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Steady state measurements in stress plateau region of entangled polymer solutions: Controlled-rate and controlled-stress modes

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Synopsis

Despite decades of efforts, reliable measurements of nonlinear flow behavior of well-entangled polymers in continuous shear have been challenging to obtain. The present work attempts to accomplish three important tasks: (A) overcome this challenge by adopting a strategy of decoupling rheological measurements from the outer meniscus region in a cone-partitioned plate (C/PP) setup; (B) determine whether well-entangled solutions indeed undergo a flow transformation under creep that can be taken to phenomenologically define an entanglement-disentanglement transition (EDT); (C) provide the velocity profiles of such solutions undergoing either controlled-stress or controlled-rate shear by carrying out in situ particle-tracking velocimetric (PTV) measurements. Upon removing any influence of edge fracture and sample loss, we are able to reach steady state during continual shear and elucidate more reliably the nonlinear flow behavior of well entangled polymer solutions with little ambiguity. Three well-entangled solutions with $Z = 40$ entanglements per chain exhibited overlapping continuous and monotonic flow curves both in controlled-rate and controlled-stress modes. The C/PP based experiments qualitatively confirm the report by Tapadia and Wang [Macromolecules 37, 9083–9095 (2004)] that at a given applied shear stress the solution evolves over time from a state of high viscosity to that of substantially reduced viscosity, i.e., EDT occurs ubiquitously in absence of any edge effects. These results, made possible by a combination of C/PP and PTV, cause us to reevaluate the objectives of polymer rheology, and are expected to impact the future development in the field of rheometry for entangled polymers and other viscoelastic materials. © 2008 The Society of Rheology. [DOI: 10.1122/1.2936869]

I. INTRODUCTION

Rheological studies of nonlinear flow behavior of entangled polymers require reliable rheometric measurements. Sliding plate (planar Couette) shear cell suffers from the inherent limitation of finite shear strain. Circular Couette setup typically possesses an intrinsic stress gradient apart from the Weissenberg effect of rod climbing that makes characterization of continuous shear behavior infeasible. One of the most convenient and potentially most accurate apparatuses for simple shear is a cone-plate assembly on a rotational rheometer. Unfortunately, because of the well-known edge fracture it has been

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challenging to make a reliable determination of steady-state flow curve in the nonlinear (strongly shear thinning) region for monodisperse entangled polymers, which we refer to below as “stress plateau” region.

In the past, only a handful of measurements of stress vs. imposed rate have been made on well entangled polymer solutions in the nonlinear regime during continuous shear [Huppler et al. (1967); Osaki et al. (1975); Menezes and Graessley (1982); Bercea et al. (1993); Mhetar and Archer (2000); Osaki et al. (2000); Pattamaprom and Larson (2001); Islam et al. (2003); Tapadia and Wang (2004)]. None of these measurements have actually been carried out without the edge fracture complication in cone-plate (C/P) shear cell. In the controlled-rate mode, startup shear measurements of well-entangled samples were often prematurely truncated to avoid severe edge fracture and potential sample loss. It is possible that the shear stress may not have settled to its steady state value in such an aborted experiment.

A recent experimental study [Tapadia and Wang (2004)] revealed that at a constant applied torque in the stress plateau region, the apparent shear rate rose over time sharply in a well entangled polymer solution. This remarkable increase in the rate over time was viewed as a flow transformation, namely, a yield-like entanglement-disentanglement transition (EDT). Although a little bit of edge fracture would affect the quantitative accuracy of the results in creep, it remains unproven whether the EDT phenomenon could be fully accounted for by the occurrence of edge fracture, as claimed by Inn et al. (2005).

In the present work, for the first time we are able to achieve steady state shear in the stress plateau region of well-entangled solutions in both controlled-rate and controlled-stress modes without any influence of edge fracture. Specifically, by adopting a clever design from the literature [Meissner et al. (1989); Schweizer (2002, 2003)], involving a partitioned stationary surface composed of a circular disk and a ring as shown in Figs. 1(a) and 1(b), we have carried out rheological measurements under both controlled-torque and controlled-velocity shear for hundreds of strain units free of edge effects. The cone-partitioned plate (C/PP) shear cell allows us to achieve true controlled-stress measurements, verify their characteristics, attain steady state shear in both modes and determine whether EDT indeed does take place in absence of any edge instability.

