INVESTIGATION OF NON-LINEAR RHEOLOGICAL BEHAVIOR OF
POLYMERIC LIQUIDS

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INVESTIGATION OF NON-LINEAR RHEOLOGICAL BEHAVIOR OF
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Entangled polymeric liquids necessarily show significant nonlinear responses to fast and large external deformation. Recent particle-tracking velocimetric measurements showed that the nonlinear behavior may involve inhomogeneous shear. But even in absence of shear banding, it remains a challenge to characterize and establish a connection between various nonlinear rheological characteristics and the molecular rearrangements in the entanglement network.

In this dissertation, the relationship between the dynamics of chain entanglement and the rheological behavior was studied under different deformation conditions. We emphasized with the present entangled polymeric liquids that nonlinearity in large amplitude oscillatory shear could arise due to rearrangement of their microstructures over time in response to large amplitude oscillatory shear. In this case, no correlation is obvious between strain dependence of the steady-state stress response and deviation of the steady-state stress from the sinusoidal wave. We investigated the nature of steady shear flow of entangled polymeric liquids by superimposing either small amplitude oscillatory shear or small step strain and analyzing the resultant mechanic responses. Our results showed that a) polymer dynamics (in terms of stress relaxation) were accelerated relative to the quiescent dynamics in direct proportion to the underlying shear rate, and b) the steady shear was a viscous state where chains were displaced past one another on a time scale comparable to the reciprocal rate, consistent with the idea of convective constraint release (CCR). We carried out rate-
switching tests to further elucidate the changes of the transient strength of chain entanglement in response to various forms of shearing. Our results showed that a) elastic yielding could occur during quiescent relaxation after a large step strain, b) the new state of chain entanglement was stable for a significant period after shear cessation from steady state, and c) the strength of chain entanglement could achieve a higher level than that of the equilibrium state during re-entanglement.
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## TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>LIST OF TABLES</th>
<th>ix</th>
</tr>
</thead>
<tbody>
<tr>
<td>LIST OF FIGURES</td>
<td>x</td>
</tr>
</tbody>
</table>

### CHAPTER

I. INTRODUCTION .................................................................................. ..... 5

II. BACKGROUND OF THIS STUDY ............................................................. 5

2.1 Rheological measurement ............................................................... 5

2.2 Rheological phenomenon of entangled polymeric liquids .................. 9

2.2.1 Linear rheological behaviors ...................................................... 9

2.2.2 Nonlinear rheological behaviors ................................................. 13

2.3 Maxwell model ............................................................................. 15

2.3.1 Small amplitude oscillatory shear: .............................................. 16

2.3.2 Stress relaxation: ....................................................................... 17

2.4 Tube model .................................................................................. 18

2.5 Particle Tracking Velocimetry (PTV) ............................................. 22

2.5.1 Setup ..................................................................................... 22

2.5.2 PVT observation ..................................................................... 22

2.6 New understanding and molecule picture ....................................... 29

2.7 Recent studies of chain entanglement ............................................. 31

III. NONLINEARITY IN LARGE AMPLITUDE OSCILLATORY SHEAR ....... 33

3.1 Introduction ............................................................................... 33

3.2 Experimental ............................................................................. 35
3.2.1 Materials ........................................................................................................35
3.2.2 Apparatus .......................................................................................................36
3.2.3 Fourier transformation (FT) analysis ............................................................37
3.2.4 Data representation .......................................................................................38
3.3 Results and Discussion ....................................................................................38
  3.3.1 Homogeneous yielding of nano-granular paste of polybutadiene particles ..........................................................38
  3.3.2 Shear banding in an entangled polybutadiene solution .........................46
  3.3.3 Wall slip of an entangled polyisoprene melt .............................................53
  3.3.4 Large amplitude oscillatory shear of a polydisperse diphenylmethylvinyl silicone gum ........................................60
3.4 Conclusion .......................................................................................................68

IV. NONLINEAR RHEOLOGICAL BEHAVIORS IN STEADY STATE ........72
  4.1 Introduction .....................................................................................................72
  4.2 Parallel mechanical superposition and theory prediction in linear regime .75
    4.2.1 Superimposed small amplitude oscillatory shear .................................75
    4.2.2 Superimpose small step strain .................................................................77
  4.3 Experimental ..................................................................................................78
    4.3.1 Materials .................................................................................................78
    4.3.2 Methods ..................................................................................................79
    4.3.3 Particle-tracking velocimetry setup .......................................................80
  4.4 Results and discussion ..................................................................................80
    4.4.1 Linear viscoelastic characters and temperature dependence .............80
    4.4.2 Particle-tracking velocimetry (PTV) observation ..................................87
    4.4.3 Superimposed small amplitude oscillatory shear at different temperatures ........................................87
    4.4.4 Stepwise rate jump in shear thinning regime ........................................98
4.4.5 Master flow curve in steady shear ........................................... 100
4.4.6 Step strain relaxation during steady shear ........................... 101
4.5 Discussion ........................................................................... 110
4.6 Conclusion ........................................................................... 114
V. CHAIN ENTANGLEMENT CHARACTERIZATION AT TRANSIENT
STATE......................................................................................... 116
5.1 Introduction .......................................................................... 116
5.2 Experimental ........................................................................ 118
5.2.1 Material ............................................................................ 118
5.2.2 $\sigma_{\text{max}}$ characterization method .................................... 118
5.3 Results and discussion ......................................................... 120
5.3.1 $\sigma_{\text{max}}$ characterization in linear regime ......................... 120
5.3.2 Characterize entanglement weaken during startup shear .. 121
5.3.3 Characterize stress relaxation after large step strain .......... 125
5.3.4 State of chain entanglement after shear cessation from steady shear .. 128
5.3.5 State of chain entanglement after stepdown from steady shear .... 130
5.3.6 Structure recovery after fast stress release ...................... 134
5.3.7 Shear direction dependence of chain entanglement .......... 136
5.4 Compare with tube model: after stepdown from steady shear .... 138
5.5 Discussion ........................................................................... 139
5.6 Conclusion ........................................................................... 141
VI. SUMMARY ............................................................................ 142
BIBLIOGRAPHY ........................................................................... 144
# LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.1</td>
<td>The crossover frequency of different samples at three temperatures</td>
<td>82</td>
</tr>
</tbody>
</table>
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Schematic illustration of rheological measurement in simple shear</td>
<td>6</td>
</tr>
<tr>
<td>2.2</td>
<td>The side view of a rotational rheometer</td>
<td>6</td>
</tr>
<tr>
<td>2.3</td>
<td>Side view of the cone-partitioned plate (CPP) device.</td>
<td>8</td>
</tr>
<tr>
<td>2.4</td>
<td>Top view of the cone-partitioned plate (CPP) device.</td>
<td>9</td>
</tr>
<tr>
<td>2.5</td>
<td>Illustration of a step strain</td>
<td>10</td>
</tr>
<tr>
<td>2.6</td>
<td>Illustration of a continuous shear</td>
<td>11</td>
</tr>
<tr>
<td>2.7</td>
<td>A typical G’ and G” curve of an entangled polymeric liquid</td>
<td>12</td>
</tr>
<tr>
<td>2.8</td>
<td>Typical shear thinning behavior of entangled polymer liquid. The shear viscosity is plotted as a function of shear rate</td>
<td>14</td>
</tr>
<tr>
<td>2.9.</td>
<td>A typical stress response of an entangled polymeric sample during a startup shear</td>
<td>15</td>
</tr>
<tr>
<td>2.10</td>
<td>A Maxwell model represented by a spring and dashpot</td>
<td>16</td>
</tr>
<tr>
<td>2.11</td>
<td>G’ and G” as a function of frequency as a Maxwell element</td>
<td>17</td>
</tr>
<tr>
<td>2.12</td>
<td>An illustration of chain entanglement</td>
<td>18</td>
</tr>
<tr>
<td>2.13</td>
<td>An illustration of tube model</td>
<td>19</td>
</tr>
<tr>
<td>2.14</td>
<td>An illustration of a typical particle-tracking velocimetry setup on cone and plate rheometer</td>
<td>23</td>
</tr>
<tr>
<td>2.15</td>
<td>An example of inhomogeneous shear: a polybutadience solution with Z=119 during a startup shear at shear rate of 0.55 s⁻¹. Reprint from ref²⁴ with permission</td>
<td>24</td>
</tr>
<tr>
<td>2.16</td>
<td>An example of homogeneous shear: polydisperse diphenylmethylvinyl silicone gum at shear rate of 2 s⁻¹</td>
<td>25</td>
</tr>
<tr>
<td>2.17</td>
<td>An example of inhomogeneous during large amplitude oscillatory shear: a polybutadience solution</td>
<td>26</td>
</tr>
</tbody>
</table>
An example of wall slip during large amplitude oscillatory shear: a polyisoprene melt

Particle-tracking velocimetric detection of total macroscopic motions during relaxation after shear ceasing of different loadings where the final positions of the tracked particles are given and the original positions of particles right after shear cessation are at 0.

Particle-tracking velocimetric detection of total macroscopic motions during relaxation after shear ceasing for SBR 250K. Reprint from ref 86 with permission.

The illustration of the force imbalance picture after a large step strain.

Dynamic and loss moduli $G'$ and $G''$ from small amplitude oscillatory shear measurements at $\gamma_0 = 2\%$ of the nano-granular polybutadiene (PB) melt.

FT analysis of the shear stress and stress-strain loop of the nano-granular polybutadiene (PB) melt at $\gamma_0 = 5\%$ and $\omega = 1$ rad/s.

Strain softening expressed in terms of the steady-state "complex modulus" $\sigma_{\text{peak}}^{ss}/\gamma_0$ as a function of the amplitude $\gamma_0$.

Decline of the storage and loss moduli corresponding to the first harmonic as well as the peak value of the shear stress as a function of time for $\gamma_0 = 40\%$ and $\omega = 1$ rad/s.

FT analysis of the stress response in steady state for $\gamma_0 = 40\%$ and $\omega = 1$ rad/s, in terms of the normalized power spectrum, where the inset showed the Lissajous plot.

Large amplitude oscillatory shear at $\gamma_0 = 200\%$, $\omega = 1$ rad/s: Stress-strain loop of the first three cycles.

Large amplitude oscillatory shear at $\gamma_0 = 200\%$, $\omega = 1$ rad/s: Explicit raw data of strain and stress in the first five cycles.

Large amplitude oscillatory shear at $\gamma_0 = 200\%$, $\omega = 1$ rad/s: Particle-tracking velocimetric observations confirming homogeneous large amplitude oscillatory shear.

Dynamic and loss moduli $G'$ and $G''$ from small amplitude oscillatory shear measurements at $\gamma_0 = 5\%$ of the polybutadiene

xi
solution PB1M-10%-10K where the inset showed an elliptical Lissajous loop for $\gamma_0 = 20\%$. .........................................................47

3.10 Strain softening expressed in terms of the steady-state "complex modulus" $\sigma_{\text{peak}}^{\text{ss}}/\gamma_0$ as a function of the amplitude $\gamma_0$ where the FT analysis in the inset showed ideal sinusoidal stress response.........................48

3.11 Large amplitude oscillatory shear of the polybutadiene solution PB1M-10%-10K at $\gamma_0 = 200\%$ and $\omega = 1$ rad/s: Time dependence of $\sigma_{\text{peak}}$ and $G_1'$ and $G_1"$. ........................................................................49

3.12 Large amplitude oscillatory shear of the polybutadiene solution PB1M-10%-10K at $\gamma_0 = 200\%$ and $\omega = 1$ rad/s: Stress-strain loops of the first three cycles........................................................................50

3.13 Large amplitude oscillatory shear of the polybutadiene solution PB1M-10%-10K at $\gamma_0 = 200\%$ and $\omega = 1$ rad/s: particle-tracking velocimetry measurements of the velocity profiles at two different moments in a steady-state cycle, where the moments of A and C are equivalent, so are moments B and D............................................................52

3.14 Large amplitude oscillatory shear of the polybutadiene solution PB1M-10%-10K at $\gamma_0 = 200\%$ and $\omega = 1$ rad/s: FT analysis of the raw shear stress data along with the Lissajous plot. .......................................................53

3.15 Dynamic and loss moduli $G'$ and $G"$ from small amplitude oscillatory shear measurements at $\gamma_0 = 2\%$ of the polyisoprene melt. ..........................................................................................54

3.16 FT analysis of the shear stress and stress-strain loop of the polyisoprene melt at $\gamma_0 = 10\%$ and $\omega = 0.5$ rad/s..............................................................55

3.17 Time dependence of $\sigma_{\text{peak}}$, $G_1'$ and $G_1"$ at $\gamma_0 = 70\%$ and $\omega = 0.5$ rad/s.........................................................................56

3.18 FT analysis of the shear stress at around $t = 300$ s, showing emergence of even harmonics as well as a strongly non-elliptical Lissajous plot in the inset..............................................................57

3.19 Particle-tracking velocimetry measurements of the velocity profiles at three moments in a steady-state cycle, where the moments of A and C are equivalent, so are moments B and D. ..............................................58

3.20 Time dependence of $\sigma_{\text{peak}}$, $G_1'$ and $G_1"$ at $\gamma_0 = 70\%$ and $\omega = 0.5$ rad/s measured with the partitioned-plate-cone device.................................59

xii
3.21 FT analysis of the shear stress at any time after \( t = 100 \) s, with a Lissajous loop that is nearly indistinguishable from that in the inset of Figure 3.18.................................60

3.22 Dynamic and loss moduli \( G' \) and \( G'' \) from small amplitude oscillatory shear measurements at \( \gamma_0 = 5 \% \) of the diphenylmethylvinyl silicone gum..................................................62

3.23 Time independence of \( G' \) and \( G'' \) at \( \gamma = 10 \% \) (filled symbols) and decrease of \( G_1' \) and \( G_1'' \) at \( \gamma_0 = 200 \% \) over time (open symbols), both at \( \omega = 5 \) rad/s.................................................................63

3.24 FT analysis of the shear stress around \( t = 37 \) s with Lissajous loop involving several cycles...........................................65

3.25 FT analysis of the raw shear stress data along with the Lissajous plot in steady state......................................................66

3.26 Time independence of \( G_1' \) and \( G_1'' \) (filled symbols) measured in the partitioned-plate-cone device in contrast to the decrease of \( G_1' \) and \( G_1'' \) (open symbols), both at \( \gamma_0 = 200 \% \) and \( \omega = 5 \) rad/s........................................67

3.27 FT analysis of the shear stress in steady state corresponding to the filled symbols of Figure 3.26, where the Lissajous loop was only slightly deviating from an ellipse..................................................68

4.1 An illustration of superimposed saos method........................................76

4.2 An illustration of superimposed small step strain method..........................78

4.3 Storage and loss moduli \( G' \) and \( G'' \) of PB1M-5%-10K at 5 \(^\circ\)C. .................81

4.4 Storage and loss moduli \( G' \) and \( G'' \) of PB2.6M-3%-9K at a reference temperature of 40 \(^\circ\)C where the curves at 10 \(^\circ\)C and 25 \(^\circ\)C were shifted horizontally by a shifting factor of \( a_{10\,^\circ\text{C}} = 4.6 \) and \( a_{25\,^\circ\text{C}} = 2.1 \) respectively. .................................................................82

4.5 Storage and loss moduli \( G' \) and \( G'' \) of PB2.6M-3%-1.8k at 10 \(^\circ\)C, 25 \(^\circ\)C and 40 \(^\circ\)C. The curves at 10 \(^\circ\)C and 25 \(^\circ\)C were shifted horizontally by the shifting factor \( a_{25\,^\circ\text{C}} = 2.8 \) and \( a_{10\,^\circ\text{C}} = 12.8 \) at a reference temperature of 40 \(^\circ\)C and shifted vertically by \( T_0/T \) where \( T \) is the thermodynamic temperature of 10 \(^\circ\)C and 25 \(^\circ\)C (283K and 298K), \( T_0 \) is 313K (40 \(^\circ\)C). .................................................................84

4.6 The shifting factor of PB2.6M-3%-9k (circle), shifting factor of PB2.6M-3%-1.8k based on \( \omega_k \) (square) and shifting factor of
4.7. Stress vs. strain of PB2.6M-3%-9k upon startup shear at \( Wi = 11 \) at respective temperatures of 10, 25 and 40 °C..........................86

4.8. Stress relaxation of PB2.6M-3%-9k from a small step strain of 10 % produced with a shear rate of 1 s\(^{-1} \)..........................87

4.9 Extracted \( G' \) and \( G'' \) curves vs. \( \omega \) of PB2.6M-3%-9K in steady shear at temperature 40 °C at different underlying rates..................88

4.10 Extracted \( G' \) and \( G'' \) curves vs. \( \omega \) of PB2.6M-3%-1.8K in steady shear at temperature 25 °C at different underlying rates..................89

4.11. Extracted \( G' \) and \( G'' \) curves vs. \( \omega \) of PB2.6M-3%-9K in steady shear at different temperatures at the same underlying rate. ...............91

4.12 Extracted \( G' \) and \( G'' \) curves vs. \( \omega \) of PB2.6M-3%-1.8K in steady shear at different temperatures at the same underlying rate 0.004 s\(^{-1} \). .................................................................92

4.13 Extracted \( G' \) and \( G'' \) curves vs. \( \omega \) of PB2.6M-3%-1.8K in steady shear at different temperatures at the same underlying rate 0.01 s\(^{-1} \)..........93

4.14 Extracted \( G' \) and \( G'' \) curves vs. \( \omega \) of PB2.6M-3%-1.8K in steady shear at different temperatures at the same underlying rate 0.04 s\(^{-1} \)..........94

4.15 The characteristic effective crossover frequency \( \omega_{\text{c,eff}} \) in presence of steady shear at the different applied rates and three temperatures in two different solutions is plotted against \( 5 \), showing a universal correlation, independent of temperature.................................95

4.16 Extracted \( G' \) and \( G'' \) curves vs. \( \omega \) of PB2.6M-3%-9K in steady shear at different temperatures at the same \( Wi=11 \).................................96

4.17 The \( G' \), \( G'' \) of PB2.6M-3%-1.8k under the background shear at \( Wi=11 \). The curves were shifted by the shifting factor based on \( \omega_{c} \) for PB2.6M-3%-1.8k in Fig. 3. \( G' \) \( G'' \) was also shifted vertically by \( T_{0}/T \) where \( T \) was the thermodynamic temperature of 10 °C and 25 °C (283K and 298K), \( T_{0} \) is 313K (40 °C).................................................97

4.18 Stress change as a function of elapsed strain upon switching from steady state at \( \dot{\gamma} = 0.04 \) s\(^{-1} \) to 0.045, 0.05, 0.07 and 0.1 s\(^{-1} \) respectively.................................................................99
4.19 Switch the shear rate from the steady state of 0.04 s$^{-1}$ to higher rate: 0.1 s$^{-1}$, 0.3 s$^{-1}$ and 1 s$^{-1}$ for PB2.6M-3%-1.8k at 10 °C. Stress overshoot could be seen.

