

## Shear Banding or Not in Entangled DNA Solutions

Pouyan E. Boukany<sup>†</sup> and Shi-Qing Wang\*

Department of Polymer Science and Maurice Morton Institute of Polymer Science, University of Akron, Akron, Ohio 44325.

<sup>†</sup> Present address: Department of Chemical Engineering, The Ohio State University, Columbus, OH 43212

Received June 7, 2010

Revised Manuscript Received July 20, 2010

Chain entanglement in concentrated polymer solutions and melts has many consequences in both linear viscoelasticity and nonlinear rheology.<sup>1,2</sup> Because of entanglement, polymeric liquids undergo a great deal of elastic strain before transforming into a state of flow under continuous external deformation. When the external rate of deformation is faster than the chain relaxation rates, the entanglement network is forced to collapse so that flow can take place. In complicated configurations such as pressure-driven channels, states of deformation and flow are unknown *a priori*, i.e., dependent on the specific constitutive properties. Therefore, particle tracking<sup>3–5</sup> and other means<sup>6–8</sup> have been used to examine channel flow behavior of entangled polymers since the 1950s. In simple-shear rheometric setups, the state of deformation had been assumed to be homogeneous, independent of the constitutive relationship.<sup>9,10</sup> Such an assumption has recently been called into question, following the discovery that wormlike micellar solutions show shear banding under simple shear.<sup>11–18</sup> Other polymer-like materials such as actin networks have also been studied to explore the validity of shear homogeneity.<sup>19–21</sup> When shear banding was reported in semidilute polyacrylamide/water solutions,<sup>22</sup> the authors attributed the origin of shear banding to presence of chain–chain association through hydrogen bonding.<sup>23</sup>

Entangled nonassociative polymer solutions<sup>24,25</sup> and melts<sup>26</sup> actually also undergo inhomogeneous shear according to the latest particle-tracking velocimetric (PTV) measurements. These PTV observations have caused us to search for alternative explanations<sup>27</sup> to the theoretical description based on the Doi–Edwards tube model.<sup>28–31</sup> Our observations revealed that well-entangled polymeric liquids tend to suffer inhomogeneous cohesive breakup after yielding<sup>32</sup> upon sudden startup shear when wall slip is absent or insufficient to prevent the bulk from undergoing high shear.

In the present PTV/rheometric study, using an entangled linear double-strand calf thymus DNA solution as model entangled polymers,<sup>33a–c</sup> we explore the cause of strong shear banding and determine whether shear inhomogeneity could be reduced or eliminated if the apparent shear rate is imposed gradually instead of suddenly. The aim is to explore the nature of simple shear behavior at long times.

Specifically, the entangled DNA solution has a concentration of 11 mg/mL, with glycerol as the solvent. The source and characterization of the DNA as well as the solution preparation have been described elsewhere.<sup>33a–c</sup> This solution has  $Z = 60$  entanglements per chain and shows a crossing of storage and loss moduli at a frequency  $\omega_c = 0.0013$  rad/s in frequency sweep measurements of small-amplitude oscillatory shear. Since the DNA is polydisperse in its molecular weight distribution, the assignment of  $1/\omega_c = 780$  s as the relaxation time  $\tau$  is only an approximate way to characterize the overall relaxation dynamics. The basic rheometric and shear

banding behavior of this solution as well as two other solutions at concentrations of 5 and 22 mg/mL have been reported before.<sup>33a–c</sup>

All the rheometric and PTV measurements were carried out at room temperature using a MCR-301 rotational rheometer (Anton Paar) equipped with a cone–plate of 25 mm diameter and 4° cone angle, where the surface roughness due to a black paint (to eliminate any optical reflection in PTV observations) is on the order of micrometers. The PTV setup has been depicted before,<sup>24</sup> involving wrapping a transparent film around the meniscus that does not touch the rotating cone.

We begin by examining characteristic responses of the solution to a sudden startup shear at an apparent rate  $\dot{\gamma} = 1$  s<sup>−1</sup>. At such a high Weissenberg number  $Wi = \dot{\gamma}\tau = 780$ , one notable nonlinear feature is the shear stress overshoot shown in the inset of Figure 1. Detailed PTV measurements show in Figure 1 that homogeneous deformation prevails up to the stress maximum. Then the “symmetry breaking” occurs; i.e., the shear field becomes strongly banded. In the limit where the measured stress appears constant, significant shear banding persists as shown by the filled circles in Figure 1. The velocity profiles at 100, 450, and 600 s are essentially indistinguishable. Such results are no longer surprising since they simply confirm the previous PTV observations<sup>24,25</sup> that shear banding occurs in well-entangled polymers during startup shear. Since the entanglement network cannot sustain indefinitely growing deformation in an elastic manner, yielding must take place.<sup>27</sup> In other words, the sample is forced to give in to a state of flow, signified by the stress overshoot. But this yielding may not occur in a spatially homogeneous way.

