

Understanding and modelling the extensional rheology of nearly monodisperse linear polymers.

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*To my Parents
and my Wife*

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Preface

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- F. Zhuge, S. Costanzo, T. Shahid, CA. Fustin, JF Gohy, D. Vlassopoulos, E. van Ruymbeke, Shear and extensional rheology of entangled bulk polymers functionalized with metal-ligand coordination, Annual European Rheology Conference, AERC 2018, Sorrento, Italy, 17-20 April, 2018.
- **T. Shahid**, C. Clasen, F. Oosterlinck., E. van Ruymbeke, The fast flow dynamics of polymer melts and solutions: Is it possible to achieve a universal scaling?, BGR/DRG – Joint Symposium 2018: Rheology 360°, Luxembourg, 19-20 March, 2018.
- T. Shahid, C. Clasen, F. Oosterlinck., E. van Ruymbeke, Inviscid-elastic filaments of dilute polymer solutions - an analytical solution for breakup time predictions. 11th Annual European Rheology Conference, AERC 2017, Copenhagen, Denmark, 3-6 April, 2017.
- **T. Shahid**, C. Clasen, F. Oosterlinck., E. van Ruymbeke, Influence of the entanglements on steady elongational viscosity for monodisperse polymer melts and solutions, Annual meeting of the Society of Rheology, Tampa, USA, 12-16 February, 2017.
- **T. Shahid**, C. Clasen, F. Oosterlinck., E. van Ruymbeke, Constraint Release effect in Entangled Polymer Solutions,

Congrès Annuel du Groupe Français de Rhéologie, Lille, France, 25-27 October, 2016.

- **T. Shahid**, C. Clasen, F. Oosterlinck., E. van Ruymbeke, Modeling the extensional rheology of model entangled linear chains, 10th Annual European Rheology Conference AERC 2015, Nantes, France, 14-17 April, 2015.

Summary

In polymer processing industries, polymeric materials are melted, processed and then solidified. Consequently, the flow properties of polymers are very critical and play an important role during this processing phase and also in defining the final properties of the product. To ensure the best product quality, it is thus essential to be able to characterize and understand the flow behavior of these different polymeric materials, which can broadly be characterized as being polymer solutions to concentrated solutions and melts.

Generally, a flow field can be of two types: shear and elongational. Today, the linear shear properties of polymers are well understood and can be described at its molecular level. Thus giving us the opportunity to tailor its properties according to our needs by setting the right conditions. On contrary, our knowledge on the non-linear counterpart is still limited mainly due to experimental difficulties, which has been recently solved with the development of new experimental setups. With the help of such a device (VADER-1000), we have produced controlled and systematic datasets that we believe will be crucial in our quest of understanding the non-linear behavior of polymer under uniaxial elongational flow. First, we start by critically assessing the contemporary molecular pictures then propose our own theory that can correctly address the existing difficulties in predicting the non-linear properties. The results obtained in this work can be considered as an important step towards finding a long desired universal model. The outline of this thesis is described in the following.

In chapter 1, we start with a detailed state of art of extensional flow, where current experimental techniques and molecular theories are presented. Also, the biggest challenges that currently prevails in this field is addressed. Then a detailed study of the materials and the

experimental techniques used throughout this work is presented respectively in chapter 2 and 3. In chapter 2, the principal criteria of choosing the materials and basic thermal properties are discussed, while details on the experimental techniques and protocols are presented in chapter 3. Next, the experimental results are presented and discussed from chapter 4 to 9.

First in chapter 4, we discuss how different factors can influence the accuracy of the filament stretching measurements. With controlled experimental results, we demonstrate how crucial setting up the right experimental conditions; starting from the correct sample preparation technique to the precise experimental conditions can be. Finally, a benchmark study of the VADER - 1000 between two laboratories

(Technical University of Denmark and Université catholique de Louvain) is carried out to comment on the reproducibility and reliability of the measurements. Despite of some discrepancies, the results from two different groups were found to be in good agreement.

In chapter 5, we investigated the linear shear properties of different polymer solutions to address the taxing question about the correct value of the dilution exponent α in the relaxation of entangled polymers. In addition to a large set of literature data, we produced systematic polymer solution dataset where a long chain PS is diluted in oligomer styrene in various concentrations. Together with these experimental observations and an improved tube model we were able to show that the correct value of α will always be equal to unity and the higher value (~ 1.3) arises due to contour length fluctuations that lead to additional tube dilation relaxation in the dynamics of the long linear chain.

In chapter 6, we prepared and measured a series of PS blends to assess the well-known stretch-orientation induced friction reduction concept. In this work, we studied the extensional behavior of a long chain PS diluted in different short chains matrices, in order to systematically vary the interaction between these long chains and their molecular environment. The experimental results were found to be in contrary to the expected behavior in flow-induced monomeric friction reduction mechanism, thus raising several new interesting questions.

In chapter 7, in search of finding a universal behavior between polymer melts and solutions, we prepared and studied a series PS solutions diluted at different concentrations. By confronting both literature and our data, indeed we were able to obtain a universal scaling within the framework of original Doi & Edward's tube model i.e without considering any additional mechanism.

In chapter 8, we propose a simple molecular theory that can correctly predict the non-linear extensional properties of polymer melts without considering any additional mechanism or criteria. According to our theory, both orientation and stretching of polymer chains can lead to significant strain hardening behavior. As one would expect, orientation of polymer chains is important at moderate flow while at high rates stretching dominates.

In chapter 9, we present an analytical solution for the evolution of the polymer stretch in an inviscid solvent base on the FENE-P model that allows us to quantitatively predict the breakup time of inviscid-elastic filaments. Predictions of this model are then compared successfully to experimental results for a number of model polymer solutions that span the relevant range of intrinsic Deborah and Elastocapillary numbers for actual applications.

Finally, we conclude the thesis with the major outcomes and future perspectives in chapter 10.

List of abbreviations

Ca	Capillary number
CaBER	Capillary Breakup Extensional Rheometer
CLF	Contour Length Fluctuations
CCR	Convective Constraint release
CR	Constraint Release
CR-CLF	Constraint Release activated Contour Length Fluctuations
CRR	Constraint Release Rouse
CS	Chain Stretching
DCR-CS	Double constraint release with chain stretch
DE	Doi-Edwards
DEMG	Doi-Edwards-Marrucci-Grizzuti model
DEP	DiEthyl Phthalate
DOP	DiOctyl Phthalate
DR	Double Reptation
DSC	Differential Scanning Calorimetry
DTD	Dynamic Tube Dilution
EC	Elasto-Capillary
EHP	Electrically heated plate
EVF	Extensional Viscosity Fixture
FENE	Finitely Extensible Non-linear Elastic
FFF	Field Flow Fractionation
MALS	Multi-Angle Light Scattering
NLVE	Non-linear Viscoelasticity
FiSER	Filament Stretching Extensional Rheometer
FSR	Filament Stretching Rheometer
GLaMM	Graham, Likhtman and Milner, McLeish model
IC	Inertia-Capillary
ICP	Inter-Chain Pressure

IV	Inertial-Viscous
LDPE	Low Density PolyEthylene
LVE	Linear Viscoelasticity
MALS	Multi-angle light scattering
MFI	Melt flow index
MHS	Mark-Houwink-Sakurada
MLD	Mead-Larson-Doi model
MSF	Molecular Stretch Function
NLVE	Non-Linear Viscoelasticity
OS	Styrene Oligomer
PBD	Polybutadiene
PDI	PolyDispersity Index
PEO	Polyethylene Oxide
PS	PolyStyrene
SAOS	Small Amplitude Oscillatory Shear
SEC	Size Exclusion Chromatography
SER	Sentmanat Extension Rheometer
SH	Strain Hardening
SORF	Stretch-Orientation induced Reduction in Friction
TGA	ThermoGravimetric Analysis
THF	Tetrahydrofuran
TMA	Time Marching Algorithm
TTS	Time Temperature Superposition
WLF	Williams–Landel–Ferry

List of symbols

Symbol	Description	Units
a	Mark-Houwink exponent	[-]
a_0	Initial width	[m]
	Initial tube diameter	[m]
a_T	WLF shift factor	[-]
$a(t)$	Width at time t	[m]
	Tube diameter at time t	[m]
A	Conformation tensor	[-]
A_{rr}	Radial normal chain conformation	[-]
A_{zz}	Axial normal chain conformation	[-]
b	Finite extensibility parameter	[-]
c	concentration	[wt%]
c^*	critical overlap concentration	[wt%]
C_∞	Characteristic ratio	[-]
d	Distance	[m]
De	Deborah number	[-]
D_e	Diffusion coefficient	[m ² /s]
D_0	Initial diameter	[m]
$D(t)$	Diameter at time t	[m]
D_{mid}	Mid-filament diameter	[m]
f	Frequency	[Hz]
Ec	Elasto-capillary number	[-]
F	Force	[N]
F_T	Tensile force in the thread	[N]
g	Gravitational acceleration	[ms ⁻²]
G	Elastic modulus	[Pa]
G^*	Complex modulus	[Pa]
G'	Storage modulus	[Pa]

G''	Storage modulus	[Pa]
$G_{\text{Rouse}}, G_{\text{R}}$	Rouse modulus	[Pa]
G_N^0	Plateau modulus	[Pa]
H	Dumbbell spring constant	[-]
h	Dimensionless filament radius	[-]
j	Number of bonds of a polymer monomer	[m]
k_B	Boltzmann constant	[J/K]
$K_{[\eta]}$	Mark-Houwink parameter	[Pa.s ⁿ]
L	Sample length	[m]
	Finite extensibility parameter	[-]
L_0	Initial gap between the plates	[m]
	Initial length	[m]
L_1, L_f	Final gap between the plates	[m]
$L(t)$	Length at time t	[m]
$L_{\text{eq}}, L_{\text{PP}}$	Primitive path of a test chain	[m]
$L_{\text{eq-CR}}$	Reduced primitive path due to CR	[m]
L_{max}	Maximum attainable length	[m]
$L_p(t)$	Maximum length between parallel plates	[m]
m	Mass	[kg]
M_e	Molar mass between entanglements	[kg/mol]
M_u	Molar mass of a monomer	[kg/mol]
M_n	Number average molecular weight	[kg/mol]
M_w	Weight average molecular weight	[kg/mol]
$M_{w, \text{matrix}}$	Molecular weight of the matrix	[kg/mol]
N	Number of sub-chains	[-]
	Number of Kuhn segments/modes	[-]
Oh	Ohnesorge number	[-]
Oh^*	Critical Ohnesorge number	[-]
p_{rept}	Survival probabilities of a chain by reptation	[-]
$p_{\text{CR-CLF}}$	Survival probabilities of a chain by CR-CLF	[-]
Q	Flow rate	[ml/s]
Q_0	Chain length of dumbbell (fully stretched)	[Å]
Q_{eq}	Equilibrium length of a polymer coil	[Å]
$\underline{R}$	End-to-end distance	[]

R	Radius	[m]
R	Gas constant	[JK ⁻¹ mol ⁻¹]
R_0	Initial radius	[m]
R_g	Radius of gyration	[m]
Re	Reynolds number	[-]
S	Surface area	[m ²]
t	time	[s]
t_b	Break-up time of a filament	[s]
t_R	Breakup time of the inertial filament	[s]
t_η	Viscous time scale	[s]
t_R	Rayleigh time	[s]
t_v	Viscous breakup time	[s]
T	Absolute temperature	[K]
	Stress tensor	[Pa]
T_m	Melt temperature	[°C]
T_g	Glass transition temperature	[°C]
T_{ref}	Reference temperature	[°C]
Wi	Weissenberg number	[-]
x_i	Normalized coordinate of a chain segment	[-]
x_{fat}	CLF of a molecular segment	[-]
z	Axial coordinate	[m]
Z	Correction term in FENE model	[-]
	Number of entanglements	[-]
Z_L	Entanglements formed by long-long chains	[-]
Z_S	Entanglements formed by short-short chains	[-]

Greek symbols

Symbol	Description	Units
α	Dynamic dilution exponent	[-]
	Power-law exponent	[-]
$\dot{\gamma}$	Shear rate	[1/s]

γ	Surface tension	[N/m]
δ_s	Solubility parameter	[-]
$\Delta\tau_p$	Elastic stress	[Pa]
ϵ_H	Hencky strain	[-]
$\dot{\epsilon}$	Extension rate	[1/s]
ζ_0	Monomeric friction of a chain	[N]
ζ_0	Total friction of a chain	[N]
η	Dynamic viscosity	[Pa.s]
	Shear viscosity	[Pa.s]
$[\eta]$	Intrinsic viscosity	[ml/g]
η^*	Complex viscosity	[Pa.s]
η_E, η_{el}	Extensional viscosity	[Pa.s]
η_s	Solvent viscosity	[Pa.s]
$\bar{\eta}_{st}$	Steady elongational viscosity	[Pa.s]
η_0	Zero shear viscosity	[Pa.s]
$\bar{\eta}_+$	Transient elongational viscosity	[Pa.s]
θ_b	Average bond angle	[-]
κ	Mean curvature of the filament	[1/m]
Λ	Aspect ratio	[-]
λ	Relaxation time	[s]
	Stretch factor	[-]
ρ	Density	[kg/m ³]
σ	Stress	[Pa]
σ_{rr}	Radial normal stress	[Pa]
σ_{st}	Steady elongational stress	[Pa]
σ_{zz}	Axial normal stress	[Pa]
τ	Relaxation time	[s]
	Dimensionless time	[-]
τ_a	Tube diameter relaxation time	[s]
τ_d, τ_{rept}	Reptation time	[s]
τ_e	Relaxation time between two entanglements	[s]
τ_{obs}	Average lifetime of a short-long entanglement	[s]
τ_p	Relaxation time of a sub-chain	[s]

$\tau_R, \tau_{\text{Rouse}}$	Rouse relaxation time	[s]
τ_{rel}	Terminal relaxation time	[s]
τ_s	Stretch relaxation time	[s]
τ_0	Kuhn segment relaxation time	[s]
τ_{Zimm}	Zimm relaxation time	[s]
ν	Volume fraction	[-]
ϕ	Volume fraction	[-]
ϕ'	Survival fraction of a tube	[-]
χ	Interaction parameter	[-]
ω	Angular frequency	[rad/s]

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Chapter 1

Introduction

1.1 Background

Since the earliest days of civilization, mankind has shown distinguishing features that separated them from the other kinds. One of them is the ability to use and develop materials to satisfy their needs. Human civilization has seen practice of different materials in different ages. When nature stopped providing options, they opted for their own creation thus leading to invention of polymers. This modern era has seen metals been taken over by polymers, thus forming “the age of polymers”.

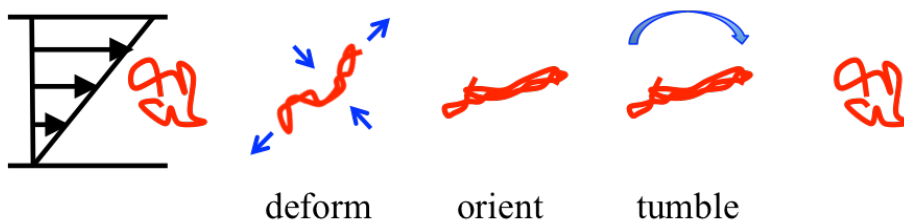
As one would expect, this contributed to the birth of polymer industries all over the globe. Over the past century the world has seen a massive growth and improvement in this industry, which led to development of a versatile product that has taken over all sectors from clothing to shelter, from transportation to communication and from entertainment to health care. However, these polymers inherently exhibit complex dynamics and rheology, which in turn affects the processing and final properties of the finished products. Understanding this complex rheological behavior as a function of molecular chemistry would enable us to overcome many complications that are currently confronted in industries. But there are limits to the human ability to understand complex systems. So often, we use simplified representational models to aid our understanding. For example, the simplest model to realize polymer chains are the bead-spring or dumbbell model, which assumes the polymer chain is represented by a series of beads connected by springs.

Generally, these representational models are based on previous scientific knowledge and advancing experimental measurements and observations. Only then it can be used to make predictions and explain future phenomena. As it stands today, the slow flow dynamics (linear behavior) of polymeric materials are very well understood, whereas the fast flow dynamics (non-linear behavior) is still unsolved, particularly due to the lack of experimental evidences. Measuring the fast flow dynamics of polymers reliably in a laboratory circumstances has proven to be very challenging. In the next section, the different kinds of flow involved in polymer processing as well as the difficulties in measuring these flow properties (non-linear) are discussed very briefly.

1.2 Different flow types

In industrial polymer processes, polymers mostly encounter a combination of shear and extensional flows. Both these flows can be classified by the relative amount of stretch versus rotation; rotational flows are weak and unable to deform microstructure whereas stretching flows are strong and may deform the microstructure (depending on the magnitude).

Polymer chain in shear flow = deform, orient and tumble.



Polymer chain in extensional flow = deform and may stretch out.

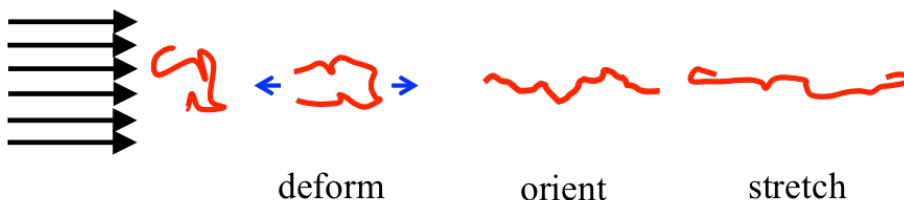


Fig. 1.1 Polymer coils under a) shear & b) extensional flow.

Shear flow is a combination of stretch and rotational flow. While the stretch component causes polymer chain to orient in the direction of flow and deform, the rotational component forces the polymer chain to tumble thus suppresses the stretch of polymer chain. On the contrary, extensional flow is purely stretching flow and given the magnitude of the flow is high, the polymer chain will stretch out as shown in Fig. 1.1 b). Understandably, polymers will exhibit different characteristics under these different flow conditions. And rheology can be a useful tool in realizing this difference. For example^{1a}, shear rheology of Boger fluids (small amount of high M_w polymer dissolved in viscous solvent) exhibit newtonian behavior (linear) whereas the extensional rheology shows prominent thickening behavior (non-linear).

So far in literature, the shear rheology (linear properties) of polymers has been studied extensively with help of commercially available shear rheometers. Consequently, molecular models could be developed which predict these properties at a quantitative level. On contrary, the extensional rheology (non-linear properties) is still not well understood largely due to scarcity of experimental data. Unlike shear, extensional flow is extremely difficult to realize and measure reliably at a laboratory scale. To generate a 'pure extensional flow', the polymer test fluid needs to be 'gripped' and actively pulled meaning extensional flows do not have 'closed' streamlines which can be accomplished with simple shear flow when rotational devices are used. Furthermore, 'gripping' the test fluid will lead to an interaction between the fluid and a solid interface (the geometry) ultimately introducing a shear component, which gives problems to generate a pure extensional flow. Also, in extensional flow the test fluid needs to be separated exponentially in time under constant strain rate. Thus extensional rheometers require the capability to produce much larger deformations to the test fluid in a short time than shear rheometers under some controlled manner (e.g. constant strain rate).

Lastly, different rheometer/setup is needed to measure different types of samples. For example, it's possible to grip high viscous sample and actively pull them apart but not for low viscous samples due to their high mobility. So different techniques had to be developed to measure low viscous polymers.

1.2.1 Definition of extensional flow

There are three types of pure extensional flows that are commonly applied in rheological measurements: uniaxial extension, biaxial extension and planar extension. Uniaxial extension, also known as simple extensional or elongational flow, comprises an extensional deformation along one axis and a contraction along the other remaining axes due to mass conservation (see Fig. 1.2). This flow type occurs near the centerline of flow in fiber spinning.

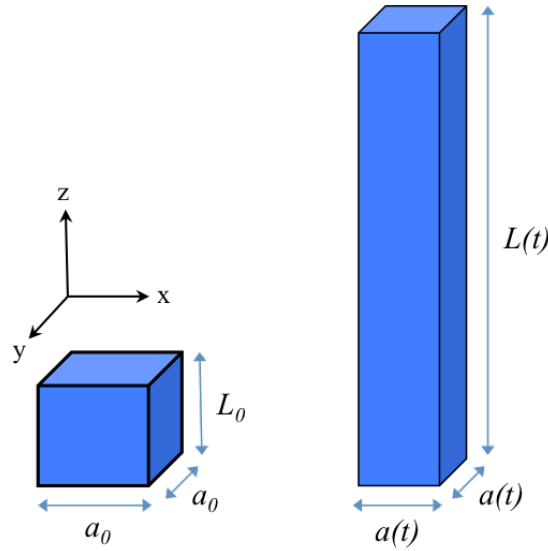


Fig 1.2: Illustration of Uniaxial extension.

Planar extension consists of an extensional deformation along one axis and contraction in the second while the third axis remains unchanged. This flow has gained the attention of experimentalists since constraining one direction of the flow makes the experiment somewhat easier. This type of extension occurs in cross-channel dies and in a four-roll mill apparatus. Biaxial extension is the inverse of a uniaxial extension and comprises of an extension along two axes while the contraction occurs along the remaining axis. This flow type may be produced by squeezing a sample between 2 lubricated surfaces. This thesis concerns only the uniaxial extension, which is the most frequently reported extensional flow in experiments; hence the other two types are not discussed further.

A common way to describe an extensional deformation is by the engineering strain or Cauchy strain, ε_c (for smaller deformations), which is defined as the ratio of increase in the length, ΔL to the initial length, L_0 . While for larger deformations ($\Delta L \gg L_0$), the Cauchy strain is replaced by the Hencky strain,

$$\varepsilon_H = \ln \left(\frac{L(t)}{L_0} \right), \quad (1)$$

where, L_0 is the initial length and $L(t)$ is the length at time, t . For an incompressible fluid, ε_H can be obtained from the change in diameter as well,

$$\varepsilon_H = -2 \ln \left(\frac{D(t)}{D_0} \right), \quad (2)$$

where, D_0 and $D(t)$ are the initial and the length at time t , respectively.

1.2.2 Importance of extensional rheology

In many industrial processes and applications, polymeric materials undergo flows, which are dominated by the extensional component. For example, in inkjet printing process, the extensional flows appear in three forms:

- a) First, the fluid undergoes a contraction flow (along the nozzle),
- b) Second, an uniaxial extension occurs when the jet is formed,
- c) Finally, a biaxial extension ensues when the drop impacts against the surface of the paper.

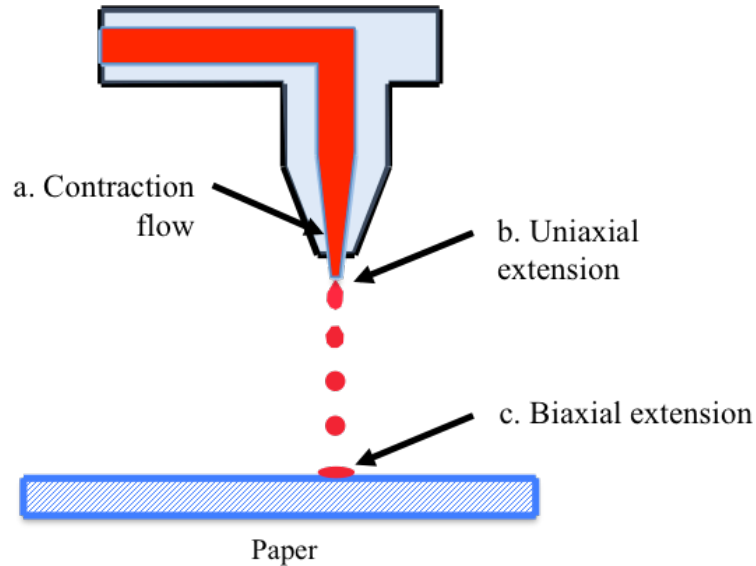


Fig 1.2: Extensional flows during inkjet printing process.

Consequently, characterization of these materials is necessary to accurately model and predict the processing/application conditions that will lead to optimum final properties of the finished product. And rheology can and has been used as an ideal tool to characterize these materials. For example, back in 1979, Meissner^{1b} reported the film blowing performance of three different LDPE resins of which two performed identically while the third one could not be processed. All three resins exhibited similar simple shear flow characteristics like the melt flow index (MFI) and the zero shear viscosity, η_0 . However, the extensional stress growth behavior showed distinctly different behavior, which later was attributed to the differences in the degree of long chain branching in these LDPEs. Apparently, subtle changes in molecular architecture like branching or presence of a high molecular weight tail in the distribution can easily influence the extensional properties with insignificant difference in the shear.

1.3 A brief history of extensional rheometers

First effort to quantify extensional properties came back in early 19th century, when an Irish physicist, Trouton² attempted to measure the viscosity of a highly viscous liquid with his own experimental setup

named the stretching of a uniform cylinder. Upon success, he established both experimentally and theoretically that a ratio of 3 exists between uniaxial extensional viscosity η_E and shear viscosity η for a simple Newtonian fluid. This relationship was later named as the “Trouton ratio”. Few years later, another pioneer in extensional flow Fano³ conducted an intensive study on the spinnability of materials. In order to determine a connection between viscosity and the thread-forming ability, he tested a wide range of materials. His name is now associated with the experimental arrangement he envisioned: the Fano flow or tubeless syphon.

During the next few decades, different polymer processing techniques were introduced in the industry fueled by the rapid growth of polymer usage. A number of these techniques involved polymers undergoing elongation deformation thus generating a common interest on this particular flow type. As a result, a number of articles concerning the extensional behavior of polymer suspensions and melts emerged. During this time, a lot of different techniques were developed, majorly focusing on molten polymers, some of which are still being used today. On the contrary, progress on measuring the less viscous samples (solutions) was relatively slower as the ‘mobile fluids’ were difficult to be placed in an extensional flow. Owing to its high mobility, these less viscous samples were difficult to grip and pulled actively, thus leading to development of new measuring techniques particularly for polymer solutions. But even at present it remains a very challenging subject.

In the next section, the evolution of different extensional measuring techniques is discussed very briefly.

1.3.1 High viscous liquids in extension

a) Rotating clamps rheometer, RME:

The first set of reliable and accurate extensional measurements of polymer melts was done with the rotating clamps rheometer also known as the Meissner device. This rheometer was originally developed by Meissner⁴ at the BASF and further improved by Laun and Münstedt⁵.

Extensional rheometers: high viscous liquids

According to this setup, a horizontal rectangular sample is placed between two “rotary clamps”, which consist of pairs of gears. Then, the sample (between the clamps) is stretched by rotating the clamps in opposite directions. During this whole process, the length of stretched sample remains constant with time as the velocity at each clamp. Assuming there is no slip between the clamp and the sample, this arrangement generates a constant Hencky strain rate between the clamped ends of the sample. To avoid gravitational sagging, the sample is supported by a fluid bath like silicone oil.

In the original device, the rotary clamp consisted a pair of gear like tooth wheels, which was later substituted due to necking instabilities by sets of metal bands that operate like tank treads. The fluid bath was also replaced by a gas cushion thus removing constrain on the maximum temperature⁶. Furthermore, a video camera was placed to aid in determining the true strain rate. The commercialized version of this device is known as the Rheometrics-Melt Extensometer or RME. A schematic diagram of the improved RME is shown in fig. 1.3.

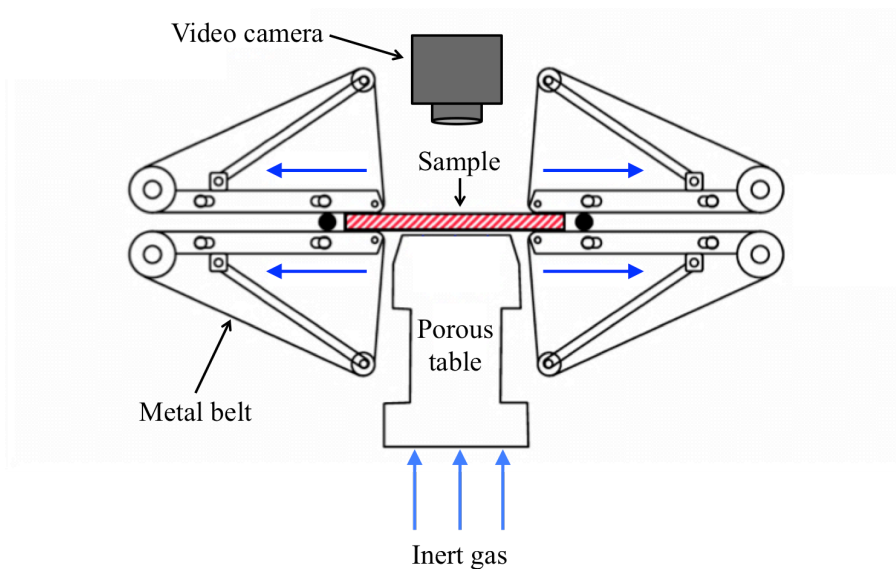


Fig 1.3: Schematic diagram of rotation clamps rheometer.

The main advantages and disadvantages of this device are listed below,

Advantages:

- Smaller apparatus,

- High attainable hencky strain ($\varepsilon_H \sim 7$),
- No oil bath: large temperature range,
- No necking instability.

Disadvantages:

- Limited strain rate ($<1 \text{ s}^{-1}$),⁷
- Low sensitivity of force transducer,
- Sample often slips from the belt,
- No longer commercially available.

b) The Münstedt tensile rheometer, MTR:

Another device that accurately measures the uniaxial extensional properties of polymer melts is the Münstedt tensile rheometer (MTR)^{8,9}.

In this device, the sample is glued to two metal plates with the lower one being mounted on a force transducer and the upper metal plate is connected to a pull rod, which is vertically displaced by a toothed belt driven by a motor. The specimen is then pulled vertically in a cylindrical oil bath, which supports the sample. Both the sample and the transducer are immersed in the oil bath. Due to its working principle, the MTR is also referred as an end-separation type of instrument.

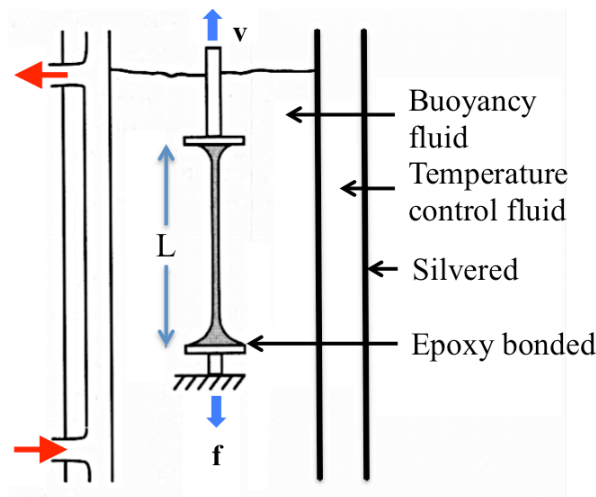


Fig 1.4: Schematic diagram of Münstedt tensile rheometer.

Extensional rheometers: high viscous liquids

The main advantages and disadvantages of this device are listed below,

Advantages:

- Moderate attainable strain rates ($\dot{\epsilon} \sim 5 \text{ s}^{-1}$),
- Limited but controlled temperature range,

Disadvantages:

- Large apparatus,
- Necking instability,
- Limited maximum temperature,
- Not commercially available (home-build device).

The modern filament stretching devices are based on similar working principles as this instrument.

c) Rotating cylinder setup, SER & EVF:

The rotating cylinders setup is based on the concept of Meissner's device and stretches the sample within a confined space by means of two rotating cylinders (instead of clamps).

The rotating cylinder rheometer was originally developed as the Sentmanat Extension Rheometer^{10,11} (SER), which consists of two counter-rotating drums upon which a rectangular sample is wound. The ends of the sample are clamped to the drums by means of securing clamps. The counter-rotating motion of the drums then stretches the sample between the clamps with a constant strain rate. The response from the sample (force measurements) is determined from the torque exerted by the drums. One of the problems with this setup is that the force measurements and deformation are not decoupled. Therefore, the sample response could be affected by the friction contributions leading to high level of noise. A schematic view of the Sentmanat extensional rheometer (SER) is shown in fig. 1.5.

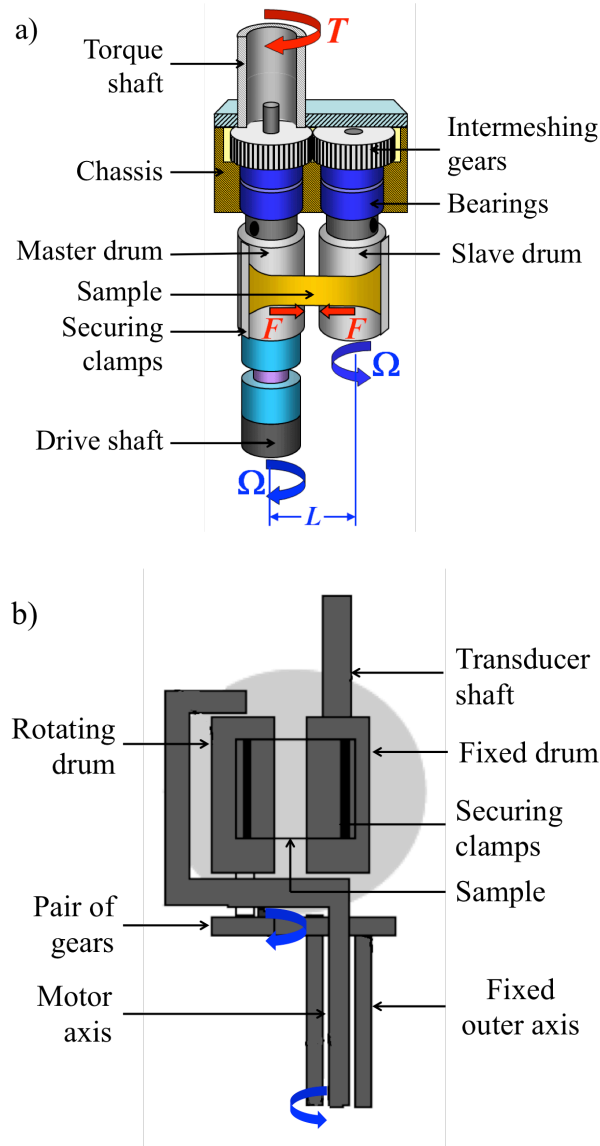


Fig 1.5: Schematic diagram of Rotating cylinder rheometer. a) Sentmanat Extension Rheometer, b) Extensional Viscosity Fixture

In a later version of the rotating cylinder rheometer, this problem was solved by decoupling the deformation of the sample and force measurements. The setup is known as the extensional viscosity fixture (EVF). In this setup, the rectangular sample was stretched by a single rotating cylinder while the other cylinder was used to measure the

force. In order to wind up the sample equally on both sides, the rotating cylinder moves on a circular orbit around the force-measuring cylinder while rotating around its own axis at the same time. However, the disadvantage with this setup is that the sample deformation cannot be visualized during the experiment; hence optical measurements are not possible during the stretching of sample (attainable with the SER setup).

The main advantages and disadvantages of both rotating cylinder rheometers are listed below,

Advantages:

- Small apparatus,
- Entire device can be mounted on a standard shear rheometer (SER on Anton Paar & EVF on ARES).
- High attainable strain rates (10 s^{-1}).

Disadvantages:

- Low viscous samples can't be measured due to gravitational sagging,
- Limited Hencky strain ($\epsilon_H < 4$).

This rotating cylinder setup has been used extensively to study the uniaxial extensional behavior of polymer melts and elastomers. But its use has been restricted due to its limited attainable Hencky strain. Especially in studies, where the steady state viscosity is needed. In general a steady state viscosity is reached around a hencky strain of 4.

d) Filament stretching rheometer, FSR, FiSER, VADER:

The problem of limited Hencky strain can be overcome with an end-separation type of instrument generally termed as the filament stretching rheometer¹²⁻¹⁴ (FSR). There are different versions of this device built in different laboratories across the globe. Most of them are home-built with the only exception is the lab at DTU, Denmark who very recently commercialized a miniature version of their filament stretching rheometer naming it the Versatile Accurate Deformation Extensional Rheometer, VADER. A common schematic diagram of FSR is shown in fig. 1.6.

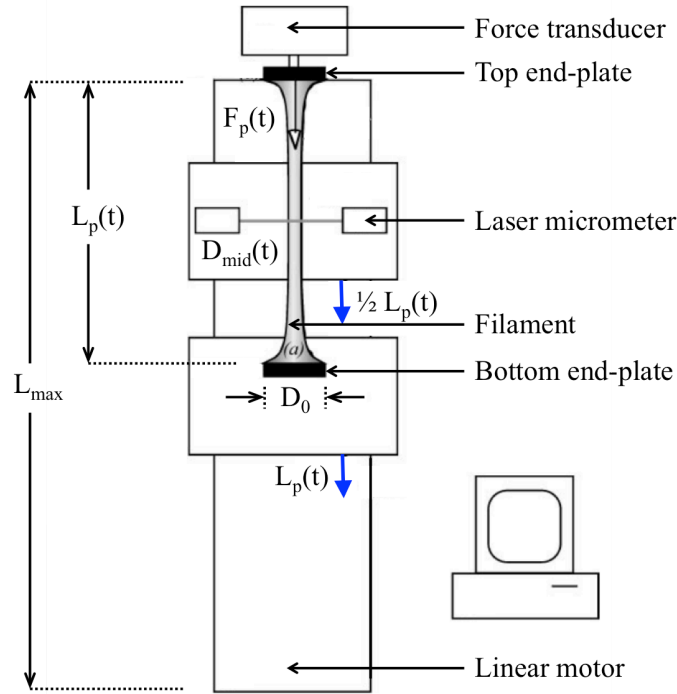


Fig 1.6: Schematic diagram¹⁵ of Sentmanat Extension Rheometer.

A polymeric fluid bridge (filament) is established between two cylindrical parallel metal plates. Similar to MTR, one plate is at stationary and connected with the force transducer while the other plate stretches the filament vertically via a motor. A laser micrometer measures the minimum diameter at the middle of the filament. An active feedback loop enforces the moving plate to accelerate and impose a constant strain rate at the middle (minimum diameter) of the filament.

The main advantages and disadvantages of this device are listed below,

Advantages:

- High attainable strain rates ($\sim 5 \text{ s}^{-1}$),
- High attainable Hencky strain (~ 7),
- Different range of samples can be measured,

Disadvantages:

- Large apparatus,

- Necking instability.

In this Ph.D. project, extensional rheometer, VADER has been used extensively. Details of this rheometer is further discussed in chapter 3.

1.3.2 Low viscous liquids in extension

Measuring low viscous samples (solutions) has proven to be more challenging as they are difficult to place in an extensional flow. The extensional rheometers discussed so far can't be used to 'grip and pull' these 'mobile fluids'. Thus leading to development of new measuring techniques for polymer solutions.

a) Opposed Nozzles:

Opposed nozzle^{16,17} was a commercially available device used for measuring very low viscous samples ($\sim 0.01 \text{ s}^{-1}$). In this setup, two opposite nozzles are mounted on rigid arms as shown fig. 1.7. One nozzle arm is fixed whereas the other arm can rotate around a pivot. During the experiment, liquid can be either drawn into the nozzles or forced out of the nozzles by means of a twin syringe pump. The resulting stagnation flow generates a uniform uniaxial or biaxial extensional field.

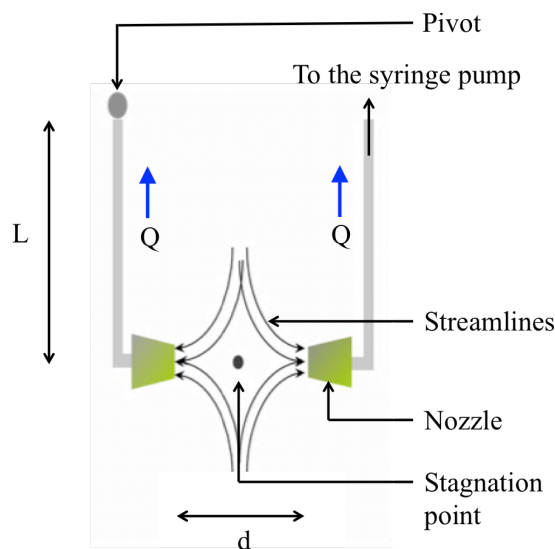


Fig 1.7: Schematic diagram of opposed nozzle device.

The main advantages and disadvantages of this device are listed below,

Advantages:

- High extensional rates ($\sim 10^3 \text{ s}^{-1}$),
- Only low viscosity device that controls rate,
- Easy sample preparation.

Disadvantages:

- Non-homogeneous flow,
- Large sample volumes ($\sim 250 \text{ mL}$),
- Limited viscosity range ($0.01\text{-}1 \text{ s}^{-1}$),
- Combination of shear and extension,
- No longer commercially available.

b) Four roll mill:

The four roll mill^{18,19} was originally invented to study the deformation and breakup of fluid drops. This classical fluid mechanics device can generate a homogenous two dimensional extensional flow and has been used in experimental investigations of a wide range of physical phenomenon. This device is excellent for visualization measurements (morphology, stream lines) and for optical experiments (birefringence, etc.) but not useful for mechanical measurements.

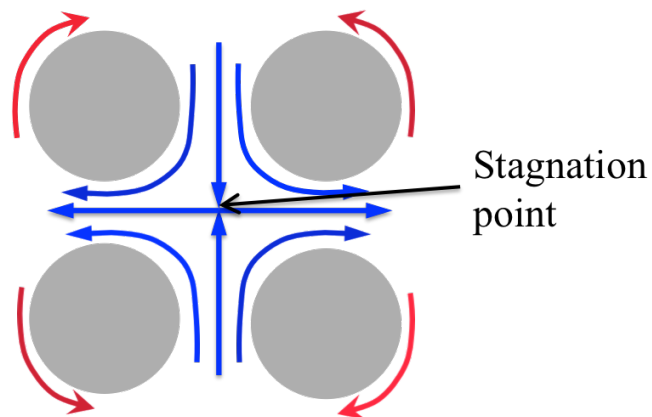


Fig 1.8: Schematic diagram of four roll mill device.

History of extensional rheometers: low viscous liquids

This device consists of four cylindrical rollers that rotate inside a container filled with the test fluid. The axes of the cylinders are parallel and symmetrically arranged in a square configuration. A broad class of homogenous two-dimensional flow can be obtained by varying the rotational direction of the rollers.

The main advantages and disadvantages of this device are listed below,

Advantages:

- Pure ‘homogenous’ extensional flow,
- Excellent for visualization and optical measurements.

Disadvantages:

- Not useful for mechanical measurements.

c) Capillary Breakup Rheometry (CaBER):

Capillary Breakup Extensional Rheometer (CaBER) is a commercially available rheometer, which is commonly used to measure the extensional properties of very diluted polymer solutions.

In a CaBER measurement, a liquid sample is placed between two circular parallel plates to form a cylindrical liquid bridge. Consequently, the sample is stretched with an exponential profile and stopped at a final length, L_f . The surface tension causes the sample to thin, which is monitored by either a laser micrometer or a camera. The breakup dynamics of the filament can be used to measure important extensional characteristics such as the breakup time or an apparent extensional viscosity.

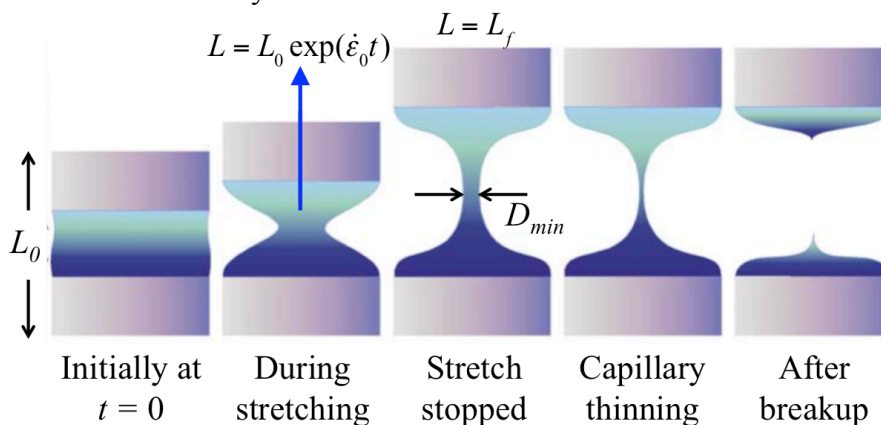


Fig 1.9: Schematic diagram of CaBER.

The main advantages and disadvantages of this device are listed below,

Advantages:

- Small sample volume required,
- Very rapid tests,
- Most used technique in industries.

Disadvantages:

- No direct force or stress measurement,
- No temperature control,
- Extensional strain rate isn't controlled.

In this Ph.D. project, the breakup dynamics of diluted solutions are studied with this device. So details on the functionality of this rheometer are further discussed in chapter 3.

Despite the recognized need for extensional measurements of polymer solutions, the development of instrumentation has proceeded slowly due to several challenges discussed previously. As a result, this subject remains an area of active research.

However, in last few years the group of Hassager has presented a large set of extensional data of linear polymers in melts^{12, 34} and concentrated solutions^{32,33} state using there home-build device, FSR. On the other hand, Sridhar and coworkers^{35, 36} also proposed a series of reference data, for very well diluted but still well entangled linear polymers. These data sets are now used as reference to spread our understanding to the fast flow dynamics, or in particular to non-linear uniaxial extensional flow. Models that are currently used to predict these properties are discussed in the following section.

1.4 Overview of models in rheology

In science, we often use models to represent complex systems. Use of these representational models is twofold; it helps us visualize a complex system and allows us to understand it in depth. Moreover, the system's future behavior can be predicted and tailored if needed, thus being both time and cost effective.

So far in rheology, different types of models have been used to predict the viscoelastic properties of polymers. They range from empirical to semi-empirical and phenomenological models. Some of them can partially or closely describe the complex rheological behaviour of fluids. However, due its nature these models don't take into account the physical origin of viscoelasticity and consequently, it's difficult to explain why they work and fail for specific cases. For example, Giesekus model explains the behaviour of polymers very well in shear flow but totally fails in elongational. Similarly, Maxwell model can predict the behaviour of linear polymer at low Deborah number but fails for high Deborah number.

Thus it's important to follow the molecular approach and build better models, which takes into account the physical origin of viscoelasticity. This approach is called molecular rheology and has been recently developed for polymers. A classification of different models used in rheology is shown in chart 1,

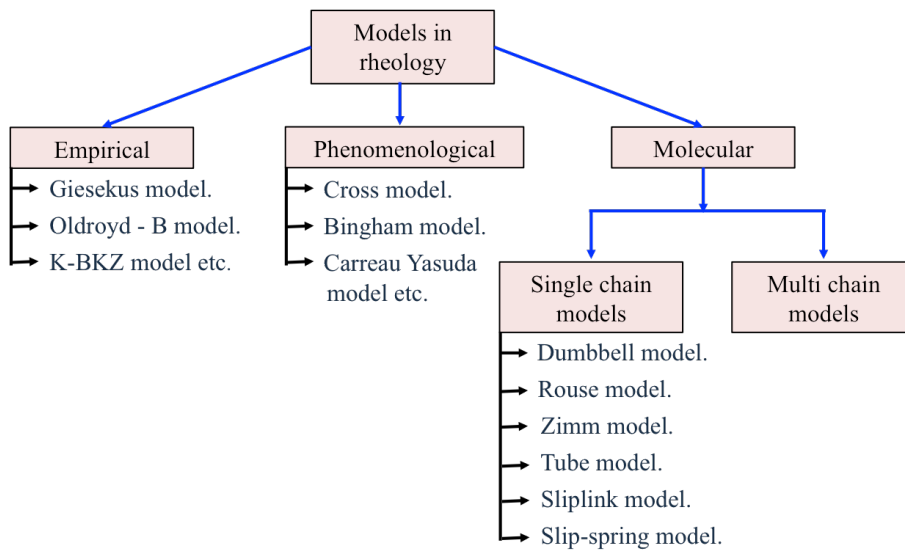


Chart 1. Classification of models in rheology.

In this Ph.D. project, we are focusing on the molecular approach and particularly on the tube model. Therefore in the next section, the focus will be mostly on the 'tube model'. Originally proposed by de Gennes²⁰ and Doi-Edwards²¹, the tube model is based on reptation of

entangled chains and so far can quantitatively predict the linear viscoelasticity of linear polymers.

1.5 Molecular models: linear chains

Different molecular models have been used in literature to describe the dynamics of linear chains. The simplest model, which can represent a single polymer chain, is the dumbbell model. At the next level of complexity, a polymer chain can be considered as an assembly of dumbbells where each dumbbell represents a Kuhn segment. This level of treatment is known as the Rouse model²² and is particularly important for describing chain dynamics at short times i.e before the system start to realize entanglements. For entangled systems however, it gets complex and more detailed theory such as the tube model has to be considered. This model is based on Edward's idea where, a 'tube' is considered around a single chain to represent the topological constraints exerted by the environment on this test chain. The tube localizes the movement of the chain prohibiting its lateral motion beyond a characteristic length scale (the tube diameter) thus allowing it to relax its configuration only by diffusing along the tube axis (reptation). Later, additional relaxation mechanisms were included in this model to reach quantitative predictions.

1.5.1 Unentangled polymer dynamics: The Dumbbell model

Polymer chains are entropic objects. In order to retain its maximum entropy, the ideal shape for a polymer chain is the random coil shape. As shown in figure 1.10 a), the random coil is not at static but always in Brownian motion. So it can take many possible configurations while keeping the end to end distance fixed.

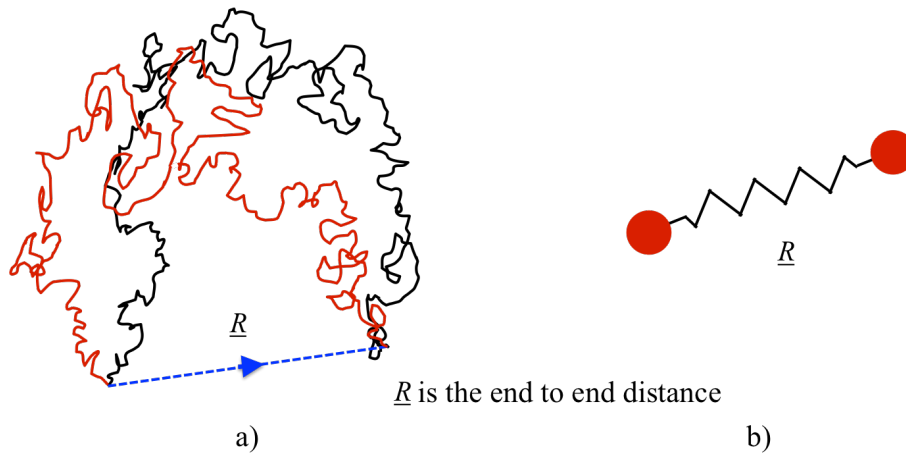


Fig. 1.10. a) Polymer chain in random coil shape; two possible configurations are shown. b) Polymer chain represented as a dumbbell.

The simplest way to describe a random coil is by considering a dumbbell, which has two major components; beads and springs. The beads represent the friction of the chain with its environment, which can be the surrounding chains or the solvent while the spring represents the elastic force generated by the Brownian motions of the chain.

1.5.2 Unentangled polymer dynamics: The Rouse model

Rouse mechanism is the dominant relaxation mechanism for unentangled systems, where polymer chains are free from the effect of surrounding chains. Entangled systems also relax by the Rouse mechanism but only at shorter times when they don't feel the constraint of the environment. Once the entanglements start to act, the tube theory needs to be considered, as the Rouse theory alone can't predict the complex behavior. This is because the Rouse relaxation is driven by the thermal motions of the chains, which allows the chains to move toward a more stable configuration thus aiding them to lose orientation. But in an entangled system the crossover of chains restricts these thermal motions thus the Rouse model isn't applicable beyond the unentangled sub chain and the tube theory needs to be considered.

In this section, we focus on the Rouse relaxation of unentangled polymer chains, for example in diluted polymer solutions or unentangled polymer melts.

In the Rouse model²², polymer chains can be considered as an assembly of dumbbells where each dumbbell represents a Kuhn segment. A Kuhn segment is defined as the smallest scale of the polymer chain having three following characteristics,

- There is no interaction between the Kuhn segments.
- There is no specific orientation of Kuhn segments.
- For one particular polymer, all Kuhn segments have the same length.

Representation of a polymer chain with N number of Kuhn segments is shown in fig. 1.11.

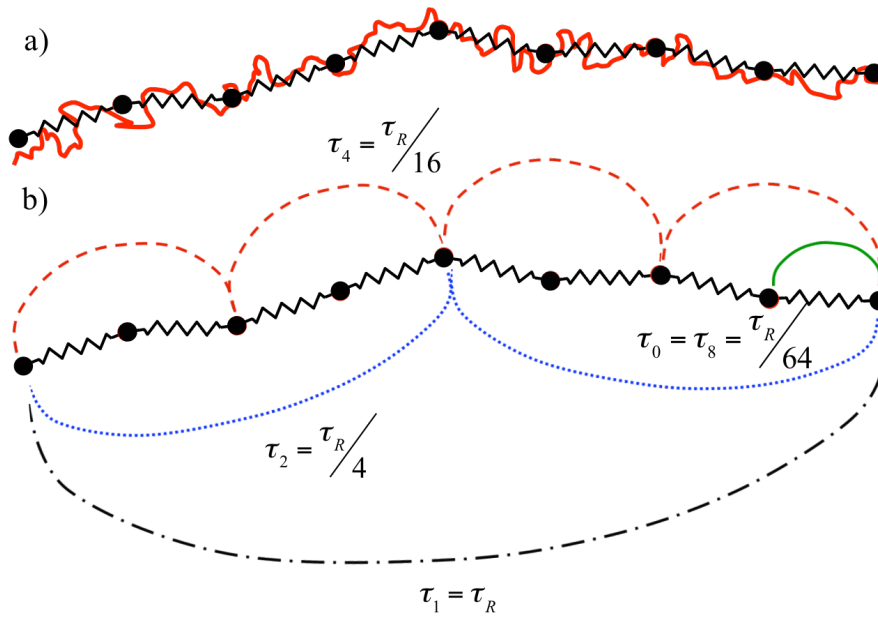


Fig. 1.11. a) A polymer chain illustrated as combination of dumbbells
b) Relaxation of different Rouse modes.

According to the Rouse theory, the relaxation process starts on a very small scale i.e. at level of a Kuhn segment (In our case, at $N = 8$, indicated by the green curve in fig. 1.11) and with time spreads to larger sub chains (i.e. $N = 4, 2, 1$ indicated by red, blue and black

curves respectively). This will continue until the whole chain has diffused along its end-to-end distance thus relaxing all applied stresses. Time needed to relax a sub chain can be calculated by,

$$\tau_p = \tau_0 \left(\frac{N}{p} \right)^2, \quad (3)$$

where, τ_0 is the Kuhn segment relaxation time, N is the number Kuhn segments/modes and $p = 1, 2, 3 \dots N$.

The longest characteristic relaxation time of an unentangled chain is defined as the Rouse time, τ_{Rouse} and is very important particularly in fast elongational flow as polymer chains are presumed to be stretched when the flow rate exceeds the reciprocal of this characteristic time. From equation 3 this becomes,

$$\tau_{Rouse} = \tau_0 N^2 \text{ or } \tau_{Rouse} \sim N^2, \quad (4)$$

The Rouse model does a very good job in predicting the viscoelastic behavior of highly concentrated unentangled solutions as well as unentangled polymer melts, where a similar scaling of relaxation time $\tau_{relaxation} \sim N^2$, has indeed been observed. However, the Rouse model fails to predict dynamics of diluted polymer solutions as it neglects the hydrodynamic interactions of the solvent molecules with the polymer chain. Experimental results show that polymers diluted in theta solvent follows a weaker M_w dependence i.e. ($\tau_{relaxation} \sim N^{3/2}$).

1.5.3 Unentangled polymer dynamics: The Zimm model

Consequently, an alternative model was proposed that adds this interaction to the original Rouse model and is known as the Zimm model. This model is an improved version of the Rouse model, which correctly takes into account the hydrodynamics interactions. According to this model, when an isolated polymer chain moves, it drags surrounding solvent with it; this in turn could drive remote polymer chains into motion. Inclusion of this mechanism results in an alternative characteristic relaxation time of the unentangled polymer

chains which scales with, $\tau_{Zimm} \sim N^{3/2}$ as observed for diluted solutions in theta solvent.

However, predictions of both Rouse and Zimm model fail for entangled systems (both melts and solutions) as they neglect the interactions between different chains i.e. the entanglement effect. Therefore, a more complex model is required which takes the mutual entanglements between chains into consideration. Such a model is discussed in the next section.

1.5.4 Entangled polymer dynamics: The tube model

In an entangled system, thermal motions of polymer chains aren't enough to relax stresses completely. In this case, the effect of entanglement has to be taken into account. As of today, the tube model has proven to be the most effective way of considering entanglements.

The tube model is based on Edward's idea, where a 'tube' is considered around a particular chain to represent the topological constraints exerted by the environment on the test chain. The tube blocks the lateral motion of the test chain, thus only allowing it to move along its contour length. The tube concept is illustrated in the fig. 1.12.

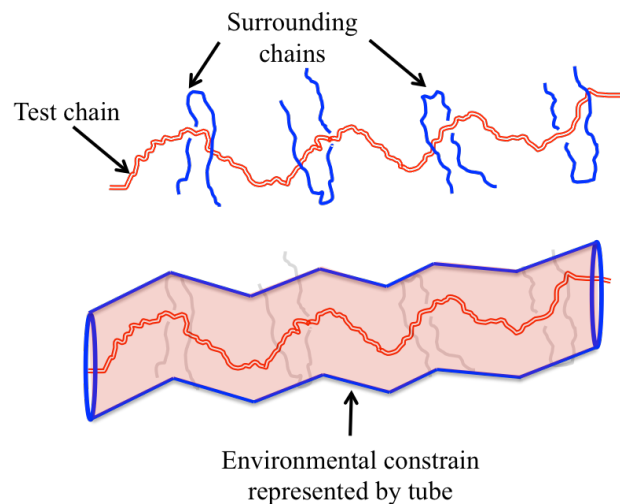


Fig 1.12: Illustration of the tube theory.

The tube theory elucidates how an entangled polymeric system relaxes the stress induced by a step strain. When a constant small deformation is applied on the system, the test chain will start to orient itself to the direction of deformation. But with constant decrease in entropy, a certain stress is needed to keep the deformation constant. Now to relax, the chains need to disorient and go back to their initial random orientation. This relaxation process is not instantaneous and occurs via two major and distinct steps: the fast Rouse relaxation and a slow disentanglement process.

a) Fast Rouse relaxation in entangled polymer

In an entangled system, polymer chains form a temporary network so Rouse relaxation takes place only in the chain segment where the effect of entanglement is not felt. Entanglements acting like cross-links (temporary) prevent the test chain to disorient more and relax in the same manner.

Generally a distinction is made at time τ_e , which is defined as the characteristic relaxation time between two entanglements. At short times $t < \tau_e$, the molecular sub chains shorter than the average molar mass between two entanglements, M_e doesn't feel the tube and can relax via Rouse relaxation taking place in all three directions. But at $t > \tau_e$, the longer modes feel the tube effect and only the longitudinal (one dimension) Rouse mode is noticed. The resulting Rouse modulus is,

$$G_{Rouse}(t) = \frac{\rho_0 RT}{M_w} \left\{ \frac{1}{4} \sum_{p=1}^Z \exp\left(-\frac{p^2 t}{\tau_R(M_w)}\right) + \sum_{p=Z+1}^N \exp\left(-\frac{2p^2 t}{\tau_R(M_w)}\right) \right\}, \quad (5)$$

where, R is the gas constant, T is temperature, ρ_0 and M_w is the respective density and molecular weight of the polymer and $Z = M_w/M_e$ is the number of entanglements.

b) Slow entanglement relaxation

At longer times, the test chain starts to feel the surrounding environment, so it can't relax by intrinsic Rouse process anymore. At this point, the tube becomes active and restricts the lateral motion of the chain. In order to relax completely, the test chain needs to go out of the tube since the tube itself carries the memory of orientation; and move on to a new tube with no preferred orientation. This 'escaping the environment' or disentanglement process is relatively slower and occurs via different relaxation mechanisms. In the next section, each of this relaxation processes is introduced very briefly.

1.6 Important relaxation mechanisms in tube model

According to the original tube model, the only significant mechanism for stress relaxation is the 'reptation', a process introduced by de Gennes²⁰. However, comparison with certain experimental data revealed some major limitations in the predictions, which could only be overcome by including additional relaxation mechanisms. Detailed studies on these various mechanisms and its implications can be found in refs [21, 23-27].

1.6.1 Orientational relaxation mechanisms

First, we discuss the orientational relaxation mechanisms, which is particularly important for predicting shear flows. The important orientational relaxation mechanisms are: reptation, contour length fluctuation, and constraint release.

a) Reptation dynamics

As discussed previously, for complete stress relaxation the test chain needs to escape its initial tube and move on to a new one with no preferred directions. The only available way for the chain to renew its configuration is by diffusing back and forth along the tube axis since its lateral movements; beyond a particular length scale are severely restricted (see fig. 1.13). This length scale is known as the tube

diameter a , which is also the distance between two entanglements. This relaxation mechanism is known as the reptation process (due to the snake-like motion) and is the dominant relaxation mechanism in tube theory. The concept of reptation process is shown in fig. 1.13.

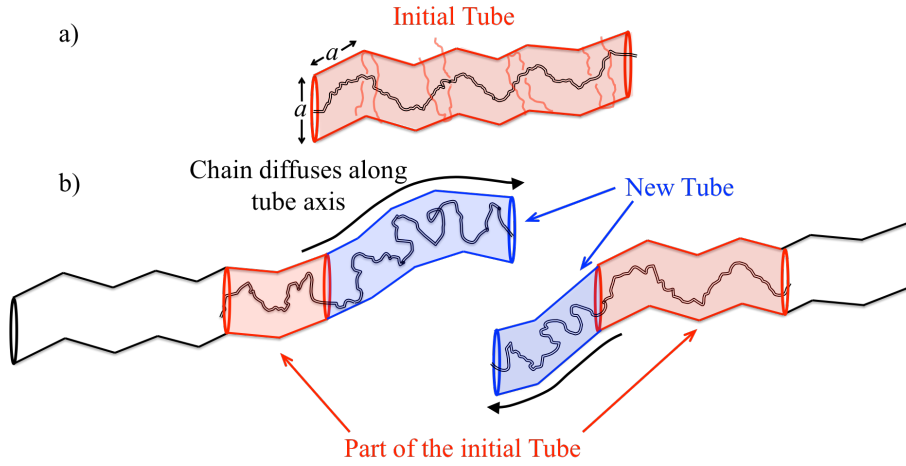


Fig 1.13: Illustration of the Reptation dynamics.

In the reptation process, the test chain diffuses out of the tube and a new tube is continuously being formed, starting from the ends. This new tube is randomly oriented meaning the test chain doesn't carry any stress to the new tube. The time needed for a chain to reptate is,

$$\tau_{rept} = \frac{L_{eq}^2}{D_e}, \quad (6)$$

where, D_e is the diffusion coefficient and L_{eq} is the primitive path of the test chain.

The diffusion coefficient is,

$$D_e = \frac{KT}{\zeta_{tot}} = \frac{KT}{N\zeta_0}, \quad (7)$$

where, ζ_0 is the monomeric, ζ_{tot} is the total friction of the chain and N represents the total number of segments in the chain.

So, the final form of reptation time is,

$$\tau_{rept} \propto \frac{N^2}{N-1} \propto N^3, \quad (8)$$

But experimental data of entangled system suggest that $\tau_{relaxation} \propto n^{3.4-3.6}$, which means reptation mechanism alone can't describe the disentanglement process of entangled chains. Therefore additional relaxation mechanism has to be taken into account, which aids the reptation process.

b) Contour length fluctuation mechanism, CLF

Contour length fluctuation^{28,40} is considered as the second key ingredient of quantitative tube model after reptation. It leads to a partial relaxation of the stress even before the chain starts to reptate. According to this concept, the constraint exerted by the tube on the test chain is maximum at the middle and minimum at the chain ends, allowing the chain extremities to vibrate and relax stress at a local level. Consequently, the effective tube length will decrease before the reptation process starts. Thus speeding up the overall relaxation process of the polymer.

From previous discussions we know that, when time, $t > \tau_e$, polymer chains start to feel the tube/entanglements and further relaxation is only possible by means of diffusion along the primitive path. But before, $t = \tau_{Rouse}$ the entire chain is not dynamically connected and segmental diffusion does not result in a diffusion of centre of mass. In other words, the reptation won't begin until $t = \tau_{Rouse}$. In this time interval (from $t = \tau_e$ to $t = \tau_{Rouse}$) this new relaxation process, CLF takes place and the extremities of the chain relaxes locally. At $t > \tau_{Rouse}$, reptation process will start but in an effectively shortened tube length. The CLF process is shown in fig. 1.14.

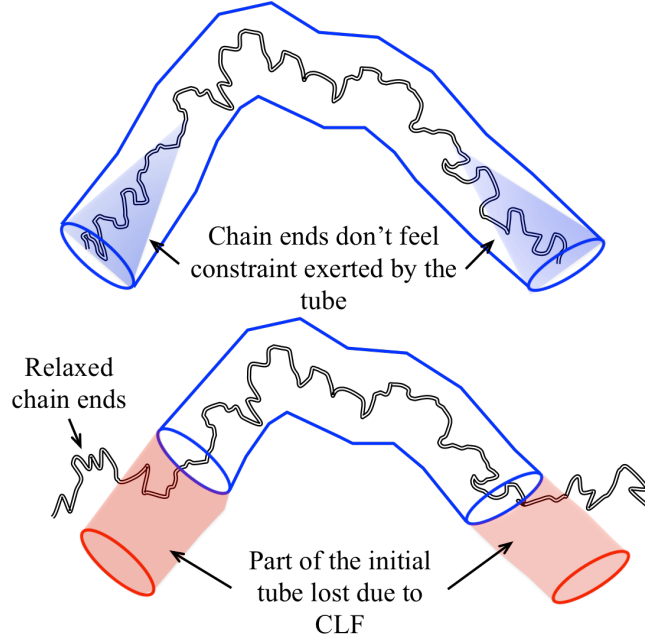


Fig 1.14: Illustration of the Contour length fluctuation dynamics.

According to CLF process, the extremities of a chain don't feel the influence of the tube and can relax by a Rouse process with a relaxation time,

$$\tau_{early}(x_i) = \frac{9\pi^3}{16} \tau_e (Z/2)^4 x_i^4, \quad (9)$$

where, x_i is the normalized coordinate of a chain segment, ranging from 0 at the extremities to 1 at the middle of the chain.

c) Thermal constraint release process, CR

As discussed earlier, tube theory is a representational model of real polymeric system, where movement of both the test and the surrounding chains can cause formation and losing of entanglements. So far, only the movement of the test chain has been considered. With constraint release process^{23, 40, 41, 58}, motion of the tube is taken into account, which allows the test chain to relax its local configuration. However, the tube motions are extremely difficult to understand so

only the simplification of real situation is incorporated. A simple illustration is shown in fig. 1.15.

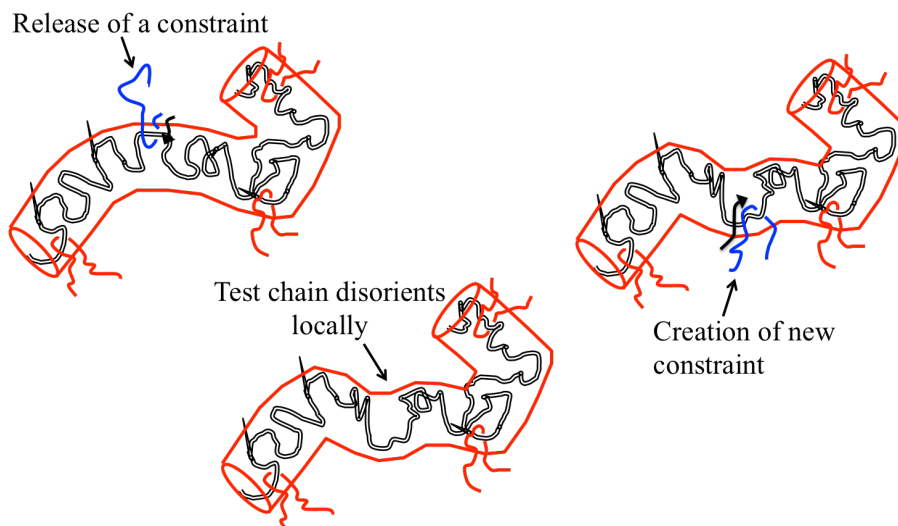


Fig 1.15: Illustration of the Constraint release process.

This process is very important for poly or bi dispersed systems, where entanglements are formed by a combination of long and short chains. Because of their length, the short chains are prone to reptate faster and cause a loss of entanglement. Allowing the test chain to disorient more and explore the space (in a lateral motion) that was previously occupied by the short chains, thus speeding up the overall relaxation process. As this constraint release event occurs due to reptation/diffusion of surround chains, it is also known as the reptative/diffusive constraint release^{23, 40, 41}.

There are different ways to incorporate this mechanism in the tube model but the most used one is the dynamic tube dilution effect. According to this concept, the polymer fraction that is already relaxed can't impose constraint to the test chain anymore, thus can only act as a solvent to the remaining polymer chains. Consequently, the test chain can explore a larger tube diameter as shown in fig. 1.16.

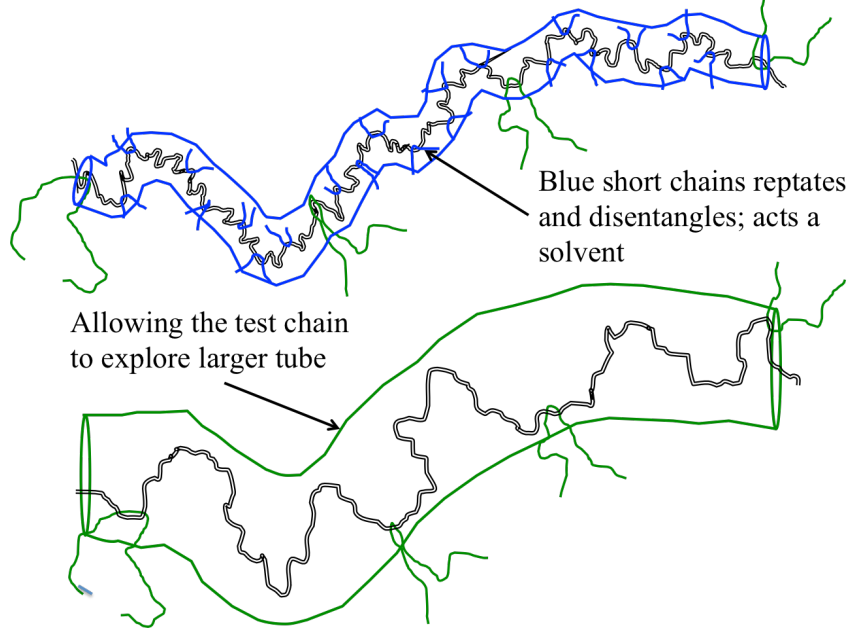


Fig 1.16: Illustration of dynamic tube dilution effect, DTD.

According to the Dynamic tube dilution theory, once relaxed the presence of blue chains can be ignored and a new effective molecular weight between entanglements is formed (only between long-long chains),

DTD theory allows us to rescale the following tube parameters by use of the unrelaxed fraction of the polymer, $\phi(t)$

Molecular weight between entanglements,

$$M_e(t) = \frac{M_{e,0}}{\phi(t)^\alpha}, \quad (10)$$

Equivalent length of the tube,

$$L_{eq}(t) = L_{eq,0} \phi(t)^{\alpha/2}, \quad (11)$$

Tube diameter,

$$a(t) = \frac{a_0}{\phi(t)^{\alpha/2}}, \quad (12)$$

and the reptation time,

$$\tau_{rept}(t, M) = \frac{L_{eq}(t)^2}{D_e} = \tau_{rept,0}(M) \phi(t)^\alpha \quad (13)$$

where, 0 refers to an initial state and α is the dynamic dilution exponent, which is an empirical value between 1 to 1.3. The value of this exponent is investigated in details in chapter 4.

On top of the orientational relaxation mechanisms described above, new experimental evidences suggest another mechanism has to be taken into account particularly for polymer solutions and bidispersed polymer melts. This relaxation mechanism has been defined as a constraint release activated, contour length fluctuation or CR-CLF mechanism. As the name suggests, this mechanism is initiated by the loss of entanglements; thus a constraint release action; and results in releasing constraint at the chain end (similar to as CLF). This relaxation mechanism is investigated in details with both literature and a new set of experimental data in chapter 4.

1.6.2 Stretch relaxation mechanisms

In the next section, we discuss other relaxation processes that become important if not dominant for non-linear flows. As discussed earlier, in these large and fast deformations, polymer chains start to unravel and may even stretch, which is not considered in the relaxation mechanisms described so far. These mechanisms are: chain stretching and convective constraint release.

a) Chain stretching, CS

Chain stretching^{29, 42} refers to a configuration in which the contour length of a chain, L exceeds its equilibrium value, L_{eq} i.e.

(stretch, $\lambda = \frac{L}{L_{eq}}$) > 1 . This increases the tension in the chain beyond the equilibrium and results in an overall increase in stress. However, due to the chain's entropic nature the stretch is not infinite and the chain can retract along the tube axis. As retraction occurs along the tube axis it is unhindered by the tube constraints and occurs at a rate determined by the Rouse time.

In the original tube model, it was assumed that the polymer chain retracts instantaneously within the tube to maintain a constant tube length, thus no stretching was allowed. But subsequent experimental data revealed that when stretched above the inverse of their stretch relaxation time, polymer solutions show strong strain hardening behavior, thus confirming stretching of chains. Therefore this mechanism has to be considered for non-linear flows.

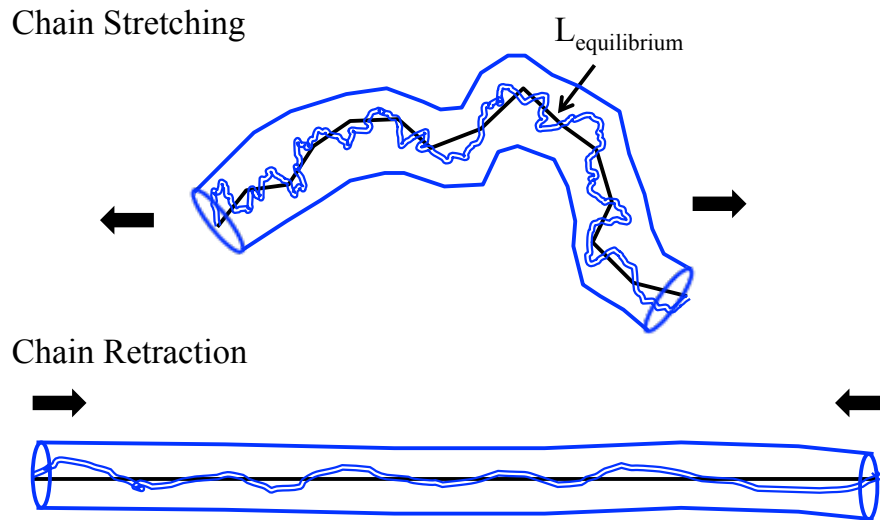


Fig 1.17: Illustration of chain stretch and retraction.

b) Convective constraint release, CCR

Constrain release mechanism has a non-linear counterpart known as convective constraint release^{30, 43}. As discussed above, in linear flow constraint release events are caused by reptation of surrounding chains. Similarly, in non-linear fast flows, retraction of a given chain

could lead to release of constraints exerted by its ends. Since tube constraints are swept away by the convection, its called convective constraint release effect.

