time constants that characterize whether a flow is strongly non-linear or moderately non-linear. The longest time constant is the time it takes for a chain to diffuse through the length of its confining tube, the reptation time $\tau_d$. The small time constant, the Rouse time $\tau_R$, is the time it takes for the stretched chain to reach its equilibrium length in surroundings with no deformation gradients. The model by Marrucci and Grizzutì (1988) incorporates the concept of chain stretch into the tube model developed by Doi and Edwards, and explains strain hardening in elongational flow faster than $1/\tau_R$, and chain orientation for flows in the intermediate region from $1/\tau_d$ to $1/\tau_R$. For elongational flow we define the dimensionless Rouse Deborah number as: $De_R \equiv \dot{\varepsilon} \tau_R$ and the reptation time Deborah number as: $De_d \equiv \dot{\varepsilon} \tau_d \dot{\varepsilon}$. Bach et al. (2003) measured the elongational viscosity for two moderately entangled polystyrene melts, with 15 and 29 entanglements, and found these to display substantial amount of strain hardening even in the intermediate regime, for $1/\tau_d < \dot{\varepsilon} < 1/\tau_R$ and no sudden change in behavior when going into the fastest regime, $\dot{\varepsilon} < 1/\tau_R$. We refer to strain hardening behavior when the transient elongational viscosity rises above the linear viscoelastic prediction. We similarly measured strain hardening for narrow molecular weight polystyrenes with 3.9 and 7.7 entanglements, Nielsen et al. (2006). This indicated that chain stretch occurred much sooner than expected, and continued so with faster and faster flow.

Motivated by Bach’s (2003) results Marrucci and Ianniruberto (2004) developed a model that introduces a new characteristic time constant for the polymer chain that deals with tube pressure, $\tau_p$. According to this model there are three regions that identifies polymeric flows: 1) For $1/\tau_d < \dot{\varepsilon} < 1/\tau_p$ the polymer is oriented and the tube diameter is constant 2) For $1/\tau_p < \dot{\varepsilon} < 1/\tau_R$ the polymer is oriented and the tube surrounding the chain is subject to pressure, that reduces the tube diameter 3) For $1/\tau_R < \dot{\varepsilon}$ the polymer is stretched.

The tube pressure time, $\tau_p$ scales with molecular weight as $M_w^2$, similarly to the Rouse time, meaning that the distance between $\tau_p$ and $\tau_d$ scales with $M_w^1$, $\tau_p \sim M_w^{-1} \tau_d$. Marrucci and Ianniruberto estimated $\tau_p$ to be equal to $\tau_d$ if the number of entanglements, $Z$, is 15. The conclusions made by Bach et al. (2003) are based on two polystyrene melts with 15 and 29 entanglement, which means that the slowest region defined as $1/\tau_d < \dot{\varepsilon} < 1/\tau_p$ is not present for $Z=15$ and very narrow for $Z=29$. In order to thoroughly investigate and identify the slowest region where $1/\tau_d < \dot{\varepsilon} < 1/\tau_p$ we need
to have a broad interval of elongational rates at which this is true to experimentally prove the existence of this region. If for instance $\tau_p/\tau_d = 10$ the region will be measurable in one elongational rate decade. This would require that $Z=150$, which for polystyrene correspond to a molecular weight of $M_w = 2 \cdot 10^6 \text{g/mol}$. This is however too high for rheological purposes with melts due to very long relaxation times at temperatures below the degradation temperature of around 200°C. Rheological characterization of polystyrene will be limited to less than 100 entanglements mainly due to its high entanglement molecular weight, $M_e = 13.3 \cdot 10^3 \text{g/mol}$ and its high glass transition temperature, 100°C. To investigate melts with more than 100 entanglements we have decided to use polyisoprene as model polymer since this polymer has some of the same advantages as polystyrene and the two materials together open a wider experimental window than may be obtained by either one alone. Both materials can be synthesized by anionic polymerization, which is the most commonly used method for making model linear polymers with low polydispersities. The side groups on the polyisoprene monomer are less bulky than is the case for polystyrene, and this results in a significant reduction of the entanglement molecular weight to $M_e = 4.82 \cdot 10^3 \text{g/mol}$. Therefore it is possible to obtain a larger number of entanglements giving a larger spacing between the reptation time $\tau_d$ and the tube pressure time $\tau_p$. A less bulky side groups also give a significantly reduced glass transition temperature, $T_g = -75°C$ compared to polystyrene, $T_g = 100°C$, giving a much larger frequency interval in small angle oscillatory shear (SAOS) measurements, since polyisoprene is stable for temperatures below 100°C, which we have determined from oscillatory shear temperature sweeps on the AR 2000 rheometer. Polyisoprene is more prone to thermal degradation due to the presence of the double bond in the backbone of the polymer, which explains the lower degradation temperature for polyisoprene compared to polystyrene.

SAOS measurements will be used to estimate the reptation time, $\tau_d$ and the Rouse time of an entanglement segment, $\tau_e$, by fitting the loss and storage moduli to the Milner and McLeish (1998) model. The size of $\tau_d$ can be roughly estimated from the position of the maximum in $G''$ at low frequencies, $\omega_{max}$ and $\tau_e$ from the reciprocal frequencies at the higher cross over point of $G'$ and $G''$. The Rouse time however cannot be seen directly from the behavior in $G'$ or $G''$, since $\tau_R$ is related to chain stretch which obviously does not occur in small amplitude shear flow. Usually one would use the relation between the reptation time $\tau_d$ and the number of entanglements to estimate the Rouse time, and this also comes out as a result of fitting the LVE data to the Milner-McLeish, MM, model, $\tau_R = \tau_e Z^2$.

As a more direct way of finding the onset of chain stretch we will measure the relaxation after a sudden shearing displacement. We hereby determine the Rouse time $\tau_R$ experimentally by observing strain-time separability $G(t) = G(t, \gamma)/h(\gamma)$ for $t > \tau_R$. 
We base most of our elongational conclusions on results obtained by two similar rheometers, the EVF and the SER, Sentmanat et al. (2005). In both of these techniques a rectangular formed polymer film is attached to two cylindrical drums that are rotated opposite to each other, stretching out the spanned film. The transient elongational results obtained using the EVF and SER rheometers have been compared with elongational results from our filament stretching rheometer, FSR, on the same polymer. To validate the strain rate in the SER-experiments we have video recorded the elongational deformations at different elongational rates and at different aspect ratios of the samples.

7.2 Theory

7.2.1 Milner-McLeish model

Doi and Edwards (1986) describes the polymer chain as confined inside a tube consisting of the constraints arising from the other chains for entangled melts or concentrated solutions. The motion of the chain is constricted to occur inside the tube, which has a fixed length, and the time it takes to diffuse, or reptate, through the tube is called the reptation time, \( \tau_d \). Milner and McLeish (1998), refined the reptation model by incorporating the concept of contour length fluctuation first studied by Doi and Kuzuu (1980). The ends of the chain do not experience the same kinds of constraints as the central part of the chain, but will instead be able to fluctuate along the tube length direction.

The original Milner-McLeish model from 1998 has been modified by Likhtmann and McLeish (2002) who included more details into the model, for instance constraint release. This new version of the MM model is however much more computationally challenging, and we have decided to use a version of the MM model that is described in detail in Ye et al. (2003), that builds on corrections by Likhtmann (2000).

7.2.2 Doi Edwards model: Transient elongational start-up

We calculate the elongational prediction for the Doi Edwards model from the formulation described in Bird et al. (1987), which uses the independent alignment approximation. For uniaxial flow the stress becomes:

\[
\sigma_{zz} - \sigma_{rr} = \int_{-\infty}^{t} M(t - t') S(\epsilon)_{DE} dt'
\]

(7.1)

Where the strain function is:

\[
S(\epsilon)_{DE} = \left[ \left\langle \frac{u'u'}{u'u'} \right\rangle_{zz} - \left\langle \frac{u'u'}{u'u'} \right\rangle_{rr} \right] = 5 \left( 2e^{3\epsilon} + 1 - 3e^{3\epsilon} \arctan \frac{\sqrt{e^{3\epsilon}} - 1}{\sqrt{e^{3\epsilon}} + 1} \right) \frac{1}{2e^{3\epsilon} - 2}.
\]

(7.2)
For startup of steady flow the Hencky strain is given as:

$$
\varepsilon(t, t') = \begin{cases} 
\dot{\varepsilon}_0 t, & t' < 0 \\
\dot{\varepsilon}_0 (t - t'), & t' > 0
\end{cases} 
$$

(7.3)

where $\dot{\varepsilon}$ is the elongational rate. As an expression for the memory function $M(t)$ we use a multi mode Maxwell spectrum:

$$
M(t) = \sum_{i=1}^{i_{\text{max}}} \frac{\eta_i}{\lambda_i^2} e^{-t/\lambda_i}
$$

(7.4)

The Maxwell model fits the SAOS-data quantitatively and gives an accurate description of the memory function, that is used to calculate the linear viscoelastic prediction in elongation as accurate as possible. No physical insight is obtained by this fit. We however also fit the SAOS-data to the Milner-McLeish model (1998), see figure 7.1, to obtain the important physical values of the number of entanglements $Z$, the reptation time, $\tau_R$ and the melt modulus $G_N^0$. The MM model does however not fit $G'$ and $G''$ quantitatively, as the Maxwell model does, which is probably due to the fact that the polyisoprene is not completely monodisperse. In the limit of rapid stretch the memory function becomes time independent, and the Doi Edwards stress function in equation 7.2 only depends on the Hencky strain, $\varepsilon$ and melt modulus, $G_N^0$.

