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# A correlation between velocity profile and molecular weight distribution in sheared entangled polymer solutions

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## Synopsis

In this work we attempt to answer several questions concerning the flow characteristics of entangled polymer solutions in a sliding plate shearing cell. We explore (a) how the molecular weight distribution affects the velocity profile in simple shear, (b) whether the observed shear banding is consistent with a nonmonotonic constitutive model, (c) whether the flow response and velocity profiles are different in simple shear depending on the different modes of shear. Our results provide a comparison with recent reports on a polydisperse polymer sample [Tapadia and Wang, *Phys. Rev. Lett.* **96**, 016001 (2006); Tapadia, *et al.*, *Phys. Rev. Lett.* **96**, 196001 (2006)] that revealed the first evidence for inhomogeneous shear during startup in cone-plate flow geometry of a rotational rheometer. Using a highly monodisperse sample, we observed the sample to partition into two fractions with different local shear rates instead of possessing a smooth spatial variation of the local shear rate as seen for the polydisperse samples. In the stress plateau, the shear banding appears to involve various local shear rates instead of just two values. © 2007 The Society of Rheology. [DOI: 10.1122/1.2424947]

## I. INTRODUCTION

Nonlinear viscoelastic flow behavior of entangled polymers has been studied for several decades. By treating them as liquids that could deform homogeneously in simple shear, the task of probing their constitutive properties has been thought to be relatively straightforward as demonstrated by both experimental [Stratton (1966); Hupler *et al.* (1967); Lee *et al.* (1970); Graessley (1974); Crawley and Graessley (1977); Ferry (1980); Wagner and Meisner (1980); Mendez and Graessley (1982); Bercea *et al.* (1993); Patamaprom and Larson (2001)] and theoretical [Doi and Edwards (1979); Graessley (1982); McLeish and Ball (1986); Cates *et al.* (1993); Marrucci (1996); Mead *et al.* (1998); Likhtman (2000); Milner *et al.* (2001); Marrucci and Ianniruberto (2003); Graham *et al.* (2003)] activities. Specifically, the experiments have proceeded by assuming that a simple shear field with a constant shear rate ( $V/H$ ) would prevail in rheometric instruments where a sample of thickness  $H$  was sheared between two parallel surfaces by moving one surface at a fixed velocity  $V$  while holding the other stationary. The standard theoretical approach has extended the basic notation of tube confinement to describe quiescent reptative chain dynamics [Edwards (1967); de Gennes (1971)] to describe

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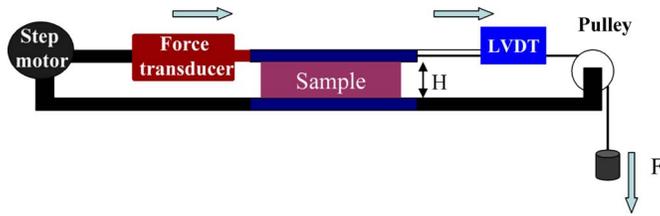
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deformation of the primitive chain and resulting stress in simple shear. The earlier versions of the tube model (up to 1993, Cates *et al.*) actually encountered a shear stress maximum that would imply a nonmonotonic constitutive curve for entangled polymers. However, because the implied shear banding instability was not observed experimentally, the consensus of the community over the past ten years has been that the stress maximum was a theoretical artifact.

Another difficulty facing us has arisen from the so-called type C behavior observed in a large step-strain/stress-relaxation experiment [Osaki (1993); Osaki and Kurata (1980); Vrentas and Graessley (1982)], typically found to involve highly entangled liquids. The excessive strain softening associated with the relaxation behavior is at odds with the initial theoretical prediction [Doi (1980)] as well as the subsequent calculations based on a slip-link model [Doi and Takimoto (2003)]. A large body of literature has been devoted to an attempt to reconcile the obvious difference between experiment and theory. The original unphysical feature in the Doi-Edwards tube model of a stress maximum for steady shear flow of entangled polymers [Doi and Edwards (1979)] led subsequent workers [Marrucci and Grizzuti (1983); Larson *et al.* (1988); Morrison and Larson (1992)] to speculate that the step shear deformation would occur inhomogeneously leading to the observed much lower relaxation modulus than that measured in the linear response regime. In other words, the Doi-Edwards theory has often been viewed as having the required ingredients to explain the stress relaxation behavior at large step strains. The stress maximum character of the Doi-Edwards model has also been thought to be [McLeish and Ball (1986)] the origin of the spurt phenomenon in capillary flow [that has subsequently been shown to be interfacial in nature (Yang *et al.*, 1998)] and to produce shear banding in steady simple shear flow [Cates *et al.* (1993)].

In the past investigations on step strain behavior of polymers, a plane-Couette sliding-plate shear cell have been constructed and employed [Demarquette and Dealy (1992); Archer and Larson (1995); Koran and Dealy (1999a)]. By placing a video camera facing the *X-Z* plane (i.e., flow-vorticity plane), Archer and Larson (1995) applied a particle-tracking technique and detected apparent slip within microns from the shearing surfaces for an entangled polystyrene solution after completion of an imposed strain. Since such a setup did not allow simultaneous determination of all particle motions along the velocity gradient direction *y*, they could only conclude that delayed slip occurred at the sample/wall interface after large step strain. For a sample with large meniscus, both groups [Archer *et al.* (1995); Reimers and Dealy (1996)] concluded that there was secondary flow as also evidenced [Mhetar and Archer (1996)] by the uneven flow birefringence. Because of these complications and lack of a reliable determination of the time-dependent velocity profile across the sample thickness, this type of experimental protocol has ceased to attract attention. Actually more than a dozen papers including [Islam and Archer (2001); Islam *et al.* (2003)] have since been published on nonlinear viscoelastic behavior of polymer solutions and melts, only Islam *et al.* (2001) cited their earlier work [Archer *et al.* (1995); Mhetar and Archer (1996)] by raising the concern that "...it might be seen that the nonlinear rheology of well entangled polymer liquids is hopelessly complicated...". The situation concerning the step strain experiment has indeed remained elusive despite recent progress [Venerus (2005)] until our first disclosure of non-quiescent relaxation behavior in step strain experiment Wang *et al.* (2006).

