Homogeneous shear, wall slip and shear banding of entangled polymeric liquids in simple-shear rheometry: a roadmap of nonlinear rheology

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Homogeneous shear, wall slip and shear banding of entangled polymeric liquids in simple-shear rheometry: a roadmap of nonlinear rheology

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Abstract

The recent particle-tracking velocimetric (PTV) observations revealed that well-entangled polymer solutions and melts tend to either exhibit wall slip or assume an inhomogeneous state of deformation and flow during nonlinear rheological measurements in simple-shear rheometric setups. Many material parameters and external conditions have been explored since 2006, and a new phenomenological picture has emerged. In this article, we not only point out the challenges to perform reliable rheometric measurements but also discuss the relation between wall slip and internal (bulk) cohesive breakdown and summarize all available findings in terms of a phase diagram. This map specifies the conditions under which shear homogeneity, interfacial slip, and bulk shear inhomogeneity would prevail respectively. The paper is closed by enumerating a number of unresolved questions for future studies.
1. Introduction

Rheometry is a widely used experimental technique in polymer science and engineering. The polymer scientist often makes rheometric measurements to characterize the linear viscoelastic properties of his polymer samples. Conversely, linear viscoelastic characteristics have been thought to yield unique information about such molecular information as the molecular weight distribution of a linear polymer melt.\textsuperscript{1,2} The rheometric measurements usually follow the standard analysis that is based on three key assumptions: (1) no-slip boundary conditions and (2) homogenous velocity profile during shear as shown in Figure 1a, and (3) quiescent relaxation upon shear cessation. These assumptions about the state of deformation hold true by definition for linear viscoelastic measurements and have been the basis of most rheometric studies in the literature. The most common rheometric setup\textsuperscript{3} is a rotational shear device involving either cone-plate (see the middle figure in TOC) or parallel-plate (disk) shear cell, where the typical sample thickness H is macroscopic, in the range of 0.1 to 1 mm.

Polymer scientists and engineers have also performed nonlinear rheological studies\textsuperscript{4} to learn more about the molecular structures including chain architecture.\textsuperscript{5} In studies involving simple shear, the dominant nonlinearity is strain softening: both the relaxation modulus and steady-shear viscosity of entangled polymers are lower than their values in the linear response regime. In absence of any direct evidence to contradict, in the past we assumed that such strain softening had occurred in a homogeneous manner.
Figure 1  (a) 3-D view of homogeneous shear at an apparent shear rate \( \dot{\gamma}_{\text{app}} = V/H \) in absence of wall slip.  (b) Side view: velocity profile in presence of wall slip on two identical shearing surfaces, when \( \dot{\gamma}_{\text{app}} > \tau \), with \( \tau \) being the dominant chain relaxation time.  When a slip velocity \( V_s \) is present, the amount of slip can be quantified by the extrapolation length \( b \) defined in the figure involving the bulk shear rate \( \dot{\gamma} \).  (c) Side view: bulk shear banding along with a small amount of wall slip is a characteristic response of well entangled linear polymer solutions during startup shear at high rates when wall slip alone can no longer prevent the sample bulk from shearing at rates higher than the dominant relaxation rate \( 1/\tau \).

To verify whether this is the case, we have recently developed an in situ particle-tracking velocimetric (PTV) method as shown in the middle figure of TOC.\textsuperscript{6} The combination of rheometric and PTV measurements revealed a clear violation of each of the three basic assumptions listed in the first paragraph.  In other words, shear inhomogeneity was found to take place cone-plate shear cell during startup shear\textsuperscript{7,8,9,10} and large amplitude oscillatory shear.\textsuperscript{11} Entangled solutions\textsuperscript{12} and melts\textsuperscript{13} were not quiescent upon shear cessation from a large step strain.  Thus, the nonlinear responses of entangled polymers appear far more complicated than previously revealed.  In other words, when using any commercial rheometer for simple shear, we could no longer assume a priori that the states of deformation and flow are homogeneous.

In this Perspective we indicate some guidance for future rheological experiments by showing when, how and why the three basic assumptions in polymer rheology may be invalid.  We first briefly review a primary type of shear inhomogeneity, i.e., wall slip, as schematically illustrated in Figure 1b.  We then describe when nonlinear rheological
measurements might be complicated by such effects as edge fracture. Subsequently we enumerate the situations where shear homogeneity prevails before discussing a relation between wall slip and shear banding. We summarize the available results in terms a phase diagram to map out the parameter space and to show where shear homogeneity, wall slip, and shear banding (schematically illustrated in Figure 1c.) are "located". We conclude by indicating what we still do not know and the theoretical implications of the emerging PTV observations.