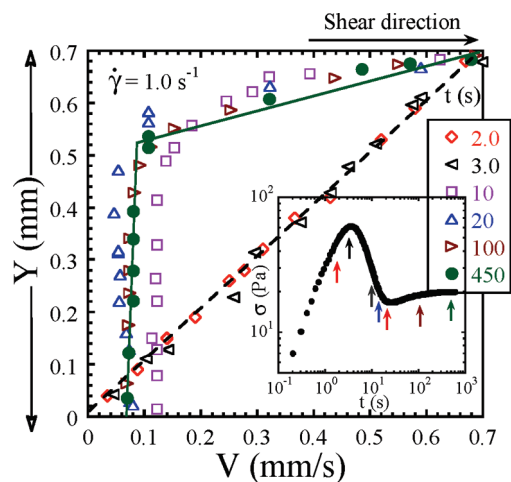
PTV measurements have been carried out at other rates to illustrate the trend. Figure 2 shows that the thickness of the high-shear band grows with the applied (apparent) rate. However, the local rate in the low-shear band is not fixed as the applied rate increases. At a rate equal to or higher than 4 s<sup>−1</sup>, the transient shear banding is weaker,<sup>33b</sup> and beyond the stress overshoot homogeneous shear returns.<sup>34</sup> Since our attention is on the steady state, we have only presented these profiles at times indicated in Figure 2 when the shear stress has become constant with respect to time.

The present work explores a different approach to the same final external condition. Instead of a sudden startup shear, we will gradually increase the imposed shear rate toward the final rate of, say, 1.0 s<sup>−1</sup>, starting with a rate lower than the quiescent relaxation rate  $1/\tau$ .

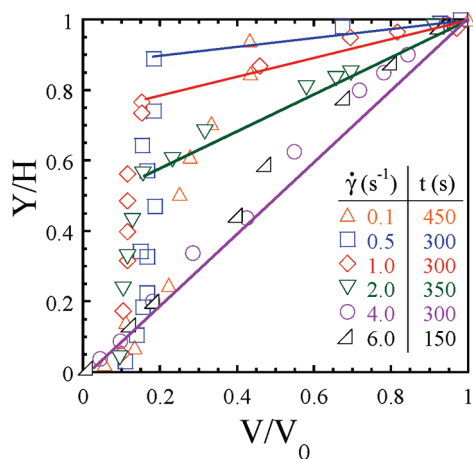
Because the present sample is also found to attain steady homogeneous shear at rates equal to or higher than 4 s<sup>−1</sup> as shown in Figure 2, we have a second procedure to produce homogeneous shear in the shear thinning regime: first shear the sample into a homogeneous steady state at a sufficiently high rate and then quench down to rates, at which startup shear produces shear banding.

Figure 3a shows a conventional startup shear at a rate of 1.0 s<sup>−1</sup> (in blue squares), a slow rate ramp-up toward the final rate of 1.0 s<sup>−1</sup> (in green diamonds), and a rate quench-down from a startup shear at 6.0 s<sup>−1</sup> down to 1.0 s<sup>−1</sup> (in red circles). The corresponding PTV observations in Figure 3b show a contrast of shear banding (resulting from startup shear due to forced yielding<sup>27</sup>) against the approximate linear variations in the velocity profiles (arising from either rate ramp-up or quench-down).<sup>35</sup> The remarkable difference indicates that the strong shear banding originates from the sudden fast deformation in startup shear. When the forced yielding is avoided, so is shear banding. This comparison suggests that shear banding is not a unique response. In other words, for the same final

\*Corresponding author. E-mail: swang@uakron.edu.