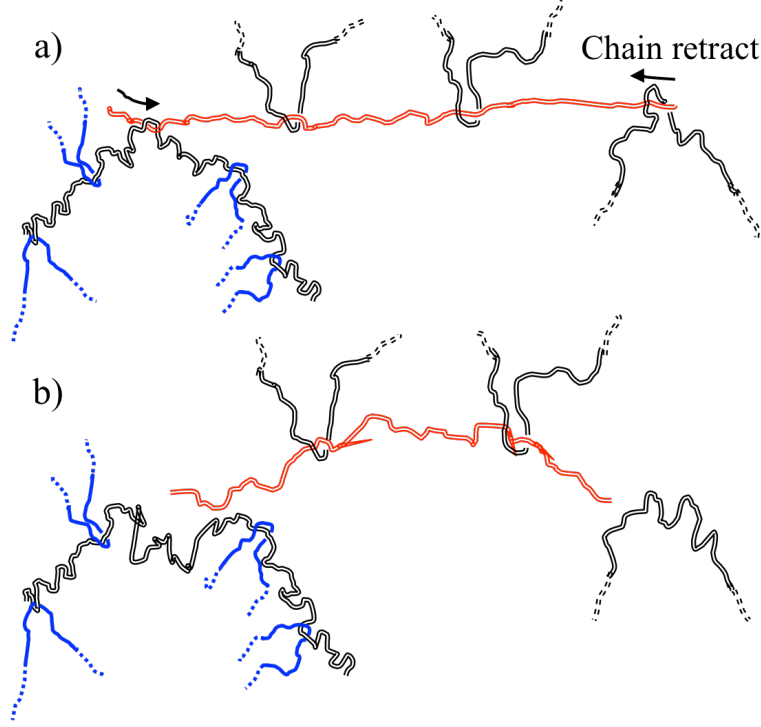


Fig 1.18: Illustration of convective constraint release event. Another important implication of this mechanism is that it suppresses stretch of molecules in simple shear at finite strain rates.

1.7 Material parameters in Tube model

The tube model uses three distinct parameters to identify a particular polymeric system, these are: plateau modulus G_N^0 , molar mass between entanglements, M_e and the characteristic relaxation time between entanglements, τ_e . All these parameters are related to the polymer segment between entanglements, which is the largest stress-carrying element of the chain.

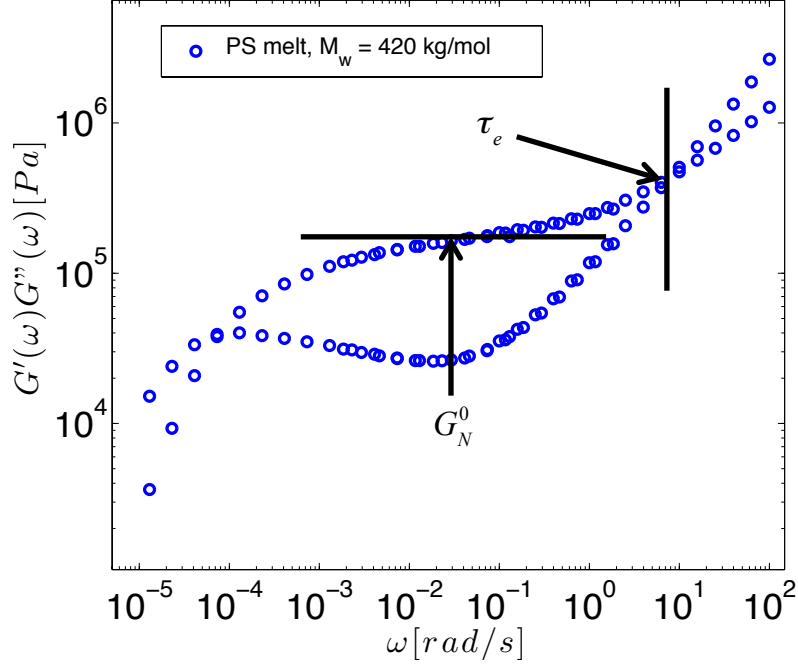


Fig. 1.19: Correlation of material parameters and linear visco-elastic response of a material.

These material parameters can be easily obtained from linear viscoelastic, LVE response (frequency sweep curve) of the material. As shown in fig. 1.19, G_N^0 is observed from the vertical position of the storage modulus, τ_e from the horizontal cross over between the loss and storage modulus (the first crossover at high frequency) and M_e , which determines the shape of the curve is interrelated with G_N^0 as shown in equation 14.

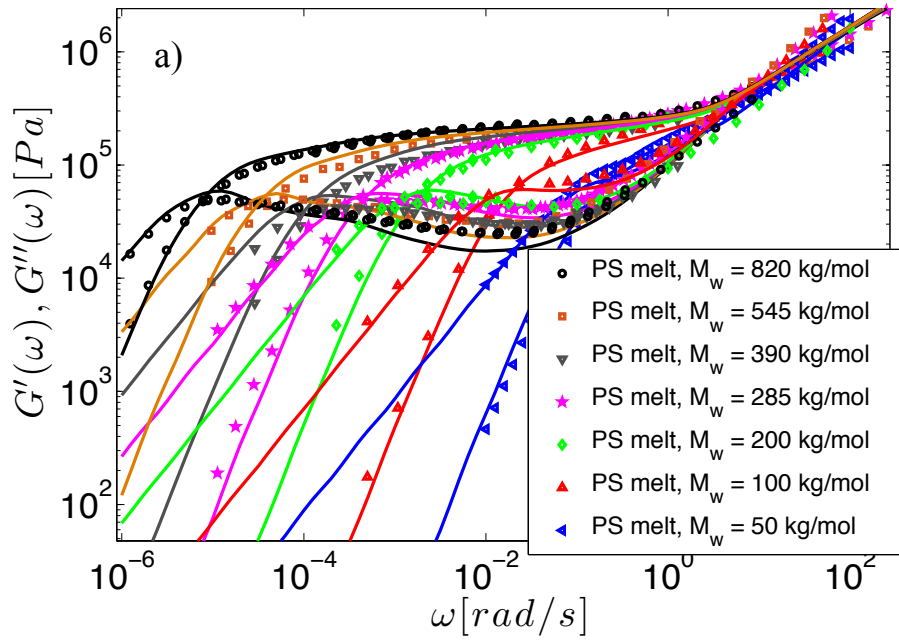
$$M_e = \frac{\rho R T}{G_N^0}, \quad (14)$$

where, ρ is the density of the polymer, R is the gas constant and T is the temperature.

These material parameters are unique for a specific polymeric system and are molar-mass and flow (same parameters are applicable for both linear and non-linear flow) independent.

1.8 Tube model in linear flow

Since its inception, the tube model has been used extensively in literature to describe both linear and non-linear rheological properties of entangled polymers. In linear regime, the tube model with the above-mentioned orientational mechanisms has proven to be highly successful. This refined tube model has been used to obtain quantitative predictions for different linear polymers, not only in melt state (see fig. 1.20) but also in diluted forms (concentrated to largely diluted solutions; see fig. 1.20c).



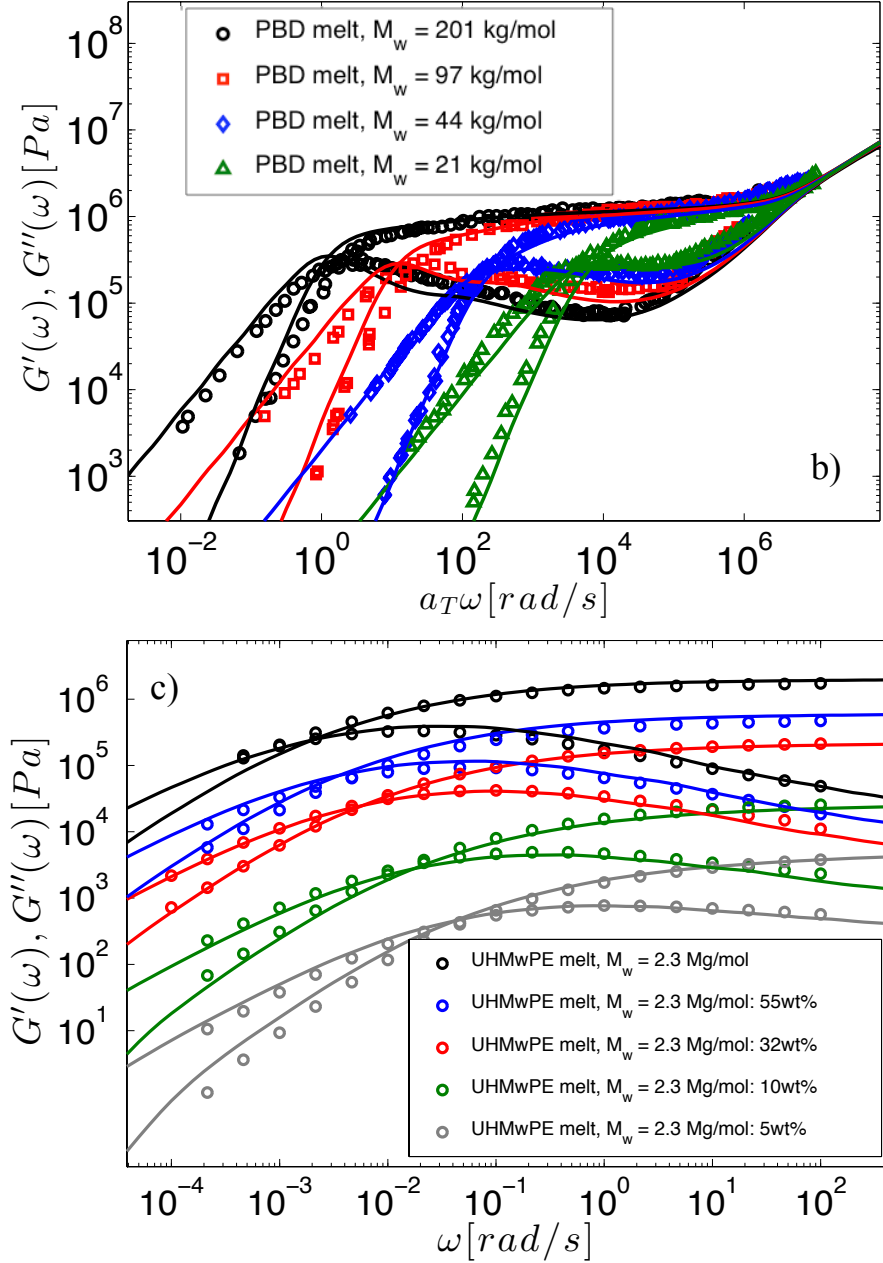


Fig. 1.20 Tube model predictions for a) PS melts, b) PBD melts of different molecular weights (both monodispersed) and c) UHMWPE (polydispersed) at different concentrations. Time marching algorithm based tube model has been used for the predictions (details in chapter 4).

Complex systems can be also be predicted by the tube model with further adjustments. For example, in star polymers, the presence of branching point restricts reptation motion of the chains. Consequently, each arm needs to retract down to the branch point to release the stress, a mechanism known as the arm retraction (similar to CLF).

Despite its overwhelming success, some fundamental questions still remains that need to be further addressed. One of them is about the value of dynamic dilution exponent, α (see equation 10-13). As previously discussed, the dynamic tube dilution concept is the most widely used method to explain the constraint release mechanism. And since entanglements can be assumed to be binary contacts of polymer chains, the value of α should be 1. But several experimental evidences point toward a higher value⁵⁹⁻⁶¹ ($\sim 4/3$). Thus, today, there is no general agreement on what should be the exact value of this exponent, α . This topic is further addressed in chapter 4 in light of a new set of model polymer solutions and other sets of samples presented in literature^{32, 33, 59, 61}.

1.9 Tube model in non-linear flow

Tube model has relished an unprecedented success in linear flow. Unfortunately, it didn't meet a similar fate in the non-linear counterpart. The refined tube models incorporating both stretching and orientational mechanisms failed miserably in non-linear elongational flows. Despite the on going progress, a general molecular theory for the non-linear viscoelastic properties is still missing. Thus, this subject remains an area of active research.

1.9.1 Evolution of the tube model in non-linear flow

A brief description on how non-linear modeling has evolved in last few decades follows. Since this Ph.D. project is focused on behaviors of polymers in uniaxial extensional flow, in this section only model predictions for this particular flow type are discussed.

I. Original Doi and Edwards model, DE

In the original DE model, reptation was considered as the only significant mechanism for stress relaxation. Both chain stretch and

convective constraint release mechanisms (dominant in strong flows) were discussed but omitted in the final constitutive model. As a result, the DE model predictions for steady uniaxial extensional viscosity, η_{el} exhibit two distinct regimes. In regime I, when the flow rate is weak (less than the reciprocal of the reptation time, $\dot{\epsilon} < \tau_{rept}^{-1}$), the polymeric fluid retains its equilibrium structure. The weak flow tries to orient the tubes in the direction of deformation but the tubes reptate and go back to its initial conformation. Consequently, the stress increases with the strain rate, keeping $\eta_{el} = \sigma/\dot{\epsilon}$ constant at the Trouton value.

Intermediate flow rates ($\dot{\epsilon} > \tau_{rept}^{-1}$) constitute the second regime, where reptation mechanism is hindered and the tubes orient parallel to the direction of deformation. In this regime, the flow is still not fast enough to stretch the chains, therefore they carry the equilibrium tension. As a result the stress saturates together with the orientation of the tubes leading $\eta_{el} = \frac{\sigma=constant}{\dot{\epsilon}}$ to scale with $\dot{\epsilon}^{-1}$. Similar behavior is expected even for fast flow rate ($\dot{\epsilon} > \tau_{Rouse}^{-1}$) as instantaneous chain retraction mechanism doesn't allow the chains to stretch out and cause an increase in stress. In principle, the DE model can be used to model linear ($\dot{\epsilon} < \tau_{rept}^{-1}$) and mildly non-linear flows ($\tau_{rept}^{-1} < \dot{\epsilon} < \tau_{Rouse}^{-1}$), where chain stretch doesn't occur.

II. Doi, Edwards, Marrucci and Grizzuti model, DEMG

A refinement to the DE model is the so-called DEMG²⁹ model, which adds chain stretch to the basic DE model in the form originally suggested by Marrucci and Grizzuti. In this modification the chain retraction wasn't considered instantaneous anymore and takes place in finite time. This allowed the previously 'inextensible' chain to stretch beyond its equilibrium length in fast flows where the rate exceeds the stretch relaxation time, τ_s ($\sim \tau_{Rouse}$). Consequently, the chain tension and in turn the stress will increase causing an upturn of η_{el} . Therefore, in DEMG model a third unique regime is observed for fast flow rates ($\dot{\epsilon} > \tau_{Rouse}^{-1}$).

Initially, in DEMG model, the chains were considered to be infinitely stretchable, which isn't practical as chain stretching occurs at a high

entropic cost. In a subsequent modification the chains were considered to be finitely stretchable thus leading to a fourth regime, where η_{el} saturates as the chains become fully stretched. All these regimes are shown in figure 1.21.

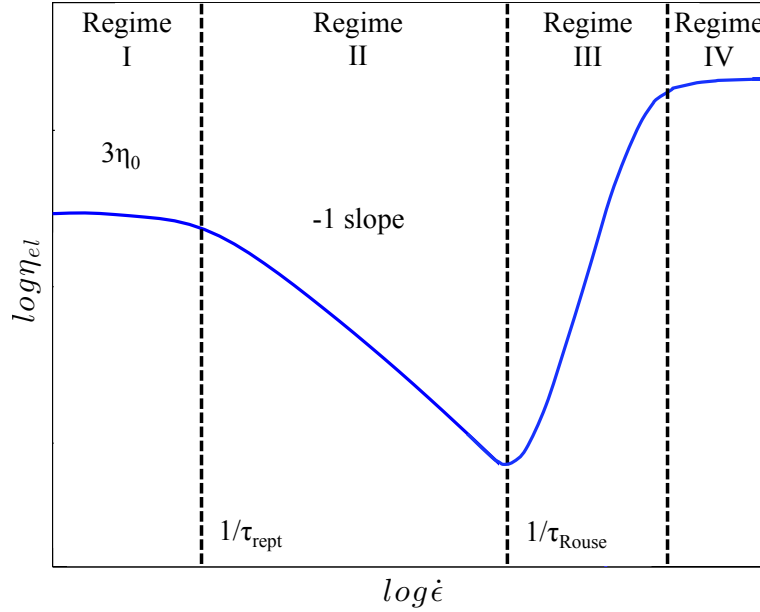


Fig 1.21: Schematic representation of steady-state elongational viscosity, η_{el} vs elongation rate, $\dot{\epsilon}$.

III. Mead, Larson and Doi model, MLD

In a further modification, Mead, Larson and Doi incorporated the other important stretch relaxation mechanism, convective constraint release (CCR) into the basic DEMG model. This improved model is known as the MLD³¹ model. According to the concept of CCR, the fast non-linear flow could cause some entanglements to sweep away (by convection) which leads to an additional mechanism for relaxation.

In MLD model, the CCR mechanism assists both the relaxation of orientational anisotropy and the segmental stretch in moderate and fast flows respectively. To ensure a smooth crossover a 'switch function' is employed. As discussed earlier, for very fast flows ($\dot{\epsilon} > \tau_{Rouse}^{-1}$)

chain stretching is the dominant dynamics so the switch function allows the segmental stretch to relax via CCR while suppressing the effect on the orientational relaxation. On the contrary, for moderate flows ($\tau_{rept}^{-1} < \dot{\epsilon} < \tau_{Rouse}^{-1}$), no chain stretching occurs so only the orientational relaxation takes place.

Both DEMG and MLD models were further modified to incorporate other important relaxational mechanisms such as the Contour Length Fluctuation^{28, 35, 40} and the diffusive constraint release mechanism (DCR-CS, MLD-toy model)^{36, 40, 41}.

IV. Double constraint release with chain stretch, DCR-CS

The DCR-CS model, proposed by Ianniruberto and Marrucci³⁷ is a simplified single-mode model that extends the boundary of the DEMG model by incorporating both diffusive and convective constraint release on top of the reptation and chain stretching mechanisms. This model considers diffusive constraint release in form of double reptation^{44, 45}, which has major influence on polydispersed systems.

Another interesting feature of this model is that it doesn't require a switch function for the CCR mechanism as in the original MLD model. In this model, only the orientational anisotropy is allowed to relax by the CCR mechanism while the segmental stretch remains uninfluenced. The only well-known relaxation mechanisms missing in this theory is the CLF. The single mode DCR-CS model, which strictly focuses on the dynamics of a single representative chain, was later extended to multi mode DCR-CS model³⁸.

V. Graham, Likhtman and Milner, McLeish model, GLaMM

The GLaMM model⁶⁴ incorporates all known orientation and stretch relaxation mechanisms as described above. Consequently, it can be used to predict the viscoelastic behavior of linear chains in the full range of deformation rates from linear to non-linear i.e. in both shear and extensional flows. Proposed by Graham, Likhtman, Milner and McLeish, it is the first model to incorporate both contour length

fluctuation and diffusive/reptative constraint release mechanisms in the same framework and thus provides accurate quantitative comparison also in the linear regime.

Reptation, contour length fluctuation and diffusive/reptative constraint release are dominant mechanisms in the linear regime (regime-1 of Fig. 1.21) whereas the convective constraint release mechanism controls the intermediate thinning regime (regime-2). The chain stretching mechanism causes the upturn in the third regime (non-linear) and since finite extensibility is missing in the original GLaMM model the fourth plateau regime is absent.

An overview of different relaxation mechanisms considered in these non-linear models are shown in table 1.1.

Table 1.1 Relaxation mechanisms considered in tube models

Model Names	Relaxation mechanisms				
	Reptation	CLF	Diffusive CR	Chain Stretch	Convec-tive CR
DEMG model	✓	✗	✗	✓	✗
MLD model	✓	✗	✗	✓	✓
Modified DEMG and MLD model	✓	✓	✗	✓	✓
Modified MLD-toy model	✓	✗	✓	✓	✓
DCR-CS model	✓	✗	✓	✓	✓
GLaMM model	✓	✓	✓	✓	✓

Presently, we have a number of comprehensive models for non-linear extensional flow, which combines well-known relaxation dynamics and perhaps can be called a “Standard model”. The progress of this “standard model” was greatly aided by the availability of accurate and

reliable experimental data^{12, 32-36}. In the next section, competence of the standard model is demonstrated by comparing with experimental data.

1.9.2. Non-linear standard tube model

The steady-state viscosity as predicted by the standard tube model (schematically represented in fig 1.21) demonstrates four distinct regimes as previously discussed. Similar nonmonotonic behavior has been reported for polymer solutions diluted in theta solvents^{35, 36}. The steady-state values first decreases with increasing strain rate, goes through a minimum and then exhibits prominent thickening behavior at rates comparable to inverse of Rouse time. In an extensive study, Bhattacharjee et al.^{35, 46} compared different standard models with experimental data of a set of PS solutions diluted in various concentrations (in DEP/DOP) with a home-built filament stretching device. Outcome for one particular PS solution is summarized in fig 1.22, where, steady state elongational viscosities are plotted with respective strain rates.

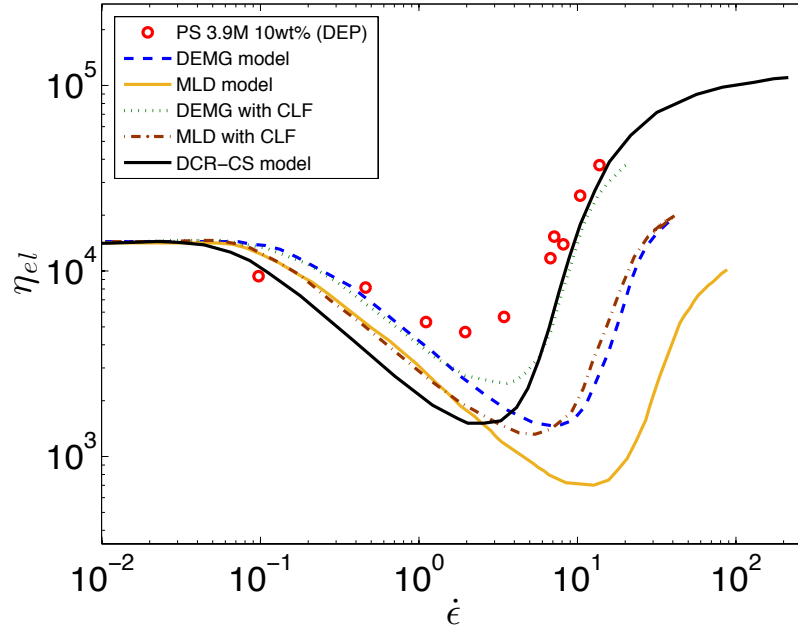


Fig 1.22: Comparison between different standard models (curves) and steady-state experimental data (symbols) of PS solution.

The comparison is qualitatively favorable especially for the models that include the CLF mechanism. From the quantitative point of view however, the predictions are off, particularly at high strain rates. Apparently, the DCR-CS model generates the best comparison with ‘almost’ quantitative predictions at low and high strain rates and qualitative in the intermediate ones. This discrepancy was attributed to the single modality of the DCR-CS model. At extreme rates, the motion of the chains are barely influenced by the environment, thus the assumption of single chain segment is not an issue.

However, things get complicated when standard models are compared with experimental data of molten polymers. In this case, qualitative discrepancy is observed at least at two levels. First, the steady state elongational data exhibit a monotonic thinning behavior with a slope of $-1/2$ instead of -1 , as predicted by standard models. And second, η_{el} shows no sign of thickening even beyond $\dot{\epsilon} > \tau_{Rouse}^{-1}$.

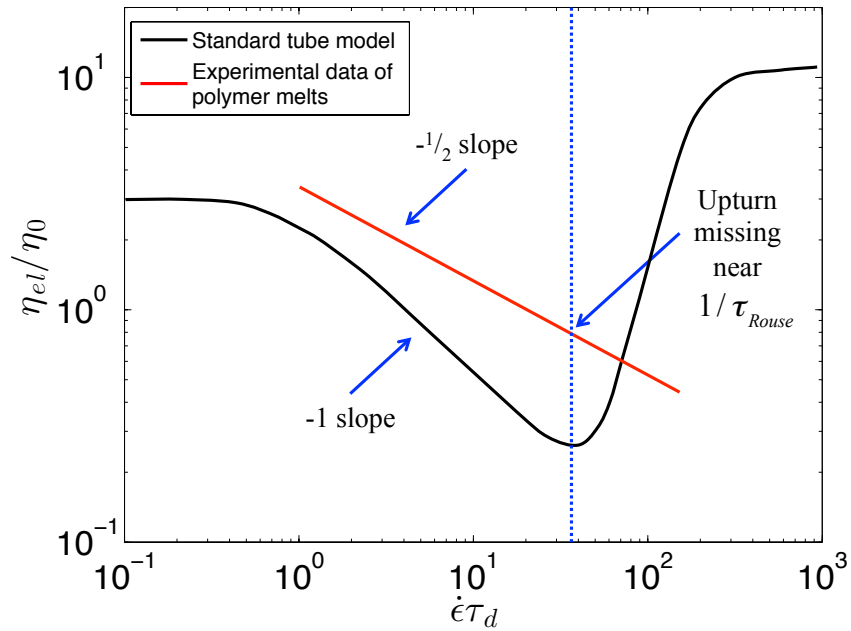


Fig 1.23 A schematic comparison of standard model and polymer melt from ref. [12].

This qualitative difference between polymer melts and solutions has baffled researchers across the globe and gave rise to the problem now known as “non-universality of polymer melts and solutions in elongational flow”.

1.9.3 Non-universality in non-linear flow

Experimental evidences point toward a non-universal behavior of polymer melts and solutions in non-linear flows, which is contrary to their behavior in linear flows. Indeed, this universal scaling has been observed in several studies in linear flows^{23, 24, 62, 63}, where the key molecular parameter was the number of entanglements, Z per a single chain. LVE responses (dynamic moduli G' and G'' in a wide range of frequencies) of different polymers in different states (from melt to diluted solutions) superimposes onto one single master curve, provided that the frequencies and moduli are suitably shifted horizontally and vertically, respectively, with corresponding concentration-dependent parameters, like a characteristic relaxation time, τ_e and the plateau modulus, G_N^0 . This phenomenon is shown in fig. 1.24.

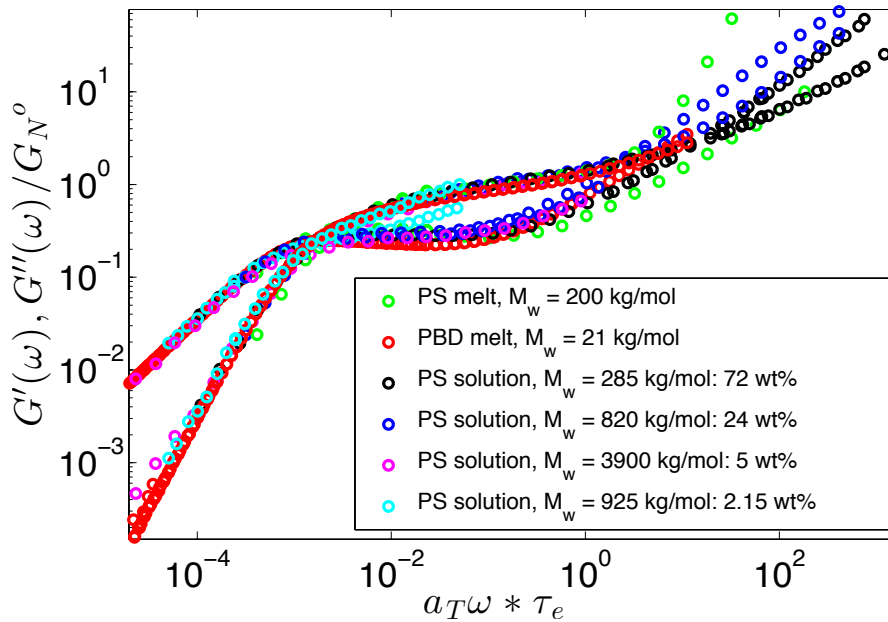


Fig 1.24 Universal LVE response of different polymer melts and solutions with same no. of entanglements ($Z \sim 13$).

Both these phenomena (universality in linear and non-universality in non-linear flow) were nicely demonstrated in a recent study⁶², where authors prepared several polystyrene (PS) solutions by tailoring the polymer molar mass and concentration in such a way that all solutions had the same number of entanglements per chain ($Z \sim 19$), same as a certain PS melt. They observed same LVE response (when nondimensionalised; fig 1.25 a) for all systems, with prominent difference in the non-linear flow as shown in fig. 1.25 b. In non-linear regime, the behavior of PS solutions changes qualitatively depending on the level of dilution. The least concentrated solution depicts strong thickening behavior while the highest one shows mostly thinning with a brief constant regime.

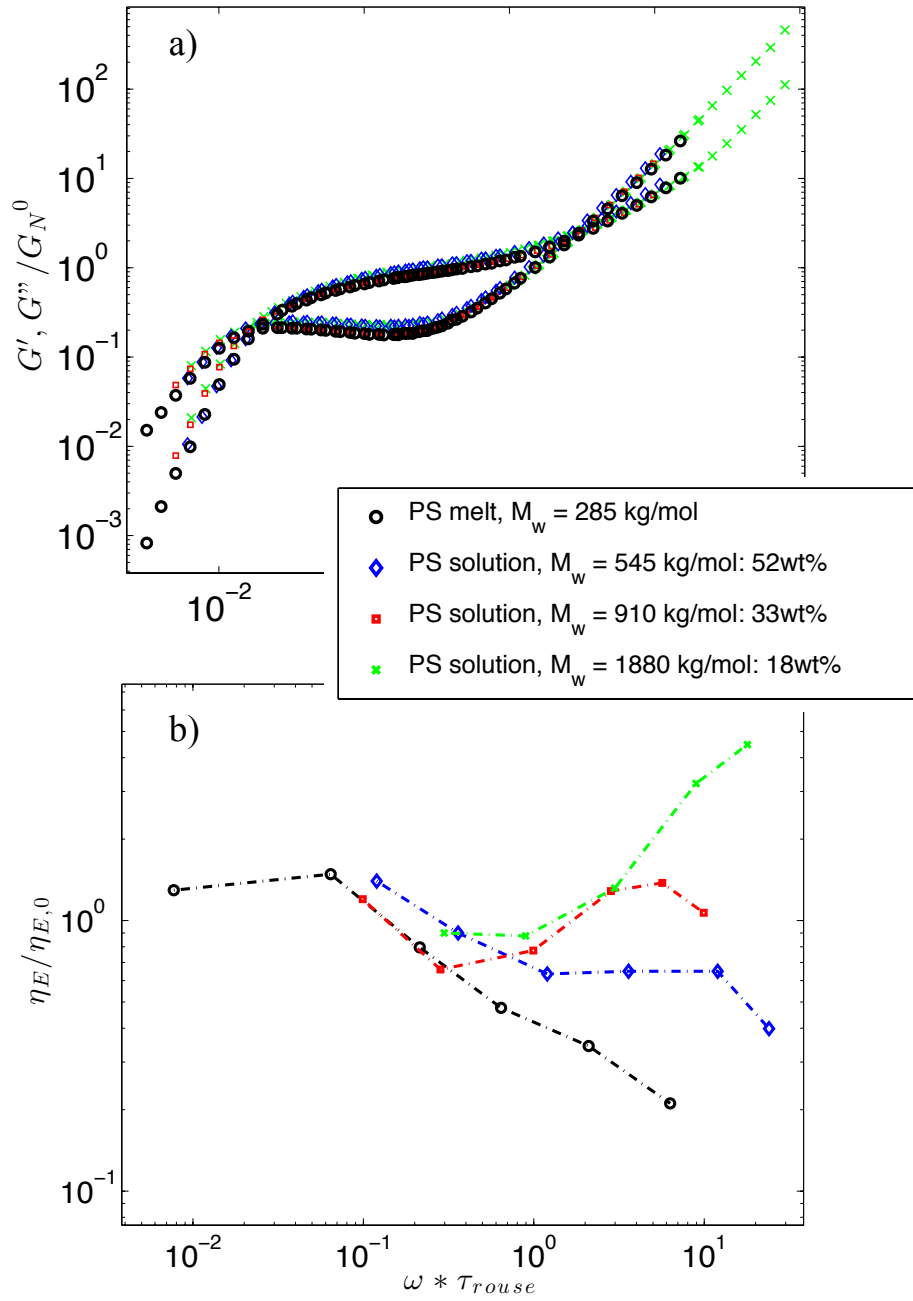


Fig 1.25 Universal and non-universal behavior of PS systems in a) linear and b) non-linear flow respectively.

1.9.4 The “missing link”

This non-universality in elongational flow is now well established but its molecular origin is not yet fully understood, particularly the absence of thickening trend for polymer melts. The Doi-Edwards Tube theory should and does predict a strong thickening behavior as soon as the polymer chains are being stretched, indifferent of polymer melt or solution. According to the tube theory, the stretching should occur at reciprocal Rouse time, which is the relaxation time of the whole unentangled chain. This triggered researchers to search for additional mechanisms predominantly important for elongational flows.

Marrucci and Ianniruberto proposed the first possible explanation, which is a flow-induced contraction of tube diameter from its equilibrium that ultimately results in a pressure induced relaxation effect⁴⁷. Known as the interchain pressure concept, it included the first non-linear parameter: tube diameter relaxation time, $\tau_a \sim \tau_R$. By incorporating this concept in the molecular stretch function (MSF) theory, Wagner et al.⁴⁸ was able to attain semi-quantitative agreement for monodisperse PS melts¹² and showed that the tube diameter relaxation time scales with the Rouse time of the chains. Later, this work was successfully extended to entangled chains diluted in oligomers⁴⁹ and small molecule solvents⁵⁰. However, this required using two different Rouse times, each for melt and solution state⁵¹, which is difficult to comprehend. Furthermore, with binary blends it was shown that τ_a varies with the sample composition, which should not be the case since it is related to a Rouse process⁵².

Recently, several works have been proposed, based on the idea⁵³ that the monotonic thinning behavior observed in the melt state is due to an alignment-induced reduction of the monomeric friction under fast elongational flow^{54, 55}. According to this concept, when the flow is faster than the stretch relaxation rate of a polymer, the local environment (at level of Kuhn segments) becomes strongly anisotropic resulting in a decrease in monomeric friction coefficient. Consequently, the flow loses ‘grip’ on the polymer and the level of stretch is reduced (and so is the stress). However, this mainly affects entangled polymer melts, since it’s very difficult if not impossible to align the small solvent molecules in solutions⁵⁴.

Presently, this concept seems to be widely accepted and different groups have incorporated this mechanism to their respective tube-based models and successfully predicted various PS melts and solutions⁵⁵⁻⁵⁷. In spite of its seemingly success, the monomeric friction reduction concept is controversial as it lacks solid experimental evidence.

1.10 Objective of this thesis

The fundamental objective of this thesis is to find the “*missing link*” in non-linear extensional flows as described in the previous section. Or in other words, to investigate the possibility of finding an universal model that can predict the non-linear elongational behavior of both linear polymer melts and solutions under one frame work. In order to simplify this complicated objective, we have sub-divided it in three parts,

i) Review the contemporary molecular pictures

First, we would like to critically assess the contemporary molecular pictures or more specifically, the tube model with the SORF concept by designing and characterizing very specific PS blends. As discussed above, this widely accepted SORF theory has been successfully applied to predict the non-linear viscoelastic properties of both melts and solutions⁵⁵⁻⁵⁷. Details of this study are presented in chapter 6.

ii) Produce systematic datasets to realize the fast flow properties

Survey of the existing literature data in elongational flow reveals several blank spots, which needs to be filled in order to perceive the complete story of what polymer chains go through during an elongational flow. And also how differently does a polymer melt or solution behave when stretched. To realize that we have designed and characterized specific PS solutions which ranges from very concentrated to diluted ones. Thus, the different NLVE behavior of polymer solutions with the level of dilution can be realized. Details of this study are presented in chapter 5 and 7.

- iii) *Propose a novel theory within the framework of tube model*

Lastly, we would like to propose a novel theory that can predict both polymer melts and solutions under the same framework, based on the understanding of the experimental results produced in this work and the literature. If possible we would like to extend the tube model in linear regime to the non-linear regime without including any additional relaxation mechanism or criteria. Details of this study are presented in chapter 8.

1.11 Summary

Extensional flow properties of polymers play a crucial part on their performance during processing techniques such as the film blowing or fiber spinning. Therefore, rheological characterization of these materials is essential to predict the processing conditions that will optimize the final properties of the finished product. Despite the industrial need, this field has progressed slowly mainly due to lack of experimental techniques. However, this last decade has seen the rise of a new home-built device, FSR, which has greatly facilitated this field of study.

Experimental evidence allowed a better understanding of fast flow dynamics of polymers and presently we have comprehensive models that combine well-known relaxation mechanisms and can predict polymer solutions (at least at a qualitative level). However, the recently observed non-universality between polymer melts and solutions is still not well understood and remains an open question. Alignment induced monomeric friction reduction seems to offer the answer but needs to be further tested with strong experimental evidence.

In this introductory chapter, an outline of different types of flow, definition and importance of extensional flow, brief history on extensional experimental rheology and a literature overview of molecular model (non-linear) are given.

Summary

This chapter is designed to offer the reader some introductory knowledge and brief literature review for the forthcoming chapter

References:

- 1a. i) D. M. Binding, D. M. Jones, K. Walters, The shear and extensional flow properties of M1, *Journal of non-newtonian fluid mechanics*, (1990), 35, 121-135. ii) M. J. Solomon, S. J. Muller, The transient extensional behavior of polystyrene - based Boger fluids of varying solvent quality and molecular weight, *Journal of Rheology*, (1996), 40, 837.
- 1b. i) M. H. Wagner, T. Raible, J. Meissner, Tensile stress overshoot in uniaxial extension of a LDPE melt. *Rheol. Acta* (1979), 18, 427-428. ii) T. Raible, A. Demarmels, J. Meissner, Stress and recovery maxima in LDPE melt elongation, *Polymer Bulletin* (1979), 1, 397-402.
2. F. T. Trouton, On the coefficient of viscous traction and its relation to that of viscosity. *Proc. Roy. Soc.*, (1906), A77, 426-440.
3. G. Fano, Contributo allo studio dei corpi filanti (Contribution to the study of thread-forming materials), *Archivio di fisiologia*, (1908), 5, 365-370.
4. J. Meissner, Dehnungsverhalten von polyäthylen-Schmelzen. *Rheol. Acta*, (1971), 10, 230-242.
5. H. M. Laun, H. Münstedt, Comparison of elongational behavior of a polyethylene melt at constant stress and constant strain rate. *Rheol. Acta*, (1976), 15, 517-524.
6. J. Meissner and J. Hostettler, A new elongational rheometer for polymer melts and other highly viscoelastic liquids. *Rheologica Acta*, (1994), 33, 1-21.
7. J.S. Schulze, T.P. Lodge, C.W. Macosko, J. Hepperle, H. Münstedt, H. Bastian, D. Ferri, D.J. Groves, Y.H. Kim, M. Lyon, T. Schweizer, T. Virkler, E. Wassner, and W. Zoetelief, A comparison of extensional viscosity measurements from various rheometers. *Rheologica Acta*, (2001), 40, 457-466.

References

8. H. Münstedt, New universal extensional rheometer for polymer melts. Measurements on a polystyrene sample. *J. Rheol.*, (1979), 223, 421–436.
9. H. Münstedt, S. Kurzbeck, and L. Egersdörfer, Influence of molecular structure on rheological properties of polyethylenes. part ii. elongational behavior. *Rheologica Acta*, (1998), 37, 21–29.
10. M. Sentmanat, Miniature universal testing platform: from extensional melt rheology to solid-state deformation behavior. *Rheologica Acta*, (2004), 43, 657–669.
11. M. Sentmanat, B. N. Wang, and G. H. McKinley, Measuring the transient extensional rheology of polyethylene melts using the ser universal testing platform. *Journal of Rheology*, (2005), 49, 585–606.
12. A. Bach, H.K. Rasmussen, and O. Hassager, Extensional viscosity for polymer melts measured in the filament stretching rheometer. *Journal of Rheology*, (2003), 47, 429–441.
13. D.M. Hoyle, Q. Huang, D. Auhl, D. Hassell, H.K. Rasmussen, A.L. Skov, O.G. Harlen, O. Hassager, and T.C.B. McLeish, Transient overshoot extensional rheology of long-chain branched polyethylenes: Experimental and numerical comparisons between filament stretching and cross-slot flow. *Journal of Rheology*, (2013), 57, 293–313.
14. G.H. McKinley and T. T. Sridhar. Filament-stretching rheometry of complex fluids. *Annual Review of Fluid Mechanics*, (2002), 34, 375–415.
15. S. L. Anna, G. H. McKinley, D. A. Nguyen, T. Sridhar, S. J. Muller, D. F. James, J. Huang, An interlaboratory comparison of measurements from filament-stretching rheometers using common test fluids. *J. Rheol.*, (2001) 45, 83–114.
16. G. G. Fuller, C. A. Cathey, B. Hubbard, and B. E. Zebrowski, Extensional Viscosity Measurements for Low-Viscosity Fluids. *J. Rheol.*, (1987), 37, 235–249.
17. P. Dontula, M. Pasquali, L. E. Scriven, C. W. Macosko, Can

extensional viscosity be measured with opposed-nozzle devices? *Rheo. Acta*, (1997), 36, 429-448.

18. G. I. Taylor, The formation of emulsions in definable fields of flow. *Proc. Roy. Soc. London Set. A*, (1934), 146, 501-523.

19. R. R. Lagnado, L. G. Leal, Visualization of three-dimensional flow in a four-roll mill. *Experiments in Fluids*, (1990), 9, 25-32.

20. P. G. de Gennes, Reptation of a polymer chain in the presence of fixed obstacles. *Journal of Chemical Physics*, (1971), 55, 572-579.

21. M. Doi and S. F. Edwards. *The Theory of Polymer Dynamics*. International series of monographs on physics. (1986), Oxford University Press, Oxford.

22. P. E. Rouse, A theory of the linear viscoelastic properties of dilute solutions of coiling polymers. *J. Chem. Phys*, (1953), 21, 1272-1280.

23. T. C. B. McLeish, Tube theory of entangled polymer dynamics. *Advances in Physics*, (2002), 51(6), 1379-1527.

24. M. Doi., *Introduction to Polymer Physics*. (1995), Oxford Science Publications, Clarendon Press, Oxford.

25. M. Rubinstein and R. H. Colby, *Polymer Physics*. (2003), Oxford University Press, Oxford.

26. J. M. Dealy and R. G. Larson, *Structure and Rheology of Molten Polymers*. (2006) Hanser Gardner Publications.

27. R. B. Bird, C. F. Curtiss, R. C. Armstrong, and O. Hassager, *Dynamics of Polymeric Liquids - Volume 2: Kinetic Theory*. (1977), John Wiley and Sons, New York.

28. M. Doi, Explanation for the 3.4 power law of viscosity of polymeric liquids on the basis of the tube model. *J. Polym. Sci. Polym. Lett.*, (1981), 19, 265-273.

29. G. Marrucci, and N. Grizzuti, Fast flows of concentrated

polymers: Prediction of the tube model on chain stretching. *Gazz. Chim. Ital.*, (1988), 118, 179–185.

30. G. Marrucci, Dynamics of entanglements: A nonlinear model consistent with the Cox–Merz rule. *J. Non Newtonian Fluid Mech.*, (1996), 62, 279–289.

31. D.W. Mead, R.G. Larson, and M. Doi. A molecular theory for fast flows of entangled polymers. *Macromolecules* (1998), 31, 7895–7914.

32. Q. Huang, N. J. Alvarez, Y. Matsumiya, H. K. Rasmussen, H. Watanabe, O. Hassager, Extensional Rheology of Entangled Polystyrene Solutions Suggests Importance of Nematic Interactions. (2013), *ACS Macro Lett.*, 2 (8), 741–744.

33. Q. Huang, O. Mednova, H. K. Rasmussen, N. J. Alvarez, A. L. Skov, K. Almdal, O. Hassager, Concentrated Polymer Solutions are Different from Melts: Role of Entanglement Molecular Weight. (2013), *Macromolecules*, 46 (12), 5026–5035.

34. J. K. Nielsen, H. K. Rasmussen, O. Hassager, and G. H. McKinley, Elongational viscosity of monodisperse and bidisperse polystyrene melts. (2006), *J. Rheol.* 50, 453–476.

35. P. K. Bhattacharjee, J. P. Oberhauser, G. H. McKinley, L. G. Leal, and T. Sridhar, “Extensional rheometry of entangled solutions”. (2002), *Macromolecules* 35, 10131–10148.

36. X. Ye, R. G. Larson, C. Pattamaprom, T. Sridhar, Extensional properties of monodisperse and bidisperse polystyrene solutions, (2003), *J. Rheol.*, 47, 443.

37. G. Ianniruberto, G. Marrucci, A simple constitutive equation for entangled polymers with chain stretch. *J. Rheol.*, (2001), 45, 1305–1318.

38. G. Ianniruberto, G. Marrucci, A multimode CCR model for entangled polymers with chain stretch. *J. Non-Newtonian Fluid Mech.*, (2002), 102, 383–395.

39. S. T. Milner, T. C. B. McLeish, Reptation and contour-length fluctuations in melts of linear polymers. *Phys. Rev. Lett.*, (1998), 81, 725-728.
40. W. W. Graessley, Entangled linear, branched and network polymer systems—Molecular theories. *Adv. Polym. Sci.*, (1982), 47, 67-117.
41. H. Watanabe, Viscoelasticity and dynamics of entangled polymers. *Prog. Polym. Sci.*, (1999), 24, 1253-1403.
42. D. S. Pearson, E. Herbolzheimer, N. Grizzuti, and G. Marrucci, Transient behavior of entangled polymers at high shear rates. *J. Polym. Sci., Polym. Phys. Ed.*, (1991), 29, 1589-1597.
43. G. Ianniruberto, and G. Marrucci, On compatibility of the Cox-Merz rule with the model of Doi and Edwards. *J. Non-Newtonian Fluid Mech.*, (1996), 65, 241-246.
44. C. Tsenoglou, Viscoelasticity of binary homopolymer blends. *ACS Polym. Prepr.*, (1987), 28, 185-186.
45. J. des Cloizeaux, Double reptation versus simple reptation in polymer melts. *Europhys. Lett.*, (1998), 5, 437-442.
46. P. K. Bhattacharjee, D. A. Nguyen, G. H. McKinley, T. Sridhar, Extensional stress growth and stress relaxation in entangled polymer solutions. *J. Rheol.*, (2003), 47(1), 269-290.
47. G. Marrucci, G. Ianniruberto, Interchain pressure effect in extensional flows of entangled polymer melts. *Macromolecules*, (2004), 37, 3934- 3942.
48. M. H. Wagner, V. H. Rolon-Garrido, Nonlinear rheology of linear polymer melts: modeling chain stretch by interchain tube pressure and Rouse time. *Korea-Australia Rheol. J.*, (2009), 21, 203-211.
49. M. H. Wagner, An extended interchain tube pressure model for elongational flow of polystyrene melts and concentrated solutions. *J. Non-Newtonian Fluid Mech.*, (2015), 222, 121-131.

50. M. H. Wagner, E. Narimissa, V. H. Rolon-Garrido, From melt to solution: Scaling relations for concentrated polystyrene solutions. *Journal of Rheology*, (2015), 59, 1113-1130.
51. M. H. Wagner, Scaling relations for elongational flow of polystyrene melts and concentrated solutions of polystyrene in oligomeric styrene. *Rheol. Acta*, (2014), 53, 765–777.
52. E. van Ruymbeke, J. Nielsen, O. Hassager, Linear and nonlinear viscoelastic properties of bidisperse linear polymers: Mixing law and tube pressure effect, *Journal of Rheology*, (2010), 54, 1155.
53. G. Ianniruberto, A. Brasiello, G. Marrucci, Friction coefficient does not stay constant in nonlinear viscoelasticity. *Proc. 7th Annu. Eur. Rheol. Conf.*, (2001), 1, 61.
54. G. Ianniruberto, A. Brasiello, G. Marrucci, Simulations of Fast Shear Flows of PS Oligomers Confirm Monomeric Friction Reduction in Fast Elongational Flows of Monodisperse PS Melts As Indicated by Rheo-optical Data. *Macromolecules*, (2012), 45, 8058.
55. T. Yaoita, T. Isaki, Y. Masubuchi, H. Watanabe, G. Ianniruberto, G. Marrucci, Primitive chain network simulation of elongational flows of entangled linear chains: stretch/orientation-induced reduction of monomeric friction. *Macromolecules*, (2012), 45, 2773.
56. G. W. Park, G. Ianniruberto, Flow-induced nematic interaction and friction reduction successfully describe PS melt and solution data in extension startup and relaxation. *Macromolecules*, (2017), 50, 4787–4796.
57. P. S. Desai, R. G. Larson, Constitutive model that shows extension thickening for entangled solutions and extension thinning for melts. *Journal of Rheology*, (2014), 58, 255-279.
58. A. E. Likhtman, T. C. B. McLeish, Quantitative theory for linear dynamics of linear entangled polymers. *Macromolecules*, 35, 6332–6343, (2002).

59. R. Colby, L. Fetters, W. G. Funk and W. W. Graessley, Effects of concentration and thermodynamic interaction on the viscoelastic properties of polymer solutions. *Macromolecules*, (1991), 24, 3873.
60. H. Watanabe, S. Ishida, Y. Matsumiya and T. Inoue, Test of Full and Partial Tube Dilation Pictures in Entangled Blends of Linear Polyisoprenes. *Macromolecules*, (2004), 37, 6619.
61. K. Osaki, Y. Nishimura and M. Kurata, Viscoelastic properties of semidilute polystyrene solutions. *Macromolecules*, (1985), 18, 1153.
62. Q. Huang, L. Hengeller, N. J. Alvarez, O. Hassager, Bridging the Gap between Polymer Melts and Solutions in Extensional Rheology. *Macromolecules*, (2015), 48, 4158–4163.
63. S. L. Wingstrand, N. J. Alvarez, Q. Huang, O. Hassager, Linear and Nonlinear Universality in the Rheology of Polymer Melts and Solutions. *Phys. Rev. Lett.* (2015), 115, 078302.
64. R. S. Graham, A. E. Likhtman, T. C. B. McLeish, S. T. Milner, Microscopic theory of linear, entangled polymer chains under rapid deformation including chain stretch and convective constraint release. *J. Rheol.*, (2003), 47(5), 1171-1200.

Chapter 2

Materials: Preparation and properties

Materials used throughout this work are introduced in this chapter. To achieve the overall purpose of this thesis, three different systems are designed and studied: two polymer solutions and a polymer blend. In this chapter, the basic ingredients of these systems are presented along with the solution/blend preparation techniques. Some basic physical and thermal properties of the systems are also presented, while more advanced characteristics (mechanical characteristics) can be found in the respective chapters. In order to avoid complexity only monodispersed model polymers have been studied in this work.

This chapter is organized as follows. First, the selection criterion of the systems is presented in section 2.1. Followed by the detail description of each system in section 2.2 and 2.3. And finally a brief summary concludes the chapter.

2.1 Selection criterion of systems

Systems were chosen considering various factors, the most important being the involved experimental techniques. No matter how appealing a system may look for the overall objective of a project, if it can't be measured with the existing technology it becomes irrelevant. This becomes even more important in extensional flows, as the measuring techniques that currently exist are subjective to the sample (discussed in details in chapter 1). Accordingly, in this thesis two different polymeric systems were prepared and studied considering the involved experimental techniques.

The first system consists of polystyrene melts and solutions and was analyzed in the filament stretching rheometer equipped with an

convection oven. Thus allowing us to measure at high temperatures (T_g of PS $\sim 100^\circ\text{C}$). On the other hand, for the capillary breakup studies; performed in a commercially available CaBER device (no oven), PEO diluted in an inviscid small molecule solvent was chosen as it could be measured at room temperature. Similar systems have been studied extensively in literature using respective experimental techniques thus allowing us to compare our results with literature data.

The main ingredients and basic properties of these systems are described in the next section.

2.2 Polystyrene blends/solutions

Depending on the objective of the study, two different PS systems were designed. The first system (designated as PS-1 in this chapter), consists of a high M_w polystyrene dissolved in a styrene oligomer at various concentrations. Whereas, in the second system (designated as PS-2 in this chapter), a high M_w polystyrene is dissolved in a series of low M_w PS chains but at the same concentration.

2.2.1 Selection criterion of the ingredients

a) System 1: PS diluted in styrene oligomer (PS-1):

One of the objectives of this thesis is to understand how the concentration level of a solution affects its strain hardening behavior. To achieve that a new system is designed where a relatively high molecular weight PS is dissolved in an oligomeric styrene at different weight fractions. A total of 9 different solutions were prepared that ranges from very concentrated to semi-dilute and diluted solutions.

In order to explore all concentration regimes (concentrated, semi-dilute and dilute) a well-entangled PS melt was needed for this study. However, too high M_w solute could lead to samples difficult to measure with current experimental techniques. So eventually, a moderate M_w (820 kg/mol) PS was chosen, which has about 55

entanglements in its melt state and remains entangled ($Z \sim 3$, assuming $M_e \sim 15$ kg/mol and $\alpha = 1$) even when diluted at 5wt%.

As for the solvent, styrene oligomers were chosen as it has the same solubility parameters as polystyrene, thus minimizing the interaction parameter, χ for the system. Indeed this was confirmed by several studies in literature, which indicate that oligomers act like real solvent to polymers¹⁻³. The molar mass of the solvent was selected well below the entanglement molar mass of PS, thus short enough to consider it as a solvent. However, too low molar mass could lead to a larger gap in glass transition temperature with the solute. So, finally an oligomer with M_w of 8.8 kg/mol (molecular weight between entanglements, M_e of PS is ~ 15000 kg/mol) was chosen.

b) System 2: PS diluted in short PS chains (PS-2):

To realize the transition from polymer melts to polymer solutions in fast flow, a set of PS blends are designed and studied in chapter 5. In this work, a total of four different blends were prepared from five different components: One high molar mass PS and four low molar mass PS/OS. The long chain PS is diluted at the same concentration in a series of oligomer/short chains matrices of different molecular weights.

There were two major selection criteria for this project. First, the molar mass of the short chains were chosen to make sure that they cover an entanglement range from unentangled to barely and fully entangled states, thus allowing a smooth transition from polymer melts to solutions in a very systematic way.

Second, the molar mass of the long and the short chain matrices were needed to be well separated from each other. So that in fast elongational flows, strain hardening of the system only occurs due to the stretching of the long chains while the matrices are short enough to retract and retain their equilibrium length, thus do not participate in overall the strain hardening (details in chapter 6).

2.2.2 Synthesis and chromatography:

Ingredients for both systems (PS-1 & PS-2) were purchased from Polymer Source (Montreal, Canada). They were synthesized by living anionic polymerization; details of the procedure can be found elsewhere^{4,5}. The molar mass and polydispersity is checked by size-exclusion chromatography technique for the oligomer and by field flow fractionation (FFF) coupled with multi-angle light scattering (MALS) for the high molar mass PS (details about the techniques in chapter 3). The results are consistent with the ones received from Polymer Source as shown in table 2.1.

Table 2.1 Specifications of the ingredients for a) PS-1 and b) PS-2

a)

Sample name	M_w^* kg/mol	M_w^{**} kg/mol	PDI*	PDI**
PS820k	790	820	1.06	1.02
OS9k	8.8	8.8	1.1	1.09

b)

Sample name	M_w^* kg/mol	M_w^{**} kg/mol	PDI*	PDI**
PS820k	790	820	1.06	1.02
PS73k	70	73	1.04	1.07
PS34k	35	34	1.02	1.08
PS23k	22	23	1.06	1.09
OS9k	8.8	8.8	1.1	1.09

*:Values provided by supplier

**:Values measured

2.2.3 PS solution/blend preparation method:

Both PS solutions and blends were prepared following a four-step procedure inspired by an earlier work⁶. In this procedure first the components are dissolved in a solvent where they are soluble and then the mixture is precipitated by another insoluble solvent. The steps are described in detail below.

First, the polystyrene and the oligomer are weighed according to the desired weight fractions and dissolved together in THF. The mixture is then stirred at the room temperature overnight to ensure that the two components are well dissolved and mixed. In a next step, the whole mixture is added to the non-solvent methanol drop by drop, using a burette. The precipitated polymer/oligomer blend was then separated and collected using paper filtration. Finally, the blends were dried at 70 °C under vacuum for 4 days to remove any remaining traces of the solvents. The drying temperature of the solution was set higher than the boiling temperature of the used solvents (~65°C).

The quantity of THF added in the first step influences the final form of the mixture. So it was controlled to obtain PS mixture in fine powder form, thus making easier to get rid of the residual solvent. Ensuring solvent-free samples is very important, especially for elongational measurements. Presence of solvent can alter the strain hardening behavior of the sample profoundly. Consequently, different drying techniques were employed in this work and the consequences are discussed in details in chapter 4.

2.2.4 Thermal characteristics:

The glass transition and the degradation temperature of both PS systems were determined by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) techniques respectively (under N₂ gas). Details on the techniques are discussed at chapter 3. Corresponding thermal characteristics of ingredients and the systems are given in table 2.2,

Table 2.2 Thermal characteristics of the ingredients and systems

a) PS - 1

Ingredients	No. of entanglements*	Glass transition temperature (°C)	Degradation temperature (°C)
OS9k melt state	<1	94.6	380
PS820k melt state	55	106.6	390
Solutions			
OS9k + PS820k (1wt%)	<1	97.6	385
OS9k + PS820k (3wt%)	1	98.1	385
OS9k + PS820k (5wt%)	3	98.4	385
OS9k + PS820k (10wt%)	5	98.6	390
OS9k + PS820k (20wt%)	11	99.8	390
OS9k + PS820k (30wt%)	17	100.7	390
OS9k + PS820k (40wt%)	22	101.3	390
OS9k + PS820k (50wt%)	27	102.3	390
OS9k + PS820k (80wt%)	44	104.6	390

*: The number of entanglements are determined based on $M_e = 15$ kg/mol

b) PS - 2

Ingredients	Number of entanglements *	Glass transition temperature ($^{\circ}\text{C}$)	Degradation temperature ($^{\circ}\text{C}$)
OS9k melt state	<1	94.6	380
PS23k melt state	1	92.4	390
PS34k melt state	2	103.3	390
PS73k melt state	5	105.6	390
PS820k melt state	55	106.6	390
Blends	$Z_L^{**} / Z_S^{\text{¥}}$		
10%PS820k – 90%PS73k	5 / 5	106.6	390
10%PS820k – 90%PS34k	5 / 2	104.7	390
10%PS820k – 90%PS23k	5 / 1	103.5	390
10%PS820k – 90%OS9k	5 / 0	98.6	390

*: The number of entanglements are determined based on $M_e = 15$ kg/mol.

** : Entanglements formed by long-long chains.

¥ : Entanglements formed by short-long chains.

Please note that the T_g of PS23 may seem odd as it's even lower than the OS9. This could be due to presence of solvent from the polymerization process. However, while preparing the blends extra cautions were taken to make sure that no solvent remains, which then

can be confirmed from the DSC and SAOS experimental data (presented in chapter 6) of blend B3.

2.3 PEO diluted in water

The model polymer solutions used for the capillary breakup studies (chapter 9), consists of a series of nearly monodisperse linear polyethylene oxide (PEO) diluted in distilled water. To have a good comparative study over a range of molecular weights, three different molecular weight PEOs were diluted in several concentrations ranging from semi-dilute to dilute ones. These samples were purchased from DOW, USA ($M_w = 200$ kg/mol & 4000 kg/mol) and Sigma Aldrich, Belgium ($M_w = 1000$ kg/mol). The details of the system are described below.

2.3.1 Selection criterion of the ingredients

Water acts like a real solvent to PEO, as a result water-based PEO have proven to be an ideal system for capillary breakup studies and is used extensively in literature⁷⁻¹⁰. Moreover, it also has industrial application as PEO is often used as a water-soluble industrial additive to enhance the rheological performance of various products. For example, it is added to water-based agricultural sprays at very low concentrations to reduce the turbulent frictional drag and to prevent misting¹¹.

2.3.2 Solution preparation method

The polymer solutions were prepared by carefully adding the polymer in distilled water. Extra cautions were taken to prevent agglomeration of polymer in the solution. During this process, the solution was gently stirred using a magnetic stirrer. This aids to the prevention of agglomeration but high stirring rate could lead to cessation of long polymer chains. So a compromise was made between these two processes. Thereafter the solution was shielded from light by using aluminum foils and stirred further on a rolling bench for 24-48 hours

to ensure a complete mixing of the components. To minimize the effect of degradation of polymer all experiments were performed within 72 hours of preparation.

A total of six different concentrations of PEO solutions were prepared. The concentrations were fixed such that the solutions range from the dilute to the semi dilute regime. The overlap concentration of the system was calculated from Graessley's definition¹²,

$$c^* = \frac{0.77}{[\eta]} \quad 2.1$$

where, η is the intrinsic viscosity of the polymer solution which depends on the molar mass of the chain in accordance with the Mark–Houwink–Sakurada equation,

$$\eta = K_{[\eta]} M_w^\alpha \quad 2.2$$

where, $K_{[\eta]}$ is a constant and the power-law exponent, α varies ($0.5 \leq \alpha \leq 0.8$) with the quality of the solvent.

2.3.3 Physical properties

Table 2.3 lists the main physical properties of the prepared blends. As we know, surface tension plays an important role in a capillary breakup experiment. Here it is measured with a platinum Wilhelmy plate (details in chapter 3).

Table 2.3. Characteristics (at room temperature) of the polymer solutions, PS-2

M_w kg/mol	Overlap concentra- -tion, c^* [wt%]	Prepared concentrat -ion, c [wt%]	Solvent Density, ρ kg/m ³	Surface tension, γ mN/m	<i>Dilution state</i>
200	0.38	1	998	62.2	Semi- dilute
		2	998	62.2	
		4	998	62.2	
1000	0.13	0.1	998	62.4	Dilute
4000	0.0055	0.005	998	62.4	
		0.01	998	62.4	

2.4 Summary

Different materials that were studied in this thesis are presented in this chapter, along with some basic properties. An overview of the different systems used in different chapters are given in table 2.4.

Table 2.4. Overview of different systems

Systems	Ingredients			Chapter
	Solute	Solvent	Concentration states	
PS solutions, PS – 1	High M_w PS	Styrene oligomer	Several concentrations: Concentrated to dilute	4, 6, 7 & 8
PS blend, PS – 2	High M_w PS	Different low M_w polystyrene s	Semi-dilute	5
PEO solution, PEO	Different M_w PEO	Water	Several concentrations: Semi-dilute to dilute	9

Different experimental techniques and protocols used to characterize our systems are discussed in details in the following chapter.

References:

1. Q. Huang, N. J. Alvarez, Y. Matsumiya, H. K. Rasmussen, H. Watanabe, O. Hassager, Extensional Rheology of Entangled Polystyrene Solutions Suggests Importance of Nematic Interactions. (2013), *ACS Macro Lett.*, 2 (8), 741–744.
2. Q. Huang, O. Mednova, H. K. Rasmussen, N. J. Alvarez, A. L. Skov, K. Almdal, O. Hassager, Concentrated Polymer Solutions are Different from Melts: Role of Entanglement Molecular Weight. (2013), *Macromolecules*, 46 (12), 5026–5035.
3. E. van Ruymbeke, V. Shchetnikava, Y. Matsumiya, and H. Watanabe, Dynamic Dilution Effect in Binary Blends of Linear Polymers with Well-Separated Molecular Weights. *Macromolecules*, (2014), 47 , 7653–7665.
4. S. Ndoni, Ch. M. Papadakis, F. S. Bates, and K. Almdal, Laboratory-scale setup for anionic polymerization under inert atmosphere, *Rev. Sci. Instrum.* (1995), 66 (2), 1090– 1095.
5. Polymer source. <https://polymersource.ca>. Accessed at: 23/05/2018.
6. Q. Huang, L. Hengeller, N. J. Alvarez, O. Hassager, Bridging the Gap between Polymer Melts and Solutions in Extensional Rheology. *Macromolecules*, (2015), 48, 4158–4163.
7. V. Tirtaatmadja, G. H. McKinley, & J. J. Cooper-White, Drop formation and breakup of low viscosity elastic fluids: Effects of molecular weight and concentration. *Physics of Fluids*, (2006), 18, 043101.
8. L. E. Rodd, T. P. Scott, J. J. Cooper-White, & G. H. McKinley, Capillary break-up rheometry of low-viscosity elastic fluids. *Applied Rheology* (2015), 15, 12–27.

9. A. U. Chen, P. K. Notz, & O. A. Basaran, Computational and experimental analysis of pinch-off and scaling. *Physical Review Letters*, (2002), 88, 174501.
10. W. Mathues, C. McIlroy, O. Harlen, C. Clasen, Capillary breakup of suspensions near pinch-off. *Physics of Fluids*, (2015), 27 (9).
11. POLYOX™ Water-Soluble Resins: Unique Resins for Binding, Lubricity, Adhesion and Emollient Performance, The Dow Chemical Company, Form No. 326-00001-0302 AMS, March 2002.
12. W. W. Graessley, Polymer chain dimensions and the dependence of viscoelastic properties on the concentration, molecular weight and solvent power, *Polymer* 21 (1980), 258–262.

Chapter 3

Experimental techniques and protocols

In this chapter, we introduce the experimental techniques and protocols used in this thesis. Both extensional and rotational rheometers were used to characterize the mechanical properties of the samples. While other basic properties were measured by several other techniques that include: differential scanning calorimetry (DSC), thermogravimetric Analyzer (TGA), size exclusion chromatography (SEC) etc.

This chapter is organized as follows. First, the different experimental techniques employed in this work are presented from section 3.1 to 3.3. Then in section 3.4, the used experimental protocols are demonstrated very briefly. Lastly, the chapter concludes with the description of home-built mold used to prepare the samples in section 3.5.

3.1 Extensional rheometry

To accomplish the overall objective of this thesis, two different extensional rheometers were used. The extensional stress measurements of the polystyrene samples were carried by the commercially available version of the filament stretching rheometer, known as the VADER-1000 (Rheo Filament, USA). And the capillary breakup studies of the diluted PEO were performed in the Capillary breakup rheometer, CaBER-1 (Thermo Haake GmbH, Karlsruhe, Germany) equipped with a high-speed camera.

3.1.1 Versatile accurate deformation extensional rheometer (VADER - 1000)

VADER-1000 is an end-separation type instrument that allows a viscous liquid to be stretched uniaxially between two parallel plates similar to a MTR device¹. Originally developed as FSR at the Technical University of Denmark, VADER - 1000 comprises of an active feedback control loop that prevents filament instabilities^{2, 3, 4} (i.e. necking instability) during experiments thus allowing filament to sustain long enough to reach steady states (in constant rate mode). The main components of the device are demonstrated in fig 3.1.

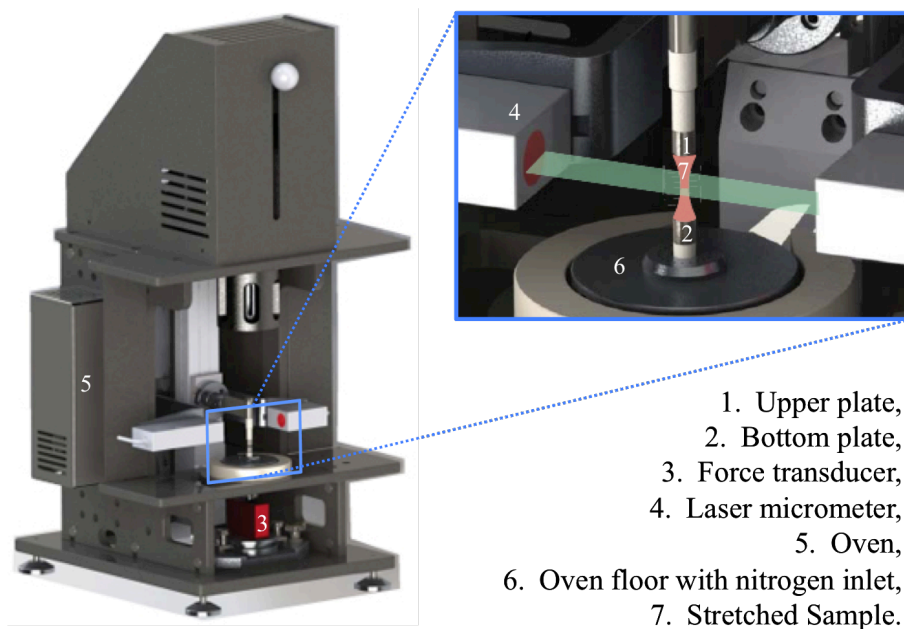


Fig. 3.1 Picture of a VADER-1000 with its main components. (image courtesy of Rheofilament¹⁰)

As illustrated, the device consists of five main components: two cylindrical steel plates, a force transducer, a motor, a laser micrometer and a convection oven. The sample is placed and sandwiched in between the cylindrical parallel plates to which is attached with direct adhesion of the sample to the metal. The top plate is connected with a linear motor and can deform the sample vertically to form a cylindrical filament between two plates. The stationary bottom plate is

connected with the force transducer that measures the force, $F(t)$ exerted by the sample during deformation, while the laser micrometer follows and measures the diameter, $2R(t)$ at mid-filament. The whole setup is enclosed by a convection oven that allows the measuring temperature to vary from room temperature to a maximum of 250°C . If needed inert gas can be purged in the oven in a controlled manner through a flow meter.

Unfortunately, an ideal filament stretching experiment is practically impossible as the no-slip boundary condition at the plates induces local shearing resulting in an inhomogeneous uniaxial deformation. As a consequence, the strain in the filament is not uniform, and the measurement is based on the mid-filament, where its diameter is at a minimum. The true Hencky strain at this point is measured from the observation of $R(t)$ (from laser micrometer) which is,

$$\varepsilon(t) = -2\ln\left(\frac{R(t)}{R_0}\right) \quad (1)$$

where, R_0 is the initial radius before the stretching started. Now assuming the mid filament has a rotational symmetry as well as axis symmetry, the mean value of the stress difference over the plane can be calculated from the observations of the laser micrometer, $R(t)$ and the force transducer, $F(t)$ as⁵

$$\langle\sigma_{zz} - \sigma_{rr}\rangle = \frac{F(t) - mg/2}{\pi R(t)^2} \quad (2)$$

where m is the mass of the sample and g is the gravitational acceleration.

Note that, the stress measured during this experiment is the true stress with respect to the mid-filament and not the engineering stress.

3.1.2 Capillary breakup extensional rheometer (CaBER)

As mentioned in chapter-1, filament stretching rheometers are used mostly to measure moderate to high viscous sample. For low viscous

samples, the surface tension comes into play and tends to destabilize the fluid filament ultimately leading to necking instabilities^{6, 7}. On contrary, the CaBER device uses the surface tension to create an extensional flow thus offering an alternative solution for low viscous samples. The main components of a CaBER device is illustrated in fig. 3.2,

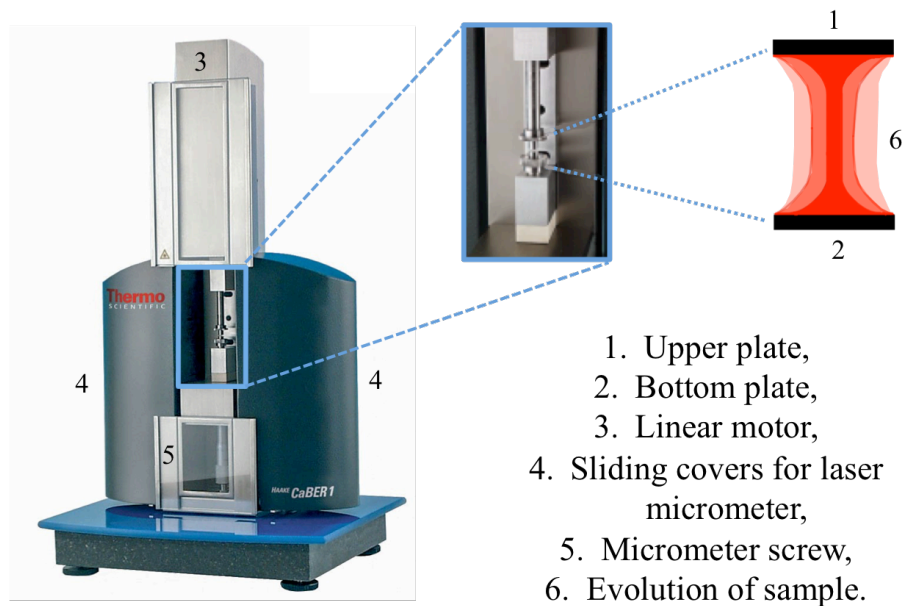


Fig. 3.2 Picture of a CaBER-1 with its main components, (image courtesy of Thermo HAAKE)

As illustrated, CaBER consists of three main components: two parallel plates, a linear motor and a laser micrometer. The upper plate is connected with the linear motor and can stretch the sample vertically whereas the bottom plate is at stationary but its position can be changed with a micrometer screw in order to vary the final gap size. Similar to a FSR measurement, a polymeric fluid bridge (filament) is placed between two cylindrical parallel metal plates to which is attached with natural adhesion of metal to sample. Afterwards, the upper plate is displaced rapidly by means of the linear motor and stopped at a final height. At this point, the capillary pressure will cause the filament to thin and ultimately to breakup (illustrated in fig 3.2). The mid-point evolution (presumed minimal diameter, where the surface tension is at maximum) of the filament is monitored with the

laser micrometer. This thinning dynamics is set by the resisting stress generating from the sample and reveals important fluid properties such as density, viscosity and elasticity.

Though, the CaBER doesn't involve any active stretching mechanism or direct force measurements, they can be estimated from the minimal diameter evolution. Thus an apparent extensional viscosity, $\eta_{E,app}$ can be calculated.

It should be noted that the laser micrometer only measures the mid-filament radius, which may not be the minimum (depends on the sample). In order to be accurate, in this work, the evolution of the minimal filament diameter was measured with a high-speed camera (Fastcam SA2, Photron, USA), connected to a tube lens system equipped with 5x and 10x microscopic objectives (Olympus, Japan). Consequently, the images were analysed with a Matlab-based software (developed at KU Leuven) that is described in details in ref. [8].

3.2 Rotational shear rheometry

The linear shear measurements of the PS systems were done with three different rheometers (due to the collaborative nature of this project): ARES-2K (TA instrument, USA), AR-2000 (TA instrument, USA) and MCR301 (Anton Paar, Austria). While the PEO systems were measured with an Ubbelohde viscometer, as the viscosity was too low to be measured with any of the conventional rotational rheometers. In order to be certain that the use of different rheometers did not affect the experimental results in any way, a comparative study between the rheometers was done with a common sample (see section 3.2.5).

3.2.1 Advanced rheometric expansion system, ARES-2K

ARES-2K is a strain-controlled rheometer that can apply rotational deformations to the sample placed between its geometries. Mostly used to measure high viscous/elastic materials, this device is capable

of subjecting a sample to either a dynamic (sinusoidal) or steady shear strain deformation, and then measure the resultant torque exerted by the sample in response to this shear strain. The main components of an ARES device are illustrated in fig. 3.3.