2. Wall slip: primary example of shear inhomogeneity and how to minimize

Entangled linear polymeric liquids can display one unique property that non-entangled liquids do not possess: They are capable of undergoing true wall slip. Phenomena involving polymer wall slip have been reported since the 1950s.14,15,16,17,18,19,20 De Gennes21 offered in 1979 the first understanding of why entangled polymers have the ability to display observable wall slip on macroscopic scales. According to de Gennes, slip can be quantified by the extrapolation length \( b \) defined in Figure 1b and can be macroscopically large due to the high shear viscosity \( \eta \) originating from chain entanglement. Specifically, it can be readily shown that\(^{21,22}\)

\[
b = (\eta/\eta_i)a,
\]

where \( \eta \) is the shear viscosity in the bulk, \( \eta_i \) is a local viscosity at the polymer/wall interface, and \( a \) is the interfacial slip-layer thickness of a molecular dimension. This viscosity ratio can be exceedingly large, allowing \( b \) to attain a macroscopic magnitude when the value of \( \eta_i \) diminishes as a consequence of either chain desorption or disengagement of adsorbed chain from the bulk entanglement network.\(^{22}\) Subsequent to
de Gennes' analysis,\textsuperscript{21} a number of studies were devoted to theoretical\textsuperscript{23,24,25} and experimental accounts\textsuperscript{26,27,28,29,30,31,32,33,34} of steady-state wall slip.\textsuperscript{22,35} Since wall slip is such an important rheological character of entangled polymers, we describe it in some detail in the Appendix A. In particular, we illustrate in the Appendix A why both entangled solutions and melts could exhibit significant wall slip.

Because polymeric materials, particularly entangled polymers, are prone to wall slip, rheometric measurements of nonlinear behavior can be difficult to interpret. Many of the nonlinear rheological measurements of entangled polymer solutions and melts in the literature might have involved wall slip. This may be particularly true in the large step strain studies\textsuperscript{36,37,38,39,40,41} of well-entangled polymer solutions made with small organic liquids. In other words, wall slip\textsuperscript{42} is likely the cause\textsuperscript{28} for the observed ultra-strain-softening\textsuperscript{37-40} in stress relaxation from step strain that deviated from the prediction\textsuperscript{43} of the Doi-Edwards tube model.\textsuperscript{44} Even when the experimental data agrees with the model calculation,\textsuperscript{38} interfacial failure can be present after shear cessation as revealed recently in a PTV study.\textsuperscript{12} More discussion on the development of the tube theory in the context of continuous shear is provided in Appendix B.

For entangled solutions, Eq A.4 in the Appendix A explains why wall slip could be present in previous studies of entangled polymer solutions in both step shear\textsuperscript{36-40} and continuous shear,\textsuperscript{45} due to use of small molecular organic solvents with a water-like viscosity $\eta_s$. Because of the low $\eta_s$ in the dominator of Eq A.4 $b_{\text{max}}$ can be comparable to or larger than the sample thickness $H$. Solutions with higher concentration $c$ or polymer molecular weight $M_w$ are more affected by wall slip in their nonlinear rheological
measurements. This explains why there is more strain softening in a step strain test when \( cM_w \) is higher.\textsuperscript{37-40}

For entangled polymer solutions that show significant wall slip,\textsuperscript{46,47} we have confirmed two ways to minimize slip. An effective way to get rid of wall slip stems from our understanding of what parameters control the magnitude of wall slip. It has been shown that the degree of wall slip can be reduced by using an entangled polymeric solvent.\textsuperscript{12,48} In other words, Eq A.4 for \( b_{\text{max}} \) not only explains why polymer solutions can undergo strong wall slip but also points to an effective way to minimize wall slip. According to a previous study,\textsuperscript{49} the solution viscosity \( \eta \) does not increase proportionally with the solvent viscosity \( \eta_s \) when the polymeric solvent's molecular weight increases. Thus, \( b_{\text{max}} \) of Eq A.4 can be considerably reduced by using a polymeric solvent of sufficiently high molecular weight.\textsuperscript{12} Surface roughness has been demonstrated to be effective in reducing wall slip.\textsuperscript{32} We have also used sandpapers as the shear surfaces to produce shear banding in a solution that would only exhibit interfacial failure on smooth surfaces.\textsuperscript{48,50}

Well-entangled melts undergo even greater amount of wall slip.\textsuperscript{21,22,34,51} The maximum value \( b_{\text{max}} \) is inherently dictated by the degree of chain entanglement, as expressed in Eq A.1. Thus, for well-entangled linear polybutadiene melts with a large \( b_{\text{max}} \), large step strain tests could only demonstrate ultra strain softening\textsuperscript{52} resulting from wall slip. We must have some means for the shear surfaces to grab polymer melts so that sufficient shear deformation can be exerted on the sample to probe its intrinsic nonlinear rheological responses. For certain melts such as styrene-butadiene rubber (SBR) with high vinyl content, we have demonstrated that various superglues can effectively adhere
the samples onto solid surfaces so that simple shear can take place in sliding-plate without wall slip.\textsuperscript{13}

3. Meniscus instability or edge fracture

Simple shear in rotational device, e.g., cone-plate or parallel-disk or circular Couette (co-concentric cylinders), can in principle reach a steady rheological state. In reality, such geometries leave a rim of meniscus exposed to the ambient air. Since the free surface is cohesively weaker, highly viscoelastic materials such as strongly entangled polymer melts and solutions are often found to undergo edge or meniscus instability upon significant strains. This finite size effect severely constrains rheometric studies of large deformation behavior.