More recent studies from Wang's laboratory [Tapadia and Wang (2004); Philips and Wang (2004); Tapadia and Wang (2006); Tapadia *et al.* (2006); Wang *et al.* (2006)] suggest that the physical picture behind shear flow of entangled polymers may be different from that portrayed in the literature. [In passing, we should note that the words "discontinuous" and "discontinuity" were inappropriately used and are self-contradicting



**FIG. 1.** A schematic depiction of our sliding-plate rheometer that can be operated in both controlled displacement and controlled force modes.

in Tapadia and Wang (2004) because the yield-like entanglement-disentanglement transition was also shown there to be free of hysteresis, i.e., only a smooth second order transition was observed instead of a discontinuous one. Subsequently, these authors tested the assertion of Tapadia and Wang (2004) that shear banding may occur in the stress plateau by applying a particle tracking velocimetric method (PTV) to determine the actual velocity profile experienced by entangled polymer solutions.] Contrary to the basic premise of experimental polymer rheology, the shearing mode of controlled rate produced nonlinear velocity profiles in the entangled polybutadiene solutions in either startup continuous shear [Tapadia and Wang (2006)] or large-amplitude oscillatory shear [Tapadia *et al.* (2006)], and macroscopic motion after step strain [Wang *et al.* (2006)].

Several key questions remain to be addressed: 1. Is the observed nonlinear velocity profile consistent with existence of a nonmonotonic flow curve? 2. Why did the velocity gradient vary smoothly across the gap in continuous shear in Tapadia and Wang (2006)? 3. Is there a non-negligible stress gradient in a cone-plate shear cell? 4. What velocity profile will result in controlled stress mode? The present work focuses on answering these questions.

To answer the first and second questions, we apply a PTV method to determine how the nonlinear velocity profile of a monodisperse sample changes with the imposed plate velocity. We suspect that the smooth variation of the velocity gradient in the previous work of Tapadia and Wang (2006) arises from polydispersity in the molecular weight distribution of the entangled solution. Thus, the present work will compare the velocity profiles among samples ranging from highly monodisperse to highly polydisperse polymer solutions. To address the third and fourth questions, we have built a sliding-plate rheometer using parallel plates that can be operated in either controlled speed or constant force mode as depicted in Fig. 1.

## II. EXPERIMENT

### A. Materials

Three well entangled 10% 1,4-polybutadiene (PBD) solutions were prepared by dissolving high molecular weight PBD of three different molecular weight distributions in a low molecular weight PBD melt, which is a phenyl terminated oligomeric PBD (oBD) with a number average molecular weight  $M_n = 1.8$  kg/mol (Aldrich 20 043-3). The first sample is based on a monodisperse high  $M_w$  PBD as indicated in Table I, made in Bridgestone America, Akron, Ohio (by courtesy of Christopher Robertson). The second was made in Goodyear Tire & Rubber, Akron, Ohio (by courtesy of Adel Halasa). The most polydisperse third sample is comprised of 80% Goodyear (1.5 M) and 20% (Aldrich 18 138-2,  $M_w = 420$  kg/mol with  $M_w/M_n = 2.6$ ). The resulting molecular weight distribution is described in Table I. All samples were prepared by dissolving both high and low

**TABLE I.** Molecular characteristics of long chain PBDs.

Sample	$T_g$ (°C)	1-2PBD	1,4-PBD	$M_n$ (g/mol)	$M_w$ (g/mol)	$M_w/M_n$	Source
700 K	-99.5	10	90	$0.74 \times 10^6$	$0.75 \times 10^6$	1.02	Bridgestone
1.50 M	-100.5	8.1	91.9	$1.30 \times 10^6$	$1.50 \times 10^6$	1.35	Goodyear
1.30 M	-100.5	7.7	92.3	$0.81 \times 10^6$	$1.40 \times 10^6$	1.72	Goodyear

molecular weight PBDs in toluene for over 48 h to obtain uniform molecular mixing. Silver-coated particles of 10  $\mu\text{m}$  diameter (Dantec Dynamics HGS-10) were first ultrasonicated in toluene and then manually mixed with the master batch that still contained sufficient toluene to have honey-like consistency. The final loading of the particles is at a level of 200–600 ppm. The toluene was then removed at room temperature first under the hood and then in a vacuum oven until the residual toluene was less than 0.2%.