4.20 Master flow curves made of steady shear stress vs. rate data at three temperatures of 40, 25 and 10 °C where the reference temperature is 40 °C and the WLF shifting factor is the same as that in Figure 4.4.

4.21 Parallel superposition of step strain (the superimpose step strain is 10%, produced with a shear rate of 1 s$^{-1}$) for PB2.6M-3%-9k at 25 °C under the shear rate of 0.04 s$^{-1}$, 0.0003 s$^{-1}$, and in absence of shear respectively. The data were obtained by subtracting from the baseline, i.e., steady state shear stress.

4.22 Parallel superposition step strain (the superimpose step strain is 10% produced with a shear rate of 1 s$^{-1}$) for PB2.6M-3%-9K at different temperatures under the same shear rate of 0.04 s$^{-1}$. The data were obtained by subtracting from the baseline, i.e., steady state shear stress.

4.23 Parallel superposition step strain (the superimpose step strain is 10% produced with a shear rate of 1 s$^{-1}$) for PB2.6M-3%-1.8K at different temperatures under the same shear rate of 0.004 s$^{-1}$. The data were obtained by subtracting from the baseline, i.e., steady state shear stress, and normalized by the stress difference right after the disturbance.

4.24 Parallel superposition step strain (the superimpose step strain is 10% produced with a shear rate of 1 s$^{-1}$) for PB2.6M-3%-1.8K at different temperatures under the same shear rate of 0.01 s$^{-1}$. The data were obtained by subtracting from the baseline, i.e., steady state shear stress, and normalized by the stress difference right after the disturbance.

4.25 Parallel superposition step strain (the superimpose step strain is 10% produced with a shear rate of 1 s$^{-1}$) for PB2.6M-3%-1.8K at different temperatures under the same shear rate of 0.04 s$^{-1}$. The data were obtained by subtracting from the baseline, i.e., steady state shear stress, and normalized by the stress difference right after the disturbance.

4.26 Parallel superposition step strain (the superimpose step strain is 10% produced with a shear rate of 1 s$^{-1}$) for PB2.6M-3%-9K and PB1M-5%-10K at different temperatures. The data obtained by
scaling the time scale with the underlying shear rate, and normalized by the stress difference right after the disturbance. .................108

4.27 Stress relaxation curve for PB2.6M-3%-1.8K at equilibrium and under different steady shear rates at 40 °C. The data were obtained by subtracting from the baseline, i.e., steady state shear stress. .................109

4.28 Stress relaxation curve for PB2.6M-3%-1.8K at equilibrium and under different steady shear rates at 40 °C. Master curves obtained by scaling the time scale with the underlying shear rate. .........................110

4.29 An illustration of convective constraint release (CCR) mechanism ..........112

4.30 An illustration of a general shear banding case. .................................113

5.1 A sketch of yield stress value \( \sigma_{\text{max}} \) characterization method. .................119

5.2 Stress relaxation curve and \( \sigma_{\text{max}} \) as a function of rest time \( t_2 \) after a step strain of 20% produced by a rate of 0.1 s\(^{-1}\) .........................................................122

5.3 Viscosity and \( \sigma_{\text{max}} \) as a function of rest time \( t_2 \) for startup rate of 0.03 s\(^{-1}\) and 0.1 s\(^{-1}\) .................................................................123

5.4 \( \sigma_{\text{max}} \) as a function of steady state at different shear rates .................124

5.5 Strain recovery measurement and \( \sigma_{\text{max}} \) for a strain of 300% produced by 1 s\(^{-1}\) ........................................................................125

5.6 Normalized stress relaxation curve and \( \sigma_{\text{max}} \) as a function of rest time \( t_2 \) after a step strain of 100% produced by a rate of 1 s\(^{-1}\). The black curve is the normalized stress relaxation curve after a small step strain of 20% as a reference curve. (Re-plot from ........................................126

5.7 Normalized stress relaxation curve and \( \sigma_{\text{max}} \) as a function of rest time \( t_2 \) after a step strain of 300% produced by a rate of 0.1 s\(^{-1}\). The black curve is the normalized stress relaxation curve after a small step strain of 20% as a reference curve. (Re-plot from Figure 5.2) ..........127

5.8 \( \sigma_{\text{max}} \) as a function of rest time \( t_2 \) after shear cessation of shear rate equaled to 0.03 s\(^{-1}\), 0.1 s\(^{-1}\), 0.3 s\(^{-1}\) .........................................................128

5.9 Stress vs. time after stepdown from steady shear ....................................131

5.10 \( \sigma_{\text{max}} \) as a function of rest time \( t_2 \) after stepdown from steady shear .........132

5.11 Stress vs. time after stepdown from steady shear ....................................133

5.12 \( \sigma_{\text{max}} \) as a function of rest time \( t_2 \) after stepdown from steady shear ..........134
5.13  Recover strain vs. time after a steady state shear...........................................135

5.14  \( \sigma_{\text{max}} \) as a function of rest time \( t_2 \) during the strain recovery
measurements........................................................................................................136

5.15  \( \sigma_{\text{max}} \) as a function of rest time \( t_2 \) after shear in different directions ..........137

5.16  Tube model prediction of \( \sigma_{\text{max}} \) recovery after stepdown from
steady shear..............................................................................................................138

5.17  An example that the system had stronger chain entanglement but
less thermal stable....................................................................................................141
CHAPTER I

INTRODUCTION

Polymers play an central role in modem chemical technology due to their richness of properties.\textsuperscript{1-7} One of the most important properties is their mechanical properties. This dissertation mainly focused on the mechanical properties of polymeric materials in their liquid state, i.e., the temperature above glassing transition temperature. For polymeric liquids with short chains or in a very dilute concentration solutions, the mechanical properties are already well understood.\textsuperscript{8-12} However, when the polymer chains are long enough and in their concentrated solutions or melt state, polymer chains will entanglement with each other due to their topological relationship. The entangled polymeric liquids show complicated nonlinear mechanical behaviors.\textsuperscript{5, 13-15} Understanding the properties of chain entanglement under different conditions could help us to develop new polymer theories, guide us in solving processing problems, and find new applications of polymers based on their special properties.

One of the most widely used methods to demonstrate the complex mechanical properties of entangled polymeric liquids is rheological measurement. The deformation and flow behavior of entangled polymeric liquids is a central subject in polymer science and has been extensively studied in the past.\textsuperscript{3,16} To link macroscopic rheological measurements to molecular responses, numerous calculations based on
different versions of the tube model\textsuperscript{17} have been successfully carried out.\textsuperscript{18,19} Such theoretical studies have also been extended to the nonlinear response regime.\textsuperscript{20,21}

A recent series of particle-tracking velocimetric (PTV) observations along with rheometric measurements increased our understanding of mechanical responses of entangled polymeric liquids to startup continuous shear.\textsuperscript{22-25} For a series of polybutadiene (PB) solutions, appearance of shear inhomogeneity during sudden startup shear provided convincing evidence for yielding\textsuperscript{26} that took place on time scales much shorter than the reputation time and preceded the eventual state of steady shear. These new findings indicated that we need to think about how the transient cohesion of the entangled chains is overcome during fast continuous shear\textsuperscript{22-25} or after a sudden step shear.\textsuperscript{27,28} In particular, the emergence of shear inhomogeneity seemed to originate from localized cohesive failure (i.e., yielding) during the initial response to sudden fast shear. particle-tracking velocimetry observations offered us fresh insight into such prominent features as stress overshoot during startup shear. Yielding, i.e., a transition from elastic deformation to irrecoverable deformation (i.e., flow) that was signified by the stress overshoot,\textsuperscript{29} could occur in a wide range of deformation conditions.

The new experimental evidence and molecular picture of yielding gave us a hint that for most materials, the changing of microstructure dictated the viscoelastic responses and determined when and how nonlinearity may arise. For example, entangled polymeric liquids originated their structure from chain entanglement, i.e., the inability for molecules to pass across one another due to their topological relationship. Almost all the nonlinear rheological behaviors of entangled polymeric liquids could be related to how the polymer chains rearrange themselves under different conditions. To better understand the physical picture behind nonlinear
viscoelastic behaviors, we started to think the origin of chain entanglement and how the dynamics of chain entanglement changes under different deformation conditions. In this dissertation, we tried to understand how the microstructure changed under different deformation conditions based on the experimental evidence, and probed the physical origin of different nonlinear rheological behaviors.

This dissertation was organized as the following: In CHAPTER II, the background of this study was introduced, including the basic concept of rheology, models and molecular picture of entangled polymeric liquids, and some previous studies of nonlinear polymer rheology.

In CHAPTER III, we showed that in contrast to most studies in the literature that treat nonlinearity in large amplitude oscillatory shear in steady state, the nonlinearity could also arise in entangled polymeric liquids due to rearrangement of their microstructures over time in response to large amplitude oscillatory shear. In this case, no correlation was obvious between strain dependence of the steady-state stress response and deviation of the steady-state stress from the sinusoidal wave. For instance, a highly viscoelastic material made of nano-sized polybutadiene particles exhibits homogeneous deformation and an approximate sinusoidal wave as well as strong strain softening. In a second example, an entangled polybutadiene solution undergoes inhomogeneous structural change, and the nonlinearity also took a finite time to develop to its fullest. In the example of wall slip of a monodisperse entangled polyisoprene melt, contrary to the literature claim that even harmonics would emerge, we show that the stress response only involves odd harmonics in absence of any meniscus instability. Lastly, a polydisperse diphenylmethylvinyl silicone gum experiences homogeneous LAOS without displaying significant harmonics.
Moreover, the Fourier transform analysis showed that meniscus failure is responsible for the emergence of *even* harmonics.

In CHAPTER IV, we investigated the properties of chain entanglement of entangled polymeric liquids at steady shear flow by superimposing either small amplitude oscillatory shear or small step strain and analyzing the resultant mechanic responses.\(^{30}\) By comparing different samples at various temperatures and shear rates, the results showed the overall relaxation behaviors at flow state were independent of solvents and temperatures, and accelerated by the underlying shear rate, consistent with the idea of convective constraint release (CCR). The dynamic picture of chain entanglement was also studies based on the modulus of entangled polymeric liquids at flow states.

In CHAPTER V, we made a connection between the stress maximum value of a fast large deformation and the strength of chain entanglement, and carried out rate-switching tests to further elucidate the changes of the transient strength of chain entanglement in response to various forms of shearing. Our results showed that consistent with other experimental evidence, elastic yielding could occur during quiescent relaxation after a large step strain. The re-entanglement process was also investigated. The new state of chain entanglement was stable for a significant period after shear cessation, and the strength of chain entanglement could achieve a stronger state during recovery than that of the equilibrium state.

Some parts of the work appeared in Journal of Rheology and Macromolecules.
CHAPTER II

BACKGROUND OF THIS STUDY

2.1 Rheological measurement

Most mechanical properties of polymers and polymer solutions could be demonstrated via rheological measurements. In simple shear, the sample is sandwiched between two plates. A typical simple shear illustration is shown in Figure 2.1. When the moving plate moves a distance $\Delta x$ and deformed the sample with a thickness of $h$, the sample suffers a deformation of strain $\gamma$:

$$\gamma = \frac{\Delta x}{h} \quad (2.1)$$

the shear rate is defined as

$$\dot{\gamma} = \frac{d\gamma}{dt} \quad (2.2)$$

And the shear stress is defined as the force per unit area of the moving plate:

$$\sigma = \frac{dF}{dA} \quad (2.3)$$

In conventional studies, people tried to build up the connection among stress, shear rate, strain, and time.$^5,^{31-33}$

In order to overcome the strain limit of the setup which is shown in Figure 2.1, rotational cone and plate rheometers are widely used.$^5$ This setup was first suggested by Mooney and Ewart$^{34}$ at the bottom part of a rotational cylinder rheometer to
eliminate the low end effect. The advantage that it could achieve almost uniform stress and shear rate distribution made it to be the most popular rheometer setup to study the nonlinear rheological behavior. Figure 2.2 showed a typical rotational rheometer setup.

![Figure 2.1 Schematic illustration of rheological measurement in simple shear](image1)

Figure 2.1 Schematic illustration of rheological measurement in simple shear

For viscoelastic materials such as entangled polymeric liquids, suspensions, the edge of the samples was unstable during shear\textsuperscript{35, 36} when relationship of second normal force difference, size of the edge and surface tension met some certain critical value.\textsuperscript{37, 38}

![Figure 2.2 The side view of a rotational rheometer](image2)

Figure 2.2 The side view of a rotational rheometer
The edge fracture needs to be overcome if we want to archive the steady flow state and study the rheological properties. The inherent experimental complication arising from edge fracture could be overcome by employing an improved setup to isolate the rheological measurements from the inevitable meniscus failure. To eliminate the edge effects on rheometric measurements, an effective strategy was adopted to extract the mechanical response of only the central portion of the sample. In other words, we could utilize a cone/partitioned-plate (CPP) assembly as shown in Figure 2.3 and Figure 2.4,\textsuperscript{39-42} where the inner disk was linked to the torque transducer of rheometer, and the outer ring as well as the bottom rotating cone has the same diameter. The clearance between the outer ring and inner disk is about 0.2 mm. Cruder methods to eliminate edge fracture were also employed numerous times in the literature, including sample overloading and introduction of a guard ring.\textsuperscript{38, 43, 44} Although edge fracture may be delayed by such a treatment, these modifications produced complicated rheometric contributions and were therefore useful only if rheological measurements could be compromised. This CPP allows rheometric measurements to be free of edge failure and enabled us to carry out steady-state rheometric measurements.
Figure 2.3 Side view of the cone-partitioned plate (CPP) device.
Rheological phenomenon of entangled polymeric liquids

The entangled polymeric liquids\textsuperscript{45, 46} showed complicated mechanical properties, which could be partially demonstrated by the following rheological measurements:

2.2.1 Linear rheological behaviors

When entangled polymeric liquids were suffered a very small deformation, or were deformed under a very small deformation rate, i.e., at the limit of $\gamma \to 0$ or $\dot{\gamma} \to 0 \text{s}^{-1}$, the intrinsic properties such as modulus, viscosity (see more details below) would be independent of strain or deformation rate. This region was called linear
region. Below were some methods which could be used to demonstrate the linear rheological behaviors.

2.2.1.1 Small step strain:

When entangled polymeric liquids were subjected a small increase of strain, as illustrated in Figure 2.5, the stress response will relax as a function of time after this step strain increase. The time dependence behavior is also call viscoelastic.\(^5\)

We could use the relaxation modulus to describe the stress relaxation behavior:\(^{47,48}\)

\[
G(t, \gamma) = \frac{\sigma(t, \gamma)}{\gamma}
\]

(2.4)

Figure 2.5 Illustration of a step strain
When the strain $\gamma$ is small enough, the relaxation modulus are independent of apply strain $\gamma$, this regime is called linear regime. Different materials showed different relaxation behavior, which depended on molecular weight distribution, molecule structure, and components of samples.$^{47,49-53}$

2.2.1.2 startup shear:

When entangled polymeric liquids are subjected to flow from a rest state (as shown in Figure 2.6), if shear rate is very low, the stress will grow monotonically to approach steady state stress value $\eta^*$, where $\eta^*$ is zero-shear viscosity independent of shear rates.$^{54-57}$ It could be defined as:

$$\eta_0 = \frac{\sigma(\dot{\gamma})}{\dot{\gamma}} \quad (2.5)$$

The regime in which the shear viscosity is a constant value is called linear regime.

![Figure 2.6 Illustration of a continuous shear](image-url)

Figure 2.6 Illustration of a continuous shear
2.2.1.3 Small amplitude oscillatory shear

Linear viscoelasticity is both conceptually and technically straightforward to characterize by using small amplitude oscillatory shear. Small amplitude oscillatory shear focuses on the stress response to an externally imposed oscillatory shear strain \( \gamma = \gamma_0 \sin \omega t \) when \( \gamma_0 \to 0 \). In general, the stress response were typically studied under the condition of steady state, where the stress responses \( \sigma^{ss}(t; \omega \gamma_0) \) was a periodic function of time.

Figure 2.7 A typical G’ and G” curve of an entangled polymeric liquid.
For viscoelastic materials, the shear stress $\sigma(t; \omega, \gamma_0)$ is also a sinusoidal wave when $\gamma_0$ is lower than a critical value $\gamma_c$. In other word, for a small amplitude oscillatory shear measurement, the stress response could be written as:

$$\sigma(t; \omega, \gamma_0) = \gamma_0 G'(\omega) \sin(\omega \tau) + \gamma_0 G''(\omega) \cos(\omega \tau)$$

(2.6)

Where $G'(\omega)$ and $G''(\omega)$ is only a function of applied frequency $\omega$. The $G'$ and $G''$ is called storage modulus and loss modulus, respectively. Figure 2.7 showed a typical $G'$ and $G''$ curve of an entangled polymeric liquids as a function of frequency, the physical meaning of the $G'$ $G''$ curve will be discussed later.

2.2.2 Nonlinear rheological behaviors

For entangled polymeric liquids, in most cases the stress response is not linear proportional to shear rate or strain, this phenomenon is called nonlinear behavior. For example:

2.2.2.1 Shear thinning

For entangled polymeric liquids, when the shear rate is high, i.e., in non-linear regime, the shear viscosity $\eta = \frac{\sigma}{\dot{\gamma}}$ at steady flow state is a function of applied shear rate $\dot{\gamma}$.\textsuperscript{68-71} A typical viscosity vs. shear rate curve is shown in Figure 2.8. This phenomenon that the shear viscosity decreases as increasing shear rate is called shear thinning.\textsuperscript{5}
2.2.2.2 Stress overshoot

When entangled polymeric liquids are subjected to flow from a rest state, if the shear rate is high, i.e., in non-linear region, unlike the shear stress grows monotonically in linear regime, the stress will reach a maximum before getting to steady state. This stress maximum after a startup shear is called “stress overshoot”.\textsuperscript{29} and the strain at when the stress reaches its maximum is called “yield strain”.\textsuperscript{73} The yield strain and the stress overshoot value strongly depends on applied shear rates.\textsuperscript{29,72} A typical stress response of an entangled polymeric liquids during a startup shear in linear and nonlinear regime is shown in Figure 2.9.
Figure 2.9. A typical stress response of an entangled polymeric sample during a startup shear.

2.3 Maxwell model

In order to describe viscoelastic behaviors of entangled polymeric liquids, different models were developed in the past. One of the most widely used model is Maxwell model given by Maxwell\(^5\). In Maxwell model, the sample could be represented by a purely viscous component and a purely elastic component connected in series, as shown in Figure 2.10.
The Maxwell model could be described by a partial differential equation connecting stress and strain:

$$\dot{\gamma} = \frac{\sigma}{G} + \frac{\sigma}{\eta} \quad (2.7)$$

We could define terminal relaxation time $\tau = \frac{\eta}{G}$, and Eq (2.7) could be re-written as:

$$G\dot{\gamma} = \sigma + \frac{\sigma}{\tau} \quad (2.8)$$

Here are two important conclusions in the Maxwell model:

### 2.3.1 Small amplitude oscillatory shear:

When we give the sample a sinusoidal deformation with a frequency of $\omega$, i.e., $\gamma = \gamma_0 e^{i\omega t}$, Eq. (2.8) becomes:

$$G\gamma_0 i \omega e^{i\omega t} = \sigma_0 i \omega e^{i\omega t} + \frac{\sigma_0 e^{i\omega t}}{\tau} \quad (2.9)$$

$$\Rightarrow \sigma = (G' + iG'') \gamma \quad (2.10)$$

Where
\[ G' = \frac{G\omega^2\tau^2}{1 + \omega^2\tau^2} \quad \text{and} \quad G'' = \frac{G\omega\tau}{1 + \omega^2\tau^2} \quad (2.11) \]

Figure 2.11 showed \( G' \) and \( G'' \) as a function of frequency \( \omega \) calculated by Eq. (2.11), the frequency where \( G' \) equals to \( G'' \) is called crossover frequency \( \omega_c \), which equals to \( 1/\tau \).