The intrinsic difficulty of meniscus instability in rotational rheometry can be successfully dealt with by using a cone-partitioned plate (CPP) setup to decouple rheometric measurements from any disturbance due to the edge fracture. Figure 1 of Ref. 10 depicted such a CPP device coupled with particle-tracking velocimetric (PTV) capability. For entangled polymer solutions, CPP appears to assure reliable characterization during a) steady-state continuous shear\textsuperscript{10} b) large amplitude oscillatory shear of linear polymer melts,\textsuperscript{53} and c) non-quiescent relaxation after a large step shear.\textsuperscript{54}

4. Particle-tracking velocimetry: a necessary tool in nonlinear rheometry

In complicated setups such as channel flow, particle tracking has been applied to visualize the state of polymer flow since 1950s.\textsuperscript{55,56,57} In most cases, capillary flow in the entrance and channel flow in die land have been observed using either particle-tracking\textsuperscript{55,57,58} or laser Doppler velocimetry.\textsuperscript{59,60,61} Such visualization is informative and
necessary because the flow field is unknown \textit{a priori}. Particle tracking velocimetry has been applied to visualize complex flow behavior of other fluids.\textsuperscript{62,63,64,65,66}

In simple-shear rheometry we have often conveniently assumed that the state of deformation or flow would be homogeneous independent of the constitutive properties of entangled polymers. This assumption would be correct in steady state if there would be a monotonic constitutive relation (i.e., one-to-one correspondence) between shear stress and shear rate. Typically, rheometric studies of entangled polymers have been carried out on the basis of shear homogeneity, and no commercial rheometers have been designed to directly probe the velocity field in such shear cells as cone-plate or parallel-disk. We have recently recognized the need to independently measure the states of deformation and flow during startup shear, large amplitude oscillatory shear and step shear. Specifically, an effective PTV method\textsuperscript{6} has been implemented to determine whether entangled polymer solutions (made with polymeric solvents) would undergo inhomogeneous shear, instead of, or, in addition to wall slip. Because of the revelation of wall slip and shear banding through the PTV observations,\textsuperscript{6} the PTV measurements should now be regarded as an indispensable part of any nonlinear rheological study of highly viscoelastic materials including entangled polymers. It is worth noting in passing that the time resolution of our PTV method is only limited by the camera speed whereas the previous attempts placed a CCD camera along the velocity gradient direction and could only image the shear-vorticity plane one layer at a time.\textsuperscript{28,67} In fact, because of the poor vertical resolution, this arrangement may only be effective to monitor wall behavior at the sample/plate interface.
5. The roadmap for nonlinear rheology of entangled polymers

In this section we begin by indicating the situations where rapid external shearing fields would not result in inhomogeneous deformation and flow. Then we discuss the relation between wall slip and shear banding. We close by presenting a phase diagram to summarize what can be expected in startup continuous shear.

5.1 Homogeneous shear with $Wi_{app} > 1$ and quiescent relaxation after step shear

We enumerate several conditions, under which homogeneous shear and quiescent relaxation prevail so that rheometric measurements may receive straightforward interpretation. When the apparent Weissenberg number $Wi_{app} = \dot{\gamma}_{app} \tau > 1$, shear homogeneity can still prevail under the following circumstances.

(a) When an entangled polymer solution is not strongly entangled, we have $b_{max}/H << 1$. Consequently, neither wall slip nor shear banding is observable. In other words, the steady state profile tends to be homogeneous although transient shear inhomogeneity may occur.$^{9,68,69}$

(b) Even when the entanglement level is high, shear inhomogeneity can be suppressed$^{10,48}$ during startup shear by reducing the extrapolation length $b_{max}$ using a polymeric solvent of sufficiently high molecular weight to produce a large $\eta_s$ in Eq A.4.

(c) When $b/H << 1$, macroscopic motions after a large step strain may not be observable. In other words, with $b/H << 1$ elastic yielding could occur quiescently.$^{48}$
(d) Preliminary evidence based on both entangled DNA\textsuperscript{70} and polymer\textsuperscript{71} solutions indicates that shear banding observed upon sudden startup shear can diminish if the shear rate is gradually approached from the Newtonian regime.