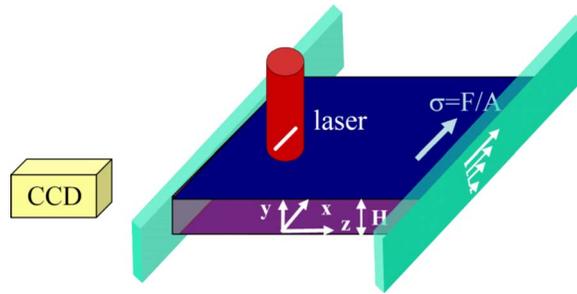
### B. Sliding Plate Rheometer

All commercially available rheometers are either capillary or rotational by design. In a rotational rheometer, a cone-plate assembly is commonly assumed to produce homogeneous shear field as long as the cone angle is less than 0.1 rad  $\sim 5.73^\circ$  [Macosko (1994)]. The current study employs a sliding-plate rheometer built in our lab by mechanist Edward Laughlin. Unlike all other sliding-plate rheometers or shear cells [Demarquette and Dealy (1992); Migler *et al.* (1993); Archer and Larson (1995); Archer *et al.* (1995); Mhetar and Archer (1998); Reimers and Dealy (1996); Koran and Dealy (1999b); Leger (2003)], our apparatus also operates in the condition of constant force as sketched in Fig. 1. With the bottom plate fixed, the moveable upper plate can be pushed by a step motor (Motion Parker Co, model No. ZETA6104-57-83) where the resulting force is measured by a pressure transducer (Dynisco Co model-PT422A). The velocity of the upper plate can be read from the program controlling the step motor as well as from an independent linear voltage differential transformer (LVDT) device (Schaevitz Sensors Co, model DC-SE 4000). The upper plate can also be moved with a constant force by either a dead weight through a pulley or an air cylinder (Festo Co) connected to a high-pressure air line.

A dynamic mechanical spectrometer (advanced rheometric expansion system) was used to obtain storage and loss moduli  $G'$  and  $G''$  at frequencies ranging from 0.001 to 100 rad/s at room temperature in a 25 mm parallel-plate geometry.

### C. Setup of particle tracking velocimetry (PTV)

The sliding-plate rheometer was designed with flexibility to make optical observations in both velocity gradient and vorticity directions during shear of polymer solutions and melts in either constant force or controlled velocity mode. Specifically, particle-tracking velocimetric observations can be made along the vorticity direction, similar to that described previously [Tapadia and Wang (2006); Tapadia *et al.* (2006); Wang *et al.* (2006)]. To determine velocity profiles, a laser beam of cylindrical cross section is incident, along the velocity gradient direction, upon a slit, as shown in Fig. 2, so that a sheet of particles in the  $XY$  plane can be illuminated. A black/white charge coupled device (CCD) camera (Panasonic, wv-BP332, sensitivity around 0.1 lux) watches the sheet of illuminated particles through a variable magnification lens (Edmund VZM<sup>TM</sup> Model 1000, No. 54-396). The focus onto a flow-gradient plane is naturally achieved by the location of the illumi-



**FIG. 2.** An illustration of the particle tracking velocimetry setup for the sliding-plate shear cell, where a cylindrical laser beam is incident on a line-shaped opening (located about 4 mm away from the sidewalls confining the sample) to illuminate a sheet of particles in the sample. The gap is typically set between 0.5 and 0.75 mm, and dimensions in  $x$  and  $z$  are approximately 4 and 10 cm, respectively.

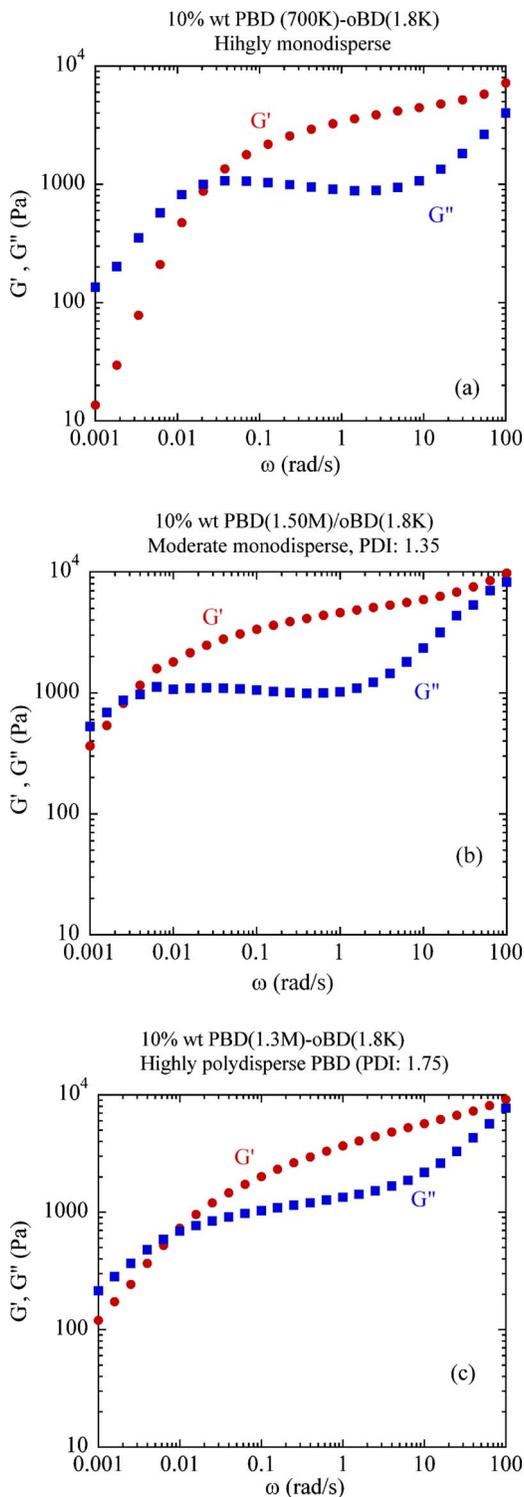
nated particles. In the present study, the laser source is a common presentation laser pointer (nexXTECH). The plane of observation is about 3–4 mm from one edge that runs parallel to the shearing direction. As illustrated in Fig. 2, the sample is confined with two sidewalls made of transparency films. A previous study has shown that the film does not alter the velocity profile at the plane of observation [Tapadia *et al.* (2006)]. We keep the side films so that the shear flow is stable and free of secondary flow. The transparent film also allows us to place a video camera horizontally that can be focused onto the interior of the sheared sample. With the samples dispersed with several hundred parts per million of ten micron-sized silver-coated particles (Dantec Dynamics HGS-10), the spatial resolution of our PTV technique can be as good as 20  $\mu\text{m}$ . The time resolution is also more than sufficient for our samples: with a conventional CCD camera, there are 30 frames/s. Typically we need to play 3–10 frames using MGI Videowave 4 software to determine the traveled distance of a given tracked particle over a range of shear rate. Thus we usually have a time resolution around 0.1–0.3 s, which is sufficient for our sluggish samples.