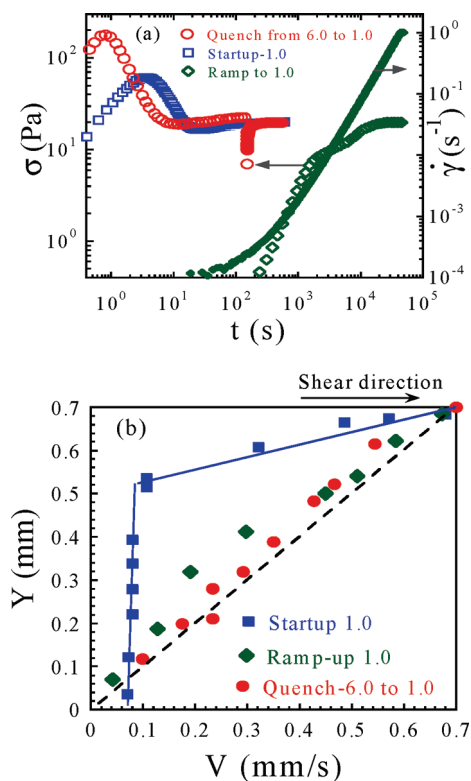
**Figure 1.** Velocity profiles during the startup shear at an apparent shear rate of  $1.0 \text{ s}^{-1}$ , where different symbols denote the profiles at different times of 2, 3, 10, 20, 100, and 450 s during shear. The inset shows stress vs time where the stress overshoot is followed by an undershoot before the stress level approaches a constant after 300 s. The solid lines are added to guide the reader's eye, and the dashed line represents the homogeneous shear (i.e., linear profile).



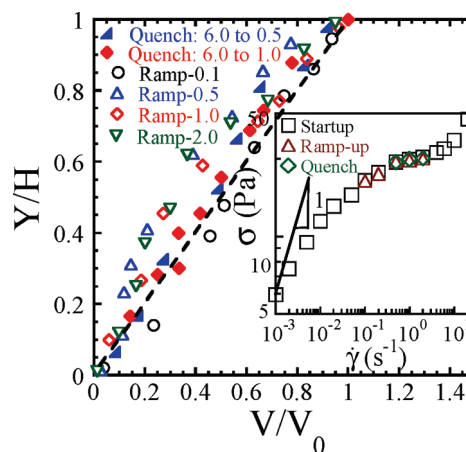
**Figure 2.** Strong shear banding produced by the sudden startup shear at apparent rates of 0.1, 0.5, 1.0, 2.0, 4.0, and 6.0  $\text{s}^{-1}$  at the times when the shear stress and velocity profiles no longer change in time. The higher rates of 4.0 and 6.0  $\text{s}^{-1}$  result in approximate shear homogeneity in the long time limit. The solid lines are here to guide the reader's eye.

apparent shear rate, the states of flow can be different. In passing, we note from Figure 3b that the local shear rate in the low-shear band  $\dot{\gamma}_{\text{low}} \sim 0.04 \text{ s}^{-1}$ , revealing an effective relaxation time<sup>36</sup>  $\tau_{\text{eff}}$  ( $\sim 1/5 \dot{\gamma}_{\text{low}}$ ) of 5 s. Thus, the shearing time of 450 s is 90 times  $\tau_{\text{eff}}$ , which we consider it to be extremely long.

Further experiments involving other rates confirm in Figure 4 that the slow rate ramp-up mode or rate quench-down tends to produce approximately linear velocity variation across the gap throughout the stress plateau region, in sharp contrast to the shear bands that emerge from startup shear as shown in Figure 2. Note that because of the polydispersity, the onset of the stress plateau is not abrupt, and the plateau width is rather narrow as revealed in the inset of Figure 4. Since the stress value resulting from rate ramp-up and rate quench-down appears identical to that produced by sudden startup shear, the flow curves are not discernibly different despite the different resulting velocity profiles. Thus, shear banding is clearly not necessary for the system to exhibit shear thinning. Clearly, mechanical (i.e., rheometric) measurements must be combined with a description of the state



**Figure 3.** (a) Shear stress as a function of time for startup shear at  $1.0 \text{ s}^{-1}$ , quenching from a startup at  $6.0$  to  $1.0 \text{ s}^{-1}$ , and a gradual rate ramp-up from an initial rate of  $10^{-4} \text{ s}^{-1}$  to the final value of  $1.0 \text{ s}^{-1}$ . Also plotted on the right-hand Y-axis is the increasing applied rate as a function of time in filled diamonds for the rate ramp-up test. (b) Velocity profiles corresponding to those depicted in (a), where the PTV measurements in squares were taken 450 s after the startup shear, those in circles were taken 300 s after the rate switching from  $6.0$  to  $1.0 \text{ s}^{-1}$ , and those in diamonds give the velocity profile at the end of the rate ramp-up when it has undergone shearing at  $1.0 \text{ s}^{-1}$  for 500 s. The solid lines are added to guide the reader's eye, and the dashed line represents the homogeneous shear (i.e., linear profile).