2.3.2 Stress relaxation:

If we shear the sample to a certain amount of strain, and then stop shearing, i.e., at time equals to zero, \( \dot{\gamma} = 0 \text{s}^{-1} \), Eq. (2.8) becomes:

\[ 0 = \sigma + \frac{\sigma}{\tau} \quad (2.12) \]

Where
The solution of Eq. (2.12) is:

\[ \sigma |_{t=0} = \sigma_0 \]

Eq. (2.13) showed that after a step strain, the stress takes a time scale of \( \tau \) to relax stress to around 1/e of the initial stress.

The conclusions from (2.13) and (2.11) are very important, we will use these conclusions in the rest chapters.

2.4 Tube model

For entangled polymeric liquids, the unique mechanical properties are mainly coming from strong interaction among chains due to their topological relationship,\(^8,9\) as shown in Figure 2.12: the fact that chains cannot cross each other creates the topological interaction (chain entanglement).

![Figure 2.12 An illustration of chain entanglement](image)

In order to link the physical properties of entangled polymeric liquids to the molecule responses, different models were developed in the past decades. Tube model\(^8\) with the idea of reputation concept\(^74\) was the most successful model to
describe the viscoelastic properties of entangled polymeric liquids in their linear regime.

Imaging that there is a test chain in an entangled polymeric liquid sample, and other surrounding chains are frozen. The obstacles for the test chain to move along the chain length direction is much less than the obstacles for the test chain to move perpendicular to the chain length direction. In other words, it is like that the test chain is confined in a tube-like region, and the most possible motion of the test chain is reptation along the tube, as shown in Figure 2.13. In tube model, the tube diameter $a$ is proportional to the end-end distance of a random coil with a molecular weight $M_e$, which is called the molecular weight between entanglements.

Figure 2.13 An illustration of tube model

Experiments showed that at thermal equilibrium state, the concept of reptation was the dominant dynamics of well entangled polymers. Here are some conclusions based on tube model:
The plateau modulus, as well as the modulus at the crossover frequency at lower frequency regime, of pure entangled polymeric liquids (polymer melts) is given by Eq. (2.14)

\[ G_N^{(0)} \sim \frac{\rho}{M_e} \]  

(2.14)

For entangled polymeric liquids with a volume fraction \( \phi \) of long chains, the entanglement molecular weight becomes:

\[ M_e(\phi) = \frac{M_e}{\phi^{1.2-1.3}} \]  

(2.15)

And plateau modulus becomes:

\[ G(\phi) = \frac{D(\phi)RT}{M_e(\phi)} = G_N^{(0)} \phi^{2.2-2.3} \]  

(2.16)

The entanglement density \( Z \) is defined as:

\[ Z(\phi) = \frac{M}{M_e(\phi)} \]  

(2.17)

Define \( \tau_e \) as the time scale when the average displacement of a segment of a long chain equals to tube diameter \( a \). After a small step strain after \( t = \tau_e \), the polymer chains start to disengage from the tube, which gives the relaxation modulus in the following form:

\[ G(t) = 3G_N^0 \psi(t) = 3G_N^0 \sum_{p: \text{odd}} \frac{8}{p^2 \pi^2} \exp(-p^2t/\tau_d) \quad (t \geq \tau_e) \]  

(2.18)

With

\[ \tau_d = Z^3 \tau_e \]  

(2.19)
After a large step shear with a strain $\gamma$, the relaxation modulus becomes:

$$G(t, \gamma) = h(\gamma)G(t) \quad (t \geq \tau_R) \quad (2.20)$$

With

$$\tau_R \approx \tau_d / 3Z \quad (2.21)$$

And

$$h(\gamma) \approx \frac{1}{1 + \frac{4}{15} \gamma^2} \quad (2.22)$$

The stress for an arbitrary shear flow history could be roughly estimated as (BKZ model)

$$\sigma(t) = 3G_N \int_{-\infty}^{t} dt' \left( \frac{\partial}{\partial t'} \psi(t-t') \right) (\gamma(t,t')) h(\gamma(t,t')) \quad (2.23)$$

With

$$\gamma(t,t') = \gamma(t) - \gamma(t') \quad (2.24)$$

Although tube model combined with different constitutive equations has been successfully carried out in linear response regime, whether the assumptions are still valid in nonlinear regime is still unclear. In the next section, a series of new findings of nonlinear rheological phenomenon were emerged thanks to Particle Tracking Velocimetry, which make the tube model and conventional constitutive equations questionable.
2.5 Particle Tracking Velocimetry (PTV)

Most previous models and rheological studies were based on the assumption that homogeneous deformation prevails during measurements. However, whether this assumption hold for all of the entangled polymeric liquids was questionable. It is important to check whether the flow field is homogeneous or not during our rheological measurements. Particle-tracking velocimetry\textsuperscript{78} has been effectively applied since 2006\textsuperscript{25, 79} to complement traditional rheometric experiments on entangled polymeric liquids, ranging from sudden startup shear,\textsuperscript{24, 25, 72, 80} large amplitude oscillatory shear,\textsuperscript{81-83} and large step shear.\textsuperscript{27, 28, 84, 85}

2.5.1 Setup

Figure 2.14 is the side view of a particle-tracking velocimetry setup. A laser sheet was passed across the gap at an angle to illuminate the sliver particles embedded in the sample. Movement of the illuminated particles could be captured by a CCD camera at a speed of 30 frames per second so that the time-dependent deformation field could be recorded by the video microscopy. In this setup, all surfaces are smooth surfaces made by steel except for a small particle-tracking velocimetry window made of glass. For the purpose of particle-tracking velocimetry observations, we incorporated about 600 ppm silver-coated particles with an average diameter of 10 \(\mu\text{m}\) (Dantec Dynamics HGS-10) into samples.

2.5.2 PVT observation

A recent series of particle-tracking velocimetry observations along with rheometric measurements have increased our understanding of mechanical responses of entangled polymers under different shear conditions. Recent studies showed that a
lot of entangled polymeric liquids made of flexible linear chains cannot undergo flow upon a startup shear or large amplitude oscillatory shear without yielding inhomogeneously. \textsuperscript{24, 81} Particle-tracking velocimetry observations also revealed non-quiescent relaxation from a large step strain. \textsuperscript{28, 86}

Figure 2.14 An illustration of a typical particle-tracking velocimetry setup on cone and plate rheometer

2.5.2.1 Startup shear

A particle-tracking velocimetry study\textsuperscript{24} on a series polybutadiene solutions during startup shear showed that the velocity profile depended on the entanglement density \( Z \). For small \( Z \) (\( Z=13 \)), the samples only underwent homogeneous shear under all shear rates. For a higher \( Z \) (\( Z=27 \)), the solution showed transient inhomogeneous flow after stress overshoot and came back to homogeneous flow at steady state. For solutions with \( Z \) higher than 40, the inhomogeneous shear could be observed after stress overshoot and it was stable at steady state for a wide range of shear rate. Figure
Figure 2.15 An example of imhomogeneous shear: a polybutadiene solution with $Z=119$ during a startup shear at shear rate of 0.55 s$^{-1}$. Reprint from ref$^{24}$ with permission.

For monodisperse entangled polymeric liquids with sufficient chain entanglement, particle-tracking velocimetry observations have revealed inhomogeneous. Apart from two publications by Boukany and Wang on polydisperse entangled solutions$^{80}$ and monodisperse melts$^{86}$ respectively using a custom-made sliding-plate rheometer, all the previous particle-tracking velocimetry investigations focused on nonlinear behavior of monodisperse entangled polymer solutions. Another work$^{39}$ explored
nonlinear responses of diphenylmethylvinyl silicone gum, which was a polydisperse melt, to startup shear. The polydisperse diphenylmethylvinyl silicone gum showed nonlinear responses in a homogeneous manner, as shown in Figure 2.16.

![Figure 2.16](image)

Figure 2.16 An example of homogeneous shear: polydisperse diphenylmethylvinyl silicone gum at shear rate of 2 s⁻¹

2.5.2.2 Large amplitude oscillatory shear:

large amplitude oscillatory shear is another leading probe of nonlinear rheological responses of viscoelastic materials. particle-tracking velocimetry technique has used to study the velocity profile dependence of amplitude and frequency for polybutadiene solutions with different entanglement density Z.\textsuperscript{82} Depends on Z, frequency and amplitude, the velocity profile could be either
homogeneous, or inhomogeneous flow could be observed in the first cycle or developed after several cycles.

Figure 2.17 An example of imhomogeneous during large amplitude oscillatory shear: a polybutadiene solution

For example, an entangled polybutadiene solution underwent inhomogeneous (as shown in Figure 2.17), and the nonlinearity also took a finite time to develop to its fullest. In another example a monodisperse entangled polysisoprene melt showed wall slip (as shown in Figure 2.18), whereas a polydisperse diphenylmethylvinyl silicone gum experienced homogeneous large amplitude oscillatory shear.\textsuperscript{83}
2.5.2.3 Large step strain:

For entangled polymeric liquids with sufficient entanglement density $Z$, macroscopic motion could be observed after large step strain. For example, for a polybutadiene solution (10% polybutadiene with molecular weight 1000 kg/mol dissolved in polybutadiene with molecular weight of 10 kg/mol, named as PB1M-10%-10k), at strains lower than 0.7, no macroscopic motion could be seen after shear cessation. When the strain was higher, macroscopic motions occurred after shear cessation. Actually, the observed macroscopic motions could be very different or random in terms of their magnitude and position along the sample thickness. On the other hand, such differences do not produce any discernible difference in the

Figure 2.18 An example of wall slip during large amplitude oscillatory shear: a polyisoprene melt
rheometric measurements. Figure 2.19 showed the macroscopic motions after shear cessation could last for around 50s and the corresponding total displacements in two different loadings after a step strain with $\gamma_0 = 3.0$, where a high shear rate of 10 s$^{-1}$,

corresponding to Weissenberg number $Wi = 500$, was used to generate the step strain. The two stress relaxation curves completely overlapped with each other.

Experiments with a series styrene-butadiene rubber (SBR)\textsuperscript{86} in sudden large step strain demonstrated that, unlike entangled polymer solutions showed non-quiescent
relaxation immediately after large step strain, the remaining elastic force in polymer melts struggle with the energy barrier quiescently for a significant induction time which could be much longer than Rouse relaxation time before the macroscopic motion. Figure 2.20 showed the macroscopic motion after a large step strain for SBR melt.

Figure 2.20 Particle-tracking velocimetric detection of total macroscopic motions during relaxation after shear ceasing for SBR 250K. Reprint from ref\textsuperscript{86} with permission.

2.6 New understanding and molecule picture

particle-tracking velocimetry observations along with rheometric measurements have increased our understanding of mechanical responses of entangled polymers to sudden large deformations. Unlike yielding in glassy polymers, entangled polymeric liquids undergo a great deal of deformation before the yield point was reached. These
new findings indicated that we need to think about how the transient cohesion of the entanglement network is overcome during fast large deformation.

New molecule pictures\textsuperscript{26} rose up based on experimental observation. In the new theory, three types of force play the dominant roles in nonlinear flow regime of an entangled polymeric sample. Let us focus on a test chain. During a startup deformation applied to a sample, the chain deforms due to the interaction, which could be represented effectively by an intermolecular locking force $f_{\text{iml}}$, between the test chain and other surrounding chains. On the other hand, the chain deformation in each “spring” between entanglements build up a retraction force $f_{\text{retract}} \sim \gamma$. The chain sliding could not occur until $f_{\text{retract}}$ reach the maximum limit of $f_{\text{iml}}$. If the sample suffers further deformation, $f_{\text{iml}}$ could not support to building up $f_{\text{retract}}$. Therefore the chain sliding must occur. This force balance-imbalance transition give us the stress overshoot during a startup shear. Base on experimental evidence, $f_{\text{iml}}$ is expected to be larger as we increase shear rate.

Since $f_{\text{iml}}$ relates to shear rate, after a large step strain, $f_{\text{iml}}$ will drop to a value lower than the retraction force $f_{\text{retract}}$. Because each chain length between entanglements has entropy $\sim k_B T$, the energy barrier for chain ends to start to sliding with other chains (disentanglement) is also $\sim k_B T$, which corresponding an entanglement force $f_{\text{ent}} \sim k_B T/ l_{\text{ent}}$, where $l_{\text{ent}}$ is the entanglement length. Therefore the disentanglement criterion after a large step strain was given by $f_{\text{retract}} > f_{\text{ent}} \sim k_B T/ l_{\text{ent}}$. Figure 2.21 showed the illustration of the force imbalance after a large step strain.
Yielding, i.e., a transition from elastic deformation to irrecoverable deformation (i.e., flow) that is signified by the stress overshoot, could also occur in absence of any visible shear inhomogeneity, as is the case whenever the system was insufficiently entangled. Shear homogeneity allows us to more straightforwardly explore various rheological characteristics of steady shear of entangled polymeric liquids.

2.7 Recent studies of chain entanglement

There have been two recent studies of the nature of steady shear in the shear thinning regime of entangled solutions. To a series of polybutadiene solutions, startup shear was first applied to produce steady state. Then, the shear was turned off for different amounts of resting time $\tau_{\text{Rest}}$ before the same startup shear was re-applied. The stress overshoot characteristics were found to return only after sufficient resting time $\tau_{\text{Rest}}$ from the preceding shear, which was found to be longer than the terminal relaxation time $\tau$. The weaker overshoot was taken as evidence for chain
disentanglement. In a second study, by superimposing small amplitude oscillatory shear at different frequencies onto a steady-state shear in the shear thinning regime, it was found based on entangled polymeric liquids that the state of steady flow possesses a basic characteristic: the effective relaxation time is universally shorter than the reciprocal imposed average shear rate $\gamma$ regardless of whether steady shear is homogeneous or not. When the Weissenberg number $Wi = \dot{\gamma} \tau$ is much greater than unity, chains bypass one another by undergoing convective constraint release (CCR) on the time scale of $1/\dot{\gamma} \ll \tau$. Such state of flow is truly a state of less entanglement or partial disentanglement because in quiescence with full entanglement, chains take a period comparable to $\tau$ to pass around one another by thermal diffusion.
CHAPTER III

NONLINEARITY IN LARGE AMPLITUDE OSCILLATORY SHEAR

3.1 Introduction

Many structured materials, either biological or synthetic, including colloids, polymers, liquid crystals, micelles, foams, gels (e.g., associating polymers, ionomers, gelatins, etc.), emulsions and membranes, exhibited viscoelastic behavior due to the microscopic organization of the constituents into cooperative structures. Characteristics of the microstructure dictate the viscoelastic responses and determine when and how nonlinearity may arise. For example, entangled polymeric liquids derive their structure from chain entanglement, i.e., the inability for chain-like molecules to freely pass across one another within their overall relaxation time $\tau$. Upon a sudden startup shear at a rate $\dot{\gamma}$ corresponding to the Weissenberg number $Wi = \dot{\gamma}\tau \gg 1$, chains in an entangled polymeric liquid are forced to pass around one another without waiting for thermal diffusion to move them past when the initial elastic deformation transforms to viscous flow.

Linear viscoelasticity is both conceptually and technically more straightforward to characterize. The work in this chapter focused on a generic study of nonlinearity in the stress response to an externally imposed single-frequency oscillatory shear strain $\gamma = \gamma_0\sin(\omega t)$. For many viscoelastic materials, the shear stress $\sigma(t;\omega \gamma_0)$ is not linearly
proportional in magnitude to $\gamma_0$ when $\gamma_0$ exceeds a critical value $\gamma_c$. In the literature, nonlinear responses to large amplitude oscillatory shear were typically studied under the condition of steady state,\textsuperscript{90-98} where $\sigma^{ss}(t; \omega \gamma_0)$ is a periodic function of time. In this case, the final response could be represented completely by a Fourier series:

$$\sigma(t; \omega, \gamma_0) = \sum_{n=1}^{\infty} \left[ a_n (\omega, \gamma_0) \sin(n \omega t) + b_n (\omega, \gamma_0) \cos(n \omega t) \right]$$  \hspace{1cm} (3.1)

where $a_n$ and $b_n$ represent respectively the elastic and viscous components of the stress responses. In terms of the generalized storage and loss moduli $G_n'$ and $G_n''$, the coefficients $a_n = \gamma_0 G_n'$ and $b_n = \gamma_0 G_n''$. A Fourier transform (FT) analysis could be made of $\sigma^{ss}(t; \omega \gamma_0)$ to determine all of $\{G_n'\}$ and $\{G_n''\}$ for all values of $\omega$ and $\gamma_0$. Wilhelm and coworkers\textsuperscript{63, 99} have advocated this Fourier transform rheology method.

In the case where the stress response is of odd symmetry with respect to directionality of shear strain and shear rate, i.e., when the material response is the same if the shearing axis is reversed and $n$ is odd in the Fourier series of Eq.( 3.1 ), Cho et al.\textsuperscript{64} avoided performing an FT rheology analysis by decomposing the stress response into elastic and viscous components. Two recent studies further discussed alternative methods to the FT analysis\textsuperscript{67, 100} where the goal is to find a more definitive way to quantify the steady-state stress response. Since the characteristics of $\sigma^{ss}(t; \omega \gamma_0)$ do not depict how the system evolves over time from its equilibrium state to the final non-equilibrium state, the mathematical features of $\sigma^{ss}(t; \omega \gamma_0)$ could hardly be regarded as the full rheological fingerprint.

It is our opinion that many, perhaps, most viscoelastic systems respond to large amplitude oscillatory shear in a time-dependent fashion, including particle-filled polybutadiene melts\textsuperscript{101} and entangled polybutadiene solutions.\textsuperscript{82} The purpose of this chapter was to elucidate four more examples of strain softening materials. These four
systems were selected to illustrate how yielding behavior is different, from a polymeric nano-granular paste, to an entangled melts of linear chains with either broad or narrow molecular weight distribution, and to an entangled polymer solution. With the assistance of particle-tracking velocimetry,\textsuperscript{26} we have identified the following four characteristics accompanying the large amplitude oscillatory shear: (i) homogeneous strain sinusoidal softening of a polymeric paste, (ii) shear banding of an entangled polymer solution, (iii) interfacial wall slip of one polymer melt, (iv) homogenous yielding of a polydisperse melt.