### III. RESULTS AND DISCUSSION

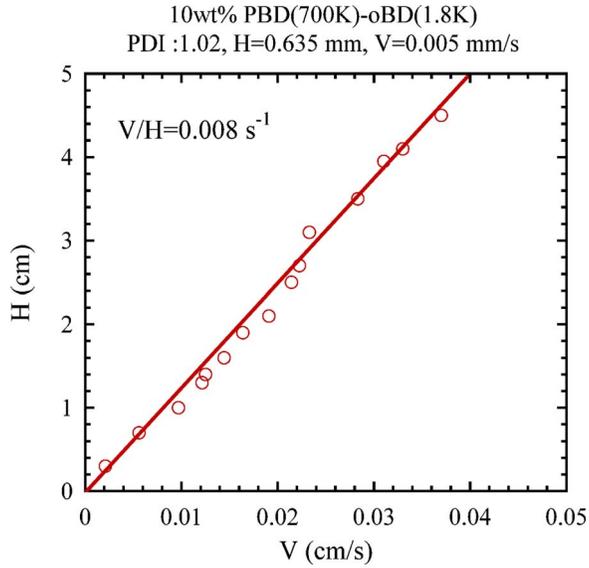
In this paper systematic measurements were carried out to explore nonlinear flow behavior of both monodisperse and polydisperse samples in a start-up shear experiment carried out in the controlled displacement mode. As a proper starting point, we first perform oscillatory shear frequency sweep measurements to illustrate the linear viscoelastic characteristics of the three different samples described in Sec. II. Figures 3(a)–3(c) are the storage and loss modulus curves of the three samples.

#### A. Multiple values of shear rate in banding (controlled displacement)

Continuous shear flow behavior of entangled fluids was conventionally studied by a sudden imposition of a constant velocity on one shearing surface and measuring the stress growth as a function of time. This approach usually produces a smooth steady state flow curve for well entangled polymer solutions. For monodisperse polymers including the present sample, a stress plateau can be rather visible [Menezes and Graessley (1982); Pattamaprom and Larson (2001); Tapadia and Wang (2004)]. Although our interest is to probe the stress plateau region, we made one PTV observation in the Newtonian region to establish a reference point. Figure 4 is the result of PTV measurements for an imposed



**FIG. 3.** Dynamic moduli  $G'$  and  $G''$  from oscillatory shear measurements at 25 °C for (a) 10% PBD(700 K)-oBD(1.8 K), which is highly monodisperse as can be seen from the shapes of the curves, (b) 10% PBD(1.5 M)-oBD(1.8 K), which is slightly polydisperse, and (c) 10% PBD(1.3 M)-oBD(1.8 K), which highly polydisperse as indicated in Table I.



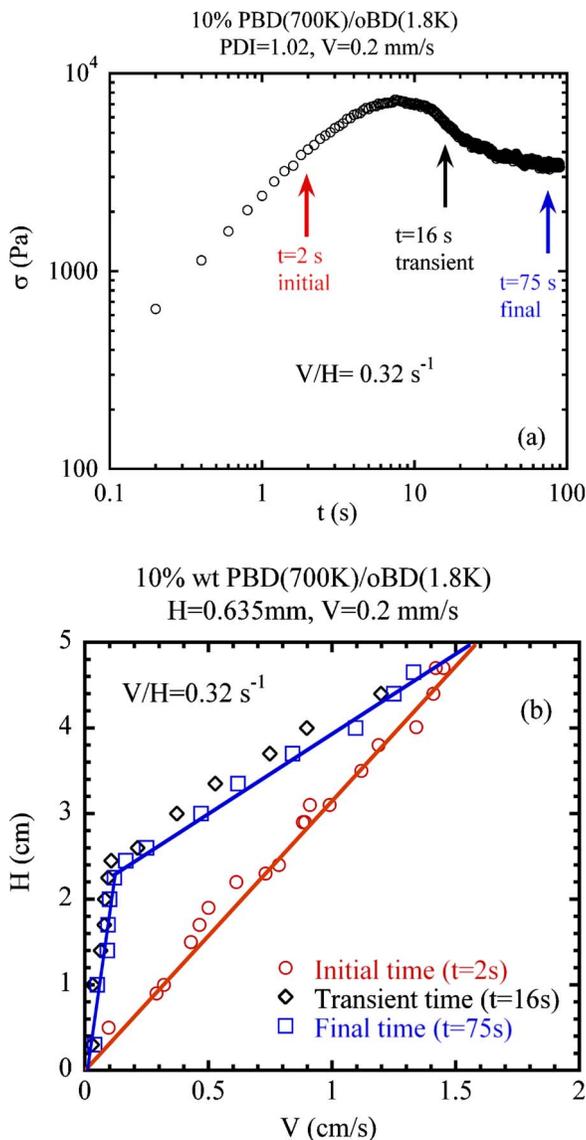
**FIG. 4.** PTV measurement at a low shear rate of  $0.008 \text{ s}^{-1}$  for 10% PBD (700 K)-oBD(1.8 K) at  $25^\circ \text{C}$ , where the length scale is that of the video monitor.

velocity of  $0.005 \text{ mm/s}$  over a gap of  $0.635 \text{ mm}$ , indicating that this low velocity indeed produces a homogeneous shear field with a constant shear rate equal to  $0.008$  throughout the sample thickness.