### 7.2.3 Marrucci Model

The chain inside the tube exerts a pressure on the tube wall, that scales with the tube diameter as $1/a^3$. Marrucci and Ianniruberto (2004) claim that the tube diameter will decrease in an elongational flow, and they set up a balance between the force pushing on the tube from the outside with the perpendicular force from the chain inside the tube. This eventually leads to an expression for a new time constant, $\tau_p$ that is found to be:

$$
\tau_p \approx \frac{a_0^2}{b^2}\tau_R
$$

(7.5)

where $a_0$ is the equilibrium tube diameter, $b$ is the length of a Kuhn step and $\tau_R$ is the Rouse time of the chain. Since $a_0$ and $b$ are related to the specific type of polymer, they are independent of molecular weight; $\tau_p$ scales with molecular weight in the same way as the Rouse time, that is: $\tau_p \sim M_w^2$. Fetters et al. (2006) reports the values for the tube diameter and the Kuhn step length as $a_0$ and $b$ for 1,4 polyisoprene, (with 7% 3,4 microstructure) as $a_0 = 61.6\text{Å}$and $b = 8.44\text{Å}$, giving the pre-factor in equation 7.5 as $\frac{a_0^2}{b^2} = 53.3$. 
7.3 Experimental section

7.3.1 Molecular characterization

The polyisoprene sample is purchased at Polymer Source Inc., Canada, which reports the weight molecular weight as: \( M_w = 1.3 \cdot 10^6 \text{g/mole} \) and the polydispersity as \( M_w/M_n = 1.1 \).

The polyisoprene is characterized by H-NMR in deuterated chloroform. We determined the content of 1,4 and 3,4 structure from the olefinic alkene protons between 4ppm and 6ppm, which gives a microstructure fraction of 3,4-polyisoprene of 8.6%.

7.3.2 Shear measurements

The oscillatory shear and step strain shear experiments are performed on an AR-G2 rheometer from TA instruments using an 8 mm parallel plate geometry. The Small Angle Oscillatory Shear (SAOS) experiments were performed over a range of temperatures from -22°C to 75°C, and the measured \( G' \) and \( G'' \) was shifted horizontally to a single master curve, shown in figure 7.1, using time-temperature shifting. Figure 7.2 shows the results of the stress relaxation after a sudden shearing displacement, found for seven different shear strains, from \( \gamma = 0.02 \) to \( \gamma = 0.75 \) at 25°C. The limited range of strains appear to be due to slip at the polymer-steel interface on the rheometer for strains higher than \( \gamma > 0.75 \). The measured moduli, \( G(t, \gamma) \) have been shifted vertically by the amount \( h(\gamma) \) to fit the strain independent relaxation modulus \( G(t) \), which is found from the Maxwell spectrum, fitted from SAOS-data.

7.3.3 Elongational viscosity measurements, SER, EVF and FSR

On the Extensional Viscosity Fixture (EVF) from TA instruments, two cylinders are used to wind up a polymer sample. One cylinder is rotating round its own axis while orbiting around the other cylinder which is fixed. The fixed cylinder is coupled onto the torque transducer of the ARES rheometer, and the orbiting cylinder is mounted on the ARES actuator. The Sentmanat Extensional Rheometer (SER), from Xpansion instruments, is also mounted onto the ARES rheometer and consists of two cylindrical drums and the polymer sample is attached onto these that are both rotated in opposite directions. The dimensions of the cylinders and the separation between the cylinders are the same for both the SER and the EVF, which makes it experimentally easy to compare the two rheometers. The thickness of the film is 0.7 mm in all experiments, and the width, \( D_0 \), is varied between 1.39 mm and 10mm. We here define the aspect ratio, \( \Lambda_0 \) as sample width divided with thickness. We also performed elongational experiments on the Filament Stretching Rheometer
Figure 7.1. Measurements of $G'$ and $G''$ obtained from oscillatory shear data at 25°C. The solid lines (—) are the Milner McLeish prediction for $Z = 282$, $\tau_e = 2.0 \cdot 10^{-5}$, and $G_0^N = 450kPa$. The dotted lines (- - -) are calculated from the Maxwell spectrum, table 7.1.

(FSR) situated at DTU in Lyngby, Denmark, to compare with the results obtained from the EVF and SER at MIT in Boston.

7.3.4 Strain validation by digital video microscopy

While the FSR has immediate strain validation due to the online measurement and control of the filament diameter, the SER and EVF-rheometers merely impose a rotation that ideally results in uniaxial deformation. To find a more direct measure of Hencky strain we have video recorded the sample deformation for different elongational rates and different aspect ratios of the samples. We use a high-speed digital CMOS video camera (Phantom 5) operating at a frame rate of 100-1000 frames per second, depending on the time of the experiment.

To determine how the strain evolves with time we have recorded the deformation of the polyisoprene film on the SER for four different elongational rates: 0.2s$^{-1}$, 2s$^{-1}$, 8s$^{-1}$ and 50s$^{-1}$ using the same aspect ratio of $\Lambda_0 = 14.3$. The result is shown in figure 7.3 as dimensionless width, $D/D_0$, against time, non-dimensionalized with the imposed elongational rate i.e. $\dot{\epsilon} \cdot t$. To examine how the measured strain depends on initial aspect ratio, we recorded the sample deformation for three different initial aspect ratios, $\Lambda_0 = 2.0$, $\Lambda_0 = 9.6$ and $\Lambda_0 = 14.3$, all experiments run at the same rate, $\dot{\epsilon} = 3s^{-1}$. Figure 7.4 displays a sequence of image frames from the videos for $\Lambda_0 = 2.0$ and 14.3, taken for frames at times at 0.0s, 0.33s, 0.66s, 1.00s and 1.33s. The width of the samples was found by digital
image processing and figure 7.5 shows how dimensionless width, \( D/D_0 \), of the sample evolves with dimensional time, \( \dot{\varepsilon}t \), for the three different aspect ratios.

## 7.4 Results and Discussion

### 7.4.1 Shear stress relaxation and Small Angle Oscillatory Shear

The measured storage- and loss moduli, \( G' \) and \( G'' \), were fitted to the MM model, and the result is shown as solid lines in figure (7.1), and the fitted parameters are listed in table 1. Moreover, a Maxwell spectrum has been fitted to the SAOS-data and is showed in figure 1 as a dotted line. The viscosity and time-spectrum is displayed in table 1.

The strain dependent modulus, found from stress relaxation measurements is nicely shifted onto a single master curve for times higher than \( \tau_k = 3s \), as seen in figure 7.2. The experimentally found damping function was found to lie below the theoretical Doi-Edwards prediction especially for high strain values, and the experimental values of \( h(\gamma) \) could not be reproduced when changing the gap size in the measurements. The reason for this may be that the adhesive strength of this high molecular weight polyisoprene on steel is weak, and the actual strain is smaller than the apparent strain for high values of \( \gamma \). This however does not affect the size of \( \tau_k \), which is independent of \( \gamma \), and since the purpose of performing step-strain experiments is to determine this value, no further attempts are done to avoid adhesive failure. The size of \( \tau_k \) is related to the Rouse chain stretch time, and it is expected that stress relaxation occurs exponentially with the Rouse time. Doi and Edwards (1986) report the relation between \( \tau_k \) and \( \tau_R \) to be \( 4.5 \tau_R = \tau_k \), and since \( e^{-4.5} = 0.01 \) it is reasonable that the chain stretch has relaxed after 4.5 Rouse times.