3.2 Experimental

In order to well study the nonlinear large amplitude oscillatory shear behaviors and investigate the origin of the distortion of stress-strain loop, we chose different materials with careful designed fixtures. This section we would describe the materials and methods in details.

3.2.1 Materials

Four materials were studied in this chapter. (A) The first sample was a highly viscoelastic material made of nano-sized spherical polybutadiene particles. The nanoparticle had a crosslinked polystyrene core and a shell of polybutadiene brushes (with 8.4 \% vinyl content). The average size of the nanoparticle was around 9 nm, and the core/shell ratio was around 1/4. The polydispersity of these particles was around 1.15. The polybutadiene brush molecular weight was around 15 kg/mol, and the average number of polybutadiene chains per particle was around 55. More details about this material could be found in the literature.\textsuperscript{102} (B) The second sample was an entangled solution at a concentration of 10 \% high molecular-weight monodisperse
1,4-polybutadiene (M\text{w} = 1,100 \text{ kg/mol}) in an oligomeric monodisperse polybutadiene (M\text{w} = 10 \text{ kg/mol}). The sample was prepared by first dissolving polybutadiene 1M in toluene and then mixing with polybutadiene 10K. Toluene was then allowed to evaporate from the uniform solution at room temperature for a week under hood. The residual toluene was completely removed under vacuum for about 3 days. This sample was named as PB1M-10\%-10K in this chapter. (C) The third sample under present study was a monodisperse 1,4-polyisoprene (PI) melt made by Goodyear Rubbers & Tires with the following characteristics: cis-1,4 (75.0 \%), trans-1,4 (16.4 \%), and -3.4 (6.6 \%), M\text{w}= 547K (g/mol) and M\text{n} = 516K (g/mol). This sample was named as PI550K in this chapter. (D) The last sample was a polydisperse diphenylmethylvinyl silicone gum from GE Silicones (product number: SE54) with M\text{z} = 1,479 \text{ kg/mol}, M\text{w} = 878.2 \text{ kg/mol} and M\text{n} = 538.6 \text{ kg/mol}.

3.2.2 Apparatus

All measurements were made with an Advanced Expansion Rheometric System (ARES), equipped with different customer-made fixtures. Measurements of 1,4-polyisoprene 550K and diphenylmethylvinyl silicone gum were performed with a 4° cone-plate fixture with diameter of 10 mm and 15 mm respectively. Wall slip behavior of 1,4-polyisoprene 550K was observed directly at the meniscus. The experiments on nano polybutadiene particle paste were carried out in a partitioned-plate-cone device that has been described previously\textsuperscript{23} (see CHAPTER II for more details). In the partitioned-plate-cone device setup, the bottom rotating cone plate had a 4° angle and a diameter of 30 mm. As part of the top surface, an inner circular disk of 15 mm in diameter was linked to the torque transducer of Advanced Expansion Rheometric System(ARES). The top outer ring was held fixed and had a gap around
0.2 mm with the inner circular disk. The ring’s outer diameter matched that of the bottom cone equal to 30 mm. This partitioned-plate-cone apparatus was also used to eliminate edge effects for 1,4-polyisoprene and the diphenylmethylvinyl silicone gum. Finally, the entangled polybutadiene solution PB1M-10 %-10K was studied with a cone-plate with a diameter of 25 mm and 4° cone angle. It was worth mentioning that in the Arbitrary Wave mode Advanced Expansion Rheometric System(ARES) was capable of delivering nearly perfect sine wave even in the initial cycle. All measurements were carried out at room temperature around 24 °C.

3.2.3 Fourier transformation (FT) analysis

When steady state was achieved, the stress response to $\gamma = \gamma_0 \sin \omega t$ was a periodic function of time and could be expressed as a Fourier series as shown in Eq. (3.1). The amplitudes $\{a_n, b_n\}$ of each term from the fundamental harmonic to other harmonics in Eq. (3.1) could be evaluated according to

$$a_n(\omega, \gamma_0) = \frac{2}{T} \int_{-T/2}^{T/2} \sigma(t; \omega, \gamma_0) \sin n\omega t dt \quad (3.2)$$

And

$$b_n(\omega, \gamma_0) = \frac{2}{T} \int_{-T/2}^{T/2} \sigma(t; \omega, \gamma_0) \cos n\omega t dt \quad (3.3)$$

where $T$ is the period of the large amplitude oscillatory shear equal to $2\pi/\omega$. The intensity of the various harmonic waves is defined by

$$I_n(\omega) = [(a_n)^2 + (b_n)^2]^{1/2} \quad (3.4)$$

Thus, any given periodic stress response of Eq. (3.1) could be expressed in terms of a normalized power spectrum of $I(\omega)/I_1(\omega)$, where $I(\omega)$ was evaluated according to
Eqs. (3.2), (3.3), and (3.4) with $n \omega$ replaced by $\varpi$. In our FT analysis, we typically evaluated $I_n$ over several cycles to reduce the noise level.

3.2.4 Data representation

Advanced Expansion Rheometric System (ARES) not only outputted in its software data on $G'_1$ and $G''_1$ during large amplitude oscillatory shear but also exported the actual data of the time-dependent torque and angular displacement respectively. The transient raw data could be captured by using a digital reading card DATAQ DI-154RS with a rate of 30 data points per second when the fundamental frequency was 0.5 rad/s and 1 rad/s. For the large amplitude oscillatory shear frequency equaled to 5 rad/s, the data collection rate could be set to 120/s. The stress power spectra were calculated by performing Fourier transform on an average of five cycles. We also presented how the peak stress value $\sigma_{\text{peak}}$ changed with time during large amplitude oscillatory shear.

3.3 Results and Discussion

In this section, we would show the large amplitude oscillatory shear behavior for the four different materials with the help of particle tracking velocimetry and Fourier transformation (FT) analysis.

3.3.1 Homogeneous yielding of nano-granular paste of polybutadiene particles

Any large amplitude oscillatory shear study of an unknown system may begin with a small amplitude oscillatory shear frequency sweep. Figure 3.1 showed the small amplitude oscillatory shear data at a strain of 2%. Figure 3.2 showed the Fourier transformation analysis of the small amplitude oscillatory shear stress signal.
at $\gamma_0 = 5\%$ and $\omega = 1$ rad/s, along with a steady-state Lissajous plot (shear stress vs. shear strain loop) in the inset. At such low strains, the Lissajous plot was perfectly elliptical and higher harmonics were negligibly small. Moreover, characteristic of linear response behavior, the peak stress $\sigma_{\text{peak}}$ was found to be constant in time. The gel-like rheological characteristic was indicative of close-packing of the nano-sized polybutadiene particles that led to jamming and inability of the paste to display terminal flow behavior on a reasonable experimental time scale.

![Diagram showing dynamic and loss moduli $G'$ and $G''$ from small amplitude oscillatory shear measurements at $\gamma_0 = 2\%$ of the nano-granular polybutadiene (PB) melt.](image)

Figure 3.1 Dynamic and loss moduli $G'$ and $G''$ from small amplitude oscillatory shear measurements at $\gamma_0 = 2\%$ of the nano-granular polybutadiene (PB) melt.
When $\gamma_0$ was higher than around 20%, $\sigma_{\text{peak}}$ became time-dependent and was no longer linearly proportional to $\gamma_0$. In steady state, the strain softening could be expressed as shown in Figure 3.3 where the slope of -1 was merely to indicate the limit of maximal strain softening. Over a range from $\gamma = 10\%$ to 40\%, the magnitude of the "complex modulus", $\sigma_{\text{peak}}^{ss}/\gamma_0$, actually decreased by a factor of nearly 3 at $\gamma_0 = 40\%$ from its value in the linear response ($\gamma_0 < 10\%$) regime.  

The emergence of the harmonic at $3\omega$ also occurred around $\gamma_0 = 20\%$. For example, at $\gamma_0 = 40\%$, the stress response (peak stress $\sigma_{\text{peak}}$) declined in magnitude over time, and $G_1'$ dropped below $G_1''$ after 200 s, as shown in Figure 3.4. In the steady state, intriguingly enough, the stress signal was almost completely sinusoidal, with the
Lissajous plot looking like a decent ellipse in the inset of Figure 3.5 although the FT analysis detects a small amount of harmonics as shown in Figure 3.5. Since the intensity of the third harmonic was only as low as 3% that of the base harmonic, the steady-state stress $\sigma^{ss}$ could be approximately written as

$$\sigma^{ss}(t) = \sigma_{\text{peak}}^{ss}(\gamma_0) \sin(\omega t + \delta)$$  (3.5)

Figure 3.3 Strain softening expressed in terms of the steady-state "complex modulus" $\sigma_{\text{peak}}^{ss}/\gamma_0$ as a function of the amplitude $\gamma_0$. 
Figure 3.4 Decline of the storage and loss moduli corresponding to the first harmonic as well as the peak value of the shear stress as a function of time for $\gamma_0 = 40\%$ and $\omega = 1 \text{ rad/s}$. 
Figure 3.5 FT analysis of the stress response in steady state for $\gamma_0 = 40\%$ and $\omega = 1$ rad/s, in terms of the normalized power spectrum, where the inset showed the Lissajous plot.

The approximate sinusoidal character of Figure 3.5 expressed in Eq. (3.5) obviously did not capture the strong strain softening depicted by $\sigma_{ss}^{\text{peak}}(\gamma_0)$ in Figure 3.3. To better comprehend the strain softening phenomenon, it was instructive to examine at a high strain $\gamma_0$ how the system initially responded to the imposed large amplitude oscillatory shear that was realized in the Arbitrary Wave mode in Advanced Expansion Rheometric System (ARES). Figure 3.6 showed how the Lissajous loops evolved in time under the condition of $\gamma_0 = 70\%$, $\omega = 1$ rad/s. Clearly, the equilibrium state had given in to the large amplitude oscillatory shear, and was developing toward a new softer microstructure over time. This process could be more clearly delineated by examining the raw stress data of strain and stress for the first
five cycles in Figure 3.7: The peak shear stress (blue dots) dropped over time. Eventually, the system arrived at a new state capable of approximate sinusoidal response to the imposed large amplitude oscillatory shear. This was possible if the new steady-state under the large amplitude oscillatory shear did not undergo further structural change within each cycle. This new state plausibly corresponded to packing of the nano-particles into layers that were long lived, i.e., stable during the large amplitude oscillatory shear.

Figure 3.6 Large amplitude oscillatory shear at $\gamma_0 = 200 \%$, $\omega = 1$ rad/s: Stress-strain loop of the first three cycles
Since the nano-particle paste was most likely free of chain entanglement, we did not expect the yielding to occur inhomogeneously. Our particle-tracking velocimetric observations indeed confirmed occurrence of uniform straining during the large amplitude oscillatory shear. Figure 3.8 showed a linearly varying velocity field in steady state at the moment when the driving surface attains the maximum speed. Thus, the present nano-granular paste of polybutadiene particles offered an example of homogeneous yielding during large amplitude oscillatory shear. To reiterate, absence of chain entanglement insured that no structural failure through the packing rearrangement would result in any drastic reduction of the local shear viscosity.
Consequently, the structure change during yielding was able to proceed homogeneously.

Figure 3.8 Large amplitude oscillatory shear at \( \gamma_0 = 200\% \), \( \omega = 1\) rad/s: Particle-tracking velocimetric observations confirming homogeneous large amplitude oscillatory shear.

3.3.2 Shear banding in an entangled polybutadiene solution.

Shear banding has been reported for entangled polymer solutions during large amplitude oscillatory shear.\(^{82}\) Figure 3.9 presented the small amplitude oscillatory shear frequency sweep measurement for the polybutadiene solution PB1M-10\%-10K, showing the crossover frequency \( \omega_c = \tau^{-1} \) to be around 0.02 rad/s. The oscillatory shear at \( \gamma_0 = 20\% \) was small amplitude oscillatory shear because the stress-strain loops of the first three cycles showed closed elliptical loops in the inset of Figure 3.9,
rather different from those observed for large amplitude oscillatory shear in Figure 3.12 below. In the present study, we chose to perform large amplitude oscillatory shear at $\omega = 1$ rad/s, corresponding to a Deborah number $\omega \tau$ of 50.

Figure 3.9 Dynamic and loss moduli $G'$ and $G''$ from small amplitude oscillatory shear measurements at $\gamma_0 = 5\%$ of the polybutadiene solution PB1M-10%-10K where the inset showed an elliptical Lissajous loop for $\gamma_0 = 20\%$.

For $\gamma_0$ between 0 and 70\%, we only observed linear response – the stress peak did not decline over time, and time-dependence was an ideal sinusoidal wave. Apparent strain softening occurred at higher amplitudes. Actually, the stress response was nearly ideal yield-like beyond 70\% as shown in Figure 3.10 – the slope of $-1$
amounted to having $\sigma_{\text{peak}}^{ss} = \text{constant}$. In contrast, the FT analysis in inset of Figure 3.10 illustrated absence of harmonics in the linear response regime, e.g., at $\gamma_0 = 10\%$.

Figure 3.10 Strain softening expressed in terms of the steady-state "complex modulus" $\sigma_{\text{peak}}^{ss}/\gamma_0$ as a function of the amplitude $\gamma_0$ where the FT analysis in the inset showed ideal sinusoidal stress response.

In large amplitude oscillatory shear, e.g., at $\gamma_0 = 200\%$, $\omega = 1\text{ rad/s}$, Figure 3.11 showed the decline of $\sigma_{\text{peak}}$, $G_1'$ and $G_1''$ respectively. Figure 3.12 of stress vs. strain loops for the first three cycles illustrated yielding behavior. The sample first elastically deformed in response to the strain of $\gamma = \gamma_0\sin\omega t$, with the shear stress $\sigma$ growing monotonically. At $\gamma = 160\%$, yielding occurred as the shear stress started to drop. This was analogous to stress overshoot because the shear stress did not return to
the initial level in the subsequent cycles, strongly indicative of a structural change in the sample. When steady state was reached, was the large amplitude oscillatory shear homogeneous? We had to resort to particle-tracking velocimetry observations.

Figure 3.11 Large amplitude oscillatory shear of the polybutadiene solution PB1M-10%-10K at $\gamma_0 = 200$ % and $\omega = 1$ rad/s: Time dependence of $\sigma_{\text{peak}}$ and $G_1'$ and $G_1''$. 
Figure 3.12 Large amplitude oscillatory shear of the polybutadiene solution PB1M-10%-10K at $\gamma_0 = 200\%$ and $\omega = 1\,\text{rad/s}$: Stress-strain loops of the first three cycles.

Our particle-tracking velocimetry observations indicated that the deformation field was homogeneous in the first several cycles. After five cycles, shear banding emerged as the stress response dropped further according to Figure 3.11. Figure 3.13 showed how the velocity profile changed in steady state when the shear banding was strongest. In each cycle, the apparent shear rate was continuously changing from 0 to $\gamma_0\omega$ and moments at A and C were equivalent, and so were points B and D as indicated in Figure 3.13. Apparently, inhomogeneous yielding occurred between A and B (or C and D) so that strong shear banding was present at both B and D. When
the driving shear rate diminished toward zero, the system healed from its "wound", and the healed sample exhibited homogeneous shear again at moments A and C as confirmed by the particle-tracking velocimetry observations. Thus, although at times A and B the apparent transient strain and shear rate were respectively of the same magnitude the deformation field was completely different. Clearly, the system was unable to settle down to a single state of entanglement within each cycle, even in steady state. This was the origin of strong non-sinusoidal response of the shear stress. Figure 3.14 indicates that the stress response contained considerable harmonics as disclosed by the FT analysis as well as the non-elliptical shape of the Lissajous plot.

Entangled polymeric liquids such as the present polybutadiene 10 % solution were a primary example for nonlinearity in large amplitude oscillatory shear where the structural change occurred even in steady state within each cycle to produce the significant non-sinusoidal responses. They also displayed strain softening in the traditional sense as illustrated in Figure 3.10.
Figure 3.13 Large amplitude oscillatory shear of the polybutadiene solution PB1M-10%-10K at $\gamma_0 = 200\%$ and $\omega = 1$ rad/s: particle-tracking velocimetry measurements of the velocity profiles at two different moments in a steady-state cycle, where the moments of A and C are equivalent, so are moments B and D.
3.3.3 Wall slip of an entangled polyisoprene melt

For entangled melts of linear chains with a high entanglement density $Z$, wall slip was often observed at high shear stresses or strains.\cite{103,104} Boukany and Wang\cite{107} have recently described how interfacial yielding arises during startup shear as a result of chain disentanglement to produce wall slip. In the case of wall slip under large amplitude oscillatory shear, Hatzikiriakos and Dealy\cite{108} and Reimers and Dealy\cite{109} observed even harmonics in their large amplitude oscillatory shear experiments and attributed its occurrence to wall slip. One theoretical study based on a memory-slip model\cite{110} also concluded that wall slip would allow even harmonics to emerge along
with odd harmonics in the shear stress response. It has also been speculated that even harmonics would occur in certain constitutive models in absence of wall slip.\textsuperscript{107} It was thus interesting and important to determine the various characteristics of large amplitude oscillatory shear in polymer melts when wall slip is the dominant response and other factors are unimportant.

3.3.3.1 Wall slip and edge fracture

![Graph showing dynamic and loss moduli](image)

Figure 3.15 Dynamic and loss moduli $G'$ and $G''$ from small amplitude oscillatory shear measurements at $\gamma_0 = 2\%$ of the polyisoprene melt.

First, a small amplitude oscillatory shear measurement was carried out to show in Figure 3.15 that the terminal relaxation time $\tau$ was approximately 54 s. In the linear
response regime, Figure 3.16 revealed completely sinusoidal stress response, where the corresponding Lissajous plot was perfectly elliptical. When $\gamma_0 > 40\%$ with $\omega = 0.5 \text{ rad/s}$, the polyisoprene melt PI550K started to show wall slip and the stress response was strongly nonlinear. Figure 3.17 showed the time dependence of $\sigma_{\text{peak}}$, $G'_1$ and $G''_1$ at $\gamma_0 = 70\%$ and $\omega = 0.5 \text{ rad/s}$, where the dashed line indicated the stress response in absence of any edge failure, which was a condition to be discussed in detail below. At around $t = 300 \text{ s}$, the stress response, characterized by the FT analysis in Figure 3.18, showed emergence of even harmonics as well as a strongly non-elliptical Lissajous plot. A careful inspection of the Lissajous loop indicated a slight loss of a rotational symmetry about the origin, consistent with the appearance of even harmonics.

Figure 3.16 FT analysis of the shear stress and stress-strain loop of the polyisoprene melt at $\gamma_0 = 10\%$ and $\omega = 0.5 \text{ rad/s}$.
Figure 3.17 Time dependence of $\sigma_{\text{peak}}$, $G_1'$ and $G_1''$ at $\gamma_0 = 70\%$ and $\omega = 0.5 \text{ rad/s}$. 
Figure 3.18 FT analysis of the shear stress at around $t = 300$ s, showing emergence of even harmonics as well as a strongly non-elliptical Lissajous plot in the inset.