To step into the stress plateau region, we chose a value of the upper plate velocity  $V$  that would result in an average shear rate ( $V/H$ ) higher than the crossover frequency  $\omega_c \sim 0.027 \text{ rad/s}$  for the first sample. Figure 5(a) shows standard characteristics of the shear stress response to startup shear where a velocity of  $0.2 \text{ mm/s}$  is applied to the upper plate over a gap distance of  $H=0.635 \text{ mm}$ , corresponding to an average shear rate of  $V/H=0.32 \text{ s}^{-1}$ .

The familiar stress overshoot has been regarded as a common flow characteristic of a homogeneously sheared sample. However, the PTV measurements show that the velocity profile is linear only up to the time ( $t \sim 8 \text{ s}$ ) when the shear stress reaches the maximum. After the stress overshoot, the sample “nucleated” into two bands with two different local shear rates as shown in Fig. 5(b). It is important to note that the “slow band” possesses a shear rate as low as  $0.05 \text{ s}^{-1}$ . In other words, the slow band was essentially sheared in the Newtonian region, whereas the fast band undergoes a considerably higher shear rate than the average shear rate. In this sliding-plate rheometer, we are limited to this level of shear strain and we cannot claim that the system has truly reached steady state after  $0.32 \times 75 = 24$  strain units.

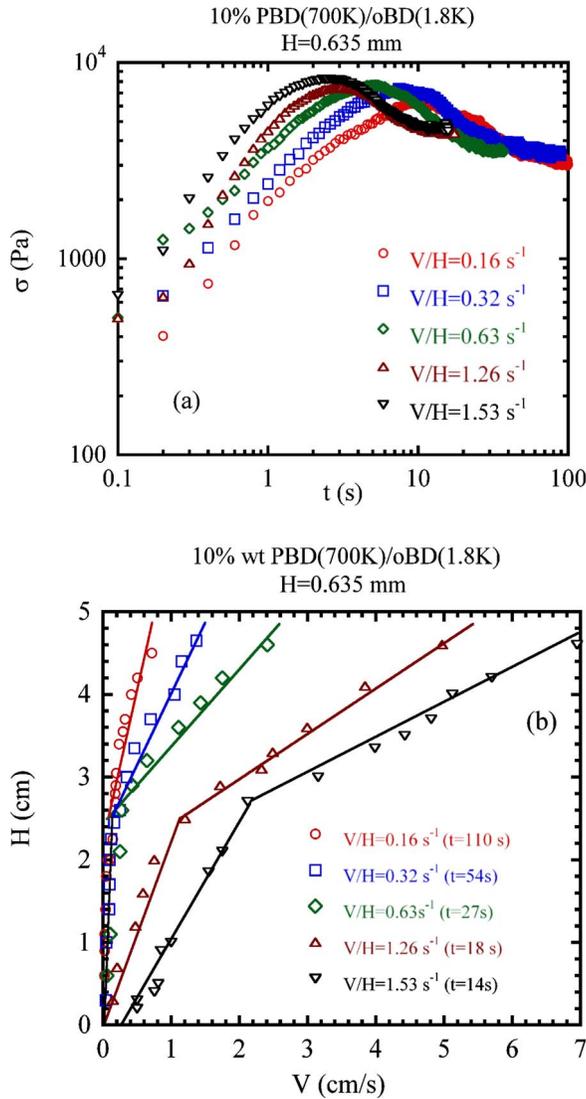
To better depict the nature of the shear banding it is useful to compare the velocity profiles at various imposed apparent shear rates. Figure 6(a) show the commonly observed shear stress overshoot at five values of the imposed velocity  $V$ . The long-time velocity profiles at the different values of the upper plate velocity  $V$  reveal in Fig. 6(b) that the “fast band” width does not grow much with increasing  $V$ , whereas its shear rate does increase proportionally with  $V$ . Although these velocity profiles cannot be claimed to correspond to the true steady states, it is likely that the behavior is inconsistent with the nonmonotonic feature of the original Doi-Edwards theory. An improved version of the



**FIG. 5.** (a) Stress growth in a start-up shear experiment for the 10% PBD (700 K)-oBD(1.8 K) solution at room temperature where the apparent shear rate  $V/H=0.32$  falls into the stress plateau region. (b) The corresponding velocity profile at the initial, transient, and final times.

Doi-Edwards tube theory [Cates *et al.* (1993)] indicates that there could only be two values of local shear rate in the stress plateau at different average shear rates of  $V/H$ .

It is important to indicate that the shear banding does not appear to be due to a change in the concentration across the sample thickness. Had the concentration been the origin of the observed nonlinearity in Fig. 6(b), the sample would still possess such a feature upon switching to a low shear rate of  $0.008$   $s^{-1}$ . Our experiment shows that the sample quickly resumes linear velocity profile shortly after such a switch. It would have taken mass transport through chain diffusion a very long time to redistribute the polymer concentration had the sample been made into two bands of polymer-rich and polymer-poor phases [Larson (1992)].