From the SAOS measurements we find a zero shear viscosity of \( \eta_0 = 3.43 \cdot 10^8 \) Pa s, which is found from the Maxwell fit as \( \eta_0 = \sum_{i=1}^{i=\text{max}} \eta_i \).

Auhl et al. (2006) examined the linear viscoelastic properties of narrow molecular weight polyisoprene over a wide range of molecular weights, and predicted the zero shear viscosity to be \( \ln_{10}(\eta_0) = -13.65 + 3.6 \ln_{10}(M_w) \). This corresponds to a molecular weight of \( M_w = 1.45 \cdot 10^6 \) s/mole for our polyisoprene. Another way of determining the molecular weight is from the number of entanglements, \( Z = 282 \), found by fitting the MM model to \( G' \) and \( G'' \). Auhl et al. (2006) determined an average value of the entanglement molecular weight for polyisoprene to be: \( M_e = 4.82 \cdot 10^3 \) s/mole, which gives a molecular weight for our polyisoprene to be: \( M_w = 1.35 \cdot 10^6 \) s/mole. The polyisoprene is purchased from Polymer Source inc., Canada, and the manufacturer reports the molecular weight to be \( M_w = 1.31 \cdot 10^6 \) s/mole. The values of \( M_w \), found by different approaches are listed in table 7.1 together with \( G_N^0 \) and \( \eta_0 \). The Rouse time found from the DE model is
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\[ G(t, \gamma) = \frac{h(\gamma)}{1000} \]

\[ \gamma = 0.02 \]
\[ \gamma = 0.10 \]
\[ \gamma = 0.20 \]
\[ \gamma = 0.30 \]
\[ \gamma = 0.40 \]
\[ \gamma = 0.60 \]
\[ \gamma = 0.75 \]

\[ \tau_R = \frac{\tau_k}{4} \cdot 0.67 \] s

\[ \tau_e = 1.4 \cdot 10^{-5} \] s

\[ G^0_n = 4.50 \cdot 10^5 \] Pa

\[ M_w \text{ from MM fit to } Z = 1.36 \cdot 10^6 \text{ g/mole} \]
\[ M_w \text{ reported by manufacturer} = 8.393 \cdot 10^6 \text{ g/mole} \]
\[ M_w \text{ calculated from } \eta_0 = 5.34 \cdot 10^6 \text{ g/mole} \]

\[ \eta_0 \text{ from Maxwell fit to SAOS data} = 3.43 \cdot 10^8 \text{ Pa s} \]
\[ \tau_d \text{ from MM fit to SAOS data} = 646 \text{ s} \]
\[ \tau_R \text{ from MM fit to SAOS data} = 0.89 \text{ s} \]
\[ \tau_e \text{ from MM fit to SAOS data} = 1.4 \cdot 10^{-5} \text{ s} \]
\[ s_d \text{ from MM fit to SAOS data} = 0.0877 \]
\[ \tau_p = \frac{a_0^2}{b^2} \tau_R = 35.5 \cdot 0.67 \] s

\[ \mu_w \text{ from MM fit to } Z = 1.36 \cdot 10^6 \text{ g/mole} \]
\[ \mu_w \text{ reported by manufacturer} = 8.393 \cdot 10^6 \text{ g/mole} \]
\[ \mu_w \text{ calculated from } \eta_0 = 5.34 \cdot 10^6 \text{ g/mole} \]

\[ \eta_0 \text{ from Maxwell fit to SAOS data} = 3.43 \cdot 10^8 \text{ Pa s} \]
\[ \eta_i \text{ from Maxwell fit to SAOS data} = 3.43 \cdot 10^8 \text{ Pa s} \]
\[ \tau_d \text{ from MM fit to SAOS data} = 646 \text{ s} \]
\[ \tau_R \text{ from MM fit to SAOS data} = 0.89 \text{ s} \]
\[ \tau_e \text{ from MM fit to SAOS data} = 1.4 \cdot 10^{-5} \text{ s} \]
\[ s_d \text{ from MM fit to SAOS data} = 0.0877 \]
\[ \tau_p = \frac{a_0^2}{b^2} \tau_R = 35.5 \cdot 0.67 \] s

\[ G^0_n \text{ from MM fit to SAOS data} = 4.50 \cdot 10^5 \] Pa

\[ \mu_w \text{ from MM fit to } Z = 1.36 \cdot 10^6 \text{ g/mole} \]
\[ \mu_w \text{ reported by manufacturer} = 8.393 \cdot 10^6 \text{ g/mole} \]
\[ \mu_w \text{ calculated from } \eta_0 = 5.34 \cdot 10^6 \text{ g/mole} \]

\[ T \] able 7.1. The properties for the polysioprene determined from linear viscoelastic measurements and the Maxwell parameters determined from small amplitude oscillatory shear data

\[ \tau_R = \tau_e Z^2 \]

\[ \eta_0 \text{ from Maxwell fit to SAOS data} = 3.43 \cdot 10^8 \text{ Pa s} \]
\[ \eta_i \text{ from Maxwell fit to SAOS data} = 3.43 \cdot 10^8 \text{ Pa s} \]
\[ \tau_d \text{ from MM fit to SAOS data} = 646 \text{ s} \]
\[ \tau_R \text{ from MM fit to SAOS data} = 0.89 \text{ s} \]
\[ \tau_e \text{ from MM fit to SAOS data} = 1.4 \cdot 10^{-5} \text{ s} \]
\[ s_d \text{ from MM fit to SAOS data} = 0.0877 \]
\[ \tau_p = \frac{a_0^2}{b^2} \tau_R = 35.5 \cdot 0.67 \] s

\[ G^0_n \text{ from MM fit to SAOS data} = 4.50 \cdot 10^5 \] Pa

\[ \mu_w \text{ from MM fit to } Z = 1.36 \cdot 10^6 \text{ g/mole} \]
\[ \mu_w \text{ reported by manufacturer} = 8.393 \cdot 10^6 \text{ g/mole} \]
\[ \mu_w \text{ calculated from } \eta_0 = 5.34 \cdot 10^6 \text{ g/mole} \]

\[ T \] able 7.1. The properties for the polysioprene determined from linear viscoelastic measurements and the Maxwell parameters determined from small amplitude oscillatory shear data

7.4.2 Strain rate confirmation and aspect ratio dependency

In order for the deformation to be uniaxial with constant elongational rate, the square section area of the sample must decrease exponentially with time. To examine this, the width of the samples have been measured and figure 7.3 shows the normalized width plotted against apparent Hencky strain (time multiplied by the imposed elongational rate). All polysioprene
samples have initial aspect ratios of $\Lambda_0 = 14.3$.

\[
\begin{align*}
\dot{\epsilon} &= 0.177 \text{s}^{-1}, \\
\dot{\epsilon} &= 1.812 \text{s}^{-1}, \\
\dot{\epsilon} &= 6.77 \text{s}^{-1} \quad \text{and} \\
\dot{\epsilon} &= 41.9 \text{s}^{-1}
\end{align*}
\]

The figure shows that the strain rate is constant for strains lower than approximately $\epsilon < 1.5$, and then the strain rate starts to decrease. This decrease is not seen in the slowest experiment $\dot{\epsilon} = 0.2 \text{s}^{-1}$ because the sample ruptures at approximately $\dot{\epsilon} \cdot t = 1.2$, nor is it seen for $\dot{\epsilon} = 50 \text{s}^{-1}$ due to rupture at $\epsilon = 2.5$. By fitting the diameter, measured for $\dot{\epsilon} \cdot t < 1.2$, to the expected exponential decrease $D/D_0 = e^{-1/2t\dot{\epsilon}}$ we find that the strain rate is around 20% smaller than the imposed strain rate. Schultze et al (2001) observed a similar deviation between the imposed strain rate and the actual strain rate on the Rheometric Scientific RME extensional rheometer for LLDPE melts. The strain rates measured from the video images are given in the legend to figure 7.3. We expected the decrease in strain rate for high Hencky strains to be related to the large initial aspect ratios and therefore a series of experiments were conducted with varying sample widths. Figure 7.5 shows the development in sample width for three different aspect ratios and do indeed show that the sample deformations depend strongly on initial aspect ratio, $\Lambda_0$. As $\Lambda_0$ approaches unity, the change in elongational rate at $\epsilon = 1.2$ fades away. This phenomena is illustrated more visually in figure 7.4.