II. EXPERIMENTAL SECTION

A. Sample preparation

Experiments have been carried out on four entangled 1,4-polybutadiene (PBD) solutions. The solutions were prepared using two high molecular weight PBD whose molecular characteristics have been listed in Table I. The molecular characteristics at room temperature of the four oligomeric PBDs utilized as solvents are listed in Table II. Table III shows the properties of these solutions at room temperature. The four samples were prepared by first dissolving the desired wt % of high molecular weight PBD in large excess of toluene. To this solution a proper amount of low molecular weight oligomeric PBDs was added and intimately mixed. Silver-coated particles with an average diameter of 10 μm (Dantec Dynamics HGS-10) were first ultrasonicated in toluene and then added to the mixture, for the purpose of particle-tracking velocimetric measurements. The final loading of the particles was at a level of 300–600 ppm. Most of the toluene was evaporated slowly under hood at room temperature over a period of two weeks and the remainder was removed under vacuum condition until the residual toluene was less than 0.5%, at which time the sample no longer gave a toluene smell. Evaporation of PBD oligomers
Negligible. Since $T_g$ of 1,4-PBD is $\sim -100^\circ$C, any residual toluene of this level is not rheologically noticeable and thus of no consequence. Throughout this paper, 1 M(10\%) -15 K sample refers to 10 wt\% of the sample 1 M (listed in Table I) dissolved

<table>
<thead>
<tr>
<th>Sample</th>
<th>$M_n$ (g/mol)</th>
<th>$M_w$ (g/mol)</th>
<th>$M_w/M_n$</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 M</td>
<td>$1.014\times 10^6$</td>
<td>$1.052\times 10^6$</td>
<td>1.03</td>
<td>University of Akron</td>
</tr>
<tr>
<td>0.7 M</td>
<td>$0.74\times 10^6$</td>
<td>$0.75\times 10^6$</td>
<td>1.02</td>
<td>Bridgestone</td>
</tr>
</tbody>
</table>

FIG. 1. (a) Side view of the cone-partitioned plate device coupled with in situ particle-tracking velocimetric setup: (1) shaft connected to ARES motor (2) bottom cone (3) glass cover slip (Fisher Scientific 12-546-2, 25CIR-2) (4) flexible plastic film (5) outer ring (6) trench ($H \times W = 1.5 \text{ mm} \times 1.3 \text{ mm}$) (7) inner circular disk (8) shaft connected to ARES transducer (9) microlens. (b) Top view of the partitioned top plate.
in 90 wt% of 15 K oligomeric PBD (listed in Table II). Similarly, the other three solutions are labeled as 1 M(10%)-5 K, 1 M(10%)-1.5 K and 0.7 M(5%)-4 K.

B. Cone-partitioned plate setup

All experiments were performed at room temperature using a TA Instruments Advanced Rheometric Expansion System (ARES) equipped with a cone-partitioned plate (C/PP) assembly as sketched in Figs. 1(a) and 1(b), as well as with a conventional cone-plate (C/P) apparatus that is for the purpose of comparison with, validation and calibration of C/PP. The bottom rotating cone has a 4° angle and radius of either 20 or 15 mm. On the top, an inner circular disk is linked to the torque transducer of ARES and the meniscus is formed by the bottom cone and an outer ring that is detached to the inner circular disk on the top. The gap between the inner circular disk and the outer ring is around 0.3 mm. The top outer ring is held fixed. For the bottom cone of $R_2 = 20$ mm, the upper stationary surface is made of an inner circular disk of $R_1 = 12.5$ mm and ring of outer radius equal to 20 mm; for the bottom cone of $R_2 = 15$ mm, we use an inner disk of $R_1 = 7.5$ mm and ring of outer radius equal to 15 mm. The smaller set is used to avoid torque overloading at high shear rates. Specifically, all data in Figs. 2–6, 8, 11, 15(a) and 15(b) were based on the larger C/PP set. Moreover, except for rates of 50 in Fig. 10, 40 and 50 in Fig. 12, all the data were also collected with the larger C/PP set. Last, two sets of data were based on the larger C/PP and one on the smaller C/PP in Fig. 7.

Once the sample was loaded, the trench ($H \times W = 1.5 \text{ mm} \times 1.3 \text{ mm}$) on the top is filled with 1 M(10%)-15 K solution to prevent any sample leaking through the 0.3 mm gap. Since there is absolutely no motion between the central disk and the outer ring on the upper stationary surface of the shear cell, the transducer (connected to the central disk) cannot be affected by the filling in the trench. Typically, a flexible plastic film was wrapped around the outer meniscus by gluing the film to the top stationary ring. Hence, the film remains stationary when the bottom cone rotates. Data (to be presented below) demonstrate that the film has no effect on the measurements. It is interesting to note that dielectric spectrometers employ a similar strategy to eliminate the edge effect and to

| Table II. Molecular characteristics of various solvents at room temperature. |
|----------------|----------------|----------------|----------------|----------------|
| Sample        | $M_n$ (g/mol) | $M_w$ (g/mol) | $M_w/M_n$     | Source         | $\eta_s$ (Pa s) |
| PBD-15 K      | 14020         | 15,000        | 1.07          | Bridgestone    | 36             |
| PBD-5 K       | 3800          | 4800          | 1.2           | Bridgestone    | 1.8            |
| PBD-4 K       | ...           | 3900          | ...           | Goodyear       | 1.2            |
| PBD-1.5 K     | 1500          | ...           | ...           | Sigma–Aldrich  | 0.7            |

| Table III. Properties of PBD solutions at room temperature. |
|----------------|----------------|----------------|----------------|
| Solution       | $M_w/M_c$     | $\tau_s$ (s)  | $\tau_R$ (s)  | $\eta_s$ (Pa s) |
| 0.7 M(5%)-4 K  | 13            | 3              | 0.2            | 2459           |
| 1 M(10%)-15 K  | 40            | 71             | 1.8            | $2.5 \times 10^5$ |
| 1 M(10%)-5 K   | 40            | 25             | 0.6            | 95618          |
| 1 M(10%)-1.5 K | 40            | 15.6           | 0.4            | 49985          |
achieve uniform electric fields. Apart from rate-controlled continuous shear measurements, measurements under controlled-stress shear were made possible by using a feedback loop available within the ARES software, where we choose the feed-in viscosity to be of the absolute value of the complex viscosity at frequency equal to 10 rad/s.