By measuring movements particles on the meniscus we obtained signature of wall slip in Figure 3.19 during the large amplitude oscillatory shear at $\gamma_0 = 70\%$ and $\omega = 0.5$ rad/s. Analogous to Figure 3.13, severe yielding occurred at both interfaces at B or D. No-slip boundary condition recovered at A and C when the instantaneous shear rate diminished to allow healing of the interface through chain re-entanglement. The video microscopy on the edge also revealed meniscus failure.
Figure 3.19 Particle-tracking velocimetry measurements of the velocity profiles at three moments in a steady-state cycle, where the moments of A and C are equivalent, so are moments B and D.

3.3.3.2 Absence of even harmonics in wall slip

To remove any influence of edge fracture on the large amplitude oscillatory shear characteristics during wall slip, we adopted a literature design\textsuperscript{23} to decouple the rheometric measurements from the edge instability. Using such a partitioned-plate-cone setup, we found that the shear stress quickly stabilized to its steady state as shown in Figure 3.20 in contrast to Figure 3.17. Contrary to all the other three cases studied in this work, $G_1'$ stayed above $G_1''$ in steady state. Because of interfacial slip, the imposed large amplitude oscillatory shear could not be effectively applied to the
bulk of the sample. Consequently, the bulk sample did not get transformed into a liquid and remains well-entangled and solid-like on the time scale of the large amplitude oscillatory shear experiment. Equally interesting and important was the FT analysis of the rheometric measurements that disclosed only odd harmonics in Figure 3.21, contrary to the result of Figure 3.18, implying the emergence of even harmonics was due to edge effects. In other words, true wall slip in large amplitude oscillatory shear appeared free of even harmonics, in odds with the previous conclusions.62, 67, 106

Figure 3.20 Time dependence of $\sigma_{\text{peak}}$, $G'_1$ and $G''_1$ at $\gamma_0 = 70\%$ and $\omega = 0.5$ rad/s measured with the partitioned-plate-cone device.

Emergence of strong harmonics were evident from Figure 3.21 even in absence of edge failure in this example of wall slip because the system alternated between slip and no-slip within each cycle, i.e., the state of deformation was oscillating instead of
stationary. Thus, wall slip in large amplitude oscillatory shear joined the example of large amplitude oscillatory shear banding of entangled polymer solutions as a case where severe nonlinear character in steady state originated from the ability of the system to respond differently during at different moments within each cycle, i.e., wall slip was at B and return to no-slip at C.

Figure 3.21 FT analysis of the shear stress at any time after $t = 100$ s, with a Lissajous loop that is nearly indistinguishable from that in the inset of Figure 3.18.

3.3.4 Large amplitude oscillatory shear of a polydisperse diphenylmethylvinyl silicone gum

Finally, we used a diphenylmethylvinyl silicone gum to depict how edge failure produced wave distortion in large amplitude oscillatory shear in absence of interfacial wall slip.
3.3.4.1 Characteristics of large amplitude oscillatory shear due to edge fracture

The small amplitude oscillatory shear in Figure 3.22 confirmed that diphenylmethylvinyl silicone gum had a broad molecular weight distribution. Figure 3.23 showed the time dependence of the stress response at both low strain $\gamma_0 = 10\%$ and high strain $\gamma_0 = 200\%$ at $\omega = 5$ rad/s. The diphenylmethylvinyl silicone gum showed linear response behavior at $\gamma_0 = 10\%$. However, at $\gamma_0 = 200\%$, $G_1'$ fell below $G_1''$ immediately, and both $G_1'$ and $G_1''$ decreased further over time. For example, around $t = 37$ s, the stress-strain loops in the inset of Figure 3.24 depicted the evolution of the stress response whose FT analysis revealed a number of odd harmonics. In quasi-steady state around $t = 120$ s, small even harmonics along with additional odd harmonics were also visible from the FT analysis in Figure 3.25. A visual inspection of the meniscus showed that the edge integrity could not be maintained during the large amplitude oscillatory shear. In a traditional cone-plate setup, the occurrence of edge fracture made the large amplitude oscillatory shear rheometric measurements of polymer melts unreliable. The strong wave distortion of the stress response and decline of the shear stress might have stemmed from the edge failure that caused the effective amount of sample under large amplitude oscillatory shear to decrease in time.
Figure 3.22 Dynamic and loss moduli $G'$ and $G''$ from small amplitude oscillatory shear measurements at $\gamma_0 = 5\%$ of the diphenylmethylvinyl silicone gum.
3.3.4.2 Characteristics of large amplitude oscillatory shear in absence of edge fracture

To separate the experimental complication of edge effects from the true and intrinsic rheological response of the polydisperse diphenylmethylvinyl silicone gum under large amplitude oscillatory shear, we again adopted the partitioned-plate-cone setup of Ravindranath and Wang.\textsuperscript{42} This effective apparatus allowed us to demonstrate in Figure 3.26 that nearly all the time-dependent drop of the shear stress observed in Figure 3.23 was due to the edge fracture. In other words, in absence of the edge effects, the diphenylmethylvinyl silicone gum quickly attained stable large amplitude oscillatory shear behavior with $G_1'$ below $G_1''$. Upon FT analysis of the
shear stress data, we confirmed that in absence of the edge effected the steady-state stress response did not deviate significantly from a sinusoidal wave depicted by Eq. (3.5). There was only a fairly weak third harmonic term in Figure 3.27 where the inset showed a very slightly distorted elliptical Lissajous loop. Furthermore, particle-tracking velocimetry observations indicated that the large amplitude oscillatory shear was homogeneous. Thus, this was an example analogous to the nano-granular polybutadiene melt where the nonlinearity of large amplitude oscillatory shear was not accompanied by shear banding or interfacial failure, and the stress response was nearly sinusoidal. The diphenylmethylvinyl silicone gum was highly polydisperse as evident from the small amplitude oscillatory shear data of Figure 3.22. The broad molecular weight distribution in the present diphenylmethylvinyl silicone gum allowed the strain-induced yielding during large amplitude oscillatory shear to occur homogeneously. Unable to shear band due to the broad molecular weight distribution, the sample in steady state was also unable to significantly re-adjust its state of entanglement in each cycle. Consequently, the stress response was almost completely sinusoidal as shown in Figure 3.27.
Figure 3.24 FT analysis of the shear stress around $t = 37$ s with Lissajous loop involving several cycles.
Figure 3.25 FT analysis of the raw shear stress data along with the Lissajous plot in steady state.
Figure 3.26 Time independence of $G_1'$ and $G_1''$ (filled symbols) measured in the partitioned-plate-cone device in contrast to the decrease of $G_1'$ and $G_1''$ (open symbols), both at $\gamma_0 = 200\%$ and $\omega = 5$ rad/s.
Figure 3.27 FT analysis of the shear stress in steady state corresponding to the filled symbols of Figure 3.26, where the Lissajous loop was only slightly deviating from an ellipse.

3.4 Conclusion

Underlying microscopic structures of various viscoelastic materials tended to yield under large fast deformations such as large amplitude oscillatory shear. As the material was forced to undergo a transition from elastic deformation to viscous flow, new states emerged in response to the large amplitude oscillatory shear. Such states may or may not be stable during the imposed large amplitude oscillatory shear. If the new state was stable, then the shear stress response tended to be fairly sinusoidal. Conversely, if the system was able to switch from one state to another within each cycle, strong wave distortion took place in the stress response. A common feature
shared by all four systems was the significant strain softening under large amplitude oscillatory shear regardless of whether the final steady state displayed appreciable sign of nonlinearity or not in the form of the stress wave distortion.

It was rare to have a viscoelastic system that would show linear response at large Deborah numbers at any amplitude of oscillatory shear. What experimental system was capable of exhibiting nonlinearity in large amplitude oscillatory shear without experiencing structural changes? How did stress response display significant non-sinusoidal time dependence without yielding or structural change? Some associative materials studied by Ma et al., Ewoldt et al. showed strain hardening within each cycle in steady state. It remains unclear whether the strain-hardening-like behavior was also due to structural changes (such as strain-induced association and dissociation) within each cycle.

Since yielding or association in large amplitude oscillatory shear may not complete within the first oscillation cycle, one had to follow the process to steady state to obtain the full "fingerprint". It was difficult to identify any rheological fingerprint in the nonlinear regime that would be analogous to \( G' \) and \( G'' \) for the equilibrium viscoelastic structure. We had presented four viscoelastic materials to illustrate a wide range of nonlinear behavior in large amplitude oscillatory shear. None of these four systems could greatly benefit from such treatments as the FT analysis and the general stress decomposition (GSD) method proposed by Cho et al. and improved by Ewoldt et al. and Yu, Wang and Zhou. Specifically, we showed two examples (i.e., a nano-particle polybutadiene melt and a polydisperse diphenylmethylvinyl silicone gum) of yielding in large amplitude oscillatory shear that involve little wave distortion, plenty of strain softening and completely homogenous deformation. We analyzed a familiar phenomenon of entangled
polybutadiene solution undergoing severe shear banding. We depicted a classical case of melt wall slip that does not produce even harmonics. Finally, we demonstrated how the commonly-encountered edge fracture resulted in production of even harmonics in both monodisperse PI melt and polydisperse diphenylmethylvinyl silicone gum during large amplitude oscillatory shear.

In summary, we reiterated the importance of identifying the yielding process in large amplitude oscillatory shear of viscoelastic fluids. Regardless of whether we could capture explicit evidence for yielding or not, it was almost inevitable to encounter structural change by large amplitude oscillatory shear in any viscoelastic liquids. The structural change induced by large amplitude oscillatory shear may not be generically depicted by classical constitutive (continuum mechanical) models where the materials parameters were all constants with respect to both space and time. Thus, to theoretically quantify nonlinear large amplitude oscillatory shear of viscoelastic materials remained a formidable task. It seemed that the first step toward depicting nonlinear large amplitude oscillatory shear behavior was to establish reliable phenomenology. Clearly, the steady-state character of large amplitude oscillatory shear did not necessarily reveal strain softening behavior. Homogeneous large amplitude oscillatory shear seemed to imply sinusoidal response. Future study might or might not encounter exception to this statement. Conversely, it has yet to be demonstrated whether or not inhomogeneous large amplitude oscillatory shear necessarily results in wave distortion. In our opinion, whether wave distortion occurs or not depends essentially on whether the new microstructure is stable during each cycle of the large amplitude oscillatory shear and little on whether the steady-state structure and deformation are homogeneous or not across the velocity gradient
direction (i.e., the sample thickness). Likewise, sinusoidal stress response to large amplitude oscillatory shear does not imply homogeneous deformation.
CHAPTER IV

NONLINEAR RHEOLOGICAL BEHAVIORS IN STEADY STATE

4.1 Introduction

Continuous shear is one of the most commonly methods in polymer rheology research to characterize the rheological properties of entangled polymeric liquids. It’s well known that when applied shear rate is larger than the inverse of terminal relaxation time $\tau_d$, polymer chains will tend to disengage from the network, i.e., disentanglement will take place after several strain units. This chain disengagement is corresponding to stress overshoot during startup shear or entangle-disentangle transition (EDT) in creep measurement. To characterize the chain dynamics in nonlinear region is still a challenge in recent polymer rheology study. This chapter mainly focused on the study of chain dynamics in steady flow state in nonlinear flow regime.

Linear viscoelastic properties of entangled polymeric liquids are already well understood based on tube model. One widely used method to characterize the relaxation dynamic of entangled polymeric liquids is step strain. The stress responds showed how the system came back to the equilibrium state after a disturbance. Another commonly employed characterize method was small amplitude oscillatory shear frequency sweep measurement. The stress responds during these measurements were usually reported in terms of $G'$ and $G''$ as a function of frequency $\omega$. For
entangled polymeric liquids, the entangled molecular weight $M_e$ is characterized by the plateau modules $G^u_e = \frac{sRT}{M_e}$, where $\rho$ is the density of entangled polymers, $R$ is the ideal gas constant and $T$ is the thermodynamic temperature (see Eq. (2.14)).\(^8\) The reptation time $\tau_d$ of polymers could be estimated from the inverse of $\omega_c$ when $G'(\omega_c) = G''(\omega_c)$.

It was useful to use small amplitude oscillatory shear to interpret the state of chain dynamics during shear.\(^3, 110-113\) Most commercial rotational rheometers were capable to combine oscillatory shear and simple shear in the same direction (parallel superposition). For entangled polymeric liquids, the effective crossover frequency $\omega_{c,\text{eff}}$ which was measured during simple shear was always higher than the background shear rate while no significant change was found for the plateau modules.\(^8\)

Marrucci\(^8\) proposed a convective constraint release (CCR) mechanism when entangled polymeric liquids were under fast flow. At steady state during simple shear, instead of taking reputation time $\tau_d$ to come back to steady state after a small disturbance, the relaxation time was accelerated by the background flow. The fast flow directly contributed a mechanism by which the surrounding chains were renewed in the time scale of the inverse of applied rate. As suggested by Marrucci, we may write the relaxation time under flow conditions as

$$\frac{1}{\tau} = \frac{1}{\tau_d} + A\dot{\gamma}$$

(4.1)

where $\tau_d$ was the terminal relaxation time without shear, $\dot{\gamma}$ was the background shear rate and $A$ was a constant number. This assumption could be checked indirectly by superimposing small amplitude oscillatory shear on a simple shear. If the effective crossover frequency $\omega_{c,\text{eff}}$ was considered to be the inverse of the effective relaxation
time during simple shear, the experiment results\textsuperscript{88} indicated that the relaxation time
during flow, i.e., the time polymers need to take to come back to their steady shear state after some small disturbance, was accelerated by the background flow. However, the physical meaning of the effective crossover frequency $\omega_{c\_eff}$ was still not clear, and whether it could present the relaxation time during shear is still questionable.

Instead of using small amplitude oscillatory shear, to use small step strain to characterize the relaxation time was more straightforward. Superimposing a small step strain during stress relaxation (double step strain) to characterize the polymer state has been studied both in theory and experiments.\textsuperscript{8, 114, 115} During shear, a small step strain could be also superimposed to directly check the stress relaxation and CCR effect.

Changing temperature was another way to change the relaxation spectrum for entangled polymeric liquids. Somma et al.\textsuperscript{113} reported that time-temperature superposition (TTS) principle holds with the background flow for polymer melts, whereas TTS failed for some polymer blends with different glass transition temperature (Tg).\textsuperscript{116}

In the other hand, yielding, i.e., a transition from elastic deformation to irrecoverable deformation (i.e., flow) that is signified by the stress overshoot, could occur in absence of any visible shear inhomogeneity, as is the case whenever the system is insufficiently entangled. Shear homogeneity allowed us to more straightforwardly explore various rheological characteristics of steady shear of entangled polymeric liquids.

In this chapter, we further explored the nature of homogeneous steady-state shear of entangled polymeric liquids beyond the yield point, i.e., beyond the shear stress overshoot, by examining additional rheological responses in the steady state to
superimposed small external mechanical perturbations. We superimposed small amplitude oscillatory shear and a small step strain at different temperature and at different shear rate for three polymer solutions. We found that if the Tg solvent was higher than the Tg of long chains, the dynamic behavior deviated more from TTS principle under background flow. Both small amplitude oscillatory shear and step strain data supported the CCR idea for our entangled polymeric liquids.

4.2 Parallel mechanical superposition and theory prediction in linear regime

In order to study the transient properties of entangled polymeric liquids, we could superimpose other rheological measurements to the state which we wanted to probe. In this section, we would introduce how we performed this type of measurements and the corresponding theory calculation in linear regime. The word “parallel superposition” meant that all the superimposed rheological measurements were in the same direction as the underlying flow direction.

4.2.1 Superimposed small amplitude oscillatory shear

We could measure the effective $G'$ and $G''$ at flow state by superimposing small amplitude oscillatory shear on top of the steady state. Figure 4.1 showed the illustration of this measurement: First, the sample was sheared to steady state at rate $\dot{\gamma}_{ss}$, and then a small amplitude sine wave deformation was superimposed and the strain and shear rate could be written as:

$$\gamma(t) = \dot{\gamma}_{ss} t + \gamma_0 e^{iat} \quad (4.2)$$

$$\dot{\gamma}(t) = \dot{\gamma}_{ss} + i \omega \gamma_0 e^{iat} \quad (4.3)$$
For superimposing small amplitude oscillatory shear in linear regime, Maxwell model could be used. At steady state, the shear stress $\sigma_{ss}$ and shear rate $\dot{\gamma}_{ss}$ could be described by Eq. (2.7):

$$\dot{\gamma}_{ss} = \frac{\dot{\sigma}_{ss}}{G} + \frac{\sigma_{ss}}{\eta}$$  \hspace{1cm} (4.4)

During superimposed small amplitude oscillatory shear, the transient shear rate and shear stress could also be described by Eq. (2.7):

$$\dot{\gamma}(t) = \frac{\dot{\sigma}(t)}{G} + \frac{\sigma(t)}{\eta}$$  \hspace{1cm} (4.5)

Subtracted Eq. (4.4) from Eq. (4.5), we could get that the stress response of this sine wave disturbance also followed Eq. (2.7), in other words, in linear regime, we could analyze the stress response by subtracting the steady state stress, and the effective $G'$ $G''$ was the same as the sample in absence of any flow.

![Figure 4.1 An illustration of superimposed saos method.](image)

76
4.2.2 Superimpose small step strain

However, if polymeric liquids were sheared in nonlinear regime, i.e., shear thinning regime, the physical meaning of the $G'$ and $G''$ was not clear, we did not know whether they also had the same meaning as they were in absence of any shear or not. In other words, could we get the information of effective relaxation time and modulus at flow state by measuring $G'$ and $G''$?

In order to answer this question, we designed a more straightforward method: instead of superimposing small amplitude oscillatory shear, a small step strain could be directly superimposed on to the steady flow state. In this method, we gave the sample a small disturbance, and observed how the disturbance disappeared. Figure 4.2 showed the illustration of this method: First, the sample was sheared to steady state at rate $\dot{\gamma}_s$, and then the shear rate was switched to a very high rate for a short time. After that, the shear rate was switched back to the original rate $\dot{\gamma}_s$. This rate switching gave the sample an extra strain $\Delta \gamma$ and stress jump $\Delta \sigma$, and the effect of this disturbance could be measured through the stress signal.

In linear regime, this process could be described by Maxwell model. After the disturbance, Eq. (2.7) becomes:

$$\dot{\gamma}_s = \frac{\sigma}{G} + \frac{\sigma}{\eta}$$

(4.6)

And the solution of Eq. (4.6) was:

$$\sigma(t) - \sigma_{ss} = \Delta \sigma e^{-t/\tau}$$

(4.7)

From Eq. (4.7), we found that if we set the stress at steady flow state as the baseline, and measure how the stress after the disturbance relaxed against the baseline, the relaxation behavior in flow regime was the same as the relaxation behavior in
absence of any shear. Therefore we could check our data in linear regime to verify our characterization methods.

Figure 4.2 An illustration of superimposed small step strain method.

4.3 Experimental

In this section, we would describe the materials, fixtures and methods we used to probe the properties of entangled polymeric liquids at steady flow states.