### 7.4.3 Comparison of SER, EVF and FSR

To validate the elongational measurements made on the SER and EVF rheometers, independent measurements on the polyisoprene were performed on an FSR-rheometer, (Bach et al. 2003). The results for three different elongational rates are plotted in figure 7.6 as engineering stress against applied elongational rate times time. Engineering stress is defined as elongational force divided with initial square sectional area and note that the y-axis is linear in order to ease visual comparison. The devi-
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\[ \dot{\varepsilon} \cdot t = 0 \quad \dot{\varepsilon} \cdot t = 1 \quad \dot{\varepsilon} \cdot t = 2 \quad \dot{\varepsilon} \cdot t = 3 \quad \dot{\varepsilon} \cdot t = 4 \]

**Figure 7.4.** Black and white image frame from the video for \( \Lambda_0 = 2.0 \) and \( \Lambda_0 = 14.3 \). The imposed elongational rate is \( \dot{\varepsilon} = 3s^{-1} \) in both experiments. Close inspection of the frames show that the kinematics depend on the aspect ratio, see figure 7.5.

The measured engineering stress does seem to obey this, for \( \dot{\varepsilon} < 0.2s^{-1} \), but by looking closely at the data and the recorded video we see that...
the engineering stress goes through a maximum and then shortly after the sample ruptures. This delay is probably due to the fact that our polyisoprene is not a purely elastic material and that viscous effects have to be considered as well. The control loop in the FSR makes it possible to delay failure even further as shown in figure 7.6.

Figure 7.8 shows the results of the same experiments as in figure 7.7, including the results for the highest elongational rate experiments, plotted as elongational viscosity against time together with the linear viscoelastic prediction. Both these figures reveal that the elongational behaviour changes radically at an elongational rate of around \( \dot{\epsilon} = 0.2 \text{s}^{-1} \).

This is visually seen as stabilization of the polymer fluid, i.e. it does not rupture until a Hencky strain of about \( \epsilon = 6 - 7 \), as also seen in figure 7.3. The measured elongational forces increase drastically, and the predicted stresses no longer follow the Doi-Edwards prediction. Likewise the viscosity becomes strain rate dependent and deviates from the generalized viscoelastic prediction from the Maxwell model. The viscosities increase strongly above the linear viscoelastic envelope, a sign of strain hardening for elongational rates higher than \( \dot{\epsilon} > 0.2 \text{s}^{-1} \).

The slow experiments in figure 7.8, at elongational rates \( \dot{\epsilon} < 0.6 \text{s}^{-1} \) are performed on samples with initial aspect ratio of \( \Lambda_0 = 14.3 \), whereas the fastest experiments, \( \dot{\epsilon} \geq 0.6 \text{s}^{-1} \) are performed on samples with \( \Lambda_0 = 2.0 \).

The reason is, that when stretching the samples to high Hencky strains, \( \epsilon > 1.2 \), the kinematics change and the imposed deformation rate decreases for large aspect ratios, as described in section 7.4.2. This phenomenon is
Figure 7.6. Measurements of the engineering stress for $\dot{\epsilon} = 0.003 \text{s}^{-1}$, $\dot{\epsilon} = 0.06 \text{s}^{-1}$ and $\dot{\epsilon} = 0.2 \text{s}^{-1}$, determined by different elongational techniques, filament stretching, EVF and SER. The Rouse Deborah numbers are $\text{De}_R = 0.002$, $\text{De}_R = 0.04$ and $\text{De}_R = 0.13$, based on the Rouse time of $\tau_R = 0.67 \text{s}$. The solid line is the Doi Edwards prediction, equation 7.2, for infinite elongational rate, with $G_n^0 = 450 \text{kPa}$.

less apparent for aspect ratios close to unity which makes the collected data for high deformations at high elongational more reliable, and is why we use smaller aspect ratio in the fastest experiments. In figure 7.9 we make a comparison between the measured stress in the startup experiments performed with two different aspect ratios, $\Lambda_0 = 14.3$ and $\Lambda_0 = 2.0$. It is seen that the stresses coincide until around $\epsilon = 3$, where the measured stresses for $\Lambda_0 = 14.3$ flattens out and the stress keeps on increasing for $\Lambda_0 = 2.0$.

The difference in elongational stresses between $\Lambda_0 = 14.3$ and $\Lambda_0 = 2.0$, figure 7.9, is only up to 30%, implying that the stress measurements are less affected by the dramatics change in kinematics seen in figure 7.5. Included in figure 7.9 is the Neo-Hookean prediction of the stress that applies for a affinely deforming crosslinked network. We see that the stress approaches this upper limit with increasing elongational rates.

The transient elongational viscosities do not show any tendency to level off and become constant in any of the experiments. At lower elongational rates, $\dot{\epsilon} < 0.2 \text{s}^{-1}$ the cut off values in viscosities are related to sample rupture, and the highest measured viscosity is probably not representative of a steady state elongational viscosity. At higher elongational rates we are
Figure 7.7. Transient engineering stress growth for elongational rates: \( \dot{\epsilon} = 0.0003 s^{-1} \) +, \( \dot{\epsilon} = 0.0006 s^{-1} \) ◊, \( \dot{\epsilon} = 0.001 s^{-1} \) ▲, \( \dot{\epsilon} = 0.003 s^{-1} \) △, \( \dot{\epsilon} = 0.006 s^{-1} \) ◦, \( \dot{\epsilon} = 0.01 s^{-1} \) ○, \( \dot{\epsilon} = 0.03 s^{-1} \) ▼, \( \dot{\epsilon} = 0.06 s^{-1} \) □, \( \dot{\epsilon} = 0.1 s^{-1} \) *, \( \dot{\epsilon} = 0.2 s^{-1} \) ■, and \( \dot{\epsilon} = 0.6 s^{-1} \) ●. The dotted lines are the prediction of the Doi Edwards model for the seven lowest elongational rates, and the solid line is the upper limit for the Doi Edwards model, equation 7.2. Inserted to the right is a picture of the polyisoprene sample at a Hencky strain of \( \epsilon = 1.7 \), stretched at \( \dot{\epsilon} = 0.2 \).

6.4. Results and Discussion

Infinite DE

Neo Hookean

\( \epsilon \) = \( \sigma_{zz} - \sigma_{rr} \)

\([kPa]\)

Figure 7.7. Transient engineering stress growth for elongational rates: \( \dot{\epsilon} = 0.0003 s^{-1} \) +, \( \dot{\epsilon} = 0.0006 s^{-1} \) ◊, \( \dot{\epsilon} = 0.001 s^{-1} \) ▲, \( \dot{\epsilon} = 0.003 s^{-1} \) △, \( \dot{\epsilon} = 0.006 s^{-1} \) ◦, \( \dot{\epsilon} = 0.01 s^{-1} \) ○, \( \dot{\epsilon} = 0.03 s^{-1} \) ▼, \( \dot{\epsilon} = 0.06 s^{-1} \) □, \( \dot{\epsilon} = 0.1 s^{-1} \) *, \( \dot{\epsilon} = 0.2 s^{-1} \) ■, and \( \dot{\epsilon} = 0.6 s^{-1} \) ●. The dotted lines are the prediction of the Doi Edwards model for the seven lowest elongational rates, and the solid line is the upper limit for the Doi Edwards model, equation 7.2. Inserted to the right is a picture of the polyisoprene sample at a Hencky strain of \( \epsilon = 1.7 \), stretched at \( \dot{\epsilon} = 0.2 \).

able to measure the elongational viscosity to much higher Hencky strains. However, the stress in figure 7.9 seem to keep on increasing at all strains. Another problem that one encounters when using the EVF-rheometer is that the polymer film at Hencky strain units above \( \epsilon = 3.8 \) has made one entire revolution on the cylindrical drum and will initially touch the clamps and eventually touch itself. This will change the effective diameter of the drum, and thereby change the imposed elongational rate. This is why we do not see a smooth transition into a steady state viscosity for the EVF measurements as opposed to when using a filament stretching rheometer, which has no inherent restrictions on a maximum number of Hencky strain.

The disturbance in the elongational startup flow caused when the EVF-rheometer has made one revolution will always result in an instantaneous increase in the measured torque, since the effective drum radius increases, and torque is force times radius. The imposed elongational rate will also increase because the radius scales linearly with the elongational rate and consequently the measured elongational forces for \( \epsilon > 3.8 \) are not reliable. Other kind of disturbances in the elongational flow, for instance decrease in elongational rate after \( \epsilon > 1.2 \) or sample rupture at elongational rates below \( \dot{\epsilon} < 0.2 s^{-1} \) will cause the elongational rate, and hereby the elongational forces to decrease.