(e) Shear homogeneity has been observed to return at sufficiently high rates where no entanglement network structure could survive\textsuperscript{9,69} This condition corresponding to a Weissenberg number $W_i_{\text{dis}}$ is discussed in some detail in the Appendix A.

### 5.2 Relationship between wall slip and bulk shear banding

Wall slip usually precedes any bulk inhomogeneous response to an external shearing field because polymer/wall interface typically has weaker adhesion than the cohesion of entangled polymers. Because of wall slip sketched in Figure 1b, the sample bulk can avoid high shear and stay in the Newtonian regime ($W_i_{\text{app}} < 1$) until an apparent rate $\dot{\gamma}_{\text{app}}$, corresponding to a critical Weissenberg number\textsuperscript{50,72}

$$W_{i_{\text{ws-sb}}} = (1 + 2b_{\text{max}}/H),$$  \hfill (2)

where the subscript "ws-sb" denotes this critical shearing condition for the transition from wall slip to (bulk) shear banding. To estimate this critical condition, we have equated the bulk shear rate $\dot{\gamma}_c$ at the borderline between the Newtonian and shear thinning regimes to the reciprocal relaxation time $1/\tau$, i.e., $\dot{\gamma}_c \tau = 1$. The expression $b_{\text{max}}$ is given by Eq A.1 for entangled melts and by Eq A.4 for entangled solutions respectively in the Appendix A. According to Eq 2, the higher the value of $b_{\text{max}}/H$, the wider range of the apparent rate is for the wall slip to be the dominant response. When $W_{i_{\text{app}}} > W_{i_{\text{ws-sb}}}$, shear banding may emerge. Moreover, bulk shear banding could emerge at a much lower value of $W_{i_{\text{app}}}$ than
When rough shearing surfaces are used to remove wall slip. For example, surfaces made of sandpaper can effectively reduce wall slip so that shear banding takes its place.\textsuperscript{48,50}

5.3 The "phase diagram"

Clearly, $b_{\text{max}}/H$ is the key parameter to control the nonlinear rheology of entangled polymers, dictating when and what type of shear inhomogeneity may occur for a given apparent Weissenberg number $W_{i\text{app}}$. Here we summarize what we know about the nonlinear rheological responses to startup shear in terms of a phase diagram as shown in Figure 2a, where for a fixed gap distance $H^*$ the X axis of $2b_{\text{max}}/H^*$ is controlled by $b_{\text{max}}$. For monodisperse linear-chain melts, Eq A.1 shows how the molecular weight dictates the magnitude of $b_{\text{max}}$. For entangled solutions made with polymeric solvents, besides the molecular weight of the solute the solvent viscosity $\eta_s$ can also alter $b_{\text{max}}$ according to Eq A.4. For a given polymeric system, i.e., for a fixed $b_{\text{max}}^*$, varying $H$ would have the consequence shown in Figure 2b.

In both Figures 2a-b, at small values of $b_{\text{max}}/H$, we have the vertical "homogeneous" strips to the left of the vertical white lines. The inclined white borderline

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2.png}
\caption{Phase diagrams in the parameter space of $W_{i\text{app}}$ vs. $2b_{\text{max}}/H$ (double log scales) to map out the different responses in terms of the state of deformation for (a) a fixed sample thickness so that $b_{\text{max}}/H^*$ simply denotes the level of chain entanglement; and (b) a given sample so that $b_{\text{max}}^*/H$ increases with lowering $H$ until the upper bound is reached at $H = 2l_{\text{ent}}$ when only wall slip is possible, moving along the red vertical line.}
\end{figure}
between wall slip and shear banding is given by Eq 2. The boundary between "uniform disentanglement" and "shear banding" is depicted by Eq A.3 or Eq. A.6, which is inclined in Figure 2a and horizontal in Figure 2b. Actually, Figure 2a is somewhat analogous to Figure 6 of Ref. 6. Both Figures 2a and 2b serve as a roadmap for the steady-state behavior of well entangled polymers in startup shear.

![Figure 2](image)

Figure 2 (c) Regions of the phase diagram where PTV studies have been carried out, including the small $b_{\text{max}}/H$ regime inside the rectangle, and six solutions of different $2b_{\text{max}}/H$ equal to 22, 26, 136, 140, 259, 1470 respectively. The open symbols indicate approximate shear homogeneity.

![Figure 3](image)

Figure 3 PTV observations of steady state shear in a gap of $H = 50 \, \mu m$ at two different rates of 0.3 and 3.0 s$^{-1}$ for an entangled solution of 13 wt. % polybutadiene ($M_w \sim 10^3$ kg/mol) in a polybutadiene solvent ($M_w \sim 10$ kg/mol).

