Universal Scaling Behavior in Startup Shear of Entangled Linear Polymer Melts

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Universal scaling behavior in startup shear of entangled linear polymer melts

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Synopsis

We have studied stress overshoot behavior in startup shear of four monodisperse polymer melts with a range of chain entanglement from $Z=24$ to 160 entanglement points per chain. In the elastic deformation regime defined by $\gamma \tau_R > 1$, where $\tau_R$ is the Rouse relaxation time, (i) the peak shear stress $\sigma_{\text{max}}$ scales with the time $t_{\text{max}}$ at the peak to $1/2$ power, in contrast to an exponent of $-1/4$ in the viscoelastic regime (for $\gamma \tau_R < 1$), (ii) $\sigma_{\text{max}}$ changes linearly with the elapsed strain at the stress peak $\gamma_{\text{max}}$, which scales with the applied shear rate as $\dot{\gamma}^{1/3}$, (iii) a supermaster curve collapses time-dependent shear stress growth curves up to the stress maximum at all shear rates for all the four styrene-butadiene rubber samples.

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I. INTRODUCTION

Polymeric liquids display interesting flow behavior such as wall slip, shear thinning, die swell, melt fracture associated with either roughness on, or distortion of extrudate surface. One of the most widely known rheological responses in entangled polymers is emergence of stress overshoot during sudden (startup) shear at a sufficiently high rate, corresponding to the Weissenberg number $Wi = \gamma \tau_R > 1$ [Huppler et al. (1967); Lee et al. (1970); Graessley (1974); Ferry (1980); Menezes and Graessley (1982)]. This transient feature has been widely reported in polymeric liquids from semidilute solutions [Osaki et al. (2000a, 2000b, 2000c)], unentangled melts [Moore et al. (1999); Santangelo and Roland (2001)] to well entangled polystyrene (PS) solutions [Osaki et al. (1975); Crawford and Graessley (1977); Attane et al. (1985); Demarquette and Dealy (1992); Pattamaprom and Larson (2001)], polybutadiene (PBD) [Menezes and Graessley (1982); Tapadia and Wang (2004); Robertson et al. (2004); Ravindranath and Wang (2008)] and polyisoprene (PIP) solutions [Pearson et al. (1989)], and melts [Vinogradov and Belkin (1965); Schweizer (2002); Schweizer et al. (2004); Collis et al. (2005); Auhl et al. (2008)].

Recent particle-tracking velocimetric (PTV) studies [Wang (2007)] in well entangled...
solutions [Tapadia and Wang (2006); Boukany and Wang (2007); Ravindranath et al. (2008)], DNA [Boukany et al. (2008); Boukany and Wang (2009a)], and wormlike micellar solutions [Boukany and Wang (2008)] have shown that entangled network suffered inhomogeneous shear after stress maximum $\sigma_{\text{max}}$, during startup shear. Similar inhomogeneous deformation was found in uniaxial extension of entangled polymer melts after maximum of engineering stress $\sigma_{\text{engr}}$ [Wang et al. (2007b); Wang and Wang (2008)]. These observations revealed that the entanglement network could yield to fast large deformation [Wang et al. (2007a)]. With $W_i \gg 1$, a significant amount of elastic deformation takes place until the point of yielding, when the resistant (elastic retractive) force measured in terms of either shear stress or tensile engineering stress can no longer grow with further external deformation. Beyond the yield point, molecular sliding occurs to cause rearrangement of the state of chain entanglement, allowing the stress to decline in time [Wang and Wang (2009)]. The PTV experiments show that the yielding becomes observable in the form of transient elastic recoil and shear banding beyond the stress overshoot in highly entangled solutions [Ravindranath et al. (2008)].