4.3.1 Materials

In order to achieve steady state without edge fracture, three entangled polybutadiene solutions were used in this chapter. For the first two samples, entangled solutions were prepared involving a low concentration of 3 % and ultra high molecular weight 1,4-polybutadiene with $M_w=2,600$ kg/mol, $M_n=1,600$ kg/mol from
Bridgestone-America. Two oligomeric polybutadienes were used as solvent to make two 3 % solutions, one being monodisperse with \( M_w = 9 \text{ kg/mol} \) from Bridgestone-America, and the other from Aldrich with \( M_w = 1.8 \text{ kg/mol} \) and a high level of vinyl content (category number 20,043-3). The polybutadiene solutions in solvent polybutadiene 9K and polybutadiene 1.8K are respectively labeled as PB2.6M-3%-9K and PB2.6M-3%-1.9K. The third sample was an entangled polybutadiene solution at a concentration of 5 % high molecular-weight monodisperse 1,4-polybutadiene (\( M_w = 1,100 \text{ kg/mol} \)) in an oligomeric monodisperse polybutadiene (\( M_w = 10 \text{ kg/mol} \)). This sample was labeled as PB1M-5%-10K.

The glass transition temperatures \( T_g \) of the pure polybutadiene melts of 2.6M, 1M, 10K and 9K were around – 98 °C. In contrast, \( T_g \) of polybutadiene 1.8K was ca. -38 °C due to the high vinyl component. The samples were prepared by first dissolving the high molecular weight polybutadiene in toluene and then mixing with oligomer. Toluene was then allowed to evaporate from the uniform solution at room temperature for a week under the hood. The residual toluene was removed under vacuum for about 3 days. For the purpose of particle-tracking velocimetry observations, we had incorporated about 600 ppm silver-coated particles with an average diameter of 10 µm (Dantec Dynamics HGS-10) into each of the samples.

4.3.2 Methods

All the rheological measurements were carried out using a controlled-torque rheometer (Physica MCR-301, Anton Paar USA) in a cone-plate cell of 25 mm diameter with a 2° cone angle. In controlled stress (CS) mode, this rheometer had the ability to perform oscillatory shear superimposed onto a steady simple shear. In such a parallel superposition small amplitude oscillatory shear experiment, we first applied a
constant shear rate in the control rate (CR) mode until steady state. Then, the rheometer was programmed to switch to the CS mode to match the steady-state shear stress, meanwhile a small amplitude oscillatory shear was superimposed. Our second experimental protocol consisted of a short "pulse" in the applied rate during steady-state shear when the shear rate was elevated for a very short duration, which amounted to performing a step strain and stress relaxation against a steady shear baseline.

4.3.3 Particle-tracking velocimetry setup

As illustrated in Figure 2.14, a particle-tracking velocimetry setup was implemented with a cone plate setup. The top cone of 25 mm in diameter had a 4 degree angle. Motions of the illuminated particles were captured by a CCD camera onto a DVD recorder at a speed of 30 fps, where the CCD was connected to a 3.2× microscope objective lens.

4.4 Results and discussion

In this section, we would describe the rheological behaviors for our materials under superimposed rheological measurements.

4.4.1 Linear viscoelastic characters and temperature dependence

Small amplitude oscillatory shear measurements were first performed to characterize linear viscoelastic properties of these solutions at several temperatures. Figure 4.3 showed the dynamic modulus curves for PB1M-5%-10K at 5 °C. Figure 4.4 showed the dynamic modulus curves for PB2.6M-3%-9K, measured at three
temperatures. The collapse indicated existence of time-temperature superposition within the explored frequency range.

![Figure 4.3 Storage and loss moduli G' and G" of PB1M-5%-10K at 5 °C.](image)

Table 4.1 listed the crossover frequency $\omega_c$ on the lower branch and $\omega_L$ at high frequencies at temperatures of 10, 25 and 40 °C respectively. From Table 4.1, we got the WLF shifting factor of PB2.6M-3%-9K $\alpha_T = \tau(T)/\tau(T_0) = \omega_c(T_0)/\omega_c(T)$ equaled to 2.1 for $T = 25$ °C and 4.6 for $T = 10$ °C at a reference temperature of 40 °C. The $\omega_c$ of PB2.6M-3%-1.8K at 10 °C was estimated from the trend of its G' and G" curves.

It was worth to note that for PB2.6M-3%-9k, the ratio $\omega_c / \omega_c$ was a constant at different temperature, i.e., TTS held for this sample, as shown in Figure 4.4. However, the ratio $\omega_e / \omega_c$ decreased with lower temperature for PB2.6M-3%-1.8k sample.
Table 4.1 The crossover frequency of different samples at three temperatures

<table>
<thead>
<tr>
<th>Temperature</th>
<th>$\omega_c$ (s$^{-1}$)</th>
<th>$\omega_L$ (s$^{-1}$)</th>
<th>$\omega_c$ (s$^{-1}$)</th>
<th>$\omega_L$ (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 °C</td>
<td>2.4x10$^{-3}$</td>
<td>8.9</td>
<td>2.8x10$^{-4}$</td>
<td>0.35</td>
</tr>
<tr>
<td>25 °C</td>
<td>5.3x10$^{-3}$</td>
<td>20.0</td>
<td>1.3x10$^{-3}$</td>
<td>2.9</td>
</tr>
<tr>
<td>40 °C</td>
<td>1.1x10$^{-2}$</td>
<td>38.6</td>
<td>3.6x10$^{-3}$</td>
<td>14.5</td>
</tr>
</tbody>
</table>

Figure 4.4. Storage and loss moduli $G'$ and $G''$ of PB2.6M-3%-9K at a reference temperature of 40 °C where the curves at 10 °C and 25 °C were shifted horizontally by a shifting factor of $a_{10^\circ C} = 4.6$ and $a_{25^\circ C} = 2.1$ respectively.
Figure 4.5 showed the $G'$ $G''$ curves for PB2.6M-3%-1.8k at these three temperatures by shifting the $\omega_c$ to the same point. Different from PB2.6M-3%-9k of which crossover frequency at low frequency and high frequency region shared the same shifting factor, the shifting factors at low frequency and high frequency region for PB2.6M-3%-1.8k were different, as shown in Figure 4.6. It was clear that TTS broke down for PB2.6M-3%-1.8k. This break down was due to the Tg of polybutadiene 1.8k which was much higher than the Tg of polybutadiene 2.6M. The solvent affected the high frequency dynamic more strongly than that at low frequency, because the high frequency dynamics more depended on local dynamics. At low temperature, the viscosity of PB1.8k increased rapidly, and this effect shifted $\omega_L$ to lower value at lower temperature.

To examine the validity of the time-temperature superposition principle in continuous shear, we applied startup shear to PB2.6M-3%-9K at three rates at three temperatures respectively such that the effective rate, i.e., the normalized shear rate Weissenberg number $Wi = \dot{\gamma} \tau_d$ was the same. Figure 4.7 showed the stress vs. strain at temperatures of 10 °C, 25 °C and 40 °C at $Wi = 11$. The perfect overlapping indicated that the dominant rheological responses obeyed the WLF relationship. We also studied the temperature dependence by performing small step strain tests to determine how the stress relaxation dynamics varied with temperature. Figure 4.8 showed that the stress relaxation behavior could be depicted at different temperatures by rescaling the time with the terminal relaxation time.
Figure 4.5 Storage and loss moduli $G'$ and $G''$ of PB2.6M-3%-1.8k at 10 °C, 25 °C and 40 °C. The curves at 10 °C and 25 °C were shifted horizontally by the shifting factor $a_{25 \, ^\circ C} = 2.8$ and $a_{10 \, ^\circ C} = 12.8$ at a reference temperature of 40 °C and shifted vertically by $T_0/T$ where $T$ is the thermodynamic temperature of 10 °C and 25 °C (283K and 298K), $T_0$ is 313K (40 °C).
Figure 4.6 The shifting factor of PB2.6M-3%-9k (circle), shifting factor of PB2.6M-3%-1.8k based on $\omega_c$ (square) and shifting factor of PB2.6M-3%-1.8k based on $\omega_L$ (diamond) at a reference temperature of 40 °C.
Figure 4.7. Stress vs. strain of PB2.6M-3%-9k upon startup shear at $Wi = 11$ at respective temperatures of 10, 25 and 40 $^\circ$C.
Figure 4.8. Stress relaxation of PB2.6M-3%-9k from a small step strain of 10% produced with a shear rate of 1 s⁻¹.

4.4.2 Particle-tracking velocimetry (PTV) observation

We also verified that these samples only underwent homogeneous deformation in all of our experiments. In other words, in this study, the really shear rate of the samples were uniform distributed and exactly matched the apparent shear rate which was measured by our rheometer.

4.4.3 Superimposed small amplitude oscillatory shear at different temperatures

Despite extensive efforts to describe rheological behavior of entangled polymeric liquids, the state of steady shear flow has essentially escaped a first-principles treatment. For example, the tube model could only depict steady shear properties
such as shear thinning by introducing the effect of convective constraint release (CCR). The idea behind CCR was to recognize that the dominant molecular relaxation time in presence of shear was accelerated in proportion to the reciprocal shear rate. In other words, the effective chain relaxation dynamics in shear was no longer Brownian diffusion in origin.

One way to measure indirectly the effective relaxation time $\tau_{\text{eff}}$ in steady shear was to superimpose small amplitude oscillatory shear during steady shear, which was a well established technique.\textsuperscript{110-113} In this method, small amplitude oscillatory shear frequency sweep measurement was carried out to evaluate $G'$ and $G''$ curves against the baseline.

![Figure 4.9 Extracted $G'$ and $G''$ curves vs. $\omega$ of PB2.6M-3%-9K in steady shear at temperature 40 $^\circ$C at different underlying rates.](image)

88
First we checked whether $G'$ and $G''$ changed or not in shear thinning regime. The difference at different underlying shear rates would confirm that the behavior of entangled polymeric liquids were changed in nonlinear regime. Figure 4.9 and Figure 4.10 showed the $G'$ and $G''$ curves at different underlying rates at the same temperature for PB2.6M-3%-9K and PB2.6M-3%-1.8K, respectively. For both samples sheared in nonlinear regime, the effective crossover frequency at low frequency regime $\omega_c$ shifted to higher value as we increased the underlying rate. While the effective crossover frequency at high frequency regime $\omega_L$ barely changed in this experiment.

![Graph](image)

Figure 4.10 Extracted $G'$ and $G''$ curves vs. $\omega$ of PB2.6M-3%-1.8K in steady shear at temperature 25 °C at different underlying rates.
We would like to apply the method of the parallel superimposed small amplitude oscillatory shear to examine any temperature dependence of $\omega_{c, \text{eff}}$ at the same applied shear rate. A lack of any temperature dependence would confirm that the accelerated chain bypassing each other is not dictated by thermal diffusion. Figure 4.11 showed that the structure of the $G'$ and $G''$ curves in the "terminal regime" remained unchanged although the Brownian dynamics had slowed down by a factor of 4.6 from 40 to 10 °C. In other words, despite the temperature changed the three curves cross at essentially the same frequency around 0.2 rad/s = $1/\tau_{\text{eff}}$, which was about 5 times higher than the applied rate $\dot{\gamma} = 0.04$ s\(^{-1}\). We had carried out similar tests at other applied rates at these temperatures for this and the other solutions (Figure 4.12, Figure 4.13, and Figure 4.14). All the data conformed to one universal scaling law as shown in Figure 4.15, which was in complete numerical agreement with a previous report.\(^{88}\)

Somma \textit{et al.}\(^{113}\) reported that TTS principle also holds with the background flow for polymer melts, i.e., $a_T$ does not change with Weissenberg number $Wi$. This conclusion was also true for entangled polymeric liquids if TTS could hold in absence of background flow. Figure 4.16 showed superimposed $G'$ and $G''$ at the same $Wi = 10.9$ for PB2.6M-3%-9K at three temperatures. The prefect overlapping of these three curves indicated that in flow state the dynamics shared the same shifting factor that in equilibrium state when Weissenberg number $Wi$ was fixed.
Figure 4.11. Extracted $G'$ and $G''$ curves vs. $\omega$ of PB2.6M-3%-9K in steady shear at different temperatures at the same underlying rate.
Figure 4.12 Extracted $G'$ and $G''$ curves vs. $\omega$ of PB2.6M-3%-1.8K in steady shear at different temperatures at the same underlying rate 0.004 s$^{-1}$. 
Figure 4.13 Extracted $G'$ and $G''$ curves vs. $\omega$ of PB2.6M-3%-1.8K in steady shear at different temperatures at the same underlying rate $0.01 \text{ s}^{-1}$. 


Figure 4.14 Extracted $G'$ and $G''$ curves vs. $\omega$ of PB2.6M-3%-1.8K in steady shear at different temperatures at the same underlying rate 0.04 s$^{-1}$. 
Figure 4.15 The characteristic effective crossover frequency $\omega_{c,\text{eff}}$ in presence of steady shear at the different applied rates and three temperatures in two different solutions is plotted against $5\dot{\gamma}$, showing a universal correlation, independent of temperature.
Figure 4.16 Extracted G' and G" curves vs. $\omega$ of PB2.6M-3%-9K in steady shear at different temperatures at the same $Wi=11$. 
In this section, we showed that, if TTS broke down for entangled polymeric liquids even without background flow, the deviation would be stronger when the measurement was superimposed with shear flow.

Figure 4.17 The $G'$ $G''$ of PB2.6M-3%-1.8k under the background shear at $Wi=11$. The curves were shifted by the shifting factor based on $\omega_c$ for PB2.6M-3%-1.8k in Fig. 3. $G'$ $G''$ was also shifted vertically by $T_0/T$ where $T$ was the thermodynamic temperature of 10 °C and 25 °C (283K and 298K), $T_0$ is 313K (40 °C).

For PB2.6M-3%-1.8k, because $T_g$ of solvent was much higher than $T_g$ of long chains, TTS broke down either in equilibrium or during shear. Figure 4.17 showed the $G'$ $G''$ of PB2.6M-3%-1.8k by shifting the $\omega_c$ to the same point with the background shear at $Wi=11$. It was clear that the plateau width shrinks more when temperature was lower. Moreover, at equilibrium state, the width of stress plateau ($\omega_e / \omega_c$) at 10
°C was around 0.31 of that at 40 °C, while under the background flow of $Wi=11$, the width of stress plateau at 10 °C was only 0.21 of that at 40 °C.

Since $\omega_c$ was proportional to shear rate, when the $Wi$ was fixed, it was easy to prove that the shifting factor of $\omega_c$ at different temperature was the same as the shifting factor in thermal equilibrium states for both samples. At high frequency region, the dynamic behavior was more locally dependent. During shear, the long chains started to lose entanglements, therefore, the interaction between solvent and long chains became more important than equilibrium state. Compared with the equilibrium state, for PB2.6M-3%-1.8k sample, $\omega_c$ shifted more when it was under shearing at low temperature.

The evidence that $\omega_c$ was always higher than $\dot{\gamma}$ showed a very important concept: flow always flow, i.e., at steady state, the system was at a state that it was sheared as if it was in its terminal region. Another interesting point was that the plateau modulus under background flow did not change much compared with the plateau modulus at equilibrium state. It meant that the chain entanglement still kept its stiffness when the measured time scale was much shorter than the inverse of rate. This result will be discussed later in this chapter.

4.4.4 Stepwise rate jump in shear thinning regime

We carried out a sequence of step-wise rate jump and monitored the stress growth over time. Figure 4.18 showed stress response in a series of discrete rate switching experiments from the steady state at a rate of 0.04 s$^{-1}$. According to Figure 4.15, the effective relaxation rate $\omega_{c,eff}$ should be ca. $5\dot{\gamma} \sim 0.2$ s$^{-1}$. If we took this effective relaxation time literally, then any rate jump with a magnitude lower than 0.2 s$^{-1}$ would only result in a monotonic change in the measured stress. Instead, stress
overshoot emerged in each of these rate switching experiments that involved a rate increment as low as 0.01 s\(^{-1}\). Similar stress overshoot could also be observed for PB2.6M-3%-1.8K, as shown in Figure 4.19. These experiments appeared to suggest that the steady state shear was a state of complete balance between intra-chain retraction force and inter-chain gripping force. An increase in the applied rate automatically resulted in high inter-chain gripping force that produced additional chain deformation. The additional chain deformation ceased when a point of force imbalance was reached at the stress peak, i.e., the point of stress overshoot as shown in Figure 4.18 and Figure 4.19. The outcome of this experiment indicated that the meaning of \(\tau_{\text{eff}}\) was not entirely equivalent to the quiescent terminal relaxation time \(\tau_d\).

Figure 4.18 Stress change as a function of elapsed strain upon switching from steady state at \(\dot{\gamma} = 0.04\) s\(^{-1}\) to 0.045, 0.05, 0.07 and 0.1 s\(^{-1}\) respectively.
4.4.5 Master flow curve in steady shear

At a given temperature in the shear thinning regime, the shear stress increased little with increasing applied rate as shown in Figure 4.20 because the chains were more oriented at a higher rate and thus offer less viscous resistance among each other during shear. Changing temperature had the consequence of changing the Brownian dynamics as well as viscous interactions among chains. The collapse of three sets of data at three temperatures onto a master flow curve in Figure 4.20 showed that the WLF shifting factor \( a_T = \tau(T)/\tau(T_0) = T_0\eta(T,\dot{\gamma})/T\eta(T_0,\dot{\gamma}a_T) \). In other words, the steady shear-thinning "viscosity" \( \eta/T \) scaled with temperature in the same manner as
the quiescent terminal relaxation time \( \tau \) as long as the viscosity \( \eta(T, \dot{\gamma}) \) was evaluated at the same effective shear rate, i.e., the same Weissenberg number \( Wi = \dot{\gamma} \tau \).

Figure 4.20 Master flow curves made of steady shear stress vs. rate data at three temperatures of 40, 25 and 10 °C where the reference temperature is 40 °C and the WLF shifting factor is the same as that in Figure 4.4.