We therefore claim that the measured maxima in the elongational vis-
\[ 7.4. \text{Results and Discussion} \]

\[ \dot{\epsilon} = 5.0 \text{s}^{-1} \]
\[ \dot{\epsilon} = 3.5 \text{s}^{-1} \]
\[ \dot{\epsilon} = 2.0 \text{s}^{-1} \]
\[ \dot{\epsilon} = 1.0 \text{s}^{-1} \]
\[ \dot{\epsilon} = 0.6 \text{s}^{-1} \]
\[ \dot{\epsilon} = 0.2 \text{s}^{-1} \]
\[ \dot{\epsilon} = 0.06 \text{s}^{-1} \]
\[ \dot{\epsilon} = 0.03 \text{s}^{-1} \]
\[ \dot{\epsilon} = 0.01 \text{s}^{-1} \]
\[ \dot{\epsilon} = 0.003 \text{s}^{-1} \]
\[ \dot{\epsilon} = 0.001 \text{s}^{-1} \]
\[ \dot{\epsilon} = 0.0006 \text{s}^{-1} \]

Figure 7.8. Transient elongational viscosity for elongational rates going from \( \dot{\epsilon} = 0.0006 \text{s}^{-1} \) to \( \dot{\epsilon} = 5 \text{s}^{-1} \). The solid line is the linear viscoelastic envelope. Included is the startup and stress relaxation viscosity for: \( \dot{\epsilon} = 0.1 \text{s}^{-1} \) stretched to \( \epsilon = 0.26 \), \( \dot{\epsilon} = 0.01 \text{s}^{-1} \) stretched to \( \epsilon = 0.23 \) and \( \dot{\epsilon} = 0.003 \text{s}^{-1} \) stretched to \( \epsilon = 0.3450 \). The dotted lines are the relaxation prediction from the linear viscoelastic Maxwell model.

Cosisties, as long as \( \epsilon < 3.8 \), must be a lower estimate of the steady state viscosities. These maximum values are plotted in figure 7.10 together with the Doi Edwards steady state prediction and included is a rough estimate of the Marrucci model. We have sketched out the three regions described in the Introduction simply by connecting straight lines obeying the Marrucci scaling:

\[
\bar{\eta}^+ \sim \begin{cases} 
\dot{\epsilon}^0 & \text{for } \dot{\epsilon} < \tau_d^{-1} \\
\dot{\epsilon}^{-1} & \text{for } \tau_d^{-1} < \dot{\epsilon} < \tau_p^{-1} \\
\dot{\epsilon}^{-0.5} & \text{for } \tau_p^{-1} < \dot{\epsilon} < \tau_R^{-1} \\
\dot{\epsilon}^0 & \text{for } \dot{\epsilon} > \tau_R^{-1}
\end{cases}
\]

It is not immediately possible to conclude whether the measured data follow the Doi Edwards or the Marrucci prediction. The biggest concern, when presenting steady state data, is that the the viscosities at the lowest elongational rates probably have not reached steady steady state, because the polyisoprene samples rupture at small Hencky strain units. The data at higher elongational rates, \( \dot{\epsilon} > \tau_R^{-1} \) are more reliable because the samples
Figure 7.9. Comparison between the startup stress for elongational experiments performed with initial aspect ratio of respectively $\Lambda_0 = 2.0$ and $\Lambda_0 = 14.3$. The imposed elongational rates are ranging from $\dot{\epsilon} = 0.6\, s^{-1}$ to $\dot{\epsilon} = 5\, s^{-1}$. The solid line is the Neo Hookean predictions, $\sigma_{zz} - \sigma_{rr} = G_0 \left( e^{2\epsilon} - e^{-\epsilon} \right)$ and the dotted line is the infinitely fast Doi Edwards limit from equation 7.2.

7.4. Results and Discussion

7.4.4.1 Thermal effects

When stretching the polyisoprene sample the applied amount of work to the sample would, at adiabatic conditions, result in a temperature increase. In the case of no radiative and convective heat transport the temperature increase in the polyisoprene sample will be:

$$\Delta T = \frac{1}{\rho C_p} \int_0^{\epsilon_f} \left[ \sigma_{zz}(\epsilon) - \sigma_{rr}(\epsilon) \right] d\epsilon$$

(7.7)

where $\epsilon_f$ is the Hencky strain, $C_p = 1930 \, J\, kg^{-1}K^{-1}$ is the heat capacity of polyisoprene and $\rho = 830 \, kg\, m^{-3}$ is the density for polyisoprene (Fetters et al. do not rupture. The most notable difference between this plot and the similar plot for narrow molecular weight polystyrene, figure 6 in Bach et al. (2003) is the transition that we observe when stretching faster that the inverse Rouse time, for $\dot{\epsilon} > \tau_R^{-1}$, which is absent in Bach et al. (2003) measurements.
Table 7.2. Estimates of the maximum possible temperature increase for adiabatically elongated samples at high rates.

<table>
<thead>
<tr>
<th>$\epsilon_f$</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta T_{\text{max}}[\degree{C}]$</td>
<td>0.53</td>
<td>2.58</td>
<td>13.5</td>
<td>37.3</td>
</tr>
<tr>
<td>$a_{25-\degree{C}}/\Delta T/a_{25-\degree{C}}$</td>
<td>0.97</td>
<td>0.85</td>
<td>0.45</td>
<td>0.15</td>
</tr>
</tbody>
</table>

1994 and Krevelen 1990). The highest measured elongational stresses in this work are found for an elongational rate of $\dot{\epsilon} = 5s^{-1}$, and the stress vs. Hencky strain has been fitted for this experiment with a sixth order polynomial. In table 7.2 we give the maximum values of the temperature increase of the polyisoprene sample for given values of the Hencky strain $\epsilon$, found by using equation 7.7 and the mentioned fitted polynomial expression for the $[\sigma_{zz}(\epsilon) - \sigma_{rr}(\epsilon)]$. It is seen, that the maximum possible temperature increase in the sample stretched 4 Hencky strain is considerable, $\Delta T = 37.3K$, and using the Williams-Landel-Ferry coefficients from Abdel-Goad et al. (2004) the temperature increase will change the time-temperature shift factor to $a_{62-\degree{C}}/a_{25-\degree{C}} = 0.15$, which is the highest estimate. However the potential temperature increase is not critical for Hencky strains below 3, meaning that the measured stresses in the slower experiments are not affected by thermal dissipation. Any increase in the temperature would eventually result in stresses and viscosities lower than the isothermal stresses and viscosities, and therefore the reported values in this work can be regarded as lower estimates of the stresses and viscosities.

### 7.4.4.2 Rupture dynamics

When stretching the polyisoprene sample on the EVF fixture we observe sample failure very close to the engineering stress maximum at elongational rates below the inverse Rouse time, $\dot{\epsilon} < \tau^{-1}_R$ whereas sample rupture occurs later for higher elongational rates. To quantify this phenomenon better figure 7.12 shows the Hencky strain at failure, $\epsilon_{\text{failure}}$ and the Hencky strain at maximum engineering stress $\epsilon_{\text{max}}$ plotted against the Rouse Deborah number, $De_R = \dot{\epsilon} \cdot \tau_R$, where $\tau_R = 0.67s$. Included in the plot is prediction for $\epsilon_{\text{max}}$ found with the Doi Edwards model.