C. Particle tracking velocimetry setup (PTV)

The silver coated particles embedded in the samples are illuminated by passing a laser sheet with a cross section of 0.2 mm × 2 mm across the gap. The laser sheet was passed at an angle of ~45° through a glass window of 3 mm radius on the top stationary plate as shown in Fig. 1(a). To eliminate reflections from the bottom cone, its surface was coated with a thin layer of black enamel (Rustoleum Corporation, specialty high heat black enamel). Movements of the illuminated particles across the entire sample thickness were captured with a black-white charge coupled device (CCD) camera (with a maximum speed of 30 frames/s) and recorded on videotape. The CCD camera is mounted with a DIN objective lens (3.2 ×) through an adaptive tube (Edmund Optics: U54-868). During imaging analysis, the distance traveled by a particle is determined by playing 1–3 frames using MGI Videowave 4 software. The PTV observation point was around 10 mm from the center. The performance of PTV is evaluated by comparison between the prescribed homogeneous shear field due to the rotating cone and that determined from PTV for a Newtonian fluid. The current PTV scheme, i.e., observing at ~45° from the stationary plate, has an inherent error of ~15% in its reading of the sample gap, resulting in a similar level of error in the determination of velocity profiles.

D. Validation of cone-partitioned plate (C/PP) setup

In this section, we take several steps to evaluate the performance of the C/PP setup and contrast results with those obtained with conventional C/P.

First, we use two materials that do not suffer edge fracture to show that the C/PP works as well as the conventional C/P. Figure 2 illustrates the shear stress growth of a monodisperse 1,4-polybutadiene melt of molecular weight equal to 44 kg/mol. Comparison is made possible because the sample does not suffer edge fracture at these shear rates of 1 and 10 s⁻¹. Similarly, a moderately entangled polymer solution such as 0.7 M-4 K having roughly Z=13 entanglements per chain suffer negligible edge fracture although it exhibits a considerable level of nonlinear viscoelasticity. Figure 3 shows the stress growth upon startup shear at two respective apparent shear rates of 1.0 and 5.0 s⁻¹ in the stress plateau region, where linear velocity profiles were obtained from PTV observations in the C/PP as shown in the inset. Both C/P and C/PP measurements were performed on the same ARES rotational rheometer involving a cone, plate, and inner plate of diameter equal to 25 mm. The overlapping of data from the C/P fixture with those from the C/PP device serves to calibrate between the C/P and C/PP measurements and thus validates rheological measurements obtained with the C/PP device.

The C/PP setup clearly shows its superiority over the conventional C/P fixture, when edge fracture has an accumulating effect as in the case of a strongly entangled solution. This is illustrated in Fig. 4, where the decline of the shear stress in C/P arises from the decreasing contact between the sample and the fixture due to edge fracture. In other words, the continuous “erosion” of the sample at the meniscus caused the measured torque to decrease monotonically in a conventional C/P, whereas the C/PP setup has successfully overcome this inherent difficulty. Edge fracture can make creep measurements even less reliable in the shear thinning region where the apparent rate changes sharply with shear stress. Figure 5 demonstrates the ability of the C/PP setup to avoid a
runaway phenomenon pointed out by Inn et al. (2005). In other words, in the absence of this C/PP improvement, a sample with strong edge fracture cannot be quantitatively reliably characterized by a creep experiment in the stress plateau region.

FIG. 2. Comparison of shear stress growth upon startup shear at two discrete shear rates between cone-plate setup (open symbols) and the cone-partitioned plate device (closed symbols).

FIG. 3. Comparison of shear stress growth upon startup shear at two discrete shear rates between C/P setup (open symbols) and C/PP device (closed symbols). Inset: Particle-tracking velocimetric (PTV) measurements of the velocity profiles at different times corresponding to the two startup shear experiments.
The performance of C/PP is further evaluated by comparing data obtained with a film wrapped around the meniscus as indicated in Fig. 1 with those absent of such a film. Figure 6 shows no difference whether the film is present or not. In Figs. 4 and 5 and all subsequent figures obtained with C/PP, a film is used to allow multiple tests within a sample loading. Moreover, we have carried out three identical experiments in three discrete sample loadings. Figure 7 shows that the rheological responses are highly reproducible with this C/PP setup.

**FIG. 4.** Comparison at two discrete applied shear rates between conventional cone-plate measurements and those made with the C/PP device of Fig. 1.