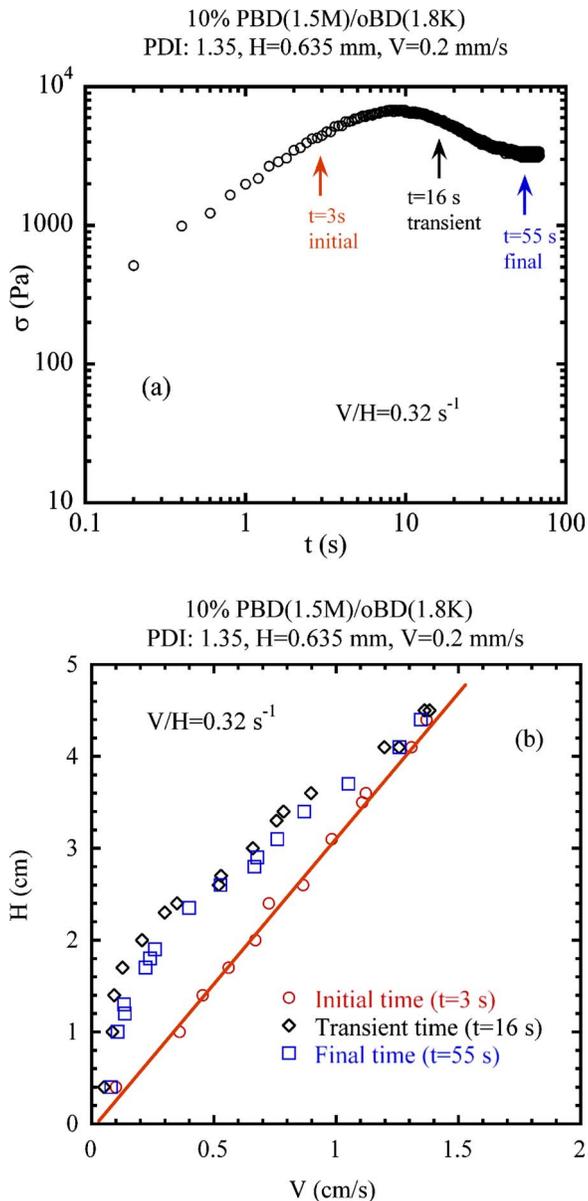


**FIG. 6.** (a) Stress growth in start-up shear experiments at five apparent shear rates all in the stress plateau region for the 10% PBD (700 K)-oBD(1.8 K) solution at room temperature. (b) Five velocity profiles at the specified times showing variation of the velocity field with the apparent shear rate.

## B. Shear banding vs. smooth variation: Monodisperse vs. polydisperse samples

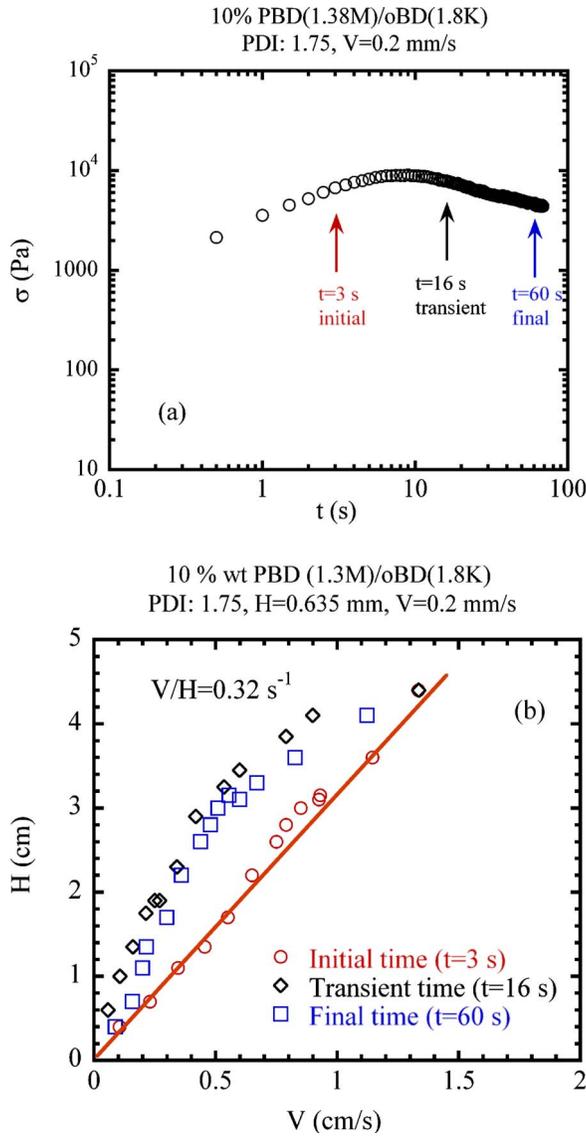
The observed shear banding of the monodisperse PBD solution in the preceding subsection provides a contrast to the previously reported smooth variation of the local shear rate in a similar experiment on a polydisperse sample [Tapadia and Wang (2006)]. It appears that the molecular weight distribution (MWD) might play a direct role in affecting the velocity profile.

In this subsection, we vary the polydispersity of the long chains in the solutions and carry out PTV measurements. First we study a 10% PBD solution with a certain level of polydispersity ( $\text{PDI}=1.35$ ), listed as the second sample in Table I. Under the same condi-



**FIG. 7.** (a) Stress growth in a start-up shear experiment for the 10% PBD (1.5 M)-oBD(1.8 K) (PDI: 1.35) under the same flow condition as Fig. 5(a). (b) The corresponding velocity profile at the initial, transient, and final times.

tion as described for Fig. 5(a), this sample also shows stress overshoot in Fig. 7(a). Our PTV observations in Fig. 7(b) show that at the beginning time of shearing ( $t < 10 \text{ s}$ ), the velocity varies linearly along the thickness direction. At a transient point  $t=16 \text{ s}$  beyond the stress overshoot, a maximum deviation from linearity was observed. At a long time of  $t=55 \text{ s}$ , there is still significant spatial variation of the local shear rate. The variation appears to be somewhat smooth for this slightly polydisperse sample in contrast to the sharp banding of Fig. 5(b) for the monodisperse sample.