We can summarize the available results from the literature in Figure 2c as well as in Table 1 that lists five PTV-based studies$^{9,10,50,72,73}$ on eleven entangled solutions. The first two papers in Table 1 focused on the phase space circled by the (red) rectangle in Figure 2c in the region of $2b_{\text{max}}/H < 1$. We specifically mark the other regions corresponding to the other six solutions listed at the bottom of Table 1, having respectively $2b_{\text{max}}/H$ equal to 22, 26, 136, 142, 259 and 1470. Particularly worth mentioning is the system with $2b_{\text{max}}/H = 26$ represented by the five circles that shows both slip dominant and shear banding prevailing features as the applied shear rate increases. Also special about this study$^{73}$ is the significantly reduced sample thickness
from a conventional rheometric dimension of ca. 1000 µm to 50 µm. Reducing H broadens the window for wall-slip-dominated rheological responses, leading some to suggest that wall slip would be the only characteristic rheological response of entangled polymers. Indeed, when we reduce H from 1 mm to 50 µm, a sample that would not show significant wall slip "suddenly" does. However, Figure 3 shows that the wall-slip dominant response switches to bulk shear banding behavior as the applied rate crosses the predicted borderline given by Eq 2, represented by the two (yellow) circles in Figure 2c. This switch would always occur until the sample thickness H becomes comparable to the entanglement spacing $l_{ent}$. Figure 2b shows that the shear banding regime shrinks to zero only at the red vertical line at $H = l_{ent}/2$. The window for shear banding is given by $W_{dis}/W_{ws-sb} = H/2l_{ent}$, as indicated in Figures 2a-b.

Table 1 Five PTV studies of entangled solutions of different ability to undergo slip

<table>
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<th>References</th>
<th>Samples</th>
<th>solution viscosity</th>
<th>solvent viscosity</th>
<th>$2b_{max}/H$</th>
<th>$W_{app}$</th>
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<tr>
<td>Macromol., 2008, 41, 2663</td>
<td>0.7M(5%)-2K</td>
<td>21(kPa)</td>
<td>97(Pa)</td>
<td>0.01</td>
<td>10 - 150</td>
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<td>Ref. 9</td>
<td>0.7M(10%)-9K</td>
<td>57(kPa)</td>
<td>10(Pa)</td>
<td>0.2</td>
<td>15-50</td>
<td>Only transient banding</td>
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<td></td>
<td>1M(15%)-9K</td>
<td>510(kPa)</td>
<td>10(Pa)</td>
<td>1.5</td>
<td>45-400</td>
<td>Banding</td>
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<tr>
<td>J. Rheol. 2008, 52, 957</td>
<td>1M(10%)-1.5K</td>
<td>50(kPa)</td>
<td>0.7(Pa)</td>
<td>3</td>
<td>16-110</td>
<td>Slip, banding</td>
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<tr>
<td>Ref. 10</td>
<td>1M(10%)-15K</td>
<td>250(kPa)</td>
<td>36(Pa)</td>
<td>0.27</td>
<td>14-140</td>
<td>No slip, no banding</td>
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<td>Macromol., 2008, 41, 2644 Ref. 72</td>
<td>1 % DNA solution water based</td>
<td>190(kPa)</td>
<td>0.001(Pa)</td>
<td>136</td>
<td>14-14000</td>
<td>Slip, banding</td>
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<tr>
<td>Diamond symbols in Fig. 2c</td>
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<tr>
<td>Soft Matter 2009, 5, 780</td>
<td>water based</td>
<td>5.8(kPa)</td>
<td>0.001(Pa)</td>
<td>1470</td>
<td>0.5-220</td>
<td>Slip</td>
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6. Unresolved questions in both shear and extensional rheometry

We close by listing a number of important issues that we have either not resolved or only obtained partial, preliminary answers. Our PTV method has its natural constraints. In particular, startup continuous shear over a large amount of strain units always requires wrapping a film around the meniscus to prevent sample loss. Sometimes, air bubbles are trapped during sample loading. Small bubbles are difficult to remove under vacuum. The role of bubbles remains to be clarified.

Moreover, many questions remain as listed in no particular order that future studies must deal with.

(1) Shear banding appears not to be a steady state property for entangled polymers. At least for solutions, we were able to remove shear banding by very gradual rate ramp-up instead of a sudden startup shear.\textsuperscript{70,71} It remains to be seen whether the same is true for entangled melts.

(2) Only a handful of studies exist in the literature on transient rheological behavior of melts during startup shear.\textsuperscript{13,75,76} Rheological measurements along with PTV observations of steady shear behavior of entangled melts remain to be carried out.
(3) During startup shear, shear banding emerges after the shear stress maximum where the high shear band is usually adjacent to the moving surface and low shear band stays next to the stationary surface. The origin of this symmetry breaking is elusive and could be related to the presence of polymer/wall interfaces although the initial elastic deformation is homogeneous.