**FIG. 5.** Comparison of creep tests at the same applied shear stress of 1800 Pa between C/P and C/PP of Fig. 1.
Finally, we are interested to find out whether the sample in the C/PP setup is still intact after shearing for a high number of strain units. Figure 8 examines this question by performing oscillatory shear measurements before and after the steady shear experiment involving a shear rate of 10 s$^{-1}$. Clearly, sound measurements can be made even after

**FIG. 6.** Comparison of shear stress growth upon startup shear at a shear rate of 1.0 s$^{-1}$ between C/P and C/PP device of Fig. 1 where a containing film was either installed or uninstalled.

**FIG. 7.** Comparison of shear stress growth upon startup shear at a shear rate of 1.0 s$^{-1}$ between three discrete sample loadings.
hundreds of strain units, free of either edge instability around the meniscus that is film wrapped or at the gap between the disk and ring that is filled up by excess sample.

III. RESULTS AND DISCUSSION

According to the recent PTV observations of entangled polymer solutions [Tapadia and Wang (2006); Boukany and Wang (2007); Ravindranath et al. (2008)], application of a constant does not guarantee that a homogeneous shear field would develop across the sample thickness. Rheometric measurements lose their conventional meaning. Throughout this paper “controlled-rate” measurements only mean that the angular velocity is fixed such that the apparent or averaged shear rate is related to angular velocity as \( \dot{\gamma}_{\text{app}} = \frac{\Omega}{\theta} \) for a cone angle of \( \theta \). Because of the C/PP setup, controlled-stress measurements refer to experiments carried out at a fixed torque as determined by the upper central disk.

A. Achieving steady state in stress plateau: Controlled-rate mode

In rotational rheometry, the routinely applied protocol to probe the shear thinning behavior in monodisperse entangled polymer solutions is to terminate a startup shear before edge instability and resulting sample loss become visible. Could such an abolishment be premature, i.e., could steady state be reached at such an arbitrary truncation?

Before confronting the intrinsic experimental difficulty in performing measurements in continuous shear in the nonlinear regime, we present in Fig. 9 linear viscoelastic properties of three similar entangled solutions to indicate regions of terminal flow and stress plateau. These solutions have the same number \( Z \) of entanglements per chain \( (Z=40) \) in the different solvents made of low molecular weight 1,4-polybutadienes. We will show subsequently that the solvent can play a crucial role in dictating the flow response of these solutions.

FIG. 8. Oscillatory shear measurements of \( G' \) and \( G'' \) at frequency \( \omega=10 \text{ rad/s} \) before and 20 s after a startup shear to steady state at shear rate 10.0 s\(^{-1}\).
Out of the three solutions, 1 M(10\%)–1.5 K is similar to that studied by Tapadia and Wang (2004). Therefore, we focus on presenting detailed results on this sample. Based on this solution, we will show that all previous controlled-rate measurements are quantitatively inaccurate in the stress plateau (nonlinear) region.

Figure 10 presents shear stress growth upon startup shear at four discrete shear rates beyond the terminal flow region based on the C/PP device of Fig. 1, along with one sheared in the terminal region for reference.
rates in the stress plateau region as well as a shear rate of 0.04 s\(^{-1}\) in the terminal region. Remarkably, the sample takes so many strain units to settle down to a steady state defined by the unchanging value of the shear stress. Stress undershoot is also noticeable in Fig. 10 beyond the overshoot at higher rates.

B. True controlled-stress shear: Confirmation of EDT

A second motivation to adopt the C/PP design stems from the speculation that the remarkable rise of apparent shear rate at a given applied torque in a conventional C/P setup observed by Tapadia and Wang\(^{2004}\) can be “fully ‘account’ed for by the occurrence of edge fracture”\(^{2005}\). In the preceding subsection II D, we have shown how the effect of edge fracture can be removed by using a C/PP setup. We proceed here to use C/PP to achieve true controlled-stress measurements by maintaining a constant torque measured through the inner disk.

Figure 11 shows the characteristic rise in the apparent shear rate at several discretely applied stresses. At the highest applied stress of 2400 Pa, the apparent rate jump over time is by nearly two orders of magnitude. The fact that the apparent shear rate eventually becomes flat with respect to time indicates that the steady state has been achieved. Note that the time is presented on a logarithmic scale that compresses the long times, and the flatness is much more impressive on a linear scale. This remarkable rise in the apparent shear rate is demonstrated experimentally here in absence of any edge effect and can be taken as evidence for an entanglement-disentanglement transition (EDT): The system is clearly seen to have made a transformation from a state of high viscosity to that of a considerably lower viscosity.

The phenomenological essence of the EDT was first visualized by Tapadia and Wang\(^{2004}\) that at a given applied stress a well entangled solution first exhibited terminal flow with a low shear rate before eventually flowing at a much higher apparent shear rate. It is this dual-state (two “plateaus”) character that elucidates the meaning of EDT as originally
stated in Tapadia and Wang (2004) on p. 9086: “As far as we are aware, yieldlike flow transition observed in Figs. 6–6 has never been reported for entangled polymer solutions or melts except in our recent communication. Upon this transition, the sample exhibits a steady-shear viscosity as low as 20 Pa s at $\sigma = 3.0$ kPa in comparison to its value of 25 000 Pa s before the transition. Since the high zero-shear viscosity is universally regarded as due to chain entanglement, the reduction of 3 decades in the shear viscosity could be due to a massive loss of chain entanglement. Thus, we term this yieldlike constitutive transition an entanglement-disentanglement transition (EDT).”