**FIG. 8.** (a) Stress growth in a start-up shear experiment for the 10% PBD (1.3 M)-oBD(1.8 K) solution (PDI: 1.72) under the same flow condition as Fig. 5(a). (b) The corresponding velocity profile at the initial, transient, and final times.

To confirm this trend, a highly polydisperse PBD solution (PDI: 1.75), listed as the last sample in Table I, was studied. The stress growth of  $\sigma$  versus time is shown in Fig. 8(a) for the same flow condition as for Figs. 5(a) and 7(a). The stress overshoot was most gradual for this polydisperse PBD solution. In Fig. 8(b), the PTV measurements show a smooth shear rate gradient across the gap at long times. This result is consistent with the first report on PTV observation by Tapadia and Wang (2006) of a polydisperse entangled PBD solution.

A comparison among Figs. 5(b), 7(b), and 8(b) clearly reveals a correlation between

the MWD and the shape of the velocity profile. Although such a link may seem rather natural, it remains to be seen in future work whether the smooth velocity profile would prevail after more strain units of shear.

### C. Linear velocity profile in creep experiment (controlled force)

We have previously proposed a theorem regarding shear flow of viscoelastic fluids [Tapadia and Wang (2004)] that a sample subjected to a constant shearing force should develop a linear steady-state velocity profile in simple shear apparatuses such as the present sliding-plate rheometer. We applied the PTV method here to explore how the velocity field of an entangled polymer solution evolves under a constant force.

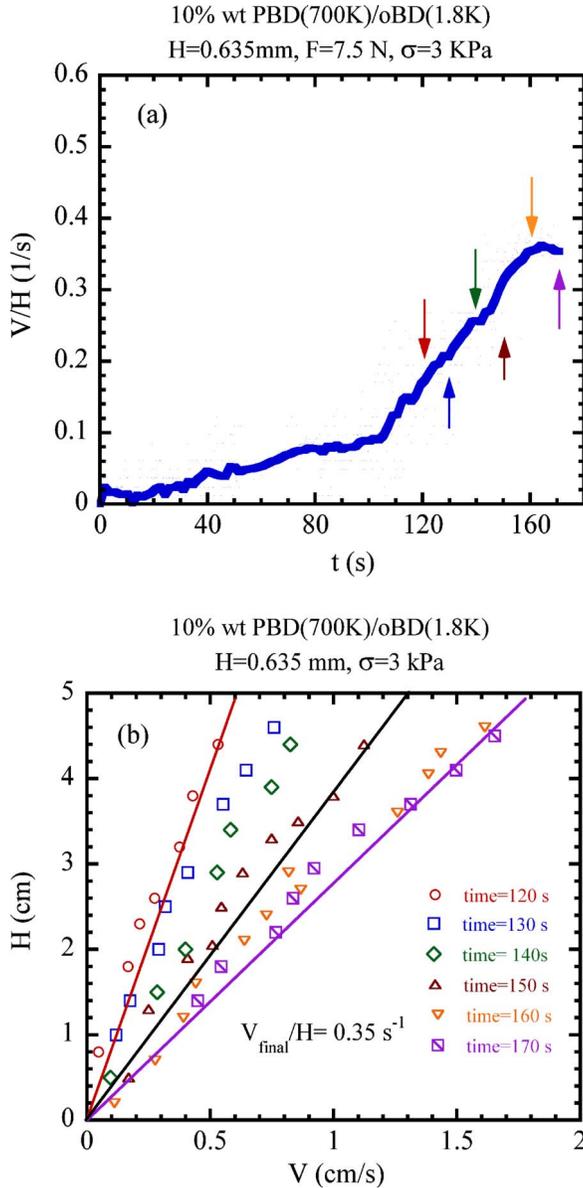
Knowing the area of sample between the two parallel plates equal to  $25 \text{ cm}^2$ , we applied a force of  $7.5 \text{ N}$  by hanging a weight of  $\sim 0.76 \text{ kg}$  through the pulley (see Fig. 1) to generate a shear stress of  $3 \text{ kPa}$  for the monodisperse entangled PBD solution. Figure 9(a) shows the growth of the upper plate velocity in time as measured by the LVDT. The apparent shear rate builds very slowly, slower than the characteristic relaxation rate of the sample so that the sample was initially sheared in the Newtonian region. After  $100 \text{ s}$ , the velocity of the upper plate gradually picks up. In contrast to the deeply nonlinear profiles of Fig. 6(b), Fig. 9(b) shows essentially linear velocity fields at all times including the end point ( $t=170 \text{ s}$ ) when the velocity appears to become steady as seen in Fig. 9(a). Comparison between this result and that of the preceding subsection shows the different responses of the entangled polymers to the force-control and displacement-control modes of shear.