(4) The cohesive breakdown, i.e., elastic yielding after a large step shear, appears to occur within the sample thickness at unpredictable locations for entangled solutions although styrene-butadiene rubbers show failure in the mid plane when they are well adhered to the shear surfaces by superglue. More data are required to show whether the failure location is truly random.

(5) Macroscopic shear inhomogeneity has been observed in various entangled polymeric liquids. However, the PTV technique does detect any microscopic structural inhomogeneity on micron to submicron length scales. Systematic small angle neutron scattering experiments should be carried out during shear banding to probe any microscopic structural inhomogeneity as a consequence of chain deformation.

(6) Other complementary methods including optical birefringence and small angle x-ray scattering along the vorticity direction would help gathering more information in a spatial-resolved manner about the nature of the shear inhomogeneity.

(7) So far, most studies focused on monodisperse samples. It remains to be demonstrated how shear inhomogeneity weakens with increasing polydispersity.
in the molecular weight distribution.\textsuperscript{8} PTV studies have yet to be carried out for miscible and immiscible blends in the nonlinear response regimes.

7. Summary: localized yielding in entangled polymers

In such standard rheometric tests as startup shear and step shear, the PTV observations offer fresh insight into the nature of rheological responses of entangled polymers. A sudden startup simple-shear produces the well-known stress overshoot, which is simply an indication of yielding\textsuperscript{78} with universal scaling characteristics.\textsuperscript{79,80} At the shear stress maximum, the system reaches a force imbalance between the growing elastic (intra-chain) retraction force and intermolecular gripping force,\textsuperscript{81} beyond which further deformation of the entanglement network is no longer possible and chains mutually slide past one another to approach a state of flow.\textsuperscript{82} This transformation is a cohesive failure that can occur in a spatially localized manner in simple-shear apparatuses.

In a large step strain test, instead of quiescent relaxation as perceived in previous experimental and theoretical studies, macroscopic motions were observed after shear cessation.\textsuperscript{12,13} For systems with sufficient $b_{\text{max}}/H$, quiescent relaxation only occurs when the amplitude of step strain is below one strain unity, implying that the entanglement network has a characteristic level of cohesion on shorter time scales than the terminal relaxation time $\tau$. The non-quiescent relaxation indicates that sufficient residual elastic retraction force can overcome the network's cohesion, transforming this elastically-strained "solid" into a liquid. When this elastic yielding occurs inhomogeneously in space, macroscopic motions naturally arise: a solid region can sustain stress but a liquid region cannot. This elastic yielding upon step strain\textsuperscript{81} is a unique nonlinear rheological response of entangled polymers and can be most straightforwardly demonstrated using
PTV without experimental difficulty such as edge fracture because of the small amount of strain involved.

Finally, a word is due about the theoretical situation. Is there any theory to account for the observed shear banding? If shear banding exists in steady state, then one needs a constitutive theory that allows the shear rate to be double-valued for a given stress. But if this shear banding can be avoided by a slow rate ramp-up, then we have to resort to a different theory that prescribes a one-to-one correspondence between stress and rate simple shear. However, such a monotonic constitutive theory would not permit any shear banding to prevail upon a sudden startup shear. Thus, if the conclusions of Ref. 70 and 71 are true, we would not be able to resort to any version of the tube model for a proper theoretical description of the experimental observations.

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Appendix A  Account of Wall Slip and Ultimate Homogeneous Shear

When the apparent shear rate $V/H$ indicated in Figure 1a is below the terminal relaxation rate $1/\tau$ of the entangled polymer, i.e., $(V/H)\tau < 1$, the amount of external shear deformation is lower than unity within the relaxation time $\tau$. The entanglement network does not deform sufficiently to break up unevenly. In other words, there is no chain disentanglement at either the polymer/wall interface or in the bulk. Homogeneous shear prevails as shown in Figure 1a. The viscosity ratio in Eq 1 is on the order of unity and $b$ is only molecularly small.

When the apparent Weissenberg number $Wi_{app} = (V/H)\tau$ is much higher than unity, the adsorbed chains cannot remain engaged with the bulk chain entanglement network due to definite intermolecular gripping forces during startup simple shear. Such interfacial yielding produces an interfacial layer (of thickness $a$) with a greatly reduced viscosity $\eta_i$. Consequently, $b$ can be millions times of $a$, i.e., macroscopically large according to Eq 1. For a monodisperse entangled linear polymer melt with (weight-average) molecular weight $M_w$, the maximum value of $b$ can be estimated upon complete interfacial chain disengagement as

$$b_{max} = (\eta/\eta_e)\ell_{ent} = (M_w/M_e)\ell_{ent},$$

for entangled melts, (A.1)

when $\eta_i$ in Eq 1 turns into $\eta_e$ which is that of a melt with entanglement molecular weight $M_e$. Eq A.1 assumes the slip layer thickness to be the entanglement spacing $\ell_{ent}$, related to $M_e$ as $\ell_{ent} = (M_e/\rho N_A p)^{1/2}$, where $\rho$ is the polymer mass density, the packing length $p$ and the Avogadro constant $N_A$. Here we adopted the empirical exponent 3.4 to depict the molecular weight dependence of $\eta$. The viscosity ratio in Eq. A.1 can readily approach $10^6$, making $b_{max}$ macroscopically large, for polymer melts, especially polyethylene, polybutadiene and polyisoprene.