The measured values of $\epsilon_{\text{max}}$ and $\epsilon_{\text{failure}}$ are almost identical for $De_R < 0.1$ and are predicted nice by both the Doi Edwards model and the Maxwell model. At $De_R > 0.1$ we seen that sample failure $\epsilon_{\text{failure}}$ occurs later and later compared to $\epsilon_{\text{eng}}$, and neither the Doi Edwards model nor the Maxwell model are able to catch the upturn in $\epsilon_{\text{max}}$ and $\epsilon_{\text{failure}}$. Keep in mind that while $\epsilon_{\text{max}}$ is a rheological phenomenon, $\epsilon_{\text{failure}}$ is instrumental specific.
7.4.5 Stress relaxation

The EVF fixture in conjunction with the ARES rheometer gives one the possibility of measuring stress relaxation experiments after transient elongational startup. Startup of elongational flow followed by stress relaxation was performed at three different elongational rates, where the flow was ceased in the linear viscoelastic regime. Figure 7.8 shows the startup and relaxation at rates of respectively \( \dot{\varepsilon} = 0.1 \text{s}^{-1} \) stretched for 2.6 seconds, \( \dot{\varepsilon} = 0.01 \text{s}^{-1} \) stretched for 23 seconds and \( \dot{\varepsilon} = 0.003 \text{s}^{-1} \) stretched for 115 seconds, which all corresponds to a terminal stretch, denoted \( \varepsilon_t \) less than 0.4 Hencky strain units. The decrease in elongational viscosity after cessation of flow in the LVE-regime is given by the general linear viscoelastic theory. By using the Maxwell spectrum found from SAOS-measurements the expression for the stress relaxation viscosity after being stretched for \( t_0 \) is given by:

\[
\eta_E(t) = 3 \int_{t_0}^{t} G(t) dt = 3 \sum_{i=1}^{i_{\text{max}}} \int_{t_0}^{t} \eta_i e^{-\frac{t}{\lambda_i}} dt = 3 \sum_{i=1}^{i_{\text{max}}} \eta_i \left[ e^{-(t-t_0)/\lambda_i} - e^{-t/\lambda_i} \right]
\]  

(7.8)

The LVE-prediction for the stress relaxation is included in figure 7.8 as dotted lines, which collapse nicely onto the experimental data. We have performed stress relaxation experiments from the non-linear regime as well. Figure 7.11 shows the startup and relaxation of stress for one elongational rates, \( \dot{\varepsilon} = 1 \text{s}^{-1} \) stretched to various Hencky strains. The stress relaxation for \( \dot{\varepsilon} = 1 \text{s}^{-1} \) stretched to \( \varepsilon_t = 4 \) is seen to decrease rapidly for about one or two seconds, and then actually goes below the stress that is measured for samples only stretched to \( \varepsilon_t = 1 \). This is an unphysical observation, and the simple explanation for this is that the highly stretched samples exhibit a rapid necking phenomenon, and the square section area at the thinnest place decreases and eventually ruptures.
7.4. Results and Discussion

**Figure 7.10.** Estimated steady elongational viscosity against elongational rate. The viscosity values are the highest measured transient viscosities in each experiment. The arrows mark the value of the Rouse time $\tau_R^{-1}$, the reptation time $\tau_d^{-1}$ and the Marrucci tube pressure time $\tau_p^{-1}$.

**Figure 7.11.** Transient elongational stress growth for $\dot{\epsilon} = 1 \text{s}^{-1}$ to respectively $\epsilon = 1$, $\epsilon = 2$, $\epsilon = 3$ and $\epsilon = 4$ followed by stress relaxation. The solid line is the Neo Hookean predictions.
Figure 7.12. Measured values of hencky strain at which the engineering stress goes through a maximum $\epsilon_{\text{max}}$ and hencky strain values at sample failure. Included is the Doi Edwards prediction of $\epsilon_{\text{max}}$. The two dotted lines are connecting the experimental data and are drawn schematically.
7.5 Conclusion

The aim of this work has been to investigate the extensional rheology of highly entangled polymer melts. For this purpose we have attained an ultra high molecular weight polyisoprene and measured the elongational properties of using a novel kind of extensional technique where sample is elongated by two opposite rotating cylinders. The following conclusion can be drawn:

- The polyisoprene melt has been tested on three extensional rheometers: the SER, EVF and the FSR. For three different elongational rates all rheometers obtain the same elongational properties within 20%.

- The kinematics of the elongating melt is found the depend on the dimension of the elongating sample. By the use of video microscopy it is found that a high aspect ratio, that is thickness-to-height ratio, results in decrease in elongational rate with extension. This is avoided by using samples with aspect ratio close to unity.

- At stretch rates smaller than the inverse Rouse time, \( D_e R < 1 \) sample failure is observed in accordance with the Considere Criterion, that is, at maxima in the engineering stress, and before the steady state in stress is reached.

- At stretch rates higher than the inverse Rouse time, \( D_e R > 1 \), the sample is stable well beyond the Considere Criterion and a significant strain hardening is measured.

- The experimentally estimated steady elongational viscosity, \( \bar{\eta} \) show a decreasing trend with the elongational rate, \( \dot{\varepsilon} \) for rates smaller than the reciprocal Rouse time, and become stable for rates higher than the reciprocal Rouse time. This is in contrast to the observed results for moderately entangled polystyrenes, and might be a feature only seen in very highly entangled melts.
Bibliography


8

Summarizing Chapter

8.1 Introduction

The theme of this thesis is experimental exploration of the extensional rheology of polymer melts. Research in the field of extensional rheology has for a long time been very limited and it was accepted in the scientific rheology community, until the 1990ties that, that it was virtually impossible to obtain accurate data from highly nonlinear extensional experiments. In shear flows steady state viscosities are relatively easy to measure, whereas this is not the case for extensional flows due to inability to reach high elongations. The steady state condition is preferred when comparing data with models since the time-dependence disappears. For experimental reasons, however the transient viscosities have been in focus, and in one of the most commonly used textbooks on the introduction to rheology, "Dynamics of Polymer liquids" Bird et al. has the following comment to extensional flows, page 135:

*It is not clear what the steady state viscosity exists for some materials and conditions*

The focus of experimental rheologists have therefore been on providing accurate data from shear measurements, and many theoretical models have been verified solely on shear results such as loss and storage-modulus data from oscillatory shear experiments. Since the 1990ties research in extensional rheology has progressed. The pioneering work was done by Sridhar and coworkers (1991) and rapid developments have continued up till today. At the time when this Ph.D. project was started measurement of the extensional properties of monodisperse polystyrenes had just been published by Bach et al. (2003). The primary result of Bach et al. work was a precise determination of the steady state extensional viscosity of monodisperse polystyrene melts. These results have since 2003 received much attention, and have had a big impact in the rheology community that works on polymer chain dynamics. Giuseppe Marrucci, an authority in the field of reptation based models and receiver of the Bingham medal in 2003 from the Society of Rheology, wrote in 2004 together with Giovanni Ianniruberto the first article that tried to explain Bach et al.’s data. In the introduction to the paper Marrucci and Ianniruberto wrote, among other things:

*In this paper we start from the recent experiments of elongational flow per-
formed by Bach et al. that, in our opinion, reveal a nontrivial crisis of the standard model. In the next section we review these findings, showing that the concepts generally accepted prove unable to explain those observations. Bach et al. (2003) described the extensional properties of two monodisperse polystyrenes that were synthesized at Risø National Laboratory. Monodisperse polystyrene is a relatively simple material that is available commercially and the shear rheology has been known for more than 20 years. What was most remarkable about the measurements is in my opinion, that Bach et al. demonstrated that it is possible to measure the extensional stress of a polymer melt accurately up till Hencky strain units of 6-7 where steady state is reached, and the claim by Bird et al. from 1987 was partly disproved.

The filament stretching rheometer located at the Technical University of Denmark, DTU, in Lyngby, delivered data that was valuable in the understanding of dynamics of polymer melts, and the purpose of starting the current Ph.D. project was to pick up the thread from Anders Bach’s Ph.D. project, and explore the rheology of polymer melts. The filament stretching rheometer at DTU was at the time the only rheometer in the world that used a closed loop control of the endplates to ensure a constant elongation rate during an extensional experiment. It was therefore the only rheometer that could measure accurately up to 7 Hencky strains on polymer melts above room temperature. I was in the favorable position that almost whatever polymer type I chose to work with, the obtained results would be the first of its kind. This work is of explorative character; there is no overall objective of this project, not one specific task. The purpose is to use the accessible facilities at DTU and at Risø National Laboratory to open new doors in the understanding of polymer rheology. Anders Bach chose to explore the simplest possible system: monodisperse linear polymers. Monodisperse polymers are often used as model molecules in the development of molecular based constitutive models such as the Doi and Edwards reptation model. However many rheological constitutive models are of more empirical character which is due to the fact that much of the accessible data for polymer melts are obtained from measurements on industrial polymers that are not well chemically characterized, and have high degreee of polydispersities. It would logical to investigate how polydisperse polymers behave in extension. Characterization of very simple polydisperse systems is one of the aims of this Ph.D. Besides this, we believe that it is relevant to measure the extensional properties of melts consisting of branched polymers. It is known that the dynamic melt properties of high density polyethylene, HDPE, which consists mostly of linear polymer chains, are very different from those of low density polyethylene, LDPE, which consists of branched polymer chains. In extension LDPE shows more strain hardening and is therefore able to elongate more that HDPE before rupture. One aim of this Ph.D. project is to characterize branched polymer melts using filament stretching rheometry. When the
FSR-rheometer at DTU in Lyngby was developed, the primary aim was to measure the uniaxial extensional properties at constant elongational rate. The focus was especially on controlling the separation of the end-plates from knowledge of the evolution of the filament diameter during the stretching experiment. The software used to control the endplates is however very robust and can be repogrammed so that the elongational rate can be changed during an experiment. In shear rheology stress relaxation is often used to describe the dynamics of polymer molecules, and this has inspired us to use the FSR to measure how the stress relaxes if the elongation is stopped at an extension where the stress has reached steady state. Measurements of this kind have to our knowledge not been published before for monodisperse polymer melts. When using the filament stretching rheometer the preferred model polymer with narrow molecular weight distributions has been polystyrene. Polystyrene is a well-suited polymer for investigating properties for lowly and moderately entangled polymers, but not for highly entangled polymers with more than 100 entanglements. We have therefore decided to measure the extensional properties for a highly entangled polyisoprene. This requires very high elongational rates that can not be obtained when using the filament stretching rheometer and are therefore performed on a newly developed extensional fixture, the Extensional Viscosity Fixture, EVF. This part of the experimental work was performed at Massachusetts Institute of Technology. In the following sections the results in the above-mentioned areas are summarized.