### D. Uniform flow birefringence

We have loaded a piece of the monodisperse sample, 10% PBD (700 K)-oBD(1.8 K) into the sliding-plate shear cell and carried out flow birefringence observation to examine the potential issue of uneven flow. Figure 10 shows the uniform blue color produced after 4.1 strain unit in a startup shear of  $V/H=1.57 \text{ s}^{-1}$ . The flow birefringence setup involves placing the shear cell as well as a full-wave retardation plate between two mutually perpendicular polarizers that are at  $45^\circ$  to the shearing direction  $X$ , with a white light source on one side of this assembly and a color CCD video camera on the other side. Unlike a previous study [Archer *et al.* (1995)] involving a plane Couette shear cell with a finite sample bounded only by air, our setup involves two sidewalls to confine the sheared sample between the two parallel plates. The homogeneous blue color shows that the sample has been strained uniformly throughout the sample even near the sidewall where the PTV observations were taken. Note also the smooth color variation at the front and end of the sample, which indicates lack of any edge rupture and distortion during shear. The video clip of this flow birefringence measurement is available online as Movie 4" at <http://www3.uakron.edu/rheology/>.

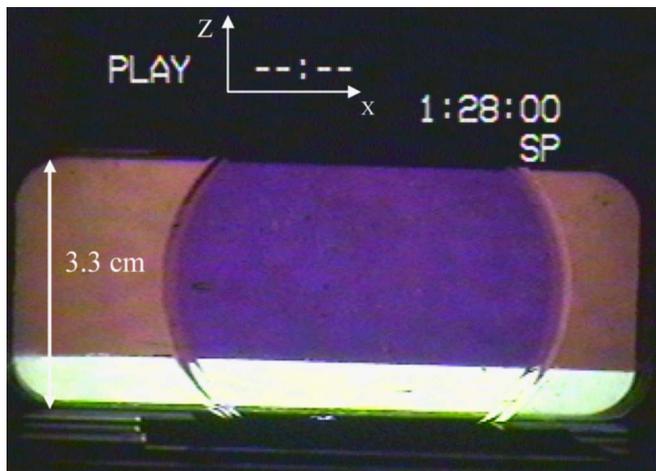
### E. Contrasting with previous work

As surveyed in the Introduction, past work [Archer and Larson (1995); Archer *et al.* (1995)] has also attempted to visualize flow deformation in a plane Couette shear cell using particle tracking. The present study implemented a PTV technique that allows the *entire* sample in the thickness direction to be monitored at all times with a spatial ( $Y$  axis) resolution of  $20 \mu\text{m}$ , whereas the 1995 papers made video imaging of the  $X$ - $Z$  plane, a method that (1) would have lower  $Y$  resolution and (2) would see only one layer at a time along the velocity gradient direction, making it unfeasible to follow the entire velocity profile at all times. The highly entangled polystyrene solutions used in the previous



**FIG. 9.** (a) Apparent shear rate  $V/H$  measured by LVDT as a function of time for the 10% PBD(700 K)/oBD(1.8 K) solution under a constant force of 7.5 N at room temperature, where the arrows indicate the times where the velocity profile is measured by PTV as shown in (b). (b) The evolving linear velocity profiles at the various times during the creep experiment described in (a).

studies [Archer and Larson (1995); Archer *et al.* (1995); Reimers and Dealy (1996)] involved a number of complications: (a) severe interfacial wall slip because the solutions were based on an inviscous small molecule solvent; (b) a sample only bounded by the air having lots of meniscus that apparently could lead to secondary flow as claimed in these papers.



**FIG. 10.** Flow birefringence under white light as viewed from the  $X$ - $Z$  plane. The boundary dividing the bright and dark areas is about 3 mm from the sidewalls. Here the bright stripe is where no polarizer was placed.

#### IV. SUMMARY

In summary, we have carried out particle-tracking velocimetric measurements during start-up shear of several entangled polybutadiene solutions in a home-built sliding-plate rheometer that can operate in both controlled displacement and force modes. We show within a certain range of polydispersity that the samples all develop a nonlinear velocity profile upon startup shear (controlled displacement) in the stress plateau region. This occurs because the sample is being sheared on a time scale on which the fluid could only respond elastically or in a solid-like manner. As a “solid” suffering from large deformation, the sample is unable to undergo homogeneous strain, and a significant fraction nucleates into a state of lower viscosity to satisfy the externally imposed boundary condition. The development of nonlinear velocity profile appears to be constitutive in origin as it has now been found to occur in the current sliding-plate shear cell where no stress gradient can be used to explain the spatial variation of local shear rate.

The shear banding for the monodisperse sample, i.e., a division of the sample into multiple layers where each layer possesses a different uniform shear rate, has the striking characteristic that the shear band width does not scale with the apparent shear rate. The existence of many uniform shear rates for a range of the imposed plate velocities presents a challenge to any simple account of shear banding by a constitutive continuum model that possesses a nonmonotonic curve. There is an indication that the shear banding is stable once created in the startup shear. One reason for why the shear banding may persist is that with the nucleation of the low viscosity layer the rest of the sample no longer suffers sufficient shear required to convert it into a state of lower viscosity.

Even the rather polydisperse PBD solution shows significant nonlinear velocity profiling upon startup shear as seen previously in our lab [Tapadia and Wang (2006)]. The nonlinearity survives over tens of strain units, making it rather difficult to deny the prevalence of the phenomenon in entangled polymeric liquids, however less dramatic it is in comparison to the sharp shear banding observed for monodisperse polymers.

Finally, the PTV observations appear to reveal a noticeable difference in the responses of the sample to controlled displacement and controlled force shear. In particular, a constant force of an appropriate magnitude seems to be able to produce homogenous

simple shear in contrast to the strongly inhomogeneous shear produced by a constant rate of displacement. More experiments must be carried out to find out whether indeed the controlled force shear would always produce a rather linear velocity profile even in the transient period and whether a smooth ramp-up in the controlled-rate mode could also result in a linear velocity profile.

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