For monodisperse melts, the local shear rate in the entanglement-free slip layer upon maximum slip is related to the bulk shear rate $\dot{\gamma}$ as

$$\dot{\gamma}_{dis} = (\eta/\eta_e)\dot{\gamma} = (\dot{\gamma}\tau)/\tau_e \sim 1/\tau_e,$$

(A.2)

where $\eta_i/\eta_e = \tau/\tau_e$ follows from the tube model, with the confinement $\tau_e$ is related to the dominant relaxation (i.e., reptation) time $\tau$ as $\tau_e = \tau(M_e/M_w)^{3.4}$, and the product $\dot{\gamma}\tau$ is only on the order of unity at the onset of complete slip. The corresponding Weissenberg number $W_i_{dis}$ is given by

$$W_{i_{dis}} = \dot{\gamma}_{dis}\tau = \tau/\tau_e = b_{max}\ell_{ent},$$

(A.3)

where the last equality follows from Eq A.1.

For an entangled polymer solution with polymer weight fraction $\phi$, complete slip corresponds to having $\eta_i$ in Eq 1 reduced to the solvent viscosity $\eta_s$, where $a$ may also be thought of as the enlarged entanglement spacing $l_{ent}(\phi) = l_{ent}\phi^{-0.6}$, so that we rewrite Eq 1 as

$$\eta = \eta_i\phi = \eta_s\phi^{-0.6},$$

for entangled solutions.
\[ b_{\text{max}}(\phi) = [\eta(\phi)/\eta_s]l_{\text{ent}}(\phi), \text{ for entangled polymer solutions.} \quad \text{(A.4)} \]

Since \( \eta_s \) can be as low as \( 10^{-3} \) Pa.s (i.e., that of water), entangled solutions could also display significant wall slip. Similar to Eq A.2, the local shear rate in the slip layer upon complete slip is given by

\[ \dot{\gamma}_{\text{dis}} = [\eta(\phi)/\eta_s] \dot{\gamma}, \quad \text{(A.5)} \]

which can be rewritten in terms of the corresponding Weissenberg number \( Wi_{\text{dis}} \) as

\[ Wi_{\text{dis}} = \dot{\gamma}_{\text{dis}} \tau(\phi) = \dot{\gamma} \tau(\phi) [\eta(\phi)/\eta_s] \sim \eta(\phi)/\eta_s = b_{\text{max}}(\phi)/l_{\text{ent}}(\phi), \quad \text{(A.6)} \]

where the last equality follows from Eq A.4, and the product \( \dot{\gamma} \tau \) is on the order of unity. Note that Eq A.6 is of the same form as Eq A.4.

Homogeneous shear should occur upon complete chain disentanglement when the imposed rate is as high as the local shear rate \( \dot{\gamma}_{\text{dis}} \) in the slip layer during maximum wall slip. This critical shear rate is given by Eq A.2 for melts and by Eq A.5 for solutions respectively corresponds to a Weissenberg number \( Wi_{\text{dis}} \) that is related to the maximum slip length \( b_{\text{max}} \) as \( Wi_{\text{dis}} = b_{\text{max}}/l_{\text{ent}} \) as shown in Eq A.3 and and A.6.

### Appendix B  Theoretical developments based on the tube model

The original 1979 tube model\(^{44}\) of Doi and Edwards revealed a non-monotonic constitutive relation in its calculation. They and subsequently others related such a feature to a flow instability (known as the stick-slip transition\(^{22}\)) observed in capillary rheometry.\(^{86,87}\) Subsequently, it was proposed in a 1993 theoretical study\(^{88}\) that shear banding could occur in entangled polymer solutions under simple shear. The experimental report for shear banding, inspired by this theoretical analysis,\(^{88}\) was made in 1996 for worm-like micellar solutions.\(^{89,90}\) Because the worm-like micelles are capable of adjusting their sizes in shear and may even suffer breakage by shear,\(^{99,100}\) shear banding in wormlike micellar solutions\(^91,92,93,94,95,96,97,98,99,100\) was not taken to imply that conventional non-charged, non-associative polymers would also shear inhomogeneously. In the decade between 1996 and 2005, a couple of studies reported a hint of shear banding in semi-dilute polyacrylamide/water solutions where chain-chain associations occur through hydrogen bonding.\(^{101,102}\) Apart from this special case, the important premise of shear homogeneity had never been observed to break down for entangled polymer liquids. In absence of a perfect stress plateau in the steady state flow curve and any direct evidence of shear inhomogeneity, major modifications\(^{103,104}\) including the introduction of convective constraint release,\(^{105}\) were made to make sure that the tube model does not predict a non-monotonic constitutive relation for entangled polymers.
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Homogeneous shear, wall slip and shear banding of entangled polymeric liquids in simple-shear rheometry: a roadmap of nonlinear rheology