4.4.6 Step strain relaxation during steady shear

The effective relaxation rate evaluated from parallel superposition of small amplitude oscillatory shear in steady shear, e.g., from Figure 4.11, was found to be proportional to the applied rate as shown in Figure 4.15. Indeed, the state of steady shear must correspond to chains passing around one another on the time scale of the reciprocal shear rate. To further probe the nature of the steady state in the shear thinning regime, we introduced a more direct means to probe the effect of steady shear on the chain dynamics, i.e., superimposing a step strain during steady shear.
Previously, such a superposition has been used to measure the elastic modulus of polystyrene solutions in steady shear.\textsuperscript{117}

For reference, we first performed a stress relaxation experiment for a small step strain of 10\% in PB2.6M-3\%-9K at 25 °C. Then, we produced a steady shear at a shear rate of 0.0003 s\(^{-1}\) (\(Wi < 0.1\)) in the terminal (Newtonian) regime. A small step strain of 10\% was superimposed onto this steady shear. The resulting elevation of the shear stress level relaxed over time toward the steady state value. Figure 4.21 showed that the stress relaxation in presence of this Newtonian flow was identical to that observed in a standard stress relaxation test. On the other hand, if the same superposition of a small step strain was performed over a steady shear in the shear thinning regime, i.e. at a shear rate \(\dot{\gamma}=0.04\) s\(^{-1}\), we could also evaluate the dynamics associated with the stress relaxation by subtraction from the baseline, i.e., the steady shear stress value. In contrast to the relaxation dynamics in quiescence or in Newtonian regime, the dynamics were much faster. Moreover, the same dynamics were observed at three different temperatures as shown in Figure 4.22, consistent with the data in Figure 4.11. It affirmed that the stress relaxation was not dictated by Brownian motions and was determined by the underlying shear that pulls the chains out of the deformed entanglement network to accelerate the stress relaxation.
Figure 4.21 Parallel superposition of step strain (the superimpose step strain is 10%, produced with a shear rate of 1 s\(^{-1}\)) for PB2.6M-3%-9k at 25 °C under the shear rate of 0.04 s\(^{-1}\), 0.0003 s\(^{-1}\), and in absence of shear respectively. The data were obtained by subtracting from the baseline, i.e., steady state shear stress.
Figure 4.22 Parallel superposition step strain (the superimpose step strain is 10% produced with a shear rate of 1 s$^{-1}$) for PB2.6M-3%-9K at different temperatures under the same shear rate of 0.04 s$^{-1}$. The data were obtained by subtracting from the baseline, i.e., steady state shear stress.

Similar results could be observed for the other samples, Figure 4.23, Figure 4.24, and Figure 4.25 summarized the superimposed small step strain results for PB2.6M-3%-1.8K at different underlying rates. Although the shapes of those curves at short time scales did not match others due to strong solvent effect, the long time relaxation behavior at the same underlying rate was independent of temperature, i.e., the stress disturbance took the same time to disappear. Without this solvent effect, the relaxation behavior in shear thinning regime for different samples under different shear conditions could be normalized to a master curve, Figure 4.26 showed the
normalized stress relaxation behavior of PB2.6M-3%-9K and PB1M-5%-10K, the identical shape indicated that the relaxation dynamics at flow state for different samples had the same physical origin.

Figure 4.23 Parallel superposition step strain (the superimpose step strain is 10% produced with a shear rate of 1 s⁻¹) for PB2.6M-3%-1.8K at different temperatures under the same shear rate of 0.004 s⁻¹. The data were obtained by subtracting from the baseline, i.e., steady state shear stress, and normalized by the stress difference right after the disturbance.
Figure 4.24 Parallel superposition step strain (the superimpose step strain is 10% produced with a shear rate of 1 s$^{-1}$) for PB2.6M-3%-1.8K at different temperatures under the same shear rate of 0.01 s$^{-1}$. The data were obtained by subtracting from the baseline, i.e., steady state shear stress, and normalized by the stress difference right after the disturbance.
Figure 4.25 Parallel superposition step strain (the superimpose step strain is 10% produced with a shear rate of 1 s\(^{-1}\)) for PB2.6M-3%-1.8K at different temperatures under the same shear rate of 0.04 s\(^{-1}\). The data were obtained by subtracting from the baseline, i.e., steady state shear stress, and normalized by the stress difference right after the disturbance.
Lastly, we superimposed the same small (10\%) step strain against steady shear at different rates respectively, for the solution of PB2.6M-3\%-1.8K. Figure 4.27 showed the stress relaxation dynamics to be controlled by the underlying shear rate. The faster relaxation was apparently realized by the higher rate of underlying shear. Instead of relaxing via Brownian motions indicated by the slowest relaxation data (0 s\(^{-1}\)) in Figure 4.27, the strained network more quickly "dissolved" due to the convective effect of the underlying shear. Actually three relaxation curves in Figure
4.27 collapsed onto one upon normalizing the time with the underlying shear rate as shown in Figure 4.28. The small perturbation in the stress due to the step strain of 10 % quickly vanished on the time scale of \(1/\dot{\gamma}\).

![Stress relaxation curve for PB2.6M-3%-1.8K at equilibrium and under different steady shear rates at 40 °C. The data were obtained by subtracting from the baseline, i.e., steady state shear stress.](image)

Figure 4.27 Stress relaxation curve for PB2.6M-3%-1.8K at equilibrium and under different steady shear rates at 40 °C. The data were obtained by subtracting from the baseline, i.e., steady state shear stress.
Figure 4.28 Stress relaxation curve for PB2.6M-3%-1.8K at equilibrium and under different steady shear rates at 40 °C. Master curves obtained by scaling the time scale with the underlying shear rate.

4.5 Discussion

From the data above, these superimposed small amplitude oscillatory shear and step strain tests clarified the nature of steady shear in entangled polymeric liquids: stress relaxation and chain dynamics were accelerated from those observed in the quiescence to time scales comparable to the reciprocal shear rate. In other words, the state of steady flow was one where chains were displaced to pass by one another by the external condition (the moving surface). In contrast, in terminal steady flow, chains "voluntarily" passed by one another by thermal diffusion (i.e., Brownian motion). This mechanism was call convective constraint release (CCR). CCR was
first given as an assumption by Marrucci\textsuperscript{89} who tried to explain the relationship between shear thinning and Cox-Merz rule. Our experiments directly proved this idea.

Convective constraint release concept could be illustrated through Figure 4.29 (a to c). Let’s focus on a rest chain in the sample at steady flow state. At steady state, the elastic force of the test chain was balanced by the gripping force given by other chains (Figure 4.29 a). During the disturbance, other surrounding chains gave the test chain a small amount of extra deformation (Figure 4.29 b). After the disturbance, the other chains were forced to bypass this test chain due to convective flow. There was no interactions between the test chain and other chains which caused the extra deformation after a certain amount of strain. As a consequence, all effect due to those chains would disappear. In other words, the topological relationship among chains were forced to renew by the convective flow after some strain units, and the stress disturbance relaxed.

It was interesting to point out that:

1. in shear thinning regime with superimposed small amplitude oscillatory shear, the effective crossover modulus $G_c$ of $G'$ and $G''$ curves barely changed with underlying rate for the same sample at the same temperature, as shown in Figure 4.9 to Figure 4.17.

2. in shear thinning regime with superimposed small step strain, the stress jump after an extra deformation of 10% barely changed with underlying rate for the same sample at the same temperature, as shown in Figure 4.21 to Figure 4.28.

All results indicated that the shear modulus did not change too much in shear thinning regime. Eq. ( 2.16 ) showed this shear modulus was in the inverse ratio of entanglement spacing $M_e$. Combined the experiment evidences above and Eq. ( 2.16 ), we could conclude that the entanglement spacing $M_e$ barely changed with shear rate.
This finding forced us to re-think the meaning of chain entanglement and disentanglement: it seemed that the concept “chain entanglement” is a dynamic concept, the average entanglement spacing $M_e$ did not change during shear, while the interaction among chains would become weaker. From the fact that the modulus dropped dramatically when the superimposed frequency was closed to the underlying shear rate, we could further think about the nature of chain entanglement: a flow state, the life time of strong chain interaction due to chain entanglement only decreased as we increased the shear rate. In other words, at short time scale, the chain entanglements still exist as they were in the thermal equilibrium state, whereas they could not survive for a time scale comparable to $1/\dot{\gamma}$.

Figure 4.29 An illustration of convective constraint release (CCR) mechanism
Previous study showed that for the same samples, the effective $G'$ and $G''$ curves which were measured by superimposed small amplitude oscillatory shear were independent of velocity profile (homogeneous vs. inhomogeneous). Here we would prove this conclusion by using Maxwell model and these two experimental evidence:

1. The relaxation time was in the inverse ratio of underlying shear rate, i.e., $\tau = A/\dot{\gamma}$, where $A$ was a constant number.
2. The plateau modulus were almost a constant value under different shear rates.

\[ \dot{\gamma}_1(t) = \frac{\dot{\sigma}(t)}{G} + \frac{\sigma(t)}{\eta_1} \]  
\[ \dot{\gamma}_2(t) = \frac{\dot{\sigma}(t)}{G} + \frac{\sigma(t)}{\eta_2} \]  

And the viscosity of each layer could be written as (remembered that the CCR effect):

Figure 4.30 An illustration of a general shear banding case.
\[ \eta_1 = G \tau_1 = GA/\dot{\gamma}_1 \quad \eta_2 = G \tau_2 = GA/\dot{\gamma}_2 \]  

(4.10)

The apparent shear rate is:

\[ \dot{\gamma} = \frac{\dot{\gamma}_1 h_1 + \dot{\gamma}_2 h_2}{h_1 + h_2} \]  

(4.11)

Insert Eq. (4.8), Eq. (4.9) and Eq. (4.10) into Eq. (4.11):

\[ \dot{\gamma} = \frac{(\ddot{\sigma}/G + \sigma/G \dot{\gamma})h_1 + (\ddot{\sigma}/G + \sigma/G \dot{\gamma})h_2}{h_1 + h_2} \]

\[ = \frac{\sigma}{GA} \dot{\gamma}_1 h_1 + \frac{\sigma}{GA} \dot{\gamma}_2 h_2 + \frac{\dot{\sigma}}{G} \]

(4.12)

Eq. (4.12) showed that the stress response which described by Maxwell model was independent of the velocity profiles. In other words, homogeneous shear or not did not affect the superimposed characterization results.

### 4.6 Conclusion

The nature of steady shear flow of entangled polymeric liquids has been somewhat elusive even without such complications as shear inhomogeneity and edge fracture. In quiescence, chain dynamics and stress relaxation behavior was dictated by thermal diffusion processes. Often the time-temperature superposition principle, as empirically depicted by the WLF relation, could be applied to extend our observation of linear viscoelasticity. In the regime of nonlinear responses, Brownian dynamics played a less important role and could not control polymer dynamics during steady shear as long as the imposed shear rate exceeded the quiescent chain relaxation rate. Based on entangled polymeric liquids that only experienced homogeneous shear, we carried out both parallel superposition of small amplitude oscillatory shear and
small step strain respectively to explore the steady shear properties. Figure 4.11 and Figure 4.22 convincingly showed that the state of steady shear was one where chains were being brought past one another at a rate equal to the imposed shear rate, independent of temperature. Although Brownian motions were faster at higher temperatures, they were ineffective in dictating the dynamic responses as long as the imposed rate was faster than the quiescent terminal relaxation rate. Figure 4.27 and Figure 4.28 showed that indeed the imposed rate governed the chain dynamics during steady shear and polymer dynamics could be significantly accelerated beyond those in quiescence due to the convective constraint release.
CHAPTER V

CHAIN ENTANGLEMENT CHARACTERIZATION AT TRANSIENT STATE

5.1 Introduction

In entangled polymeric liquids, the polymer chains strongly interact with other chains due to their topological relationship. How the chain interaction due to topological relationship changes under different conditions is the fundamental question on theoretical study of polymer dynamics. Different versions of reputation theory and tube model have successfully linked the linear viscoelastic property of polymer solutions to molecular responses. Recent theory studies have developed this model to explain the rheological behavior in nonlinear regime.

At rest, thermal equilibrium state, the polymer topological structure kept renewing itself through thermal diffusion of individual chains. When entangled polymeric liquids were subjected to flow from a rest state, if shear rate is very low, i.e., shear Weissenberg number $\dot{\gamma} \ll 1$, polymer chains suffer negligible deformation because the thermal diffusion is faster than the deformation rate. The stress would grow monotonically to approach steady state stress value $\eta_0 \dot{\gamma}$, where $\eta_0$ is zero-shear viscosity independent of shear rates. This phenomenon could be well explained by Boltzmann superposition principle assuming that the modulus (i.e., chain interaction) did not change during the whole process. The regime where the chain interaction was independent of shear rates was called linear regime. If the shear rate was high, i.e., in
non-linear regime, the thermal diffusion was slower than the deformation rate. Particle-tracking velocimetry measurements showed that, for entangled polymeric liquids, shear inhomogeneity could occur for well entangled polymer solutions under fast startup shear or after large step strain. These new findings indicated that we need to think about how the transient topological interaction of polymer chains was overcome during fast continuous shear. At the beginning of a startup shear at high rate, polymer coils would be stretched and the retraction force was balanced by the intermolecular force $f_{im}$ due to topological interaction of other chains. However, the polymer coils cannot be deformed further when the retraction force reached the limit of $f_{im}$ and polymer chains were forced to bypass each other. This force balance and imbalance picture gave the stress overshoot during startup shear. It was reported that the steady flow state was a weak chain interaction state. Measurements on polystyrene solutions showed that the elastic modules at steady state decreases with increasing shear rate.\textsuperscript{117} Another measurement showed that the elastic modules show stability after shear cessation.\textsuperscript{119}

We thought that the limit of $f_{im}$ depended on the topological relationship between chains, and for the same startup shear rate, $\sigma_{\text{max}}$ could achieve to a higher value for higher $f_{im}$. In this chapter, we called the state of chain entanglement was stronger if the topological structure could afford a larger $f_{im}$. Studies on recovery behavior of entangled polymers already suggested that the stress overshoot value $\sigma_{\text{max}}$ depended on the state of chain entanglement. In those studies, shear was first applied to produce a steady state. Then the shear was turned off for a rest time $\tau_R$ before the shear restarted.\textsuperscript{120} It is found that the magnitudes of stress overshoot to return back only after a rest time $\tau_R$ which was much longer than terminal relaxation time.\textsuperscript{87, 121} The
weaker overshoot was taken as an evidence for the weaker state of chain entanglement. This experimental evidence indicated that we could use the yield stress value to investigate the strength of chain entanglement. This method could be used in a more general way to study the properties of entangled polymeric liquids at any given transient state. In this chapter, we used the yield stress value $\sigma_{\text{max}}$ to study how the state of chain entanglement changed under different shear conditions.

5.2 Experimental

In this section, we would describe the materials, fixtures and methods which were used to probe the state of chain entanglements of entangled polymeric liquids under different deformation conditions.

5.2.1 Material

In order to achieve homogeneous steady state without any edge fracture, an entangled polybutadiene solution PB2.6M-3%-9K which was described in CHAPTER III was used. The entanglement density $Z = 26$. All the rheological measurements were carried out using a controlled-torque rheometer (Physica MCR-301, Anton Paar USA) in a cone-plate cell of 25 mm diameter with a $2^\circ$ cone angle at 25 $^\circ$C.

5.2.2 $\sigma_{\text{max}}$ characterization method

In this chapter, we used the yield stress value $\sigma_{\text{max}}$ which was produced by a fixed high shear rate to study the change of the strength of chain entanglement. First we described how we performed this $\sigma_{\text{max}}$ characterization method. The measurement profile could be divided into three regions (as shown in Figure 5.1):
In region 1, the sample was first sheared at a constant shear rate $\dot{\gamma}_1$ for a time $t_1$. In this chapter, $\dot{\gamma}_1$ was also called “first rate”.

In region 2, the measure profile was switched to another shear rate $\dot{\gamma}_2$ (in control rate mode) or shear stress $\sigma_2$ (in control stress mode) for a time $t_2$. The strength of chain entanglement at the end of region 2 was the state to be studied by the $\sigma_{\text{max}}$ characterization method.

\[
\text{Figure 5.1 A sketch of yield stress value } \sigma_{\text{max}} \text{ characterization method.}
\]

After region 2, the shear rate was immediately switched to a rate $\dot{\gamma}_3$ which was much higher than $\dot{\gamma}_1$ and $\dot{\gamma}_2$. Previous studies on this measurement usually chose $\dot{\gamma}_3 = \dot{\gamma}_1$,\textsuperscript{87,121} the reason why we chose $\dot{\gamma}_3$ to be much higher than $\dot{\gamma}_1$ and $\dot{\gamma}_2$ was: For
a startup shear, the sample took more than 100% strain (usually 200% to 1000% strain) to reach the stress overshoot, therefore, the kinetics which happened in a time scale shorter than \(1/\dot{\gamma}\) could not be caught. In this report, in order to catch the kinetics in short time scale, the rate \(\dot{\gamma}_3\) to produce the stress overshoot was chosen to be 5 \(s^{-1}\) (weissenberg number \(Wi = 943\)).

In this chapter, the stress overshoot value \(\sigma_{\text{max}}\) was taken as a character parameter of the stress growth curve in region 3. It was measured as a function of shear history \((\dot{\gamma}_1, t_1, \dot{\gamma}_2 \text{ or } \sigma_2, t_2)\). For the case of \(\dot{\gamma}_2 = 0 \text{ s}^{-1}\) or \(\sigma_2 = 0 \text{ Pa}\) and \(t_2\) went to a very long time, \(\sigma_{\text{max}}\) approached the stress overshoot value of 5 \(s^{-1}\) initially in its rest, thermal equilibrium state.

5.3 Results and discussion

In this section, we would first verify the \(\sigma_{\text{max}}\) characterization in both linear regime and nonlinear regime at steady state. An then we would demonstrate how the strength of chain entanglement of our samples changed in startup shear, large step strain, and after stepdown from a steady shear.

5.3.1 \(\sigma_{\text{max}}\) characterization in linear regime

To examine the validity of this \(\sigma_{\text{max}}\) characterization method, small step strain in linear response regime was first tested. Because the strength of chain entanglement due to their topological relationship could not be changed in linear response regime in a statistic sense, \(\sigma_{\text{max}}\) during stress relaxation was expected to be the same as the stress overshoot value of a startup shear from a fully relax, thermal equilibrium state.
The sample was first sheared to a strain of 20% at a rate of 0.1 s\(^{-1}\), and then the shear rate was switched to 0 s\(^{-1}\) for a time \(t_2\) before the shear rate was switched to 5 s\(^{-1}\). (As shown in Figure 5.1, where \(t_1 = 2\text{s}\) and \(\dot{\gamma}_1 = 0.1\text{ s}^{-1}\), \(\dot{\gamma}_2 = 0\text{ s}^{-1}\)) \(\sigma_{\text{max}}\) in region 3 was measured as a function of \(t_2\).

Figure 5.2 proved that \(\sigma_{\text{max}}\) was independent of \(t_2\). This plot also showed that the experimental error range in the measurements was around \(\pm 1.5 \text{ Pa}\). In the following section, this value of \(\sigma_{\text{max}}\) was marked as the “base line” in the \(\sigma_{\text{max}}\) characterization method.