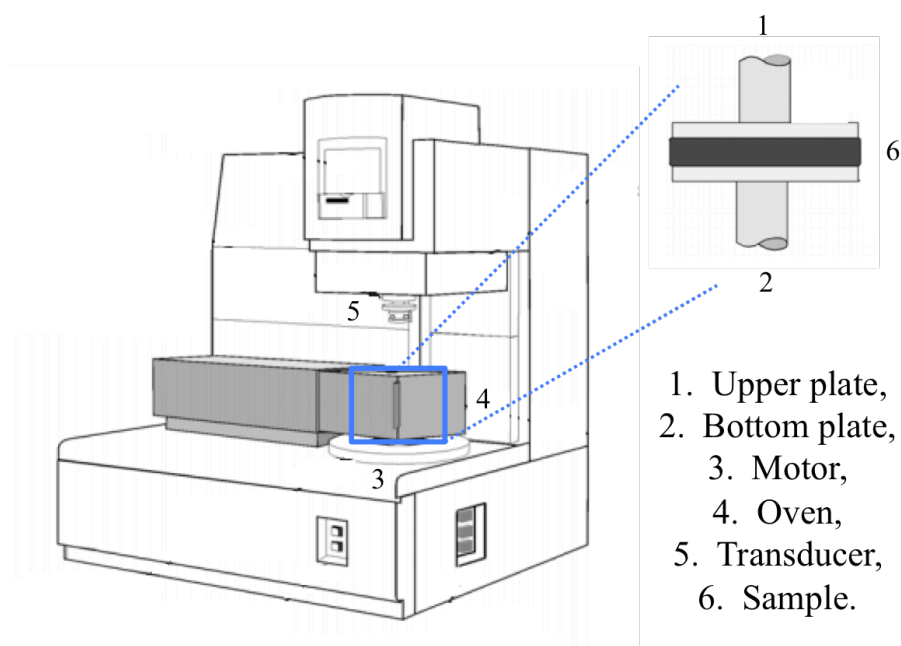


Fig. 3.3 Schematic diagram of ARES-2K with its main components. In inset, an example of a typical geometry is shown with parallel plate configuration, (image courtesy of TA instruments).

As illustrated, this device consists of four main components: upper & bottom geometries, a force transducer, a motor and a convection oven. The bottom and the upper geometries are connected to the motor and the force transducer respectively. The sample is placed and sandwiched in between the geometries. Shear strain is applied to the sample via the motor while the force rebalance transducer measures the resultant torque. The forced convection oven helps to ensure the right experiment conditions ensue. If needed, nitrogen, N_2 gas can be purged inside the oven either directly or following the liquid Nitrogen Dewar, thus allowing the usage of liquid N_2 .

The advantage of a strain-controlled rheometer is that the motor and the transducer are decoupled from each other. So the motor friction and inertia do not effect the torque measurements.

3.2.2 AR-2000

AR-2000 (TA instrument, USA) is a stress-controlled rheometer, which applies a certain torque on the test sample and the resultant angular displacement is measured via a displacement sensor. A schematic diagram of the device is illustrated in fig. 3.4,

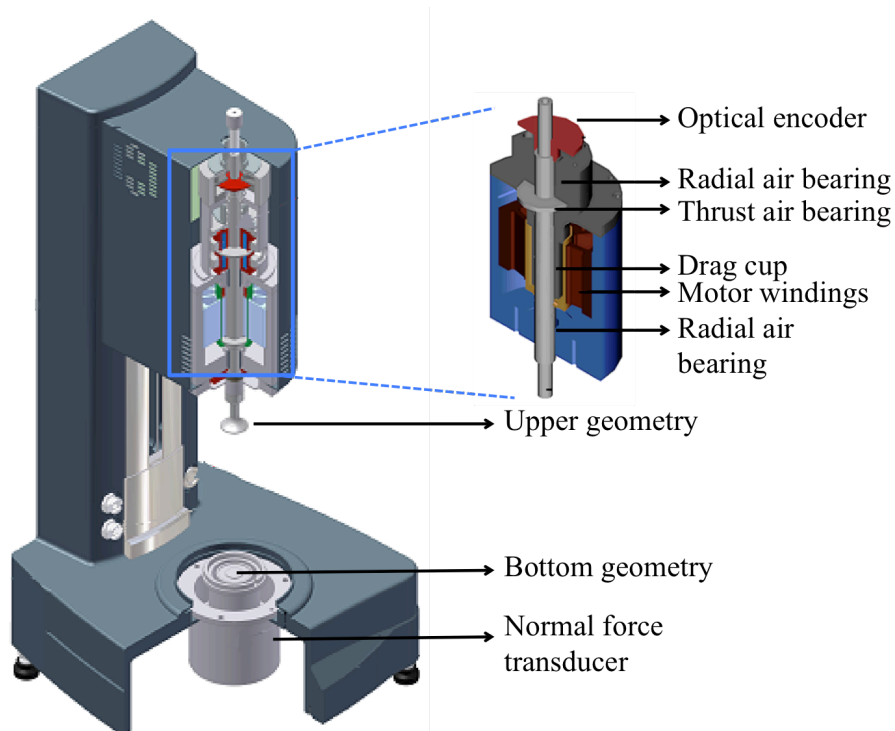


Fig. 3.4 Picture of a AR-2000 with its main components, (image courtesy of TA instruments).

AR-2000 has five main components: upper and bottom geometries, an induction motor, an optical encoder device, air bearing and a normal force transducer. The sample is placed in between two parallel plates, where the upper plate is connected with the induction motor while the

bottom plate is at stationary and is placed on top of the normal force transducer. The optical encoder is positioned on top of the motor, which is supported by the air bearing, thus they are isolated from each other.

A temperature-controlled environment can be ensured by either attaching the Peltier setup or the electrically heated plate (EHP) temperature system. In this work, this was achieved by the later setup (EHP) together with an environmental cover.

3.2.3 MCR 301

In this study, an MCR301 equipped with a convection oven was used. This device is also a stress-controlled rheometer like the AR-2000 and runs on similar working principle. A MCR301 is illustrated in fig 3.5,

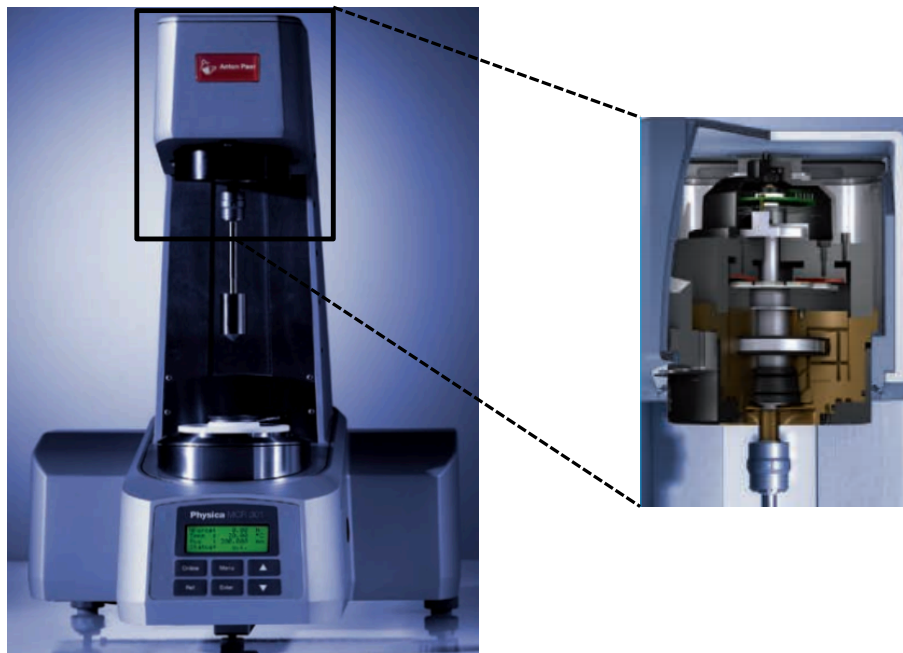


Fig. 3.5 Picture of a MCR301. Magnified measuring head is shown in inset, which constitutes motor, air bearing, optical encoder and a normal force transducer. (Image courtesy of Anton Paar).

Similar to the AR-2000, this device also has five main components: upper and bottom geometries, a synchronous motor, a rigid air bearing, an optical encoder device and a normal force transducer. The major difference in MCR 301 is that the normal force transducer isn't positioned below the bottom plate but within the air bearing on top of the upper plate geometry.

The major advantage of using a stress controlled rheometer over a strain controlled is that it can measure normal force exerted by the sample very precisely. This is particularly important for systems (colloids, suspensions) that become effectively inelastic under steady shear and can display negative normal forces due to inertial effects.

3.2.4 Ubbelohde viscometer

The base viscosities of polymer solutions used in chapter 9 (high M_w PEO diluted in water), were below the lower detection limit of the conventional rotational rheometers. So more sensitive Ubbelohde viscometer was used. A schematic diagram of a typical Ubbelohde viscometer is shown in fig. 3.6,

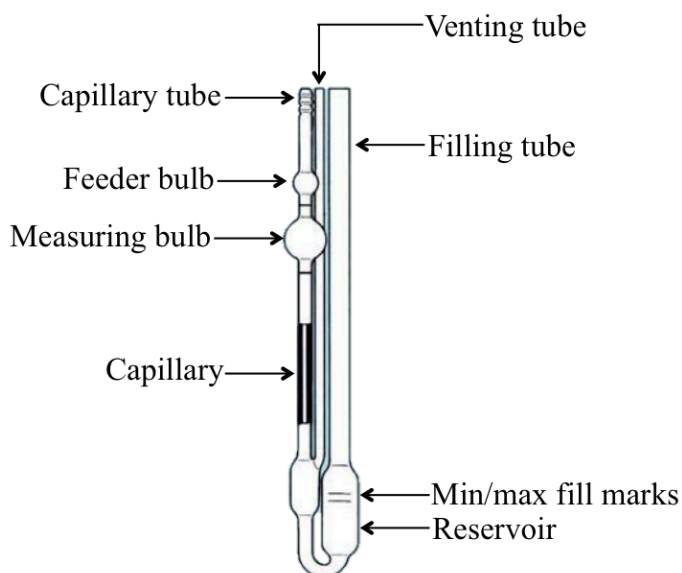


Fig. 3.6. Schematic diagram of Ubbelohde viscometer (image courtesy of Schott instruments¹¹).

Comparison between different shear rheometry

The dynamic viscosities of the solutions were measured with an Ubbelohde viscometer equipped with a capillary with a diameter of 0.53 mm (Schott Instruments).

3.2.5 Comparison between different rheometers

The comparative study between different rheometers was done with a standard linear PDMS at 25°C. The result is demonstrated in fig. 3.7,

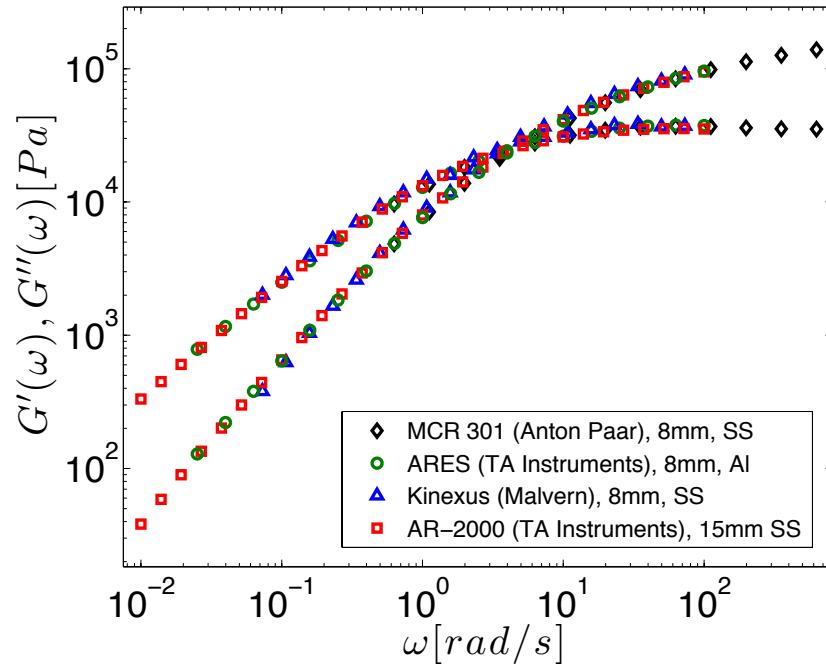


Fig. 3.7 Comparative study of standard PDMS with different rheometers. SS: Stainless steel and Al: Aluminum.

Fig 3.7 compares experimental data of standard PDMS measured by a) different rheometers, b) different geometry materials and c) different geometry dimensions. The results are in very good agreement and validates the further use of different rheometers in this project.

3.3 Other techniques

Differential Scanning Calorimetry, DSC:

Differential scanning calorimetry is a very useful thermal analysis tool that can detect phase transitions of a material very precisely. During a DSC measurement, the heat flow required to increase the temperature of the sample and a reference is recorded. Any difference in the heat flow suggests phase transition of the sample as it involves change in energy.

In this thesis, this method was used to determine the glass transition temperatures of both the ingredients and the final solutions. The measurements were done in a Q2000 (TA instruments, USA) instrument equipped with an auto-sampler. This device can work under a broad temperature range from -90°C to 550°C and can run upto 50 automated sample using 5 reference pans at a time. About 5 mg of sample was placed in an aluminum pan and carefully sealed with a cap. Then the DSC measurement was carried out using a standard heat-cool-heat procedure with a heating rate of $10^{\circ}\text{C}/\text{min}$ under constant nitrogen gas supply.

Measurement of three different molecular weight PS melts used in this work are shown in fig. 3.8.

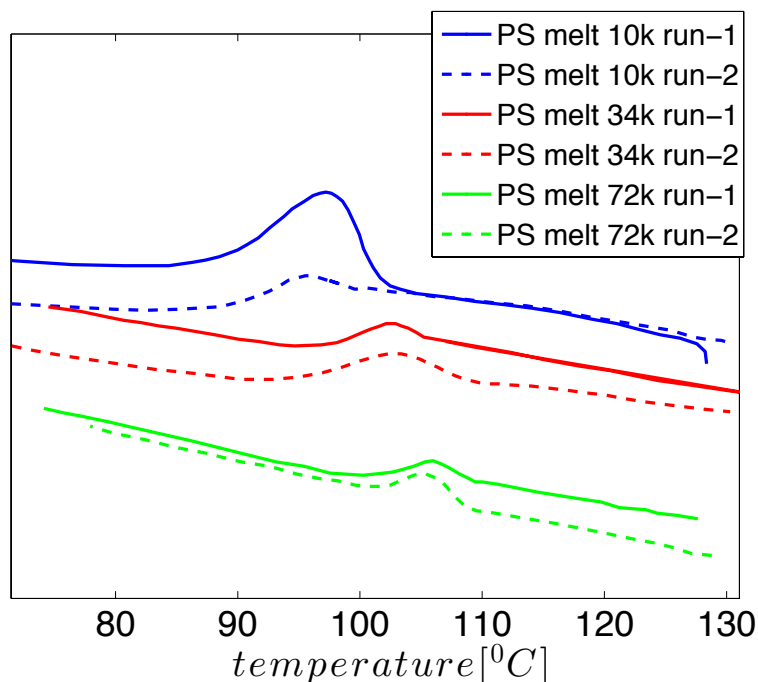


Fig. 3.8 Measuring the glass transition temperatures of PS melts by DSC.

Thermogravimetric Analyzer, TGA:

Thermogravimetric analyzer is another important thermal analysis tool, which can detect important physical and chemical phenomena such as phase transition, absorption, degradation etc. TGA measures mass loss of a sample very accurately over time versus the temperature.

In this thesis, a Q500 Thermogravimetric Analyzer (TA instruments, USA) was used to measure the degradation temperature of both ingredients and the final solutions. The Q500 consists of a low mass (from 5mg upto 1g) furnace with a rapid, precise temperature and rate programming. The temperature can be varied from room to a maximum of 1000°C. In this work, the TGA was carried out with a 5-10 mg of sample and in between room temperature to 500°C with a heating rate of 10°C/min. TGA measurements of two PS melts and a solution are illustrated in fig. 3.9.

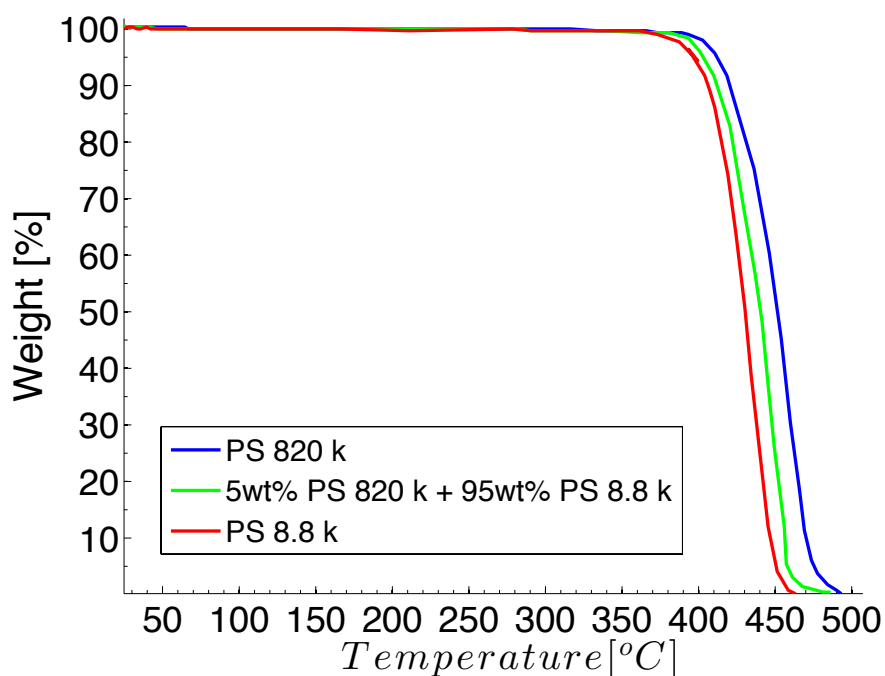


Fig. 3.9 Measuring the degradation temperature by TGA.

Size exclusion chromatography, SEC:

In this thesis, Size exclusion chromatography was performed to determine the molecular architecture (molar mass and polydispersity indexes) of the ingredients.

SEC was performed in *N,N*-dimethylformamide containing 2.5 mM NH_4PF_6 to determine molar mass distributions with respect to polystyrene standards. The measurements are carried out on a system composed of two PSS Gram columns (100 Å and 1000 Å) connected to a Waters 410 differential refractive index (DRI) detector operating at 1 mL/min flow rate and a temperature of 35°C.

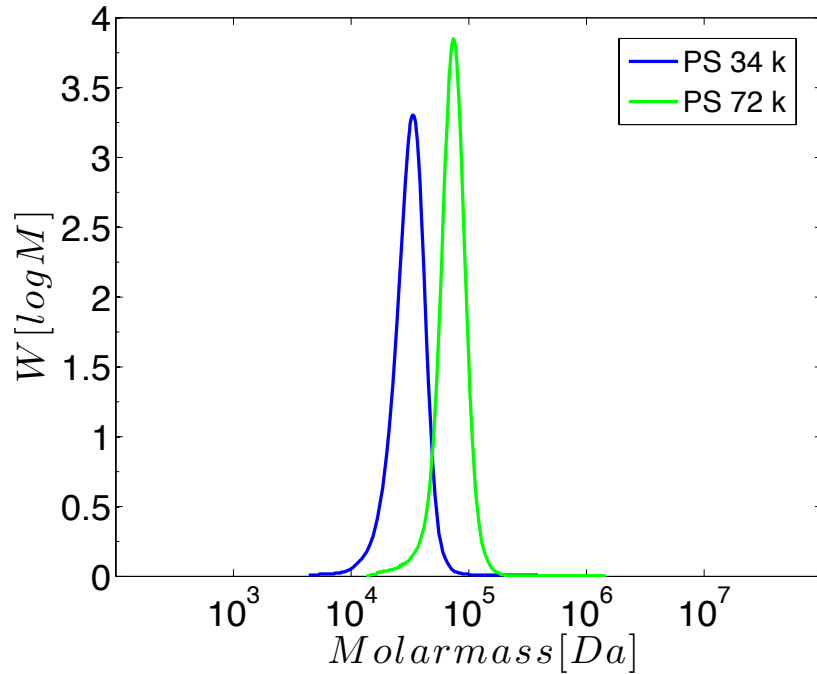


Fig. 3.10 Measuring the molecular architecture of PS melts by SEC.

Wilhelmy plate:

The surface tension at the air-sample interface is measured with a platinum Wilhelmy plate with a wetted length of 20 mm, which is attached to an electrobalance (KSV Nina).

3.4 Experimental protocols

In order to generate good and consistent dataset, it's imperative to use a well-defined measuring protocol. In this section, we present the protocols used for measuring both linear and non-linear viscoelastic properties of the samples.

3.4.1 Linear shear measurements

The measuring protocol for linear shear measurement consisted of three sub-tests:

a) Amplitude sweep test:

First an amplitude sweep test was carried out to find the limit of linear regime. This test was done at 1 rad/s and upto 5-10% of the sample's initial amplitude. No significant deformation was observed over the whole range, meaning the sample deforms linearly at least up to 5-10% of the initial length. An example of an amplitude sweep test is shown in fig. 3.11.

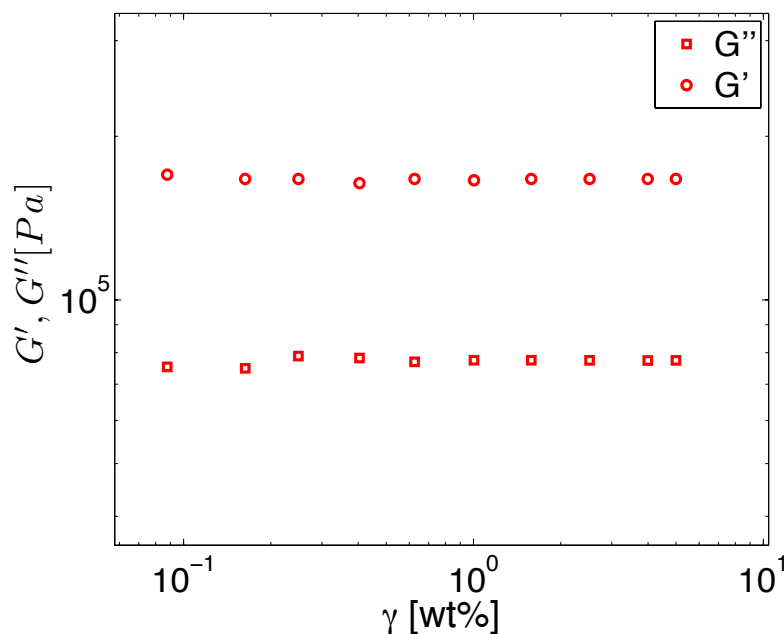


Fig. 3.11 Amplitude sweep test of a PS solution (80wt% PS 820 kg/mol - 20wt% OS 9kg/mol).

b) Time sweep test:

The amplitude sweep test was followed by a time sweep, which was done to make sure all the residual stress in the sample is relaxed and it is well equilibrated with the experimental temperature. During the preparation of the sample, rapid cooling could induce some additional stress in the sample, which needs to be relaxed before measurements. The time sweep test was done at 1 rad/s and at least for one hour.

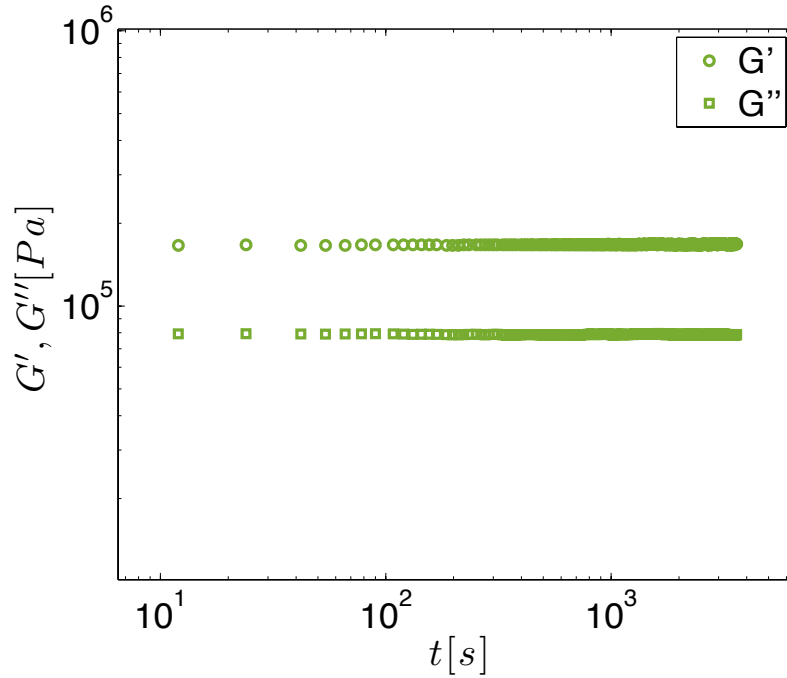


Fig. 3.12 Time sweep test of a PS solution (80wt% PS 820 kg/mol - 20wt% OS 9kg/mol).

c) Frequency sweep test:

This is the most important test in the context of this thesis. Frequency sweep tests were done at different temperatures to measure the entire relaxation spectrum of the samples. The chosen temperature range varied with the level of dilution of the samples.

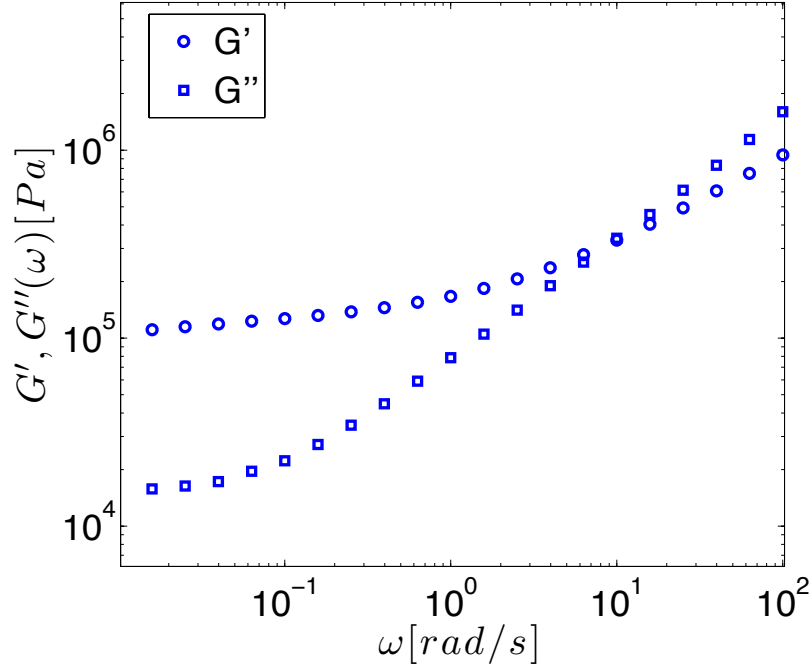


Fig. 3.11 Frequency sweep test of a PS solution (80wt% PS 820 kg/mol - 20wt% OS 9kg/mol).

For both time and frequency sweep test, the applied strain was altered as per the level of dilution but never exceeded 10% of the initial length (linear regime).

3.4.2 Non-linear extensional measurements

Again a three-step measuring protocol was followed for the non-linear uniaxial measurement.

a) First, the sample was slightly squeezed at an elevated temperature (above the T_g or T_m of the sample) to ensure adequate contact between the sample and the parallel plates.

b) Next, it was pre-stretched to a smaller radius to minimise the risk of sample detachment during the next step. This also helps to eliminate the local shearing effect at the plates (to some extent).

c) Finally, the temperature was decreased to the experimental temperature and subsequently the time-dependent stress growth coefficient was measured at constant Hencky strain rates.

3.5 Sample preparation mold

Two major issues influencing the visco-elastic properties of PS systems are: thermal degradation and the atmospheric humidity. These systems are prone to absorb water from the environment and degrade at elevated temperature in presence of oxygen known as the thermo-oxidative degradation⁹. Thus making it very important to process PS systems at inert conditions all the time. Therefore, a custom home-built mold was made to prepare the PS samples at suitable condition prior to the measurements. The mold is shown in fig. 3.8,

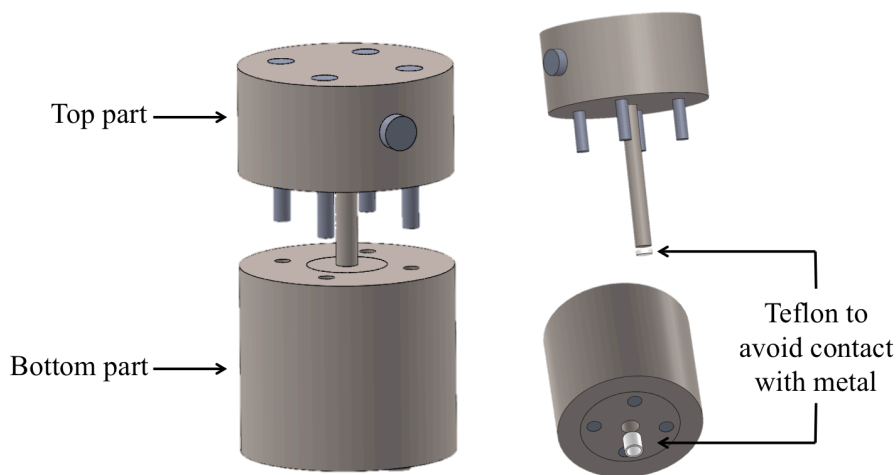


Fig. 3.8 Home-built mold to prepare PS samples.

As we know PS samples has the tendency to stick with metal thus making it difficult to detach the sample. The use of teflon at the end of cylinder prevents that problem specially for less viscous samples. The whole setup is kept inside a vacuum oven on top of a Teflon sheet. A major advantage of this mold is that multiple samples can be pressed at the same time under vacuum.

On the other hand, the PEO systems studied in this work were all liquid-like in room temperature and could be put in the rheometer directly without any preparation.

3.6 Summary

All experimental techniques and protocols used in this work have been summarized in this chapter. The main reasons and major advantages behind using these techniques and protocols are also explained. Finally, a brief description on the custom mold used to prepare the PS samples is presented.

The corresponding experimental results are presented and discussed in details in the following chapters.

References:

1. H. Münstedt, New universal extensional rheometer for polymer melts. Measurements on a polystyrene sample. *J. Rheol.* ,(1979), 223, 421–436.
2. S. M. Fielding, Criterion for Extensional Necking Instability in Polymeric Fluids. *Phys. Rev. Lett.*, (2011), 107(25), 258301.
3. D. M. Hoyle and S. M. Fielding. Criteria for extensional necking instability in complex fluids and soft solids. Part I: Imposed Hencky strain rate protocol. *Journal of Rheology*, (2016), 60(6), 1347-1375.
4. D. M. Hoyle and S. M. Fielding. Criteria for extensional necking instability in complex fluids and soft solids. Part II: Imposed tensile stress and force protocols. *Journal of Rheology*, (2016), 60(6), 1377-1397.
5. P. Szabo, Transient Filament stretching rheometer. *Rheologica Acta*, (1997), 36(3), 277.
6. S. L. Anna, G. H. McKinley, D. A. Nguyen, T. Sridhar, S. J. Muller, J. Huang, D. F. James, An interlaboratory comparison of measurements from filament-stretching rheometers using common test fluids. *Journal of Rheology*, (2001), 45, 83–114.
7. O. Hassager, M. I. Kolte, & M. Renardy, Failure and nonfailure of fluid filaments in extension. *Journal of Non-newtonian Fluid Mechanics*, (1998), 76, 137–151.
8. W. Mathues, Filament stabilisation in free-surface flows of complex fluids. Ph.D. thesis, KU Leuven (2015).
9. J. D. Peterson, S. Vyazovkin, C. A. Wight, Kinetics of the Thermal and Thermo-Oxidative Degradation of Polystyrene, Polyethylene and Poly(propylene), *Macromol. Chem. Phys.*, (2001), 202, 775–784.
10. Rheo filament. <http://rheofilament.com>. Accessed at: 28/05/2018.

11. Schott instruments. http://www.si-analytics.com/fileadmin/upload/Informationen/Kapillarviskosimetrie/INT/Technical-Data_Viscometers_400-KB_PDF-English.pdf.
Accessed at: 28/05/2018.

Chapter 4

Choosing the right operating conditions for filament stretching experiments

Filament stretching rheometry is a robust and reliable method to measure the uniaxial elongational properties of moderate to high viscous polymeric systems given the optimum experimental conditions has been chosen. Thus, in this chapter we discuss the importance of choosing the right conditions, starting from the most suitable sample preparation techniques to the best experimental protocols. At the end, a brief benchmark study of VADER-1000 between two laboratories (Technical University of Denmark and Université catholique de Louvain) is discussed to comment on the reproducibility and reliability of the measurements. Please note that all samples are individual and needs special considerations. Therefore, the operating conditions chosen in this work is strictly sample-specific (for PS systems diluted in its oligomers) and may not be suitable for other systems.

This chapter is organized as follows. The criteria and importance of removal of sample impurities and the appropriate experimental protocols are discussed in section 4.1 and 4.2 respectively. Then the chapter concludes with a benchmark study between two institutes with common samples (section 4.3).

4.1 Sample impurities

In order to obtain the best result from a filament stretching device, the sample has to be treated properly before it is placed inside the device. Presence of residual solvent or humidity can alter the behavior of a

polymeric system to a large extent. The effect of these impurities is discussed below.

4.1.1 Presence of water

PS samples are prone to absorb water from the air even at ambient conditions, which influences the overall rheological properties. When heated, the presence of moisture in the sample can lead to formation of bubbles. Presence of such a bubble in the mid-filament would decrease the cross sectional area, leading to an inaccurate stress calculation. Therefore, the PS samples are needed to be stored in a moisture-free environment like a desiccator all the time. And prior to molding, they must be dried under vacuum at an elevated temperature (near the T_g of the sample). This removes the external surface moisture. Also during the molding process, the system needs to be under vacuum, as PS tends to absorb more water at elevated temperature.

4.1.2 Presence of residual solvent

The presence of residual solvent is more significant than the humidity and should be handled with greater care. It may appear in our systems either during the polymerization of PS or the preparation of PS blends/solutions. Presence of residual solvents can decrease the overall glass transition temperature, T_g of the system, as PS are extremely sensitive to temperature, a small change in T_g could lead to a substantial different elongational behavior as discussed in the following section.

To realize how significant the presence of impurities can be, we prepared and studied a PS solution (40wt% PS 820 kg/mol - 60wt% OS 9kg/mol) that was treated in two different ways. The first sample, PS-1 was cleaned extensively to remove all impurities, while the second sample, PS-2 was left without any treatment thus containing impurities in form of both moisture and solvent. The comparison between these two systems is shown in fig.4.1.

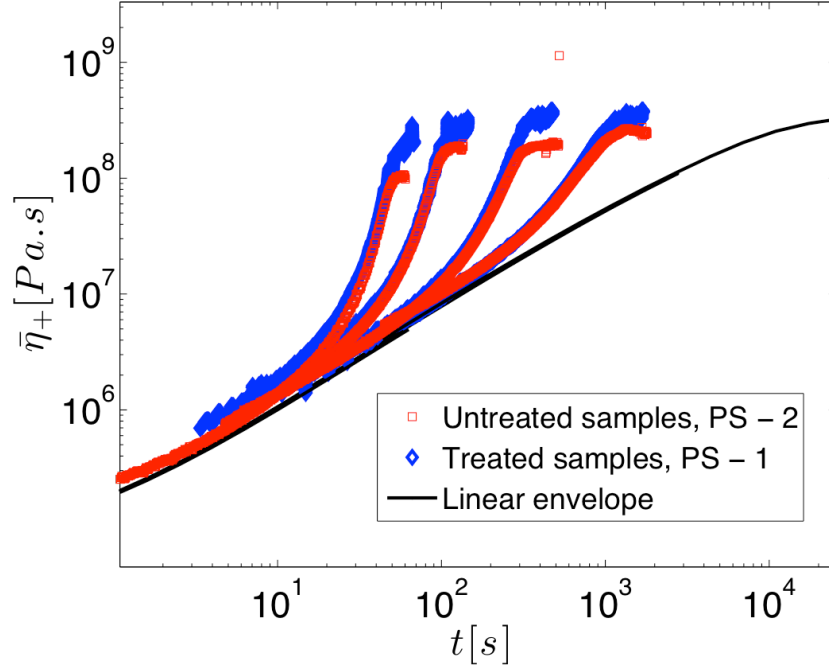


Fig. 4.1. Comparison of FSR measurements between well dried and undried samples of a PS solution measured at 130°C (strain rates, $\dot{\epsilon} = 0.01, 0.03, 0.06, 0.09 \text{ s}^{-1}$).

The presence of impurities clearly alters the elongational behavior of PS solutions. The effect is much prominent at higher Hencky strains when the steady value is achieved. It should be noted that at low Hencky strains, both systems follow the linear viscoelastic envelopes closely, so following the linear envelope doesn't guarantee a reliable measurement. Our results agree with the trend observed in ref [1].

4.1.3 Comparison between different treatment methods

In order to make sure that the system is completely cleansed of any type of impurities, we have employed two different sample-treating techniques. The first technique (T-1) is a rather simple one, where the PS systems were dried inside a vacuum oven at a temperature higher than the boiling temperatures of the solvents and close to the glass transition temperature of the PS systems. THF and methanol were used to prepare the PS solutions, both of which have a boiling temperature of around 65°C while the glass transition temperature of the PS systems is around 100°C . So they were dried at 90°C for

Comparison between different treatment methods

several hours and at 70°C for about three days. Please note that the samples were dried as powders rather than in solid blocks to ensure an easier diffusion of the solvent.

In the second technique (T-2), the PS systems were first dissolved in benzene solution and then precipitated into methanol. Then the precipitant was re-dissolved in benzene at concentration ~ 5 wt% and freeze-dried for two days in vacuum. This method results in porous PS sample, which is something like styro-form and is efficient for removal of solvent. Finally, the porous sample was dried in vacuum at an elevated temperature (85-90°C) for a week to completely remove any residual solvent. This technique (T-2) was carried out at Kyoto University in collaboration with Professor H. Watanabe and Y. Matsumiya².

A comparison between these two drying procedures with a common sample (20wt% PS 601 kg/mol - 80wt% OS 9kg/mol) is shown in fig. 4.2.

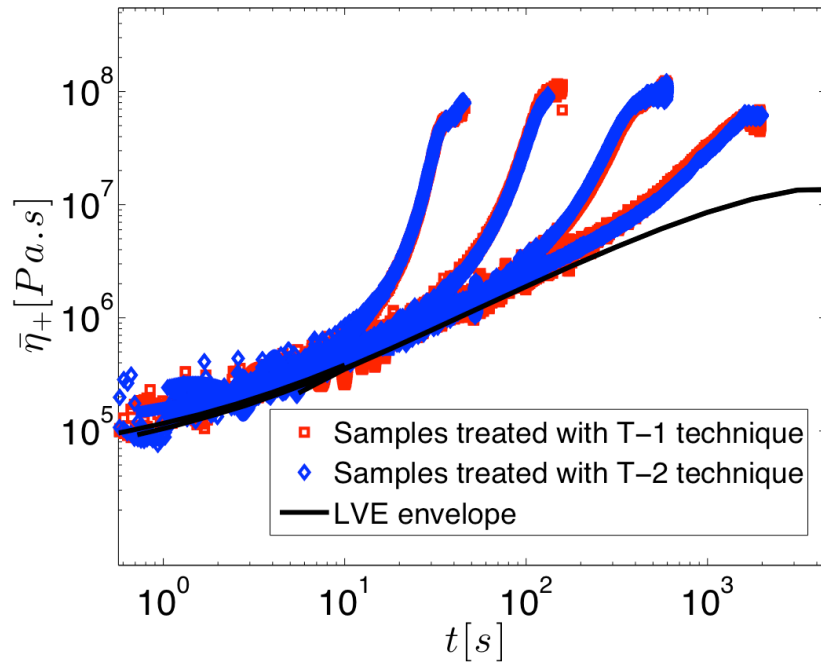


Fig. 4.2. Comparison of FSR measurements between different drying techniques of a PS solution measured at 130°C (strain rates, $\dot{\epsilon} = 0.1, 0.03, 0.01, 0.003 \text{ s}^{-1}$).

Both these techniques result in similar reproducible data indicating that both of them can be used to remove the impurities. In this work, we mostly employ the technique T-1 due to its simplicity.

4.2 Importance of good experimental protocol:

Good robust experimental protocol is a pre-requirement to produce reliable data. In this section, we discuss such important aspects that we need to consider during filament stretching experiments. Please note these specifications are directed for PS systems diluted in oligomers and may need adjustment for other systems.

4.2.1 Sample aspect ratio:

Inherently present no-slip boundary condition in the filament stretching experiments results in significant deviations from ideal uniaxial deformation, particularly in the start-up of the flow. Expectedly, this effect becomes significant for initially low aspect ratio ($\Lambda_0 = L_0/R_0$) samples. Luckily, expressions were mathematically derived³ and successfully applied⁴ in order to correct for this kinematics. The VADER software incorporates the correction factor that decouples the extensional stress contribution from the shear contribution at small aspect ratios. However, this empirical correction factor is based on a certain aspect ratio ranging from 0.48 to 0.59. Therefore, measuring samples with lower initial aspect ratios ($\Lambda_0 < 0.48$) could result in some discrepancy especially at the start-up of the flow (typically a small deviation from linear viscoelastic envelop). To check the significance of this effect, in this work we have measured our samples with different initial aspect ratios (from 0.4 to 0.5) and the results were found to be satisfactorily overlapping as shown in fig. 4.3. This specific example is for a PS solution (20wt% PS 601 kg/mol - 80wt% OS 9kg/mol).

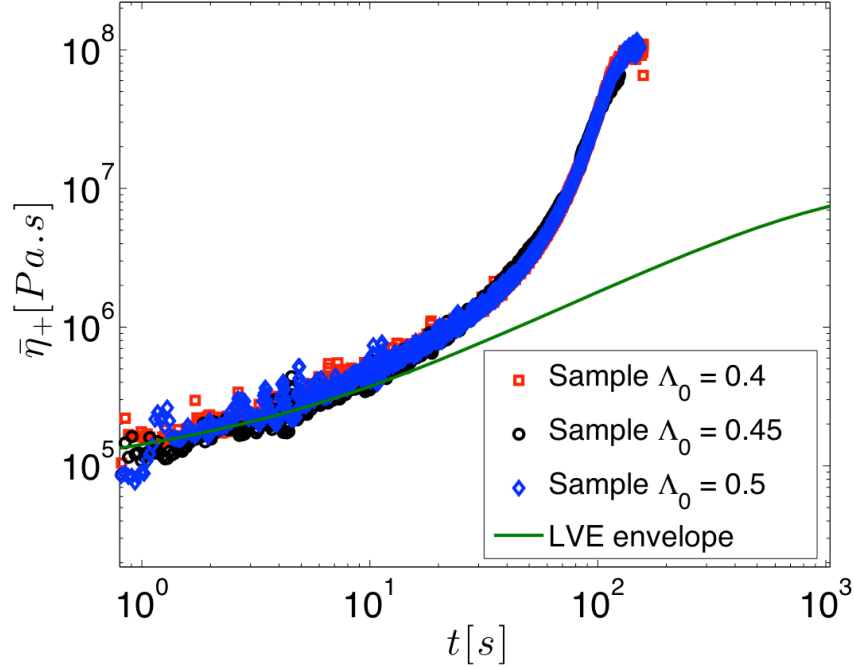


Fig. 4.3. Comparison of FSR measurements for samples with different aspect ratio at 130°C (strain rate $\dot{\epsilon} = 0.03 \text{ s}^{-1}$).

Lower aspect ratio sample could also lead to end-plate instability, especially if the fluid exhibits strong strain hardening phenomenon. One such example as encountered in ref [5] and is illustrated in fig 4.4.

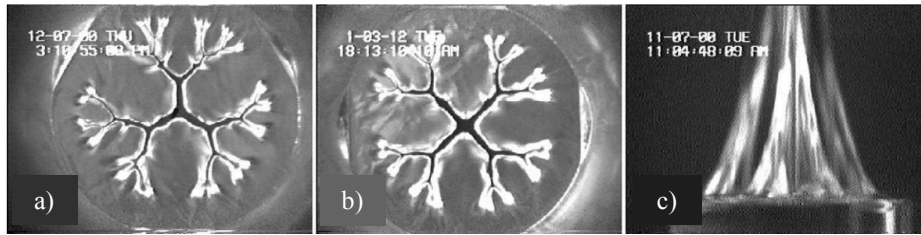


Fig. 4.4 End-plate instability observed in high molecular weight polystyrene ($M_w = 2 \text{ Mg/mol}$, $\text{PDI} = 1.2$) diluted at 12 wt% in tricresyl phosphate. The picture was taken from below the bottom glass cylinder (a, b) and from the side (c). Image courtesy of Bach et al.⁵.

If this end-plate instability propagates all the way to the mid-filament, the plane measured by the laser micrometer is not cylindrical anymore, thus could lead to irreproducible measurements.

Therefore, an initial aspect ratio between 0.48-0.59 is recommended for PS samples, particularly for largely diluted PS solutions that show strong strain hardening behavior.

4.2.2 Flow rate inside the oven

Continuous flow of inert gas/ air is needed to ensure a good homogeneous temperature profile inside the oven of the VADER. The gas inlet is placed just beneath the bottom plate, so if the flow rate is too high, the gas is not equilibrated with the set temperature and the bottom end of the filament will be at a lower temperature than the other parts. Since PS samples are very sensitive to temperature this would then result in a vertical shift in the experimental result.

High flow rate can easily be detected towards the end of an experiment. If the flow is too high, the middle of the thinning filament will start to move i.e. flap back and forth. The effect of different flow rate was studied with a PS solution (10wt% PS 820 kg/mol - 90wt% OS 9kg/mol) and illustrated in fig. 4.5.

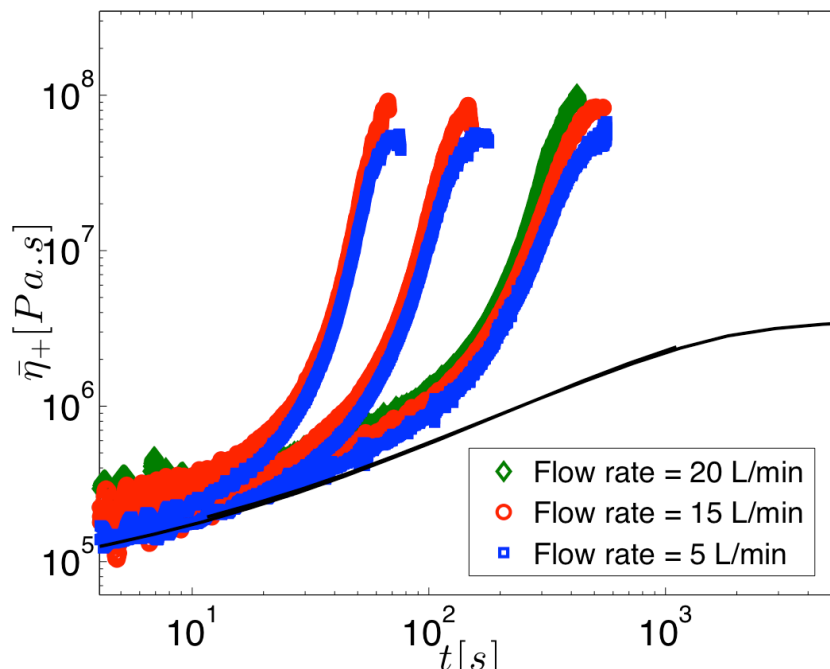


Fig. 4.5. Comparison of FSR measurements with different air / N₂ flow rate at 130°C (strain rates, $\dot{\epsilon} = 0.01, 0.03, 0.06 \text{ s}^{-1}$ from left to right).

As we can see from fig. 4.5, with increase in flow rate, the elongational stress measurements shifts vertically (away from the LVE envelope), indicating the temperature inside the oven is non-homogeneous. The optimal flow rate inside the oven is estimated to be around 4-6 L/min. On an average, 5 L/min N₂ gas flow is used in this work.

4.2.3 Inert atmosphere inside the oven

The viscoelastic properties of PS systems are largely influenced by two atmospheric conditions: temperature and the humidity. These systems are prone to absorb water from the environment, which affects their properties. Also at elevated temperature, they could degrade in presence of oxygen, which is known as the thermo-oxidative degradation⁶. Thus it is very important to measure PS systems at inert conditions all the time. In particular, prior to a

VADER measurement, PS samples are squeezed and pre-stretched at a higher temperature compared to the experimental temperature. This is usually done to facilitate the relaxation of the sample. However, too high temperature could lead to degradation of PS samples even at inert condition.

A comparison between different environments is shown in fig. 4.6 a) and b).

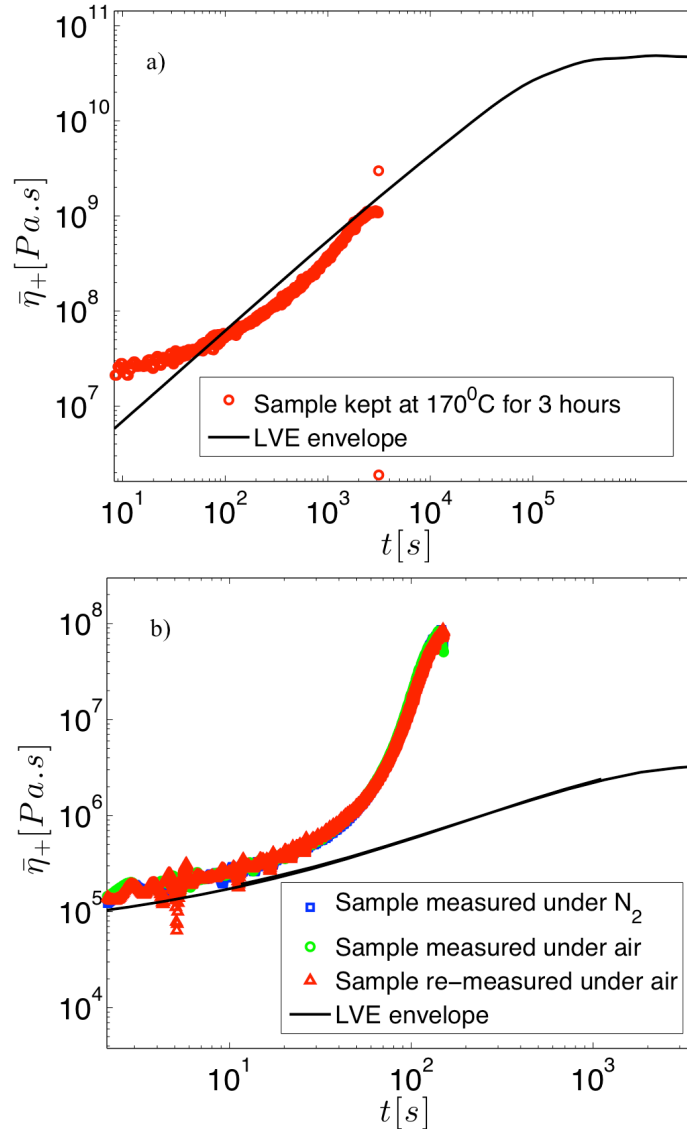


Fig. 4.6. Comparison of FSR measurements with different environments inside the oven a) sample kept at 170°C for $t > 3$ hours

_____ Importance of good experimental protocol: inert atmosphere

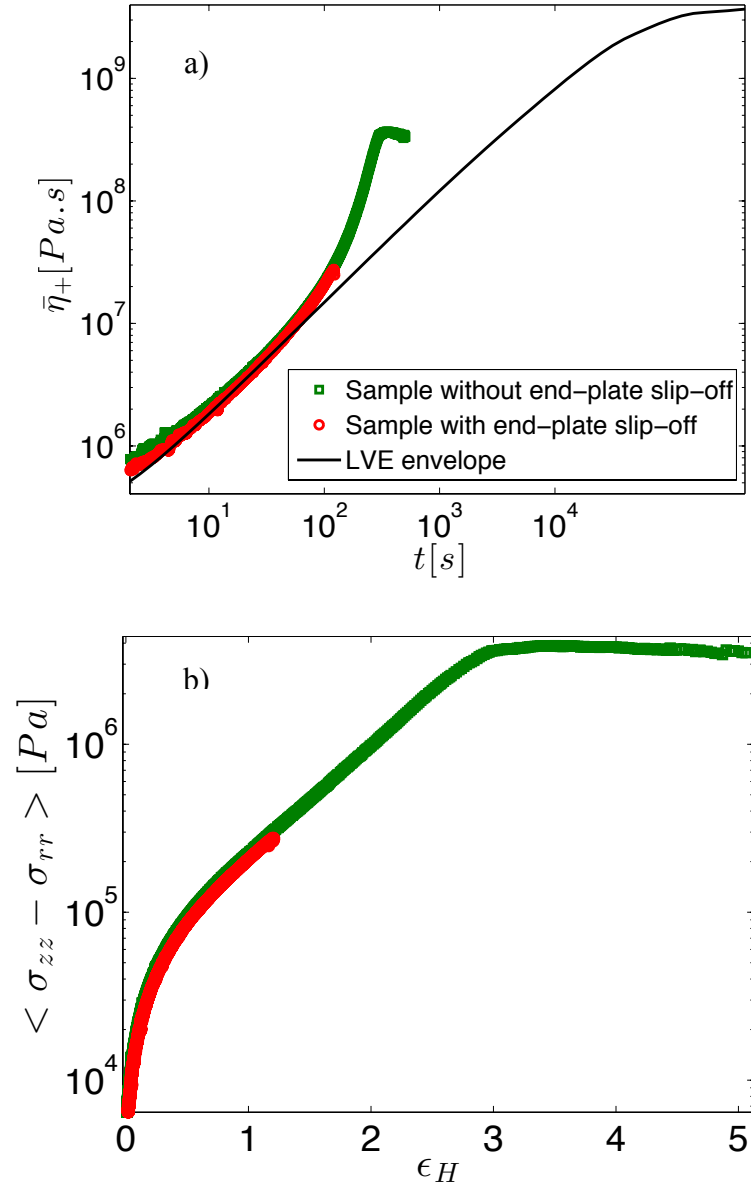
under N₂ b) sample measured under air and N₂ at 130⁰C (strain rate $\dot{\epsilon} = 0.03 \text{ s}^{-1}$).

As shown in fig. 4.6 a, the PS melt (PS 820 kg/mol) does not follow the linear envelope when kept at 170⁰C under N₂ for about 3 hours. This behavior can be attributed to thermal degradation, which results in chain scission. Note that the measured degradation temperature of this sample was around 400⁰C (TGA).

Interestingly, when the same PS sample (10wt% PS 820 kg/mol - 90wt% OS 9kg/mol) is measured separately under air and N₂ supply at temperature less than 160⁰C, reproducible data are obtained as shown in fig. 4.6 b. This suggests that it is more important to measure PS samples at moderate temperature range (<170⁰C) than using the inert condition, although it is highly recommended. However to avoid any risk, all measurements in this work were done under constant N₂ supply.

4.2.4 Sample pre-stretching:

Prior to the elongational stress measurements, the sample should be pre-stretched to a smaller radius. The purpose of this pre-stretch is two-fold; first it increases the initial aspect ratio of the sample, thus reducing the local shearing effect at the plates and secondly, it minimizes the possibility of sample slip-off due to the high force buildup during the stress measurement. The importance of sample pre-stretching is illustrated in fig. 4.7 a-c.



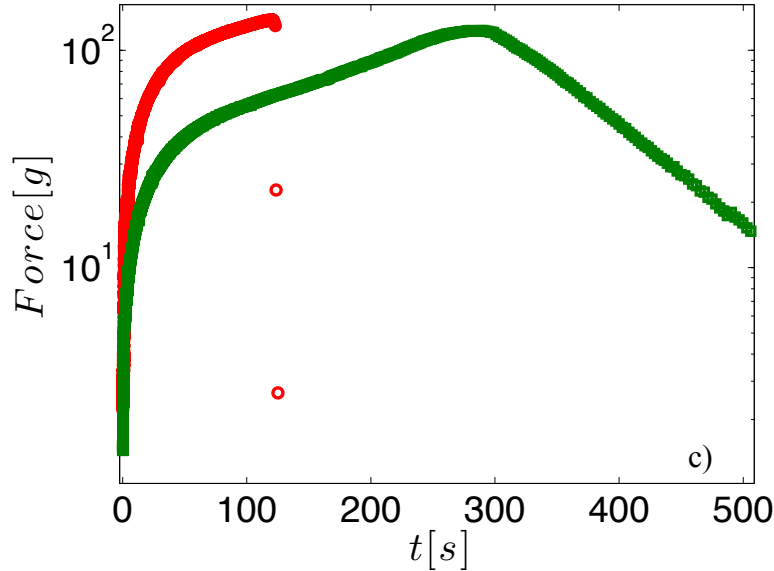


Fig. 4.7. FSR measurements with and without end-plate slip-off at 130°C and $\dot{\epsilon} = 0.01 \text{ s}^{-1}$. a) Transient elongational viscosity as a function of time b) elongational stress as a function of Hencky strain and c) force build up vs time.

As illustrated in fig. 4.7, the sample (50wt% PS 820 kg/mol - 50wt% OS 9kg/mol) can be stretched till higher Hencky strain by application of pre-stretching. The sample (red curve) slips-off when pre-stretched to 4.6 mm from an initial diameter, $d_0 = 5.5\text{mm}$. This can be avoided by pre-stretching the sample to a reduced diameter of 2.95 mm (green curve).

4.2.5 Other experimental issues

a) Brittle fracture:

Brittle fracture is defined as a rapid plastic deformation that takes place without any dissipative process. Although mostly common for solid materials, viscoelastic materials can exhibit brittle fracture⁷⁻¹⁰ when submitted to large deformation rates. At these high rates, viscoelastic materials can fracture in the elastic limit where the viscous dissipation is not relevant. Brittle fracture has been frequently

observed in our measurements, taking place at low Hencky strain, $\epsilon_H < 3$, i.e. much before the steady state is attained. Thus, this process restricts the maximum applied strain rate for a sample.

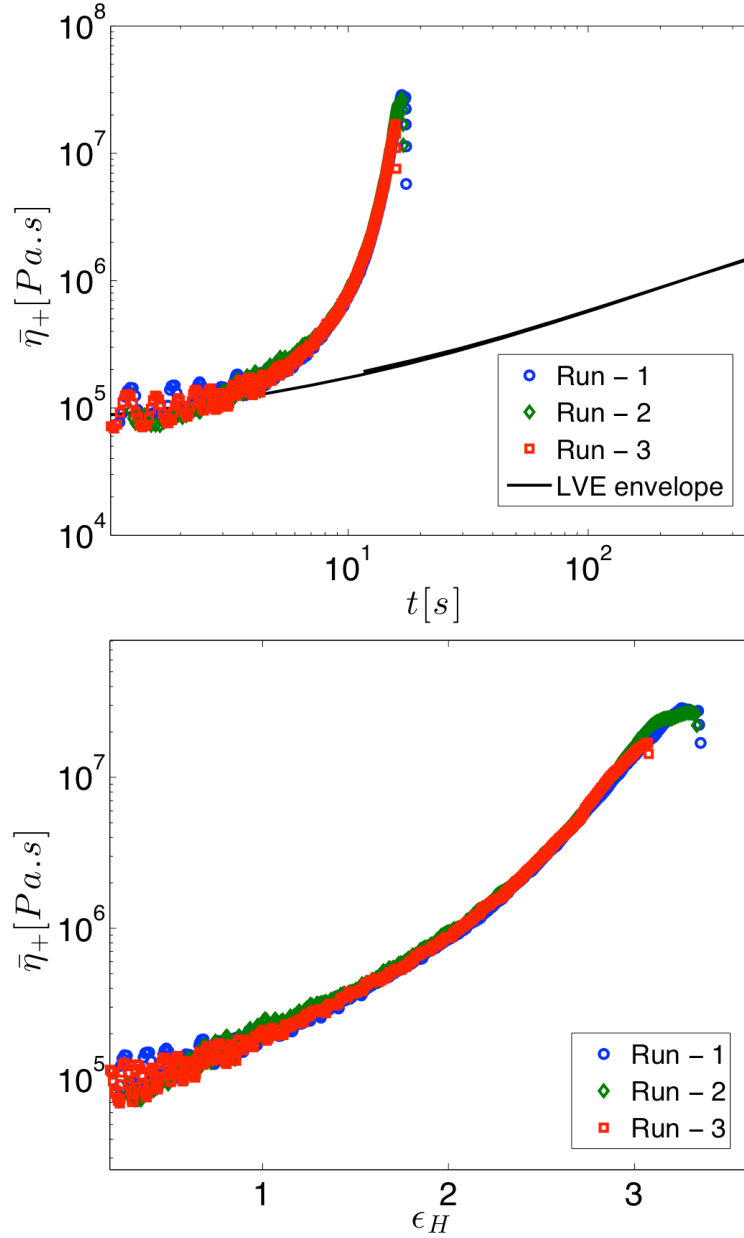


Fig. 4.8. Brittle fracture in FSR measurements at 130^0C and $\dot{\epsilon} = 0.2 s^{-1}$.

As we can see from figure 4.8, a sample (10wt% PS 820 kg/mol - 90wt% OS 9kg/mol) has been measured 3 times at the same rate and brittle fracture is observed in all cases at similar Hencky strain. This instability usually occurs at a combination of temperature and strain rate, so changing these parameters according to time temperature superposition does not help.

b) Phase separation:

PS diluted in its oligomer has been studied extensively in filament stretching experiments and so far phase separation has not been reported. However, for other systems, phase separation has indeed been observed¹². To check, if our system phase separates or not, we tried to facilitate the separation by two possible/reported ways: enthalpy driven and flow induced polymer migration.

Since polymers are large molecules, the entropic gain in mixing is small and it may not be able to overcome even a tiny enthalpic cost. So as a first attempt to phase separate, we kept our system at high temperature (160°C) for different time durations (15 minutes to 4 hours). If enthalpy driven phase separation occurs, it will occur at various degrees depending on the time duration. In fig. 4.9, we observe that the experimental results overlap nicely with each other indicating the system (10wt% PS 820 kg/mol - 90wt% OS 9kg/mol) did not phase separate at the mentioned conditions. Small discrepancy at low times, particularly for the sample equilibrated for 15 minutes, is observed because the sample didn't have enough time to relax the induced stress in the previous (pre-stretching) step.

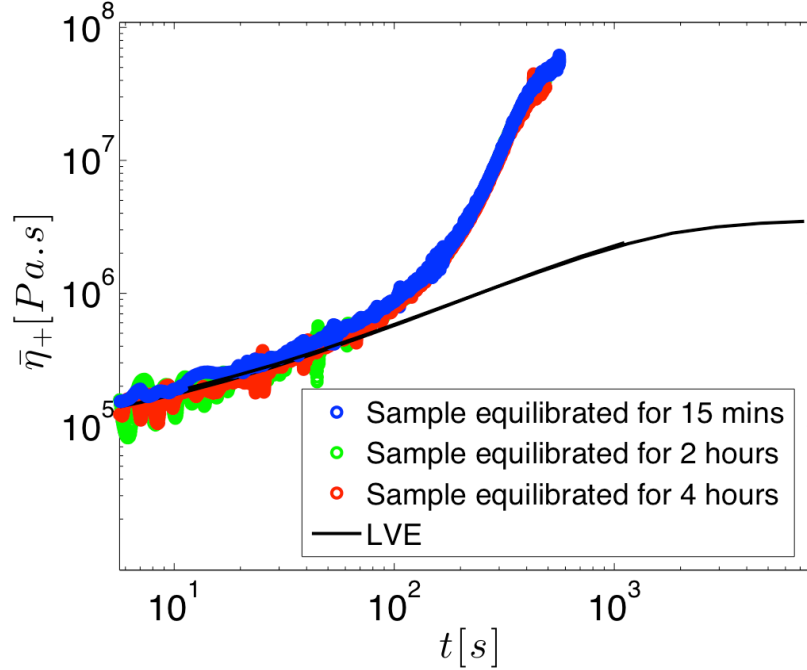


Fig. 4.9. Comparison of FSR measurements done at different time durations at 130°C, with a strain rate, $\dot{\epsilon} = 0.01 \text{ s}^{-1}$.

Strong stretching of polymers could induce polymer migration resulting in concentration inhomogeneities. Very recently, Malkin and co-workers¹¹ have demonstrated that stretching of polymer chains in semi-dilute polymer solutions could lead to a concentrated core that squeezes out solvent leading to flow instabilities. However, the flow induced phase separation should lead to arbitrary concentration inhomogeneities thus generating irreproducible stress measurements. Thus re-producible measurements can ensure the non-existence of flow induced phase separation. Most of the experimental results presented in this work were measured at least twice to check both reproducibility and possible phase-separation.

4.3 Inter-laboratory test: VADER - 1000

In order to test the reproducibility and reliability of the new commercial extensional rheometer (VADER-1000), we initiated an inter-laboratory test of the device, involving four institutes (Kyoto

University (in collaboration with Prof. H. Watanabe), Changchun Institute of Applied Chemistry (in collaboration with Prof. Q. Chen), DTU (in collaboration with Dr. Q. Huang) and UCL). In order to perform a diverse study, two different classes of samples were chosen: a PS melt and a PS solution. The detail of the study follows.

4.3.1 Selection criteria of ingredients:

Depending on the strain rate and state of the polymer, PS samples can show moderate to strong strain hardening behavior. According to the literature, molten PS exhibit moderate strain hardening^{13, 14} while well-diluted PS solutions can show strong hardening phenomenon^{15, 16}. Therefore in this work, both systems were studied at different elongational rates.

A PS melt with moderate molar mass (well-entangled in its melt state $Z \sim 28$), was chosen for the study. While for the solution, a high molar mass PS was diluted at low concentration in styrene oligomers. The combination of molar mass and the concentration were chosen in order to invoke strong hardening behavior from the sample but at the same time to keep the measurements well within the capability range of the VADER device. The main characteristics of the components and the systems are shown in table 1.

Table 1. Main characteristics of the systems

PS melt			
Molar mass, M_w Kg/mol	PDI	T_g $^{\circ}C$	Concentration wt%
427	1.06	106.6	100

PS solution				
Components	Molar mass, M_w Kg/mol	PDI	T_g $^{\circ}C$	Concentration wt%
Solute	601	1.07	106.6	20
Solvent	9.5	1.06	95	80
Solution	-	-	100.1	-

4.3.2 Preparation of PS solution:

The PS solution was prepared at UC Louvain, Belgium following the four-step procedure, described in details in chapter 2. To ensure a complete removal of solvents, the solution was treated at Kyoto University, Japan with the more intense drying technique (T-2) as described earlier in this chapter.

4.3.3 Elongational experimental protocol:

A robust three step elongational experimental protocol was chosen in an attempt to produce reproducible results. The steps are following,

a) First, the sample was squeezed at an elevated temperature (at $150^{\circ}C$ for PS solution and $160^{\circ}C$ for PS melt). This was done to ensure adequate contact between the sample and geometries.

b) Then, the sample was pre-stretched at same temperature to prevent slip/detachment of the sample during stretching.

c) Finally, the elongational stress measurement was performed at the experimental temperature ($130^{\circ}C$ for both PS melt and solution).

Four suitable strain rates for each system were chosen following a discussion with the partner institutes. Higher strain rates could and

indeed leads to brittle fracture before the steady state is reached. The chosen rates are shown in table 2,

Table 2. Selected strain rates

PS melt s^{-1}				PS solution s^{-1}			
0.001	0.003	0.01	0.03	0.003	0.01	0.03	0.1

4.3.4 Results and discussion:

Experimental results obtained in two different labs (UCL and DTU) are compared and discussed in this section. It must be noted that the results from the two other labs should be received soon. First, we discuss the PS melt.

a) PS melt:

First, the LVE properties were measured by small amplitude oscillatory shear tests (SAOS) performed on a MCR 301 (Anton Paar, Austria) rheometer using a stainless steel parallel plate geometry (with diameter of 8 mm), with a convection oven for temperature control ($\sim 0.1^{\circ}\text{C}$) under constant nitrogen gas supply. After carrying an amplitude sweep test to estimate the linear visco-elastic (LVE) region, frequency sweep tests were done at three different temperatures (ranging from 130°C to 170°C) and shifted onto a single master curve at 130°C . The linear experimental results are shown in fig. 4.10.

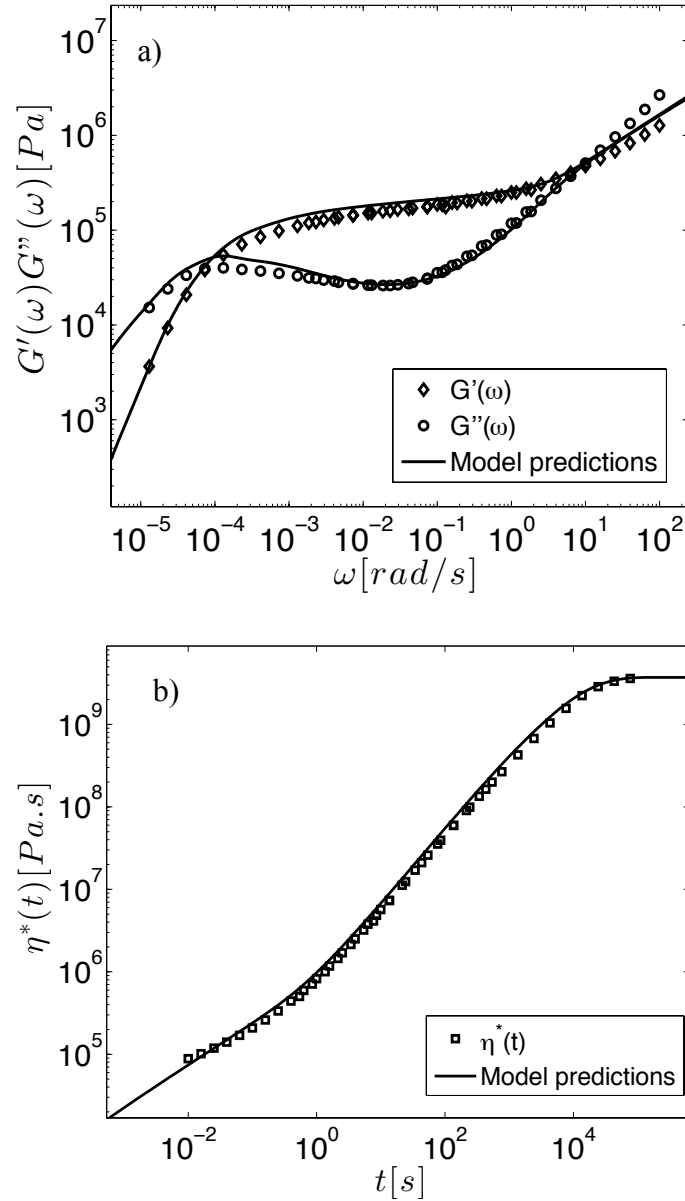


Fig. 4.10. Experimental (symbols) and predicted (lines) SAOS data a) relaxation moduli b) linear viscoelastic envelope of the monodisperse PS melt.

These experimental data are used to create the LVE envelopes for the elongational data. Any upward deviation from these envelopes is a signature of strain hardening (SH).

Transient elongational stress measurements were performed with the VADER-1000 (Rheo Filament, USA) under constant nitrogen supply. Prior to the measurements, all samples were dried under vacuum at 65 °C overnight to remove surface humidity. Then these samples were molded into discotic specimens with a fixed radius of 2.75 mm using a home-build mold under vacuum. The samples were pressed at 160 °C and annealed at the same temperature (at least for 20 minutes) under vacuum. The measurements were then carried using the three-step protocol as mentioned above. The experimental results are shown in fig. 4.11.

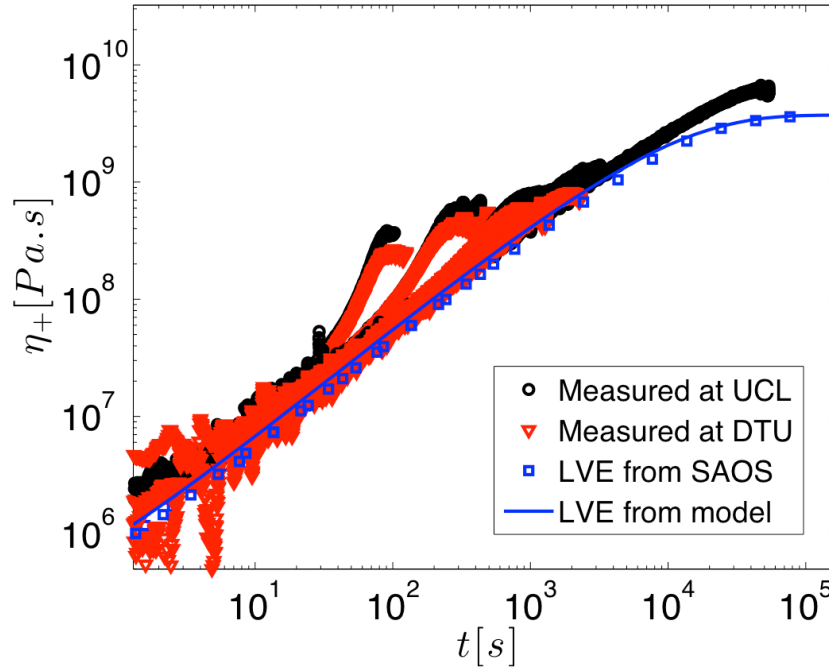


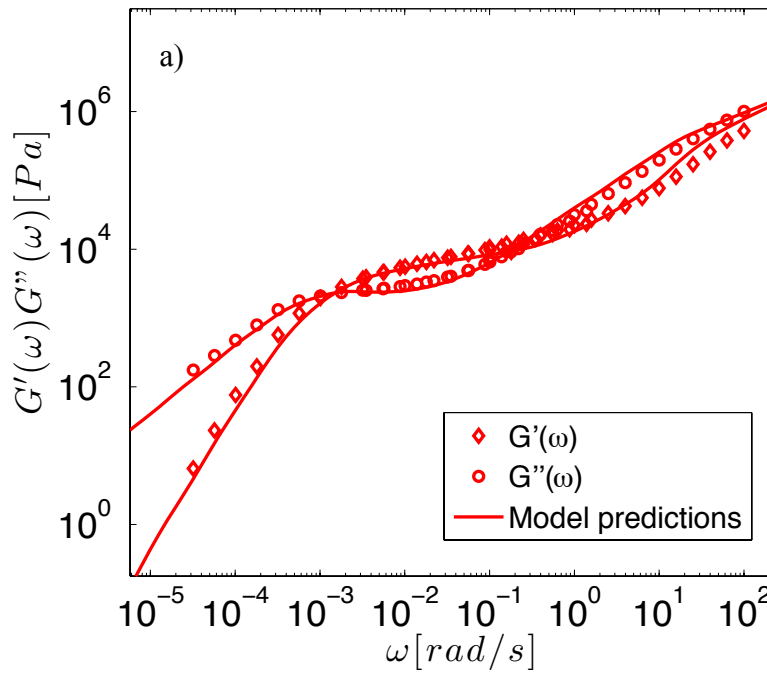
Fig. 4.11 Transient response of PS melt (symbols) under elongational flow at strain rates 0.03, 0.01, 0.003, 0.001 s⁻¹ respectively (from left to right). An extra strain rate was measured at UCL (0.00003 s⁻¹) in an attempt to recreate the linear viscoelastic envelope.

At low times, the transient response measured at both laboratories follows the LVE envelope closely and satisfactorily overlap with each other for all measured strain rates. However at high times, particularly at the steady regime slight discrepancy is observed. Indeed, it seems the data measured at UCL has a vertical shift (~ 1.2) compared to the

data measured at DTU. This discrepancy could be due to inaccurate temperature inside the oven. As we know, PS samples are very sensitive to temperatures and a variation of 1-2⁰C could result in such a discrepancy. However, in that case a similar shift should be present at lower times as well. Nevertheless, in general the comparison between the experimental results is quite satisfactory.

b) PS solution:

Next we compare with the PS solution, which is expected to show high strain hardening behavior. The shear and elongational properties of the solution is measured similarly as described in the last section and are shown in figure 4.11 and 4.12 respectively.