Shi-Qing Wang, S. Ravindranath and P. E. Boukany

Particle tracking velocimetry for commercial rotational rheometers in two different schemes A and B
References and notes


Nonlinear rheological responses occur in (a) continuous shear, (b) large amplitude oscillatory shear and (c) large step shear. In (a), one finds the steady-state shear stress is no longer linearly proportional to the shear rate $\dot{\gamma}_{app}$ when $\dot{\gamma}_{app} \tau > 1$, where $\tau$ is the dominant chain relaxation time. In (b), the measured time-dependent shear stress is no longer linearly proportional to the strain amplitude $\gamma_0$ when $\gamma_0$ exceeds a critical value (which is on the order of unity for monodisperse entangled linear polymers) and the oscillatory frequency $\omega$ is higher than $1/\tau$. In (c), the resulting shear stress after a step shear no longer relaxes in a quantitatively different way (from its relaxation behavior after a small step shear) when the amplitude of the step shear is large.


12 Ravindranath, S.; Wang, S. Q. Macromolecules 2007, 40, 8031. This important PTV study of step strain pointed out that only a subset of experimental data happened to agree with the tube model calculation that assumes quiescent relaxation. Actually, Osaki et al. first found the disagreement in 1980 (i.e., Ref. 37) before reporting the far better known agreement in Ref. 38 of 1982. We showed in this paper that the agreement between the stress relaxation data and the tube model prediction was completely fortuitous because the simultaneous PTV observations revealed significant macroscopic motions after shear cessation, and yet the calculation was only valid for quiescent stress relaxation.
Verlag, Berlin. Apparently, the view that wall slip in spurt flow is related to the sample undergoing a "fluid-to-rubber transition" has persisted to this date: Malkin, A. Y.; Semakov, A.V.; Kulichikhin, V.G. Adv. Colloid and Interface Sci. 2010, 157, 75.


42 Osaki, K. Rheol. Acta 1993, 32, 429. Although Osaki speculated about the possibility of wall slip, he was actually inclined toward a different explanation given by Marrucci, G J. Rheol. 1983, 27, 433, which was prompted by the ultra strain softening data of Ref. 52 on step strain of polybutadiene melts that could readily experience massive wall slip.


50 Boukany, P. E.; Wang, S. Q. Soft Matter 2009, 5, 780


Hu, Y. T. et al. J. Rheol. 2007, 51, 275. This rheometric setup is a circular Couette that has a finite shear stress gradient across the sample thickness. Sharp shear banding may not survive in presence of such a stress gradient for the moderately entangled polymer solutions under study.


“In engineering, the transition from elastic behavior to plastic behavior is yield” according to Wikipedia: http://en.wikipedia.org/wiki/Plasticity_%28physics%29. The flow is possible only after the underlying structure has yielded. This yielding concept is not very different from “yield” in the concept of yield-stress that describes mechanical response to external stress of materials such as ketchup and yogurt. In such yield-stress materials, the viscosity is very high, and abruptly drops greatly over a narrow range of shear stress due to some stress-induced structure rearrangements, i.e., the structure that survives at low stresses yields to a new state of flow beyond a particular stress level. Yield-stress materials are usually amorphous and non crystalline (i.e., ordered solids). Evans, I. D. (J. Rheol. 1992, 36, 1313) settled the controversy brought up by Barnes and Walters (Rheol. Acta 1985, 24, 323).


It was concluded that "the origin of shear banding in (relatively polydisperse) polyacrylamide solutions is associated with hydrogen bond breakage above a critical shear rate". Such a conclusion was reached because other polymer (PS and PEO) solutions and poly(dimethyl siloxane) melt were found to display no shear banding: private communication with Paul T. Callaghan. The PS solution examined in Ref. 101 was barely entangled involving $M_w = 600 \text{ kg/mol}$ and concentration of 0.115 g/cm$^3$. PDMS is naturally polydisperse and consequently does not show shear banding, see Li, X.; Wang, S. Q., *Rheol. Acta* 2010, 49, 89. We can indeed find a more recent example where hydrogen bonding seems to play a dominant role. See van der Gucht, J. *et al.* *Phys. Rev. Lett.* 2006, 97, 108301.