Regarding the stress peak in startup shear as the yield point, we are interested in determining salient features associated with the stress overshoot as a function of the level of chain entanglement in melts. In the present study, we have carried out systematic rheometric measurements to explore the transient rheological responses to fast startup shear of monodisperse styrene-butadiene rubber (SBR) melts with the number of entanglements per chain ranging from $Z=24$ to 160. This is made possible by employing a sliding plate rheometer. PTV measurements confirm that homogenous deformation prevails up to the stress overshoot, as expected based on previous studies of solutions [Tapadia and Wang (2006); Boukany and Wang (2007, 2008); Ravindranath et al. (2008); Boukany et al. (2008)]. Further flow birefringence observations indicate that the sample is intact during shear toward the stress overshoot. All four monodisperse SBR melts of different levels of chain entanglement show the same yielding characteristics in the elastic deformation regime and can be described by the same simple scaling laws that were previously observed in entangled polymer solutions [Ravindranath and Wang (2008)].

II. EXPERIMENTAL

A. Materials and linear viscoelastic properties

A series of monodisperse styrene-butadiene rubber (SBR) with a range of molecular weight $M_w$ from 100 to 500 K was synthesized by anionic polymerization in Bridgestone-America. The microstructural details of these SBR melts are presented in Table I. Small amplitude oscillatory shear [(SAOS) strain amplitude $\gamma=5\%$] was carried out to determine linear viscoelastic properties of these melts with an advanced rheometric expansion system (ARES) using a parallel plate geometry with a diameter of 15 mm and a gap of

<table>
<thead>
<tr>
<th>Sample</th>
<th>$M_w$ (g/mol)</th>
<th>$M_w/M_n$</th>
<th>Styrene (%)</th>
<th>Butadiene (%)</th>
<th>Vinyl (1,2-BD) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBR100K</td>
<td>94 800</td>
<td>1.05</td>
<td>10</td>
<td>90</td>
<td>78.8</td>
</tr>
<tr>
<td>SBR170K</td>
<td>174 000</td>
<td>1.07</td>
<td>20</td>
<td>80</td>
<td>65.2</td>
</tr>
<tr>
<td>SBR250K</td>
<td>250 000</td>
<td>1.04</td>
<td>20</td>
<td>80</td>
<td>65.0</td>
</tr>
<tr>
<td>SBR500K</td>
<td>497 000</td>
<td>1.19</td>
<td>20</td>
<td>80</td>
<td>52.1</td>
</tr>
</tbody>
</table>

TABLE I. Molecular characteristics of SBR melts.
about 1 mm at room temperature (T=23 °C). Figure 1 shows storage and loss moduli $G'$ and $G''$ as a function of frequency $\omega$ for all four SBR melts. The molecular characteristics of these samples based on linear viscoelastic measurements are listed in Table II. The plateau modulus $G_N^0$ was estimated from the value of $G'$ at the frequency where $G''$ shows a minimum from which the entanglement molecular weight $M_e$ is estimated according to $G_N^0=\rho RT/M_e$, with the melt mass density $\rho=0.93$ g/cm$^3$, and $R$ being the gas constant. SBR 100 K has slightly higher styrene content, thus lower $G_N^0$. The terminal relaxation time $\tau$ is estimated as the inverse of the crossover frequency $\omega_c$ where $G'=G''$. The Rouse relaxation time $\tau_R$ of these entangled melts can be estimated from the terminal relaxation time $\tau$ as $\tau_R=\tau/(M_w/M_e)$. One can also estimate $\tau_R$ in an empirical way that satisfies its quadratic scaling with $M_w$ [Osaki et al. (2001)]. The value estimated from the melt viscosity $\eta$ is slightly lower and also involves the assumption of 3.4 molecular weight scaling of $\eta$. See the footnote following Osaki et al. (2001).

FIG. 1. Small amplitude oscillatory shear (SAOS) measurements of storage and loss moduli $G'$ and $G''$ for SBR melts of different molecular weights ($T=23$ °C; PP-15 mm).