Clearly, the creep mode provides a more vivid way of revealing the shear thinning character in such entangled systems.

The EDT character, i.e., a temporal rise of apparent shear rate from the initial state of full entanglement at a fixed applied shear stress, is a necessary phenomenological consequence related to the existence of a stress plateau region as shown in Fig. 12, which shows a steady-state flow curve acquired from controlled-rate measurements as well as a curve from controlled-stress measurements in steady state. The flow curves appear continuous, monotonic, and overlapped, exhibiting a sizable slope of 0.08. The transient data given in the open squares are also rather revealing. The overlapping of open squares onto the open circles indicates that the transient states in both modes of shear are equivalent, where the open circles are taken at the stress overshoot point from data such as those in Fig. 10 and open squares from the initial states of full entanglement such as those initial rate values in Fig. 11. The absolute complex modulus $|G^*|$ vs. the oscillation frequency curve provides a contrast to reveal the severe breakdown of the Cox–Merz rule.
C. What do flow curves say about constitutive relationship?

Traditionally, one way to peek into a constitutive relationship of an unknown viscoelastic material is to obtain steady-state flow curves. From Fig. 12, one could automatically infer, since it is monotonic with an appreciable slope of 0.08, that homogeneous shear would prevail in each of these discrete measurements in the stress plateau region. Based on the feature of dual-states observed in creep in Fig. 11, Tapadia and Wang (2004) were led to suggest that the universally held premise of shear homogeneity in polymer flow be verified. Prior to Tapadia and Wang (2004), such monotonic flow curves of entangled polymer solutions had only affirmed the consensus [Graham et al. (2003)] that shear banding would not exist even in the stress plateau region for entangled polymers.

Recent studies have only indicated that shear banding can take place transiently [Tapadia and Wang (2006); Boukany and Wang (2007)] where achieving steady state had been an assumption rather than fact. Now that steady state is truly possible to reach using the C/PP, we have incorporated a PTV setup to determine whether shear banding is permanent, i.e., whether it prevails in steady state. Figure 13 shows the velocity profiles at different times during a startup shear of an apparent rate of 1 s\(^{-1}\). Note that the initial flow field was actually uniform up to the stress overshoot at t = 2.0 s. Recoil like motion occurred near the lower sample/cone interface as shown by the squares. Eventually, the solution settled to highly inhomogeneous shearing where much of the bulk experienced an immeasurably low shear rate and there is an immeasurably thin layer of high shear near the moving bottom surface.

However, interfacial slip, i.e., disentanglement of one monolayer at the interface, is insufficient to produce such a velocity profile. To appreciate this point, we need to estimate the slip length \(b\) of this solution. We can evaluate the upper bound of \(b\) according to \(b_{\text{max}} = (\eta_s/\eta_l)\ell_{\text{ent}}\) where the entanglement spacing \(\ell_{\text{ent}} \approx 20\) nm, \(\eta_l\) can be read to be \(\approx 25\) kPa s from Fig. 12 as |\(G^*/\omega\)| at |\(G^*\)| = 2000 Pa and \(\eta_s\) is taken as the solvent viscosity of 0.7 Pa s from Table II. These numbers produce \(b_{\text{max}} \approx 0.7\) mm. This level of wall slip can only accommodate the imposed rate up to \(V/H = \dot{\gamma}_c(1+2b_{\text{max}}/H) \approx 0.1\) s\(^{-1} \ll 1\) s\(^{-1}\) where \(\dot{\gamma}_c\) indicated in Fig. 12 is around 1/\(\tau = 0.06\) s\(^{-1}\) and \(H\) is taken to be around 1 mm. Thus, at this apparent shear rate of 1 s\(^{-1}\), for the bulk of the sample to undergo shear at a level of \(\dot{\gamma}_c\), chain disentanglement must occur in the sample interior as well. In other words, the rapidly sheared layer must have a thickness much greater than that of a monolayer although our PTV technique does not have adequate spatial resolution to determine its thickness. Figure 13(b) summarizes steady state PTV measurements at several applied shear rates. Clearly, the steady state profiles are nonlinear at these rates in the stress plateau region. Consequently, there is no guarantee that a monotonic steady flow curve would be synonymous to shear homogeneity, contrary to the conclusion of Hu et al. (2007).

With the C/PP setup, it becomes possible for the first time to carry out PTV observations under the condition of true creep. Figure 14(a) shows velocity profiles during the rise of the apparent shear rate at 2000 Pa. The velocity profiles are again reminiscent of an interfacial stick-slip transition although the final apparent shear rate of 0.4 s\(^{-1}\) indicates that the apparent slip would actually involve more than one monolayer. At an applied shear stress of 2400 Pa, the velocity profiles are also suggestive of apparent slip as shown in Fig. 14(b). Since all three profiles correspond to an apparent shear rate much higher than 0.1 s\(^{-1}\), there is plenty of chain disentanglement in the bulk to produce the apparent slip visible on both surfaces.