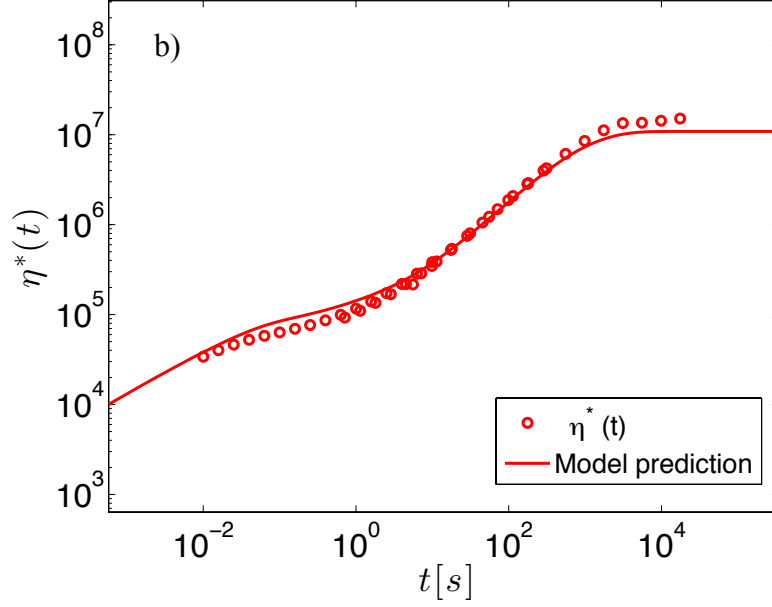


Fig. 4.11 Experimental (symbols) and predicted (lines) SAOS data a) relaxation moduli & b) LVE envelope of the PS solution.

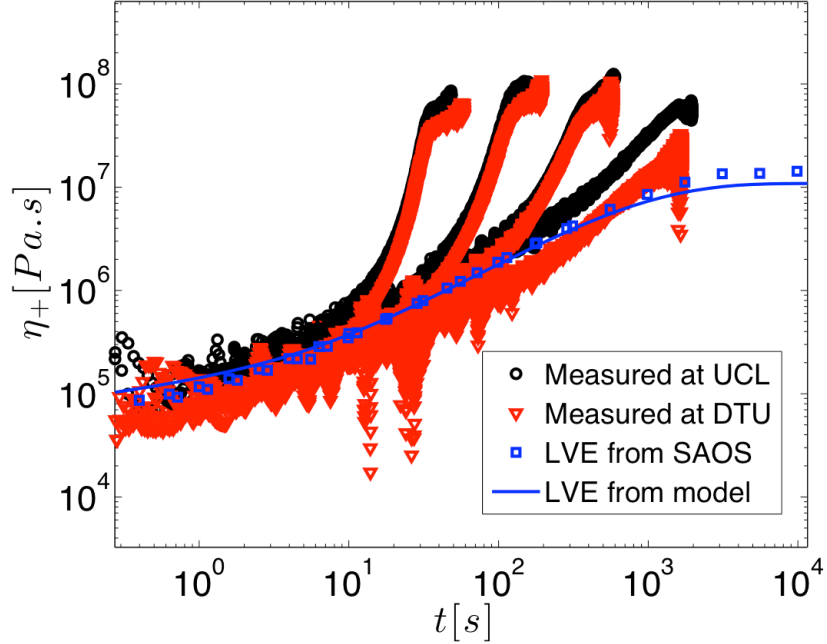


Fig. 4.12 . Transient response of PS solutions (symbols) under elongational flow at strain rates 0.1, 0.03, 0.01, 0.003 s⁻¹ respectively (from left to right).

A clear discrepancy is observed in the transient response of the PS solution both at low and high times. For the highest strain rates ($\dot{\epsilon} = 0.1, 0.03$ and 0.01), the data measured at UCL has a vertical shift of about 1.3, compared to the ones measured in DTU. This discrepancy can be traced back to the inaccurate temperature inside the oven as observed for the PS melt. However, a larger shift (~ 2) is noticed at the lowest strain rate, $\dot{\epsilon} = 0.003$. The origin of this large discrepancy is probably not related to the temperature and is currently unknown. Please note that at low times, the data measured at UCL follows the LVE envelope closely before the strain hardening sets in, whereas data measured at DTU is slightly under the envelope, especially the one measured at the lowest strain rate. The expected inputs from Kyoto and Changchun universities should allow us to better understand the origin of this issue.

4.4 Conclusion

Filament stretching rheometry has proven to be a reliable method to measure the uniaxial elongational properties of different classes of polymeric materials. And like any other measuring techniques, good and consistent experimental results need practice of well-defined measuring and sample preparation techniques. In this chapter we summarized a list of concerns that a FSR user needs to keep in mind and also discuss different ways to deal with them. A comparative study between the two FSR devices in two different labs are also presented along with the possible reasons causing the observed discrepancies.

In our quest to develop a universal model in extensional flows, we investigate the viscoelastic properties of the prepared samples in the following chapters. First the linear viscoelastic properties are compared with the tube model in chapter 5, where we look into the long unresolved question about the correct value of dynamic dilution exponent in entangled polymer solutions.

References:

1. Q. Huang, Molecular Rheology of Complex Fluids. Ph.D. thesis, Technical University of Denmark (2013).
2. H. Watanabe and Y. Matsumiya, private communications (2018).
3. G. H. McKinley and T. Sridhar, Filament–stretching rheometry of complex fluids, *Annu. Rev. Fluid Mech.*, (2002), 34, 375–415.
4. H. K. Rasmussen, A. G. Bejenariu, O. Hassager, and D. Auhl, Experimental evaluation of the pure configurational stress assumption in the flow dynamics of entangled polymer melts, *J. Rheol.* (2010), 54(6), 1325–1336.
5. A. Bach, H. K. Rasmussen, P. Y. Longin, & O. Hassager, Growth of non-axisymmetric disturbances of the free surface in the filament stretching rheometer: Experiments and simulation, *J. Nonnewton. Fluid Mech.*, (2002), 108, 163–186.
6. J. D. Peterson, S. Vyazovkin, C. A. Wight, Kinetics of the Thermal and Thermo-Oxidative Degradation of Polystyrene, Polyethylene and Poly(propylene), *Macromol. Chem. Phys.*, (2001), 202, 775–784.
7. Y. Ide, and J. White, Investigation of failure during elongational flow of polymer melts polymer melts, *J Non-Newtonian Fluid Mech.*, (1977), 2, 281–298.
8. A. Y. Malkin, and C. J. S. Petrie, Some conditions for rupture of polymer liquids in extension, *J. Rheol.*, (1997), 41, 1–25.
9. Y. Wang, P. Boukany, S.-Q. Wang, and X. Wang, Elastic breakup in uniaxial extension of entangled polymer melts, *Phys. Rev. Lett.*, (2007), 99, 237801.
10. Q. Huang, N. J. Alvarez, A. Shabbir, and O. Hassager, Multiple cracks propagate simultaneously in polymer liquids in tension, *Phys. Rev. Lett.*, (2016), 117, 087801.

11. A. Y. Malkin, A. Arinstein, & V. G. Kulichikhin, Polymer extension flows and instabilities, *Prog. Polym. Sci.*, (2014), 39, 959–978.
12. S. L. Wingstrand, L. Imperiali, R. Stepanyan, O. Hassager, Extension induced phase separation and crystallization in semidilute solutions of ultra high molecular weight polyethylene, *Polymer*, (2017), 136, 215-233.
13. A. Bach, H.K. Rasmussen, and O. Hassager, Extensional viscosity for polymer melts measured in the filament stretching rheometer. *Journal of Rheology*, (2003), 47, 429–441.
14. J. K. Nielsen, H. K. Rasmussen, O. Hassager, and G. H. McKinley, Elongational viscosity of monodisperse and bidisperse polystyrene melts. *J. Rheol.*, (2006), 50, 453–476.
15. Q. Huang, O. Mednova, H. K. Rasmussen, N. J. Alvarez, A. L. Skov, K. Almdal, O. Hassager, Concentrated polymer solutions are different from melts: Role of entanglement molecular weight, *Macromolecules*, (2013), 46, 5026-5035.
16. Q. Huang, L. Hengeller, N. J. Alvarez, O. Hassager, Bridging the Gap between Polymer Melts and Solutions in Extensional Rheology. *Macromolecules*, (2015), 48, 4158–4163.

Chapter 5

The contents of this chapter have been published in Soft Matter (2017), 13 (1), 269.

Dynamic Dilution Exponent in Monodisperse Entangled Polymer Solutions

We study and model the linear viscoelastic properties of several entangled semi-dilute and concentrated solutions of linear chains of different molar masses and at different concentrations dissolved in their oligomers. We discuss the dilution effect by the oligomers on the entangled long chains. In particular, we investigate the influence of both concentration and molar mass on the value of the effective dynamic dilution exponent determined from the level of the storage plateau at low and intermediate frequencies. We show that the experimental results can be quantitatively explained by considering the tension re-equilibration process along the chains, in agreement with [van Ruymbeke et al., Macromol. 2014], i.e. by considering that the real dilution exponent α is always equal to 1, while larger values of dilution exponent ($1 < \alpha < 1.3$) found experimentally are attributed to the enhanced relaxation of the long chain extremities. Then we discuss the influence of the polymer concentration on the terminal relaxation time of the solutions and how this can be modelled by the enhanced contour length fluctuations process (CR-CLF). We point out that this larger dilution effect is not only a function of concentration but also depends on the molar mass of the chains.

While the proposed approach successfully explains the viscoelastic properties of a large number of semi-dilute solutions of polymers in their own oligomers, important discrepancies are found for semi-dilute entangled polymers in small-molecule theta or good solvents. Possible explanations for the differences between these sample sets are proposed, based on a comparison of their viscoelastic behavior.

5.1. Introduction

Today, the linear viscoelastic properties of linear entangled polymer melts are quite well understood and can be predicted on a quantitative level, based on coarse-grained models such as tube-models¹⁻⁴ or slip-link models⁵⁻⁸. Beside the melt state, these models can also be used to describe the properties of entangled polymer solutions or of long polymer chains diluted in a matrix of very short chains or oligomers⁹⁻¹¹. However, this requires accounting for constraint release mechanisms in order to describe the influence of the fast motion of shorter and oligomeric chains on the relaxation of the long chains. To this end, most of the present tube models are using the concept of dynamic tube dilution (DTD) proposed by Marrucci et al.¹², according to which the effective diameter of the tube, a , which represents the constraining effect of the surrounding chains on the motion of a specific molecule, is increasing if the polymer concentration is reduced, as well as if part of the sample is moving fast enough so that they do not constrain the motions of the long chains anymore^{1,2}. Consequently, the entanglements involving these chains can be ignored and the effective average molar mass between two entanglements, M_e , becomes larger^{11,12}:

$$a(t) = \frac{a_{0,melt}}{(c \cdot \phi(t))^{\frac{\alpha}{2}}}, \quad (1)$$

$$M_e(t) = \frac{M_{e0,melt}}{(c \cdot \phi(t))^\alpha}, \quad (2)$$

with c , the polymer concentration, $M_{e0,melt}$, the average molar mass between two entanglements in the melt state at time $t = 0$, $\phi(t)$, the fraction of unrelaxed polymer which still contribute to the constraining tube at time t , and α , the dynamic dilution exponent. As a consequence of rescaling M_e , the plateau modulus G_N^0 and the relaxation modulus $G_d(t)$ of an entangled polymer solution can be defined as¹³:

$$G_N^0 = \frac{\rho RT}{M_e} = \frac{c \rho_0 RT}{\frac{M_{e0,melt}}{c^\alpha}} = G_{N,melt}^0 c^{\alpha+1}, \quad (3)$$

$$G_d(t) = (G_N^0 \cdot \phi(t)^\alpha) \cdot \phi(t) = G_{N,melt}^0 c^{\alpha+1} \phi(t)^{\alpha+1}, \quad (4)$$

with ρ , the density of the solution, and ρ_0 and $G_{N,melt}^0$, the density and plateau modulus of the corresponding melt.

Constraint Release (CR) mechanisms also affect the terminal relaxation time, $\tau_{rel}(M)$, of the polymer solutions and in particular their reptation time, $\tau_{rept}(M)$.¹² The latter can be compared to the initial reptation time in the melt, $\tau_{rept0,melt}(M)$, by accounting for the fact that the corresponding Rouse time of an entanglement segment, τ_e , is becoming longer (since M_e is longer), while the number of entanglement segments along the chain, Z , is decreasing (since $Z=M/M_e$):

$$\begin{aligned} \tau_{rept}(M) &= 3 \tau_e Z^3 = 3 \left(\frac{\tau_{e0,melt}}{(c \cdot \phi(t))^{2\alpha}} \right) (Z_{0,melt} (c \cdot \phi(t))^\alpha)^3 \\ &= \tau_{rept0,melt}(M) (c \cdot \phi(t))^\alpha, \end{aligned} \quad (5)$$

The c^α scaling of the reptation time can also be found by considering that reptation time is proportional to L^2/D , with L , the length of the primitive path of the chain (which scales with $c^{\alpha/2}$), and D , the diffusion coefficient.

It must be noted that, in addition to the reptation process, a contour length fluctuations process (CLF) must be taken into account in order to determine the terminal relaxation time of the chain. This further speeds up the relaxation of the chains (see Section 5.3).

The objective of this work is to discuss the value of the dynamic dilution exponent α in case of long linear chains diluted in oligomers or in real solvents. While this parameter should be *a priori* equal to 1 if we consider that entanglements are binary contacts, several works have shown that, in the specific case of entangled solutions, its effectively observed value is rather equal to 4/3.¹⁴⁻²¹ This effective

value was determined based on experimental data, by looking at the scaling of the level of the plateau modulus in the terminal regime with the concentration c , based on Eq. 3, where the plateau modulus can be conveniently approximated as being 3.56 times the value of the loss moduli at its maximum G''_{max} ¹⁸ (or 3.24 in ref.[14]) in case of monodisperse samples. In the following we will refer to an *effective* α whenever this is obtained from the scaling of G''_{max} (or G_δ see below) with concentration.

An explanation of the observed effective value of α close to 1.3 (or 4/3) was suggested by Colby and Rubinstein¹⁷, based on the level of the second (low frequency) plateau modulus of the longer chains and its scaling with concentration. They proposed that an entanglement is created only if a fixed number of binary contacts between the chains is reached. Based on this assumption, they estimated the size of the ‘blob’ needed in order to ensure the creation of an effective entanglement at equilibrium, and they could show that such a blob size is proportional to $c^{-2/3}$. As for the entangled solution, an effective value of α of 4/3 was also found for polymer blends composed of two monodisperse linear polymers¹⁵ with very different molar masses. However, in other cases such as for binary blends of linear chains with similar molar masses, or for branched molecules, the effective dynamic dilution exponent was found to be equal to 1.^{9, 22-25} Then again, from results obtained with slip-link simulations it appears that the (second) plateau modulus scales with concentration as if the dynamic dilution exponent was equal to an effective value of 4/3, despite the fact that its actual value was fixed to 1 in the model itself^{7,8}. Thus, today, there is not a real consensus on what the effective value of α should be and how it is related to the actual value.

Recently, it was proposed by van Ruymbeke and co-workers¹¹ that the actual dilution exponent α should be equal to 1, whatever the composition of the sample is. In order to explain a possible lowering of the plateau modulus with concentration (that would lead, following Eq. (3), to an increase of the effective α to values above 1), for solutions of longer polymer chains in their shorter oligomers the existence of an extra relaxation process was pointed out, originating from a tension re-equilibration along the chain²⁶, which takes place at the time scale of the release/re-formation of the entanglements

between a long and a short chain (i.e. a ‘short-long’ entanglement), and which leads to the loss of some initial ‘long-long’ entanglements at the chain extremities, independently from the reptation/fluctuations of the long chains. This process is usually slow and does not significantly affect the relaxation of the long component, leading to a clearly observable plateau modulus of this component and consequently to an experimentally determined effective α exponent equal to 1. However, in specific cases, for example when the relaxation times of the short component is much shorter than the one of the long component, this process can speed up the relaxation of the long chain and consequently, the observable second plateau modulus is apparently lowered, leading to a scaling of G_N^0 with concentration *as if* the effective dilution exponent α was equal to 4/3.

In order to include this mechanism in tube models, a dual approach was proposed, which considers two different pictures related to two different length scales (tube diameters) and time scales¹¹: According to the first picture the long chains are relaxing in a thin tube of diameter $a_{0,melt}$, this thin tube being able to move and wriggle (by Constraint Release mechanisms) in a larger tube of diameter a defined as^{7,12,27,28}:

$$a = \frac{a_{0,melt}}{(v_2)^{\frac{\alpha}{2}}}, \quad (6)$$

with v_2 , the volume fraction of the long chains. In such a case, the reptation and fluctuation processes take place in a thin tube composed of entanglements from both long and short chains, and the corresponding main time unit is $\tau_{e0, melt}$. On the other hand, according to the second picture, the thin tube is not effective anymore and the long chains are moving and relaxing in a dilated tube of diameter a .²⁹ In such a case, the short chains can be compared to a solvent except for the fact that an extra friction, coming from their slower motions, must be taken into account to determine how fast the long chains can move. Indeed, the long chains can only move at the time scale of the release/re-formation (or ‘blinking’) of the short-long entanglements, which slows down their relaxation processes (compared to a real solvent), and the importance of the delay depends on the relaxation

time of the short chains¹¹. This requires defining a new Rouse relaxation time $\tau_{long-long\ eq\ell}$, which represents the necessary time for a long-long entanglement of mass $M_e (=M_{e0,melt}/v_2^\alpha)$ to relax by a Rouse process, and which takes into account this possible delay from the motion of the short chains. If the long chains contain at least two long-long entanglement segments, this time has been defined as¹¹:

$$\tau_{long-long\ eq\ell} = \max\left(\frac{\tau_{e0,melt}}{v_2^{2\alpha}}, \tau_{short-long} \left(\frac{v_1}{v_2}\right)^{2\alpha}\right), \quad (7)$$

with v_1 , the volume fraction of the short chains and $\tau_{short-long}$, the average relaxation time of a short-long entanglement. Thus, according to this second picture, the chains are moving in a dilated tube, which speeds up their reptation and fluctuations processes, but their ‘internal clock’, defined by $\tau_{long-long\ eq\ell}$, can become slower than the intrinsic Rouse time of this segment, since it depends on the motion of the short chains. Therefore, depending on which process is faster and dominates, the long chains relaxation will be better described according to the first or the second tube picture.

In ref. [11], it was shown that for binary blends of linear chains, where the second picture (i.e. long chains moving in a dilated tube with an internal clock defined by Eq. 7) is applicable, the long chains are relaxing faster than expected from the classical tube picture, and the observable part of the second plateau modulus is effectively lowered, resulting in an *effective* dynamic dilution exponent α larger than 1 when this is obtained from the scaling the second plateau modulus with concentration following Eq. 3. Furthermore, it was shown that in the extreme case of binary blends composed of very short unentangled chains (or oligomers), the ‘second picture’ must be considered, but with the specificity that there is no extra delay in the Rouse time of a long-long entanglement segment. Indeed, in such a case, the limiting relaxation process of a long-long entanglement is its intrinsic Rouse relaxation. Therefore, eq. 7 reduces to:

$$\tau_{long-long\ eq\ell} = \frac{\tau_{e0,melt}}{v_2^{2\alpha}}, \quad (8)$$

and an effective α exponent of 4/3 was found for a specific set of samples, even if α was fixed to 1 in equation (1), (6) and (8).¹¹

Thus, by considering that the long chains in binary blends can relax according to two different length-(and time-) scales, which corresponds to two different tube diameters, the experimental data of many binary blends could be correctly described, based on an actual α value of 1.

However, several questions remain that we would like to address in the present work. In particular, we would like to test this approach on a larger set of semi-dilute or concentrated solutions of entangled polymers, diluted either in oligomers or in real solvents, in order to validate our picture. In particular, while it is expected that for such samples the second picture, which considers the long chains moving in a dilated tube, should always be active, it is to our opinion not obvious that the effective α for entangled solutions should always be equal of 4/3 (as proposed in literature for entangled solutions¹⁴⁻¹⁸). The effective α obtained from the scaling of G''_{max} with concentration should rather depend on the equilibration state of the long chain¹¹ in the terminal regime where the effective plateau modulus (which is approximated by $3.56 G''_{max}$) is determined. Also, we would like to investigate if an effective α larger than 1 is also obtained when using the value of the storage modulus detected at the higher frequency ω_* , where the $\tan\delta$ curve exhibits a minimum, a criterion that is often used to define the plateau modulus. As a last point, we would like to investigate the role of the solvent in the terminal relaxation time of the samples.

In order to address these points, a new set of model polymer solutions based on a very long polystyrene linear chains diluted in oligomers at several concentrations has been prepared and measured, and the corresponding linear viscoelastic data are discussed, also in comparison to other sets of samples presented in literature^{10,14,19,30-32}. To do so, we use our tube-based model¹¹ in order to determine, based on both experimental and theoretical data, how the value of the effective α is affected by the chains concentration, their molar mass and nature of the solvent.

The chapter is organized as follow. At first, in Section 5.2 the material used for this study as well as the experimental techniques are presented. Then, in Section 5.3 we present the model used for binary blends of linear chains, and reduced to the specific case of entangled polymer solutions. The results are presented and discussed in Section 5.4, where the experimental and theoretical data for several sets of samples are compared. The comparisons are first made for entangled polymers diluted in oligomers, and subsequently for the case of entangled polymers diluted in small-molecule solvents. Finally conclusions are drawn in Section 5.5.

5.2. Materials and experimental details

5.2.1. Materials and sample preparation

The samples investigated in this work are monodisperse linear polystyrene chains either diluted in styrene oligomers or in the melt state. Some of these samples have been studied in previous works³⁰⁻³² and their viscoelastic data have already been presented in literature. These samples are listed in Table 1, together with their corresponding references. Among them, there are several monodisperse PS samples in the melt state, which will be mainly used to define and validate the material parameters used in our tube model. There is also a set of PS samples diluted in oligomers, which has been presented in ref. [30] by Huang et al., and which has been designed in order to ensure that each of these samples contains a similar number of entanglements.

Besides these two first sets of samples, a new set of entangled solutions has been designed and prepared for the purpose of this study. These new samples consist on a very high molar mass PS polymer ($M_w = 820$ kg/mol) diluted in oligomers ($M_w = 8.8$ kg/mol) at different concentrations, ranging from 3 wt% to 100 wt% of polymer (see Table 1).

Table 1: Main characteristics of the samples used in this work

Samples	M _w	M _n	PDI	Concentration	Ref.
OS4	3,630	3424	1.06	-	30
OS8.8	8,800	8000	1.1	-	-
PS50	51,700	50,380	1.026	100%	33
PS100	102,800	100,600	1.022	100%	33
PS200	200,000	192,000	1.04	100%	33
PS285	285,000	261,500	1.09	100%	31
PS390	390,000	367,000	1.06	100%	33
PS545	545,000	486,600	1.12	100%	31
PS545	545,000	486,600	1.12	52% in OS4	30
PS900	910,000	784,500	1.16	33% in OS4	30
PS1760	1,880,000	1,663,700	1.13	18% in OS4	30
PS3200	3.140,000	2.275,000	1.38	13% in OS4	30
PS3900	3.900,000	3,714,300	1.05	10% in DEP	34
PS820	820,000	805,000	1.02	100%, 80%, 50%, 40%, 24%, 10%, 5%, 3% in OS8.8	-
PS8420	8420,000	7200,000	1.17	5%, 4%, 3%, 2.5% in chlorinated biphenyl	19
PBD410	411,500	410,800	1.01	100%, 5% in PBD 3kg/mol	10
PBD925	925,000	/	<1.1	52.3%, 30.6%, 15.7%, 8.06%, 3.08%, 2.14% in DOP	14

Both the polystyrene and oligomers were purchased from Polymer Source (Montreal, Canada). The molar mass of the oligomers has been fixed in order to be short enough to be considered as a solvent, while long enough in order to avoid a too large decrease of their glass transition temperature compared to the high molecular weight sample (see Section 5.2.2.). The high molar mass sample was selected to ensure a polydispersity as low as possible. Its molar mass and polydispersity were checked by Field Flow Fractionation (FFF) coupled with Multi-angle light Scattering (MALS) (performed at BASF, Germany). The results were found to be consistent with the ones received from Polymer Source, and are presented in Table 1.

The solutions were prepared by diluting the high molecular weight Polystyrene, PS820, in the oligomeric styrene, OS8.8, at seven different weight fractions ranging from very concentrated to semi-dilute and dilute solutions regimes.

A 4-step procedure inspired by ref [30] was used to prepare the solutions. For this we dissolved first the polystyrene and the oligomer according to the desired weight fractions together in THF. The mixture was stirred at room temperature overnight to ensure that the two components were well dissolved and mixed. In a next step, the THF solution was added to the non-solvent methanol drop by drop, using a burette. The precipitated polymer/oligomer blend was then separated and collected using paper filtration. Finally, the blends were dried at 70⁰ C under vacuum for 4 days to remove remaining traces of the solvents.

In addition to polymer/oligomers blends, semi-dilute or concentrated solutions of polymers diluted in small molecule solvents, which are investigated in Section 5.4.4, are also listed in Table 1 with their corresponding references.

5.2.2. Linear viscoelastic properties

The linear viscoelastic properties of the polystyrene melt and the solutions were measured by small amplitude oscillatory shear (SAOS) tests. These tests were performed on an AR2000 rheometer using an 8 mm parallel plate geometry and under constant nitrogen supply. Each

SAOS test contained three different sub-tests. First, an amplitude sweep test was done to estimate the linear region of each sample. This was done at 1 rad/s and up to 10% of initial amplitude of the sample. Then a time sweep test was done to make sure the sample was well equilibrated with the experimental temperature and all the residual stresses were relaxed. Finally, a frequency sweep test was done to determine the linear viscoelastic data of each sample.

For the PS melt, the frequency sweep test was performed at four different temperatures ranging from 140°C to 190°C, while the solutions were measured at three different temperatures ranging from 130°C to 170°C. Subsequently the data for each temperature was shifted per sample onto a single master curve using the time-temperature superposition (TTS) procedure³⁵.

Working under the iso- T_g conditions:

As shown in Table 2, the glass transition temperature T_g of the polymer solutions, which has been determined by Differential Scanning Calorimetry (DSC), varies with the polymer concentration. This difference must be taken into account in order to allow a comparison of the viscoelastic responses of the different solutions. To this end, as proposed in ref. [36], master-curves have been created at different reference temperatures $T_{ref.}$, such that these temperatures correspond to iso- T_g condition, i.e. these temperatures are at a constant distance from the corresponding T_g (i.e. $T_{ref.} - T_g = \text{constant}$).

Table 2: T_g of the different solutions.

Solutions	Number of entanglements ^a	T _g (°C)
OS8.8 melt state	-	94.6
OS8.8 + PS820 (3%)	2	98.1
OS8.8 + PS820 (5%)	3	98.4
OS8.8 + PS820 (10%)	5	98.6
OS8.8 + PS820 (25%)	14	100.4
OS8.8 + PS820 (40%)	22	101.3
OS8.8 + PS820 (50%)	27	102.3
OS8.8 + PS820 (80%)	44	104.6
PS820 melt state	55	106.6

^a: The number of entanglements are determined based on $M_e = 15$ kg/mol.

In this work, the experimental data of the PS820 in the melt state at 130°C were chosen as the reference point, leading to a difference between the reference and glass transition temperature, $T_{ref} - T_g$, of 23.4°C. The storage and loss moduli of the other solutions measured at 130°C were then horizontally shifted in order to ensure a good overlap of the viscoelastic response in the high frequency region, in which the chain relaxation is controlled by local Rouse dynamics and will thus depend only on $(T_{ref} - T_g)$. As discussed below, the validity of the shift factors to this specific reference temperature can then be confirmed by comparing their value to the shift factors vs temperature curve used to build the different TTS master-curves for the differently concentrated solutions.

Master-curves:

The shifted iso-T_g data measured at 130°C are then used as reference curves to shift the other experimental data measured at higher

temperatures and thus, to create general master-curves. It must be noted that no vertical shift has been considered here, since the range of temperature used is rather limited. In fig. 5.1, all shift factors used to create the master curves are plotted against $(T-T_g)$.

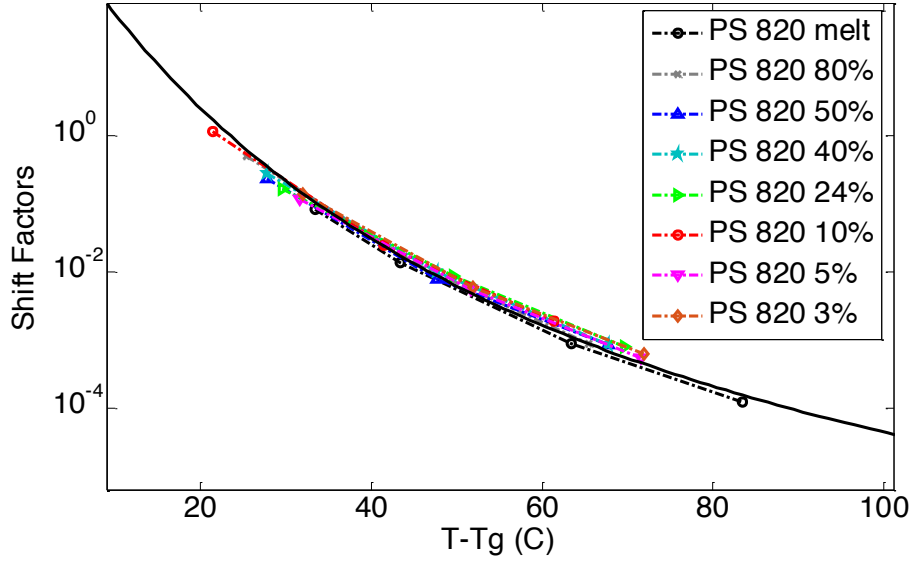


Fig. 5.1: Time Temperature Superposition shift factors as a function of $T-T_g$, determined for the different polymers solutions and melt. The continuous curve represents the WLF equation used in ref. [30].

As it can be seen, when plotted in such a way, the values used for PS solutions and the melt nicely coincide. Also, their T -dependence is very close to the dependence found in ref. [30] for the other PS samples described in Table 1, which is represented in Fig. 5.1 by the Williams–Landel–Ferry (WLF) equation³⁵.

$$\log a_T = \frac{-c_1^0(T-T_{ref})}{c_2^0+(T-T_{ref})}, \quad (9)$$

with $c_1^0 = 8.99$, $c_2^0 = 81.53K$, $T_{ref} = 130^\circ C$ and T , the temperature expressed in $^\circ C$.

The fact that all these curves superimpose also validates the factors used for shifting the data at iso- T_g condition. Indeed, these shift

factors are shown in fig. 5.1 at $T = 130^\circ\text{C}$, i.e. at $(T-T_g)$ ranging from 23.4°C (for PS820) to 35.4°C (for the OS8.8), and they are in good agreement with the WLF equation.

5.3. Tube-based Model for entangled linear solutions

In this Section, the viscoelastic response of the entangled linear solutions is modeled based on the Time Marching Algorithm (TMA) that we have developed, based on the tube theory, for predicting the relaxation modulus of linear and branched entangled polymers³⁷⁻³⁹. The main equations are summarized here below for the specific case of long linear chains of mass M_2 blended with short chains or oligomers of mass M_1 . Since this approach should also correctly describe the viscoelastic properties of monodisperse chains (of mass M_2) in the melt state, and in order to keep the model as general as possible, the equations are described as a function of the reference material parameters $M_{e,0,\text{melt}}$, $G_{N,\text{melt}}^0$, and $\tau_{e,0,\text{melt}}$ of the melt state, and short-long entanglements are considered at very short times even for PS/oligo-S blends.

As mentioned in the Introduction, this approach considers the existence of two length and time scales, the first one being related to the motions of the long chains in their thin (initial) tube, while the second one is related to the motions of the long chains in their dilated tube. Since this second relaxation takes place at the rhythm of the motions of the short chains, i.e. $\tau_{\text{short-long}}$ (see Eq. 7), the necessary time to relax one long-long entanglement segment by tension is usually delayed compared to its intrinsic Rouse time, $\frac{\tau_{e0,\text{melt}}}{v_2^{2\alpha}}$. Within this framework, using oligomers as short component represents an extreme case: the relaxation of the long chains in a thin tube (i.e. the first length scale) has a negligible effect since it is always slower than their relaxation in the dilated tube (i.e. the second length scale), this last process being not delayed by the motion of the short chains. Thus, in this specific case, the necessary time to relax one long-long entanglement segment is simply described by its minimum intrinsic value, $\frac{\tau_{e0,\text{melt}}}{v_2^{2\alpha}}$ (see Eq. 8)¹¹ and the short-long entanglements do not

play any role in the relaxation of the long chains, despite the fact that it is considered that they exist at time $t = 0$.

Following ref. [11], since the short chains only relax by Rouse process, the general expression of the relaxation modulus can be described as:

$$G(t) = \left(\nu_1 G_{R,1}(t) + \nu_2 G_{R,2}(t) \right) + G_d(t), \quad (10)$$

The first term of this equation describes the full relaxation of the short, unentangled chains by the intrinsic Rouse process⁴¹:

$$G_{R,1}(t) = \frac{\rho_0 RT}{M_1} \sum_{p=1}^n \exp\left(-\frac{2p^2 t}{\tau_R(M_1)}\right), \quad (11)$$

with $\tau_R(M_1)$, the Rouse time of the short chains, while the second term describes the fast Rouse relaxation of the long chains, taking place in all directions for molecular sub-chains shorter than the average molar mass between two entanglements, $M_{e,0,melt}$ and along the tube axis (longitudinal modes) for the longer modes⁴:

$$G_{R,2}(t) = \frac{\rho_0 RT}{M_2} \left\{ \frac{1}{4} \sum_{p=1}^{Z_{2,0}} \exp\left(-\frac{p^2 t}{\tau_R(M_2)}\right) + \sum_{p=Z_{2,0}+1}^n \exp\left(-\frac{2p^2 t}{\tau_R(M_2)}\right) \right\} \quad (12)$$

with $Z_{2,0} = M_2/M_{e0,melt}$, the number of entanglement segments of a long chains in the melt state.

In addition to this Rouse relaxation, the chains must disentangle in order to reach their full relaxation state. This is described by the term $G_d(t)$:

$$G_d(t) = G_{N,melt}^0 \varphi'(t) \{\phi(t)\}^\alpha, \quad (13)$$

with, in this case, the survival fraction of initial (thin) tube at time t , $\varphi'(t)$, which only accounts for the unrelaxed segments of the long component: $\varphi'(t) = \nu_2 \varphi_2'(t)$ (since the short chains are fully relaxing by Rouse dynamics), and with $\phi(t)^{-\alpha}$ representing the number of initial entanglement segments *per dilated segment*. While $\phi(t)$ is often equal to $\varphi'(t)$, this is not the case here due to the very fast relaxation of the short chains, and it is therefore important to consider that $\phi(t)$ cannot decrease faster than by a Constraint Release Rouse process (CRR)^{2,11,42}:

$$\phi(t_i) = \max \left\{ \varphi'(t_i), \phi(t_{i-1}) \left[\frac{t_{i-1}}{t_i} \right]^{\frac{1}{2}} \right\}, \quad (14)$$

with t_{i-1} representing the time step before the time t_i and with the initial condition $(\phi(t=\tau_e)=1)$.⁴⁷ Thus, this CRR condition prevents the function $\phi(t)$ to decrease faster than with a slope of -1/2. In fact this is crucial here since it will ensure that the long chains will relax by Rouse dynamics from their initial, undiluted tube ($\phi=1$) to their dilated tube, corresponding to ($\phi=\nu_2$). This Rouse relaxation makes sense since the short chains are oligomers and therefore the undiluted tube does not really exist.

For such extreme blends, the contour length fluctuation of their initial, undiluted, tube (i.e. including the short-long entanglements) can be neglected. Therefore, the survival proportion $\varphi_2'(t)$ of initial tube segments of the long chains at time t , can be described by considering only their relaxation by reptation and their relaxation by tension equilibration process or constraint release activated fluctuations (CR-CLF)^{11,37}:

$$\varphi_2'(t) = \int_0^1 p_{rept}(x, t) p_{CR-CLF}(x, t) dx, \quad (15)$$

with $p_{rept}(x, t)$ and $p_{CR-CLF}(x, t)$, the survival probabilities of a chain segment x at time t , considering the chain relaxation either by reptation or by CR-CLF. These probabilities depend on the reptation and CR-CLF times of the long chains^{11,13} and are approximated by single exponential functions which compare the time t to these relaxation times, for each segment x . Since the relaxation by tension

equilibration is a Rouse process along the axis of the dilated tube, the corresponding relaxation times are well described by the Constraint-Release activated fluctuations process (CR-CLF) taking place in the dilated tube:

$$\tau_{\text{CR-CLF}}(x) = \left(\tau_{\text{long-long, eq.}} \right) \frac{9\pi^3}{16} (v_2 Z_{2,0} / 2)^4 x^4, \quad (16)$$

with v_2 the weight fraction of the long chains, x the normalized coordinate of a chain segment, ranging from 0 at the extremities to 1 at the middle of the chain, and $Z_{2,0}$ as the number of entanglement segments along the long chain at time 0 (i.e., considering both long-long and long-short entanglements). As already mentioned, for long chains diluted in oligomers, the Rouse time of a long-long entanglement segment, $\tau_{\text{long-long, eq.}}$, is well described by Eq. 8. On the other hand, according to the Struglinsky-Graessley criterion, reptation is taking place in a dilated tube⁴⁰:

$$\tau_{\text{rept}}(M_2) = 3 \tau_{e,0} Z_{2,0}^3 v_2^\alpha, \quad (17)$$

5.4. Results and Discussion

5.4.1. Comparison between experimental and theoretical viscoelastic data

First, the viscoelastic properties of monodisperse entangled PS samples in the melt state (see Table 1) are modelled, based on the approach presented in Section 5.3. This requires defining the values of the three materials parameters corresponding to the melt state, $G_{N,\text{melt}}^0$, $M_{e0,\text{melt}}$ and $\tau_{e0,\text{melt}}$. The values of $G_{N,\text{melt}}^0$ and $M_{e0,\text{melt}}$ have been set in agreement with previous works^{37,38,43} as 230 kPa and 15 kg/mol respectively, while $\tau_{e0,\text{melt}}$ has been fixed to 0.55 s at the reference temperature of 130°C. Comparison between experimental and predicted results is shown in fig. 5.2. A good agreement is found,

which validates the values taken for these parameters, as well as the experimental data, which come from three different works and two different research groups.

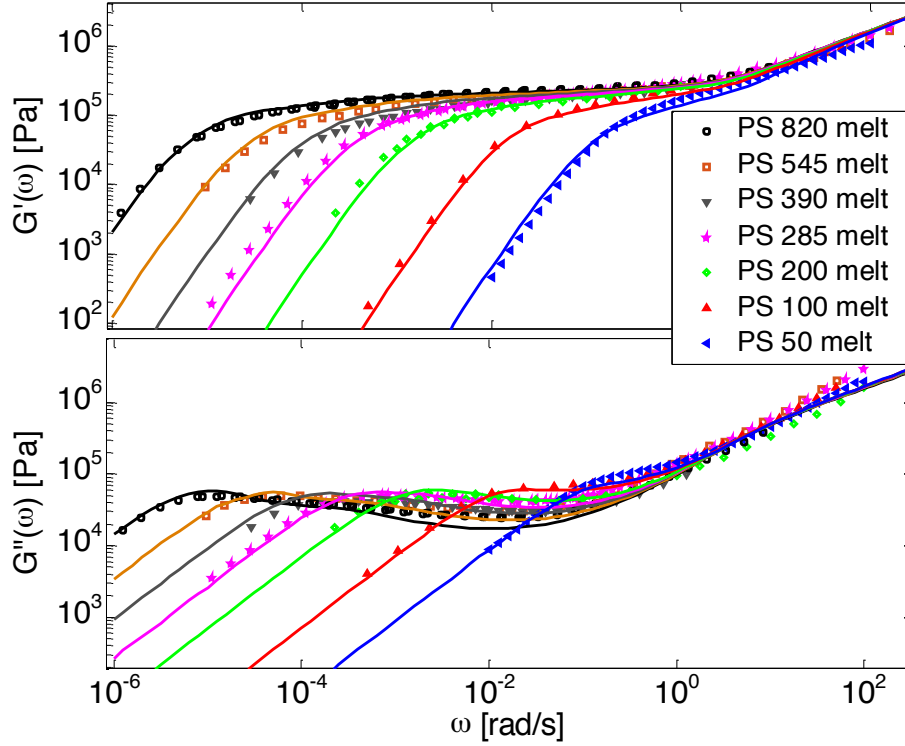


Fig. 5.2: Experimental (symbols) and predicted (line) storage and loss moduli of monodisperse PS samples in the melt state at a reference temperature of 130°C, with M_w = (from left to right:) 820 kg/mol, 545 kg/mol³¹, 390 kg/mol³³, 285 kg/mol³¹, 200 kg/mol³³, 100 kg/mol³³ and 50 kg/mol³³.

The model is then used, without any degree of freedom using only the set melt parameters, to calculate and predict the linear viscoelastic data of the two PS solutions series presented in Table 1. The comparisons between predicted and experimental data are shown in figs 5.3 and 4. While the blends presented in fig. 5.3 are all based on PS820 and OS8.8, fig. 5.4 presents viscoelastic data of solutions based on different molecular weights PS diluted in OS4 at different concentrations, but with a similar number of (long-long) entanglement segments, Z_2 . It was shown in ref. [30] that the G' , G'' curves of these

different solutions superimpose very well if horizontally and vertically shifted.

One can observe that the approach proposed here allows obtaining very good predictions for different masses and concentrations, spanning the whole range from concentrated and semi-dilute solutions down to only few entanglements per chain. In particular, it should be noted that this good agreement of the different plateau moduli between experiment and calculation is found when the actual dilution exponent α has been fixed to $\alpha = 1$ in the model.

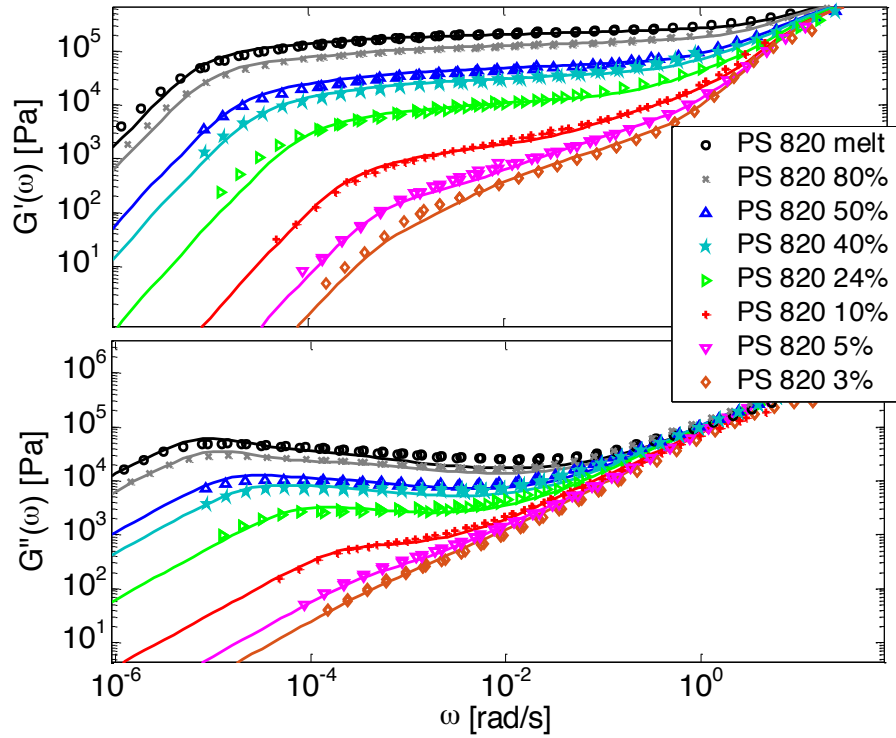


Figure 5.3: Experimental (symbols) and predicted (line) storage and loss moduli of monodisperse PS sample PS820 diluted in oligomeric styrene OS8.8, at different concentrations. The experimental data are shifted to iso- T_g condition.

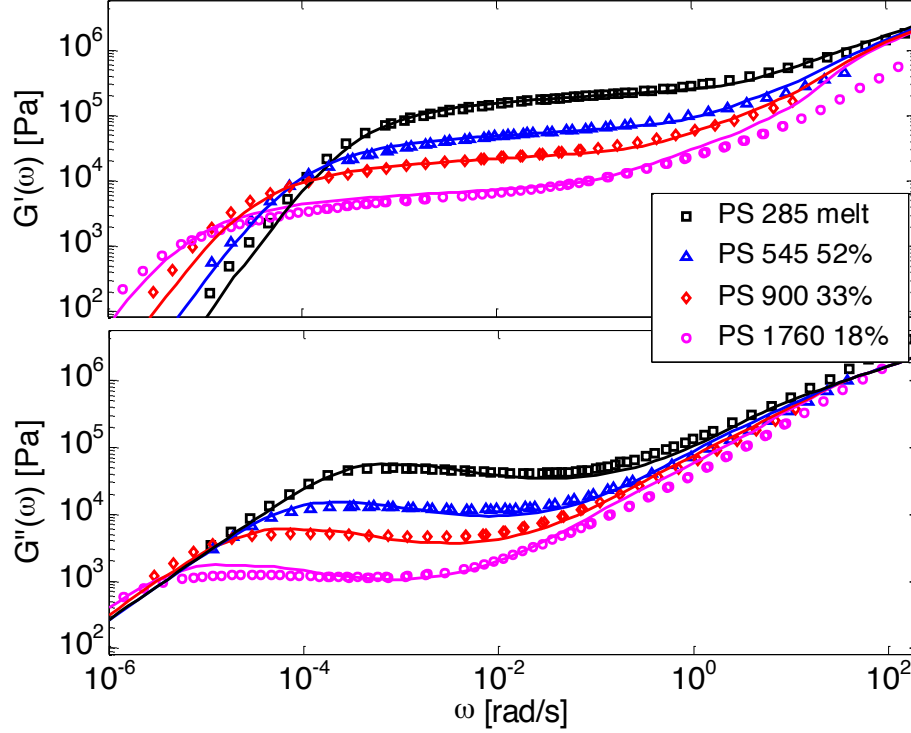


Figure 5.4: Experimental (symbols) and predicted (line) storage and loss moduli of monodisperse PS samples in the melt state or in solution in the styrene oligomers OS4, at different concentrations. The experimental data are shifted to iso- T_g condition.

Based on these results, several observations can be made. First, one can observe in Fig 5.3 that the shape of the viscoelastic data at intermediate and high frequencies is rather complex. In particular, when the long chains are strongly diluted, we observe the appearance of different slopes in this frequency region. This can be attributed to the fact that these curves include both the relaxation of the short component (with $M_w = 8.8$ kg/mol) and the Rouse relaxation of the long chains up to molecular segments of mass $M_{e,0,melt}/\nu_2$ (see Eq. 14). This is illustrated in fig. 5.5, which presents the predicted storage and loss moduli of sample PS820 diluted at 5 wt% in OS8.8, and shows the specific contributions of the different relaxation processes to the sample relaxation.

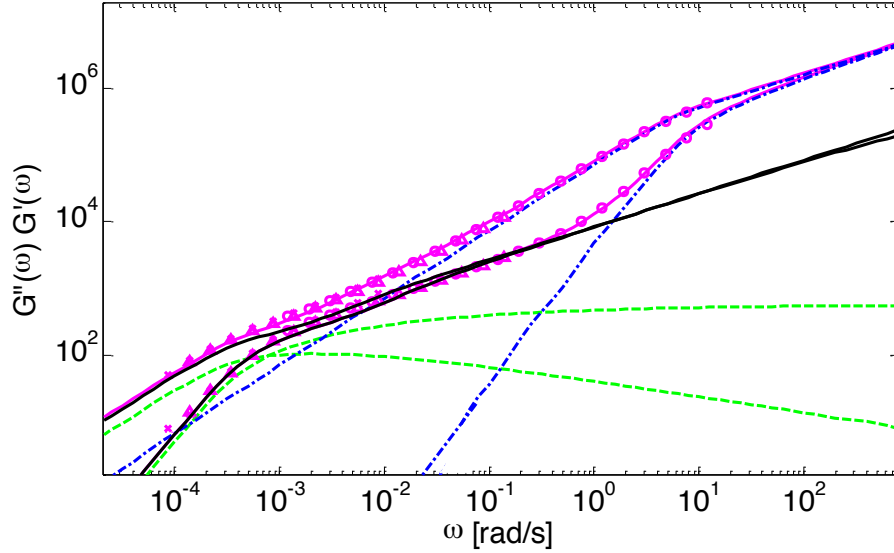


Figure 5.5: Experimental (symbols) and predicted (lines) storage and loss moduli of the sample PS820 diluted to 5 wt % in OS8.8. The data have been divided into the contribution of the oligomers (blue dash dot curves) and of the long chains, including the Rouse and Constraint Release Rouse modes (black curves) or neglecting them (green dashed curves).

As it can be seen, the curves observed in the frequency window between 1 and 20 rad/s correspond to a transition state between two Rouse domains with typical slopes of $\frac{1}{2}$: The first (high frequency) process includes the relaxation of both the short and the long chains and corresponds to the fast modes of Rouse, i.e. the Rouse relaxation of polymer strands shorter than M_I , while the second Rouse relaxation only involves the longest modes of the long chains and is associated with the relaxation of polymer strands of masses between M_I and $M_e = M_{e,0,melt}/\nu_2$. The existence of this second frequency domain governed by Rouse relaxation shows the importance of accounting for the Constraint Release Rouse modes of the long chains, taking place up to the long-long entanglement segments of mass M_e in order to properly capture the relaxation behavior of such blends with large difference in M_w . Though this might be obvious for the case of polymer solutions, this point becomes more delicate for binary blends of short and long molecules. Indeed, as described in Section 5.3, this

Rouse-like relaxation, which allows the long chains to move from a thin tube to a dilated tube, is usually described by the Constraint Release Rouse process (CRR) through Eq. 14.¹¹ However, this requires to accurately define the relaxation state of the chains at the time the CRR becomes active. While it is easy to determine this state in case of long chains diluted in oligomers (by imposing $\phi(t=\tau_e)=1$), for longer short chains the starting time of CRR and the corresponding relaxation state are not known *a priori*.

In fig. 5.5, one can also observe that the rubbery plateau is quite low and not well defined. This can be understood based on the fact that when diluted to 5 wt%, sample PS820 only contains an average of 2.7 entanglement segments per chain, which is at the limit of the entangled state. In the terminal zone, the chains are therefore moving by CR-CLF in a very dilated tube. In order to observe an actual (rubbery) plateau, the concentration of sample PS820 must be at least 10 wt% (see fig 5.3).

As seen in fig. 5.2 for the monodisperse samples, the high frequency data are not accurately captured by the model. This is due to the contribution of the terminal tail of glassy relaxation⁴⁴, which is not included in the model. On the other hand, the discrepancy observed in Figure 5.4 at high frequency has two different origins: in addition to be effected by the glassy relaxation⁴⁴, large part of the disagreement comes from the fact that our model predicts slower Rouse relaxation of the oligomers when compared to the experimental results. This cannot be corrected by considering another value for the material parameter $\tau_{e0,melt}$ (used to define the intrinsic Rouse time of the oligomers) since this would strongly affect the other data. However, since this discrepancy is observed only at very high frequency, it does not influence the curves around the rubbery plateau, i.e. in the frequency area where we would like to discuss the results and the value of the effective dilution exponent.

The good agreement found between experimental and theoretical curves allows us to take advantage of the model for further investigating how the effective (i.e. experimentally determined from the scaling of G_s or G''_{max} with c) value of α varies with the sample composition. This is the objective of the next section.

5.4.2. Influence of concentration on G_N^0 , G_s , G''_{max} and on the effective α

As already mentioned, the plateau modulus of the different blends in fig. 5.2-5.4 is well described by the model in which the actual dilution exponent is fixed to the *a priori* expected value of $\alpha = 1$. This good agreement between theoretical and experimental values means that the real plateau modulus of these samples, G_N^0 , must scale with v_2^2 , or equivalently, with c^2 (see Eq. 3). However, due to the CR-CLF (tension equilibration) process, the observable level of the plateau measured at lower frequency, is expected to change so that the effective value of α , measured at longer times, is expected to be larger than 1. It is therefore interesting to determine its value for the sets of samples analyzed here, based on approaches usually used in literature in the case of monodisperse samples. Such approaches are the determination of the effective α by looking at the c -dependence of the maximum loss modulus, G''_{max} , localized in the terminal regime^{14,17,18}. On the other hand, in order to estimate the influence of the tension equilibration at intermediate frequency regime, another approach is to look at the c -dependence of G_s , defined as the value of the storage modulus at the frequency ω_s where the $\tan\delta$ curve ($= G''/G'$) shows a minimum.^{45,46} G_s is usually used to approximate the value of the plateau modulus G_N^0 .

Results obtained for the two sets of solutions are shown in fig. 5.6. The theoretical G_s values have also been determined and are represented by the cross symbols in fig. 5.6.a.

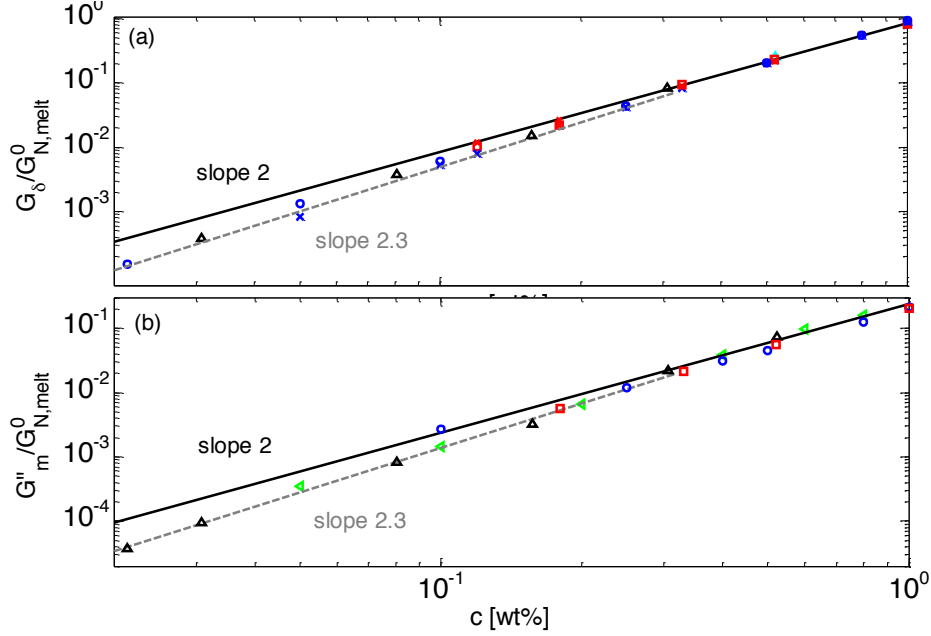


Figure 5.6: Values of (a) G'_δ , and (b) G''_{max} determined from the experimental ($\square, o, \Delta, <$) or the predicted (X) data of the blends. The data correspond to PS/OS blends with similar number of entanglements (Red $\square$), the PS820/OS8.8 blends (blue o), the PBD410/PBD3 blends (green $<$) and the PBD925 diluted in small-molecule solvent (black Δ) (see Table 1). Solid and dashed line represent the slope of 2 and 2.3. The line in figure (b) are plotted a factor 3.56 times lower than in figure (a).

As a first comment, it must be noted that G''_{max} cannot be determined for low concentrations of PS in oligomers since there is no clear maximum in the corresponding loss modulus curves, due to the overlap between constraint release Rouse process and terminal relaxation of the chains (see fig. 5.5). Only the plateau of the PBD samples could be measured, the long chains being much more entangled than the PS long chains. On the other hand, G'_δ could be measured only for the samples with experimental data in the intermediate-high frequency region.

Fig. 5.6 reveals important features:

- From the comparison between G''_{max} and G'_δ , we can see that the G''_{max} values are indeed around a factor 3.56 lower than the values of

G_s .¹⁸ Also, we observe that the c -dependence of G''_{max} and G_s are very similar and that they both differ from the real plateau modulus G_N^0 (represented by the continues line in fig. 5.6.a), this discrepancy increasing with decreasing polymer concentration. From this result, we conclude that the CR-CLF process can already affect the viscoelastic properties at the intermediate frequency ω_s . Thus, the G_s obtained from the $\tan\delta$ method cannot be used to determine G_N^0 for polymer/oligomers blends since it is already influenced by the fast tension equilibration process.

We also see that the G''_{max} data are a little more scattered than the G_s data. This is most probably due to the fact that G''_{max} is much more sensitive to polydispersity than G_s .

- At high concentrations (> 40 wt%), G''_{max} and G_s show a c^2 -dependence, which corresponds to an effective value of α equal to 1. Then, at lower concentration, most of the blends show a transition from c^2 - to $c^{2.3}$ - dependence of their plateau values. This demonstrates that the value of the effective α determined from either G''_{max} or G_s , is not a constant and depends on the concentration.

- Looking at the G_s extracted from both the experimental and the theoretical curves (see fig. 5.6.a), it is interesting to note that the set of PS/OS4 blends prepared from different molecular weight PS samples in order to keep Z_2 constant (set 2, see the red symbols), keeps a c^2 -dependence also at lower concentrations, while this is not the case for the other blends, made from long chains with a specific, constant molar mass and varying concentrations. In particular, the value of G_s of PS3200 diluted to 13 wt% is well above the G_s found for a solution of 13 wt% of PS820. From this observation, one can conclude that the effective α determined from G_s (at intermediate frequency) is not only a function of concentration, but also seems to depend on the molar mass of the chain.

This is further illustrated in fig. 5.7, which compares the viscoelastic response of two solutions of PS chains, both at the same concentration of 10 wt%, but with chain molar masses of either 820 kg/mol or 3900 kg/mol³⁴: despite the fact that they are diluted to the same concentration and thus have the same entanglements density, it is obvious that the value of G_s is much lower for sample PS820 (which contains 6 long-long entanglements) in comparison to the G_s value of

the PS3900 sample (which contains around 28 long-long entanglements).

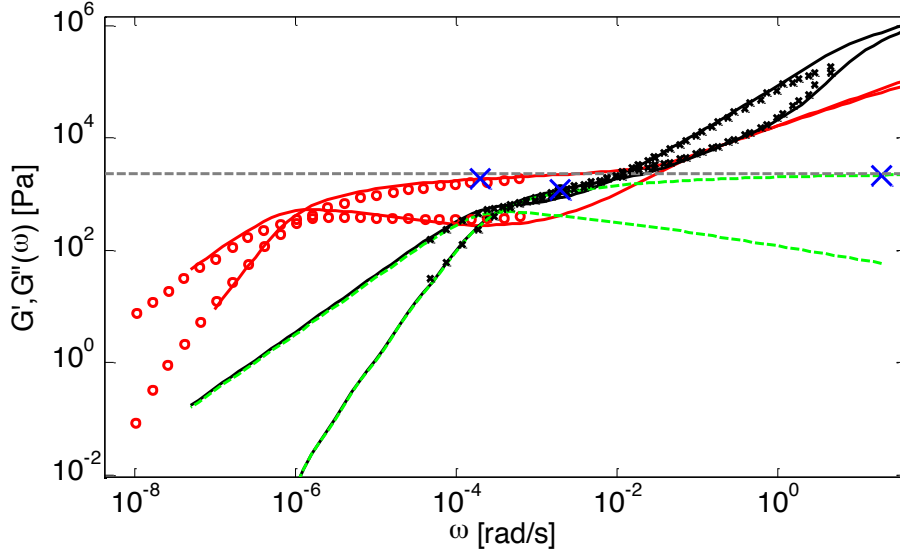


Figure 5.7: Experimental (symbols) and predicted (line) storage and loss moduli of monodisperse PS samples in solutions, for sample PS820 diluted to 10 wt% (black x) and for sample PS3900 diluted to 10 wt% (red, o). The X symbols on the predicted curves indicate the storage modulus which corresponds to the minimum of the $\tan \delta$ curve. The predicted curves of PS820 are shown with (black lines) and without (green lines) Rouse contributions. The dashed line corresponds to the rubbery plateau (based on $\alpha = 1$).

From these observations, a global picture can be drawn: while the effective value of α in binary blends of long and short linear chains must be determined from moduli in the frequency range close to the terminal relaxation of the long chains¹¹, for polymer/oligomers blends a larger effective α can also be determined from moduli at higher frequencies, with no significant difference between the c -dependence of the values of G''_{max} and G_{∞} . This is due to the fact that, in the case of polymer/oligomer blends, the tension equilibration process, which is modelled here by the CR-CLF process, is very fast since it does not include any delay due to the motions of the short component (see Equations 7 and 8), and the long chains can explore their dilated tube as fast as their intrinsic Rouse process allows. Since these fast Rouse

motions are already taking place at times shorter than the inverse of the frequency ω_s at which G_s is determined, the effective α at intermediate frequency is found to be larger than 1.

If we consider that a large value of the effective α is related to the tension equilibration process, as it is suggested in this work, one can easily explain that its value can vary between 1 (no influence of the CR-CLF) and 4/3 (fully equilibrated long chains¹⁷), depending on both concentration and molar mass of the long chains. Indeed, from Equation 16 it is expected that the importance of the CR-CLF process increases with decreasing chain length or the concentration, i.e. the effective α increases with a decreasing number of long-long entanglements per chain, Z_2 .⁴⁷ This Z_2 dependence of the effective α is consistent with the c^2 -dependence found for G_s with the second set of PS-OS blends, for which Z_2 was kept constant for all concentrations³⁰⁻³¹: in such a case the importance of CR-CLF process is exactly the same for all the samples since they all have a constant number of entanglements. Thus, they are all characterized by a similar effective α and the slope of the G_s values continues to scale with c^2 . On the contrary, the dependence of G_s for the PS820/OS8.8 blends shows a power law which is relatively well defined by a slope of 7/3 at low concentrations: by diluting PS820 in oligomers, the number of (long-long) entanglement segments is decreasing; this enhances the CR-CLF process, which is already observed at intermediate frequency since it is not delayed by the short chains. As a consequence, the difference between G_s and G_N^0 is increasing when the PS820 is diluted in the oligomers.

Thus, the tension equilibration process allows us to explain the non-constant value of the effective α found experimentally from G''_{max} and G_s , as well as its dependence on concentration and molar mass. According to the CR-CLF process, its value should depend on Z_2 , which is further validated in Section 5.4.3.

Another consequence of this fast CR-CLF process is that for such blends, G_s cannot be considered as a good approximation of the plateau modulus G_N^0 , which scales with c^2 for all concentrations (as defined in our model). This is illustrated in fig 5.7, which shows the storage modulus corresponding to G_s for the two blends, and

compares this value to the real plateau modulus G_N^0 determined by removing the contribution of the high frequency Rouse relaxation as well as the CR-Rouse modes (see Eq. 14) from the theoretical curves⁴⁶⁻⁴⁸. It is seen that, due to the overlap between Rouse relaxation and CR-CLF process, the minimum of the $\tan\delta$ curve is found at a rather low frequency ω_δ (see the X symbols), at which the sample has already partially relaxed by tension equilibration.

5.4.3. Influence of Z_2 on the terminal relaxation time, CR-CLF process and effective α .

As described in Section 5.4.2., it seems that the value of the effective α depends on the importance of the CR-CLF process: the more the chains are able to relax by CR-CLF before their terminal relaxation, the larger is the effective α , which is usually determined based on the scaling of G''_{max} with concentration, but which can also be determined from G_δ in the specific case of polymer/oligomers blends. Thus the transition between an effective α of 1 (negligible effect of CR-CLF) and 4/3 (fully equilibrated chains¹⁷) could, in principle, take place at any possible concentration, depending on the entanglement state of the long chains, Z_2 . In this Section, we first try to point out the existence and importance of the CR-CLF process as a function of Z_2 , based on the experimental terminal relaxation time of the solutions, and then relate this process to the effective α determined from G_δ .

As mentioned in the Introduction, the terminal relaxation time of the solutions is expected to be a function of both reptation and CR-CLF processes. Since the real dynamic dilution exponent α is equal to 1, the reptation time of the monodisperse long chains diluted in oligomers (or theta solvent) should therefore scale with concentration (see Eq. 17): $\tau_{rept,0}(M_2) = \tau_{rept,0,melt}(M_2) \cdot c$. Therefore, by comparing this theoretical reptation time to the experimental terminal relaxation times of these samples, one should be able to extract the importance and scaling of the CR-CLF process. In order to do so, the experimental terminal relaxation time τ_{rel} , must be determined. This is achieved by superimposing terminal slopes of 1 and 2 to the experimental loss and storage moduli curves in the terminal regime

and by defining τ_{rel} as the inverse of the frequency at which these two lines cross each-other³.

Terminal and reptation times are compared in fig. 5.8.a, as a function of the concentration, and fig. 5.8.b as a function of the number of long-long entanglement segments, Z_2 , which leads to several observations:

First, one can clearly see that reptation alone is not enough to explain the relaxation of the samples: as expected, Contour Length Fluctuations (CLF) process (for the monodisperse PS samples) and CR-CLF (for the solutions) are needed in order to explain the shorter terminal relaxation times. Also, the ratio between terminal and reptation relaxation time cannot be seen as a simple function of concentration; it is rather a function of the number of long-long entanglement segments along the long chains, $Z_2 (=Z_{2,0} \cdot c)$. Indeed, as shown in fig. 5.8.b., all the data superimpose when plotted in this way and create a master curve, except for the PBD925/DOP solutions, which are discussed in Section 5.4.4.

In fig. 5.8.b., a transition is observed around $Z_2=20$, from a terminal time dominated by reptation at high Z_2 , towards much shorter terminal times at low Z_2 , for which another scaling is observed: the terminal relaxation time of the diluted chains containing less than 20 long-long entanglement segments is found to scale with $(Z_{2,0}^3 c) \cdot Z_2$, i.e. with $(c^2 Z_{2,0}^4)$. This scaling is identical to the scaling of the CR-CLF process (see Eq. 16) and therefore validates this relaxation mechanism and demonstrates its importance for moderately entangled linear chains diluted in oligomers. In fact, for such chains the reptation process (taking place in a tube only formed by the long-long entanglements) is becoming very slow compared to the CR-CLF process, and its influence becomes negligible.

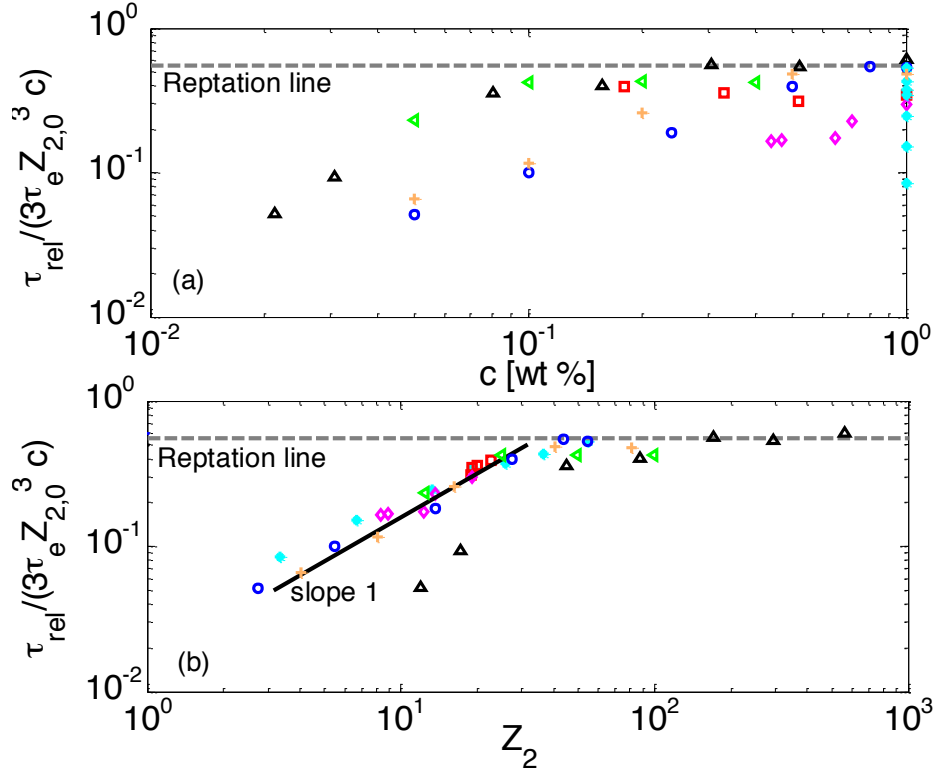


Figure 5.8: (a) Terminal relaxation time of the long chains normalized by their reptation time in the melt state, $\tau_{rept,0,melt}$, versus the polymer concentration, (b) Terminal relaxation time of the long chains normalized by their reptation time $\tau_{rept,0,melt}$ in solution, $\tau_{rept,0}$, versus the number of long-long entanglement segments $Z_2 = Z_{2,0} \cdot c$, for the set of samples with similar number of entanglements (red $\square$), the PS820/OS8.8 blends (blue o), the PBD410/PBD3 blends (green $<$), PI308kg/mol /PI2kg/mol blends from ref. [15] (orange +), the PS285kg/mol/OS4kg/mol from ref. [49] (magenta $\diamond$), the monodisperse PS samples (cyan $*$) and the PBD925 diluted in small-molecule solvent (black Δ) (see Table 1).

Similarly to the terminal relaxation time, the c -dependence of G_s data can be rationalized when they are plotted as a function of Z_2 . This is illustrated in fig. 5.9, based on theoretical moduli: the values of G_s determined from theoretical storage and loss moduli are shown in fig. 5.9.b. for three different molar masses and for a large range of

concentrations, while fig. 5.9.b. shows the same data but plotted as a function of Z_2 .

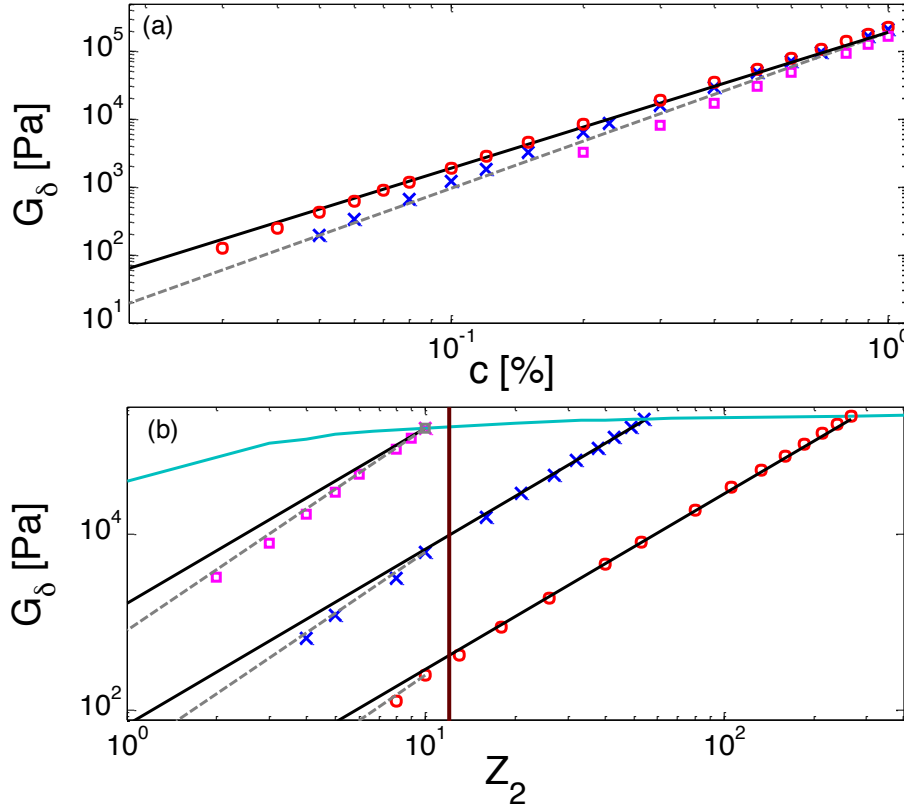


Fig. 5.9: Theoretical predictions of the $\tan\delta$ plateau modulus of PS solutions with $M_w=4000k$ (red o), $M_w=820k$ (blue x) and $M_w=150k$ (magenta $\square$) at different concentrations, (a) versus concentration, and (b) versus number of entanglements. The black and grey straight lines have slope of 2 and 2.3 respectively. The light blue curve represents the plateau modulus of monodisperse linear chains.

As it can be seen in fig. 5.9.a, the c -dependence of G_δ varies with the molar mass of the chains, as it has been observed from the experimental data. Furthermore, it also depends on the range of concentrations, which is considered. However, when plotted as a function of Z_2 (see fig. 5.9.b.), one can see that, despite the different levels of G_δ (which comes from the different concentrations (see Eq. 3)), all the curves show a transition from an effective α equal to 1 to a

larger value at the same number of entanglements, corresponding to around 12 entanglements. While the fact that the effective α tends to 4/3 at low concentrations cannot be determined from the equations, this scaling is clearly observed in fig. 5.9.

While the CR-CLF process starts to affect the terminal relaxation time around $Z_2 = 20$, it starts to have a large influence on G_s only at $Z_2 = 12$. This difference in the transition can be understood by the fact that G_s is less sensitive to Z_2 than the CR-CLF process (see Eq. 16). These results suggest that, in order to experimentally determine an effective α equal to 1 from G''_{max} or G_s , the diluted chains should at least conserve 12 (long-long) entanglements. This is in good agreement with the experimental results shown in fig. 5.6 (apart from the PBD925/DOP solution – see Section 5.4.) as well as with other results found in literature. For example, in ref. [15,16], Watanabe et al. found an effective α of 1.3 for polyisoprene chains of mass of 308 kg/mol diluted in oligomers. Indeed, when diluted at 10 wt%, these long chains only contain around 8 long-long entanglements and therefore are already largely influenced by the CR-CLF process. This is also consistent with the results found by Wang et al. [10], who showed that c-dependence of G''_{max} for long polybutadiene chains of 410 kg/mol diluted in oligomers at concentrations larger than 5%, i.e. with $Z_2 > 12$, leads to an effective α of 1 (see 5. 7 in ref. [10]), as well as Tao et al. in ref. [50], who showed that solutions of linear hydrogenated polybutadiene chains with a molar mass of 200, 350 and 440 kg/mol and concentrated above 20 wt% of polymer chains (i.e. with at least 24 entanglements) are well described with an effective α of 1. Another interesting example has been recently proposed by Park et al., who studied the dilution effect of ultra-high M_w polyethylene ($M_w > 10^6$ g/mol) diluted in paraffinic oil⁵¹. The molar mass of such sample is so high that even at the lowest investigated concentration of 2.5 wt%, the sample shows a clear rubbery plateau. In this work also, it was found that the viscoelastic data of this sample in solutions correspond to an effective α of 1.

In this part, it has been shown that the chains containing less than 20 long-long entanglements mainly relax by CR-CLF process, and their terminal relaxation time, which is well predicted based on $\alpha=1$, scales with $(c^2 Z_{2,0}^4)$. The chain equilibration through CR-CLF process leads

to a partial relaxation of the long chains and thus to a decrease of the corresponding level of the storage modulus. This effect is a function of Z_2 , and is already detected at intermediate frequency in the case of polymers/oligomers blends. This larger dilution effect of the oligomers leads to larger value of the effective α , especially for blends with $Z_2 < 12$.