5.3.2 Characterize entanglement weaken during startup shear

At high rate limit, the initial stress response was linear, i.e., \(\sigma = G\dot{\gamma}\), the deviation from this linear relationship could be considered as the weaker chain entanglement under large deformation.\(^{72}\) However, when shear rates were not in the high rate limit, the initial stress-strain dependence could be weaker than linear\(^{3, 5}\) without any network broken due to a wide spectrum of relaxation. In other words, we could not directly answer the question that when the state of chain entanglement started to become weaker during startup shear by just simply reading the stress curve. The \(\sigma_{\text{max}}\) characterization method could give us a brief picture to investigate this process.
Figure 5.2 Stress relaxation curve and $\sigma_{\text{max}}$ as a function of rest time $t_2$ after a step strain of 20% produced by a rate of $0.1 \, \text{s}^{-1}$. 

stress relaxation after $\gamma_0 = 20\%$ in region 3
We first sheared the sample under certain rates for different time and then the rate was switched to 5 s$^{-1}$ (i.e., we omitted region 1 in Figure 5.1). The $\sigma_{\text{max}}$ was recorded as a function of shear time $t_2$. The evidence that initial $\sigma_{\text{max}}$ matched the base line indicates that the state of entanglement kept its strength even though the stress-strain (transient viscosity vs. time in Figure 5.3) was weaker than linear relationship. Figure 5.3 showed that the state of entanglement became weaker before stress overshoot. The minimum of $\sigma_{\text{max}}$ was corresponding to the weak stress undershoot before reaching steady state. Figure 5.4 showed the $\sigma_{\text{max}}$ as a function of different pre-shear rates at steady state. The lower $\sigma_{\text{max}}$ at higher rate indicates that the topological interaction decreased as the shear rate increased. This phenomenon could be explained in the following: At higher shear rate, the polymer chains were more sorted.
out, the chains tended to align in the shear direction to reduce the interaction due to the topological relationship.

Although the state of entanglement became weaker before reaching stress overshoot, the sample could still 100% recover its deformation in a strain recover experiment, as shown in Figure 5.5. The fully recovery could be explained by introducing some global topological relationship was unchanged, i.e., flow did not take place, but the state of entanglement was already weaker.

Figure 5.4 $\sigma_{\text{max}}$ as a function of steady state at different shear rates.
5.3.3 Characterize stress relaxation after large step strain

Recent particle-tracking velocimetry studies showed that macroscopic motion could be observed after a large step strain for entangled monodisperse polymeric liquids with high enough entanglement density. This non-quiescent relaxation was due to the chain entanglement in one monolayer became weaker after a large step strain. This phenomenon that the chain entanglement became weaker after a large step strain, which was called elastic yielding, could possible occur homogeneously for insufficient entangled polymeric liquids such as PB2.6M-3%-9K. This process was a good example to show how the $\sigma_{\text{max}}$ characterize method worked because elastic yielding was corresponding to weaken chain entanglements during stress relaxation.
The Rouse relaxation time $\tau_R$ of the sample is around 3s at 25 °C. Figure 5.6 showed how $\sigma_{\text{max}}$ changed as a function of $t_2$ after a large step strain of 100% produced at shear rate of 1 s$^{-1}$ where $\dot{\gamma}_R > 1$. (t$_1$ = 1s and $\dot{\gamma}_1$ = 1 s$^{-1}$, $\dot{\gamma}_2$ = 0 s$^{-1}$ in Figure 5.1) Unlike the case that the state of chain entanglement kept the same strength during relaxation after a small step strain, $\sigma_{\text{max}}(t_2)$ showed a significant non-monotonic behavior. The V-shape curve indicated that the state of chain entanglement still kept the strength (i.e., the topological structure did not change) right after shear cessation. The chain entanglement could become weaker even without any further deformation after a certain amount of time which could be longer than the Rouse relaxation time.
relaxation time $\tau_R$. Similar result could be observed when the shear rate to produce the deformation met the condition $\gamma > \tau_R$. Figure 5.7 showed the stress overshoot recovery curve after a large step strain of 300% produced by a shear rate of 0.1 s$^{-1}$. These evidences were consistent with the elastic yielding concept. The time for the sample in both cases to reach the minimum $\sigma_{\text{max}}$ was larger than Rouse relaxation time $\tau_R$.

Figure 5.7 Normalized stress relaxation curve and $\sigma_{\text{max}}$ as a function of rest time $t_2$ after a step strain of 300% produced by a rate of 0.1 s$^{-1}$. The black curve is the normalized stress relaxation curve after a small step strain of 20% as a reference curve. (Re-plot from Figure 5.2)
5.3.4 State of chain entanglement after shear cessation from steady shear

After shear cessation in nonlinear regime, entangled polymeric liquids must recover from their weak entangle state to the thermal equilibrium state which was stronger. The recover process has been reported to be much longer than terminal relaxation time. In this section, we mainly focused on the effect of previous shear rate on the recover kinetics.

We first sheared the sample at three different rates ($\dot{\gamma}_1$ equals to 0.03 s$^{-1}$, 0.1 s$^{-1}$, 0.3 s$^{-1}$) respectively to steady state. After the cessation of shear, we waited a time $t_2$ before the shear rate switched to $\dot{\gamma}_3 = 5$ s$^{-1}$. Figure 5.8 is $\sigma_{\text{max}}$ as a function of $t_2$ for the three previous rates $\dot{\gamma}_1$.

![Figure 5.8](image)

Figure 5.8 $\sigma_{\text{max}}$ as a function of rest time $t_2$ after shear cessation of shear rate equaled to 0.03 s$^{-1}$, 0.1 s$^{-1}$, 0.3 s$^{-1}$
At steady state, because the chain entanglement was weaker as shear rate went higher, the initial $\sigma_{\text{max}}$ value (i.e., $\sigma_{\text{max}}(t_2-t_0)$) was lower at higher previous shear rate. We found that $\sigma_{\text{max}}(\dot{\gamma}_2, t_2)$ did not change until a characterize time $\tau_{\text{begin}}(\dot{\gamma}_2)$ was reached. In other words, the strength of chain entanglement did not recover before $\tau_{\text{begin}}(\dot{\gamma}_2)$. This time lag of $\sigma_{\text{max}}$ increasing indicated that the topological structure of polymer chains had a stability after shear cessation. The time $\tau_{\text{begin}}(\dot{\gamma}_2)$ that the strength of chain entanglement started to recover depended on previous shear rate. This phenomenon could be explained by that at higher shear rate, viscosity was lower at steady state, therefore polymer chains could be easier to start to rearrange themselves to the new steady state.

Although the time scale that $\tau_{\text{begin}}$ of the strength of chain entanglement started to recover depended on previous shear rate, the time scale of the chain entanglement fully recovered after shear cessation was independent of previous rate. The $\sigma_{\text{max}}$ recovery curves merged to a single curve after around 1000s. It was interesting to show that $\sigma_{\text{max}}$ was not monotonic as a function of $t_2$. A weak but repeatable peak could be observed after these curves merged to a single curve. More importantly, the peak value was larger than the base line. It meant that during stress relaxation after shear cessation, before reached to thermal equilibrium, the state of chain entanglement could be transiently stronger than that at equilibrium state. However, this stronger state was not the most thermal stable state. In other words, the thermodynamic stable state was not the state that had the strongest chain entanglement.
5.3.5 State of chain entanglement after stepdown from steady shear

Stress relaxation after shear cessation in a special case of stepdown from steady shear (\( \dot{\gamma}_2 = 0 \text{ s}^{-1} \)). In this section, we studied more general cases in which \( \dot{\gamma}_1 > \dot{\gamma}_2 \geq 0 \text{ s}^{-1} \). In nonlinear regime, after stepdown from a higher rate to a lower rate, shear stress showed a stress undershoot before reaching to the new steady state. The recovery time had also been studied by measuring the time scale to reach new steady states.\(^\text{121}\) However, the origin of this stress undershoot was still not clear. In this section, we used \( \sigma_{\text{max}} \) characterize method to study how the state of chain entanglement changed before it reached to new steady states.

5.3.5.1 Switch from the same previous rate to different lower rates

We first studied how the stress approached to new steady states from the same previous rate. Figure 5.9 showed the stress responses produced by switch from steady state of \( \dot{\gamma}_1 = 0.3 \text{ s}^{-1} \) to different lower rates \( \dot{\gamma}_2 = 0 \text{ s}^{-1}, 0.003 \text{ s}^{-1}, 0.01 \text{ s}^{-1}, 0.03 \text{ s}^{-1} \), respectively. Unlike the stepdown from steady shear in linear response regime which only showed a monotonic decrease in shear stress, in nonlinear regime, stress undershoot showed up before reaching new lower rate steady state. For a constant previous rate \( \dot{\gamma}_1 \), the initial stress responses after switching to lower rates composed to a single curve which was independent of second rate \( \dot{\gamma}_2 \). The corresponding \( \sigma_{\text{max}} \) vs. \( t_2 \) also indicated that the states of chain entanglement were independent of \( \dot{\gamma}_2 \) during a short time scale and could not recovery immediately (As shown in Figure 5.10). Compared Figure 5.9 and Figure 5.10, we concluded that the initial stress drop was not due to any chain entanglement change.

Like the stress relaxation after shear cessation, the structure recovery also showed a time lag independent of \( \dot{\gamma}_2 \). Weak peaks of \( \sigma_{\text{max}} \) showed up before reaching...
steady state when \( \dot{\gamma}_1 \) was much lower than \( \dot{\gamma}_2 \). It indicated that the chain entanglement could also reach a stronger state during adjusting itself to new steady states.

Figure 5.9 Stress vs. time after stepdown from steady shear
Figure 5.10 $\sigma_{\text{max}}$ as a function of rest time $t_2$ after stepdown from steady shear

5.3.5.2 Switch from different previous rates to the same lower rate

Similar to the structure recovery after shear cessation at steady state, the long time behavior was independent of previous rates. Figure 5.11 was the plot of stress vs. time after switching from previous rate $\gamma_1 = 0.03 \text{ s}^{-1}$ and $0.3 \text{ s}^{-1}$ to the same second rate $\gamma_2 = 0.003 \text{ s}^{-1}$. It took almost the same mount of time for the stress finally stabilized. Figure 5.12 showed $\sigma_{\text{max}}$ as a function of time corresponding to Figure 5.11. The curves initialized at different previous rates merged to a single curve and showed the same peak. This result indicated that the long time behavior of recovery only
depended on the second rate, whereas the time for the sample to reach new steady state was independent of pre-shear rates.

Figure 5.11 Stress vs. time after stepdown from steady shear
5.3.6  Structure recovery after fast stress release

Previous section showed that the strength of chain entanglement had stability after deviation from previous steady state. Here we wanted to find the answer to this question: Could we accelerate the recover process by letting it revert to its thermal equilibrium rest state freely? In this section, instead of doing a stress relaxation after shear cessation, we used $\sigma_{\text{max}}$ characterize method to study how the state of chain entanglement recovered during strain recovery experiment.

We first pre-sheared the sample to steady state at shear rate $\dot{\gamma}_1 = 0.03 \, \text{s}^{-1}$ and $0.3 \, \text{s}^{-1}$ respectively. And then the rheometer was switched to control stress mode to apply a zero shear stress on the sample for a time $t_2$ ($\sigma_2 = 0 \, \text{Pa}$ in Figure 5.1). The
shear of $\dot{\gamma}_3 = 5 \text{ s}^{-1}$ was restarted after $t_2$ and $\sigma_{\text{max}}$ was measured as a function of $t_2$. Figure 5.13 showed how the strain recovered for these two previous shear rates. Figure 5.14 was the corresponding states of chain entanglement, which was characterized by $\sigma_{\text{max}}$, as a function of $t_2$. Compared with the case of stress cessation, our results indicated that the structure stability of steady state still existed even we allow the sample to revert freely. It meant that the reverse flow after shear cessation could not accelerate the recover process.

![Figure 5.13 Recover strain vs. time after a steady state shear.](image-url)
5.3.7 Shear direction dependence of chain entanglement

From the data shown above, the $\sigma_{\text{max}}$ characterization method provided us a powerful tool to study the chain entanglement at any transient state. Here came an interesting question: Did the chain entanglement depend on shear direction? In other words, was the chain entanglement an isotropic or anisotropic property?

Physica rheometer MCR301 offered us this opportunity to switch shear rate between different directions. In order to probe the direction dependence, the sample was first sheared at a shear rate of 0.1 s$^{-1}$ and -0.1 s$^{-1}$ respectively to steady state. Here

![Figure 5.14 $\sigma_{\text{max}}$ as a function of rest time $t_2$ during the strain recovery measurements.](image-url)
the negative shear rate meant the sample was sheared in the opposite direction of the shear rate in region 3 in Figure 5.1.

Due to the experimental error in different sample loadings, Figure 5.15 showed the normalized $\sigma_{\text{max}}$ as a function of time after shear cessation. It was very clear that the state of chain entanglement was sensitive to shear directions: Although the system will take the same amount of time to fully recover, it tended to show stronger chain entanglement in the shear direction than in the opposite direction.

Figure 5.15 $\sigma_{\text{max}}$ as a function of rest time $t_2$ after shear in different directions
5.4 Compare with tube model: after stepdown from steady shear

Figure 5.16 Tube model prediction of $\sigma_{\text{max}}$ recovery after stepdown from steady shear.

Tube model was the most successful model in describing linear viscoelastic properties of entangled polymeric liquids. In this section, we did the theory calculation based on tube model and showed that the tube model could not catch all the polymer dynamics which was demonstrated by our experimental data. For a simple case, we would use Eq. (2.23) and neglect the Rouse relaxation part. This equation was calculated through numerical integration written by C language. Figure 5.16 showed that the tube model predicted that $\sigma_{\text{max}}$ recovered monotonically to the new steady state after stepdown from steady shear. Leaking of a peak during the recovery process was not consistent with our experimental observation. In other
words, whether the tube model could catch the real physical picture of polymer dynamics was still questionable.

5.5 Discussion

There was no one to one relationship between shear stress and state of chain entanglement. Combination of conventional rheological values and $\sigma_{\text{max}}$ characterize method could give us a better understanding of polymer rheology.

The stepdown from steady shear measurement showed a stress undershoot before reaching new steady states. After the shear rate decrease, we could conclude that the initial stress response was mainly elastic because the stress did not show a jump down after rate decreased. If there was significant viscosity contribution, the stress would show a jump which is comparable to $\eta(\dot{\gamma}_1 - \dot{\gamma}_2)$, where $\eta$ was the viscosity at previous steady state. Although the stress response was mainly elastic, which was related to chain deformation, chain deformation relaxation in the beginning did not change the topological relationship among polymer chains. After the stress undershoot, the stress growth was mainly due to the viscosity increase. The reason was: At previous steady state, due to CCR effect, the effective relaxation time was around $0.2/\dot{\gamma}_1$, while the effective relaxation time in the new steady state after stepdown from steady shear was around $0.2/\dot{\gamma}_2$. Because the effective relaxation time could only monotonic decrease, there was no any transient state which had an effective relaxation time longer than $5/\dot{\gamma}_2$. Therefore in the stress growth part, the sample was sheared as it was in its “effective” terminal state, and the elastic deformation could not occur. This growth was mainly coming from the increase of viscosity. This argument was also confirmed by Figure 5.10 and Figure 5.12.
Section 5.3.6 proved that $\sigma_{\text{max}}$ was a good parameter to characterize the topological relationship among polymer chains. After shear cessation, the stress was set to be zero, and the sample had the freedom to revert to its lower elastic energy deformation state. However, this “turn back” only released the stretch of local chain, but could not change the overall topological relationship of chains. In other words, the initially strain recovery just let the relationship among chains become “looser”, but it still had the same topological structure. This molecular picture could explain the reason why strain recovery could not accelerate the recovery of the strength of chain entanglement.

Our results showed that the topological relationship among chains had stability at steady state, while this stability did not exist after a large step strain. This indicates that the system did not suffer any further elastic yielding after shear cessation. The stability also indicated that the topological relationship among chains needed time $\tau_{\text{begin}}(\dot{\gamma}_1)$ to change. The time to reach new steady state mainly depended on the second rate $\dot{\gamma}_2$. It was because the surrounding of chains is forced to renew at a time scale comparable to $1/\dot{\gamma}_2$ (CCR effect).

The peak of $\sigma_{\text{max}}$ after shear cessation from steady shear indicated that the thermal equilibrium state was not the strongest chain entanglement state. It was possible because at thermal equilibrium state polymer chains tended to form a random coil due to entropic and thermal diffusion. Some states with stronger chain entanglement may not have the lowest free energy. For example, the chain entanglement on the left side of Figure 5.17 obviously had a stronger chain entanglement than that on the right side, but the chains were more favorable to form random coils, as shown on the right side of Figure 5.17. It was possible that the peak
of $\sigma_{\text{max}}$ after shear cessation from steady shear was due to density change of the sample, or polymer chains shrunk to coils which were smaller than the coils at equilibrium state.

![Image](image_url)

Figure 5.17 An example that the system had stronger chain entanglement but less thermal stable.

5.6 Conclusion

The states of chain entanglement have been studied by stress overshoot characteristic method. In small step strain, the stress relaxed without changing the state of chain entanglement. In the nonlinear regime, chain entanglement suffered further weaken after a large step strain (elastic yielding). After stepdown from steady shear, no further elastic yielding could be observed. The states of chain entanglement of steady state had stability, and it only started to recover after a time lag which depended only on previous rate. Although the time for the system to start to recover was independent on the second rate, the time to reach new steady state mainly depended on second rate. Before reaching to new steady state, chain entanglement could reach to a transient state which was stronger than steady state. It meant that the most thermal equilibrium state was not the strongest state for polymeric liquids.
CHAPTER VI

SUMMARY

It is rare to have a viscoelastic system that would show nonlinear rheological behavior without changing its microstructure. For entangled polymeric liquids, nonlinear rheological behavior often arises from changes in the state of chain entanglement that apparently could survive for only a limited amount of applied strain.

In large amplitude oscillatory shear, strong wave distortion would happen if the system was able to alter from one state to another at either sample/fixture interface or in the bulk within each cycle. During each cycle of a sinusoidal wave, the transient shear rate would continuously change from 0 to the maximum rate. As a consequence, entangled polymeric liquids could disentangle when the transient shear rate was in the nonlinear region, and re-entangle in the rest of the cycle. If the materials did not have a chance to recover, i.e., the time when the materials were sheared in linear region was much shorter compare to the time required to re-entangle, the new state would be stable, and the shear stress response tended to be fairly sinusoidal. Conversely, if the system was able to switch from one state to another with in each cycle, strong wave distortion in the stress response would occur. Clearly, the steady-state character of large amplitude oscillatory shear did not necessarily reveal strain softening behavior.

For entangled polymeric liquids, there were two major relaxation mechanisms: thermal diffusion and convective constraint release. The thermal diffusion was
controlled by temperature, whereas the convective constraint release was dominated by the flow rate. The overall relaxation behavior was dictated by the faster relaxation mechanism. In the deeply nonlinear region, the relaxation due to convective constraint release would be much faster than the thermal diffusion relaxation. As a consequence, the apparent polymer dynamics were independent of temperature. The imposed rate governs the chain dynamics during steady shear, so that polymer dynamics could be significantly accelerated beyond those in quiescence due to the convective constraint release.

Our experimental data showed that the chain entanglement was a dynamic concept. Disentanglement occurs when strands from different chains slide past one another on time scales much shorter than the equilibrium relaxation time. The strength of chain entanglements can be probed by using a combination of rate-switching experiments. Similarly, loss of entanglement as a result of elastic yielding after a large step strain can be examined by application of a sequence of shearing histories. The rate-switch protocol allowed us to uncover that, under certain conditions, entangled polymer solutions could reach a transient state that possessed a higher degree of chain entanglement than it has in equilibrium or in steady state.


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