It is clearer to see from Fig. 14(b) that the sample has undergone inhomogeneous shear inside the gap as the apparent rate grew from 0.2 to over 20 s\(^{-1}\), i.e., over two decades.
Due to the limitation of our current PTV method, we cannot monitor the flow field at times much longer than 350 s as the apparent rate further built. However, it is evident that the phenomenologically defined EDT does not appear to involve a uniform acceleration of the motion due to chain disentanglement. In other words, shear banding is also present, even in creep mode. Thus, although the flow curves of this sample seem continuous and monotonic according to Fig. 12, the points on the curves do not involve uniform shear rates and therefore do not represent a constitutive curve in the conventional sense.

**FIG. 13.** (a) Particle-tracking velocimetric observations of startup shear at an apparent shear rate of 1.0 s$^{-1}$ at initial, intermediate and long times. (b) Particle-tracking velocimetric determination of the normalized velocity profiles at four discrete shear rates upon startup shear, revealing inhomogeneous shear in steady state.
The current C/PP device allows us to make a detailed comparison with the previous study of Tapadia and Wang (2004). The following remarks can be made:

(a) The characteristic rise over time of apparent shear rate at a fixed shear stress indeed takes place in absence of any edge effect. As long as there is a stress plateau region as amply demonstrated in previous studies involving rate-controlled experiments, the rate rise observed and asserted by Tapadia and Wang (2004) to reflect an

**FIG. 14.** (a)–(b) Particle-tracking velocimetric (PTV) determination of the velocity profiles at different stages during creep at stress of 2000 Pa and stress of 2400 Pa respectively corresponding to the time-dependent rises of the apparent shear rate in Fig. 11, where the open symbols represent the rheometric values of velocity, not PTV measurements.
entanglement-disentanglement transition (EDT) will inevitably take place. On the other hand, it is true that any edge fracture and resulting sample loss would significantly affect the accuracy of such a creep measurement as pointed out by Inn et al. (2005) and Sui and McKenna (2007).

(b) The present study reveals a continuous flow curve even in the controlled-stress mode, whereas Tapadia and Wang (2004) had a self-conflicting description about the nature of the EDT. The transition was said both to be second order and to produce a discontinuous steady-state flow curve. The alleged discontinuity could only be understood in the sense that the system would access two different values of apparent shear rate during creep at a fixed value of shear stress. Our PTV observations reveal that different local shear rates coexist at the same shear stress. This multiplicity can be taken to imply flow discontinuity.

c) The two flow curves obtained in controlled-rate and controlled-stress modes essentially overlap in sharp contrast to the results of Tapadia and Wang (2004). The mismatch between the flow curves in Tapadia and Wang (2004) was most likely due to the premature truncation of the startup shear (controlled-rate) experiment, a procedure all previous experiments adopted as a protocol to conduct “steady state” measurements in simple shear.

d) Tapadia and Wang (2004) speculated upon observing EDT that controlled-rate shear may not always involve homogeneous flow across the sample thickness. Indeed, the present PTV observations have provided direct evidence in support of their anticipation. Moreover, the EDT only reflects the rise of the apparent shear rate, and only the PTV observations allow us to determine whether or not the EDT process occurs in a spatially homogeneous manner.

E. Another example of shear banding: 1 M(10%)-5 K solution

In the preceding 1 M(10%)-1.5 K solution inhomogeneous shear occurs in the appearance of apparent slip. Appreciable bulk shear banding is only observed at higher rates as shown Fig. 13(b). By choosing an oBD of \(M_w=5\ \text{kg/mol}\), the slip length \(b\) can be significantly reduced as demonstrated recently [Ravindranath and Wang (2007)]. As a consequence, shear banding can be more readily seen in the sample interior. Before reporting on the PTV observations, we first apply C/PP to obtain steady state measurements of the shear stress from the startup experiments. Figure 15(a) confirms Fig. 9 that it takes several hundred strain units to reach the steady state. Taking the steady values from such startup continuous shear measurements, we can plot a flow curve as shown in Fig. 15(b).

Our PTV observations reveal that the velocity profiles are sharply nonlinear even in steady state as shown in Figs. 16(a) and 16(b). The local shear rates in the fast sheared layers can be higher than those in the slowly sheared bulk by a factor of over 10. Currently, it remains elusive why shear inhomogeneity could remain stable over time although a tentative explanation has been offered elsewhere [Ravindranath et al. (2008)].