5.4.4. Solutions in a small-molecule solvent versus polymer/oligomer blends

From the examples above, we can conclude that the proposed model leads to a unified picture, which is in good agreement with the experimental data. However, while this picture holds for the different polymers/oligomers blends which have been tested, it does not seem to describe the linear viscoelastic properties of entangled polymers strongly diluted in a small-molecule solvent. This is discussed in this Section.

We first focus on the set of solutions proposed by Colby et al.¹⁴, from which an α value of 4/3 has been obtained. These are solutions of polybutadiene chains of mass $M_w=925$ kg/mol dissolved in dioctyl phthalate (considered as theta solvent). Figure 5.10 shows the comparison between their experimental and predicted storage modulus. Parameters used in the tube model are the material parameters usually used with the TMA model for polybutadiene samples (i.e. a plateau modulus of 1.2MPa, $M_e=1650$ g/mol and $\tau_e=2.3 \cdot 10^{-7}$ s)³⁸. As it can be seen, while the model accurately captures the viscoelastic properties of the higher concentrated solutions (polymer concentration of 100 wt%, 52.3 wt% and 30.6 wt%), it starts to deviate at intermediate concentrations (15.7 wt% and 8.06 wt%), and the deviation becomes very large at very low concentration (3.08 wt% and 2.14 wt%): it is clear that the level of the predicted plateau modulus is too high compared to the experimental data, despite the fact that the CR-CLF process is taken into account. In fact, as discussed in Section 5.4. 3., this latter process becomes really effective only if $Z_2 < 12$, while here, $Z_2 = 17$ and 12 for the solutions at 3.08 wt% and 2.14 wt% respectively (based on $\alpha=1$).

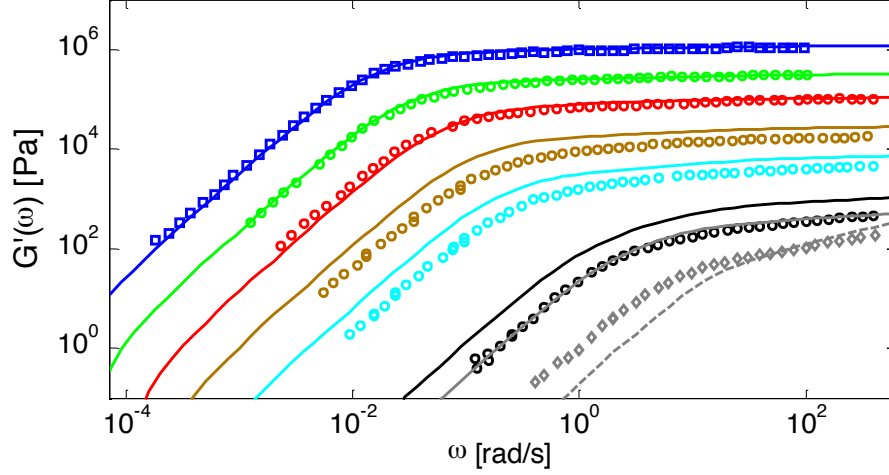


Figure 5.10: Experimental (o) and predicted (-) storage modulus of PBD925 diluted in DOP at a polymer concentration from 100% (blue $\square$), to 52.3% (green), 30.6% (red), 15.7% (brown), 8.06% (cyan), 3.08 wt% (black) and 2.14% (grey $\diamond$). The dashed curve shows the Rouse relaxation of 2.14 wt% of PBD925 (i.e. considered as unentangled).

Also, as observed in fig. 5.10, the sample PBD925 diluted at 2.14 wt% shows a viscoelastic behavior close to full relaxation by Rouse (see the dashed curve), as if the long chains were nearly not entangled, which definitely does not correspond to the behavior of a chain containing 12 entanglements. Thus, when highly diluted, these PBD chains seem less entangled than the predicted number of entanglements based on $\alpha = 1$ and accounting for CR-CLF. In such a case, using a larger value of the real dilution exponent α could, indeed, lead to better agreement.

However, considering a larger exponent α would have large consequences for the predictions of the viscoelastic properties of the polymers/oligomers blends, which are well described with $\alpha=1$. We thus face a situation in which our tube model cannot correctly predict the linear viscoelastic properties of both the polymer/oligomers blends and these solutions in a small-molecule solvent. This is illustrated in fig 5.11, which compares a PBD solution of ref. [14], composed of 2.14 wt% of sample PBD925 in DOP, to the blend composed of 5 wt% of PBD410 in PBD3¹⁰: although of different composition, these two samples have a similar number of entanglements ($Z_2=12$ and 12.4

respectively) if we consider $\alpha=1$ (by considering $\alpha=1.3$, $Z_2=3.8$ and 5 respectively).

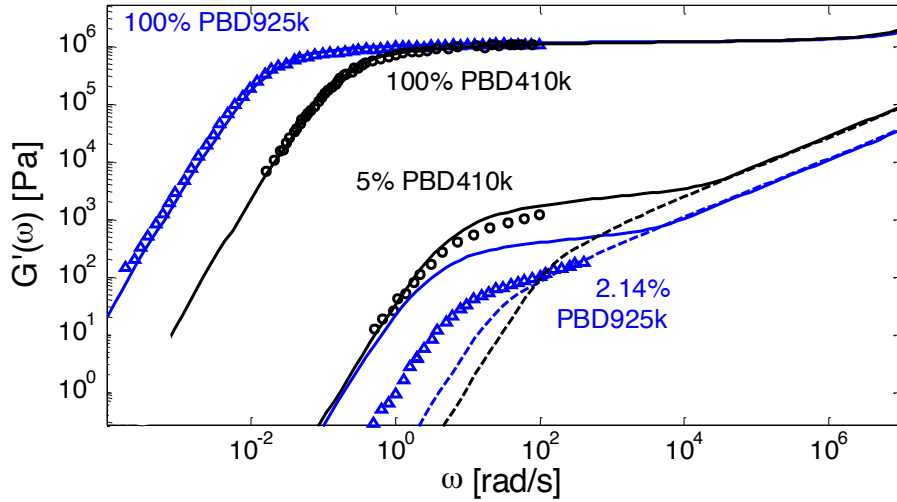


Figure 5.11: Experimental (o) and predicted (-) storage modulus for PBD samples with $M_w=410$ kg/mol and 925 kg/mol, in monodisperse state or diluted in oligomers (for PBD410) or in DOP (for PBD925). The dashed curves show the corresponding Rouse relaxation.

From this figure it is clear that the two solutions have a very different viscoelastic behavior: contrary to the viscoelastic response of the PBD925k diluted in DOP, the response of the PBD410k sample diluted in oligomers strongly differs from a Rouse-like response and is well described by our model with a real α exponent of 1. Furthermore, the level of its plateau could not be captured by considering an α value of 1.3. Indeed, in such a case, the storage plateau would have been 2.5 times lower than the present plateau, which does not correspond to the experimental data.

One can also observe that the two solutions have similar terminal relaxation times, which is somehow surprising since the reptation time of the diluted PBD925k should be higher by a factor of 4.9 (based on $\alpha=1$) or at least by a factor 3.8 (based on $\alpha=1.3$) than the reptation time of the PBD410k/PBD3k blend. This is also seen in figure 5.8.b.: at low Z_2 , the terminal relaxation times of the solutions in small-

molecule solvent are much shorter than the relaxation times of all polymer/oligomers blends, as if the long chains were less entangled.

Other examples of PS solutions in small-molecule solvent can be found in literature. In particular, in ref. [34], Bhattacharjee et al. studied the rheology of PS chains of mass $M_w=3900$ kg/mol dissolved in diethyl phthalate (DEP), dibutyl phthalate (DBP) or dioctyl phthalate (DOP). However, due to the use of different solvents with different qualities (from good for DEP and DBP, to theta for DOP), it is difficult to determine the origin of the observed discrepancy for this last set of solutions. Another, systematic set of data has been presented by Osaki et al.¹⁹, who studied very long PS chains (with $M_w = 2890, 4480$ and 8420 kg/mol) dissolved in a good solvent (chlorinated biphenyl). Similarly to the results found with the PBD solutions, these curves cannot be modelled based on the approach used for the polymer/oligomers blends. This is illustrated in Fig. 5.12, which compares experimental and predicted curves for the PS solution containing 5 wt% of PS8420: since Z_2 is equal to 28 (with $\alpha=1$), the predicted dilution effect is very small and at intermediate frequency, the storage modulus is close to its rubbery plateau, which has been determined based on $\alpha=1$. In contrast, we observe that the experimental plateau corresponds rather to an α value close to 1.3, which is the scaling found by Osaki et al., after having removed the high frequency Rouse contribution from the experimental data in order to determine G_N^0 .

On the other hand, the shape of the moduli is similar to the ones found for the blend composed of 40% of PS820 in OS8.8 (see the dashed curves compared to the star symbols), i.e. corresponds to long chains with 22 entanglements. For PS8420 diluted at 5 wt%, a value of Z_2 equal to 22 corresponds to an α value close to 1.08 (since $8420k/(M_{e0, melt}/0.05^{1.08})=22$). Thus, for this sample, it seems that the scaling in term of plateau modulus and relaxation time is different.

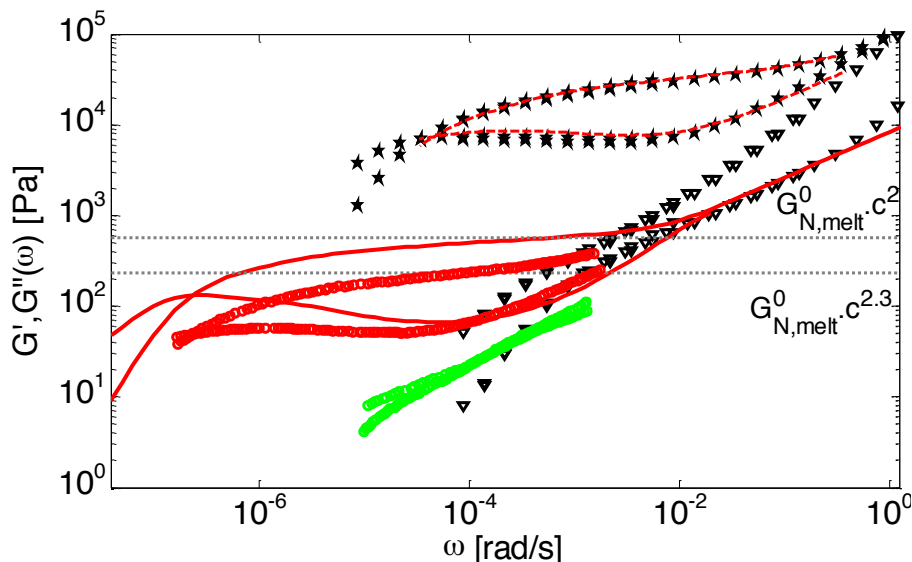


Figure 5.12: Comparison between the experimental storage and loss moduli of the blends PS820/OS8.8 containing 40 wt% (*) or 5 wt% (∇) of long chains, and the (horizontally shifted) moduli of sample PS8420 diluted at 5wt% (red o) or 2wt% (green o) in good solvent. The thick curves represent the predicted G' and G'' of sample PS8420 diluted at 5 wt%, while the dashed curves represent the experimental data of this sample, which have been horizontally and vertically shifted in order to superimpose the data of the blend composed of 40 wt%PS820 in OS8.8.

The reason why the diluted PBD925k behaves differently compared to the polymer/oligomers blends is not clear and should be further investigated. While it could come from the fact the solvent used is a small-molecule solvent, which possibly affects the ability of the chains to create entanglements, it could also be due to a difference in the cooperativity between the long chains and the oligomers or the small-molecule solvent: the high- M chains in the small-molecule solvent determine their entanglement mesh size just according to the solubility of the solvent, without any time needed to reach their equilibrium state. Thus, the high- M chains in those solutions obey the Colby-Rubinstein argument and their plateau modulus is proportional to $c^{2.3}$ in semi-dilute solutions. In contrast, in the high- M /oligomers blends, there is a very strong cooperativity between the oligomers and high- M chains, at least up to the length scale of the oligomer chains,

since the motion of the Rouse segments of the high-M chain occurs together with that motion of the oligomers. Consequently, this strong cooperativity leads to a slower equilibration, which is well described by the CR-CLF process.

In order to validate this proposition, one should compare these data to the viscoelastic behavior of very long chains (similar to PS8420k) blended in few percent to short chains or oligomers and check if their effective α continue to be equal to 1 until $Z_2=12$ (as the theoretical values shown for PS4000 in fig 5.9.a).

5.5. Conclusions

We have studied and modelled the viscoelastic properties of several polymer/oligomers blends, with various molar masses and concentrations of long chains, in order to discuss the dilution effect from the oligomers on the entanglement state of the long chains. In particular, we have shown that, at low concentration, the effective dynamic dilution exponent determined from the scaling of level of the storage modulus corresponding to G_s or G''_{max} with concentration is larger than the real or actual dilution exponent α , which is fixed to 1. This is due to the fast contribution of the CR-CLF process, which can take place without any delay coming from the oligomers. Consequently, in case that the number of (long-long) entanglements of the long chain falls below 12 (either by lowering the molecular weight or the solution concentration), G_s is found to scale with $c^{2.3}$ and cannot be used as a measure of the plateau modulus.

These results are in good agreement with ref. [11], where a larger value of the effective α in binary blends of linear chains was attributed to the partial re-orientation of the long-long entanglement segments, taking place through the tension re-equilibrium process along the chains. A similar picture is used here to analyze the viscoelastic properties of the polymer/oligomers blends, by considering that the relaxation time of a long-long entanglement segment is well described by its intrinsic Rouse time, with no extra delay due to the motion of the short chains.

While this approach could successfully explain the viscoelastic properties of a large number of polymer/oligomers blends, an

important discrepancy was found for semi-dilute solutions of entangled polymers in theta or good solvents: their plateau moduli scaled with $c^{2.3}$ rather than with c^2 . It has been shown that this behavior was not comparable to the viscoelastic behavior of the polymer/oligomers blends and that we could not describe the moduli of both types of samples with a single tube model. Possible origin of this difference has been proposed, based on the difference in cooperativity between the long chains and the oligomers or the small-molecule solvent.

In perspective, one should study the viscoelastic properties of very long chains (i.e. still entangled when diluted at few percent) blended in short chains or oligomers, in order to validate our proposition. This question needs, indeed, to be solved if we want to compare the extensional behavior of these different blends and solutions.

In the following chapters, we focus on the non-linear extensional properties of our samples. First we investigate the PS blends in details in chapter 6, followed by the PS solutions in chapter 7.

References

1. J.M. Dealy and R. G. Larson, Structure and rheology of molten polymers, Hanser Publishers, Munich, 2006.
2. H. Watanabe, Prog. Polym. Sci., 1999, 24, 1253; T. C. B. McLeish, Adv. Phys., 2002, 51, 1379.
3. E. van Ruymbeke, C. Y. Liu and C. Bailly, Quantitative tube model predictions for the linear viscoelasticity of linear polymers, Rheol. Rev., 2007, 53–134.
4. A. E. Likhtman and T. C. B. McLeish, Macromolecules, 2002, 35, 6332.
5. R. N. Khaliullin and J. D. Schieber, Macromolecules, 2010, 43, 6202.
6. Y. Masubuchi, H. Watanabe, G. Ianniruberto, F. Greco and G. Marrucci, Macromolecules, 2008, 41, 8275.; Y. Masubuchi, J. I. Takimoto, K. Koyama, G. Ianniruberto, G. Marrucci and F. J. Greco, Chem. Phys., 2001, 115, 4387.; Y. Masubuchi, G. Ianniruberto, F. Greco and G. Marrucci, J. Chem. Phys., 2003, 119, 6925.
7. S. Shanbhag and R. G. Larson, Macromolecules, 2004, 37, 8160.
8. M. E. Shivokhin, E. van Ruymbeke, C. Bailly, D. Kouloumasis, N. Hadjichristidis and A. E. Likhtman, *Macromolecules*, **2014**, 47, 2451; A. E. Likhtman, S. K. Sukumaran and J. Ramirez, Macromolecules, 2007, 40, 6748.
9. J. Park and R. G. Larson, Rheol. Acta, 2005, 44, 319. ; S. J. Park and R. G. Larson, Macromolecules, 2004, 37, 597.; Park, S. J. and Larson R. G., Journal of Rheology, 2006, 50, 21.
10. S. Wang, S.Q. Wang, A. Halasa and W. L. Hsu, Macromolecules, 2003, 36, 5355.
11. E. van Ruymbeke, V. Shchetnikava, Y. Matsumiya, and H. Watanabe, Macromolecules, 2014, 47, 7653.

12. G. Marrucci, J. Polym. Sci., Polym. Phys. Ed., 1985, 23, 159. ; R. C. Ball and T. C. B. McLeish, Macromolecules, 1989, 22, 1911.
13. M. Doi and S. F. Edwards, The Theory of Polymer Dynamics, Oxford, 1986.
14. R. Colby, L. Fetters, W. G. Funk and W. W. Graessley, Macromolecules, 1991, 24, 3873.
15. H. Watanabe, S. Ishida, Y. Matsumiya and T. Inoue, Macromolecules, 2004, 37, 6619. ; H. Watanabe, S. Ishida, Y. Matsumiya and T. Inoue, Macromolecules, 2004, 37, 1937.
16. T. Sawada, X. Qiao and H. Watanabe, Nihon Reorojo Gakkaishi (J. Soc. Rheol. Japan), 2007, 35, 11; Y. Matsumiya, K. Kumazawa, M. Nagao, O. Urakawa and H. Watanabe, Macromolecules, 2013, 46, 6067.
17. R. H. Colby, and M. Rubinstein, Macromolecules 1990, 23, 2753.; M. Rubinstein, and R.H. Colby, *Polymer Physics*; Oxford University Press: New York, 2003.
18. V.R. Raju, E.V. Menezes, G. Marin and W.W. Graessley, Macromolecules 1981, 14, 1668.
19. D. Auhl, P. Chambon, T. C. B. McLeish, and D. Read, Phys. Rev. Lett., 2009, 103, 136001.
20. C. Das, N. J. Inkson, D. J. Read, M. A. Kelmanson and T. C. B. McLeish, J. Rheol., 2006, 50, 207.
21. D. J. Read, D. Auhl, C. Das, J. den Doelder, M. Kapnistos, I. Vittorias and T. C. B. McLeish, Science, 2011, 333, 1871.
22. Z. W. Wang, X. Chen and R. G. Larson, J. Rheol., 2010, 54, 223.
23. E. van Ruymbeke, Y. Masubuchi and H. Watanabe, Macromolecules, 2012, 45, 2085.

References

24. M. Kapnistos, D. Vlassopoulos, J. Roovers and L. G. Leal, *Macromolecules*, 2005, 38, 7852.
25. M. Ahmadi, C. Bailly, R. Keunings, N. Nekoomanesh, H. Arabi and E. van Ruymbeke, *Macromolecules*, 2011, 44, 647.
26. H. Watanabe, O. Urakawa and T. Kotaka, *Macromolecules*, 1994, 27, 3525.
27. D.J. Read, K. Jagannathan, S.K. Sukumaran and D. Auhl, *Journal of Rheology*, 2012, 56, 823.
28. J. L. Viovy, M. Rubinstein, and R. H. Colby, *Macromolecules*, 1991, 24, 3587.
29. M Doi, W. W. Graessley, E. Helfand and D. S. Pearson, *Macromolecules*, 1987, 20, 1900.
30. Q. Huang, L. Hengeller, N. J. Alvarez and O. Hassager, *Macromolecules* 2015, 48, 4158.
31. Q. Huang, O. Mednova, H. K. Rasmussen, N. J. Alvarez, A. L. Skov, K. Almdal and O. Hassager, *Macromolecules* 2013, 46, 5026.
32. Q. Huang, N. J. Alvarez, Y. Matsumiya, H. K. Rasmussen, H. Watanabe and O. Hassager, *ACS Macro Letters* 2013, 2, 741.
33. J. K. Nielsen, H. K. Rasmussen, M. Denberg, K. Almdal and O. Hassager, *Macromolecules*, 2006, 39, 8844.; A. Bach, K. Almdal, H. K. Rasmussen and O. Hassager, *Macromolecules* 2003, 36, 5174.
34. P.K. Bhattacharjee, J.P. Oberhauser, G.H. McKinley, L.G. Leal and T. Sridhar, *Macromolecules* 2002, 35, 10131.
35. M. L. Williams, R. F. Landel, and J. D. Ferry, *J. Am. Chem. Soc.*, 1955, 77, 3701.
36. C.Y. Liu, J. He, R. Keunings and C. Bailly, *Macromolecules* 2006, 39, 8867.

37. E. van Ruymbeke, J. Nielsen and O. Hassager, *J. Rheol.*, 2010, 54, 1155.
38. E. van Ruymbeke, C. Bailly, R. Keunings and D. Vlassopoulos, *Macromolecules*, 2006, 39, 6248.
39. Shchetnikava, V., J. J. M. Slot, and E. van Ruymbeke, *Macromolecules*, 2014, 47, 3350.
40. M. J. Struglinski and W. W. Graessley, *Macromolecules*, 1985, 18, 2630.
41. P. E. Rouse, *The Journal of Chemical Physics*, 1953, 21, 1272.
42. Milner, S. T., T. C. B. McLeish, R. N. Young, A. Hakiki, and J. M. Johnson, *Macromolecules*, 1998, 31, 9345.
43. E. van Ruymbeke, M. Kapnistos, D. M. Knauss and D. Vlassopoulos, *Macromolecules*, 2007, 40, 1713.
44. T. Inoue, H. Okamoto, and K. Osaki, *Macromolecules*, 1991, 24, 5670; E. van Ruymbeke, E.B. Muliawan, D. Vlassopoulos, H. Gao and K. Matyjaszewski, *European Polymer Journal*, 2011, 47, 746.
45. C. Liu, J. He, E. van Ruymbeke, R. Keunings and C. Bailly, *Polymer*, 2006, 47, 4461.
46. Y. Matsumiya, N. Rakkapao and H. Watanabe, *Macromolecules*, 2015, 48, 7889.
47. E. van Ruymbeke, R. Keunings and C. Bailly, *J. Non-Newtonian Fluid Mech.*, 2005, 128, 7.
48. E. van Ruymbeke, M. Kapnistos, D. Vlassopoulos, C. Y. Liu and C. Bailly, *Macromolecules*, 2010, 43, 525.
49. S. Costanzo, Q. Huang, G. Ianniruberto, G. Marrucci, O. Hassager and D. Vlassopoulos, *Macromolecules*, 2016, 49, 3925.

References

50. H. Tao, C. Huang and T.P. Lodge, *Macromolecules* 1999, 32, 1212.
51. J. W. Park, J. Yoon, J. Cha and H. S. Lee, *Journal of Rheology*, 2015, 59, 1173.

Chapter 6

Short chains in polymer mixtures influence the transient hardening, but not the steady viscosity in uniaxial extension

It is now established that the huge qualitative difference between entangled polymer melts and solutions in non-linear elongational flows cannot be explained in the framework of the ‘standard’ tube model. Instead, the additional relaxation mechanism of alignment-induced friction reduction, acting primarily in melts, has been successfully tested in experiments and simulations. Here, we critically assess this mechanism by means of a systematic experimental investigation of the extensional response of long polystyrene chains diluted in different short chains matrices of varying molar mass, hence spanning the range from melts to solutions and varying the interaction between long chains and their molecular environment. We find that, surprisingly all polystyrene blends exhibit the same steady-state elongational viscosity, i.e. the long chains reach the same final stretch state, as long as the short chain exceeds a critical molar mass of about 4 kg/mol, well below the entanglement limit. This observation contradicts, in part, the basic assumption of alignment-induced friction reduction mechanism and raises new fundamental questions, in particular on the relationship between strain hardening and stretch state of the chains and its consequences on the non-universal behavior of melts and solutions in non-linear flows.

6.1 Introduction

Predicting the linear viscoelastic (LVE) properties of monodisperse polymers has reached a quantitative level, based on the Doi-Edwards tube-model theory¹ combined with established relaxation mechanisms

such as reptation, contour length fluctuations and constraint release (CR)²⁻⁶. The latter mechanism is particularly important for binary blends since it describes the influence of fast relaxation of shorter chains on the relaxation of longer chains⁷⁻⁹. This approach has been confirmed by demonstrating the universality of linear viscoelastic response of polymers with different chemical structures and concentrations as long as they have the same number of entanglements^{2,10,12}. However, it was shown recently that the universality between polymer melts and solutions breaks down under non-linear elongational flows^{11,12}: while polymer melts exhibit a monotonic extension-thinning behavior for all applied strain rates¹⁴, polymer solutions with the same number of entanglements exhibit an initial thinning behavior followed by a strong extension-hardening, which occurs at rates comparable to the reciprocal Rouse time of the chains¹³. As a result, molecular theories for linear flows cannot be extended to non-linear flows without further considerations.

This non-universality is now well established experimentally, however its molecular origin and in particular the absence of an extension thickening for polymer melts is not yet fully understood^{14,15}. This indicates that there is an important missing relaxation mechanism in polymer physics. Marrucci and Ianniruberto¹⁶ proposed a first explanation, which is a flow-induced contraction of tube diameter from its equilibrium that ultimately results in a pressure induced relaxation effect. Known as the inter-chain pressure concept, it included a novel non-linear parameter: the tube diameter relaxation time, τ_a . By incorporating this concept in the molecular stretch function theory, Wagner et al.¹⁷ were able to attain a semi-quantitative agreement for monodisperse PS melts¹⁴, and showed that the tube diameter relaxation time scales with the Rouse time of the chains. Later, this work was successfully extended to entangled chains diluted in oligomers¹⁸ and small molecule solvents¹⁹. However, this required using two different Rouse times, each for melt and solution state²⁰, which is difficult to comprehend. Furthermore, with binary blends it was shown that τ_a varies with the sample composition, which should not be the case since it is related to a Rouse process²¹.

Recently, it was proposed²² that the monotonic thinning behavior observed in the melt state is due to an alignment-induced reduction of the monomeric friction under fast elongational flow^{23,24}. This

mechanism calls for stretching of the chains in fast flows, inducing strong local anisotropy and resulting in a decrease of their (monomeric) friction coefficient. A priori, this should mainly affect entangled polymer melts, since in solution the small molecules do not align²³. However, recent work by Huang et al.²⁵ suggests that in oligomeric solution, friction reduction can also take place due to nematic interactions⁴¹⁻⁴³ between the oligomers and the polymer molecules, the importance of this process increasing with the size of the oligomers. Subsequently, a nematic interaction parameter, ε was included in the non-linear tube model²⁶, defined as the ratio of the order parameter of the short molecules to the average order parameter of the system. The resulting model successfully predicted the properties of various polystyrene (PS) melts and solutions²⁶⁻²⁸. Very recently, Park and Ianniruberto²⁸ established the dependence of ε on the molar mass of PS oligomer. Four different regions were distinguished as shown in Fig. 6.1. Initially, ε increases with the oligomer molar mass (for $M \ll M_e$), followed by a regime where ε is constant (up to $M \approx M_e$). Then ε decreases and finally becomes constant when the chains are fully entangled. Only the first regime has been observed experimentally^{25, 28}, whereas the other regimes are not yet confirmed with the exception of the work of Ylitalo *et al.*²⁹ (for polybutadiene). However, this is in contrast to the work of Tassin et al.³⁰, who found a constant value of ε for 10k and 27k styrene oligomers.

From the above it is evident that role of oligomer size on the extension-hardening reduction and its consequences on advancing the state-of-the-art in polymer physics in the direction of developing molecular constitutive equations represents an outstanding challenge. In this work we address this challenge with a systematic dataset that allows exploring the transition from polymer melts to polymer solutions in uniaxial extension by means of long PS chains diluted in oligomeric matrices of different sizes. We identify the origin of non-universal polymeric behavior of polymer melts in elongation and critically assess the monomeric friction reduction mechanism. To this end, long chain polystyrene PS is diluted at same concentration in different polystyrene matrices of molecular mass, $M_{w, matrix}$, ranging from unentangled to fully entangled states. These samples have been selected to ensure that friction reduction is solely governed by the long chain-matrix nematic interaction, i.e., their reciprocal Rouse time

exceeds the elongation rates, hence they do not stretch (details can be found at appendix).

The new results provide the ingredients to understand why and how the transition from polymer-oligomer to polymer-polymer interaction affects the strain hardening behavior, and raise new questions on physics of polymeric response in strong flows.

Specifically, the outcome of this study is both surprising and significant since it contradicts the existing picture of friction reduction. The experimental results suggest that all PS blends have the same steady elongational viscosity when compare at the same distance from their glass temperature T_g . This observation leads us to conclude that, as long as the matrix length is above a ‘critical molar mass’ (around 4 kg/mol²⁵), the long chains/matrix nematic interaction is constant, and *independent* of the length and entanglement state of the matrix molecules. In addition, the departure of the transient viscosity curves from their linear viscoelastic (LVE) envelopes is much more pronounced in oligomeric matrix than in entangled matrix, demonstrating the large influence of partial relaxation of the longer matrix chains on strain hardening.

6.2 Materials and methods

Four different blends were prepared by diluting a long PS chain (PS820) at a concentration of 10 wt% in four different matrices (from Polymer Source, Montreal, Canada). The long component was always self-entangled. The short chains ranged from oligomers (OS9) to a fully entangled state (PS73), but they never stretched at the particular experimental conditions. Their weight average molar mass M_w and polydispersity PDI were assessed by gel permeation chromatography, and for PS820 by field flow fractionation coupled with multi-angle light scattering (at BASF, Germany), yielding: 820 kg mol⁻¹ and 1.02 for PS820; 8.8 kg mol⁻¹ and 1.11 for OS9; 23 kg mol⁻¹ and 1.09 for PS23; 34 kg mol⁻¹ and 1.11 for PS34, and 73 kg mol⁻¹ and 1.08 for PS73.

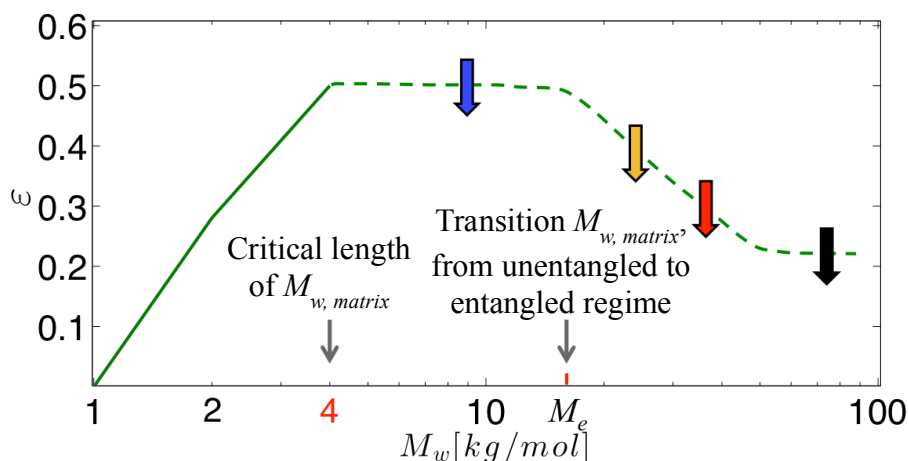


Fig. 6.1. Nematic interaction parameter, ε vs styrene molar mass M_w . The dashed part of the curve is hypothetical^{28,29}. The M_w of the PS matrices used in the current study (symbols) were chosen to explore all three hypothetical regimes.

The PS blends were prepared using the procedure described in ref. 34. Their main characteristics are listed in Table 1. T_g was determined by differential scanning calorimetry. The number of entanglements along the long and short chains (Z_L and Z_S , respectively) and the isofrictional Rouse relaxation time of the matrix (τ_R) are also given (details in the appendix).

Table 1 Main characteristics of the blends.

	Blend composition	Z_L / Z_S	Blend T_g [°C]	$\tau_R(\text{matrix})$ at $T_g + 31.4^\circ\text{C}$ [s]
B1	10% PS820 – 90% PS73	5 / 5	106.6	2.9
B2	10% PS820 – 90% PS34	5 / 2	104.7	0.63
B3	10% PS820 – 90% PS23	5 / 1	103.5	0.29
B4	10% PS820 – 90% PS9	5 / <1	98.6	0.04

The LVE properties were measured by small amplitude oscillatory shear tests performed on a MCR 301 (Anton Paar, Austria) rheometer using a stainless steel parallel plate geometry (with diameter of 8 mm), with a convection oven for temperature control ($\sim 0.1^\circ\text{C}$) under constant nitrogen gas supply. After an amplitude sweep to estimate the LVE region, frequency sweep tests were performed at three different temperatures (ranging from 130°C to 170°C for samples B1, B2 and B3, and from 120°C to 160°C for sample B4 with lower T_g) and shifted onto a single master curve at a reference temperature T_{ref} , using time-temperature superposition³⁵. Master curves were then brought to iso- T_g conditions ($T_{ref} - T_g = 31.4^\circ\text{C}$)³⁶ in order to compensate for the different T_g of the blends. Details are provided in the appendix.

Transient elongational stress measurements were performed with a filament stretching rheometer (VADER-1000, Rheo Filament, USA) using stainless steel parallel plate geometry (with diameter of 6mm), with an oven for temperature control ($\sim 0.1^\circ\text{C}$) under constant nitrogen gas supply. Prior to the measurements, all samples were dried under vacuum at 65°C overnight. Then these samples were molded into discotic specimens with a fixed radius of 2.75 mm using a home-made mold under vacuum. The samples were pressed at $140\text{--}150^\circ\text{C}$ and annealed at the same temperature (at least 20 minutes) under vacuum. A three-step protocol was followed: first, the sample was slightly squeezed at $150\text{--}160^\circ\text{C}$ to ensure adequate contact between the sample and the plates. Next, it was pre-stretched to a smaller radius R_0 ranging from 1 mm to 2.5 mm (this reduced the risk of sample detachment during the next step). Finally, the temperature was decreased to the $(T - T_g) = 31.4^\circ\text{C}$ (i.e., for samples B1, B2, B3 and B4 to 138°C , 136°C , 135°C and 130°C , respectively) and subsequently the time-dependent stress growth coefficient was measured at constant Hencky strain rates between 0.001 s^{-1} and 0.2 s^{-1} .

The linear and non-linear responses of the PS blends are shown in Figs. 6.2 & 6.3 respectively. The tube-based model used to predict the LVE properties of the blends, is discussed briefly in the appendix.

6.3 Results and discussion

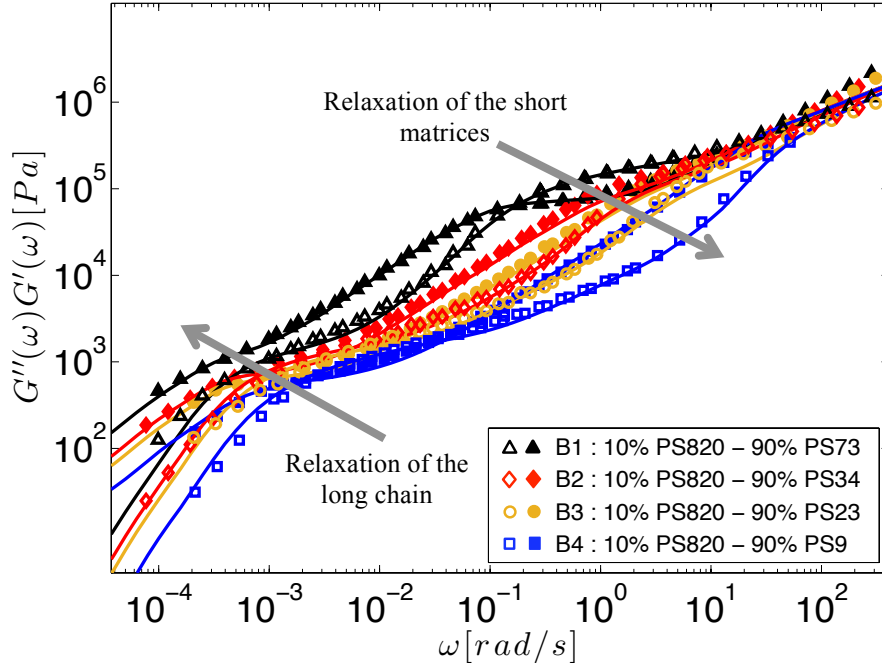


Fig. 6.2. Experimental (symbols) and predicted (lines) storage (open symbols) and loss (closed symbols) moduli of the PS blends, at iso- T_g condition.

The LVE data clearly show a fast relaxation of the short matrix at high frequencies, followed by the relaxation of the long chains at lower frequencies. While the short chains in sample B1 with about 5 entanglements form a rubbery plateau, its extend gradually diminishes with shorter matrix molecules and it disappears for B4. Despite the fact that the same concentration of long chains is used for all blends, their terminal relaxation time decreases with decreasing length of the matrix, due to a larger CR effect^{8, 9, 20, 34}. These experimental data are used to create the LVE envelopes for the elongational data of Fig. 6.3. Any upward deviation from these envelopes is a signature of strain hardening (SH). As already mentioned, the observed SH results entirely from the stretching of the long chains (see Fig. A1 in appendix) and should be influenced by their interaction with the different matrices. It should be noted that in this work, the term ‘steady elongational viscosity’ represents the constant elongational

viscosity reached by the transient viscosity curve after a certain time, but does not especially refer to a steady-state³¹⁻³³.

We first interpret the extend of SH via the deviation from the linear envelope, and by comparing normalized curves with respective LVE envelopes (inset of Fig. 6.3). While all blends depict strong strain hardening, the deviation from the LVE envelope is reduced with increasing $M_{w, matrix}$. A similar trend, going from polymer solution to melt, has been reported in the literature¹² and attributed to stretch-induced friction reduction. However, this explanation cannot hold for the present samples since the matrices are not stretched (see appendix). An alternative scenario is the monomeric friction reduction due to enhanced nematic interactions. In such a case, our experimental observations would suggest that ε increases monotonically with $M_{w, matrix}$ even when the matrix is fully entangled, which contradicts the results of Ylitalo et al.²⁹ and Park and Ianniruberto²⁸ (see Fig. 6.1). Moreover, this interpretation is physically questionable since nematic interactions cannot be enhanced in entangled polymer melts. These important discrepancies render a re-examination of strain hardening necessary.

Indeed defining SH with respect to the LVE envelope, as typically done in the literature^{10,12,25,38,39} raises concerns in the case of blends where the entanglement state of the linear matrix may strongly affect the LVE envelope. Consequently, we expect that part of SH coming from the long chains is masked by the viscoelastic response of the matrix itself, especially if the latter takes time to relax. In order to rationalize this effect, we used our tube model^{37, 40} to extract the contribution of the long chains to the LVE envelope of the blend, which is depicted with dotted lines in Fig. 6.3. Comparing this to the measured LVE envelope of the blend (solid lines) it becomes evident that for samples B1, B2 and B3 the long chain stretching should start well below the level of the full LVE envelope (illustrated further in Fig. A6), but is masked by the matrix contribution. Contrary, for sample B4 the oligomer matrix relaxes fast enough and contributes weakly to the LVE envelope, so the SH arising from the long chains is fully detectable and seems stronger. Therefore, the LVE envelopes influence the way the curves are normalized and consequently the final level of SH (inset of Fig. 6.3). These observations demonstrate the large effect of the linear response on the actual magnitude of SH,

and justify our proposal of an alternative way to quantify the actual stretch state of the long chains that is independent of the LVE properties of the blends.

To achieve this we directly relate the final long-chain stretching to the steady values of the elongational stress growth curves, as the short component has no effect at this level (given the choice of $M_{w, matrix}$ and $\dot{\epsilon}$) and all blends contain the same proportion of long chains. Interestingly, it is observed that all tested PS blends reach the same steady-state value (for $Wi_R = \dot{\epsilon} * \tau_{Rouse} > 1$), implying that the particular choice of matrix chains has no impact on the final stretch of the long chains. We can then conclude that beyond a ‘critical molar mass’ of the matrix (about 4 kg/mol²⁵), the polymer-matrix interaction remains unaltered and friction reduction doesn’t depend on the length of the matrix anymore. This unambiguous experimental observation, which suggests a constant nematic interaction for all blends, contradicts the behavior proposed in Fig. 6.1.

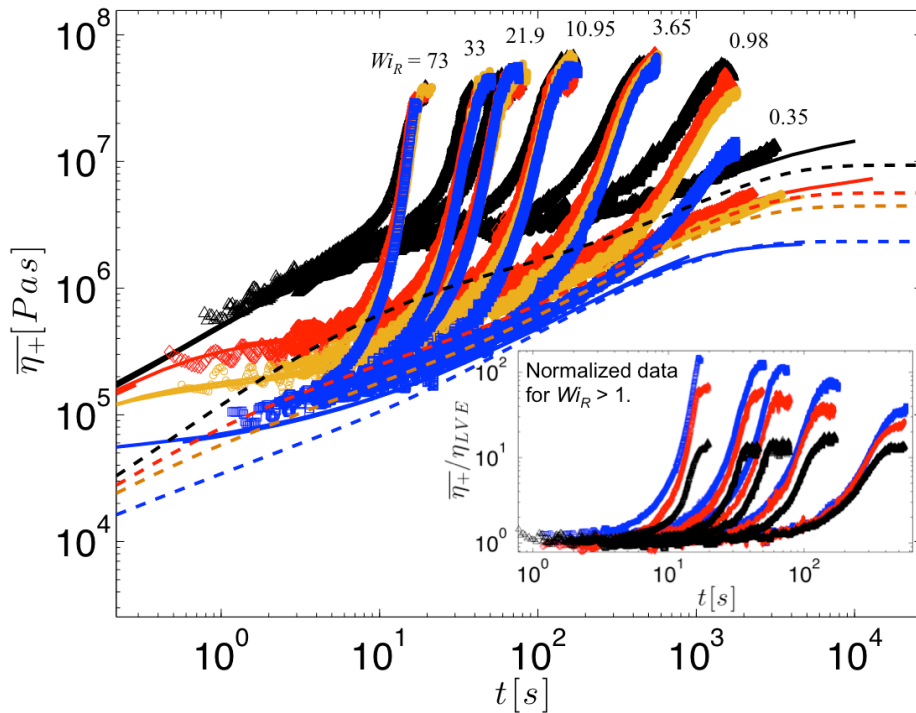


Fig. 6.3. Transient response of PS blends (symbols: legends are same as Fig. 6.2) under elongational flow at

various rates as indicated. Solid lines are the LVE envelopes, while the dashed lines are predictions of the contribution of long chains to the LVE envelop. Inset: Responses of blends B1, B2 and B4 are normalized by respective LVE (blend B3 is excluded for clarity). Slight discrepancy at short times with highest W_{IR} (defined with respect to the long chain) is discussed in the appendix.

Our results illustrate the large ambiguity in relating the extend of transient SH (i.e., departure from linear envelope) to the stretch state of the chains: while Fig. 6.3 suggests that the long chains reach the same steady-state stretch level, hence same final SH properties, the transient SH strongly decreases with $M_{w, matrix}$ (inset of Fig. 6.3).

As already discussed, this large difference in transient hardening mainly comes from the LVE response of the matrix, which masks the initial SH of the long chains. But even if we compare with the LVE of the long chains, the transient SH still decreases with increasing $M_{w, matrix}$. This is due to a second process which influences transient SH, namely the capability of the long chains to partially relax before starting to stretch. Indeed, long chains diluted in a fast-relaxing matrix will rapidly relax a part of their orientation through the CR process, since the continuous loss/creation of entanglements with short chains enables them to explore a larger effective tube diameter. Another consequence of CR is the reduction of the effective length of their primitive path, L_{eq-CR} (Fig. 6.4 a), in comparison to their initial value, $L_{eq,0}$ (which accounts for entanglements with both long and short chains). Thus, while $L_{eq,0}$ is constant for all PS blends, the rhythm at which L_{eq-CR} decreases through time strongly depends on the matrix relaxation time. This is important since, as explained by Auhl et al.¹⁵, under non-linear elongation flow, transient strain hardening appears as soon as the long chains are stretched above L_{eq-CR} , not above $L_{eq,0}$. This indicates that the importance of transient SH is proportional to the efficiency of the CR process. Therefore, the total strain hardening consists of an *apparent* CR-induced stretching when the primitive path length L_{PP} is increased from L_{eq-CR} ($< L_{eq,0}$) to its original value $L_{eq,0}$ (see Fig. 6.4 b), followed by the *real* stretch of the primitive path beyond $L_{eq,0}$, defined as $\lambda = L_{PP}/L_{eq,0} \geq 1$ (see Fig. 6.4 c). Since the same long chains are used for all samples, their *real*

stretch is identical, as well as their final length, L_{pp} . However their *apparent* stretch increases with decreasing $M_{w, matrix}$, leading to an enhancement of the transient SH (see Fig. 6.3). The results illustrate the key role of the matrix in transient SH and should have large consequences for blends in which the proportion of long chains is varied.

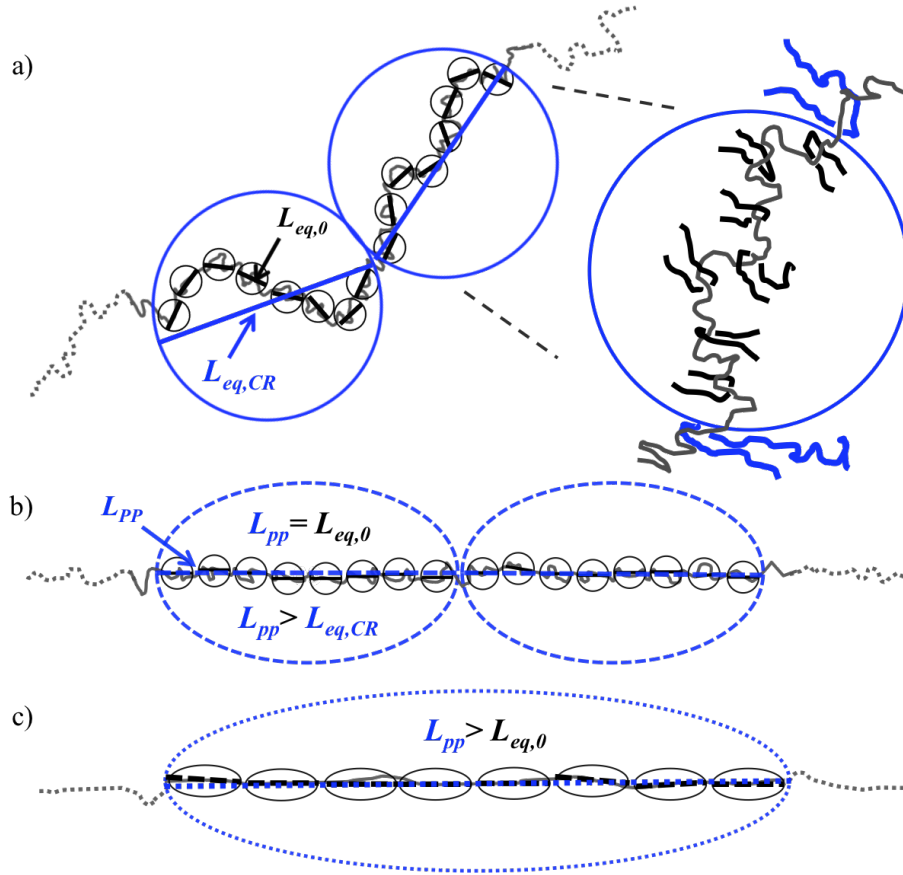


Fig. 6.4 a) Relaxation state reached by the long chain (blue curve) through CR process before stretch occurs. The black blobs correspond to the initial entanglement segments and $L_{eq,0}$. b) Chain conformation corresponding to $L_{pp}/L_{eq,0}=1$: Transition state between ‘apparent’ stretch (taking place from $L_{eq,CR}$ to $L_{eq,0}$ (see the evolution of the dashed blue blobs) and ‘real’ stretch. c) Onset of ‘real stretch’, $\lambda = L_{pp}/L_{eq,0} \geq 1$ (shown for one long-long entanglement blob).

6.4 Conclusion

In conclusion, we have demonstrated that above a critical molar mass (of about 4kg/mol^{25} for PS), probe polymer-matrix interactions remain unaltered and the size of the matrix does not play a role anymore on the final stretching of the long chains. Our results put into question the existing framework for understanding polymer stretching and provide new ingredients in this direction: there exists a clear distinction between transient strain hardening and steady-state stretching of the long chains. The former strongly depends on the polymer matrix, whereas the latter depends solely on the elongation strain rate (as well as the long chain M_w and concentration). This distinction is important for the fundamental understanding of the transition from polymer melts to polymer solution under extensional flow, and will have consequences in our continuing quest to establish conditions for universal viscoelastic behavior under strong flows.

In the next chapter, we investigate the polymer solutions diluted in different concentration levels to develop an understanding of how differently does a polymer melt and solution behave under non-linear elongational flows.

I. Appendix

1. Rouse time of the short chains matrix and related stretch state

In this section, the different characteristics of PS blends (as presented in table S-1) are defined. The number of entanglements along the short and long chains was calculated from the ratio of the molecular weight of the corresponding component and the molecular weight between entanglements, $Z = M_w/M_e$. Following our previous works, the value of M_e is fixed to 15 kg/mol³⁴.

Table S-1. Main characteristics of different components & blends.

Molecular Weight [kg/mol]	Z	PDI	T _g [°C]
820	56	1.02	106.6
73	5	1.08	105.6
34	2	1.11	103.3
23	1	1.09	92.4
8.8	--	1.1	94.6

	Blend composition	Z _L / Z _S	T _g [°C]	τ _R (matrix) at T _g +31.4°C [s]
B1	10% PS820 – 90% PS73	5 / 5	106.6	2.9
B2	10% PS820 – 90% PS34	5 / 2	104.7	0.63
B3	10% PS820 – 90% PS23	5 / 1	103.5	0.29
B4	10% PS820 – 90% PS9	5 / 0	98.6	0.04

The Rouse time, which is the longest relaxation time of an unentangled chain, is very important in elongational flow as polymer chains are presumed to be stretched when the flow rate exceeds the reciprocal of this characteristic time. In typical tube model, this relaxation time is defined as $\tau_{Rouse} = \tau_e * Z^2$, where τ_e is the relaxation time of a molecular segment between entanglements. The value of τ_e depends on the iso- T_g condition and in this work is set to 0.12s at $\Delta T_g = 31.4^\circ\text{C}$, in agreement with our previous works³⁴. Consequently, the short chains should start to stretch at strain rates of $1/\tau_{Rouse}$, i.e. 0.35, 1.59, 3.45 & 25 s^{-1} for the matrix of molar mass equal to 73, 34, 23 & 8.8 kg/mol respectively. To avoid stretching of the short components the highest strain rate used in this work is 0.2 s^{-1} .

The fact that strain rates selected here do not lead to strain hardening of the matrix can be further validated by looking at literature elongational data of PS melts² similar to the ones used in this work. In Fig. A1, it is observed that PS melt with a molar mass of 50 kg/mol do not show strain hardening (which results from stretch of chains) at strain rates lower than 0.4 s^{-1} , while the PS melt with a molar mass of 100 kg/mol starts to strain harden at rates above 0.13 s^{-1} . This last strain rate corresponds to a critical rate of $(0.13 \text{ s}^{-1} \cdot (\frac{100}{70})^2 =) 0.265 \text{ s}^{-1}$ in case of polymer chains of mass equal to 70 kg/mol. This value is indeed above the maximum Hencky strain rate used in this work.

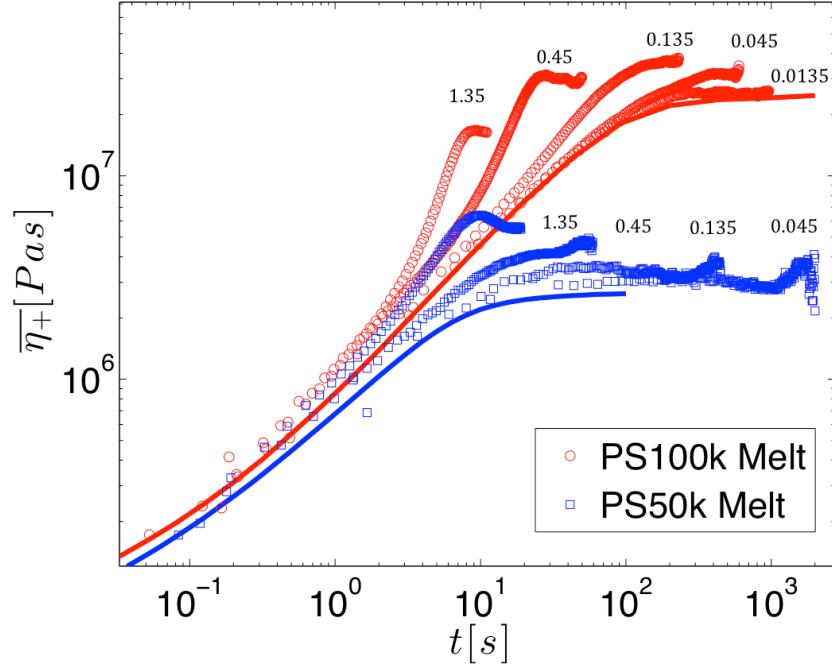


Fig. A1. Transient response (symbols) of PS melts, coming from ref. [14]. Solid lines represent the linear viscoelastic envelopes. Strain rates are shifted to $\Delta T_g = 31.4^\circ\text{C}$ from 23.4°C .

2. Experimental issues and corrections:

(i) Working at iso- T_g condition:

For the purpose of this study, four different blends were prepared from five different polystyrene components (four PS and one styrene oligomer). The longest chain PS (PS820) was diluted in the short chain matrices at same concentration (10-wt%). Consequently the T_g of each blend was found to vary, depending on the molecular weight of the short components. The important characteristics of these different components and blends are given in table S-1. Please note that the T_g of PS23 may seem odd as it's even lower than the OS9. This could be due to presence of solvent from the polymerization process. However, while preparing the blends extra cautions were taken to make sure that no solvent remains, which then can be confirmed from the DSC and SAOS experimental data of blend B3.

This difference in T_g values must be taken into account to allow a comparison of the viscoelastic responses. This can be achieved by working under iso- T_g condition³⁶ i.e. by keeping the same temperature difference between the experiment and the glass transition temperature of each blend. The importance of working at iso- T_g condition is very substantial particularly for amorphous polymers such as PS because of its high T_g ($\sim 100^\circ\text{C}$) and therefore low temperature difference between the glass transition and the experimental temperature.

In this work, the iso- T_g condition ($T - T_g$) was fixed at 31.4°C for all blends. For linear measurements, the master curves (from SAOS data) were generated at the corresponding temperatures (given on table S-2) while all the non-linear measurements were done directly at these temperatures.

Table S-2. Experimental temperatures.

Blends	T_g $^\circ\text{C}$	Experimental temperature, T $^\circ\text{C}$
B1 : 820 – 73 K	106.6	138
B2 : 820 – 34 K	104.7	136
B3 : 820 – 23 K	103.5	135
B4 : 820 – 8.8 K	98.6	130

a) Linear measurements (SAOS):

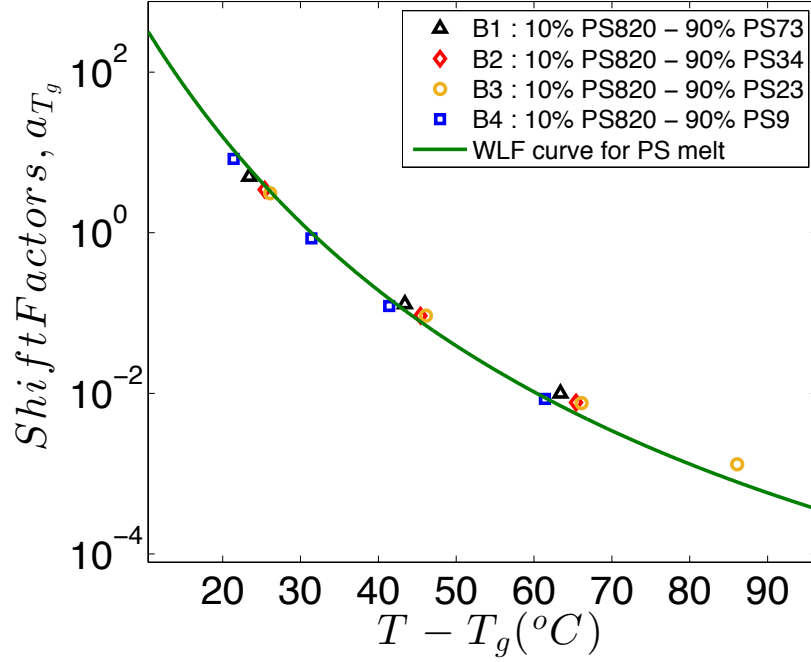


Fig. A2. Time temperature superposition shift factors as a function of $(T - T_g)$, determined for the different polymer blends. The continuous curve represents the WLF equation used in ref. [12].

The storage and loss moduli measured at 120 °C (for Blend B4) and at 130 °C (for Blend B1, B2 and B3) were horizontally shifted in order to ensure a good overlap of the viscoelastic response in the high frequency region, in which the chain relaxation is controlled by local Rouse dynamics and thus depends only on $(T_{\text{ref}} - T_g)$. As discussed below, the validity of the shift factors to this specific reference temperature can then be confirmed by comparing their value to the shift factors vs. temperature curve used to build the different TTS master-curves for different blends.

The shifted iso- T_g data measured at 120 °C (for Blend B4) or 130 °C (for Blend B1, B2 and B3) are then used as reference curves to shift the other experimental data measured at higher temperatures and thus to create general master-curves. It must be noted that no vertical shift has been considered here, since the range of temperature used is rather

limited. In Fig. A2, all shift factors used to create the master curves are plotted against $(T - T_g)$. As it can be seen, when plotted in such a way, the values used for PS blends nicely coincide with each other and the WLF equation for melts ³⁴.

$$\log a_T = \frac{-c_1^0(T - T_{ref})}{c_2^0 + (T - T_{ref})}$$

where, $c_1^0 = 8.19$, $c_2^0 = 89.53$ K, $T_{ref} = 138$ °C and T , the temperature is expressed in °C. The fact that all these curves superimpose also validates the factors used for shifting the data under iso- T_g conditions.

b) Non-linear measurements (Uniaxial extension):

All uniaxial extension measurements were performed at iso- T_g conditions as mentioned in table S-2. This is very important as T_g of blends containing the highest and lowest $M_{w.matrix}$, B1 and B4 correspondingly differs almost by 8°C. This temperature difference can't be ignored specially for PS, whose activation energy is very high so even a small change in temperature can cause huge variation in its viscoelastic properties as shown in Fig. A3 a)

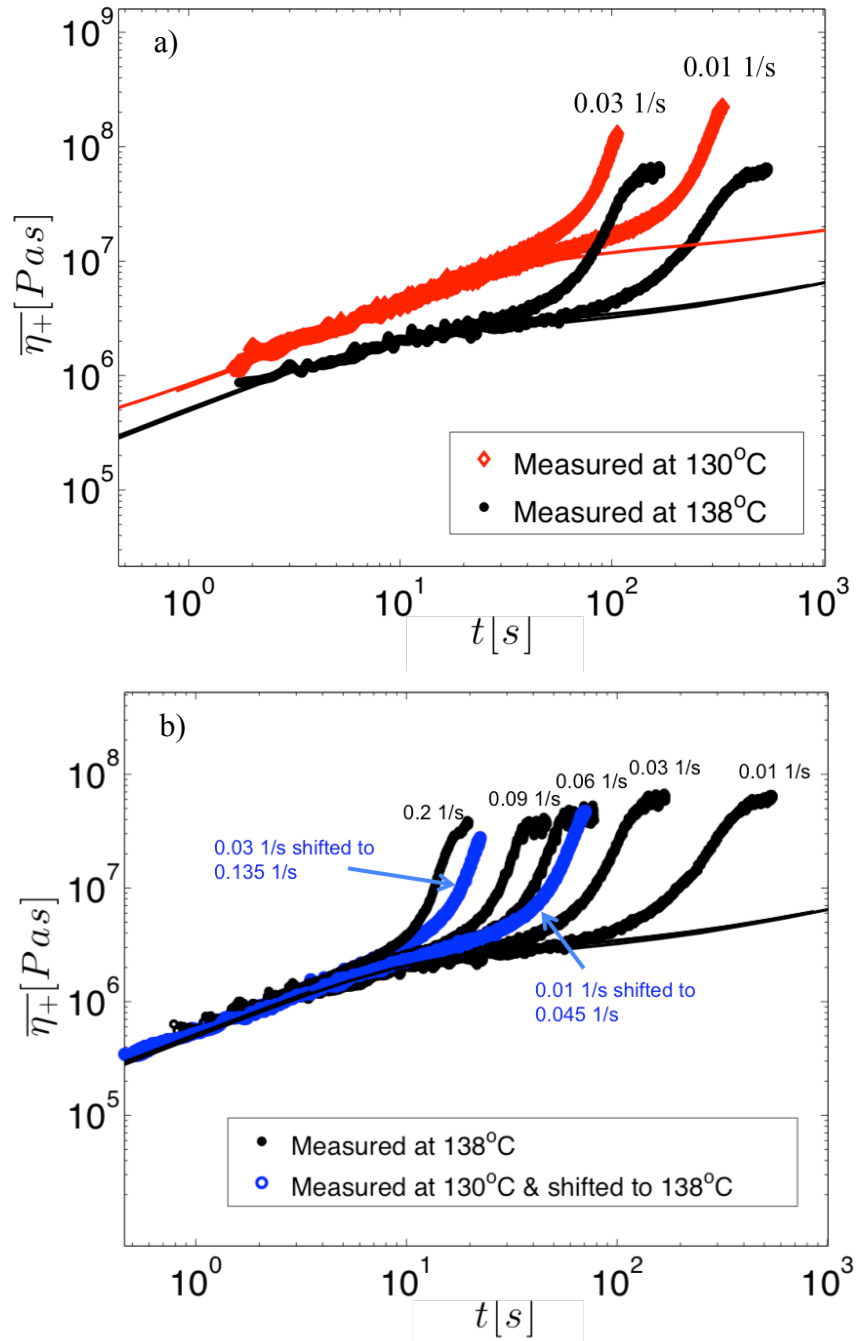


Fig. A3. a) Blend B1 measured at different temperatures. b) Data shifted according to TTS shift factor.

An alternative way of measuring at iso- T_g condition is to measure the blends at same temperature and then shift using the TTS shift factors as mostly done in literature (also shown in Fig A3 b). But to avoid any shifting (which might induce certain degree of freedom), in this work all measurements are done at same iso- T_g condition.

(ii) Influence of sample pre-stretching:

For blend B4, there is a slight deviation from the LVE envelope for high strain rates at low times. Owing to its high strain-hardening nature the blend, B4 had to be pre-stretched more to avoid detachment of sample from plates (due to high force build-up). This pre-stretch could often result in residual stress, which takes long time to relax. However this phenomenon only influences the data at short times. The steady value at long times are unaffected as the stress involved is few order of magnitude higher.

(iii) Steady value at high W_{iR} :

All blends in Fig. 6.3 (main text) seem to reach the same steady value for all applied W_{iR} apart from the one at highest W_{iR} , of 73. Indeed, for this particular W_{iR} , blends B1, B2 and B3 reach the same steady value while B4 doesn't. This is due to the fact that, as shown in Fig. A4, blend B4 suffers brittle fracture at high Hencky strain, before the steady state can be achieved. Measurements were repeated three times at this specific strain rate and brittle fracture was observed at a similar Hencky strain in all measurements. However, the experimental data shows an onset of the steady state right before the fracture suggesting the steady state would soon be reached.

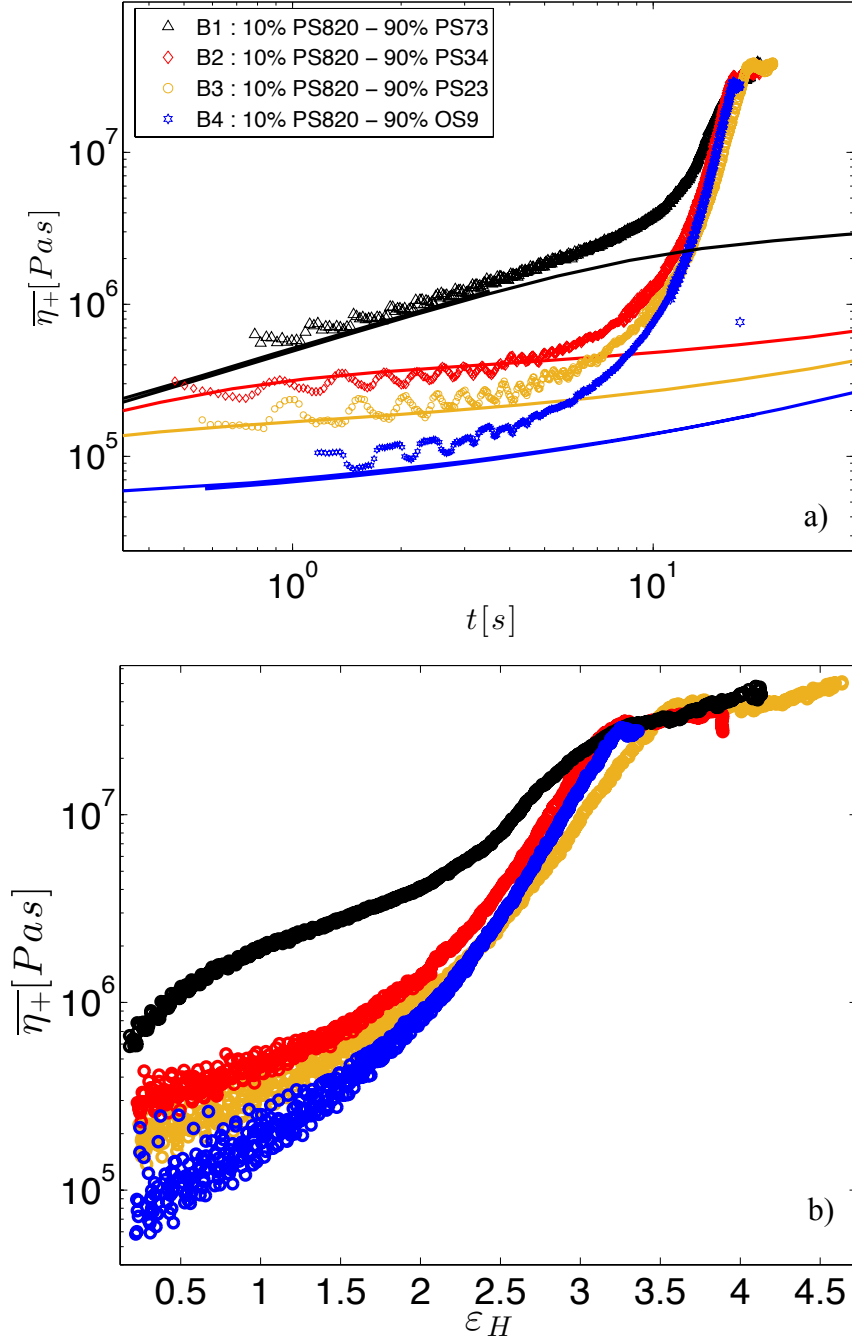


Fig. A4. Transient elongational viscosity at $W_{IR} = 73$ as a function of
a) time & b) Hencky strain.

(iv) Averaging of the data at low strain rates:

Data measured at low strain rates (0.003 s^{-1} for all blends and 0.01 s^{-1} for blend B4) were averaged to get rid of the noise. Indeed, at these low rates, the viscoelastic response of the blends was close to the sensitivity of the force transducer, thus leading to important noise as shown in Fig. A5. In order to get rid of this noise the data were averaged. As observed this averaging has little effect at long times and has almost no effect on the steady value.

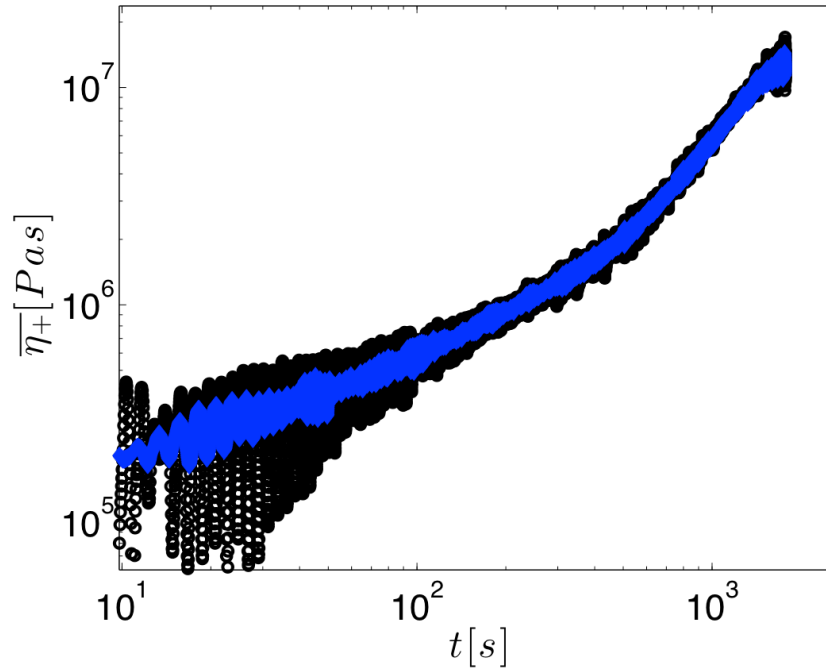


Fig. A5. Comparison between measured (black circles) and averaged data (blue diamonds) for blend B4 at 0.003 s^{-1} .

Measurements were done at very low strain rates (0.001 s^{-1}) in an attempt to recreate the linear viscoelastic envelopes. Unfortunately, the responses from the materials turned out to be too noisy (for $\varepsilon_H > 2$) and the steady state couldn't be attained. Please note that Blend B4 couldn't be measured for this particular rate, as the sample base viscosity was simply too low.

3. Modelling of the linear viscoelastic data:

In order to model the linear viscoelastic properties of the long linear chains in different oligomers/short chains matrices, we used the tube-based model (TMA) developed at UCL, and follow the approach described in refs. [34] and [40] in case of binary blends with well separated relaxation times. We summarize the main concepts here.

After the relaxation of the short chains, the long chains start to explore their dilated (fat) tube, which is only composed of long-long entanglements. These motions, which take place at the rhythm of the motion of the short chains, are well described by a Constraint Release Rouse process, and end as soon as the long-long entanglements segments (i.e. the segments between two entanglements formed by the long chains) are relaxed. The corresponding relaxation time of these latter ones is:

$$\tau_{\text{long-long ent}} = \max(\tau_{\text{obs}}, \tau_e) \left(\frac{v_1}{v_2} \right)^2,$$

where v_1 and v_2 are the weight proportion of the short chains (90 wt%) and of the long chains (10 wt%), τ_e is the Rouse time of a segment between two (short or long) initial entanglements and τ_{obs} is the average lifetime of a short-long entanglement. Following ref. [40], this last one can be defined as:

$$\tau_{\text{obs}} = 3 \frac{\tau_1}{Z_1^2},$$

with Z_1 and τ_1 , the initial number of entanglements and the terminal relaxation time of the short chains matrix, respectively.

The influence of the fast motion of the matrix on the contour length fluctuations of the long chains must also be taken into account. Following ref. [40], when the long component is diluted in a matrix with a much lower molar mass, we consider that the fluctuations of the long components take place in a dilated (or fat) tube at the rhythm of the short chains motions. Therefore, the contour length fluctuations

of the molecular segments, x_{fat} , localized along the dilated tube ($x_{fat}=0$ at the chain extremities and $x_{fat}=1$ in the middle of the chain) are activated by the constraint release events coming from the short component, and the corresponding relaxation times are described as:

$$\tau_{CR-CLF}(x_{fat\ tube}) = \tau_{long-long,ent} \frac{9\pi^3}{16} (v_2 Z_{arm,2})^4 x_{fat\ tube}^4,$$

where $Z_{arm,2}$ is the number of initial entanglements along half of the long chains.

In addition to CLF, the long chains can reptate. We consider that the reptation process is also taking place in a dilated tube. On the other hand, the relaxation of the short chain matrix is described by a Rouse process (for the 9k matrix) or, in case it is entangled, by considering its relaxation by contour length fluctuations, reptation and constraint release, as it is usually done⁴⁰.

The material parameters of the models are the plateau modulus, the average molar mass between two entanglements and the Rouse time of an entanglement segment. They have been fixed according to ref. [34], i.e. equal to 230kPa, 15 kg/mol and 0.12s (at a ref. temperature of $T_g + 31.4$ °C), respectively. The relaxation times of the short matrices have been fixed to 15s, 1s, 0.3s and 0.014s for the matrix in blends B1, B2, B3 and B4, respectively.

4. Onset of long chain stretching:

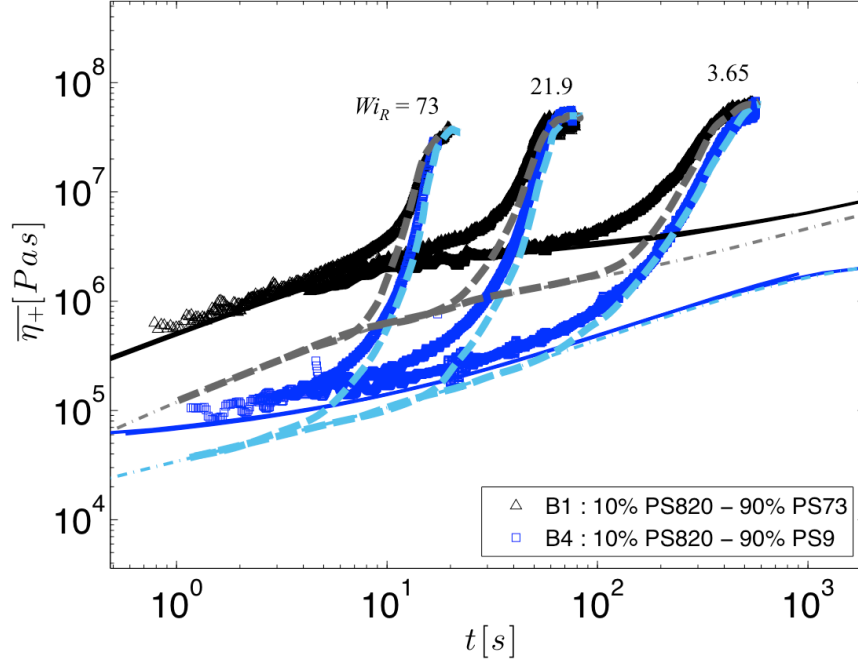


Fig. A6. Transient strain hardening of blend B1 & B4 (symbols) with respect to the full LVE envelopes (solid lines) and the long chain LVE (dash-dot lines; from model). Dash lines are drawn to illustrate the onset of long chain stretching. (for clarity only blend B1 & B4 are shown)

As discussed in the main text, the stretching of the long chains is masked under the full LVE envelope of the blends. As it can't be observed experimentally, we used our model to extract the LVE contribution of the long chains and detect the onset of the chain stretching (as illustrated in Fig. A6). And indeed the long chain stretching of blend B1 starts well below the level of the full LVE envelope in comparison to blend B4.