<table>
<thead>
<tr>
<th>Sample</th>
<th>$M_e$ (g/mol)</th>
<th>$G_N^0$ (MPa)</th>
<th>$Z=M_w/M_e$</th>
<th>$\tau$ (s)</th>
<th>$\tau_R=\pi(M_w/M_e)$</th>
<th>$G_{coh}$ a (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBR100K</td>
<td>4000</td>
<td>0.55</td>
<td>24</td>
<td>25</td>
<td>1.1</td>
<td>0.27</td>
</tr>
<tr>
<td>SBR170K</td>
<td>3300</td>
<td>0.67</td>
<td>53</td>
<td>120</td>
<td>2.3</td>
<td>0.33</td>
</tr>
<tr>
<td>SBR250K</td>
<td>3300</td>
<td>0.68</td>
<td>76</td>
<td>310</td>
<td>4.1</td>
<td>0.30</td>
</tr>
<tr>
<td>SBR500K</td>
<td>3100</td>
<td>0.72</td>
<td>160</td>
<td>2100</td>
<td>13</td>
<td>0.34</td>
</tr>
</tbody>
</table>

aCalculated according to $G_{coh}=\sigma_{max}/\gamma_{max}$ in startup shear mode when $\gamma>>\tau_R^{-1}$.
B. Experimental apparatus and measurements

In this work, a custom-built sliding plate rheometer (SPR) was employed to produce startup simple shear. The schematic depiction of our SPR involving a stationary bottom plate and movable top plate has been provided previously [Boukany and Wang (2007)]. In a typical startup shear experiment, the step motor is programmed to move suddenly at a prescribed velocity until reaching a given displacement. All of our measurements took place at room temperature ($T \approx 23^\circ C$).

Bubble-free films of SBR melts were prepared by solution casting and CRA VER press to produce uniform thickness. A sample with a sufficient length $L$, width $W$, and thickness $H$ on the orders of $L \approx 3$ cm, $W \approx 1$ cm, and $H \approx 0.05–0.08$ cm, was used. A thin layer around $10\mu m$ in thickness of a commercial cyanoacrylate-based super glue (e.g., Instant Krazy® glue) was used to adhere the sample to the two plates so that wall slip is prevented during shear.

In addition, direct visual inspection was carried out during and after measurements. When interfacial failure was observed, the measurement would be discarded. Moreover, flow birefringence observations were conducted from the transparent sliding plates to confirm integrity of the sample during rheological measurements. Armed with such evidence, it is permissible to compute the shear stress from the force read with a load cell and the actual area of the sample in each loading that is determined by knowing the gap distance and weight of the sample, along with its mass density $\rho$.

III. RESULTS AND DISCUSSIONS

A. Stress overshoot in startup shear for SBR-100 K ($Z=24$)

Typically, when imposed shear rate $\dot{\gamma}$ is greater than $1/\tau$, stress overshoot emerges during startup shear. The peak position can be specified by its coordinates in terms of the stress maximum $\sigma_{\text{max}}$, the corresponding time $t_{\text{max}}$, or the elapsed strain at the peak $\gamma_{\text{max}}=\dot{\gamma}t_{\text{max}}$. Figure 2(a) shows the time-dependent stress as a function of time at various discretely imposed shear rates ($\dot{\gamma}\tau>1.0$) for the SBR100K melt. Two scaling regimes appear in terms of how $\sigma_{\text{max}}$ varies with $t_{\text{max}}$,

$$\sigma_{\text{max}}(t, \dot{\gamma}) \sim (t_{\text{max}})^{-1/2}, \quad \dot{\gamma} \geq \tau_R^{-1},$$

which has been labeled the elastic deformation regime [Wang et al. (2007a)] and

$$\sigma_{\text{max}}(t, \dot{\gamma}) \sim (t_{\text{max}})^{-1/4}, \quad \tau^{-1} < \dot{\gamma} < \tau_R^{-1},$$

which is the viscoelastic regime.