F. A case of homogeneous shear: 1 M(10%)-15 K solution

Further increasing the molecular weight of PBD solvent to 15 kg/mol, we completely suppress interfacial wall slip in the 1 M(10%)-15 K solution. Rheologically speaking, startup shear in both rate and stress modes produces similar responses as observed in the other two solutions. Figures 17(a) and 17(b) show, respectively, the shear stress growth during startup shear and characteristic rise of the apparent shear rate in creep, where the
initial data points of high rate reflect the elastic response of the sample to a suddenly applied stress. Remarkably, our C/PP allows so many hundreds of strain units to elapse without any difficulty before reaching steady state, as shown in Fig. 17. These steady-state measurements in both modes allow two flow curves to be presented in Fig. 18. This figure confirms the salient features of Fig. 12, including a finite slope of 0.12, overlapping of the two curves, overlapping of the open circles and squares and significant departure from the Cox–Merx rule.

FIG. 15. (a) Shear stress growth upon startup shear at four discrete shear rates beyond the terminal flow region based on the C/PP device of Fig. 1, along with one near the end of the terminal region, all plotted against the elapsed shear strain. (b) Steady-state flow curves obtained with controlled-rate mode using the C/PP of Fig. 1, along with the oscillatory shear data of $|G^*|$ versus the oscillation frequency $\omega$. 
However, contrary to the responses of the two preceding solutions of the same level of chain entanglement, the PTV observations reveal linear velocity profiles at all times in both startup rate-controlled and creep modes. Specifically, Fig. 19(a) indicates that the velocity profile is basically linear both right after the shear stress overshoot and after hundreds of strain units for three discretely applied rates. Equally impressive are the profiles measured with PTV in creep at two preset shear stresses of 2000 and 2600 Pa as shown in Figs. 19(b) and 19(c). The profiles are essentially linear both at an intermediate

FIG. 16. (a)–(b) Particle-tracking velocimetric (PTV) determination of the velocity profiles at six discrete shear rates during startup shear, revealing inhomogeneous shear in steady state, where the open symbols represent the rheometric values of velocity not PTV measurements.
stage and in steady state as the apparent shear rate gradually rises over time as shown in the inset. Thus, unlike the EDT observed in the preceding two samples, the EDT in 1 M(10\%) -15 K actually occurs due to a uniform acceleration resulting from homogeneous chain disentanglement throughout the sample. The meaning of dual states is more precise here: The sample first took a state of homogeneous shear at a low rate and evolved to a second state of homogeneous shear at a rate two orders of magnitude higher.

To understand why this sample is capable of undergoing homogeneous shear upon startup shear, we must ask why the other samples with the same number of entanglements per chain (Z=40) suffer shear banding. When sheared at a high Weissenberg number in a startup experiment, a well-entangled solution initially undergoes elastic deformation like a solid until the point of yield [Wang et al. (2007)], i.e., the point of cohesive failure at the stress maximum. This cohesive breakdown inevitably takes place through chain disentanglement, which is a molecular event that eventually nucleates to produce at least one macroscopic fault plane where the entanglement network locally breaks down. For
1 M(10\%) \text{-} 1.5 K solution, any initial failure produced by one monolayer of chain disentanglement yields a sufficient correction to the boundary-imposed shear field, allowing the rest of the sample to recoil and avoid high shear, because the slip length $b$ is as large as $\sim 1$ mm. In other words, upon a strong transient shear band, much of the sample would no longer be subjected to the imposed average rate and can flow at a much lower rate as long as the fault layer or the high-shear band remains, thus avoiding sequential failure. Because of the high MW solvent, the ability of 1 M(10\%) \text{-} 15 K to undergo interfacial wall slip is reduced by a factor that can estimated by the solvent viscosity ratio equal to $36/0.7 \sim 51$ (cf. Table II). A monolayer of chain disentanglement would produce little correction to the imposed initially homogeneous shear field. As a consequence, every other molecular layer continues to undergo the same rate of deformation that causes the first monolayer to disentangle. In other words, this sample is capable of enjoying uniform chain disentanglement everywhere across the sample thickness. This essentially ensures that the shear field remains homogeneous.

**IV. SUMMARY**

Three entangled polybutadiene solutions have been studied by employing a critically improved rheometric setup and particle-tracking velocimetry (PTV). We have successfully overcome an inherent limitation in traditional rheometric measurements that has previously made it impossible to elucidate without ambiguity the nonlinear flow behavior of well-entangled polymer solutions in continuous shear. The cone-partitioned plate setup allows us to achieve steady state in both controlled-rate and controlled-stress modes in...
the stress plateau (shear thinning) region. These new rheological measurements reveal overlapped (steady state) flow curves from both controlled-rate and controlled-stress shearing in all the three well-entangled solutions.