References:

1. Doi, M.; Edwards, S. F. *The Theory of Polymer Dynamics*; Clarendon Press: Oxford, (1986).
2. Likhtman, A. E.; McLeish, T. C. B. Quantitative theory for linear dynamics of linear entangled polymers. *Macromolecules*, 35, 6332–6343, (2002).
3. McLeish, T. C. B. Tube theory of entangled polymer dynamics. *Adv. Phys.*, 51, 1379–1527, (2002).
4. Watanabe, H. Viscoelasticity and dynamics of entangled polymers. *Prog. Polym. Sci.*, 24 (9), 1253–1403, (1999).
5. Park, S. J.; Larson, R. G. Tube Dilation and Reptation in Binary Blends of Monodisperse Linear Polymers. *Macromolecules*, 37 (2), 597–604, (2004).
6. van Ruymbeke, E.; Vlassopoulos, D.; Kapnistos, M.; Liu, C. Y.; Bailly, C. Proposal to Solve the Time-Stress Discrepancy of Tube Models. *Macromolecules*, 43, 525–531, (2010).
7. Marrucci, G. Relaxation by reptation and tube enlargement: A model for polydisperse polymers. *J. Polym. Sci., Polym. Phys. Ed.*, 23, 159, (1985).
8. Watanabe, H.; Ishida, S.; Matsumiya, Y.; Inoue, T. Viscoelastic and Dielectric Behavior of Entangled Blends of Linear Polyisoprenes Having Widely Separated Molecular Weights: Test of Tube Dilation Picture. *Macromolecules*, 37 (5), 1937–1951, (2004).
9. van Ruymbeke, E.; Shchetnikava, V.; Matsumiya, Y.; Watanabe, H.; Dynamic dilution effect in binary blends of linear polymers with well-separated molecular weights, *Macromolecules* 47 (21), 7653–7665, (2014).
10. Ferry, J. D. *Viscoelastic Properties of Polymers*, 3rd ed.; John Wiley & Sons: New York, (1980).

11. Yaoita, T.; Isaki, T.; Masubuchi, Y.; Watanabe, H.; Ianniruberto, G.; Marrucci, G.; Primitive Chain Network Simulation of Elongational Flows of Entangled Linear Chains: Role of Finite Chain Extensibility, *Macromolecules*, 44, 9675-9682, (2011).
12. Huang, Q.; Hengeller, L.; Alvarez, N. J.; Hassager, O. Bridging the Gap between Polymer Melts and Solutions in Extensional Rheology. *Macromolecules*, 48, 4158–4163, (2015).
13. Bhattacharjee, P. K.; Nguyen, D. A.; McKinley, G. H.; Sridhar, T.; Extensional stress growth and stress relaxation in entangled polymer solutions, *J. Rheol.*, 47, 269, (2003).
14. Bach, A.; Almdal, K.; Rasmussen, H. K.; Hassager, O.; Elongational viscosity of narrow molar mass distribution polystyrene. *Macromolecules*, 36, 5174–5179, (2003).
15. Auhl, D.; Chambon, P.; McLeish, T. C. B.; Read, D. J. Elongational Flow of Blends of Long and Short Polymers: Effective Stretch Relaxation Time. *Phys. Rev. Lett.*, 103, 136001 (2009).
16. Marrucci, G.; Ianniruberto, G.; Interchain pressure effect in extensional flows of entangled polymer melts. *Macromolecules*, 37, 3934– 3942, (2004).
17. Wagner, M. H.; Rolon-Garrido, V. H.; Nonlinear rheology of linear polymer melts: modeling chain stretch by interchain tube pressure and Rouse time. *Korea-Australia Rheol. J.*, 21, 203–211, (2009).
18. Wagner, M. H. An extended interchain tube pressure model for elongational flow of polystyrene melts and concentrated solutions. *J. Non-Newtonian Fluid Mech.*, 222, 121–131, (2015).
19. Wagner, M.H.; Narimissa, E.; Rolon-Garrido, V. H. From melt to solution: Scaling relations for concentrated polystyrene solutions. *Journal of Rheology*, 59, 1113-1130, (2015).

20. Wagner, M. H.; Scaling relations for elongational flow of polystyrene melts and concentrated solutions of polystyrene in oligomeric styrene. *Rheol. Acta* 53, 765–777, (2014).
21. van Ruymbeke, E.; Nielsen, J.; Hassager, O.; Linear and nonlinear viscoelastic properties of bidisperse linear polymers: Mixing law and tube pressure effect, *Journal of Rheology* 54, 1155, (2010).
22. Ianniruberto, G.; Brasiello, A.; Marrucci, G.; Friction coefficient does not stay constant in nonlinear viscoelasticity. *Proc. 7th Annu. Eur. Rheol. Conf.*, 1, 61, (2011).
23. Ianniruberto, G.; Brasiello, A.; Marrucci, G.; Simulations of Fast Shear Flows of PS Oligomers Confirm Monomeric Friction Reduction in Fast Elongational Flows of Monodisperse PS Melts As Indicated by Rheooptical Data. *Macromolecules*, 45, 8058, (2012).
24. Yaoita, T.; Isaki, T.; Masubuchi, Y.; Watanabe, H.; Ianniruberto, G.; Marrucci, G.; Primitive chain network simulation of elongational flows of entangled linear chains: stretch/orientation-induced reduction of monomeric friction. *Macromolecules*, 45, 2773, (2012).
25. Huang, Q.; Alvarez, N. J.; Matsumiya, Y.; Rasmussen, H. K.; Watanabe, H.; Hassager, O. Extensional Rheology of Entangled Polystyrene Solutions Suggests Importance of Nematic Interactions. *ACS Macro Lett.*, 2, 741–744, (2013).
26. Ianniruberto, G.; Extensional Flows of Solutions of Entangled Polymers Confirm Reduction of Friction Coefficient. *Macromolecules*, 48, 6306–6312 (2015).
27. Costanzo, S.; Huang, Q.; Ianniruberto, G.; Marrucci, G.; Hassager, O.; Vlassopoulos, D.; Shear and Extensional Rheology of Polystyrene Melts and Solutions with the Same Number of Entanglements. *Macromolecules*, 49, 3925–3935, (2016).
28. Park, G. W.; Ianniruberto, G. Flow-induced nematic interaction and friction reduction successfully describe PS melt and solution data in extension startup and relaxation. *Macromolecules*, 50, 4787–4796, (2017).

29. Ylitalo, C. M.; Zawada, J. A.; Fuller, G. G.; Abetz, V.; Stadler, R.; Oligomers As Molecular Probes of Orientational Coupling Interactions in Polymer Melts and Networks. *Polymer*, 33, 2949–2960, (1992).
30. Tassin, J. F.; Baschwitz, A.; Moise, J. Y.; Monnerie, L.; Relaxation of Binary Blends of Long and Short Chains - Evidence for Orientational Coupling. *Macromolecules*, 23, 1879–1881, (1990).
31. Wang, Y.; Boukany, P.; Wang, S. Q.; Wang, X.; Elastic breakup in uniaxial extension of entangled polymer melts, *Phys. Rev. Lett.* 99, 237801 (2007).
32. Lyhne, A.; Rasmussen, H. K.; Hassager, O.; Simulation of Elastic Rupture in Extension of Entangled Monodisperse Polymer Melts, *Phys. Rev. Lett.* 102, 138301, (2009).
33. Wang, S. Q.; *Nonlinear Polymer Rheology: Macroscopic phenomenology and Molecular foundation*, Wiley: Hoboken, NJ, (2017).
34. Shahid, T.; Huang, Q.; Oosterlinck, F.; Clasen, C.; van Ruymbeke, E.; Dynamic dilution exponent in monodisperse entangled polymer solutions. *Soft Matter*, 13 (1) 269, (2017).
35. Williams, M. L.; Landel, R. F. and Ferry, J. D.; The temperature dependence of relaxation mechanisms in amorphous polymers and other glass-forming liquids. *J. Am. Chem. Soc.*, 77, 3701, (1955).
36. Liu, C. Y.; He, J.; Keunings, R.; and Bailly, C.; New linearized relation for the universal viscosity– temperature behavior of polymer melts. *Macromolecules*, 39, 8867, (2006).
37. Please see the appendix.
38. Huang, Q.; Mednova, O.; Rasmussen, H. K.; Alvarez, N. J.; Skov, A. L. and Hassager, O.; Concentrated polymer solutions are different from melts: Role of entanglement molecular weight. *Macromolecules* 46, 5026 (2013).

39. Wingstrand, S.L.; Alvarez, N.J.; Huang, Q.; Hassager, O.; Linear and Nonlinear Universality in the Rheology of Polymer Melts and Solutions. *Phys. Rev. Lett.* 115, 078302, (2015).
40. Ebrahimi, T.; Taghipour, H.; Griebel, D.; Mehrkhodavandi, P.; Hatzikiriakos, S. G.; van Ruymbeke, E.; Binary blends of entangled star and linear poly (hydroxybutyrate): Effect of constraint release and dynamic tube dilation, *Macromolecules* 50 (6), 2535-2546, (2017).
41. Deloche, B.; Samulski E.T.; Short-range nematic-like orientational order in strained elastomers: a deuterium magnetic resonance study, *Macromolecules*, 14 (3), 575–581, (1981).
42. Thulstrup, E. W.; Michl, J.; Orientation and linear dichroism of symmetrical aromatic molecules imbedded in stretched polyethylene, *J. Am. Chem. Soc.*, 104 (21), 5594–5604, (1982).
43. Doi, M.; Watanabe, H.; Effect of nematic interaction on the Rouse dynamics, *Macromolecules*, 24 (3), 740–744, (1991).

Chapter 7

Non-linear universal scaling law between polymer melts and solutions

Methodical experimental results have established that polymers of various chemical structures and concentrations exhibit universal linear viscoelastic properties as long as they have the same number of entanglements, Z per chain¹⁻⁴. This universality is the fundamental basis of the most successful theoretical model in polymer rheology known as the ‘tube model’^{2,5}. Thus this model can be used to predict the linear properties of polymers. Unfortunately, a similar universal behavior is yet to be observed in the non-linear fast flows. To the contrary, experimental results have shown that polymers with similar characteristics (same Z) perform differently even at a qualitative level^{3,6}. Consequently, the tube model for linear flows could not be extended to non-linear flows without further considerations.

In a very recent work⁷, Wingstrand et al. were able to manipulate a polymer melt into showing the exact same properties as a solution. This very first universal behavior in non-linear elongational flow was based on the alignment-induced monomeric friction reduction concept, SORF^{8,9}. To match the same potential for friction reduction two different polymers were used (PS as melt and PMMA for solution). However, the friction reduction concept is still controversial as discussed in chapter 5 and thus requires further validation.

In this chapter, we aim to find a universal scaling between polymer melts and solutions within the framework of the refined tube model, i.e., without considering any extra relaxation mechanism (like SORF). For this purpose, a new system is designed and analyzed systematically to find the right scaling between melt and solution. As we believe, the disagreement between the two systems might be due to the inadequate scaling used so far in literature.

7.1 Introduction

While the linear viscoelastic properties of linear polymers are quite well understood and can be predicted at the quantitative level^{2, 10-20}, many questions still need to be answered in order to understand and model their non-linear extensional rheology. Initially, this task was not possible due to lack of accurate experimental data, as it was proven to be very difficult to apply a uniform elongational flow field and obtain a steady elongational flow. However, in the last years many studies have been performed on this topic, triggered by the large progress in measuring the transient elongational viscosity of entangled polymers. In particular, using a home-made filament stretching rheometer, the group of Hassager has obtained a large set of extension data of model linear polymers, in the melt state or in solution, which are now used as reference data for further developing models to describe the dynamics of entangled polymers under elongation^{3, 6, 21, 22}. On the other hand, Sridhar and coworkers also obtained a series of reference data with solutions of very long entangled linear polymers^{23, 24}. From the confrontation of these results, qualitative difference was pointed out between the steady-state extensional viscosity, $\bar{\eta}_{el}$ of entangled polymers in the melt state or in solution. For the entangled solutions, a very brief thinning regime is usually observed in the curve of the steady viscosity ($\bar{\eta}_{el}$ versus elongation rate $\dot{\epsilon}$) which is then followed by an upturn occurring at rates larger than the inverse Rouse time of the chain, i.e. $\dot{\epsilon} > 1/\tau_{Rouse}$. On the other hand, polymer melts exhibit a monotonic elongational thinning behaviour with no sign of upturn even at strain rates larger than the inverse Rouse time of the chain.

In a recent work³, a series of polystyrene solutions and a melt were studied, where the concentrations and molar mass of the systems were selected in order to have the same no. of entanglements. Those systems exhibited exact identical linear behavior, provided that the frequencies and moduli were suitably shifted in log scales horizontally and vertically, respectively; thus regulating the concentration-dependent parameters such as the monomer characteristic relaxation time, τ_e and the plateau modulus, G_N^0 . Unlike the linear behavior, the non-linear behavior (normalized) was found to be strikingly different from each other, changing qualitatively with the level of dilution. While this work could successfully bridge between the behavior of

previously observed melt and solution by the level of dilution, it was also clear that the universal behavior in non-linear flow could not be attained by only keeping the same Z value. This triggered researchers to look for additional relaxation mechanisms predominantly important for elongational flow. Among the proposed mechanisms, the alignment-induced monomeric friction reduction concept^{8, 9} (introduced and discussed in detail in chapter 6) has been well received and was very recently applied to establish the first non-linear universal behavior. In addition to the same Z , the authors designed two polymeric systems (one melt and one solution) with the same potential for monomeric friction reduction⁷. Consequently, universal behavior was observed for a wide range of applied strain rate (both at $\dot{\epsilon} < 1/\tau_{reptation}$ and $\dot{\epsilon} > 1/\tau_{Rouse}$).

The objective of this present work is to attain similar universal scaling between polymer melt and solution but without considering the alignment-induced reduction in friction concept; assuming that the non-universality observed in earlier works^{3, 21, 23} could be due to a combination of lack of systematic experimental data and inadequate scaling used in literature. Indeed, the experimental results are usually compared under non-dimensional parameters (scaled with η_0 vertically and τ_e horizontally) as the glass transition temperature and concentration of a PS melt and solution will be different. Consequently, if the scaling in fast flows is different from the one in the linear regime, it could incorrectly lead to a non-universal behavior.

In order to address this question, we have designed and investigated a new set of data, where a relatively high molecular weight PS is dissolved in an oligomeric styrene at different weight fractions ranging from very concentrated to semi-dilute solutions. We then study the non-linear properties of the system and show that indeed different scaling is observed in the linear and non-linear regime. As a result, they can't be scaled in both regimes using the same normalization factor. A universal scaling can only be achieved by explicitly normalizing the experimental data in non-linear regime. This outcome is very important especially in terms of modeling as it allows us to extend our understanding of linear flow directly to non-linear range without considering any additional mechanisms i.e. extra parameter or criteria.

7.2 Materials & sample preparation

In this section, we discuss all materials and the sample preparation technique that have been used in this work.

7.2.1 Materials

To have a clear perspective on how the non-linear characteristics of polymer solution change with its dilution level, we designed and characterized our own system that consists of a high molar mass PS diluted in its oligomers. The PS is well entangled in its melt state, thus gives us an opportunity to dilute it to different concentrations and obtain different classes of solutions, which are still entangled. Both the PS and OS were purchased from Polymer Source (Montreal, Canada) and a total of eight different concentrations were prepared that varies from very concentrated to barely entangled solutions, as shown in table 1. The detail study of the linear viscoelastic data of the system has already been presented in chapter 5.

To check if our observation agrees with the literature results, we also investigated the non-linear properties of a series of monodisperse linear Polystyrene chains in both melt and solution state already presented in the literature. In order to be consistent only the samples diluted in styrene oligomers have been included in this work. As discussed in chapter 5, the choice of solvent plays an important part in tailoring the properties of the solutions. All investigated samples are listed in Table 2 together with the corresponding references.

Table 1: T_g and no. of entanglements of different solutions.

Ingredients	Number of entanglements [*]	Glass transition temperature [§] ($^{\circ}\text{C}$)	Degradation temperature [#] ($^{\circ}\text{C}$)
OS9k melt state	<1	94.6	380
PS820k melt state	55	106.6	390
Solutions			
PS – 1 : OS9k + PS820k (1wt%)	<1	97.6	385
PS – 2 : OS9k + PS820k (3wt%)	1	98.1	385
PS – 3 : OS9k + PS820k (5wt%)	3	98.4	385
PS – 4 : OS9k + PS820k (10wt%)	5	98.6	390
PS – 5 : OS9k + PS820k (20wt%)	11	99.8	390
PS – 6 : OS9k + PS820k (30wt%)	17	100.7	390
PS – 7 : OS9k + PS820k (40wt%)	22	101.3	390
PS – 8 : OS9k + PS820k (50wt%)	27	102.3	390

^{*}: The number of entanglements are determined based on $M_e = 15$ kg/mol.

[§]: T_g was measured with Differential Scanning Calorimetry.

Materials & sample preparation

*: Degradation temperature was measured with Thermogravimetric analysis.

Table 2. Main characteristics of the PS samples used in this work

Sample	M _w	M _n	PDI	Concentration	Ref.
PS2	1,920	1,770	1.08	-	25
PS4	3,630	3,424	1.06	-	3
PS8.8	8,800	8,000	1.1	-	-
PS50	51,700	50,380	1.02	100%	21, 22
PS100	102,800	100,600	1.02	100%	21, 22
PS133	133,000	131,600	1.01	100%	26
PS185	185,000	179,600	1.03	100%	26
PS200	200,000	192,000	1.04	100%	21, 22
PS285	285,000	261,500	1.09	100%	25
PS390	390,000	367,000	1.06	100%	21, 22
PS545	545,000	486,600	1.12	100%	3
PS545	545,000	486,600	1.12	58% in PS2 & 52% in PS4	3
PS900	910,000	784,500	1.16	33% in PS4	3
PS1760	1,880,000	1,663,700	1.13	18% in PS4	3
PS285	285,000	261,500	1.09	72%, 65%, 47%, 44% in PS2	25, 26
PS820	820,000	805,000	1.02	100%, 50%, 40%, 30%, 20%, 10%, 5%, 3% & 1% in OS8.8	-

PS solutions were prepared following a four-step procedure inspired by an earlier work³. In this method, first the polystyrene and the oligomer are weighted according to the desired weight fractions and dissolved together in THF. The mixture is then stirred at the room temperature overnight to ensure that the two components are well dissolved and mixed. In a next step, the whole mixture is added to the non-solvent methanol drop by drop, using a burette. The precipitated polymer/oligomer blend was then separated and collected using paper filtration. Finally, the blends were dried at 70 °C under vacuum for 4 days to remove any remaining traces of the solvents. The drying temperature of the solution was set higher than the boiling temperature of the used solvents (~65°C).

7.3 Experimental details

Mechanical characterizations of the PS solutions were performed using two different rheometers. The linear and non-linear characterization was done with AR2000 (TA instrument, USA) and VADER-1000 rheometers (Rheofilament, USA) respectively.

7.3.1 Linear viscoelastic properties

Small amplitude oscillatory shear (SAOS) tests were performed to measure the linear viscoelastic properties of our system. These tests were performed in an AR2000 rheometer using a stainless steel parallel plate geometry with a diameter of 8 mm and under constant nitrogen gas supply. Prior to the measurements, samples were molded into discotic test specimens using a custom mold with a fixed diameter of 8 mm. The custom mold was placed in a vacuum oven during the whole molding procedure to prevent any sort of degradation of the sample. The initial thickness of the sample was controlled (~1.2 mm) by putting proper amount of the powder sample into the mold.

To ensure the best result and reproducibility, each SAOS test contained three different sub-tests: first, an amplitude sweep test to make sure that the experiments were performed in linear regime of each sample, followed by a time sweep test to ensure all the residual stresses of the sample are relaxed and finally the frequency sweep test

to determine the LVE properties of each sample. For each solution, the frequency sweep test was done at three different temperatures ranging from 130⁰C to 170⁰C. Subsequently, these data were shifted onto a single master curve at a reference temperature (130⁰C) using the time-temperature superposition²⁹ (TTS) procedure.

The concentrations of all solutions were confirmed from the level of plateau modulus of the linear viscoelastic data.

7.3.2 Non-linear viscoelastic properties

The transient elongational stress measurements were performed in the VADER-1000 using stainless steel parallel plate geometry (with diameter of 6mm), with a convection oven for temperature control ($\sim 0.1^{\circ}\text{C}$) and under constant nitrogen gas supply. Prior to the measurements, all samples were dried in a vacuum oven at 65⁰C overnight. Then these samples were molded into discotic test specimens with a fixed radius of 2.75 mm using a custom mould under vacuum. The initial thickness, L_0 of the sample was maintained by controlling the amount of sample into the mould. The aspect ratio $\Lambda_0 = L_0 / R_0$ ranged between 0.38 and 0.55. Depending on the level of dilution, the samples were pressed at 140-150⁰C and annealed at the same temperature (at least 20 minutes) under vacuum to let the polymer chains relax completely.

All filament stretching measurements were done using a three-step protocol. First, the sample was squeezed at an elevated temperature 140-160⁰C, just enough to ensure adequate contact between the sample and the geometries. Inadequate contact could result in slip/detachment of the sample from the geometry before a steady value is reached. Next, the samples were pre-stretched to a smaller radius R_0 ranging from 1.5 mm to 3.3 mm, again at an elevated temperature of 140-160⁰C. This pre-stretch is normally done to reduce the force build up during stretching, which can also cause slip/detachment of the sample from the geometry. Lastly, the temperature was decreased to the experimental temperature 130⁰C and the elongational stress measurements were performed. During these measurements, the force $F(t)$ was measured by a load cell and the diameter $2R(t)$ at the mid filament plane was monitored by a laser micrometer. During the startup of elongational flow, part of the force

comes from the radial variation due to the shear component of the deformation field, which can be compensated by a correction factor as mentioned in ref. 27. Subsequently for larger strains, the correction vanishes, and the radial variation of the stress in the symmetry plane becomes negligible²⁸.

7.4 Working under the iso- T_g condition

The glass transition temperatures of polymer solutions vary with its dilution level and the T_g of the corresponding oligomer as shown in table 1. This difference must be taken into account to allow a comparison of both linear and non-linear viscoelastic responses of different solutions. To this end, as proposed in ref. 30, master-curves have been shifted to a different reference temperatures $T_{ref.}$, such that these temperatures correspond to the iso- T_g condition, i.e. these temperatures are at a constant distance from the corresponding T_g (i.e. $T_{ref.} - T_g = \text{constant}$).

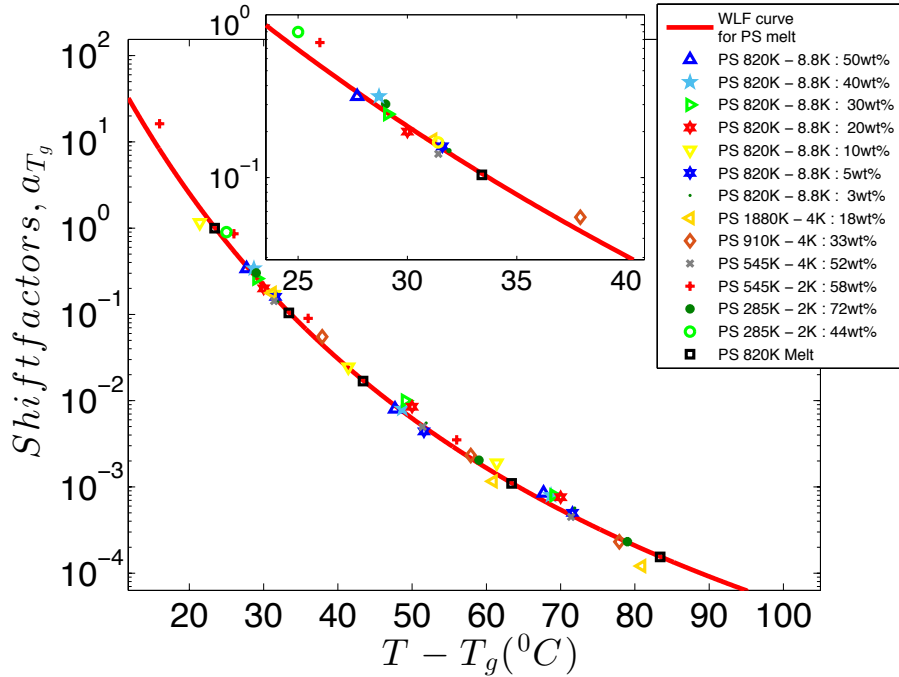


Fig 7.1. Time temperature superposition shift factors as a function of $T - T_g$, determined for the different polymer solutions. The continuous curve represents the WLF equation used in ref. [3]. The inset figure

represents the shift factors due to the change in glass transition temperature, T_g of the solutions.

In keeping with chapter 5, the experimental data of PS820 in the melt state at 130 °C were chosen as the reference point, leading to a difference between the reference and glass transition temperature, $T_{ref} - T_g$, of 23.4°C. The storage and loss moduli master curves of the other solutions created at 130°C were then horizontally shifted (see inset if fig. 7.1) in order to ensure a good overlap of the viscoelastic response in the high frequency region, in which the chain relaxation is controlled by local Rouse dynamics and will thus depend only on $(T_{ref} - T_g)$.

The validity of the shift factors to this specific reference temperature can then be confirmed by comparing their value to the shift factors vs. temperature curve used to build the different TTS master-curves for the differently concentrated solutions as shown in fig. 7.1. As it can be seen, when plotted in such a way, the values used for PS solutions and the melt nicely coincide. Also, their T-dependence is very close to the dependence found in ref. 3 for the other PS samples described in Table 1, which is represented in Fig. 7.1 by the Williams–Landel–Ferry (WLF) equation²⁹:

$$\log(a_T) = \frac{-c_1^0(T - T_{ref})}{c_2^0 + (T - T_{ref})} \quad (1)$$

with $c_1^0 = 8.99$, $c_2^0 = 81.53$ K, $T_{ref} = 130^\circ\text{C}$ and T , the temperature expressed in °C.

Data of other solutions taken from literature are also shifted according the same principle and also coincides nicely with the WLF equation as shown in fig. 7.1. Please note that no vertical shift was considered here since the range of temperature is rather limited.

Then, the same shift factor has been used to analyze both linear and non-linear data throughout this work. To ensure that the TTS shift factors can be extended to the non-linear regime, we measured the non-linear characteristics of a sample at different temperatures and rates in such a way that they are equivalent according to the TTS theory. The result is demonstrated in the next section.

7.4.1 TTS shift factors in elongational flow:

In this work, we have compared systems studied in different works at different temperatures. So it is very important that we compare them under iso- T_g condition. Accordingly, the shear and elongational experimental data have been shifted using the TTS shift factors as shown in fig. 7.1 and can be validated by the good overlapping with the WLF curve of PS melts. In this section, we confirm that TTS shift factors are also applicable in the non-linear elongational regime by testing a sample at different temperatures and corresponding rates.

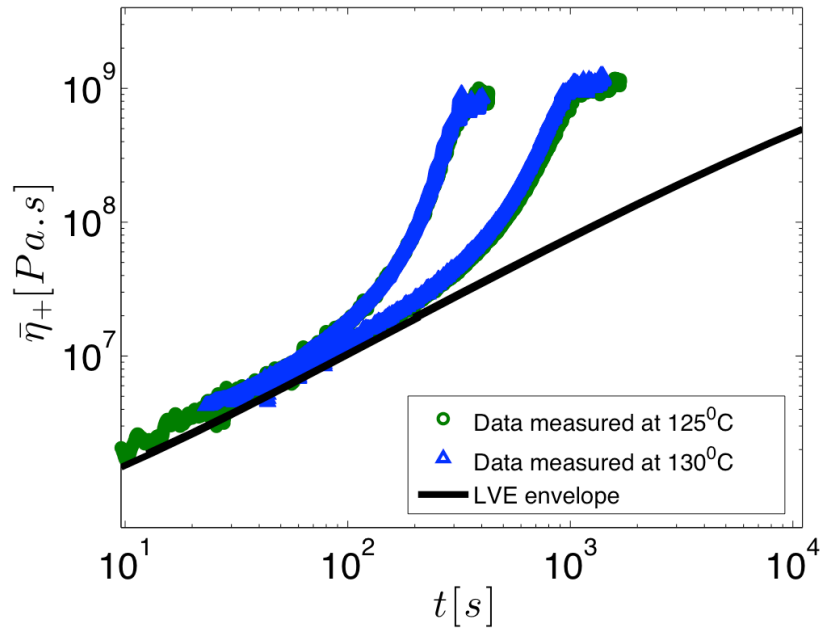


Fig. 7.2. Validating TTS shift factor in non-linear flow. Green symbols represent data measured at 125°C at 0.003 and 0.01 s⁻¹ and blue symbols represent data measured at 130°C at 0.01 and 0.03 s⁻¹

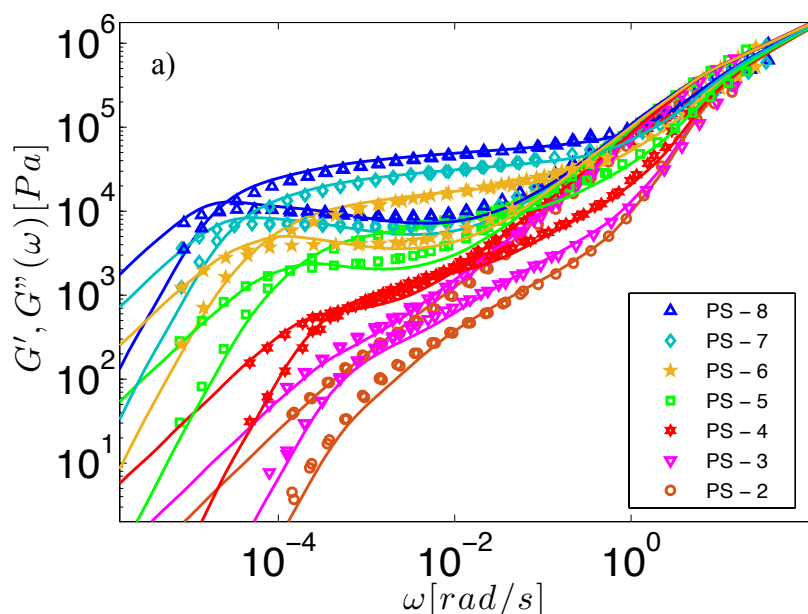
As shown in fig. 7.2, we re-measured our sample PS – 7 at two different strain rates 0.003 and 0.01 s⁻¹ at 125°C i.e. at the same iso- T_g condition used in this work. With TTS shift factor of 0.34 (from 125°C to 130°C), these strain rates correspond to 0.009 and 0.03 s⁻¹ at 130°C. As we can see, these shifted data coincides very nicely with the data measured at 130°C at corresponding rates, thus ensuring that the TTS theory works well in the non-linear regime.

7.5. Experimental results and discussion

The linear and non-linear responses of the PS solutions are presented in section 7.5.1 and 7.5.2 respectively. The tube-based model used to predict the LVE properties of the blends, is discussed in details in chapter 5 and thus is not repeated here.

7.5.1. Linear shear viscoelastic properties

The loss & storage moduli and the LVE envelopes of the solutions are presented in fig 7.3 a) and b) respectively. Please note that the most diluted solution, PS 820k – 9k: 1wt%, couldn't be measured due to thermal degradation. The sample degraded inside the oven of the rheometer (turned yellowish) within an hour even under constant nitrogen gas supply. Since reproducibility couldn't be ensured, this sample isn't considered further in this study.



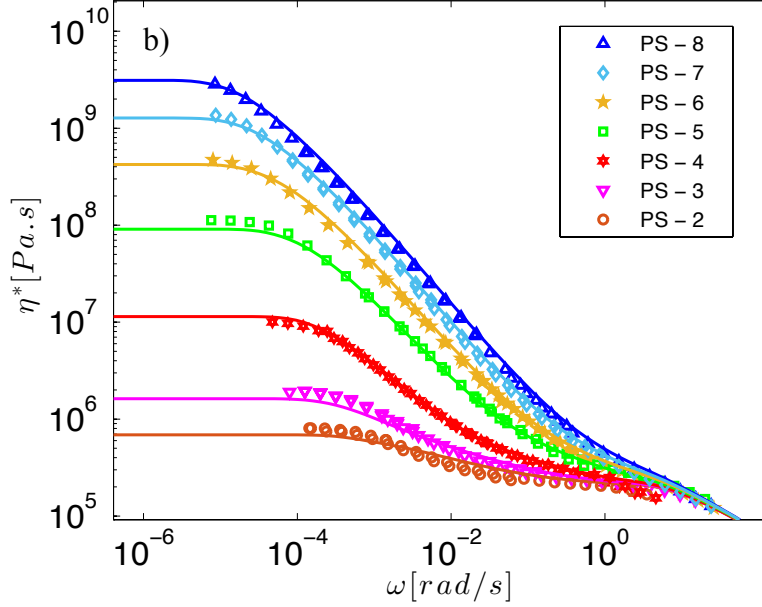


Fig. 7.3 Experimental (symbols) and predicted (lines) a) storage & loss moduli and b) LVE envelopes of PS solutions. The experimental data are shifted to the iso- T_g condition.

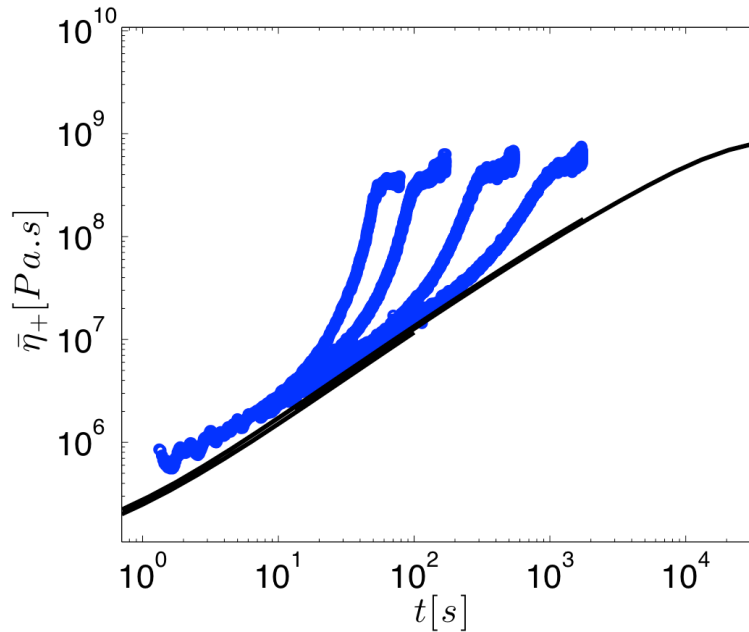
As we can see from fig. 7.3, all PS solutions overlap very nicely at high frequencies thus ensuring the validity of shift due to the iso- T_g condition. At intermediate frequencies, the concentrated solutions show a clear rubbery plateau, which gradually decreases with the level of chain dilution and disappears completely for the diluted solutions. Also, the plateau modulus and the longest relaxation time decreases with decreasing the concentration, as expected. The detailed study on the LVE properties of the solutions is presented in chapter 5. These experimental data are then used to create the LVE envelopes for the elongational data as represented in fig. 7.4 and can be reconstructed when elongational measurements are done at very low strains rates ($\dot{\epsilon} < \tau_d^{-1}$). Any upward deviation from these envelopes is a signature of strain hardening.

7.5.2. Start-up elongational viscoelastic properties

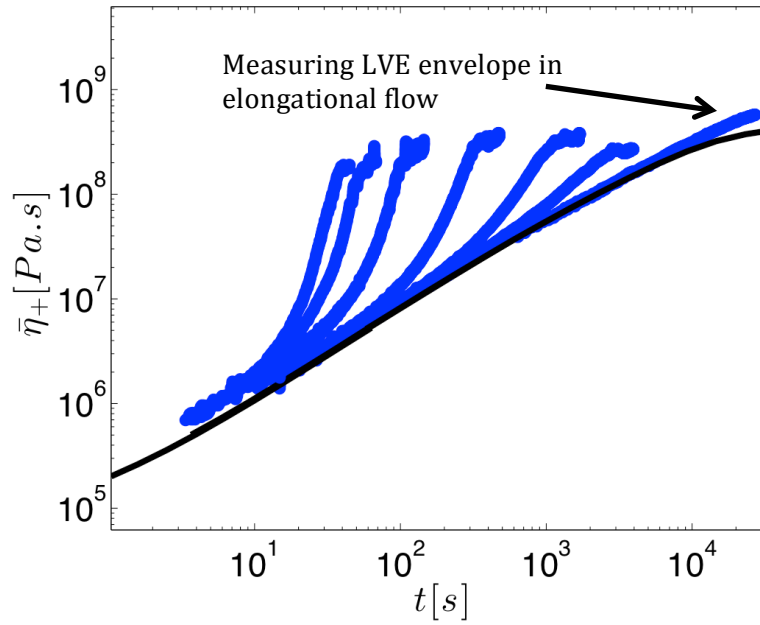
The experimental results of the transient elongational measurements along with their linear viscoelastic envelopes are shown in figures 7.4

a-g and 7.5 a-c. Expectedly, in the linear regime (for rates, $\dot{\epsilon} < \tau_d^{-1}$), the transient elongational viscosity follows the LVE envelope. However, we couldn't measure the LVE envelopes for the diluted solutions as the viscoelastic response of these samples as these very low rates were below the sensitivity of the force transducer, thus leading to important noise.

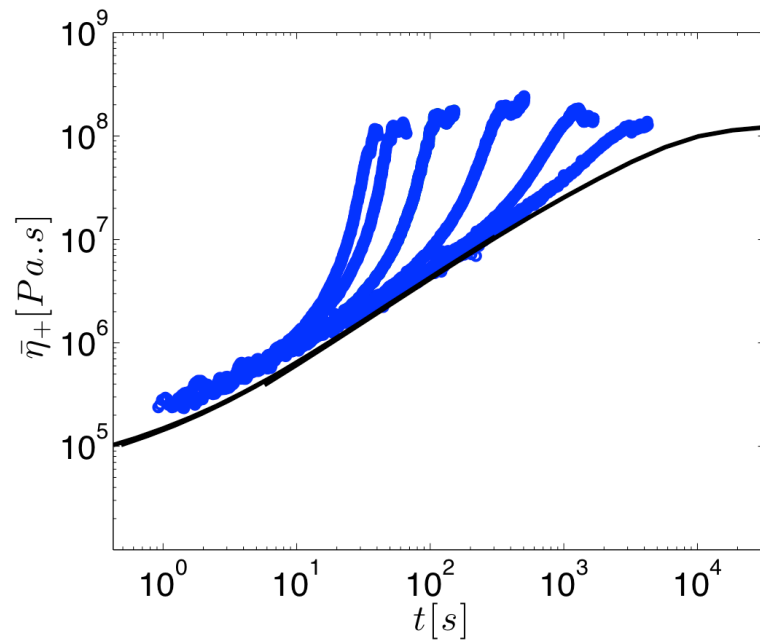
In general, at short times, the non-linear data follow quite well the linear envelope. However, for concentrated solutions, there is a slight deviation from the LVE at high strain rates as observed in fig 7.4. This deviation results from high pre-stretching which is needed to avoid detachment of the sample from the plates due to high force build-up. However this only influences the data at short times, the steady state and data at longer times being unaffected as the stress involved is few orders of magnitude higher. Another interesting point is that the concentrated polymer solutions reach clear steady values while for the largely diluted solutions the steady values are not as prominent as at high concentration and keeps on increasing steadily (see fig. 7.5 a-c). Nevertheless, for most of the strain rates presented here, at least the onset of steady value is reached.



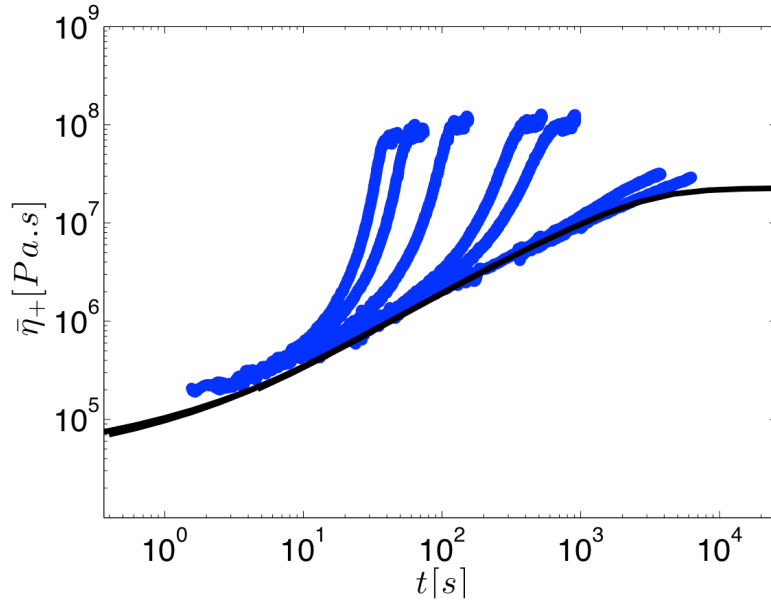
a) Strain rate for PS -8 (PS820k: 50wt% - OS9k: 50wt%): 0.06, 0.03, 0.01, 0.003 s⁻¹.



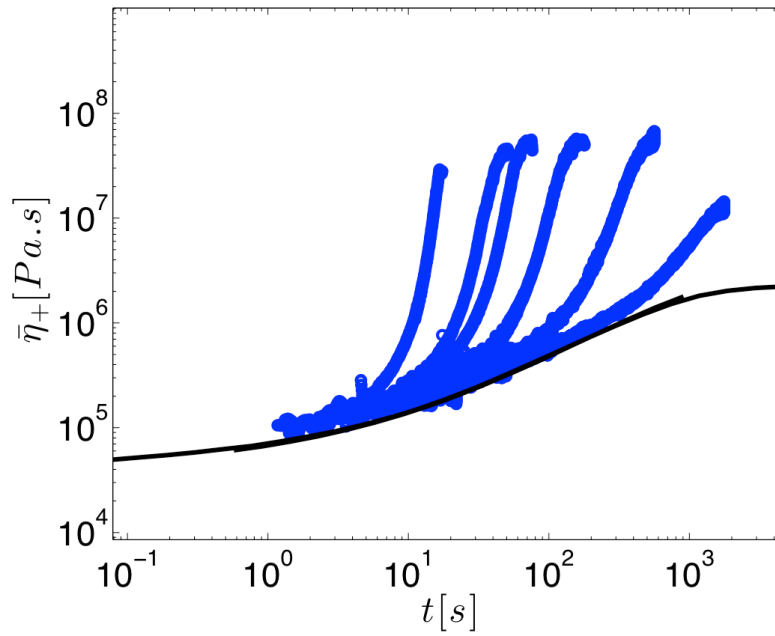
b) Strain rate for PS – 7 (PS820k: 40wt% - OS9k: 60wt%): 0.09, 0.06, 0.03, 0.01, 0.003, 0.001, 0.0001 s⁻¹.



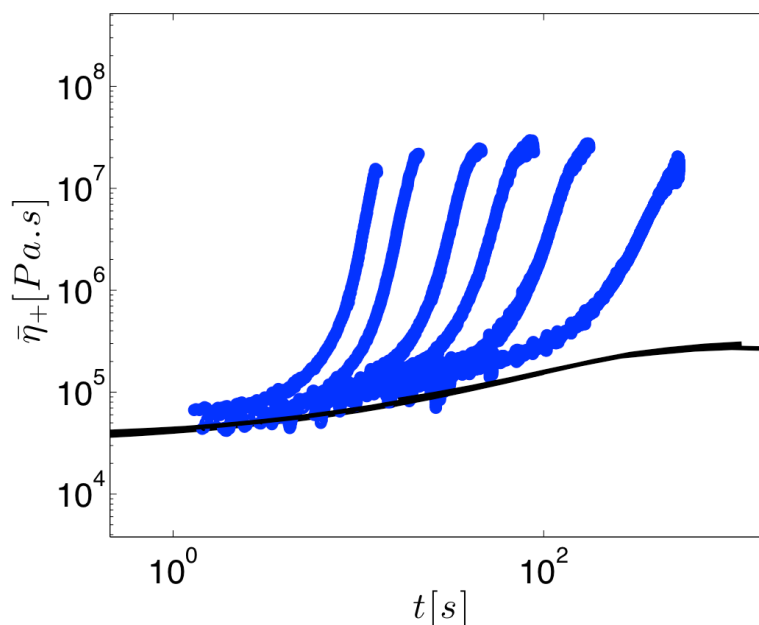
c) Strain rate for PS – 6 (PS820k: 30wt% - OS9k: 70wt%): 0.09, 0.06, 0.03, 0.01, 0.003, 0.001 s⁻¹.



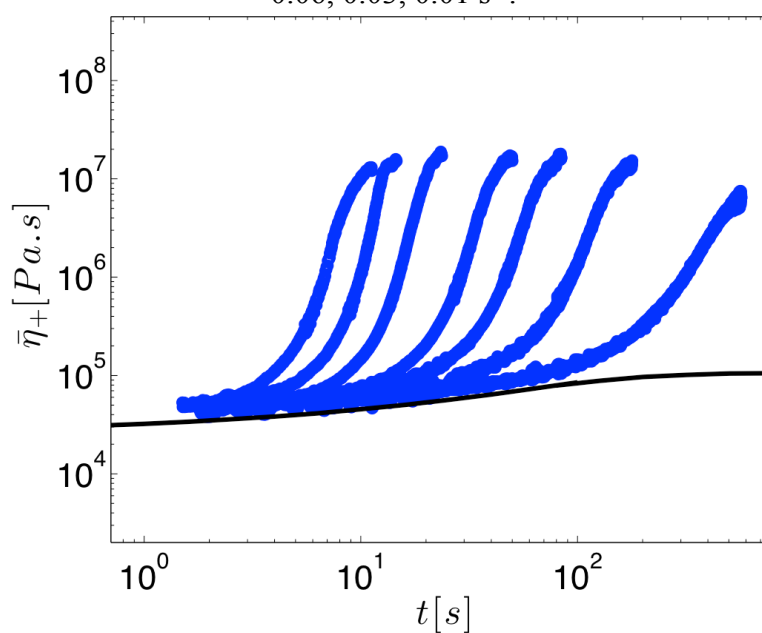
d) Strain rate for PS – 5 (PS820k: 20wt% - OS9k: 80wt%): 0.09, 0.06, 0.03, 0.01, 0.003, 0.0001, 0.00003 s^{-1} .



e) Strain rate for PS – 4 (PS820k: 10wt% - OS9k: 90wt%): 0.2, 0.09, 0.06, 0.03, 0.01, 0.003 s^{-1} .

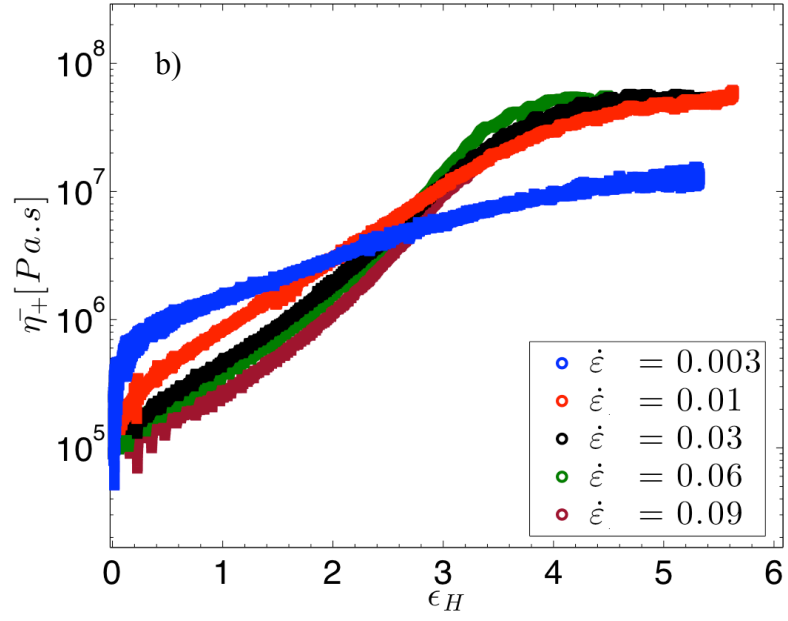
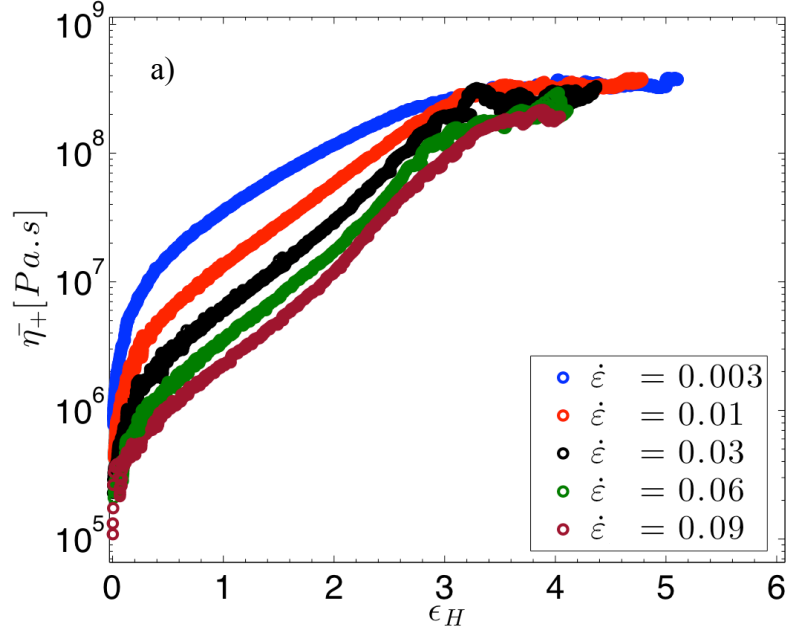


f) Strain rate for PS – 3 (PS820k: 5wt% - OS9k: 95wt%): 0.3, 0.2, 0.1, 0.06, 0.03, 0.01 s⁻¹.



g) Strain rate for PS – 2 (PS820k: 3wt% - OS9k: 97wt%): 0.45, 0.3, 0.2, 0.1, 0.06, 0.03, 0.01 s⁻¹.

Fig. 7.4. Transient response (symbols) of PS solutions measured at 130°C. Solid lines represent the linear viscoelastic envelopes.



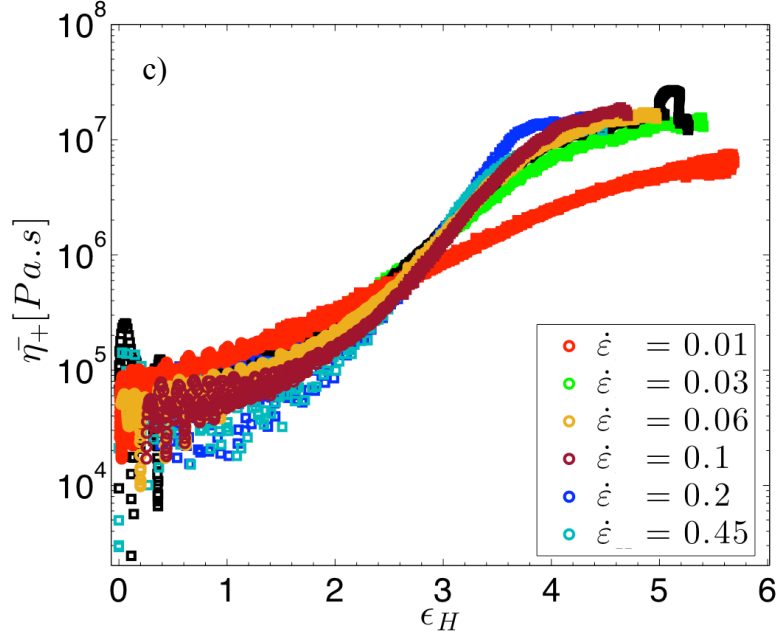


Fig. 7.5. Measured extensional stress as function of Hencky strain shown for a) PS820k: 40wt% - OS9k: 60wt%, b) PS820k: 10wt% - OS9k: 90wt% and c) b) PS820k: 3wt% - OS9k: 97wt%.

In fig. 7.4, it is observed that in the non-linear regime, the solutions show strong strain hardening behavior as the polymer chains start to stretch out thus increasing tension along the chains. More importantly, this hardening behavior depends on the level of dilution and increases significantly with decreasing concentration levels. As we can see from fig. 7.4, sample PS -8 (820k – 9k: 50wt%) shows the least strain hardening behavior and the steady values remain below the zero shear viscosity, η_0 for all measured strain rates, thus showing transient thickening but steady thinning behavior. On the other hand, the most diluted sample PS -2 (820k – 9k: 3wt%) shows the most prominent strain hardening behavior with the steady value being few magnitude higher than its η_0 , thus showing both transient and steady thickening behavior. This steady behavior becomes clear when they are plotted as a function of the applied strain rates as shown in fig. 7.6. This behavior is thus in agreement with the LVE envelopes as presented in section 7.5.1. Therefore, this systematic set of data gives us a good base to discuss the existence of a universal scaling in the non-linear regime of deformation.

It should be noted that in this work, the term ‘steady elongational viscosity’ represents the constant elongational viscosity reached by the transient viscosity curve after a certain time, but does not especially refer to a steady-state³¹⁻³³ (see fig. 7.5).

7.6. Scaling in steady-state elongational flow:

In this section, we investigate the steady elongational viscosity of our PS solutions to search for any potential scaling in between them. To check if this outcome is universal or not we also studied other polymeric systems presented in literature so far.

7.6.1. Scaling in polymer solutions

Figure 7.6 depicts the normalized steady elongational viscosity of the PS solutions as a function of the applied strain rates. To ensure that iso- T_g condition is considered, all experimental results are shifted both horizontally and vertically using the same shift factors as discussed in section 7.2. Additionally these experimental results are shifted horizontally ($\omega = \dot{\epsilon} * 0.25$) by a factor of 0.25, which is explained in detail in appendix I.

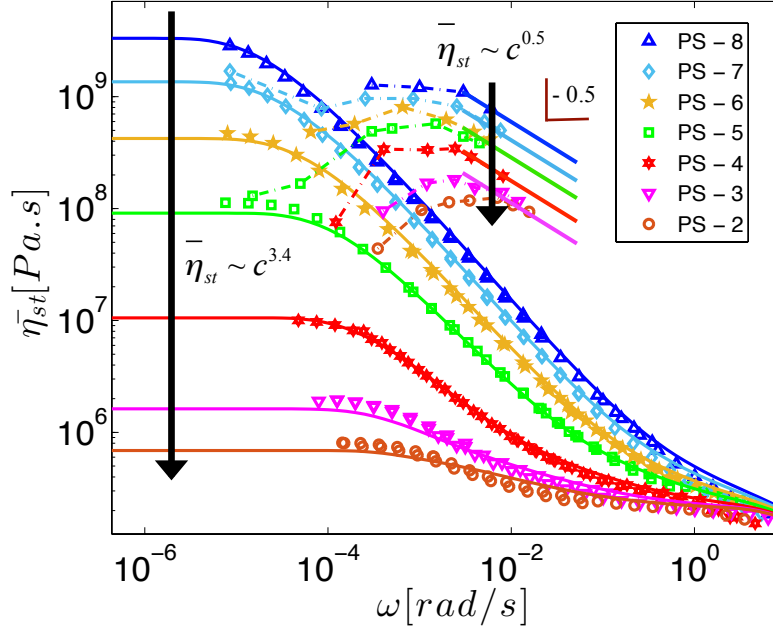


Fig 7.6 Elongational steady viscosities of PS solutions as a function of the strain rates ($\omega = \dot{\epsilon} * 0.25$). Both shear and extensional experimental data are shifted at iso- T_g conditions.

As we can see from fig. 7.6, indeed the concentrated solutions exhibit thinning behavior while the semi-dilute and dilute solutions show strong thickening behavior. Another interesting point is that at high strain rates all these solutions show a similar decrease i.e. with a slope of $-1/2$, which one might find comparable to the one observed in case of polymer melts. Particularly the largely diluted solutions are very much alike (at least qualitatively) the low molecular weight polymer melts where similar behavior i.e. an upturn followed by decrease has been observed in literature²¹. Thus, these observations already give us an impression that the behavior of polymer melts and solutions might not be that different.

In fact, a close inspection of fig. 7.6 reveals three distinct regimes and interestingly the dependence of the dilution level on the steady elongational viscosity is different in each regime. At low strain rates, all PS solutions follow the LVE envelopes thus depicting linear behavior and expectedly the steady viscosity scales with $c^{3.4}$, which is well observed in literature, and well captured by our tube-based

model. At high strain rates, i.e. in the third regime, polymer chains are predominantly stretched and exhibit strong non-linear behavior. Clearly in this non-linear regime, the concentration dependence is much lower than in the linear regime and apparently the steady viscosity scales with $\bar{\eta}_{st} \sim c^{0.5}$. It must be noted that for concentrated solutions a better fit can be obtained for $\bar{\eta}_{st} \sim c$ but in that case a large discrepancy is seen for the diluted solutions. So we have considered $\bar{\eta}_{st} \sim c^{0.5}$ scaling, which gives us an overall better result.

At intermediate frequencies we observe another regime, which acts like a transition regime between the linear and non-linear regime. As the dependence on the concentration is much higher in the linear than its non-linear counterpart, it results in an upturn that is inevitable for the transition between these two regimes. Accordingly, the upturn is missing for concentrated solutions, where the zero-elongation viscosity is high and where the transition takes place by a brief constant regime. An interesting implication of this observation is that for largely diluted solutions strain hardening is not always caused by chain stretching. Indeed, it could result from other mechanisms as well, which is further studied in chapter 8.

7.6.2. Scaling in polymer melts

A similar scaling in polymer melts would allow us to understand the transition from polymer melts to solutions. So in this section, we investigate the elongational steady viscosity of PS melts to check if a relevant scaling is observed. We study the monodispersed PS melts from literature^{21, 22, 25} ranging from very low to moderate molecular weights.

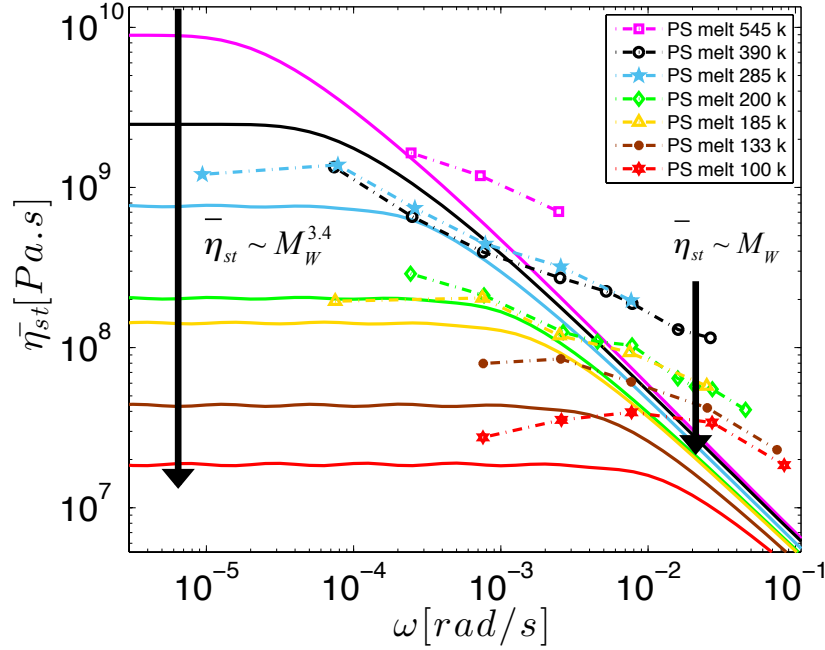


Fig 7.7 Elongational steady viscosities of PS melts as a function of the strain rates ($\omega = \dot{\epsilon} * 0.25$). The experimental data are shifted at iso- T_g conditions.

Interestingly, a similar three-regime picture is present for PS melts as well. As we can see from fig. 7.7, in the linear regime, the well known scaling is observed as the steady viscosity scales with $\bar{\eta}_{st} \sim M_w^{3.4}$. In the non-linear regime, the dependence of steady viscosity with molecular weight is much lower and scales with $\bar{\eta}_{st} \sim M_w$. In between, there is a transition regime, which becomes much prominent with low M_w PS melts. In this regime, an upturn is noticed (similar to as PS solutions) for the lowest M_w samples (< 133 kg/mol), which again occurs to balance the different scaling in the two regimes.

7.6.3. Universal behavior of polymer melt and solution

So far, we have witnessed different scaling in linear and non-linear regime. Thus it is evident that the systems can't be scaled together in both regimes. In this work, we intend to derive and use the right scaling exclusively in the non-linear regime where the flow is strong enough to stretch the polymer chains. Based on our current

observation the scaling between polymer melts and solutions in this regime is, $\bar{\eta}_{st} \sim M_W \sqrt{c}$. Now if this scaling is indeed correct then the polymer melts and solutions satisfying this scaling criterion should show similar steady viscosity values. In order to verify this scaling we first compare two solutions and a melt that follows the scaling criteria as shown in fig. 7.8.

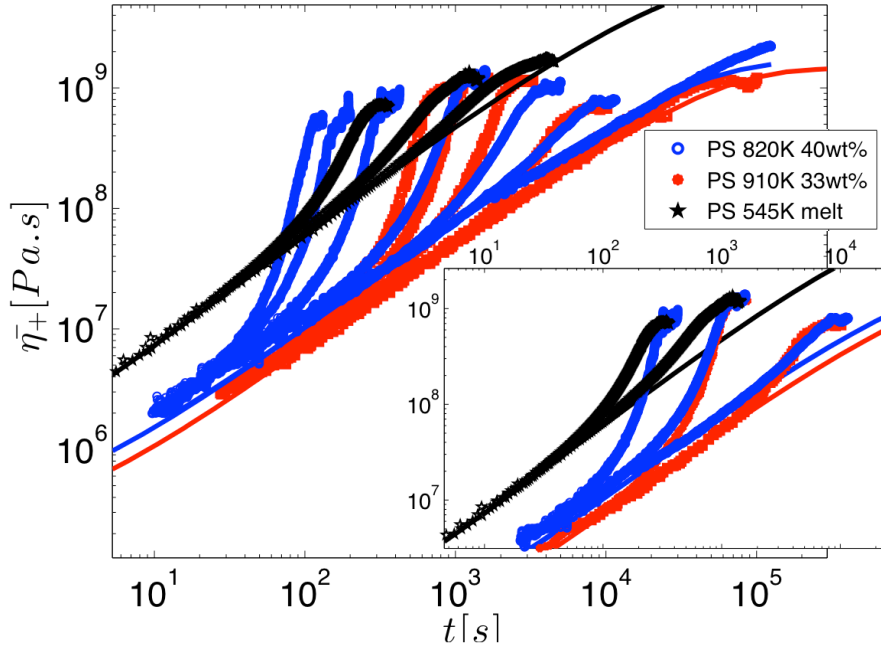


Fig. 7.8. Validation of the scaling observed in non-linear elongational flow with two PS solutions and a PS melt.

As we can see at high strain rates ($Wi_R = \dot{\epsilon} * \tau_{Rouse} > 1$), even though the transient hardening behavior of the samples are very different, with the most diluted PS solution showing strongest hardening phenomenon, the steady viscosity values are in similar range and overlap nicely with each other. This behavior is observed at least for three different strain rates as shown in inset of fig. 7.8. For small strain rates, i.e. in linear regime, there is a clear difference between the samples even with respect to the steady viscosity values. But as the strain rate is increased the difference starts to decrease and finally vanishes in the non-linear regime. Thus this comparison validates the proposed scaling in the non-linear regime where polymer chains are stretched.

We can then test this scaling, $\eta_{steady} \sim M_w \sqrt{c}$ on a large set of data, in order to capture the universal behavior between polymer melts and solutions. First, we start with PS solutions from both literature and measured in this work. As discussed in chapter 5, the solvent quality plays a huge role and can largely alter the uniaxial visco-elastic properties; therefore only PS solutions diluted in styrene oligomers have been included. The result is shown in fig. 7.9.

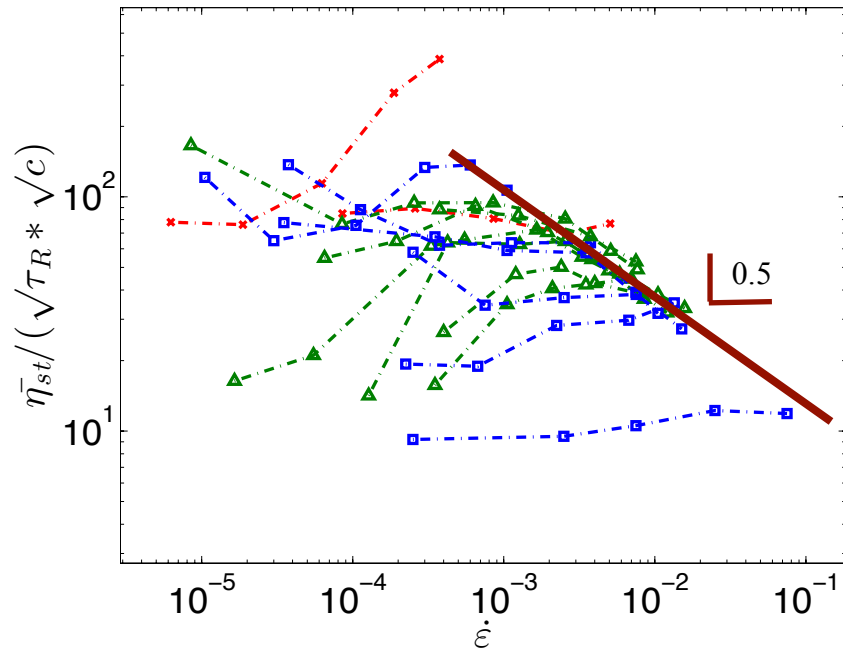


Fig. 7.9. Non-linear universal behavior of PS solutions. Blue and green symbols represent PS solutions respectively from literature and measured in this work. Two PS solutions marked in red do not exhibit universal behavior at high rates.

As we can see from fig. 7.9, a master curve is formed at the stretch regime where all PS solutions follow a common slope of $-1/2$. This indeed confirms our observed scaling for polymer solutions. However, to be consistent with literature, we can further normalize this figure in both horizontal and vertical axes with a characteristic relaxation time, τ_R and the plateau modulus, G_N^0 respectively. In fig. 7.10, we plot the normalized steady viscosity values of all polymer melts and solutions (both measured in this work and from literature).

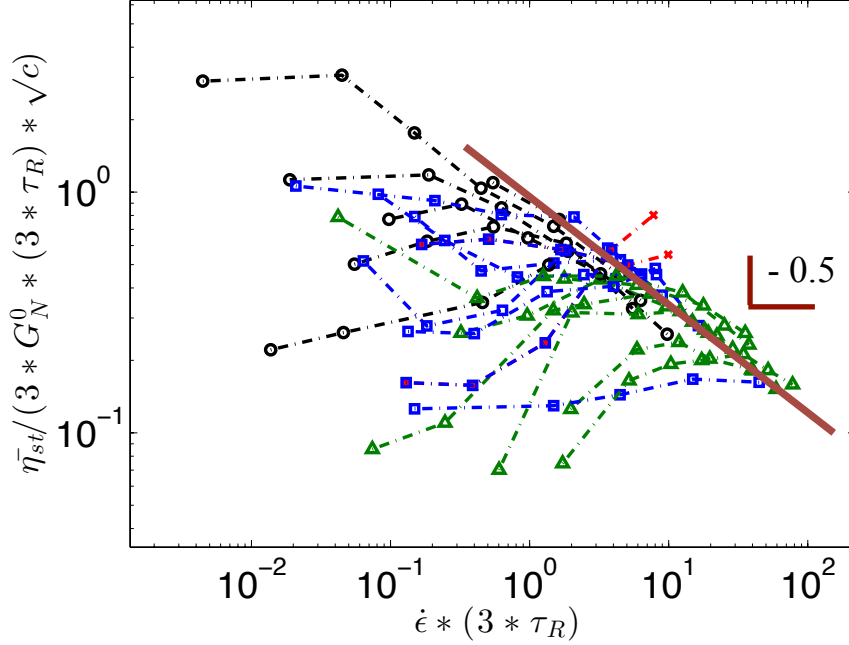


Fig. 7.10. Non-linear universality of polymer melts and solutions.

Black symbols represent Polymer melts, blue and green symbols represent PS solutions respectively from literature and measured in this work. Two PS solutions marked in red don't follow the scaling.

As we can see, in the non-linear regime all PS samples seemingly exhibit identical behavior and scales with a slope of $-1/2$, which is typical Rouse like behavior. Again two strain rates of two particular PS solutions are inconsistent with the scaling (marked in red symbols: PS 545k: 58wt% in 2k OS and PS 1880k: 13wt% in 4k OS). The true origin of this discrepancy is not clear. However, it must be mentioned that the two data points, which do not fit the scaling, are measured at very high strain rates and both samples have high molar mass difference between the PS and corresponding styrene oligomers. This could cause high strain rate induced phase separation in the sample, which in turn results in much higher strain hardening effect due to the high concentrated polymer regime.

In an earlier work, Wagner et al.^{34,35} used a similar approach to find an universal scaling between polymer melts and solutions. But their scaling is different than the one found here as the data of the polymer solutions was not shifted at iso- T_g condition.

7.7 Conclusion

Literature data suggests that polymer melts and solutions under uniaxial elongational flows behave differently. Consequently, pursuit of universal behavior between these systems has failed within the framework of Doi-Edward's tube model. This fact motivated this work where we set out on the belief that this well observed discrepancy is due to lack of systematic experimental data. Subsequently, we designed and characterized a new system to study how the level of dilution affects the strain hardening behavior of a polymer. Interestingly, a clear difference between the scaling in linear and non-linear regime was observed for the first time. This indeed explains the discrepancy observed previously where experimental data in both regimes were normalized using the same parameter thus the same scaling. In this work, we were able to capture the long awaited non-linear universal behavior of polymer melts and solutions by using the right scaling.

From a more general point of view, this work allows us to conclude that the steady viscosity reached in the non-linear regime must be interpreted independently from the linear viscoelastic envelope or from the importance of the transient hardening (since this last one depends on the linear envelop). Indeed, the final stretch state reached by the molecules in the non-linear regime seems to only depend on the molar mass and concentration of the chains, as well as on the Hencky strain rate. This shows the large ambiguity, which exist when zero-elongation rate viscosity is considered to normalize the viscoelastic response under large flow.

In closing, we remark that indeed it's possible to attain a universal behavior between different polymeric systems within the framework of the refined Doi-Edward's tube model. This result is particularly important as it allows us to extend our understanding of linear regime directly to the non-linear regime without considering any additional relaxation mechanism such as the interchain pressure or monomeric friction reduction mechanism.

In the following chapter, we use this idea and propose a simple molecular model that can predict the non-linear steady viscosity of

polymer melts under the framework of refined Doi-Edward's tube model.

I. Appendix

In this work, all non-linear steady-state experimental data have been shifted horizontally by a factor of 4. In this section, the validation of this shifting is discussed.

The transient extensional viscosity, $\bar{\eta}_+(t)$ measured at low extensional rates, $\dot{\epsilon} < \tau_d^{-1}$, (i.e. in the linear regime) has been compared with corresponding LVE envelopes $\eta(t)$, measured from linear SAOS experiments with good agreement. Following a similar approach, the steady extensional viscosity $\bar{\eta}_{st}(\dot{\epsilon})$ can be compared with corresponding LVE envelope $\eta^*(\omega = 1/t)$ with the assumption that the steady state is reached at a time, $t = 1/\dot{\epsilon}$ and the Cox-Merz rule is valid for this rate. But a close observation of the extensional experimental data reveals that the steady state is essentially reached at $t = 4/\dot{\epsilon}$ as shown in fig 7.11 (cross symbols). Consequently, in order to be compared with the LVE envelope (which is at steady state), the steady extensional viscosity $\bar{\eta}_{st}(\dot{\epsilon})$ are needed to be plotted as function of the rate at which they reach the steady state. Otherwise it gives a wrong impression of occurrence of strain hardening even when the transient elongational viscosity follows the linear viscoelastic envelope (like the magenda curves in fig. 7.11).

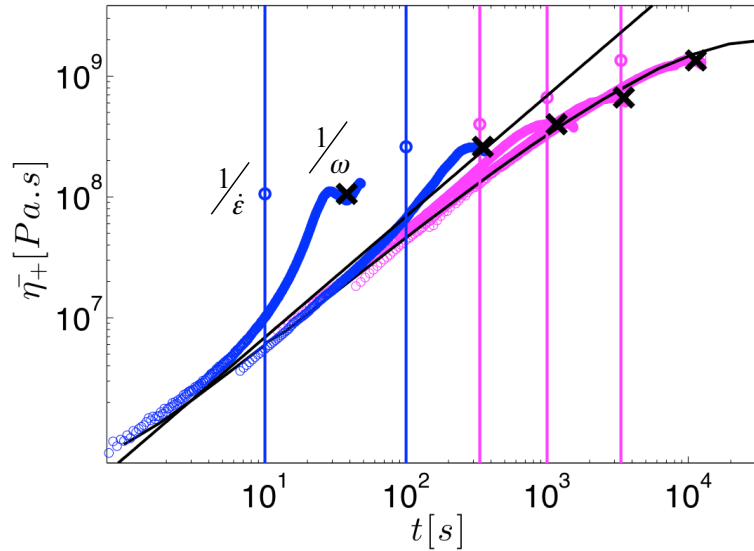


Fig 7.11. Transient elongational viscosity of a PS²¹ melt (390k at 130°C). Strain rates: 0.1, 0.01, 0.003, 0.001, 0.0003 1/s (from left to right).

In the non-linear regime when $W_{iR} > 1$ (blue symbols in fig. 7.11), this is easy to realize as the polymer chains completely orient and start to be stretched at $t > 1/\dot{\epsilon}$ and the steady value is attained at $t = 4/\dot{\epsilon}$ (Strain rates: 0.1, 0.01 in figure 7.11). However, when $W_{iR} < 1$ (magenta symbols in fig. 7.11), the flow field is not strong enough to stretch the polymer chains and surprisingly it still takes $t = 4/\dot{\epsilon}$ to reach the steady value. In this case, we believe this steady value is caused by the disentanglement of polymer chains, which also takes similar time ($t = 4/\dot{\epsilon}$) to attain. Thus in order to be compared with the LVE envelopes the steady elongational viscosities are required to be shifted horizontally with a factor of 4.

Only for the “linear” extensional flow, where the transient viscosity completely follows the LVE envelope (measured from linear flow), the steady state is reached at $t = 1/\dot{\epsilon}$ as can be seen fig. 7.12 for different M_w PS melts.

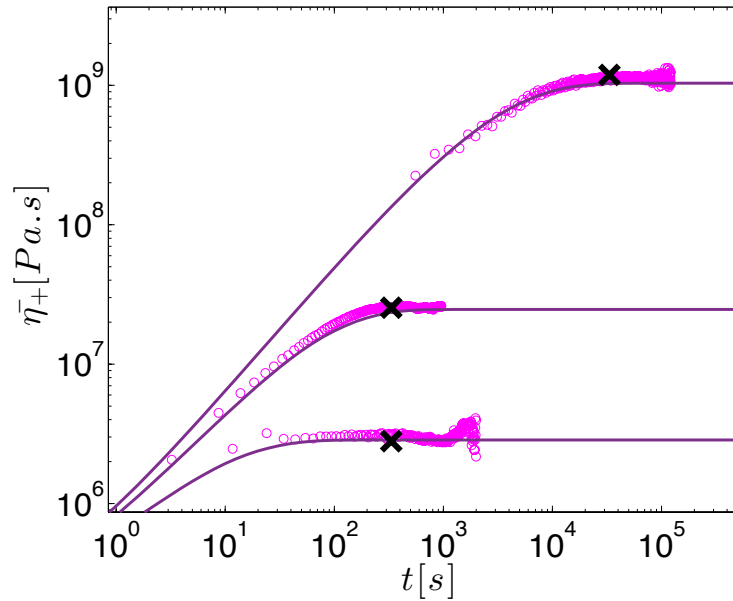


Fig. 7.12. Transient elongational viscosity of different PS melts ($M_w = 285k, 100k \text{ \& } 50k$).

Please note that this shift doesn't influence the main outcome (i.e. the universal scaling) of this chapter. The universal scaling persists with or without the shift. However, this is necessary for the following

chapter, where we present a model to predict the non-linear properties of polymer melts.