This overshoot character can also be represented on linear scales to show how the stress changes with the elapsed strain $\gamma = \dot{\gamma}t$, as shown in Fig. 2(b). Remarkably, the peak stress $\sigma_{\text{max}}$ is seen to be linear in $\gamma_{\text{max}}$ for the startup shear involving rates in the elastic deformation regime. The slope represented by the dashed line actually reveals a specific modulus $G_{\text{coh}}$,

$$\sigma_{\text{max}} = G_{\text{coh}} \times \gamma_{\text{max}},$$

where the subscript “coh” stands for the material stiffness at the point of yield or cohesive failure. Emergence of such a linear relationship implies that the elastic deformation might be understood to be entropic in origin and to involve linear deformation of a Gaussian chain network. This modulus $G_{\text{coh}}$ also tabulated in Table II for all four melts is lower than the initial (intrinsic) modulus $G_{\text{int}}$ by a factor of 2.3. It is also interesting to note that $G_{\text{int}} \approx 0.6$ MPa is very close to the plateau modulus $G_N$ determined from Fig. 1. Thus, we
conclude that $G_{coh} = G_{int}^{0.4}/2.3$. The subsequent data show that this relationship holds approximately true for all the four SBR melts.

It is instructive to normalize the shear stress $\sigma$ and strain $\gamma$ with their respective peak values. Figure 2(c) shows that all data obtained at different rates collapse onto a single master curve. Existence of such a master curve in the elastic deformation regime suggests that the physical origin of stress maximum is the same and the system approaches the yielding point in the same manner at all rates in this elastic deformation regime.

**B. Universal scaling laws in all entangled SBR melts (from Z=24 to Z=160)**

It is important to determine whether the characteristics associated with the stress overshoot revealed in Sec. III A remain universal and can be depicted in the same way for melts of different levels of chain entanglement. By increasing the SBR molecular weight, we are able to increase the number of chain entanglements per chain from 24 to 160. Performing startup shear experiments in our sliding plate rheometer, we observe the same features as seen for SBR100K. For example, Figs. 3(a)–3(c) indicate for the other three melts the same relationship of shear stress versus shear strain as shown in Fig. 2(b).
under the condition of \( \dot{\gamma}_R > 1 \), where the "cohesive modulus" \( G_{\text{coh}} \), evaluated from these plots as the slope of the dashed line and listed in Table II, is universally a factor of approximately 2.3 below the plateau modulus \( G_N^0 \) and the intrinsic modulus \( G_{\text{int}} \) defined in Figs. 2(b) and 3(a)–3(c). Actually, all these curves collapse onto a single super master curve in the normalized coordinates as shown in Fig. 4.

Another way to represent the scaling results in the elastic deformation regime is to make a master curve as shown in Fig. 5(a) where the linearity between \( \sigma_{\text{max}} \) and \( \gamma_{\text{max}} \) is demonstrated to involve the same modulus independent of the value of \( Z \), i.e., the slope of 0.43 \( \sim \) 1/2.3 being the same for all four samples. Similarly, extracting from the raw data such as those presented in Fig. 2(a), we obtain in Fig. 5(b) a master curve that depicts the characteristics of the shear stress overshoot, i.e., scaling behavior of the peak stress \( \sigma_{\text{max}} \) versus the elapsed time \( t_{\text{max}} \) at the stress maximum, for different applied rates, spanning both the elastic deformation and viscoelastic regimes. Not only do the data collapse together but they also reveal a rather clear separation of dynamic regimes at the Rouse relaxation time \( \tau_R \). In particular, Eq. (3) can be rewritten as

\[
\sigma_{\text{max}} = G_N^0 (\dot{\gamma}/\tau_R)^{1/2}, \quad \dot{\gamma} > \tau_R^{-1}.
\]

Since the elastic deformation regime is found to occur for \( t_{\text{max}} < \tau_R \), the peak stress is always higher than the elastic plateau modulus \( G_N^0 \).
Because of the linear relationship of Eq. (3) shown in Fig. 5(a) and the scaling behavior of Fig. 5(b), it is easy to extract an auxiliary scaling law detailing how the position of the yield point, i.e., the shear strain at which the shear stress peaks, \( \gamma_{\text{max}} \), scales with the shear rate. Inserting \( \gamma_{\text{max}} = \dot{\gamma}_{\text{max}} \) into the combination of Eq. (3) and Eq. (4), we have

\[
\gamma_{\text{max}} = \left( \dot{\gamma}_{R} \right)^{1/3}, \quad \dot{\gamma} > \dot{\gamma}_{R}^{-1}.
\]

(5)

Figure 6 shows the data from all four SBR melts revealing a universal scaling law of Eq. (5) independent of \( Z \), where partial data on polyisoprene melts from Auhl et al.
are incorporated to show agreement and we omitted comparison with the previous data of Schweizer et al. (2004) that restricted to just one polystyrene sample and to lower rates.