8.2 Bidisperse polystyrenes

The simplest possible polydisperse system is a blend of two monodisperse polymers, and we have chosen to use bidisperse polymer melts as model systems in investigating the effect of polydispersity on the extensional properties. Three bidisperse polymer melts have been made that consist of polystyrene with a molecular weight of 390 kg/mol, PS390K that is blended into low molecular weight polystyrene with a weight of 52 kg/mol in two different concentrations. Besides this PS390K is blended with polystyrene with molecular weight of 103 kg/mol, PS100K. The monodisperse melts, PS50K, PS100K and PS390K have all been characterized in elongation, and one of the features observed is that the highest measured value of the extensional viscosity at the rates measured, does only not exceed the value of $3\eta_0$ significantly. 3 times the zero shear viscosity is the limit reached for infinitesimally slow rates of extension. However we show that the highest measured extensional viscosity for the bidisperse melts, which is also identical to the steady state viscosity, is up to 700% above $3\eta_0$ where the similar value for the monodisperse melts is 100%. This difference between mono- and bidisperse melts can be explained using a simple differential constitutive model that includes effects of finite extensibility of a dumbbell and anisotropic drag. Manfred Wagner et al.
8.3 Branched polymers

Branched polymer melts, for instance LDPE, are often described in the literature, and much data is available on these polymer types. Heike Bastian published in 2001 data for both the shearing and extensional properties of LDPE, and in 2003 Bach et al. reproduced Heike’s data using the filaments stretching rheometer on the same LDPE polymer. At the beginning of this Ph.D.-work I measured the extensional properties of a high molecular weight LDPE and saw that the transient extensional stress developed qualitatively differently to that of mono- and bidisperse polystyrene: the stress went through an overshoot in time followed by a steady plateau. This overshoot was assumed to be caused by a collapse of the arms of the LDPE at the branch points, but we could not explain this in terms of the molecular architecture of the polymer because the exact nature of the branching was not known. It was decided to synthesize well defined branched polystyrenes as model polymers using anionic polymerization. Two branched polystyrenes were made: an asymmetric star and a so called pompom, which is double star. The extensional properties of these two polymers were measured in the filament stretching rheometer and the existence of an overshoot was shown for the pompom, but steady state was not reached due to sample failure. The asymmetric star did not have an overshoot. The extensional data for the pompom and asymmetric star were analyzed for time-strain severability. In this method the linear viscoelastic contribution to the stress is filtered out, and a time-independent strain function for each transient data point is obtained. We found that the determined strain functions for the pompom collapsed onto one single curve, a behavior that was also seen in the LDPE-measurements. The interesting thing was that the linear polystyrenes and the asymmetric star did not obey time-strain severability. The conclusion is that the branched pompom behaves like a network in high extension, where the relaxation dynamics is linear viscoelastic whereas the relaxation dynamics of linear polystyrene in extension is highly non-linear.

8.4 New experimental techniques for characterization of polystyrene

One of the goals of this Ph.D. work is to use the filament stretching rheometer to observe how the stress relaxes after cessation of extensional flow. If a polymer melt is elongated 3 to 4 Hencky strain units and the motion of the end plates is then stopped, the filament diameter continues to decrease, meaning that the elongational flow is not stopped. This
problem was solved by using a closed loop control of the end plate motion to keep the filament diameter constant in the stress relaxation part of the experiment. To interpret the measurements we use a constitutive model that assumes that there are two contributions to the stress: a contribution from the orientation of the polymer chains and a contribution from the stretch of individual chain. In stress relaxation the stretch can be expressed by a stretch factor, $\lambda$, which is a scalar greater than unity, and is multiplied with the orientation part, which is found from the Doi and Edwards reptation model. The stress relaxation experiments were done on a linear polystyrene with a molecular weight of 145 kg/mol, PS145K, and the motion of the filament diameter was ceased after 3 Hencky strains of stretching, which is were the stress reached steady state. The stretch factor was calculated from each experiment and we find that the steady state values of $\lambda$ increase with elongational rate but during stress relaxation the stretch factors for each elongational rate converge to a universal envelope and continue towards unity. The stretch reaches unity after approximately one reptation time-unit, and we conclude that the effect of the stretch relaxes faster than the orientation in stress relaxation. The filament stretching rheometer was also repurposed to be able to measure the stress for a startup and reversing extensional-flow experiment for PS145K. The samples were all elongated 3 Hencky strains and we find that the recovery strain, where the stress changed sign, increase with increasing elongational rate, but reaches a maximum value of 1.45 Hencky strains, and even decreases at very high elongational rates.

8.5 Highly entangled polyisoprene

The extensional properties of a monodisperse polyisoprene melt with approximately 280 entanglements are measured. We use a new kind of rheometer, the "Extensional Viscosity Fixture", EVF, from TA instruments to measure over a wide range of elongational rates, and the results are compared with measurements done on the well known filament stretching rheometer at DTU. It is found that the results are the same within 20A low elongational rates sample failure occurs, which is both observed on the EVF and FSR rheometers. However at elongational rates larger than the inverse Rouse time the samples are stable and significant strain hardening is observed. We believe that we are seeing the onset of chain stretch, since the transition in extensional behavior occurs at the inverse Rouse time. The Rouse time is the characteristic time constant that describes chain stretch. This type of transition is not seen for monodisperse polystyrenes, and therefore future work in the field of extensional rheology of polymers melts should focus on understanding this.
8.6 Outline for future work

Most conclusions in this Ph.D. project are drawn from measurements on polystyrene, which we have used as model molecule. Polystyrene is synthesized by anionic polymerization, which is a favorable method because the obtained polymers have low polydispersities, and it is relatively easy to reach the desired molecular weight. The primary reason for using polystyrene, and not other polymer types, is its high glass transition temperature that is above room temperature. The filament stretching rheometer is equipped with heating elements, and works for temperature above room temperature. By measuring close to the glass temperature the extensional properties can be determined over a wide range of elongational rates varying up to a factor of $10^5$ using time temperature superpositioning. It could be very interesting to investigate if the conclusions made for polystyrene also apply for other polymer types, for instance polyisoprene or polybutadiene. First step would be to synthesize a number of polymers by anionic polymerization that have the same number of entanglements as the polystyrenes that Anders Bach and myself measured on. In order to measure at rates that are comparable to the ones performed on polystyrene, the measurements would have to be done at 30-70 degrees centigrade above the glass transition temperature of the particular polymer. For polyisoprene and polybutadiene this is below zero degrees centigrade. The previously described EVF rheometer is able to measure at sub zero temperatures, but only up to a Hencky strain of 3.8, and it does not give sufficiently accurate results because there is no control of the extension. The filament stretching rheometer in Lyngby is at the present time the most accurate extensional rheometer, and if it was equipped with a cooling mechanism, it could be used to measure at low temperatures, and compare the elongational results for polystyrenes with other polymer types having the same number of entanglements.

Bibliography


Appendices
A

Joint Author Statements
Joint author statement

If a thesis contains already published articles made in collaboration with other researchers, a joint author statement about the PhD-student's part of the article shall be made by each of the co-authors, cf. article 14, section 3 of the Ministerial Order No. 114 about the PhD degree.