References:

1. T. C. B. McLeish, Tube theory of entangled polymer dynamics. *Advances in Physics*, (2002), 51(6), 1379–1527.
2. M. Doi., *Introduction to Polymer Physics*. (1995), Oxford Science Publications, Clarendon Press, Oxford.
3. Q. Huang, L. Hengeller, N. J. Alvarez, O. Hassager, Bridging the Gap between Polymer Melts and Solutions in Extensional Rheology. *Macromolecules*, (2015), 48, 4158–4163.
4. J. D. Ferry, *Viscoelastic Properties of Polymers*, 3rd ed.; John Wiley & Sons: New York, (1980).
5. M. Doi, S. F. Edwards, *The Theory of Polymer Dynamics*; Clarendon Press: Oxford, (1986).
6. Q. Huang, N. J. Alvarez, Y. Matsumiya, H. K. Rasmussen, H. Watanabe, O. Hassager, Extensional Rheology of Entangled Polystyrene Solutions Suggests Importance of Nematic Interactions. *ACS Macro Lett.*, (2013), 2, 741–744.
7. S. L. Wingstrand, N. J. Alvarez, Q. Huang, O. Hassager, Linear and Nonlinear Universality in the Rheology of Polymer Melts and Solutions. *Phys. Rev. Lett.* (2015), 115, 078302.
8. G. Ianniruberto, A. Brasiello, G. Marrucci, Friction coefficient does not stay constant in nonlinear viscoelasticity. *Proc. 7th Annu. Eur. Rheol. Conf.*, (2011), 1, 61.
9. G. Ianniruberto, A. Brasiello, G. Marrucci, Simulations of Fast Shear Flows of PS Oligomers Confirm Monomeric Friction Reduction in Fast Elongational Flows of Monodisperse PS Melts As Indicated by Rheoptical Data. *Macromolecules*, (2012), 45, 8058.
10. J. M. Dealy and R. G. Larson, *Structure and rheology of molten polymers*, Hanser Publishers, Munich, (2006).

11. H. Watanabe, Viscoelasticity and dynamics of entangled polymers. *Prog. Polym. Sci.*, (1999), 24, 1253–1403.
12. E. van Ruymbeke, C. Y. Liu and C. Bailly, Quantitative tube model predictions for the linear viscoelasticity of linear polymers, *Rheol. Rev.*, (2007), 53–134.
13. A. E. Likhtman, T. C. B. McLeish, Quantitative theory for linear dynamics of linear entangled polymers. *Macromolecules*, (2002), 35, 6332–6343.
14. R. N. Khaliullin and J. D. Schieber, Application of the slip-link model to bidisperse systems. *Macromolecules*, (2010), 43, 6202.
15. Y. Masubuchi, H. Watanabe, G. Ianniruberto, F. Greco and G. Marrucci, Comparison among slip-link simulations of bidisperse linear polymer melts. *Macromolecules*, (2008), 41, 8275;
16. Y. Masubuchi, J. I. Takimoto, K. Koyama, G. Ianniruberto, G. Marrucci and F. J. Greco, Brownian simulations of a network of reptating primitive chains. *Chem. Phys.*, (2001), 115, 4387.
17. Y. Masubuchi, G. Ianniruberto, F. Greco and G. Marrucci, Entanglement molecular weight and frequency response of sliplink networks. *J. Chem. Phys.*, (2003), 119, 6925.
18. S. Shanbhag and R. G. Larson, A slip-link model of branch-point motion in entangled polymers. *Macromolecules*, (2004), 37, 8160.
19. M. E. Shivokhin, E. van Ruymbeke, C. Bailly, D. Kouloumasis, N. Hadjichristidis and A. E. Likhtman, Understanding constraint release in star/linear polymer blends. *Macromolecules*, (2014), 47, 2451;
20. A. E. Likhtman, S. K. Sukumaran and J. Ramirez, Linear viscoelasticity from molecular dynamics simulation of entangled polymers. *Macromolecules*, (2007), 40, 6748.

21. A. Bach, H.K. Rasmussen, and O. Hassager, Extensional viscosity for polymer melts measured in the filament stretching rheometer. *Journal of Rheology*, (2003), 47, 429–441.
22. J. K. Nielsen, H. K. Rasmussen, O. Hassager, and G. H. McKinley, Elongational viscosity of monodisperse and bidisperse polystyrene melts. *J. Rheol.*, (2006), 50, 453–476.
23. P. K. Bhattacharjee, J. P. Oberhauser, G. H. McKinley, L. G. Leal, and T. Sridhar, Extensional rheometry of entangled solutions. (2002), *Macromolecules* 35, 10131–10148.
24. X. Ye, R. G. Larson, C. Pattamaprom, T. Sridhar, Extensional properties of monodisperse and bidisperse polystyrene solutions, (2003), *J. Rheol.*, 47, 443.
25. Q. Huang, O. Mednova, H. K. Rasmussen, N. J. Alvarez, A. L. Skov, K. Almdal, O. Hassager, Concentrated polymer solutions are different from melts: Role of entanglement molecular weight, *Macromolecules*, (2013), 46, 5026-5035.
26. S. Costanzo, Q. Huang, G. Ianniruberto, G. Marrucci, O. Hassager and D. Vlassopoulos, Shear and extensional rheology of polystyrene melts and solutions with the same number of entanglements, *Macromolecules*, (2016), 49, 3925.
27. H. K. Rasmussen, A. G. Bejenariu, O. Hassager, and D. Auhl, Experimental evaluation of the pure configurational stress assumption in the flow dynamics of entangled polymer melts, *J. Rheol.*, (2010), 54(6), 1325–1336.
28. I. M. Kolte, H. K. Rasmussen, and O. Hassager, Transient filament stretching rheometer II: Numerical simulation, *Rheol. Acta*, (1997), 36, 285–302.
29. M. L. Williams, R. F. Landel, and J. D. Ferry, The temperature dependence of relaxation mechanisms in amorphous polymers and other glass-forming liquids. *J. Am. Chem. Soc.*, (1955), 77, 3701.

30. C. Y. Liu, J. He, R. Keunings, and C. Bailly, New linearized relation for the universal viscosity– temperature behavior of polymer melts. *Macromolecules*, (2006), 39, 8867.
31. Wang, Y.; Boukany, P.; Wang, S. Q.; Wang, X.; Elastic breakup in uniaxial extension of entangled polymer melts, *Phys. Rev. Lett.* 99, 237801 (2007).
32. Lyhne, A.; Rasmussen, H. K.; Hassager, O.; Simulation of Elastic Rupture in Extension of Entangled Monodisperse Polymer Melts, *Phys. Rev. Lett.* 102, 138301, (2009).
33. Wang, S. Q.; *Nonlinear Polymer Rheology: Macroscopic phenomenology and Molecular foundation*, Wiley: Hoboken, NJ, (2017).
34. M. H. Wagner, E. Narimissa, V. H. Rolon-Garrido, From melt to solution: Scaling relations for concentrated polystyrene solutions. *Journal of Rheology*, (2015), 59, 1113-1130.
35. M. H. Wagner, Scaling relations for elongational flow of polystyrene melts and concentrated solutions of polystyrene in oligomeric styrene. *Rheol. Acta*, (2014), 53, 765–777.

Chapter 8

Modeling the non-linear viscoelastic properties of polymer melts

The molecular picture presently used to represent the chain dynamics under extensional flow fails to predict the different scaling laws observed experimentally; specifically the monotonic thinning behavior of polymer melts. Additional mechanisms have been proposed to explain this peculiar behavior, which is difficult to comprehend in the framework of the standard tube model. In this work, we revisit the extensional rheological data of PS melts provided in literature and propose a different point of view to interpret them. In particular, we define different levels of stretch that a chain can reach as function of the extensional rate, and their implication in the steady viscosity value. To this end, we employ the standard tube model with prevailing relaxation processes without considering any additional mechanism or criteria.

We also discuss the important role played by reptation and contour length fluctuations in the dynamics of a stretched chain. We show that this simple approach well matches the experimental observations, providing new directions to explore, towards the understanding of extensional rheology.

8.1 Introduction

As discussed in previous chapters, the linear viscoelastic properties of monodisperse linear polymers are quite well understood and have been successfully described by mesoscopic models such as the tube models¹⁻⁵ or slip-link models⁶⁻¹², which allow accounting for the effect of entanglements between the different chains. However, many

fundamental questions remain in order to understand and describe their non-linear behavior under extensional flow. More specifically, the monotonic extensional thinning behavior of polymer melts, which shows no sign of upturn even at strain rates larger than the reciprocal Rouse time of the chain has not been elucidated. Furthermore, in the thinning area, the polymer melts show a clear scaling law described as $\eta_{st} \sim M_w \dot{\epsilon}^{-1/2}$, which cannot be explained by the tube theory^{1, 13}. Because of these discrete experimental observations, the molecular picture that was previously proposed to describe the steady extensional viscosity needs to be revisited¹⁴⁻¹⁷. Indeed, according to these models both entangled polymer melts and solutions should lead to similar strain hardening properties i.e. a brief thinning regime followed by strong thickening behavior.

The monotonic behavior of monodisperse polymer melts under uniaxial extension is now well established from different studies¹⁸⁻²⁰. This unique behavior has been termed as extensional thinning, since the steady viscosity η_{st} decreases when increasing extensional rate $\dot{\epsilon}$. However, a closer look to the transient extensional viscosity in function of time (see fig. 8.1) clearly reveals that the transient viscosity curves start to depart from the linear envelope at high extensional rates $\dot{\epsilon}$ (blue curves in fig. 8.1). This means that the transient viscosity of chain under large extensional rate increases faster than the transient viscosity of the chain deformed in the linear regime, which indeed can be described as a strain hardening effect. However, the effect is not as strong as in polymer solutions thus no upturn of the steady viscosity is observed.

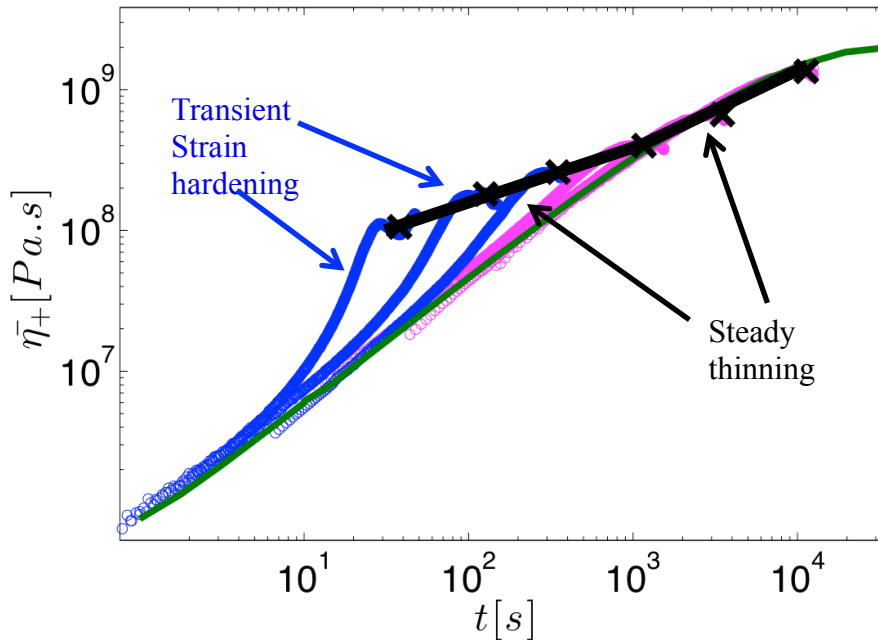


Fig. 8.1 Polymer melts: extension thinning vs strain hardening behavior.

The first proposed mechanism, which could successfully explain this reduced strain hardening effect in polymer melts was the interchain tube pressure concept (ICP) proposed by Marrucci and Ianniruberto²¹. According to this concept, a strong elongational deformation causes the tube to contract, thus decreasing the tube diameter from its equilibrium value. As the tube diameter decreases, pressure starts to build up against the tube wall and after a while, this growing pressure would stop the contraction process and a steady state would be reached. This concept included a novel non-linear parameter: the tube diameter relaxation time, τ_a . By incorporating this concept in the molecular stretch function theory, Wagner et al.²² were able to attain a semi-quantitative agreement for monodisperse PS melts¹⁸, and also showed that the tube diameter relaxation time scales with the Rouse time of the chains. Despite its success with polymer melts, the key physics behind the interchain tube-pressure cannot differentiate between polymer melts and solutions. Indeed for polymer solutions, the ICP concept requires two separate Rouse times (each for polymer melt and solution), which is difficult to comprehend. Therefore the

ICP theory is obviously missing some ingredients to correctly describe the elongation properties of an entangled polymer in general.

Recently, several works have been proposed²³⁻²⁵, based on the idea that extensional thinning observed in the melt state originates from a reduction of the monomeric friction under fast extensional flow (SORF). According to this concept, when the extensional flow is faster than the stretch relaxation rate, the local environment of the polymer deviates from its equilibrium state and becomes strongly anisotropic. This local anisotropy then leads to a decrease in monomeric friction. Consequently, the flow “loses grip” on the polymer molecule and its corresponding stretch saturates at a lower level. This mechanism is predominant for polymer melts, as the small molecules in the solution do not align²³ with the flow. This well received concept has been successfully implemented for both PS melts and solutions³⁰⁻³². However, our previous works (see chapter 6 and 7) have raised some fundamental questions about the universality of this mechanism, which needs to be further addressed.

The objective of the present work is to re-analyze the experimental steady elongational viscosity data proposed in literature for monodisperse polymer melts, with the help of a tube-based model and look at the orientation and stretch behavior of the chains at the different length scales. Even if it is expected that in the limit of high extension rate, the role of entanglements becomes negligible due to the fact that the chains are largely extended²⁹, analyzing the results with a tube model allows us to further follow the relaxation state of the chains through time and to study the role of reptation, fluctuations and constraint release as function of the extensional rate. In particular, we would like to understand the influence of these mechanisms in the transition zone from linear to non-linear flow. As discussed in the previous chapter, at low extensional rates the zero-elongational viscosity scales with $\eta_0 \sim M_W^{3,4}$, whereas at high rates, when the polymer chains are stretched, the steady viscosity values follow a different scaling, $\bar{\eta}_{st} \sim M_W$. Thus, between these two regimes, there is a transitional region that we would like to further investigate.

In this work, we propose an alternative approach to describe the extensional thinning of polymer melts, which is strictly based on experimental observations and according to which both chain stretch and orientation can lead to strain hardening. Different from the models

previously proposed, we hope that the simplicity of the approach proposed here, which does not require any additional parameters or finite extensibility criterion for correctly describing the experimental data, will open the debate towards a better description of the strain hardening behavior of polymer melts and solutions.

8.2 Materials

In this study, we have investigated a range of entangled monodisperse linear polystyrene melts, which varies from low to high molar masses. These samples have been studied in previous works¹⁸⁻²⁰ and their linear and non-linear viscoelastic data have already been presented in the literature. They are listed in Table 1, together with some basic physical characteristics.

Table 1 Main characteristics of the PS melts used in this work

Sample	M _w	M _n	PDI	T _g	Ref.
PS50	51,700	50,380	1.026	102.5*	18, 19
PS100	102,800	100,600	1.022	105.5*	18, 19
PS133	133,000	131,600	1.01	106*	26
PS185	185,000	179,600	1.03	106.5*	26
PS200	200,000	192,000	1.04	106.5*	18, 19
PS285	285,000	261,500	1.09	107.5	20
PS390	390,000	367,000	1.06	106.5*	18
PS545	545,000	486,600	1.12	106.5	20
PS820	820,000	803,900	1.02	106.5	28

*Calculated, data not available.

8.3 Establishing the material parameters

As stated before, in this work we intend to re-analyze the non-linear viscoelastic properties of monodispersed linear polymer melts with help of the TMA based tube model. The detail of the model in linear regime can be found in chapter 5. This TMA based tube model comprises of three different material parameters, i.e. the plateau modulus G_N^0 , the molecular weight between two entanglements M_e and the Rouse relaxation time of an entanglement segment, τ_e , which are needed to be defined corresponding to the melt state. All these parameters are related to the polymer segment between entanglements, which is the largest stress-carrying element of the chain. The values of these parameters have been set by best fitting procedure on the linear data of the melts and are in agreement with previous work²⁷ as 230 kPa and 15 kg mol⁻¹ respectively for G_N^0 and M_e , while $\tau_{e,0,melt}$ has been fixed to 0.55 s at a reference temperature of 130°C.

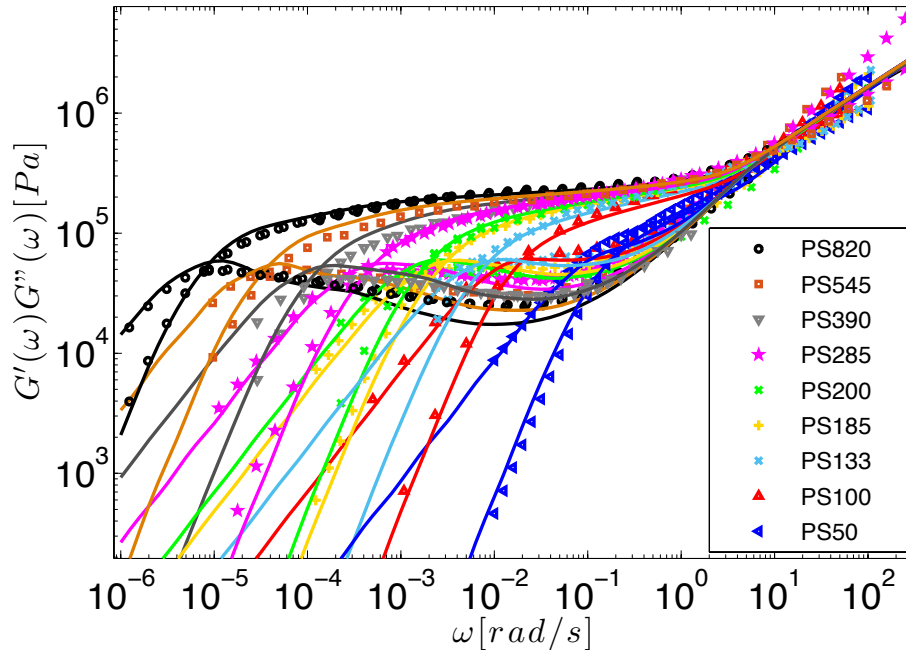


Fig. 8.2 Comparison between experimental (symbols) and theoretical (lines) storage and loss moduli of different M_w PS at 130°C. Experimental data have been described in ref. [18-20].

As we can see from fig. 8.2, a very good agreement between the model predictions and experimental viscoelastic properties is achieved with the defined material parameters. Since the chains are linear, their main relaxation process is reptation. However, it must be noted that a non-negligible part of the short samples, PS50 and PS100 (see Table 1), also relaxes by contour length fluctuations, which take place before the reptation of the chains.

The theoretical linear transient viscosity of these samples are then determined, based on the predicted shear relaxation modulus $G(t)$:

$$\eta^+(t) = 3 \int_0^t G(t') dt' \quad (1)$$

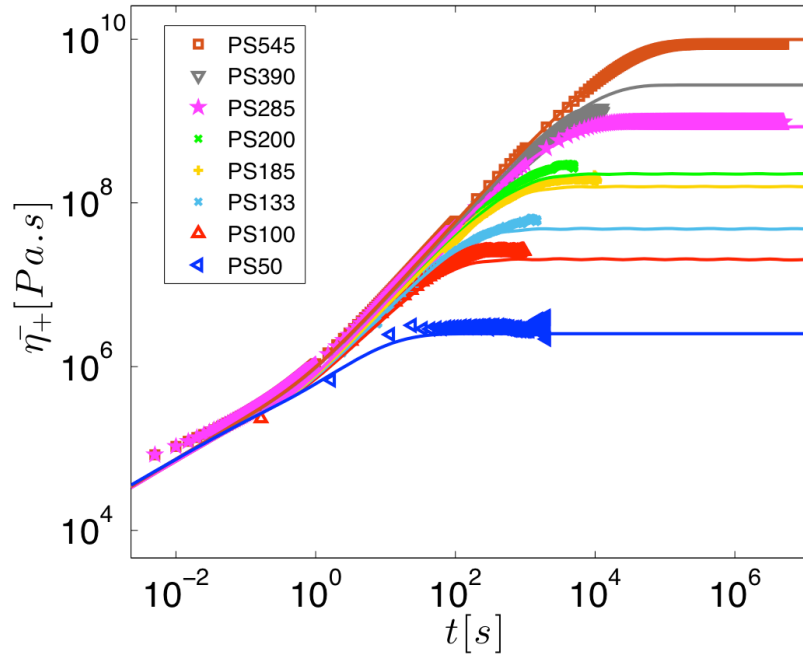


Fig. 8.3 Comparison between experimental (symbols) and theoretical (lines) linear extensional viscosity of different M_w PS at 130°C . Experimental data have been described in ref. [18-20].

Figure 8.3 compares the obtained predictions to the experimental transient data measured at low extensional rates, i.e. in the linear regime. As it can be observed, the agreement is very good, which

gives a good starting point to analyze the steady elongation viscosity at larger extensional rates.

The same set of material parameters derived in this section will be used to predict the non-linear viscoelastic properties in the following sections.

8.4 Modelling the non-linear elongation properties for PS melts

As we know, non-linear extensional flow field is strong and capable of stretching the polymer chains beyond its equilibrium length. If the flow rate is higher than the stretch relaxation rate ($\sim 1/\tau_R$), the chains are becoming stretched, i.e. the length of their primitive path, L_{eq} , is becoming longer than its length at equilibrium, $L_{eq,0}$, the stretch factor, λ , being defined as the ratio between these two lengths, $L_{eq}/L_{eq,0}$. Under such conditions, it has been shown that the polymer melt exhibits strain-hardening. The existing molecular theories suggest that beyond this critical rate ($\dot{\epsilon} > 1/\tau_R$), the polymer chains are fully stretched i.e. reach finite extensibility. In this work, we look at the stretch of polymer chains from a different perspective and propose that they can stretch at different levels depending on the rate of the flow. Furthermore, we propose that strain hardening can be observed at strain rates lower than this critical rate. These ideas are described and confronted with experimental results in the following section.

8.4.1 Strain hardening occurs at different levels

Thus, we propose here that strain hardening of polymer chains can be observed at two different levels. More specifically, while strain hardening is present when the largest stress carrying element, M_e are stretched, i.e. at high extensional flow rates ($\dot{\epsilon} > 1/\tau_R$), it seems from the experimental data that strain hardening can also be observed at rates lower than the reciprocal of the Rouse time but higher than the

reptation time ($1/\tau_{\text{Reptation}} < \dot{\epsilon} < 1/\tau_R$). Since in this regime, the chains are not stretched in the sense that $\lambda = 1$, we rather speak about strain-induced strain hardening, in comparison to stretch-induced strain hardening at high strain rates. These different chain stretching phenomena are illustrated in fig. 8.4.

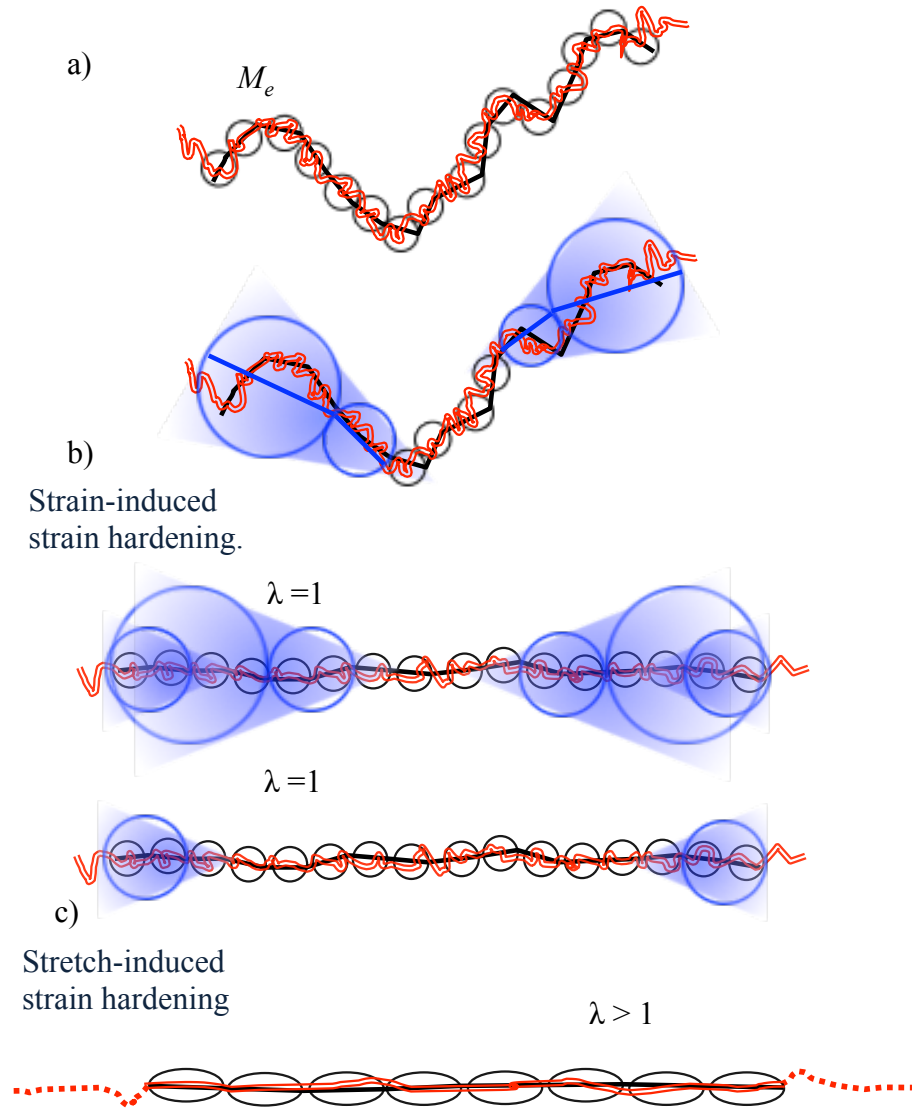


Fig. 8.4 a) At $\dot{\epsilon} < \frac{1}{\tau_{\text{Rel}}}$, (with τ_{rel} being the terminal relaxation time of the polymer), the polymer chain can relax via reptation and CLF (shown in blue highlighted area). Furthermore, the flow rate is low

enough to allow the chains to create new entanglements. Consequently, the polymer chain stays unperturbed at the level of the whole chain b) At intermediate rates $\frac{1}{\tau_{Reptation}} < \dot{\epsilon} < \frac{1}{\tau_R}$, the chain orients at the direction of flow thus initiating full orientation of the entanglement segments. At the local level i.e. M_e it stays unperturbed, so we define the stretch factor, $\lambda = 1$. At this level, strain hardening occurs due to gradual suppression of CLF (details in section 8.4.1 a). c) At $\dot{\epsilon} > \frac{1}{\tau_R}$, the flow gets strong enough to stretch polymer chain at a local level of an entanglement segment M_e , resulting in an increase in stretch factor, $\lambda > 1$.

Transition from fig. 8.4.a to fig. 8.4.b describes the strain-induced strain hardening, while the transition from fig. 8.4.b to fig. 8.4.c defines the stretch-induced strain hardening. Both mechanisms are described in the section below.

a) Strain-induced strain hardening

In order to visualize strain-induced strain hardening, transient extensional response of a low molar mass PS melts ($M_w = 100\text{kg/mol}$) are analyzed, as shown in fig. 8.5.

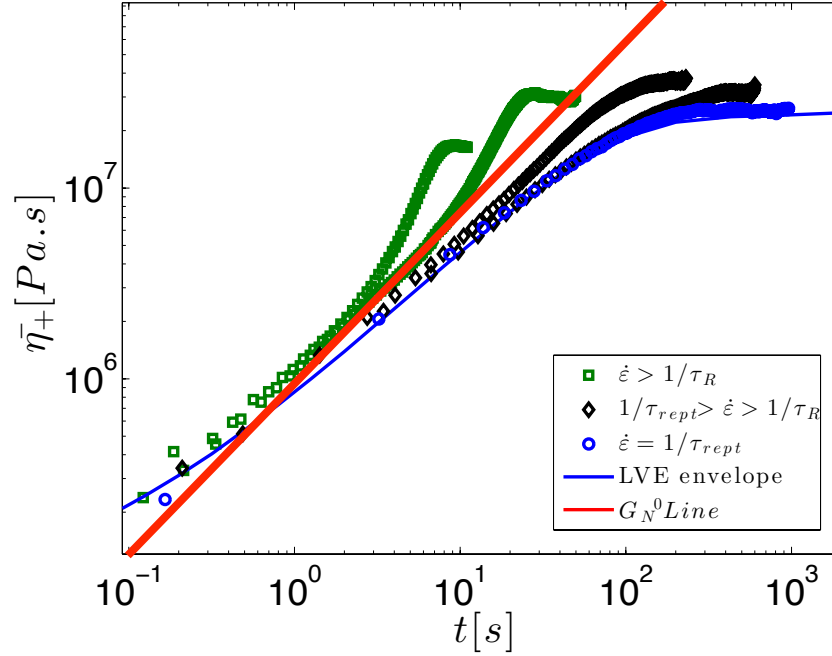


Fig. 8.5 Transient extensional viscosity (symbols) of PS100 with corresponding LVE envelope (blue curve) and G_N^0 line (red curve) at $\dot{\epsilon} = 0.3, 0.1, 0.03, 0.01, 0.003 \text{ s}^{-1}$ (from left to right). The sample was measured in ref. [18] with $1/\tau_R \sim 0.05 \text{ s}^{-1}$.

In this figure, the G_N^0 line (red line) represents the condition at which the polymer chains behavior is fully elastic. Thus, in the linear regime of extension, the chains follow this G_N^0 line as long as the time t is shorter than their relaxation time. In this regime, the corresponding transient viscosity is well described by $\eta^+(t) = 3 \int_0^t G_N^0 dt' = 3 G_N^0 t$ (see Eq. 1). All the curves above this line (green) are measured at high rates, $\dot{\epsilon} > \frac{1}{\tau_R}$, at which the chains are stretched and cannot relax. On the other hand, at very low rates (see the blue curve), the polymer chains have time to relax by reptation and CLF mechanisms, and follow the linear envelope. But the most interesting regime is the one observed at intermediate strain rates, as presented by the black curves. Indeed, in this regime, the transient viscosity deviates from the LVE envelope, apparently showing strain-hardening characteristic even if the corresponding strain rates are lower than their reciprocal

Rouse time, $\dot{\epsilon} < 1/\tau_R$. For obvious reasons, this cannot be associated with the chain stretching as defined in literature. Note that this behavior was identified earlier in chapter 7, where we discussed this upturn/hardening as a way to balance/transit between the different scaling observed in the linear and non-linear regime. Indeed, since in linear regime, η_{st} scales with $M_W^{3.4}$ whereas in non-linear regime the scaling is very different, $\eta_{st} \sim M_W$, there is necessarily a transition zone between these two regimes.

Here we would like to explain this behavior in light of the strain-induced strain hardening concept: in the linear regime of strain rates, the chains show a low zero-elongational viscosity due to the fact that most of stress-bearing segments (i.e. the entanglement segments) have time to explore their surrounding, relaxing by reptation and contour length fluctuations (CLF). Therefore their contribution to the stress is limited. However, by increasing the strain rates, the chains start to orient in the direction of the flow. We believe that this orientation should affect the motion and disentanglement of the chains. In particular: how a chain, which is fully oriented, is still be able to relax by CLF?

Obviously, in the stretch regime, the chains are not able to relax by reptation or CLF anymore, and the strain hardening appears while the transient viscosity is still following the G_N^0 line (see the green curves), i.e. before the chains start to disentangle. Between the linear regime and this extreme case of very high strain rates, we believe that in the transition regime, the chains cannot or only partially relax by CLF, i.e. with a smaller contribution of CLF compared to the CLF process taking place in the linear regime. In other words, as represented in fig. 8.6, CLF is limited to the molecular segments able to move very fast compared to the flow rate. For example, we could easily imagine that in order to be able to relax by CLF, a specific molecular segment x must have a fluctuations time shorter than the reciprocal of the strain rate, $\tau_{fluc}(x) < 1/\dot{\epsilon}$.

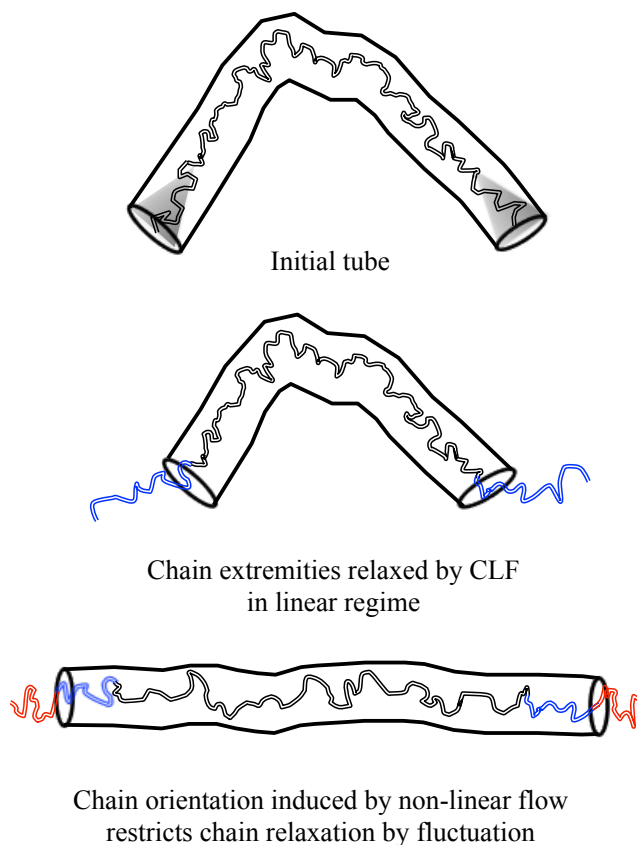


Fig. 8.6. Polymer chain relaxing at extremities by CLF, in the linear regime or at intermediate regime. The tube which is drawn represents the remaining part of the initial tube, after CLF.

This limited effect of CLF can also be seen in fig. 8.5. (see the black curve): while the transient viscosity follows the linear envelop during a longer time compared to the (green) curves at high strain rates, they deviate at some point, in the middle of the CLF process (at $\tau_e < t < \tau_{reptation}$). Furthermore, the fact that the curves stay below the G_N^0 line validates the fact that 1) a small fraction of chain end is still able to relax, 2) the chain segments are not stretched, i.e. $\lambda=1$.

Thus, fig. 8.5 suggests that as the strain rate increases, the effect of the fluctuations decreases, which directly affects the level of the steady elongation viscosity. This should be especially important for polymers such as the PS100, as we know the CLF mechanism is more effective

for polymers with low molar mass. The progressive suppression of CLF process with increasing the strain rate is further validated in fig. 8.7, where the steady elongation viscosity of the monodisperse linear polymers (see Table 1) is plotted as function of the strain rate: First, it is seen that the increase of the steady elongation viscosity takes place at rates below the rate corresponding to the G_N^0 line (represented in black), which represents the stress we should obtain if all entanglement segments were fully oriented, without being stretched. Second, we observe that only the steady viscosity of the shorter chains show a clear maximum, which is in agreement with the larger importance of CLF process with shorter chains. Further validation of the suppression of CLF process can be found in Section 8.4.2.

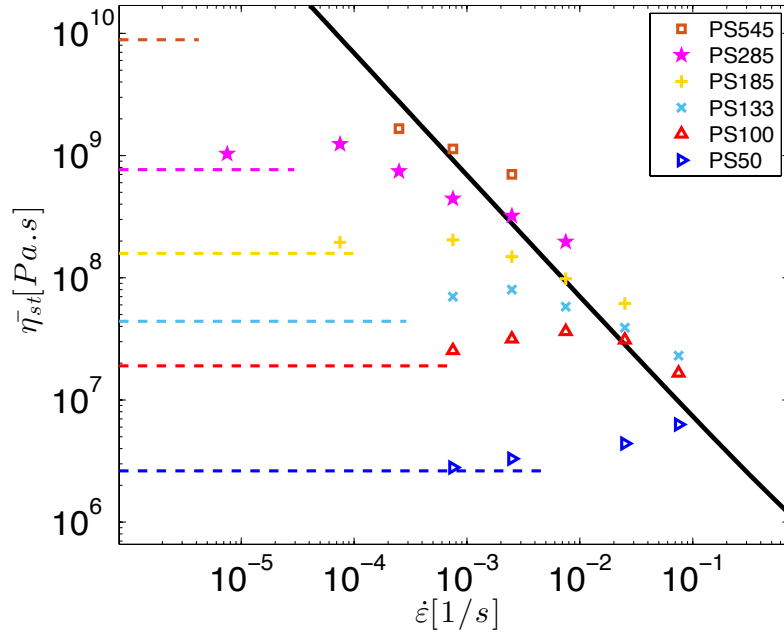


Fig. 8.7. Steady elongation viscosity (symbols) versus Hencky strain rate with corresponding zero shear viscosities and G_N^0 line.

To conclude this part, strain hardening observed below the G_N^0 line is not due to chain stretching, but is rather due to the (partial) suppression of CLF process, which does not have time to take place, and leads to an increase of the steady elongation viscosity. The observed strain hardening is therefore an ‘orientation-induced’ strain hardening.

While this viscosity increase observed in the intermediate regime is discussed here for polymer melts, this concept can easily be extended to polymer solutions. Indeed, the more a chain is diluted, the less it contains entanglements, the more it can relax by CLF. Consequently, by diluting a polymer, the gradual suppression of the CLF process with increasing the strain rate (before reaching the stretch regime) becomes more and more pronounced leading to a larger viscosity increase (see chapter 7).

b) Stretch-induced strain hardening

For extensional rates higher than $\dot{\epsilon} > 1/\tau_R$, the flow field gets strong enough to stretch the polymer chain at the level of the entanglement segment M_e , thus showing strong strain hardening effect, with a stretch factor $\lambda > 1$.

So, from the experimental observation, it is seen that the entanglement segments start to stretch as soon as $\dot{\epsilon} > 1/\tau_R$. This situation is very different from its linear counterpart, where an entanglement segment takes only a time τ_e to relax and equilibrate, not a time equal to the Rouse relaxation time of the whole chain.

Here, we propose to explain this difference by the fact that in order to relax the stress of an entanglement segment stretched by a high deformation, this is the tension along the whole chain, which has to re-equilibrate, which corresponds to a time τ_R and not τ_e . Indeed, unlike the linear regime, local relaxation (i.e. at the level of an entanglement segment) does not suffice anymore to release the stretch. This concept is illustrated in fig. 8.8.

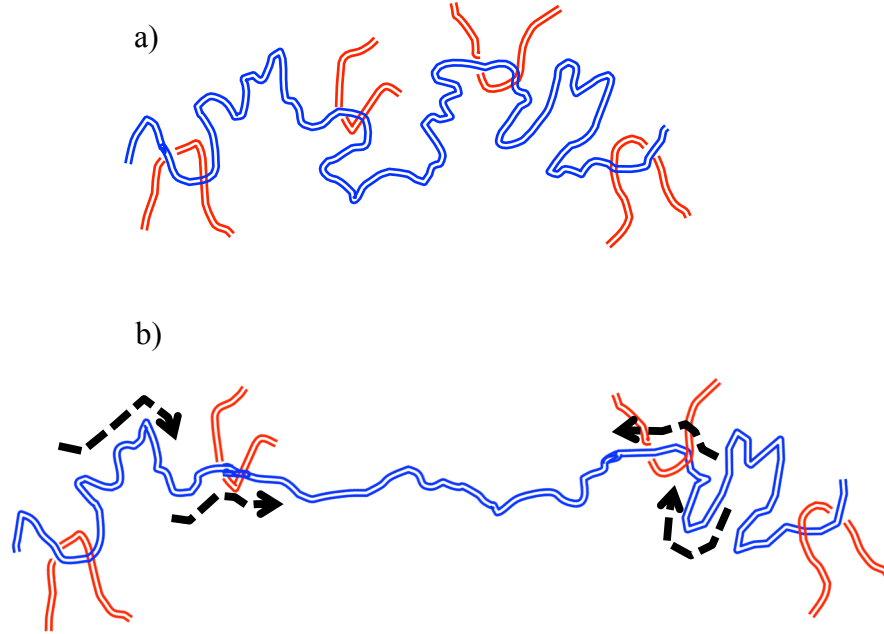


Fig. 8.8 Illustration of stretched chain relaxing along its contour length. a) In the linear regime, relaxation of an entanglement segment corresponds to the time it takes to explore its surrounding (i.e. an entanglement blob), which is a local process. b) On the other hand, when the chain is stretched, equilibration of the entanglement segment located in the middle of the chain requires the motion of the whole chain.

The proposition that the entanglement segments take a time τ_e to equilibrate in the linear regime and a time τ_R to equilibrate in the non-linear regime can be further visualized in fig. 8.9., in which the normalized steady stress is plotted against the normalized deformation rate. While the curves have a similar shape to $G'(\omega)$ in the linear regime, as we can see, the steady stress data transits from a non-stretched regime ($\sigma_{st} < 3G_N^0$) to a stretched regime ($\sigma_{st} > 3G_N^0$) exactly at the Rouse time of corresponding melt rather than at $1/\tau_e$. This confirms that the stress carrying element M_e in elongational flow relaxes with the characteristic Rouse time of the whole chain. In other words, the largest stress carrying element, M_e starts to stretch out when the strain rate gets higher than $1/\tau_R$, initiating the (stretch-induced) strain hardening of polymers. Furthermore, it is observed

that in the stretch regime, data follow a common slope of $\frac{1}{2}$. This suggests that similarly to the linear regime, the chain can be stretched at different levels, related to different modes of relaxation, as function of the strain rates: the larger the strain rate, the less the equilibration of the monomeric tension along the chain can take place, the more the entanglement segments are stretched.

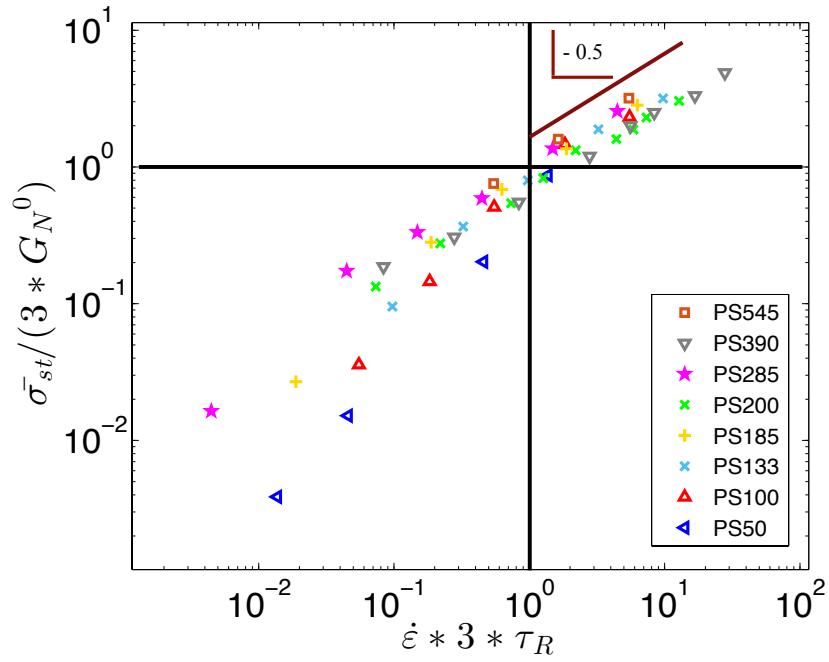


Fig. 8.9 Normalized non-linear steady stress of PS melts. Black lines separate linear and non-linear regime.

8.4.2 Exploring link between linear and non-linear flow

As discussed earlier, in linear flow we have fully developed constitutive models such as the refined tube model, which can predict the viscoelastic properties at a quantitative level. In this section, we aim to extend our understanding of linear flow to the non-linear one purely based on experimental observations. Therefore, we revisit the linear viscoelastic experimental data of PS melts in quest of finding a common background.

It is a well-known fact that linear flows comprise of weak flow field that can only deform and orient entangled polymer chains in the direction of flow. Consequently, the largest stress carrying element of the unperturbed chain, M_e can relax with its own characteristic relaxation time, τ_e via intrinsic Rouse-like motion. This phenomenon is well known and has been observed experimentally from linear SAOS viscoelastic data of PS melts as shown in fig. 8.10.

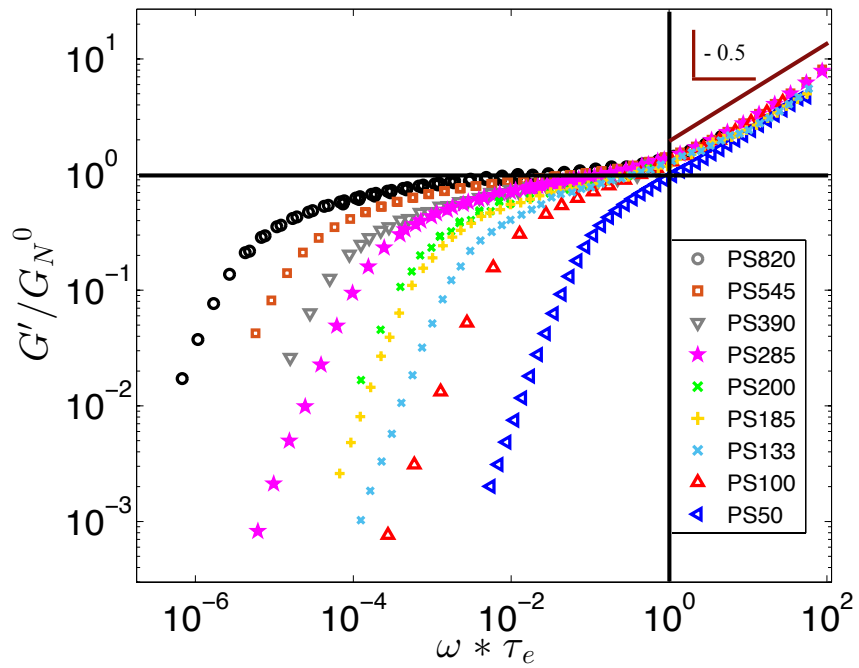


Fig. 8.10 Normalized linear moduli of PS melts.

In the Rouse regime, all PS melts exhibit a slope of $1/2$, which portrays typical Rouse like motion. This behavior of PS melts in linear flow is unmistakably similar to that of its non-linear counterpart, the only difference being a different characteristic time at which the entanglement segments are relaxed. Therefore, we propose here to extend our model to predict the linear viscoelastic properties of the chains to determine the steady stress (or viscosity) in the non-linear regime since it only requires minor alterations.

In the next section we first simplify the well-established linear relaxation modulus equation (as per the tube theory) so that it still

allows us capturing the characteristic relaxation modulus observed in fig. 8.10, but can easily be extended to the non-linear predictions. Then, we modify this equation in order to describe the steady elongation stress data.

As we know in the linear tube model, the relaxation of the entangled chains takes place via two important mechanisms. The first component, $G_R(t)$ represents the fast relaxation of the polymer subchains shorter than M_e which occur via intrinsic Rouse motion, while the second component, $G_d(t)$ represents the slow tube disentanglement process of the entangled polymer chains, which is dominated by relaxation processes such as, reptation, CLF and CR (detailed Eq. are presented in chapter 5). In this work, we combine these two components (see Eq. 2) and merge them into a simple equation to match the scaling observation (see Eqs. 3 or 4). However, this modification doesn't change the overall functionality of the model as shown in fig. 8.11.

$$G(t) = G_R(t) + G_d(t) \quad (2)$$

$$G(t) = G_N^0 * \max\left(1, \left(\frac{\tau_e}{t}\right)^{\frac{1}{2}}\right) * \phi_{tube}(t) * \varphi'(t) \text{ or} \quad (3)$$

$$G(\omega) = G_N^0 * \max\left(1, \left(\frac{\tau_e}{\frac{1}{\omega}}\right)^{\frac{1}{2}}\right) * \phi_{tube}\left(\frac{1}{\omega}\right) * \varphi'(1/\omega) \quad (4)$$

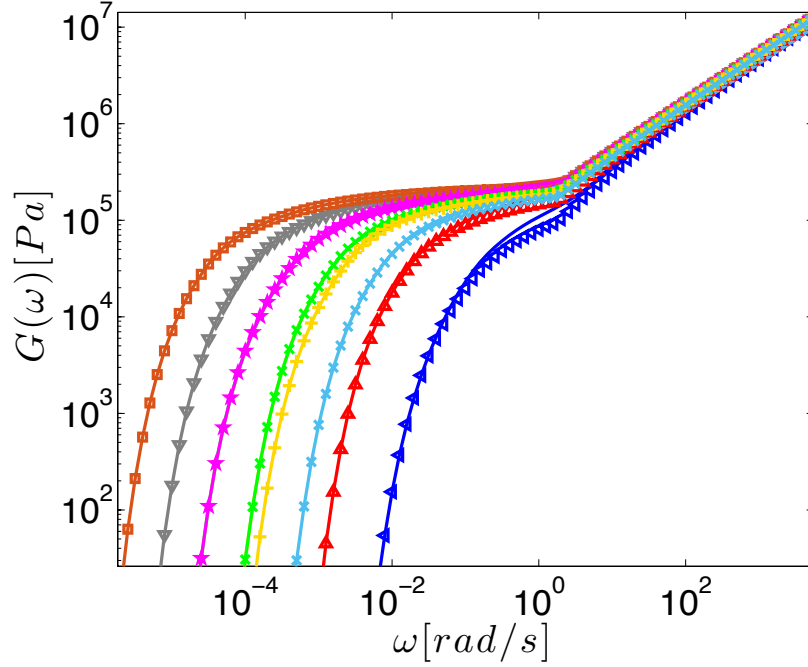


Fig. 8.11 Comparison between the simplified (curves) and the standard tube model (symbols) predictions.

In fig. 8.11, our modified modulus predictions (straight lines) are compared with the standard tube model predictions (symbols). In spite of the simplicity of our proposed equation, it works very well for the entire frequency and molar mass range of PS melts. In Eq. 3, the local Rouse relaxation is taken into account by the term $\max\left(1, \left(\frac{\tau_e}{t}\right)^{\frac{1}{2}}\right)$, which ensures that the contribution of the Rouse modes to the modulus disappears (becoming equal to 1) as soon as the entanglement segments are relaxed, i.e. at time τ_e . It also ensures that in this Rouse regime, $G(t)$ decreases with time, with a slope of $1/2$. The major advantage of this new equation is to give continuity between this local Rouse process and the Constraint Release process (taken into account by the term $\phi_{tube}(t)$): while the Rouse term decreases with time until reaching a value of 1 at time τ_e , the term $\phi_{tube}(t)$ is equal to 1 at time τ_e , at which it starts to decrease. In fact, both terms are related to the larger ‘blob’ that the chains can locally explore at time t .

Based on our observation from fig. 8.9 we can then extend this equation (Eq. 3) from linear to the non-linear regime simply by considering the inverse strain rate, $1/\dot{\epsilon}$, in place of the time t , and by modifying the relaxation time (inverse strain rate) at which an entanglement segment is relaxed. As discussed, in non-linear regime the largest stress carrying element, M_e equilibrates with τ_R instead of τ_e . The resulting stress equation is shown in Eq. 5.

$$\sigma_{steady}(\dot{\epsilon}) = 3 * G_N^0 * \max \left(1, \left(\frac{3 * \tau_{Rouse}}{1/(\dot{\epsilon})} \right)^{\frac{1}{2}} \right) * \phi_{tube}(1/\dot{\epsilon}) * \varphi'(1/\dot{\epsilon}) \quad (5)$$

As we can see, our final form of stress equation has a close resemblance to the well-known theoretical stress equation for non-linear flow as presented in Eq. 6.

$$\sigma_{steady}(\dot{\epsilon}) = 3 * G_N^0 * \lambda^2 * S, \quad (6)$$

where, λ is the stretch factor and S is the orientational component. By comparing Eq. 5 and 6 we get that at high strain rates, $\lambda^2 = l/l_0 = \sqrt{\dot{\epsilon} \tau_{Rouse}} \propto M \dot{\epsilon}^{1/2}$, which correctly depicts the scaling law observed in non-linear experimental results and $S = \phi_{tube} * \varphi'$.

According to Eq. 5, at low extensional rates $\dot{\epsilon} < 1/\tau_{reptation}$, the polymer chains can relax with processes such as reptation and CLF thus exhibiting similar behavior as in linear regime. Whereas at high rates $\dot{\epsilon} > 1/\tau_R$, the polymer chains will cease to relax as they stretch out at the local level and the stress will follow a slope of $1/2$, which depicts typical Rouse like motion. However in the intermediate regime as discussed earlier, the polymer chains orient in the direction of flow and consequently the CLF process, which acts in the reverse direction is gradually hindered with increasing the strain rate; thus allowing the polymer chains to relax only by reptation. This

assumption is particularly important for low M_w PS melts, which dominantly relax by CLF. The implication of this assumption as well as the validity of the proposed description of the steady viscosity, $\eta_{st} = \sigma_{st}/\dot{\epsilon}$, can be realized from fig. 8.12, which compares the experimental data to the predicted curves obtained based on Eq. 5, both with and without considering CLF process at rates $\dot{\epsilon} > 1/\tau_{Reptation}$.

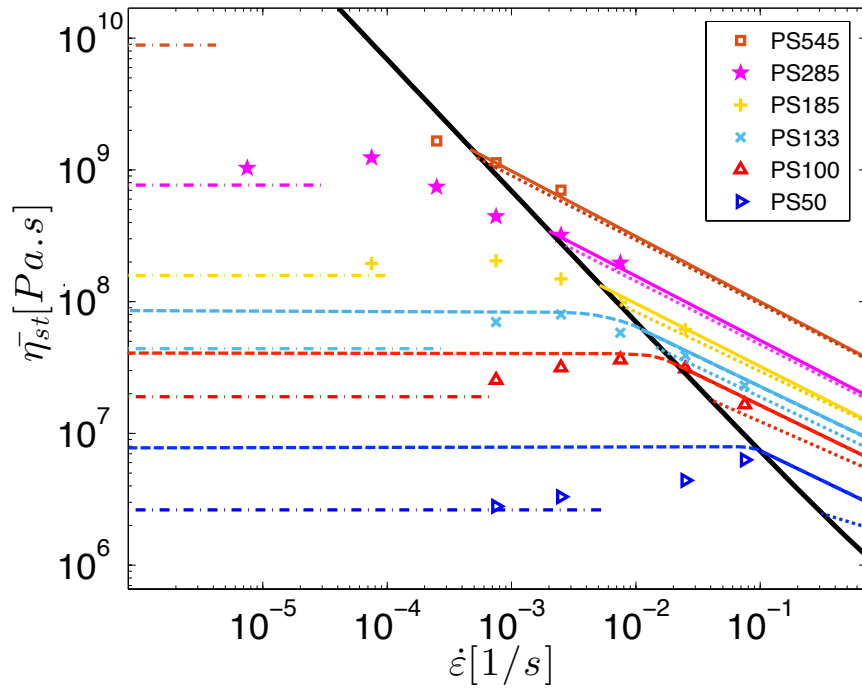


Fig. 8.12 Comparison between the experimental results (symbols) and model predictions with G_N^0 line. Dash-dot lines are linear zero shear viscosities, $3\eta_0$. Solid lines are non-linear model predictions (Eq. 5) with fluctuation and dashed lines are without fluctuation.

As we can see, quantitative predictions have been obtained for all PS melts in the two extreme regimes (linear and non-linear). In between, we have the transition regime, where strain hardening is occurring by gradual suppression of CLF process (i.e. going from the dashed-dotted lines to the dashed line) so expectedly this regime is very important

for low M_w polymer melts. The importance of suppressing the CLF can be realized from the predictions obtained in the non-linear regime, with and without considering the CLF process. Clearly, the predictions obtained while allowing the CLF to take place (see the dotted lines) under predict the experimental results.

8.5 Conclusion

In recent years, a number of molecular models have emerged that can predict the extensional viscoelastic properties of polymers. All these models address to the observed non-universality in extensional flows with some additional mechanisms. Although these models can predict the data at a quantitative level, additional mechanism often brings in extra complexity that has to be taken care with fitted parameter or by including extra criterion. In this chapter we have proposed a novel approach that can predict the non-linear extensional viscoelastic properties of PS melts without considering any additional mechanism or criteria, thus avoiding any complexity. Furthermore, the assumptions made in our theory can readily be verified with experimental observations.

Here, we have proposed a simpler model according to which polymer chains can show both strain-induced strain hardening, which is related to the (partial) suppression of CLF process, and stretch-induced strain hardening which takes place at high strain rates of deformation. While strain-induced strain hardening leads to an upturn in the steady viscosity curve plotted in function of the Hencky strain rate, the stretch-induced strain hardening leads to a slow extension thinning process, which is characterized by a slope of $-1/2$ (rather than -1 in case the chains do not stretch).

In the stretch regime, we have shown that the characteristic time to relax an entanglement segment is the Rouse time of the whole chain, which differs from the linear regime where the segments are relaxed after τ_e . We attributed the $1/2$ slope observed in the steady stress curves vs the strain rate to different relaxation states of the stretch entanglement segments, similarly to the different Rouse relaxation modes observed in the linear regime. Based on this assumption, we

Conclusion

proposed a simple equation which is capable to predict, without including any new parameter, the steady elongation viscosity of the linear polymer melt at low and high strain rates.

While the beginning and the end of the intermediate regime is well captured by the model, a full description of this part, which takes into account the gradual suppression of CLF, still needs to be done.

References:

1. M. Doi., Introduction to Polymer Physics. (1995), Oxford Science Publications, Clarendon Press, Oxford.
2. J. M. Dealy and R. G. Larson, Structure and rheology of molten polymers, Hanser Publishers, Munich, (2006).
3. H. Watanabe, Viscoelasticity and dynamics of entangled polymers. Prog. Polym. Sci., (1999), 24, 1253–1403.
4. E. van Ruymbeke, C. Y. Liu and C. Bailly, Quantitative tube model predictions for the linear viscoelasticity of linear polymers, Rheol. Rev., (2007), 53–134.
5. A. E. Likhtman, T. C. B. McLeish, Quantitative theory for linear dynamics of linear entangled polymers. Macromolecules, (2002), 35, 6332–6343.
6. R. N. Khaliullin and J. D. Schieber, Application of the slip-link model to bidisperse systems. Macromolecules, (2010), 43, 6202.
7. Y. Masubuchi, H. Watanabe, G. Ianniruberto, F. Greco and G. Marrucci, Comparison among slip-link simulations of bidisperse linear polymer melts. Macromolecules, (2008), 41, 8275;
8. Y. Masubuchi, J. I. Takimoto, K. Koyama, G. Ianniruberto, G. Marrucci and F. J. Greco, Brownian simulations of a network of reptating primitive chains. Chem. Phys., (2001), 115, 4387.
9. Y. Masubuchi, G. Ianniruberto, F. Greco and G. Marrucci, Entanglement molecular weight and frequency response of slip-link networks. J. Chem. Phys., (2003), 119, 6925.
10. S. Shanbhag and R. G. Larson, A slip-link model of branch-point motion in entangled polymers. Macromolecules, (2004), 37, 8160.
11. M. E. Shvokhin, E. van Ruymbeke, C. Bailly, D. Kouloumasis, N. Hadjichristidis and A. E. Likhtman, Understanding constraint

- release in star/linear polymer blends. *Macromolecules*, (2014), 47, 2451;
12. A. E. Likhtman, S. K. Sukumaran and J. Ramirez, Linear viscoelasticity from molecular dynamics simulation of entangled polymers. *Macromolecules*, (2007), 40, 6748.
 13. M. Doi and S. F. Edwards. *The Theory of Polymer Dynamics*. International series of monographs on physics. (1986), Oxford University Press, Oxford.
 14. G. Marrucci, and N. Grizzuti, Fast flows of concentrated polymers: Prediction of the tube model on chain stretching. *Gazz. Chim. Ital.*, (1988), 118, 179–185.
 15. G. Ianniruberto, G. Marrucci, A simple constitutive equation for entangled polymers with chain stretch. *Journal of Rheology*, (2001), 45, 1305.
 16. G. Marrucci, G. Ianniruberto, Flow-induced orientation and stretching of entangled polymers, *Phil. Trans. R. Soc. Lond.*, (2003), 361, 677–688.
 17. D.W. Mead, R.G. Larson, and M. Doi. A molecular theory for fast flows of entangled polymers. *Macromolecules* (1998), 31, 7895–7914.
 18. A. Bach, H.K. Rasmussen, and O. Hassager, Extensional viscosity for polymer melts measured in the filament stretching rheometer. *Journal of Rheology*, (2013), 47, 429–441.
 19. J. K. Nielsen, H. K. Rasmussen, O. Hassager, and G. H. McKinley, Elongational viscosity of monodisperse and bidisperse polystyrene melts. (2006), *J. Rheol.* 50, 453–476.
 20. Q. Huang, O. Mednova, H. K. Rasmussen, N. J. Alvarez, A. L. Skov, K. Almdal, O. Hassager, Concentrated Polymer Solutions are Different from Melts: Role of Entanglement Molecular Weight. (2013), *Macromolecules*, 46 (12), 5026–5035.
 21. G. Marrucci, G. Ianniruberto, Interchain pressure effect in

extensional flows of entangled polymer melts. *Macromolecules*, (2004), 37, 3934– 3942.

22. Wagner, M. H.; Rolon-Garrido, V. H.; Nonlinear rheology of linear polymer melts: modeling chain stretch by interchain tube pressure and Rouse time. *Korea-Australia Rheol. J.*, 21, 203–211, (2009).

23. G. Ianniruberto, A. Brasiello, G. Marrucci, Friction coefficient does not stay constant in nonlinear viscoelasticity. *Proc. 7th Annu. Eur. Rheol. Conf.*, (2001), 1, 61.

24. G. Ianniruberto, A. Brasiello, G. Marrucci, Simulations of Fast Shear Flows of PS Oligomers Confirm Monomeric Friction Reduction in Fast Elongational Flows of Monodisperse PS Melts As Indicated by Rheoptical Data. *Macromolecules*, (2012), 45, 8058.

25. T. Yaoita, T. Isaki, Y. Masubuchi, H. Watanabe, G. Ianniruberto, G. Marrucci, Primitive chain network simulation of elongational flows of entangled linear chains: stretch/orientation-induced reduction of monomeric friction. *Macromolecules*, (2012), 45, 2773.

26. S. Costanzo, Q. Huang, G. Ianniruberto, G. Marrucci, O. Hassager and D. Vlassopoulos, Shear and extensional rheology of polystyrene melts and solutions with the same number of entanglements, *Macromolecules*, (2016), 49, 3925.

27. E. van Ruymbeke, V. Shchetnikava, Y. Matsumiya and H. Watanabe, Dynamic dilution effect in binary blends of linear polymers with well-separated molecular weights. *Macromolecules*, (2014), 47, 7653;

28. T. Shahid, Q. Huang, F. Oosterlinck, C. Clasen, E. van Ruymbeke, Dynamic dilution exponent in monodisperse entangled polymer solutions. *Soft Matter*, (2017), 13 (1), 269.

29. P. S. Desai, R.G. Larson, Constitutive model that shows extension thickening for entangled solutions and extension thinning for melts. *Journal of Rheology*, (2014), 58, 255.

References

30. Ianniruberto, G.; Extensional Flows of Solutions of Entangled Polymers Confirm Reduction of Friction Coefficient. *Macromolecules*, 48, 6306–6312 (2015).
31. Costanzo, S.; Huang, Q.; Ianniruberto, G.; Marrucci, G.; Hassager, O.; Vlassopoulos, D.; Shear and Extensional Rheology of Polystyrene Melts and Solutions with the Same Number of Entanglements. *Macromolecules*, 49, 3925–3935, (2016).
32. Park, G. W.; Ianniruberto, G. Flow-induced nematic interaction and friction reduction successfully describe PS melt and solution data in extension startup and relaxation. *Macromolecules*, 50, 4787–4796, (2017).

Chapter 9

Analytical analysis of capillary thinning and breakup of inviscid FENE-P fluids.

The applicability of dilute polymer solutions in free surface flow processes that involve a strong extensional component depends to a large extent on the longevity of the filament that forms after the development of a Rayleigh instability on an initial liquid bridge and that connects two consecutively forming droplets. Based on the analysis of V. Entov and J. Hinch⁵, the stability and thinning dynamics of this liquid bridge has been described theoretically in great detail, and the predicted dynamics have been confirmed experimentally in several publications^{14, 17}. In particular, a recent publication by C. Wagner et al.⁶ describes an analytical solution for this elastocapillary (EC) balance regime, that allows a quantitative description of the breakup time for a known relaxation time and finite extensibility of the polymer in solutions once the onset point of this EC regime. However, their analysis for the description of this onset point was based on the assumption of a viscous fluid. Since many dilute polymer in practical applications involve solvents that behave initially inviscid, we present in this paper an analytical solution for the evolution of the polymer stretch in an inviscid solvent base on the FENE-P model, that allows us to quantitatively predict the breakup time of inviscid-elastic filaments. Predictions of this model are compared to experimental results for a number of model polymer solutions that span the relevant range of intrinsic Deborah and Elastocapillary numbers for actual applications.

9.1. Introduction:

The extensional properties of elastic liquids such as polymers play an important role during their processing phase or in application. In many industries and during processing samples experience mixed flow fields that can be partially of strong extensional flows: like spray coating, calendering, film blowing etc. Furthermore, a lot of these elastic liquids are also applied in extensional flow. Also the cobwebbing behavior of printing ink^{1,2} formulations during flexographic printing can be linked to their elongational flow behaviour. Thus, it is essential to characterize and understand the elongational properties of polymer melts and solutions.

As discussed in chapter 1, in recent years a variety of techniques have been developed to measure the extensional properties of a wide range of viscoelastic fluids. Following the work of Entov et al.^{3, 4, 5}, the capillary thinning rheometry became popular with polymer solutions especially in the industries.

Capillary Breakup Extensional Rheometer (CaBER) is a commercially available rheometer, which is commonly used to measure the extensional properties of very dilute polymer solutions. In a CaBER measurement, a liquid sample is placed between two circular parallel plates to form a cylindrical liquid bridge. Then one of the plates is moved such that the sample is subjected to strong extensional flow. The surface tension then causes the sample to thin, which is monitored by either a laser micrometer or a camera. During a CaBER measurement, two different types of active stress are present. One is the driving stress on the sample caused by the capillary pressure and other is the resisting stress coming from the fluid sample itself. Initially, the polymer molecules remain at coil state but with time they start to stretch out with increasing strain rate. As stated in the recent work of Wagner et al.⁶, the resistance at the initial stage mostly comes from the contribution of the solvent as the polymers are not stretched enough to have any kind of impact on the stress. However

with time the radius of the fluid sample decreases and the strain rate increases so that eventually the polymer starts to stretch and at a critical point this polymer stress contribution becomes dominant over the solvent contribution. The resisting stress of the sample now entirely comes from the elasticity of the polymer⁷. Assuming that the solvent contribution originates in its viscosity, the Wagner et al.⁶, developed an analytical solution, which could predict the time evolution of the radius of the filament and the breakup time. However, viscosity is not the only contribution to the stress that the solvent will deliver. In particular for lower viscous fluids as for example the above listed spraying applications or ink-jet printing utilize low viscosity solvents that contribute to the resisting stress dominantly with their inertia rather than with their viscosity.

The inviscid characteristic of such fluids in a jetting operation is easily determined via the Ohnesorge number, $Oh = \frac{\eta}{\sqrt{\rho\gamma R}}$ that compares viscous time scale $t_\eta = \frac{\eta R}{\gamma}$ to the inertial (or Rayleigh) time scale⁷ $t_R = \sqrt{\frac{\rho R^3}{\gamma}}$. A rough estimate of Oh , assuming a surface tension of γ (60 mN/m), density of ρ (1 g/cm³) and dimensions of spraying or jetting nozzle of R (1mm), yields viscosity of ~ 50 mPas at the critical or transitional Ohnesorge number of $Oh = 0.2$ ¹⁸. Thus one can expect for solvents below this viscosity level to exhibit a dominating inertia controlled thinning before viscosity sets it. Other dimensionless groups relevant in this work and will appear later are the Deborah number and the Elastocapillary number. The Deborah number is defined as the ratio of the characteristic elastic relaxation time λ of the fluid to the characteristic process time. Depending on whether viscous or inertial forces are dominant, this characteristic process time is either t_η or t_R . On the other hand, the elastocapillary number is defined as the ratio between the elastic modulus G of the fluid and the initial capillary pressure γ/R_0 .

The objective of this work is very similar to the work of Wagner et al.⁶ that established a solution for a viscous/elastic system: here we would like to introduce a solution for an inertial/elastic system, which we believe, is for several applications more relevant. Due to the ever-growing interest in capillary thinning rheometry in industries, it is worthwhile to have a complete analytic solution. So we do a full-scale analysis of capillary breakup of FENE-P fluids and obtain analytical solution for the evolution of the minimum-filament radius, $R(t)$ and the breakup time, t_b .

In order to achieve this, we start with the Entov and Hinch⁵ form of the FENE-P constitutive model. First, we evaluate the evolution of minimum-filament radius, $R(t)$ in the inertial capillary regime where the fluid inertia is the dominant factor and the elastic stress from the polymer is negligible. Then in the elasto-capillary regime, where the elastic stress from the polymer chain becomes dominant and the inertial stress is negligible. Now to have the complete solution, we need to determine the transition conditions from the inertial capillary regime to the polymer stress dominated regime.

Usually the breakup time is tuned via the elastic thinning regime. This is because the inertial regime is usually fixed by the chosen solvent (variation by changing the solvent is rather limited due to the limited range of solvent densities). Furthermore the elastic thinning regime is usually longer than the inertial regime, so variation of this regime is much more effective to vary the total breakup time.

The elastic thinning regime depends solely on the relaxation time λ (as shown later in eq. 1). For dilute systems, where inertia/elasticity controlled thinning consideration are applicable, the (Zimm) relaxation time is solely controlled by the molecular weight (an independent of concentration),

$$\lambda = \frac{[\eta] \eta_s M_W}{RT}, \quad (1)$$

so that adjustments to λ or the Deborah number, $De = \lambda/t_R = \sqrt{\lambda^2 \gamma / \rho R^3}$ as for inertial/elastic systems applicable non-dimensional group, are usually done via the molecular weight M_w (and in particular high M_w molecules are chosen as most effective). Polymer concentration is also going to affect the thinning process (and in particular when leaving the dilute regime λ will no longer remain concentration independent but rise). However, in that case also the viscosity will rise so that one leaves the inviscid, inertia controlled regime.

For our considerations the concentration is mainly affecting the modulus, $G = \eta/\lambda$ in the solution, which we capture with the non-dimensional elastocapillary number $Ec = GR/\gamma = \lambda R/\eta\gamma$. For a constant λ in the dilute regime, the concentration is thus affecting the modulus,

$$G = nkT, \quad (2)$$

via an increase of G directly proportional to the number concentration of molecules n . For the problem at hand, G (and thus concentration) are mainly controlling the build up of elastic stress during the initial inertial controlled thinning, and therefore the time (and filament radius) at the transitional point. (This is usually less effective for adjusting the breakup time then controlling λ). Although it is easy to span numerically the full range of De and Ec values, we will focus in this chapter on combinations and ranges of De and Ec that are possible (since they are linked via λ) and that are feasible with respect to De and Ec values that can actually be achieved with available polymers. This will be made possible also by experimentally determining the actual values of G, λ and η to absolutely compare experimental results to numerical simulations as well as analytical solutions.

By combining all these results, we end-up with a full analytical solution for CaBER measurements of initially inertia-dominated FENE-P fluids. Also, we propose a simple approach to evaluate the break-up time of these samples, which is influenced by the finite extensibility of the polymer. At the end, we compare our analytical solution with the full numerical solution, as well as experimental results. In this work, high molar mass polyethylene oxide was used as polymer sample, which is also used as a water-soluble industrial additive to enhance the rheological product performance.

This chapter is organized as follow. At first, in Section II, the material used in this study as well as the experimental technique is presented. Then, in Section III, the derivation of the analytic solution is presented very briefly. The results are presented and discussed in Section IV, where the analytic solution is compared with experimental results and numerical simulations. In section V, a simple approach to evaluate the breakup time of the samples is presented. Finally in Section VI, conclusions are drawn.

9.2. Materials and methods:

To check the efficiency of the analytical solution, it was compared with experimental results obtained from CaBER measurements in addition to numerical simulations. In this section, a brief description of the material used in this study and the experimental technique is presented.

9.2.1 Materials and solution preparation:

The polymer samples investigated in this work are nearly monodisperse linear polyethylene oxide diluted in distilled water. Similar solutions have been used in literature to study the capillary breakup behavior⁸⁻¹². To have a good comparative study over a range

of molecular weights, three different molecular weight PEO samples were used in this work. The samples were purchased from DOW, USA ($M_w = 200$ Kg/mol & 4000 Kg/mol) and Sigma Aldrich, Belgium ($M_w = 1000$ Kg/mol).

The solutions were prepared by allowing the polymer to dissolve in distilled water on a rolling bench for 24 hours. The samples were shielded from light by using aluminum foil. To minimize the effect of degradation of polymer all experiments were performed within 72 hours of preparation.

A total of six different concentrations of PEO diluted in water were prepared. The concentrations were chosen such that the solutions range from the dilute to the semi dilute regime. The critical overlap concentration of our system was calculated from Graessley's definition¹³,

$$c^* = \frac{0.77}{[\eta]}, \quad (3)$$

where η is the intrinsic viscosity of the polymer solution which depends on the molar mass of the chain in accordance with the Mark–Houwink–Sakurada equation $[\eta] = K_{[\eta]}M^a$, where $K_{[\eta]}$ is a constant and the power-law index, a varies ($0.5 \leq a \leq 0.8$) with the quality of the solvent. All prepared samples and their different properties are listed in the table 1.

9.2.2 Methods:

The experiments were performed with the CaBER-1 extensional rheometer (Thermo Haake GmbH, Karlsruhe, Germany), with a high-speed camera (Fastcam SA2, Photron, USA) to track the evolution of the minimum-filament diameter. This high-speed camera replaces the

usual laser micrometer to give us a better view and resolution of the minimum-filament diameter evolution.

The experiments were done at room temperature (22°C) with parallel circular disks of radius $R_0 = 2$ mm. These small disks were used to reduce the gravitational sagging. The initial gap for all the CaBER measurements was $L_0 = R_0 = 2$ mm and the final gap was $L_1 = 5$ mm. The fluid samples were loaded between the plates with a syringe to avoid air bubbles in the fluid. Images were taken at 3000 fps and with a shutter time of 1~10 μ s. The images were analysed with the Matlab based algorithm Edgehog, developed at KU Leuven²⁷.

Each measurement was repeated at least 3 times (with fresh samples) to confirm the reproducibility of the results.

The viscosities of the entire polymer solutions used in this work are near the lower detection limit of the rotational rheometer. So more sensitive Ubbelohde viscometer was used. All samples with corresponding properties are listed in table 1,

Table 1 a) Properties of different samples. The E_c is calculated based on the numerically observed elastic modulus.

Samples	Molecular Weight, M_w [Kg/mol]	Critical Concentration c^* [%] wt	Prepared Concentration c [%]	Dynamic Viscosity η [mPa s]
1	200	0.38	1	2.87
2	200		2	6.34
3	200		4	24.53
4	1000	0.13	0.1	1.72
5	4000	0.055	0.005	1.08
6	4000		0.01	1.15

continued...

Samples	Elasto-Capillary number, Ec	Deborah number, De	Ohnesorge number, Oh	Relaxation time, λ [s]
1	0.2822	0.07	0.0103	$0.4 \cdot 10^{-3}$
2	0.2096	0.12	0.0224	$0.702 \cdot 10^{-3}$
3	0.0149	0.44	0.0858	$2.65 \cdot 10^{-3}$
4	0.0082	0.43	0.0069	$1.78 \cdot 10^{-3}$
5	0.0024	1.56	0.0043	$6.1 \cdot 10^{-3}$
6	0.0025	1.78	0.0047	$7.14 \cdot 10^{-3}$

Table 1 b) Comparison of elastic modulus of different samples and methods.