C. Universality among all entangled liquids

The universal character associated with the shear stress overshoot may actually go beyond these SBR melts. To further explore the universality of the observed scaling laws, we combine the present results with those obtained previously from entangled PBD solutions [Ravindranath and Wang (2008)]. Figures 7(a) and 7(b) show that both entangled solutions and melts are governed by the same scaling laws in both elastic and viscoelastic regimes, where the collapse of data for the different samples onto a single line in Fig. 7(a) is made possible by normalizing the shear stress with the cohesive modulus \( G_{\text{coh}} \) of each system. A supermaster curve analogous to Fig. 5(a) can also be constructed by adding the data of PBD solutions from Ravindranath and Wang (2008). Figure 8 shows an impressive overlapping of all data onto a universal linear relationship between \( \sigma_{\text{max}} \) and \( \gamma_{\text{max}} \) valid for the different entangled solutions and melts.

Finally, it is instructive to summarize the yielding response to sudden startup shear of a variety of entangled liquids including wormlike micellar, DNA, synthetic polymer solutions, and melts. The supermaster curve in Fig. 9 asserts that such entangled liquids approach to the yield point in a universal way.

D. PTV measurements and flow birefringence visualization

In this section we carried out PTV and flow birefringence measurement to determine how the deformation takes place and find out whether the sample has suffered any failure.
up to the stress maximum. Figures 10(a) and 10(b) show the temporal evolution of stress and velocity profile at \( \dot{\gamma} = 1.4 \text{ s}^{-1} \) for SBR250K. As shown in Fig. 10(b), the deformation is homogeneous until \( t = 3.3 \text{ s} \), well after the stress overshoot, although inhomogeneous deformation is clearly visible at \( t = 4.8 \text{ s} \).

Since we rely on measurements of the total force to determine the shear stress, it is necessary to ensure that the sample is intact during startup shear to the point of stress overshoot. At a shear rate of 5.7 \text{ s}^{-1}, SBR100K shows its shear stress maximum around

![Figure 7](image1.png)

**FIG. 7.** (a) Supermaster curves for normalized peak stress \( \sigma_{\text{max}}/G_{\text{coh}} \) as a function of the normalized time \( t_{\text{max}}/\tau_R \) for four melts and solutions with different levels of entanglement obtained from Ravindranath and Wang (2008) [RW], (b) the \( \gamma_{\text{max}} \) vs \( \dot{\gamma} \tau_R \) for all entangled melts and solutions.

![Figure 8](image2.png)

**FIG. 8.** Supermaster curves for the normalized peak stress \( \sigma_{\text{max}}/G_{\text{coh}} \) as a function of strain for four melts and solutions with different levels of entanglement [Ravindranath and Wang (2008)].
\( \gamma_{\text{max}} = 3.0 \), i.e., at \( t_{\text{max}} = 0.5 \) s, according to Fig. 2(b). A flow birefringence setup [Boukany and Wang (2008)], involving placing a halfwave retardation plate between two mutually perpendicular polarizers at 45° to the shearing direction, is used to monitor the sample integrity. Under a white light source, our color charge-coupled device video camera reveals evolution of the optical retardation in Fig. 11 during a startup shear and shows that neither edge fracture nor glue failure takes place during deformation up to the stress maximum.

**FIG. 9.** Supermaster curves for the normalized stress growth \( \sigma / \sigma_{\text{max}} \) as a function of normalized strain \( \gamma / \gamma_{\text{max}} \) for all entangled melts obtained from Fig. 5 entangled PBD from [Ravindranath and Wang (2008)], DNA solutions from Boukany and Wang (2009a) [BWa], and wormlike micellar solution from Boukany and Wang (2008) [BWB].