The modestly entangled 0.7 M(5%)–4 K solution exhibits homogeneous shear at all applied shear rates in transient and steady states. Both controlled-rate and controlled-stress modes appear to produce inhomogeneous shear during transient and steady shear in 1 M(10%)–1.5 K and 1 M(10%)–5 K solutions. The emergence of inhomogeneous shear signals uneven structural breakdown of the entanglement network upon fast external deformation. In other words, for these solutions, the forced structural rearrangement, e.g., chain disentanglement, cannot take place in a spatially homogeneous manner upon startup shear. The localized failure of the entanglement network produces the observed shear inhomogeneity. The characteristics of a “continuous” and “monotonic” flow curve no longer reflect anything constitutive: A continuous monotonic flow curve does not guarantee or imply a priori that inhomogeneous shear would not take place. A comparison

**FIG. 19.** (a) Particle-tracking velocimetric (PTV) determination of the velocity profiles at three discrete shear rates upon startup shear, revealing approximately homogeneous shear both transiently and in steady state. (b)–(c) Particle-tracking velocimetric determination of the velocity profiles during creep at constant shear stress of 2000 and 2600 Pa, respectively, based on C/PP of Fig. 1, where the inset shows the gradual rise (EDT) of the apparent shear rate as a function of time, and the open symbols represent the rheometric values of velocity, not PTV measurements.
between 1 M(10%)-15 K and 1 M(10%)-1.5 K solutions shows a striking difference in the velocity profiles although both have the same level of chain entanglement. The high molecular-weight solvent of PBD-15 K greatly slowed down the kinetics of chain disentanglement allowing the system to respond to the suddenly imposed shear in a uniform and homogenous manner.

Apart from completing the tasks to improve upon the conventional rotational rheometric protocol (cone plate), to describe steady-state behavior of continuous shear in the nonlinear regime, and to test the basic premise of rheometry (homogeneous shear) in both controlled-rate and controlled-stress modes, the present study also attempted to resolve the discrepancy in literature surrounding a previous rheological study [Tapadia and Wang (2004); Inn et al. (2005)]. In absence of any discernible edge effects, we still observed a characteristic rise in the apparent shear rate over time at a given applied true shear stress, dispelling any doubt that a flow transformation (i.e., an entanglement-disentanglement transition-EDT) occurs leading to a state of considerably lower viscosity or state of diminished chain entanglement. Several features are consistent with the concept of an EDT: (a) at a given average rate the sample can break up into different states of chain entanglement where layers of different local shear rates coexist; (b) at a given shear stress the average shear rate rises considerably as the initial state of full entanglement transforms into either a homogenous or an inhomogeneous distribution of less entangled states; (c) the apparent shear rate increases sharply over a very narrow range of the shear stress. Strikingly, the disentanglement process can take place in a spatially inhomogeneous manner in both modes of shear, suggesting that well-entangled polymers tend to respond to fast deformation by yielding as if they were solids. It is beyond the scope of this work to elucidate why an entanglement network would break down upon deformation, how chain disentanglement takes place and what the yield criterion is. A theoretical discussion of these issues has been presented in some detail elsewhere [Wang et al. (2007)].

In conclusion, the ability to obtain reliable steady-state rheological measurements as well as the corresponding velocity profiles during continuous shear in the nonlinear (shear thinning) regime offers us the first peek into how rheometric measurements may or may not represent. Clearly, it appears imperative that in situ PTV observations be always carried out along with the conventional rheometric experiments on nonlinear flow behavior of well-entangled polymers. The traditional meaning and usefulness of a flow curve is clearly in question when many data points on the curve involve inhomogeneous shear. Conversely, monotonicity of such a curve does not ensure that there is shear homogeneity in steady state. At a deeper level, one must consider how to realign the objectives in polymer rheology since the conventional approach to acquire a constitutive relationship may not yield straightforward results.

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**APPENDIX: ESTIMATING VISCOSOUS HEATING DURING SHEAR**

For an order of magnitude estimate, we consider the following equation governing the heat transfer:
\[ \sigma \dot{\gamma}(t) = \rho c_p \frac{dT}{dt} + 4\kappa(T - T_{pl})/H^2, \quad (A1) \]

where \( \rho \) is the mass density of the solution, \( c_p \) is the specific heat of the polymer, \( \kappa \) is the thermal conductivity coefficient for the polymer, \( T \) is the average sample temperature, \( T_{pl} \) the plate temperature, and \( H \) is the traveling distance of thermal conduction, on the order of the sample thickness. In thermal equilibrium when the first term on the right-hand side of Eq. (A1) is zero, we can estimate the final sample temperature \( T_s \). Taking one of the worse cases in Fig. 23 where \( \sigma \sim 5 \text{kPa} \) and \( \dot{\gamma} \sim 11 \text{s}^{-1} \), we have \( T_s - T_{pl} \sim \sigma \dot{\gamma} H^2/4\kappa = 0.14 \text{°C} \), taking \( \kappa = 0.1 \text{W/m°C} \) [Incropera and DeWitt (1996)] and \( H = 1 \text{mm} \). This estimate shows that any viscous heating is insufficient to cause a measurable drop in shear viscosity at room temperature and produce the transient visible decrease of the measured shear stress before complete leveling off.

References

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Sui, C., and G. B. McKenna, “Instability of entangled polymers in cone and plate rheometry,” Rheol. Acta 46, 877 (2007). This paper made a rather thorough survey of the current knowledge of edge fracture that we will omit here. This paper pointed out “If an EDT transition proceeds, the edge distortion and mass loss cannot be ascertained by the present work.” In other words, it could not be ruled out that a genuine EDT would occur in well-entangled polymers when sheared at a constant stress comparable to the elastic plateau modulus.