Title of the article: Viscosity overshoot in the start-up of uniaxial elongation of low density polyethylene melts

Author(s): Henrik Kobliitz Rasmussen, Jens Kromann Nielsen, Anders Bach and Ole Hassager

Journal: Journal of Rheology

PhD-student: Jens Kromann Nielsen  Cpr.nr: 2206782873

Signature of the PhD-student: Jens Kromann Nielsen  Date: 24 January 2007

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Description of each author's contribution to the above-mentioned article:

Henrik Kobliitz Rasmussen:
Engaged in discussions about the results and wrote the first draft of the article manuscript.

Jens Kromann Nielsen:
Carried out the experimental work and post processing of the experiments.

Anders Bach:
Did preliminary stretching experiments, which were the inspiration of the article. The results are not presented in the article.

Ole Hassager:
Contributed to the article by supervising the first author and engaged in discussions about the results and the manuscript.
Joint author statement

If a thesis contains already published articles made in collaboration with other researchers, a joint author statement about the PhD-student's part of the article shall be made by each of the co-authors, cf. article 14, section 3 of the Ministerial Order No. 114 about the PhD degree

Title of the article: Viscosity overshoot in the start-up of uniaxial elongation of low density polyethylene melts

Author(s): Henrik Koblit Rasmussen, Jens Kromann Nielsen, Anders Bach and Ole Hassager

Journal: Journal of Rheology

PhD-student: Jens Kromann Nielsen

Signature of the PhD-student:

Co-author: Ole Hassager

Description of each author's contribution to the above-mentioned article:

Henrik Koblit Rasmussen:
Engaged in discussions about the results and wrote the first draft of the article manuscript.

Jens Kromann Nielsen:
Carried out the experimental work and post processing of the experiments.

Anders Bach:
Did preliminary stretching experiments, which were the inspiration of the article. The results are not presented in the article.

Ole Hassager:
Contributed to the article by supervising the first author and engaged in discussions about the results and the manuscript.
Joint author statement

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Title of the article: Elongational viscosity of monodisperse and bidisperse polystyrene melts

Author(s): Jens Kromann Nielsen, Henrik Koblitz Rasmussen, Ole Hassager and Gareth H. McKinley

Journal: Journal of Rheology

PhD-student: Jens Kromann Nielsen

Signature of the PhD-student: [Signature]

Co-author: Henrik Koblitz Rasmussen

Description of each author’s contribution to the above-mentioned article:

Jens Kromann Nielsen:
Carried out the experimental rheology work and did the post processing of the experiments and wrote the first draft of the article.

Henrik Koblitz Rasmussen:
Engaged in discussions about the results and the manuscript.

Ole Hassager:
Contributed to the article by supervising the first author and engaged in discussions about the results and the manuscript.

Gareth H. McKinley
Engaged in discussions about the results and the manuscript, and did the asymptotic analyses of the Wiest model.
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Title of the article: Elongational viscosity of monodisperse and bidisperse polystyrene melts

Author(s): Jens Kromann Nielsen, Henrik Kobliitz Rasmussen, Ole Hassager and Gareth H. McKinley

Journal: Journal of Rheology

PhD-student: Jens Kromann Nielsen

Signature of the PhD-student: Jens Kromann Nielsen

Date: 24 January 2007

Co-author: Ole Hassager

Description of each author’s contribution to the above-mentioned article:

Jens Kromann Nielsen:
Carried out the experimental rheology work and did the post processing of the experiments and wrote the first draft of the article.

Henrik Kobliitz Rasmussen:
Engaged in discussions about the results and the manuscript.

Ole Hassager:
Contributed to the article by supervising the first author and engaged in discussions about the results and the manuscript.

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Title of the article: Nonlinear Branch-point Dynamics of Multiarm Polystyrene

Author(s): Jens Kromann Nielsen, Henrik Kobitz Rasmussen, Martin Denberg, Kristoffer Almdal and Ole Hassager

Journal: Macromolecules

PhD-student: Jens Kromann Nielsen Cpr.nr: 2206782873

Signature of the PhD-student: Jens Kromann Nielsen Date: 23 January 2007

Co-author: Kristoffer Almdal Signature: [Signature]

Description of each author's contribution to the above-mentioned article:

Jens Kromann Nielsen: Carried out the experimental synthesis and rheology work, and did the post processing of the experiments and wrote the first draft of the article.

Henrik Kobitz Rasmussen: Engaged in discussions about the results and the manuscript.

Martin Denberg: Contributed to the synthesis of the pompom and asymmetric star.

Kristoffer Almdal: Contributed to the article by supervising the polymer synthesis work, and engaged in discussions about the results and the manuscript.

Ole Hassager: Contributed to the article by supervising the first author and engaged in discussions about the results and the manuscript.
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Author(s): Jens Kromann Nielsen, Henrik Koblitz Rasmussen, Martin Denberg, Kristoffer Almdal and Ole Hassager

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PhD-student: Jens Kromann Nielsen

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Description of each author's contribution to the above-mentioned article:

**Jens Kromann Nielsen:**
Carried out the experimental synthesis and rheology work, and did the post processing of the experiments and wrote the first draft of the article.

**Henrik Koblitz Rasmussen:**
Engaged in discussions about the results and the manuscript.

**Martin Denberg:**
Contributed to the synthesis of the pompom and asymmetric star.

**Kristoffer Almdal**
Contributed to the article by supervising the polymer synthesis work, and engaged in discussions about the results and the manuscript.

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Author(s): Jens Kromann Nielsen, Henrik Koblitz Rasmussen, Martin Denberg, Kristoffer Almdal and Ole Hassager

Journal: Macromolecules

PhD-student: Jens Kromann Nielsen  Cpr.nr: 2206782873

Signature of the PhD-student:  Date: 25 January 2007

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Description of each author’s contribution to the above-mentioned article:

Jens Kromann Nielsen:
Carried out the experimental synthesis and rheology work, and did the post processing of the experiments and wrote the first draft of the article.

Henrik Koblitz Rasmussen:
Engaged in discussions about the results and the manuscript.

Martin Denberg:
Contributed to the synthesis of the pompom and asymmetric star.

Kristoffer Almdal:
Contributed to the article by supervising the polymer synthesis work, and engaged in discussions about the results and the manuscript.

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Contributed to the article by supervising the first author and engaged in discussions about the results and the manuscript.
Joint author statement

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Title of the article: Nonlinear Branch-point Dynamics of Multiarm Polystyrene

Author(s): Jens Kromann Nielsen, Henrik Koblitz Rasmussen, Martin Denberg, Kristoffer Almdal and Ole Hassager

Journal: Macromolecules

PhD-student: Jens Kromann Nielsen

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Co-author: Henrik Koblitz Rasmussen

Description of each author's contribution to the above-mentioned article:

Jens Kromann Nielsen:
Carried out the experimental synthesis and rheology work, and did the post processing of the experiments and wrote the first draft of the article.

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Title of the article: Stress Relaxation of Narrow Molar Mass Distribution Polystyrene Following Uni-axial Extension

Author(s): Jens Kromann Nielsen, Henrik Kobliitz Rasmussen and Ole Hassager

Journal: Journal of Rheology

PhD-student: Jens Kromann Nielsen Cpr.nr: 2206782873

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Date: 24 January 2007

Co-author: Henrik Kobliitz Rasmussen Signature: [Signature]

Description of each author's contribution to the above-mentioned article:

Jens Kromann Nielsen:
Carried out the experimental work and post processing of the experiments and wrote the first draft of the article.

Henrik Kobliitz Rasmussen:
Engaged in discussions about the results and the manuscript.

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Title of the article: Stress Relaxation of Narrow Molar Mass Distribution Polystyrene Following Uni-axial Extension

Author(s): Jens Kromann Nielsen, Henrik Koblitz Rasmussen and Ole Hassager

Journal: Journal of Rheology

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Co-author: Ole Hassager Signature: 

Description of each author's contribution to the above-mentioned article:

Jens Kromann Nielsen:
Carried out the experimental work and post processing of the experiments and wrote the first draft of the article.

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Title of the article: Reversed extension flow of monodisperse polystyrene

Author(s): Jens Kromann Nielsen, Henrik Kobliitz Rasmussen

Journal: Physical Review E

PhD-student: Jens Kromann Nielsen Cpr.nr: 2206782873

Signature of the PhD-student: Jens Kromann Nielsen  Date: 24 January 2007

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Description of each author’s contribution to the above-mentioned article:

Jens Kromann Nielsen:
Carried out the experimental work and post processing of the experiments and wrote the first draft.

Henrik Kobliitz Rasmussen:
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