Samples	Theoretical Elastic Modulus (Zimm-Rouse theory) [Pa]	Elastic Modulus observed in numerical simulation [Pa]	Elastic Modulus observed in analytical solution [Pa]	$G = \eta/\lambda$ [Pa]
1	121.83	14	14	7.18
2	243.66	10	10	9.03
3	487.32	0.7	0.7	9.25
4	2.16	0.5	0.5	0.96
5	0.03	0.15	0.15	0.17
6	0.061	0.16	0.16	0.16

9.3. Definitions and derivation of the analytical solutions:

In this work, we analyze dilute polymer solution systems in low-viscosity solvents. So we start by considering a polymer of molecular weight, M_w , diluted in a solvent with solvent viscosity, η_s (negligible). The polymer has finitely extensible chains, which can be assumed as dumbbells with spring constant H and fully stretched chain length of Q_o . For a capillary breakup measurement the fluid sample is loaded between two parallel plates to form a cylindrical filament. We consider for this sample a uniform initial radius of R_o at temperature T , and the surface tension that acts upon the filament is γ .

9.3.1. Entov and Hinch form of the FENE-P model:

We are going to solve in the following a 0D model description of the filament, the axial stress balance at the minimum radius. In principle an axisymmetric object as the filament considered here would require at least a 1D model description to capture correctly the axial tension in the liquid filament. However, it has been shown in the past that the self-similar shape of a slender filament allows to describe the axial tension simply with the evolution of the filament radius, which justifies the use of a 0D description or simple stress balance for thinning regimes for which such similarity solutions have been established. According to Tirtaatmadja et al.⁸, the relevant stress balance of a FENE-P liquid is

$$\frac{\gamma}{R} = \frac{F_T}{\pi R^2} - \frac{1}{2} \rho \dot{R}^2 - 3\eta_s \dot{\epsilon} - \Delta\tau_p, \quad (4)$$

where $\frac{\gamma}{R}$ contains the radially driving surface pressure $-\frac{\gamma}{R}$ and the line tension contribution $+\frac{2\pi R\gamma}{\pi R^2}$ that strives to contract the filament in the

axial direction to minimize the free surface¹⁷. $\frac{1}{2}\rho\dot{R}^2$ is the resisting stress from the inertia of the fluid, $3\eta_s\dot{\epsilon}$ is the resisting stress from the solvent viscosity with the uniaxial extension rate

$$\dot{\epsilon} = -\frac{2\dot{R}}{R}, \quad (5)$$

and $\Delta\tau_p$ is the elastic resistance stress caused by from the elasticity of the polymer in sample. F_T represents the tensile force throughout the filament that remains when balancing all the other stress and that shows up as an integration constant when solving the full Navier-Stokes equations²⁴.

Whereas the inertial, viscous and surface tension contributions in the stress balance of eq. (4) simply depend on R or dR/dt , the elastic stress $\Delta\tau_p$ and the axial tension F_T contributions are more complex. F_T depends on the shape and thus curvature and surface pressure and line tension distribution along the whole filament. However, the specific filament shape at a given time is generally related to the dominance of certain fluid properties in the stress balance. This allowed to formulate analytical solutions for F_T for certain thinning regimes, and we will show in the following analytical solutions for the overall thinning dynamics in regimes dominated by a certain fluid parameter

For a uniform, cylindrical filament and a time varying uniaxial elongational flow, the tensile force is $F_T = 2\pi\gamma R$. (and takes on in this specific case the value of the line tension).

For an actual CaBER experiment the filament is connected to two fluid drops on the stationary end plates. The curvature at the transition to the droplets disturbs uniformity and adds an extra contribution to the axial tension F_T (in addition to the line tension). For a viscous filament the stress balance balance of eq. (4) reduces to

Definitions & derivation of the analytical solution

$$\frac{\gamma}{R} = \frac{F_T}{\pi R^2} - 3\eta_s \dot{\epsilon}, \quad (6)$$

and the extra contribution to F_T can only be compensated by a change of the extension rate in the viscous term in eq. (6). McKinley et al.¹⁴ showed that the observed faster thinning dynamics of a viscous filament still indicate a linear relation of the axial tension to the radius, but with $F_T = 2X\pi\gamma R$. Furthermore, they showed that the observed factor X was close to the one theoretically predicted by ref. [25] from a similarity analysis of the evolution of a viscous filament connected to spherical enddrops, which gave $X = 0.7127$.

For an elastically dominated stress the balance of eq. (4) reduces to

$$\frac{\gamma}{R} = \frac{F_T}{\pi R^2} - \Delta\tau_p, \quad (7)$$

The elastic stress $\Delta\tau_p$ can be described for a dilute polymer solution by the FENE-P model as done in the original work of Entov and Hinch⁵. The elastic stress $\Delta\tau_p$ is expressed in terms of the dimensionless microstructural configuration tensor $A = \frac{\langle QQ \rangle}{Q_{eq}^2}$ that relates the ensemble average of the second moment tensor $\langle QQ \rangle$ to the equilibrium size of the polymer coil, Q_{eq} . Here, Q is the connector vector between the two ends of the dumbbell, Q_{eq} is the end-to-end distance at equilibrium and $\langle . \rangle$ represents an ensemble average over all dumbbells. Replacing $\Delta\tau_p$ in eq. (7) in terms of the microstructural configuration tensor yields,

$$\frac{\gamma}{R} = \frac{F_T}{\pi R^2} - GZ(A_{zz} - A_{rr}), \quad (8)$$

Here, A_{rr} & A_{zz} are the radial and axial components of the microstructural configuration tensor respectively. The evolution equations for the two components following the FENE-P model are,

$$\dot{A}_{zz} = 2\dot{\epsilon}A_{zz} - \frac{1}{\lambda}(ZA_{zz} - 1), \quad (9)$$

and,

$$\dot{A}_{rr} = -\dot{\epsilon}A_{rr} - \frac{1}{\lambda}(ZA_{rr} - 1), \quad (10)$$

where

$$Z = \frac{1}{1 - \frac{A_{zz} + A_{rr}}{L^2}}, \quad (11)$$

and L is the finite extensibility parameter, which represents the ratio of fully extended polymer dumbbell to its equilibrium length. The parameter L can be calculated for a polymer coil in solution from molecular parameters via²⁸

$$L = \sqrt{3} \left(\frac{j \sin^2(\theta_b/2) M_w}{C_\infty M_u} \right)^{1-\nu}, \quad (12)$$

where θ_b is the average bond angle in the monomer, j is the number of bonds of a monomer, M_u is the monomer molar mass, C_∞ is the characteristic ratio and ν the excluded volume exponent for a given polymer-solvent system.

For the axial tension F_T in the viscoelastic filament Entov and Hinch²¹ assumed again a cylindrical filament but neglected the line tension term contained in eq. (8) and consequently set the total axial tension F_T in the jet to be equal to the bulk contribution, which they assumed to vanish. Later, Fontelos & Li¹⁶ and Clasen et al.¹⁷ solved the stress balance with an asymptotical analysis in the center of the thread and on the end drops to obtain a complete expression for the tensile force F_T with a similarity analysis in the corner region where the filament is attached to the end drops. This analysis showed that the tensile force

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in eq. (8) of the viscoelastic filament for a CaBER experiment is also linearly related to the filament diameter so that still $F_T = 2X\pi\gamma R$ albeit with a different front factor of $X = 3/2$. Inserting this into so equation in eq. (8) yields,

$$\frac{\gamma}{R} = \frac{1}{2} GZ(A_{zz} - A_{rr}), \quad (13)$$

Following Entov & Hinch we assume that finite extensibility starts to influence only at the end and causes the breakup of the filament. In particular at the onset of the elastic capillary regime that we are going to focus on in the following we can set $Z = 1$. Furthermore, as the elastic capillary regime follows the inertial thinning regime during which the polymers get stretched, the axial deformation is much more prominent than the radial deformation so that $A_{zz} \gg A_{rr}$ and the stress balance further simplifies to

$$\frac{\gamma}{R} = \frac{1}{2} G A_{zz}. \quad (14)$$

Following Entov & Hinch we solve eq. (9) in this elasto-capillary regime with $Z = 1$ and $A_{zz} \gg 1$ and the definition of extension rate in eq. (5). Since the elasto-capillary regime follows after a transition from the initial inertial thinning regime, we denote this transition with a superscript $*$ such that the boundary conditions at the onset of the elasto-capillary regime are $t = t^*$, $A_{zz} = A_{zz}^*$ and $R = R^*$, so that

$$A_{zz} = A_{zz}^* e^{\frac{t-t^*}{\lambda}} \left(\frac{R^*}{R}\right)^4. \quad (15)$$

Combining this solution with eq. (13) one obtains for the evolution of A_{zz} and the radius in the elasto-capillary regime

$$A_{zz} = A_{zz}^* e^{\frac{t-t^*}{3\lambda}} \quad (16)$$

and

$$R = R^* e^{\frac{t^* - t}{3\lambda}}. \quad (17)$$

We can non-dimensionalize eqs. (15) and (16) with $h = \frac{R}{R_o}$ and $\tau = \frac{t}{t_R}$ to

$$A_{ZZ} = A_{ZZ}^* e^{\frac{\tau - \tau^*}{3De}} \quad (18)$$

$$h = h^* e^{\frac{\tau^* - \tau}{3De}}. \quad (19)$$

Here, $De = \lambda/t_R$ is a Deborah number using the Rayleigh time t_R as the characteristic time scale. In the above equation we have two unknown terms, A_{ZZ}^* and τ^* which are the axial polymer deformation and time respectively at the transition point between the inertial thinning regime and the elasto-capillary regime. This requires a description of the thinning dynamics of this inertial regime

In case that the initial thinning regime is dominated by inertia, the 0D model of eq. (8) reduces for such an inviscid filament to

$$\frac{\gamma}{R} = \frac{F_T}{\pi R^2} - \frac{1}{2} \rho \dot{R}^2. \quad (20)$$

It should be noted that the axial force F_T in a filament that thins with inertial contributions to the stresses is not necessarily constant along the filament, different from a visco-capillary or elasto-capillary balance where the absence of inertial contributions Newton's third law implies that the axial force along the filament is constant^{14, 24}. However, capillary thinning experiments of inertia dominated fluids have shown a pinching of the filament near the end drops with a self-similar profile when rescaling dimensions with the length scale

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$\left(\frac{\gamma(t_i-t)^2}{\rho}\right)^{1/3}$ (where t_i is the breakup time of the inertial filament, and which is easily obtained from the Rayleigh time $t_R = \sqrt{\frac{\rho R_0^3}{\gamma}}$), and similarity solutions show that the filament radius should indeed scale with this length scale²⁴. This points to the fact that it is possible to formulate the low-dimensional representation of the stress balance of eq. (20) with an integrated (average) force F_T . Indeed the basic stress balance equation of eq. (20) has a solution in form of

$$R = \tau_i^{-2/3} \left(\frac{\gamma}{\rho}\right)^{1/3} (t_i - t)^{2/3}, \quad (21)$$

where t_i is the break-up time of a purely inertia controlled thinning filament, and the prefactor $\tau_i = \frac{t_i}{t_R}$ is the rescaled breakup time. This scaling and the appearance of a constant prefactor $\tau_i^{-2/3}$ have first been confirmed by simulations of Day et al.¹⁵. It can easily be shown that eq. (20) is obtained when differentiating eq. (21) once and eliminating time. Representing the axial tension in eq. (20) again in form of $F_T = 2X\gamma\pi R$, then the prefactor X is related to the constant $\tau_i^{-2/3}$ as

$$X = \frac{1}{9\tau_i^2} + \frac{1}{2}, \quad (22)$$

and we can reformulate eq. (20) as

$$\frac{\gamma}{R} = \frac{9\tau_i^2}{4} \rho \dot{R}^2. \quad (23)$$

The value of the constant prefactor $a = \tau_i^{-2/3}$ in eq. (21) has been determined by Wagner et al.¹⁹ from the Day paper as $a = 0.7$ and by Tirtaatmadja et al.⁸, calculated from a full numerical simulation in Chen, Notz et al.²⁰, also as 0.7 in ref [8], and later recalculated by

Rodd et al.²¹ as $a = 0.64$. We are going to use the latter value of $\tau_i^{-2/3} = 0.64$ or $\tau_i = 1.953$ for the radius evolution of filament in the inertial-capillary regime in eq. (20) in the following, which gives from eq. (21) for the prefactor in the axial force $F_T = 2X\pi R$ a value of $X = 0.529$. Finally, non-dimensionalising eq. (20) with $h = \frac{R}{R_o}$ and $\tau = \frac{t}{t_R}$ yields

$$h = \left(1 - \frac{\tau}{\tau_i}\right)^{2/3} \quad (24)$$

This defines the time required for a filament to break only in presence of the inertial resistance to the capillary pressure (if elastic resistance from the polymer was absent during entire time in the system).

In the following we are going to introduce analytical solutions for the evolution of the polymer deformation $\mathbf{A}$ in the initial, inertia controlled regime, based on the above presented solutions of the filament thinning dynamics in eq. (23). This will then be used to determine $\mathbf{A}^*$ in eq. (18) to calculate the remaining thinning. These analytical results will be compared to numerical solutions of the polymer stress of the evolution Eqs. (9) and (10) with (11) and (5) and the relevant stress balance over the whole range (obtained from eq. (4) neglecting only the viscous contribution, and using the FENE description for the polymer stress):

$$\frac{\gamma}{R} = \frac{F_T}{\pi R^2} - \frac{1}{2}\rho\dot{R}^2 - GZ(A_{zz} - A_{rr}) \quad (25)$$

The normalized forms of this coupled set of ODEs,

$$De\dot{A}_{zz} + 4De\frac{\dot{h}}{h}A_{zz} = -ZA_{zz} + 1 \quad (26)$$

$$De\dot{A}_{rr} - 2De\frac{\dot{h}}{h}A_{rr} = -ZA_{rr} + 1 \quad (27)$$

$$-\dot{h} = \sqrt{\frac{4}{9\tau_i^2} - 2hEcZ(A_{zz} - A_{rr})} \quad (28)$$

with eq. (11), are solved numerically in Matlab with an implicit BDF-solver (routine ode15s) in order to describe the evolution of the filament radius and microstructural configuration in time.

9.3.2 Transition from Inertia capillary regime to Elastocapillary regime:

During a capillary thinning measurement, initially the polymer chains are at coil state. So the resisting force opposing the capillary pressure comes entirely from the fluid inertia. With time, the strain rate increases and with that the polymer chains become stretched. Eventually the polymeric stress $\Delta\tau_p$ caused by the stretching polymer chains increases to a similar order of magnitude as the inertial stress, resulting in a transition from the inertia-capillary thinning regime of eq. (23) to the elastocapillary thinning of eq. (18). Assuming thus an equal contribution from both stresses opposing the driving capillary pressure at this transition point we can balance eqs. (13) and (22)

$$\frac{9\tau_i^2}{4}\rho\dot{R}^{*2} = \frac{1}{2}GA_{zz}^*. \quad (29)$$

Since we assume that up to this point the flow was controlled by the inertial-capillary balance, we can obtain $\dot{R}$ from differentiating eq. (21) as

$$\dot{R} = -\frac{2}{3\tau_i^{2/3}}\left(\frac{\gamma}{\rho}\right)^{\frac{1}{3}}(t_i - t)^{-\frac{1}{3}} \quad (30)$$

By equating Eqs. (28) and (29) we obtain the time t^* of inertial thinning that it takes to reach the transition

$$\left(\frac{\tau_i\sqrt{\rho\gamma}}{(t_i - t^*)}\right)^{2/3} = \frac{GA_{ZZ}^*}{2}. \quad (31)$$

Non-dimensionalising we have,

$$\left(1 - \frac{\tau^*}{\tau_i}\right)^{-2/3} = \frac{EcA_{ZZ}^*}{2}. \quad (32)$$

What remains now is to determine what A_{ZZ}^* is at the transition point t^* or τ^* . In order to obtain the relation of A_{ZZ} and τ we need to calculate the evolution of the axial microstructural deformation A_{ZZ} in the inertia capillary regime and determine its value at the transition conditions. For this we need to solve again the evolution equation for A_{ZZ} , but now with the extension rate for an inertia controlled thinning. Inserting the inertial radius evolution of eqs. (20) and (29) into eq. (5) we obtain for this strain rate in the inertial regime $\dot{\epsilon} = 4/3(t_i - t)$ or in dimensionless form:

$$\dot{\epsilon} = \frac{4}{3(\tau_i - \tau)}. \quad (33)$$

We can now insert this strain rate into equation (9), and applying the usual assumption $A_{ZZ} \gg 1$ and $Z = 1$ (similar to the approach of Entov and Hinch⁵ used for eq. (13) to derive eq. (14) for the elasticity dominated regime) we can solve to obtain a simple analytical solution for the A_{ZZ} evolution in an inertia dominated filament:

$$A_{ZZ} = e^{-\frac{\tau}{De}} \left(1 - \frac{\tau}{\tau_i}\right)^{-8/3} \quad (34)$$

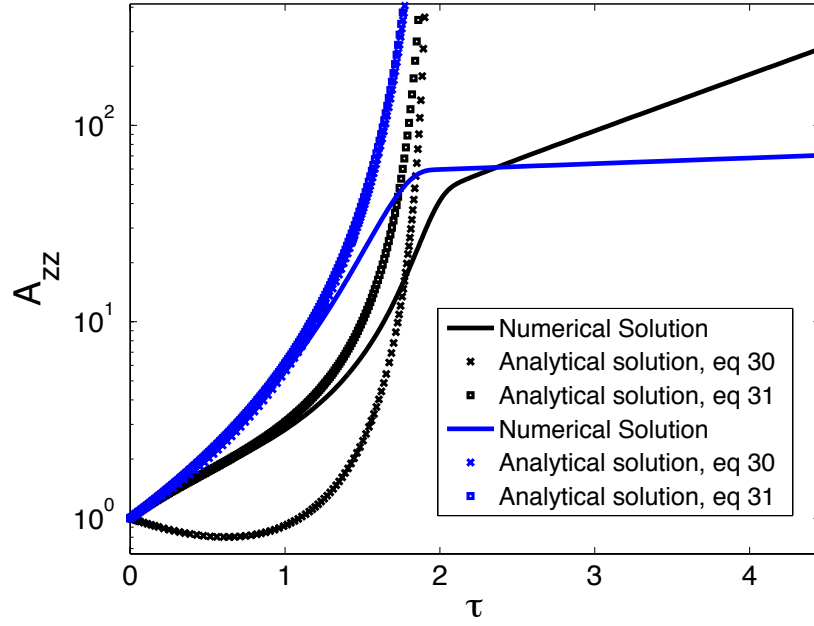


Fig. 9.1. Comparison of axial microstructural configuration with and without the assumption (between numerical and analytical) in Inertia capillary regime. Blue line and symbols corresponds to a solution with $De = 5$, $Ec_0 = 0.05$ and black line and symbols corresponds to a solution with $De = 0.5$, $Ec_0 = 0.1$.

Comparing in Fig. 9.1 this analytic result with the numerical solution shows that the assumption $A_{ZZ} \gg 1$ that was necessary to obtain the simple solution in eq. (33) is a delicate one. It is obvious from the evolution eq. (9) that the negative second term on the right hand side (which is affected by the assumption that $A_{ZZ} - 1 \approx A_{ZZ}$) will only be negligible at early stages if λ or De is large. And this can be seen in Fig. 9.1 for $De = 5$ where the simple solution of eq. (33) matches the initial regime of the numerical simulations.

However, for small De the second term on the right hand side of eq. (9) becomes larger and non-negligible, and the assumption $A_{ZZ} - 1 \approx A_{ZZ}$ causes an overprediction of the relaxation of A_{ZZ} at small deformations. And this is indeed obvious in Fig. 9.1 for $De = 0.5$ where the overprediction of the relaxation term causes A_{ZZ} to drop to unrealistic values < 1 .

However, it is possible to find an analytical solution for the combined eqs. (9) and (32) also without the unrealistic assumption that $A_{ZZ} \gg 1$, so assuming only $Z = 1$ for eq. (9). This gives

$$A_{ZZ} = e^{\frac{-\tau}{De}} \left(1 - \frac{\tau}{\tau_i}\right)^{-8/3} + \left(\frac{\tau_i - \tau}{De}\right)^{-8/3} e^{\frac{\tau_i - \tau}{De}} \left(\Gamma\left(\frac{11}{3}, \frac{\tau_i}{De}\right) - \Gamma\left(\frac{11}{3}, \frac{\tau_i - \tau}{De}\right) \right), \quad (35)$$

where $\Gamma(s, x)$ is the lower incomplete gamma function,

$$\Gamma(s, x) = \int_0^x t^{s-1} e^{-t} dt. \quad (36)$$

As we see from Fig. 9.1, the full analytical solution eq. (34) matches the numerical solution also for low De .

For the sake of completeness, we would like to point out that a similar derivation of an analytical solution for when $A_{ZZ} \sim 1$ can also be made for the viscous case, for which Wagner et al.⁶ had already introduced a simple solution similar to our eq. (33). This is further discussed in Appendix 1.

It should be noted that this approach is fundamentally different from the one used in Wagner et al.⁶. They obtain A_{ZZ}^* by making the assumption that at and after the transition A_{ZZ} will not change as drastically as before and assume thus that after the transition $\dot{A}_{ZZ} = 0$ in ref. [6]. This assumption allows an easy solution of the evolution

eq. (9), with the main advantage that their equation still contains the finite extensibility and is thus applicable also for smaller molecules that can reach their stretch limit within the initial regime, which indeed requires $Z > 1$. However, our numerical solutions for A_{zz} in fig. 9.1 show clearly that $\dot{A}_{zz} \neq 0$ after the transition, in particular for smaller values of De (and this is independent from an initially viscous or inertia dominated flow), so for smaller molecules for which the inclusion of finite extensibility effects and $Z > 1$ was intended. Furthermore, De will be lowered for the same molecular weight when the solvent viscosity is decreased, making the Wagner approach less applicable for inviscid solutions. On the other hand, our approach to obtain the evolution of A_{zz} up to A_{zz}^* as presented in eq. (34) is independent of assumption $\dot{A}_{zz}$ after the transition, but ignores finite extensibility effects during the initial stage and is thus also prone to deviations for smaller molecules as the Wagner approach.

We can now finally solve eqs. (34) and eq. (31) for an implicit expression for τ^* as well as for A_{zz}^* . This analytical solution for τ^* is compared in Fig. 9.2 to the numerically obtained results for different values of De and Ec . (A comparative study of these transition time compared to the approach of Wagner et al is presented in Appendix 2.)

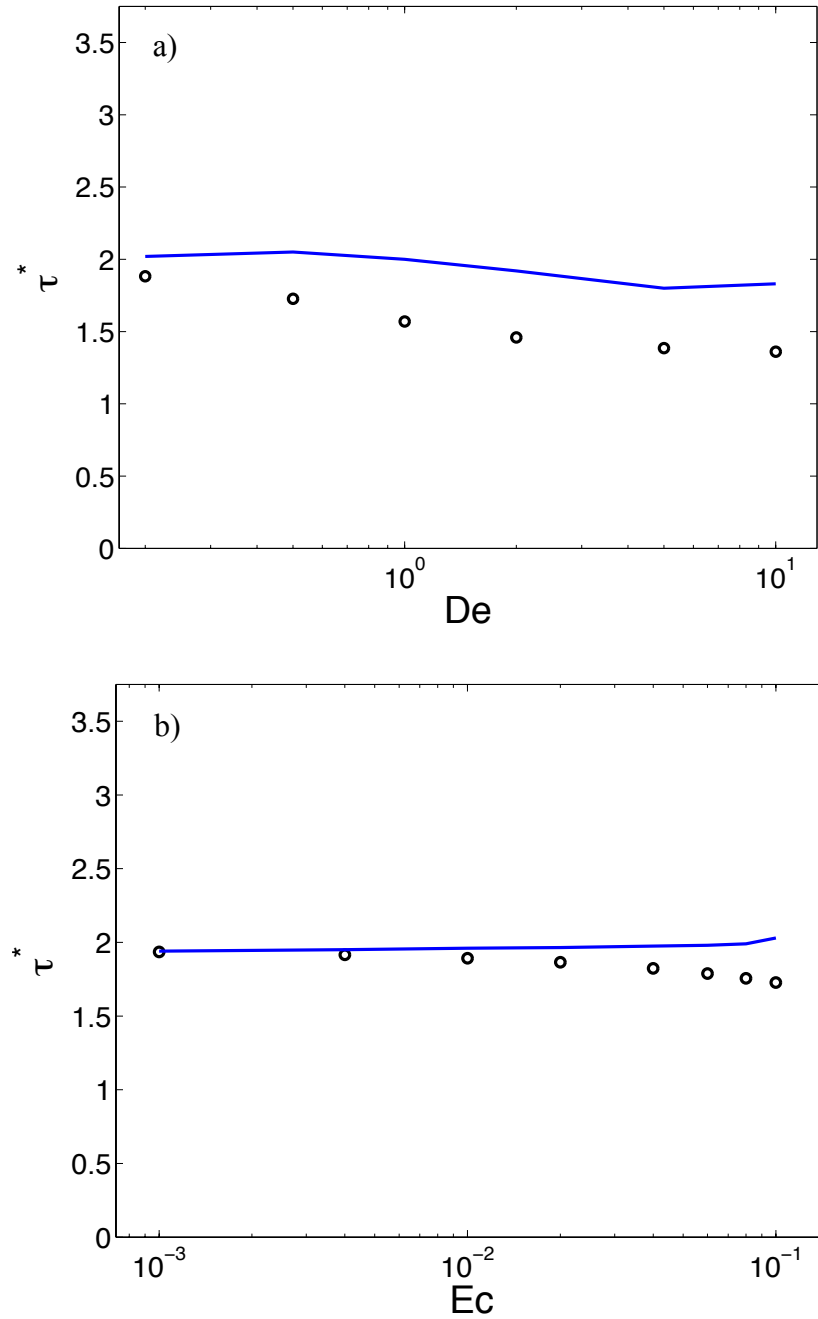


Fig. 9.2. Comparison of the transition time between our analytical (black circles) and numerical solutions (blue lines). a) Ec is kept

constant (= 0.1) b) De is kept constant (= 0.5). The used parameters in this calculations are noted in Appendix 2.

It is obvious that the transition time τ^* shifts to earlier times for an increasing Deborah number as well as an increasing elastocapillary number. This is expected, as with increasing De and thus relaxation time λ the polymer coils experience less relaxation during the inertial thinning and reach A_{zz}^* earlier. Similarly, a higher concentration and thus via eq. (2) a larger modulus G in Ec lowers the A_{zz}^* necessary in the analytical solution to reach the stress equilibrium at τ^* . An upper limit for τ^* in Fig. 9.2 can be easily obtained from eq. (31). This is reached for large Deborah numbers, for which we can use the simple solution of eq. (33) for the A_{zz} evolution. Solving eqs. (33) and (31) for τ^* yields

$$\frac{\tau^*}{\tau_i} = 1 - e^{\frac{-\tau^*}{2De}} \sqrt{\frac{Ec}{2}}. \quad (37)$$

For $De \gg \tau^*$ and non-relaxing polymers this simplifies to

$$\frac{\tau^*}{\tau_i} = 1 - \sqrt{\frac{Ec}{2}}, \quad (38)$$

Obviously for $Ec = 0$ and no polymer contribution this results in $\tau^* = \tau_i$. For $Ec = 2$, τ^* becomes 0, which is equivalent to the balance between capillary pressure and polymeric stress in eq. (13) being reached right from the beginning, and thus $A_{zz} \geq 1$ during the whole thinning process.

Fig. 9.2 gives also results for the numerical solution of eqs. (34) – (35), using again the balanced stresses of eq. (28) as the criterion for reaching τ^* . It is obvious that the analytical solution is underpredicting τ^* , and the reason for this could already be seen in Fig. 9.1 that compares the evolution of A_{zz} in time. While the

analytical solutions of eqs. (33) or (34) give the evolution of $A_{zz}(t)$, they are not considering the effect of this extra polymeric stress for the evolution of the filament and thus on the extension rate of eq. (32). The numerical simulation that incorporates this is thus exhibiting an additional deceleration when approaching A_{zz}^* that slightly delays τ^* . Within the range of Ec and De that we are experimentally probing with our polymer solutions, the effect of Ec on the numerically calculated τ^* is, however, much less pronounced. An increasing modulus in eq. 25 and subsequent equation lowers the A_{zz}^* necessary in the analytical solution to reach the stress equilibrium, so τ^* is reached earlier. In the numerical simulations the increasing modulus causes also an increase of the polymer stress in the inertial regime, which counter balances the lowering of τ^* to the point that τ^* is virtually independent of Ec .

Despite the differences observed between the transition times of the numerical and analytical solutions, the values of minimum filament radius h^* (and axial microstructural configuration A_{zz}^*) at the transition point agree quite well. This can be seen clearly in fig. 9.3a and 9.3b, in terms of A_{zz} and h respectively. Also here it is possible to formulate a simple solution for larger De by inserting eq. (36) into eq. (23)

$$h^* = e^{\frac{-\tau^*}{3De}} \left(\frac{Ec}{2} \right)^{\frac{1}{3}}, \quad (39)$$

Which simplifies for $De \gg \tau^*$ to

$$h^* = \left(\frac{Ec}{2} \right)^{\frac{1}{3}}, \quad (40)$$

The green and red curves in fig. 9.3a intersect each other before the transition period but the level of A_{zz} at this point is almost the same as the value of A_{zz} in the intersection point (see fig. 9.3a).

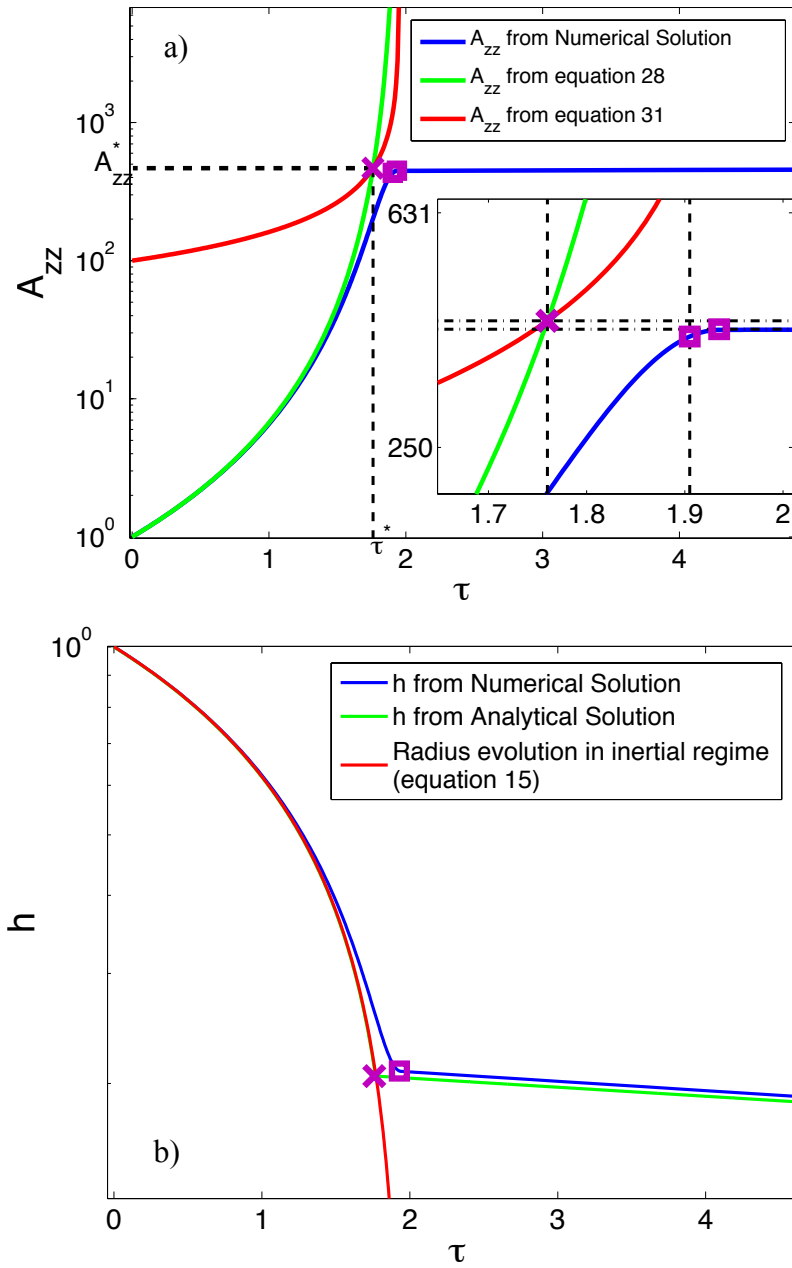


Fig. 9.3. Determining the transition point between inertia capillary and elasto-capillary regime with $De = 10$ and $Ec = 0.01$.

9.3.3 Comparison between the full analytic and the numerical solution:

Combining the results of the previous sections, now we have a full analytical solution of the minimum filament radius and the axial microstructural deformation for initially inertia controlled thinning of weakly elastic polymer solutions:

$$A_{zz} = e^{\frac{-\tau}{De}} \left(1 - \frac{\tau}{\tau_i}\right)^{-\frac{8}{3}} + \left(\frac{\tau_i - \tau}{De}\right)^{-\frac{8}{3}} e^{\frac{\tau_i - \tau}{De}} \left(\Gamma\left(\frac{11}{3}, \frac{\tau_i}{De}\right) - \Gamma\left(\frac{11}{3}, \frac{\tau_i - \tau}{De}\right) \right);$$

for $\tau < \tau^*$ and

$$A_{zz} = A_{zz}^* e^{\frac{\tau - \tau^*}{3De}}; \text{ for } \tau > \tau^*$$
(41)

with τ^* and A_{zz}^* obtained from solving eqs. (34) and eq. (31), and $\tau_i = 1.953$, and

$$h = \begin{cases} \left(1 - \frac{\tau}{\tau_i}\right)^{2/3} & ; \text{ for } \tau < \tau^* \\ h^* \left(e^{\frac{\tau - \tau^*}{3De}}\right) & ; \text{ for } \tau > \tau^* \end{cases}$$
(42)

with h^* obtained from solving eqs. (34), (31) and (23).

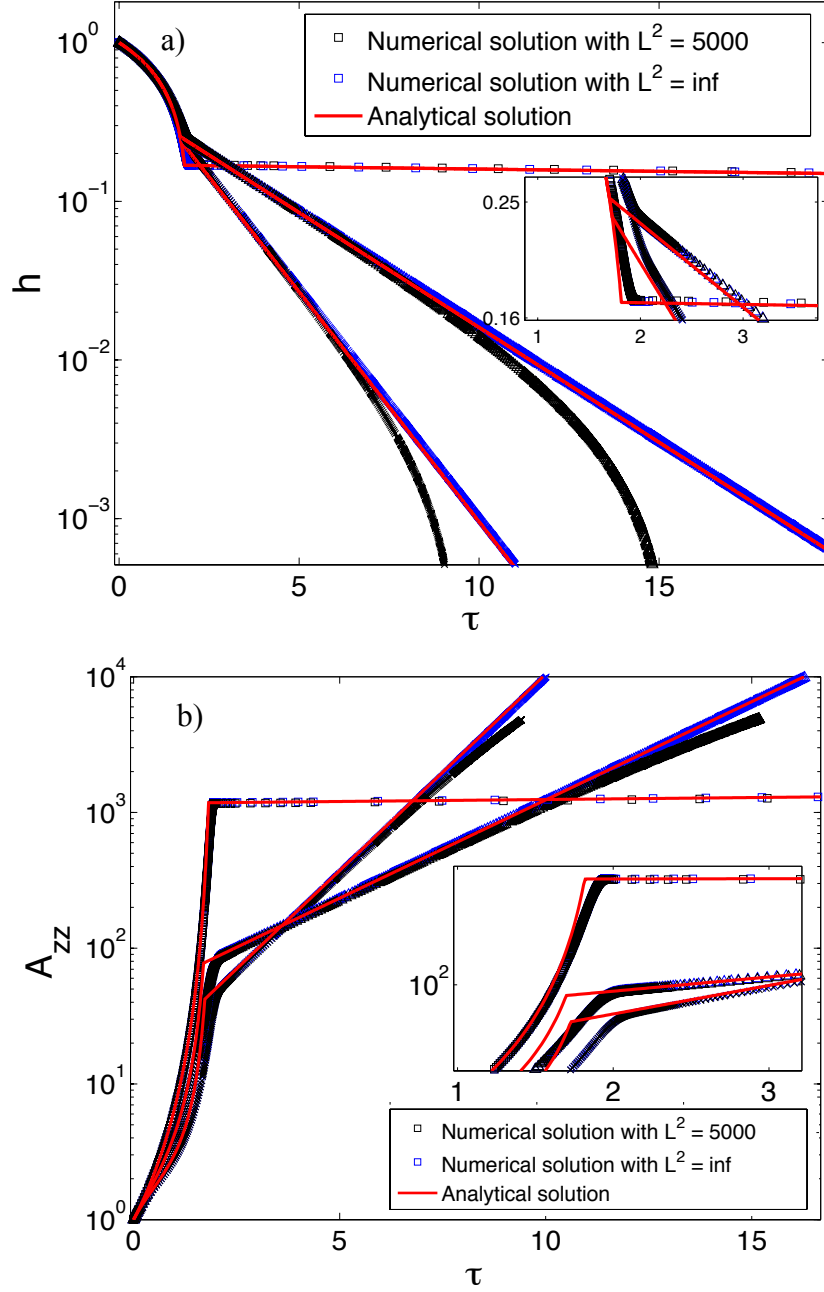


Fig. 9.4. a) Comparison of evolution of minimum-filament radius h from the numerical solution of eqs. (25) – (27) (symbols) with the analytical solution of eq. (41) (straight line), for $De = 0.50$ and $Ec =$

0.1 (X), $De = 1$ and $Ec = 0.05$ (Δ), $De = 50$ and $Ec = 0.005$ ($\square$) and two different values of finite extensibility as indicated in the legend (all other parameters are same as mentioned in Appendix 2). b) comparison of the A_{zz} evolution.

We compare now in Fig. 9.4 our full analytic solution with the numerical simulations. As we can see the analytical solution agrees very well with the numerical simulation during the initial inertial regime but also after the transition period. This might be on a first glance surprising when compared to the observed differences in τ^* in Fig. 9.2. However, it is the good agreement of the transitional radius h^* as demonstrated in Fig. 9.3 that leads eventually to a very similar diameter decay after over the range of investigated elastocapillary and Deborah numbers, albeit with a much sharper transition at h^* for the analytical solution when compared to the numerical.

It is only later in the elasto-capillary regime that deviations can be observed when compared to the numerical results that include effects of finite extensibility. This is not surprising as the derivation of eqs. (17) and (18) for A_{zz} and h in the EC regime, that went in our analytical solutions of eqs. (40) and (41), were based on the assumption that the finite extensibility term of eq. (11) is $Z = 1$. However, in particular for low values of the finite extensibility parameter L this assumption is not correct, as the strong extensional flow causes the polymer chain conformation A_{zz} in eq. (11) to approach L in the elasto-capillary regime already for diameters that are still in an experimentally relevant range. This causes the diameter decay in Fig. 9.4 to deviate from the exponential law of (18) for the lower value of $L^2 = 5000$ and to break in finite time.

To capture this, Wagner et al.⁶ developed recently an analytical solution of the evolution equations, assuming only $A_{zz} \gg A_{rr}$ in the elasto-capillary regime. By combining Eqs. (9) and (5) with the stress balance of eq. (8) (albeit neglecting the axial tension and assuming $F_z = 0$ in eq. (8)), and solving the resulting differential equation they obtained:

$$\left(\frac{1}{1+Ec(L^2+3)} - \frac{1}{1+hEc(L^2+3)}\right) + 3 \ln\left(\frac{1+hEc(L^2+3)}{1+Ec(L^2+3)}\right) +$$

$$4Ec \frac{(L^2+3)}{(L^2+2)}(h-1) = \frac{(L^2+3)^2}{(L^2+3)^2 L^2} \frac{\tau}{De}, \quad (43)$$

This solution was obtained with the boundary $h = 1$ at $\tau = 0$. While an assumption of an already initially valid elasto-capillary balance is obviously not correct, it is possible to match this solution onto an initially solvent dominated thinning regime, as there must be a unique solution of eq. (42) through the linked parameters $Ec' = Ec \frac{R'_0}{R_0}$, that starts at a (lower) initial radius R'_0 such that $h' = \frac{R}{R'_0}$ crosses through $h' = h^*$ at τ^* . Although this requires numerically solving eq. (42) to obtain the Ec' that fulfils this condition, once this is done eq. (42) represents an analytical solution for h that can be used in eq. (41) for $\tau > \tau^*$ to describe the diameter evolution in the elasto-capillary balance regime including the effects of finite extensibility. Fig. 9.4 shows then also this solutions of eq. (43) for $\tau > \tau^*$ with the appropriate Ec' to start the elastocapillary regime at h^* . The comparison to the numerical solutions shows a remarkable agreement even for smaller values of the finite extensibility parameter L .

9.4. Result & discussion:

In this section we compare our analytical solution with experimental data for the different aqueous solutions of PEO described in section III. The experimental results of Caber measurements along with our analytical solutions (as well as the numerical results using the same parameter sets) are shown in the fig. 9.5 and exhibit generally a good agreement.

Of the parameters necessary to feed into the analytical and numerical solutions, the relaxation time λ is kind of a self-fulfilling prophecy, as it is usually obtained from the experimental data to which we compare to, by fitting eq. (16) to the exponentially decaying filament diameter.

Still, once λ is determined for a given polymer concentration, the solutions presented in eqs. (41) and (42) allow to predict the thinning dynamics and break-up times for any given initial filament radius R_0 . The other necessary parameters as surface tension γ and modulus G (for the elastocapillary number), as well as finite extensibility L can be determined independently or directly calculated from molecular parameters via eqs. (2) and (11). However, since the relaxation time is already determined directly from the thinning experiment, an effective modulus G or effective elastocapillary number Ec can also readily be obtained from the experimentally observed h^* and τ^* by solving eqs. (34), (31) and (23) for Ec .

This is in particular useful for larger filament diameters, as gravitational sagging and drainage effects (that have so far been ignored) can be lumped into this effective Ec . Also in case that the experimental observation of the filament thinning is done with a high resolution objective (that prohibits to observe the initial filament radius R_0 as this larger than the field of view), the determination of an effective $Ec = G R_0 / \gamma$ from the transitional h^* and τ^* allows to use and effective R_0 in the calculations.

And finally the finite extensibility can also be obtained from fitting eq. (42) from h^* and τ^* onwards to experimental data to obtain an effective value. Also this concept can be justified, as several other observations have shown that the L determined from molecular parameters is underpredicting the experimentally effective values. The effective values obtained for the data in Fig. 9.5 are given in Table 2.

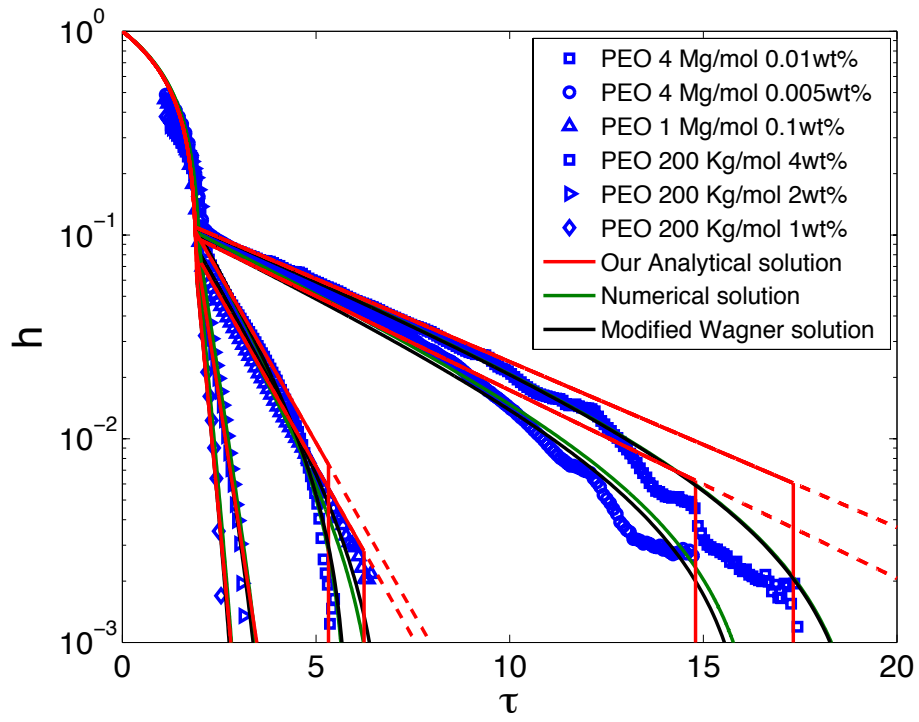


Fig. 9.5. Comparison between the numerical, analytical and experimental data.

Another possibility to capture an otherwise unobservable initial radius R_0 is by introducing a temporal shift factor to fit the observed τ^* . The applicability of such a shift was verified with measurements with a wider field of view, and the factors are also given in Table 2.

Table 2. Characteristics of different samples.

Samples	Concentration c wt%	Dynamic viscosity η Pa. s	Initial radius R_o mm	Finite Extensibility Parameter	
				Theoretical L^2	Effective L^2
1	1	2.87	1.25	3100	9000
2	2	6.34	1.3	3100	9000
3	4	24.53	1.32	3100	9000
4	0.1	1.72	1.02	14000	42000
5	0.005	1.08	0.98	46000	65000
6	0.01	1.15	1	46000	65000

Samples	Elastic Modulus		Time shifting factor, τ ms
	Theoretical, η/λ G Pa	Effective G Pa	
1	7.18	14	1.2
2	9.03	10	1.23
3	9.25	0.7	1.25
4	0.96	0.5	1.1
5	0.17	0.15	1.12
6	0.16	0.16	1.15

As we can see from the fig. 9.5, the analytical solution of the combined in eqs. (41) and (42) predict the experimental data and the numerical simulation very well. However, as discussed when introducing eq. (42), matching the solution of Wagner et al. for the elasto-capillary balance onto the inertial thinning regime required a numerical iteration to determine Ec' and R_0' in the following we present therefore a criterion based on the finite extensibility parameter

L that allows to estimated the breakup time of the filament also from the more simple eq. (41).

9.5. Analytic expression for the breakup time:

To obtain a full analytic result for the break-up time τ_b , we need to define an additional criterion for the analysis done so far. But first we briefly review the available alternative methods in literature.

Entov and Hinch⁵ assumed that the transition from the middle elastic regime to the finite extensibility regime occurs when the slopes of the $R(t)$ curves of both regimes are equal. In the finite extensibility regime, the fluid behaves as a suspension of rigid rods and the thinning dynamics are determined by the finite extensibility limit of the extensional viscosity²². The radius decreases linearly in time with a rate that is inversely proportional to the effective Ohnesorge number,

$$h = \frac{1}{Oh_{FE}}(\tau_b - \tau), \quad (44)$$

where the Ohnesorge number is defined as in ref [23],

$$Oh_{FE} = 2L^2 Ec De \left(1 - \frac{1}{2Wi}\right). \quad (45)$$

This results in the following expression of the breakup time for large values of the Weisenberg number $Wi = \lambda \dot{\epsilon}$:

$$\tau_b = De \left(3 \ln \left(\frac{4L^2}{3} \right) + 4 \ln(Ec) + 3 \right). \quad (46)$$

However, in order to apply eq. 46 for aqueous solutions the break-up time has to be corrected to incorporate the initial inertial regime,

which is missing from this solution. In the corrected version, the transition time, τ^* between the inertia-capillary and elasto-capillary regime has to be defined. And also the initial radius in EC regime will no longer be R_0 instead it will be R_0^* as there has already been capillary thinning during the inertia-capillary regime. This will result in a change in effective elastocapillary number from Ec to Ec^* and eq. 39 becomes,

$$\tau_b = \tau^* + De \left(3 \ln \left(\frac{4L^2}{3} \right) + 4 \ln(Ec^*) + 3 \right) \quad (47)$$

An alternative approach to calculate the break-up time was proposed by Wagner et al.⁶ for viscid fluids. They obtained the break-up time by simply putting the breakup condition, $h = 0$ in their analytical solution (shown in eq. 43). However, similar modification has to be done to adjust for aqueous solutions as done for the Entov and Hinch solution in the previous section. This modified breakup solution is shown in eq. (48).

$$\begin{aligned} \tau_b = \tau^* + \frac{b(b+2)}{(b+3)^2} & \left(\frac{Ec^*(b+3)}{1+Ec^*(b+3)} \right. \\ & \left. + 3 \ln(1+Ec^*(b+3)) + 4Ec^* \frac{(b+3)}{(b+2)} \right) \end{aligned} \quad (48)$$

Here τ^* is the transition time between inertia capillary regime and elasto-capillary regime and $Ec^* = h^* Ec_0$.

In the following we propose another simple approach to capture the breakup time, assuming that the axial polymer stretch A_{zz} increases exponentially in the middle elastic regime until it reaches its finite extensibility value, L^2 and the filament breaks at this time τ_b . We use the definition of L in terms of molecular parameters as shown in eq. 12.

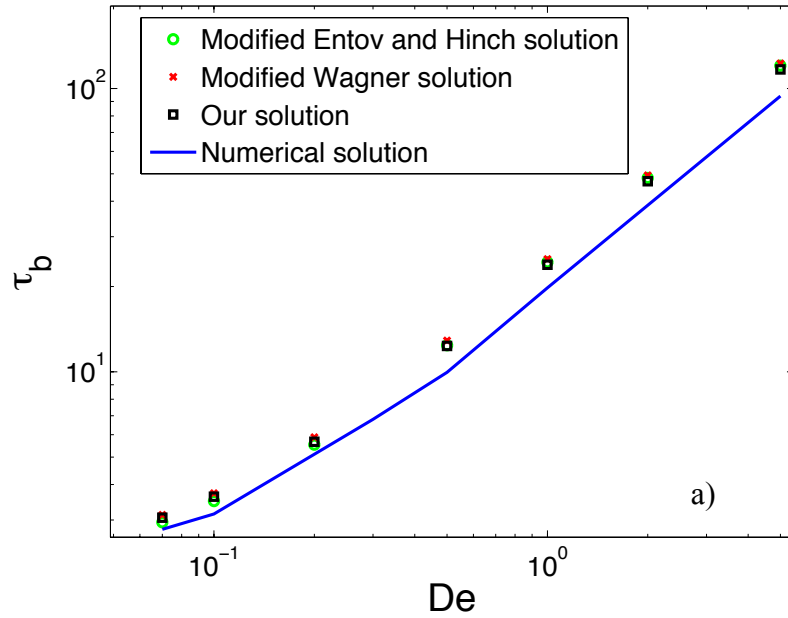
With $A_{zz} = A_{zz}^*$ at τ^* , at the onset of the elastocapillary regime, we can calculate from eq. (41),

$$A_{zz} = A_{zz}^* \exp\left(\frac{\tau_b - \tau^*}{3 De}\right) = L^2, \quad (48)$$

and the breakup time,

$$\tau_b = \tau^* + 3De \ln\left(\frac{L^2}{A_{zz}^*}\right), \quad (49)$$

Using this equation in combination with 39 and 42 for A_{zz}^* and τ^* its possible to evaluate the breakup time of a fluid sample undergoing capillary thinning. Subsequently, we assess these analytic breakup time solutions by comparing with numerical simulation results. In order to quantify this we need to use following polymer parameters: the Deborah number, elastocapillary number and the finite extensibility parameter. The comparison is shown in fig. 9.6.



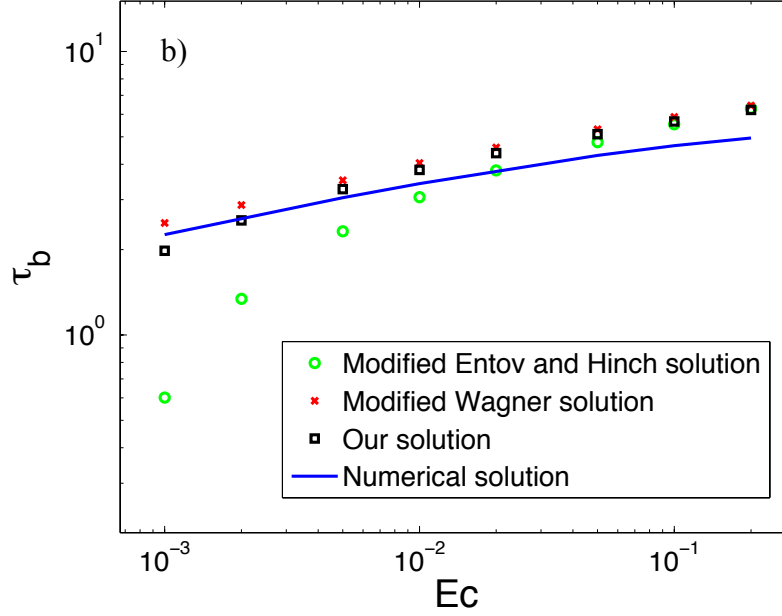


Fig. 9.6. Comparison between different (methods) breakup time t_b . a) Elasto capillary number, $Ec_0 = 0.1$ and $L^2 = 50000$. b) Deborah number, $De = 0.2$ and $L^2 = 50000$. Parameters used in these calculations are same as in Appendix 2.

In fig. 9.6 a), the elasto-capillary number is kept constant ($= 0.1$) and the Deborah number has been varied. Its clear that for the entire range of Deborah numbers that all solutions yield good results and despite the strong approximation, our solution shows the best agreement with the numerical results. On the other hand, in fig. 9.6 b), the Deborah number is kept constant ($= 0.2$) and the elastocapillary number is varied. As we see, both our and modified Wagner analytical predictions gets better as the value of Ec decreases. But the modified Entov and Hinch solution starts to deviate and the prediction goes wrong for very low elastocapillary numbers ($Ec < 0.05$). Lastly, we compare the different analytic solutions for break-up time with the experimentally observed break-up times. This is shown in fig. no. 8,

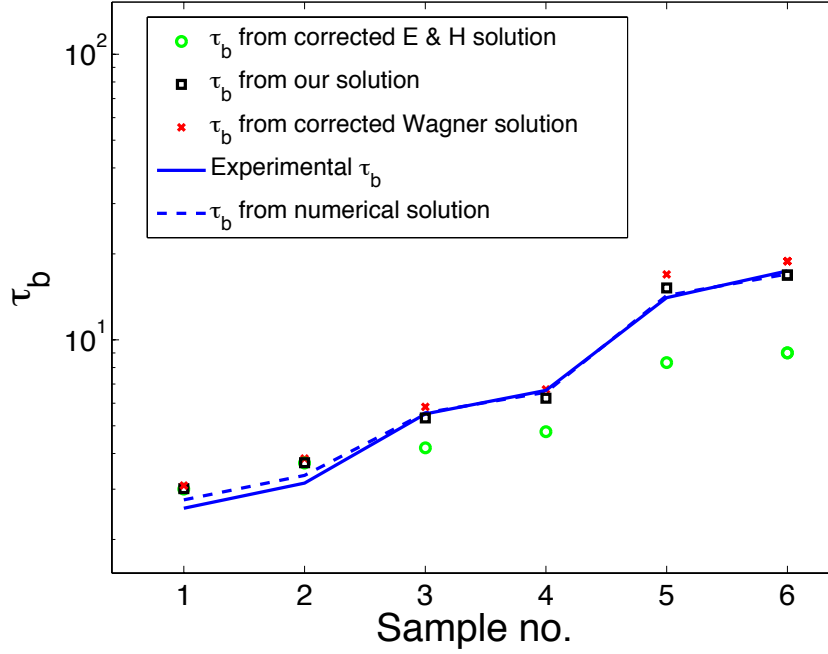


Fig. 9.7. Comparison between experimental, numerical and analytical (three methods) break-up times.

As we can see, the numerical solution has the best predictions for the experimentally observed break-up time of our samples. And for the analytical solutions both the modified Wagner and our solution predicts the break-up time quite well with our solution yielding the best results. However, the Entov and Hinch solution again predicts wrong break up time for samples having lower elasto-capillary number (<0.01 , similar to that observed in fig. 6 b).

9.6. Conclusion:

In this work, we have obtained analytical solutions for the evolution of the minimum-filament radius and the breakup time similar to the one in Wagner et al.⁶, but now for initially inertia controlled systems where solvent viscosity can be considered negligible. In this case, the

initial inertial stress originating from the liquid sample can't be ignored, so that, the capillary pressure is balanced by this inertial stress rather than the negligibly low solvent viscosity. Later, when the polymer molecules are adequately stretched the capillary pressure is balanced by the elastic stress⁷ coming from the polymer chain as demonstrated in Wagner's work⁶. Also for the elastically controlled thinning, we have expanded the analysis of Wagner et al.

Our analytic solution was subsequently compared with numerical and experimental measurements of a number of model polymer solutions. Despite of few strong approximations, the analytic solution is in very good agreement with both numerical and experimental results.

Appendix 1.

Similar to the inertia dominated case presented in eq. (34), one can calculate the evolution of A_{ZZ} also for an initially viscous controlled thinning regime. Assuming again $A_{ZZ} \gg 1$ and $Z = 1$ Wagner et al.⁶ have presented a simple solution of eq. (9), using the appropriate form of the extension rate $\dot{\epsilon} = 2/(\tau_v - \tau)$ in the viscopillary thinning regime

$$A_{ZZ} = \left(\frac{\tau_v}{\tau_v - \tau} \right)^4 e^{-\frac{\tau}{De}} \quad (50)$$

where $De = \frac{\lambda}{t_R}$, $\tau_v = \frac{t_v}{t_R}$ and t_v is the viscous breakup time at which a Newtonian filament would break. Mathues et al. showed that also here an enhanced analytical solution of eq. (9) with $\dot{\epsilon} = 2/(\tau_v - \tau)$ can be obtained by assuming only $Z = 1$ ²⁶:

$$\begin{aligned} A_{ZZ} = (\tau_v - \tau)^{-4} & \left((\tau_v - \tau)^4 + 4De(\tau_v - \tau)^3 \right. \\ & + 12De^2(\tau_v - \tau)^2 + 24De^3(\tau_v - \tau) \\ & + 24De^4 \\ & - (4De\tau_v^3 + 12De^2\tau_v^2 + De^324\tau_v \\ & \left. + De^424) e^{-\frac{\tau}{De}} \right). \end{aligned} \quad (51)$$

A more detailed analysis of a comparison of eqs (51) and (52) on the evolution of A_{ZZ} and the effect on the thinning dynamics for different values of Ec can be found in ref. [26].

Appendix 2.

Here, we compare the calculated transition time with the ones derived in Wagner et al. As discussed before, in their work the authors

assumed that initially resisting stress comes entirely from the solvent viscosity ignoring the inertia of the fluid. So to make sure that we compare everything in the same platform, we used the same assumptions made in their work but by replacing the viscous stress with the inertial stress. This comparison is done as we believe that few assumptions made in their work are weak (discussed later) and should lead to erroneous transition time.

Other parameters used in this calculation are,

Solvent density, $\rho = 998, \text{ Kg/ m}^3$,

Surface tension, $\gamma = 62 \cdot 10^{-3} \text{ N/m}$ and

Initial radius, $R_0 = 10^{-3} \text{ m}$.

Average bond angle (for PEO monomer), $\theta_b = 109.6^\circ$,

Number of bonds (for PEO monomer), $j = 3$,

Monomer molar mass, $M_u = 44 \text{ g/mol}$,

Characteristic ratio for PEO-water system, $C_\infty = 4.1$.

Table 3. Comparison between different transition times.

Deborah Number	Elasto capillary number	Numerical Solution	Our Approach ($b=\text{inf}$)	Wagner et al ⁶ with criterion, $\dot{A}_{zz} \sim 0, \text{ at } \tau^* (b=2 \cdot 10^4)$	Wagner et al. with ($b=\text{inf}$)
1	0.05	2	1.6993	1.771	1.773
10	0.05	1.9	1.5377	1.542	1.548
50	0.01	1.930	1.7602	1.758	1.761
10	0.01	1.942	1.7695	1.771	1.774
0.2	0.1	2.02	1.889	1.942	1.948
0.5	0.1	2.05	1.727	1.854	1.856
1	0.1	2	1.569	1.682	1.687
2	0.1	1.92	1.458	1.523	1.532

Interestingly, we see that the transition time obtained using these different assumptions are very similar. Depending on the system, different criterion has better result. In spite of some strong approximations the criteria set in Wagner et al. seems to work well.

When determining the transition regime, Wagner et al. assumed that at the transition point, the axial microstructural deformation doesn't change with time ($\dot{A}_{ZZ} \sim 0, at \tau^*$). This assumption is not true, as we know the A_{ZZ} in the elasto capillary regime varies with the slope of relaxation time of the polymer. So $\dot{A}_{ZZ}$ is not constant in this regime.

To determine the transition point in case of infinitely extensible polymers (middle elastic), Wagner et al. assumed that in elastocapillary regime, $A_{ZZ} = 1, when t = t^*$, which for obvious reasons cannot be true. In the elasto-capillary regime, the A_{ZZ} should be much higher than unity.

References:

1. N.F. Morrison, O.G. Harlen, Viscoelasticity in inkjet printing, *Rheol. Acta*, (2009), 49, 619–632.
2. S.D. Hoath, D.C. Vaddillo, O.G. Harlen, C. McIlroy, N.F. Morrison, W-K. Hsiao, T.R. Tuladhar, S. Jung, G.D. Martin, I.M. Hutchings, Inkjet printing of weakly elastic polymer solutions, *JNNFM*, (2014), 205, 1–10.
3. A.V. Bazilevsky, V.M. Entov, A.N. Rozhkov, Liquid filament microrheometer and some of its applications, in: D.R. Oliver, (Ed.), *Third European Rheology Conference and Golden Jubilee Meeting of the British Society of Rheology*, Elsevier Science Publishers, Ltd., pp., (1990), 41–43.
4. A.V. Bazilevsky, V.M. Entov, A.N. Rozhkov, Failure of an Oldroyd liquid bridge as a method for testing the rheological properties of polymer solutions, *Poly. Sci. Ser. A*, (2001), 43, 1161–1172.
5. V.M. Entov, E.J. Hinch, Effect of a spectrum of relaxation times on the capillary thinning of a filament of elastic liquid, *JNNFM*, (1997), 72, (31–53).
6. C. Wagner, L. Bourouiba, G. H. McKinley, An analytic solution for capillary thinning and breakup of FENE-P fluids, *JNNFM*, (2015), 218, 53–61.
7. G.H. McKinley, Visco-elasto-capillary thinning and break-up of complex fluids, *Rheol. Rev.* (2005) 1–48.
8. V. Tirtaatmadja, G. H. McKinley, and J. J. Cooper-White. Drop formation and breakup of low viscosity elastic fluids: Effects of

References

molecular weight and concentration. *Physics of Fluids*, (2006), 18(4), 043101.

9. R. P. Mun, J. A. Byars & D. V. Boger. The effects of polymer concentration and molecular weight on the breakup of laminar capillary jets. *JNNFM*, (1998), 94, 285-297.

10. L. Campo-Deaño, C. Clasen, The slow retraction method (SRM) for the determination of ultra-short relaxation times in capillary breakup extensional rheometry experiments, *JNNFM*, (2010), 165, 1688–1699.

11. Y. Christani & L. M. Walker. Effect of fluid relaxation time of dilute polymer solutions on jet breakup due to a forced disturbance. *Journal of Rheology* , (2002), 46, 733-748.

12. L. E. Rodd, T. P. Scott, J. J. Cooper-White, G. H. Mckinley. Capillary break-up rheometry of low-viscosity elastic fluids. *Applied rheology*, (2005), 1512-27.

13. W. W. Graessley, , Polymer chain dimensions and the dependence of viscoelastic properties on the concentration, molecular weight and solvent power, *Polymer*, (1980), 21, 258–262.

14. G. H. Mckinley, A. Tripathi. How to extract the Newtonian viscosity from capillary breakup measurements in a filament rheometer. *Journal of rheology*, (2000), 44, 653-670.

15. R. F. Day, E. J. Hinch, and J. R. Lister. Self-similar capillary pinchoff of an inviscid fluid. *Physical Review Letters*, (1998), 80(4), 704-707.

16. M.A. Fontelos and J. Li, "On the evolution and rupture of filament in Giesekus and FENE models". *JNNFM*, (2004), 118, 1-16.

17. C. Clasen, J. Eggers, M.A. Fontelos, J. Li, and G.H. McKinley, The beads-on-string structure of viscoelastic threads. *J. Fluid Mech.*, (2005), 556, 283-308.
18. C. Clasen, P.M. Phillips, L. Palangetic, J. Vermant, Dispensing of rheologically complex fluids: the map of misery, *AIChE J.*, (2012), 56, 3242-3255.
19. C. Wagner, Y. Amarouchene, D. Bonn, J. Eggers, Droplet detachment and satellite bead formation in viscoelastic fluids, *Phys. Rev. Lett.*, (2005), 95(16), 164504.
20. A.U. Chen, P.K. Notz, O.A. Basaran, Computational and experimental analysis of pinch-off and scaling, *Phys. Rev. Lett.*, (2002), 88(17), 174501-4.
21. L. E. Rodd, T. P. Scott, J. J. Cooper-White, G. H. McKinley, Capillary break-up rheometry of low-viscosity elastic fluids, *Applied Rheology*, (2005), 15(1), 12-27.
22. L. Palangetic, N. K. Reddy, S. Srinivasan, R. E. Cohen, G. H. McKinley, C. Clasen, Dispersity and Spinnability Why Highly Polydisperse Polymer Solutions are Desirable for Electrospinning, *Polymer*, (2014), 55, 4920–4931.
23. C. Clasen, J. P. Plog, W.-M. Kulicke, M. Owens, C. Macosko, L. E. Scriven, M. Verani, G. H. Mckinley, How dilute are dilute solutions in extensional flows?, *Journal of Rheology*, (2006), 50, 849-881.
24. J. Eggers, M. A. Fontelos, Singularities: Formation, Structure, and Propagation, *Cambridge Texts in Applied Mathematics*, (2015).
25. D. T. Papageorgiou, On the breakup of viscous-liquid threads. *Physics of Fluids*, (1995), 7, 1529–1544.

References

26. W. Mathues, T. Shahid, J. Hendricks, C. Clasen, An analytical solution for the initial polymer stretch evolution in thinning viscoelastic filaments. BSR Bulletin, (2016), 57 (3), 57-62.
27. W. Mathues, Filament stabilisation in free-surface flows of complex fluids. Ph.D. thesis, KU Leuven (2015).
28. J. Brandrup & E. Immergut, Polymer Handbook (John Wiley & Sons, Inc, 1999), 4th edn.

Chapter 10

Conclusions and perspectives

In this summarizing chapter, we present the key outcomes of this thesis and propose topics that could be worth investigating in future.

10.1 Conclusions

The elongational flow properties of polymers play a significant part in their performance during both processing and application. Unfortunately, the non-linear (fast flow) properties are not well understood like its linear (slow flow) counterpart principally due to the non-universal behavior between polymer melts and solutions. As a result, molecular models used to predict the linear properties couldn't be extended to the non-linear regime. The aim of this thesis was to find the origin of this non-universality and propose a universal model that could predict both polymer melts and solutions under the same framework.

In order to attain the overall objective, this thesis was divided into three parts. First, the contemporary molecular pictures were investigated in light of especially designed polymer blends. In this work (see chapter 6), the stretch oriented reduction in friction (SORF) mechanism was tested with a series of PS blends where a long chain polystyrene was diluted in a series of short styrene oligomers that cover an entanglement range of unentangled, barely entangled and well-entangled. Depending on the degree of entanglements of the solvent, the nematic interaction between the solvent and the polymer was expected to vary and therefore alter the fast flow dynamics of the blends. Surprisingly, the experimental results showed that all polystyrene blends behave similarly, which is contrary to the expected

behavior for SORF mechanism thus raising several new interesting questions referring to the universality of this mechanism.

Carrying on with our quest to develop a universal model, next we investigated the origin of the non-universality between polymer melts and solution in extensional flow. This work (chapter 5 and 7) was influenced by the idea that the existing non-universality between polymer melts and solutions could result from an inadequate scaling resulting due to lack of systematic experimental data. Consequently, a new set of PS solutions was prepared where a high molecular weight polystyrene was diluted in a styrene oligomer at several concentrations. Consequently, non-linear elongational experiments were carried out in order to find the right scaling between them. Using these and literature data, we were able to show that it is possible to obtain universality between melts and solutions by explicitly normalizing them in the non-linear regime and at an iso- T_g condition. Amazingly, this observation was found to be universal for all investigated samples. Also, this universality was observed without considering any additional relaxation mechanisms outside the framework of the refined Doi and Edwards's tube model.

Based on these experimental results and the ones from literature, we were then able to propose a novel theory (chapter 8) that can predict polymer melts within the framework of the refined tube model. The best feature of this proposed model is that it doesn't feature any additional parameter or controversial criterion like the finite extensibility. According to this proposed theory, both orientation and stretching of polymer chains can lead to strain hardening phenomenon. Orientation of polymer chains stimulates mild "strain-induced" strain hardening, which takes place due to suppression of CLF process at intermediates strain rates, $\frac{1}{\tau_R} > \dot{\epsilon} > \frac{1}{\tau_{Reptation}}$. On the other hand, when polymer chains are stretched beyond its equilibrium length ($\lambda = \frac{L_{eq}}{L_{eq,0}} > 1$), tension along the whole chain increases, which leads to strong strain hardening phenomenon.

The proposed strain-hardening phenomena are equally valid to both polymer melts and solutions. Unlike the SORF concept, which predominantly affects the polymer melts. The strong thickening

properties observed in case of polymer solutions are due to “strain-induced” strain hardening (see the intermediate regime of fig. 10.1) and can be attributed as a mean of transition between two different scaling regimes as shown in fig. 10.1. Since the scaling in the non-linear regime is different for polymer melts the upturn is weaker and only observed for very low M_w polymers.

On the other hand, the “stretch-induced” strain hardening (non-linear regime of fig. 10.1) is similar for both polymer melts and solutions and results in a similar slope of $-1/2$, which is well observed for PS melts and not that prominently for PS solutions as the transition (intermediate regime) between two regimes delays the on-set of the non-linear regime as shown in fig. 10.1. The stretch-induced strain hardening doesn't result in an thickening behavior but causes the slope of $\bar{\eta}_{st}$ to change from -1 to $-1/2$.

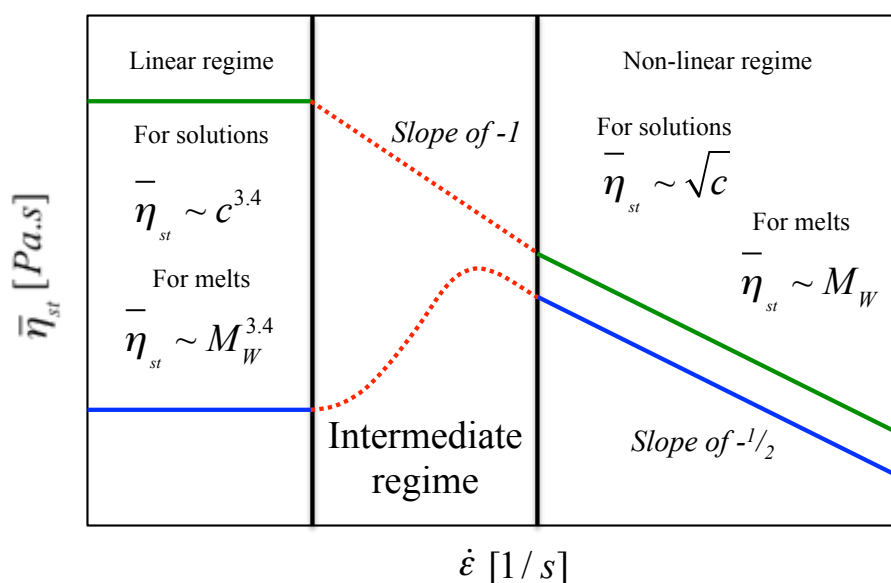


Fig. 10.1 Behavior of polymer melts and solutions in different regimes.

Using this concept, we were able to predict the steady elongational viscosity of different M_w PS melts both at linear and non-linear regime. The intermediate regime can also be predicted by gradual suppression of CLF mechanism, which becomes increasingly important for low M_w melts and largely diluted solutions.

Thus, this work can be considered as an important step toward achieving a universal model in extensional flow, where we not only raise important questions towards the controversial friction reduction concept but also propose a theory that can correctly predict the experimental results. And most importantly, this theory fits well within the established tube model. However, due to the limitation of time and resources, the focus of this thesis was limited in certain aspects as described in the following section.

10.2 Future perspectives

As concluding remark, we would like to present few future prospects that we would like to continue investigating.

10.2.1 Investigate influence of solvent quality

The solvent quality or the solvent-polymer interaction plays an important role in setting the rheological properties of polymer solutions. As we have shown in chapter 5, changing from oligomers to small molecules solvent can largely alter the shear LVE behavior, especially for the diluted solutions. Therefore, larger consequence can be expected in non-linear extensional properties, which is worth investigating. It must be noted such study has indeed been performed by Sridhar et al.¹, where PS diluted in DOP/DEP has been investigated. However more controlled experiments are needed in order to identify the fundamental influence of solvent quality in the non-linear properties of solutions.

10.2.2 Develop time-dependent NLVE model

In this thesis, we have limited ourselves on predicting the steady extensional viscosities of polymeric systems. Therefore, full constitutive equation that can describe the time dependent non-linear transient extensional viscosity is still missing. As a next step, we would like to continue in the same direction i.e. polymer chains are stretched at different levels thus perhaps activating different Rouse

modes and see how well our model assumptions perform against the experimental results.

10.2.3 Test the finite extensibility

Today, most of the molecular models used to predict the NLVE properties of polymers assume finite extensibility criteria of polymer chains. According to this criteria, when polymer chains are stretched beyond its stretch relaxation time it reaches its fully stretched state that ultimately leads to the steady state regimes as mostly observed in experimental results. However, in this work we propose polymer chains can be stretched at different levels depending on the strain rate. This assumption has been based on recent observations but is not straightforwardly verified due to experimental limitations. Therefore, verifying this assumption with experimental results would be much desirable.

10.2.4 Extend the NLVE model to polymer solutions

Two major outcomes of this thesis are: a) introducing a simple constitutive equation that can predict the elongation steady properties of polymer melts at a quantitative level b) capture the identical behavior of polymer melts and solutions in non-linear flow. Therefore, by combining these two outcomes we should be able to find the long-desired unified model for polymer melts and solutions and most appealingly even within the framework of the original tube model.

10.2.5 Study brittle fracture for polymer blends and solutions

Brittle fracture is one of the biggest impediments of extensional filament stretching measurements that is frequently observed and severely restricts the maximum applied strain rate for a specific sample. Therefore it is important to understand why and how exactly it occurs. In this thesis, we have prepared and investigated versatile sets of polymer samples that consist of different concentrated polymer

solutions to polymer blends in different matrices. Studying these samples would indeed give us a nice opportunity to explore how the surrounding environment influences the brittle behavior of a polymer.

References:

1. P. K. Bhattacharjee, J. P. Oberhauser, G. H. McKinley, L. G. Leal, and T. Sridhar, Extensional rheometry of entangled solutions. (2002), *Macromolecules* 35, 10131–10148.
2. X. Ye, R. G. Larson, C. Pattamaprom, T. Sridhar, Extensional properties of monodisperse and bidisperse polystyrene solutions, (2003), *J. Rheol.*, 47, 443.