**FIG. 10.** Time evolutions of (a) shear stress (b) velocity profile for SBR 250 K at \( \dot{\gamma} = 1.4 \) s\(^{-1} \), from \( t = 0 \) to 4.8 s.
IV. CONCLUSIONS

In this work, we have investigated universal scaling characteristics associated with stress overshoot that occurs during startup shear in SBR melts whose level of chain entanglement ranges from $Z = 24$ to $160$ entanglements per chain. Specifically, in the elastic deformation regime defined by $\gamma H_{9253}^{\dot{\gamma}} H_{9270}^{R}$ $1$, we found that at the point of yield, i.e., the moment when the shear stress peaks, the peak shear stress $\sigma_{\text{max}}$ scales linearly with the strain $\gamma_{\text{max}}$ at the peak and both $\sigma_{\text{max}}$ and $\gamma_{\text{max}}$ scales with the applied shear rate with an exponent of $1/3$. At lower rates yet still above the terminal flow regime, we see a crossover behavior with $\sigma_{\text{max}} / G_{N} H_{9270}^{R} / t_{\text{max}}^{1/4}$ and $t_{\text{max}} > \tau_{R}$ instead of $\sigma_{\text{max}} \sim G_{N} H_{9270}^{R} / t_{\text{max}}^{1/2}$ with $t_{\text{max}} < \tau_{R}$. These scaling laws turn out to be universal, independent of $Z$, and of whether the sample is a present SBR melt or a previous PBD solution or an entangled DNA solution.

Actually, the whole process of stress growth up to the point of overshoot is universal in the sense that a single supermaster curve can be obtained for the shear stress normalized by its peak value vs the elapsed strain normalized by its value at the stress maximum for all shear rates and all different entangled liquids ranging from PBD, wormlike micellar solutions to DNA solutions, and SBR melts. Existence of such a supermaster curve is likely to encourage us to look for a universal theory that can depict the elastic yielding during startup deformation of well entangled polymeric liquids.

Since the reported universal scaling behavior occurs before any inhomogeneous deformation is to take place subsequently, we expect its theoretical depiction to be more tractable than a full molecular theory for polymer deformation and flow. The latest version of tube model [Graham et al. (2003)] seemed to be able to quantitatively describe the observed scaling laws [Auhl et al. (2008)]. However, it also appears to be the case [Wang (2008)] that the same theory of Graham et al. (2003) cannot depict or anticipate the experimental observations of nonquiescent relaxation in the simpler step strain experiments on both entangled solutions [Ravindranath and Wang (2007)] and melts [Boukany and Wang (2009b)]. It is true that the tube theory does not envision the stress maximum as a yield point, where the entanglement network ceases to undergo further molecular deformation due, according to our understanding [Wang et al. (2007b); Wang and Wang (2009)], to a force imbalance between the intermolecular locking force that is causing the

![FIG. 11. (Color online) The flow birefringence images at times from $t=0$ to $0.6$ s along the velocity gradient direction for SBR 100 K obtained using a full wave retardation plate between two crossed polarizers that are $45^\circ$ to the shearing direction at $\dot{\gamma}=5.7$ s$^{-1}$, where the initial transparency arises from the use of the retardation plate as shown in the Michel-Levy chart with other corresponding retardations also indicated from (a) to (e).](image)
chain deformation and the intramolecular elastic retraction force. Beyond this yield point, the entanglement structure inevitably gets torn apart. This is a concept that is not embedded in the tube theory.

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References


Using Eq. 7 from this paper, i.e., \( \tau_{\eta} = (6M_w \eta/\pi^2) (M_c/M_w)^{2.4} \), and taking \( M_c \) to be twice \( M_w \), where \( \eta \) is the zero-shear viscosity, we estimate \( \tau_{\eta} \) to be ca. 0.78, 1.9, 3.7, and 9.9 s, respectively, for SBR100K, SBR170K, SBR250K, and SBR500K instead of 1.1, 2.3 and 4.1 and 13 s listed in Table II. These two groups of values are quite similar. Since \( \tau_{\eta} \) for SBR500K is not reliable with the crude estimate of \( \eta \) from Fig. 1, we choose to plot the master curves such as Fig. 6 based on \( \tau_{\eta} \) tabulated in Table II.