**Figure 4.** Velocity profiles from both rate ramp-up and quench-down experiments involving discretely the following four rates: 0.1, 0.5, 1.0, and 2.0  $\text{s}^{-1}$ . They are to contrast those in Figure 2. The inset shows that for a given rate the shear stress level is the same, regardless of whether this rate was produced by startup shear, rate ramp-up or quench-down. The dashed line represents the homogeneous shear (i.e., linear profile).

of flow, enabled here by the PTV measurements, to provide a full characterization of the rheological state for entangled liquids.

In this Communication, we showed how an entangled DNA solution can either undergo strong shear banding at long times

due to a sudden startup shear or display little shear inhomogeneity if it is subjected to either gradual rate ramp-up or rapid quench-down to the same rate. The contrast among the different velocity profiles in Figure 3b elucidates the origin of shear banding: localized collapse of the entanglement network in response to sudden fast shear. The shear banding persisted for a very long period, during which a steady rheological state appears to have emerged. It remains elusive why for the same final rate of apparent shear both shear banding and homogeneous shear state have the same shear stress. Since both shear banding and homogeneous shear appear stable at long times, the observed phenomena may not be explained either by a non-monotonic constitutive relation (derivable from the original Doi–Edwards tube theory<sup>29</sup>), which would always expect shear banding, or by a monotonic constitutive equation<sup>30</sup> (derivable after introduction of the convective constraint release), which would not allow shear banding to prevail.

Efforts are ongoing in our lab to determine where the entangled polybutadiene solutions and even nonvulcanized styrene–butadiene rubbers would display the same behavior as reported here. If the emergence of shear banding would depend on the shear history, there would be profound theoretical implications, concerning how to formulate the correct constitutive description for nonlinear flow behavior of entangled polymers. Specifically, it would not be possible for a nonmonotonic constitutive equation to describe such shear banding behavior because nonmonotonicity in constitutive relationship would always prescribe shear banding independent of shear history.

Finally, in passing it is worth noting that for associative polymers such as wormlike micelles shear history has been shown to influence the final rheological states.<sup>37–39</sup> The present finding in a nonassociative polymer system enriched our existing knowledge about the complex rheological behavior of entangled liquids. In contrast to wormlike micelles that can re-form their structures during shear over a time much longer than its equilibrium relaxation time, polymer solutions appear to approach the time-independent state within a fraction of their overall (equilibrium) relaxation time.

**Acknowledgment.** We appreciate the helpful comments by Sham Ravindranath. This work is supported, in part, by a grant (DMR-0821697) from the National Science Foundation.

## References and Notes

- Graessley, W. W. *Adv. Polym. Sci.* **1974**, *16*, 1.
- Ferry, J. D. *Viscoelastic Properties of Polymers*, 3rd ed.; Wiley: New York, 1980.
- Tordella, J. P. *J. Rheol.* **1957**, *1*, 203.
- Galt, J. C.; Maxwell, B. *Mod. Plast.* **1964**, *42*, 115.
- White, J. L. *Appl. Polym. Symp.* **1973**, *20*, 155.
- Ramamurthy, A. V. *Trans. Soc. Rheol.* **1974**, *18*, 431.
- Munstedt, H.; Schmidt, M.; Wassner, E. *J. Rheol.* **2000**, *44*, 413.
- Schwetz, M.; Munstedt, H.; et al. *J. Rheol.* **2002**, *46*, 797.
- Reiner, M. *J. Rheol.* **1929**, *1*, 5.
- Macosko, C. W. *Rheology - Principles, Measurements and Applications*; VCH: New York, 1994.
- Callaghan, P. T.; et al. *J. Phys. II* **1996**, *6*, 375.
- Britton, M. M.; Callaghan, P. T. *Phys. Rev. Lett.* **1997**, *30*, 4930.
- Britton, M. M.; Mair, R. W.; Lambert, R. K.; Callaghan, P. T. *J. Rheol.* **1999**, *43*, 897.
- Salmon, J. B.; Colin, A.; Manneville, S.; Molino, F. *Phys. Rev. Lett.* **2003**, *90*, 228303.
- Salmon, J. B.; Manneville, S.; Colin, A. *Phys. Rev. E* **2003**, *68*, 051503.
- Becu, L.; Manneville, S.; Colin, A. *Phys. Rev. Lett.* **2004**, *93*, 018301.
- Olmsted, P. D. *Rheol. Acta* **2008**, *47*, 283.
- Manneville, S. *Rheol. Acta* **2008**, *47*, 301.
- Head, D. A.; Levine, A. J.; MacKintosh, F. C. *Phys. Rev. E* **2003**, *68*, 061907.
- Liu, J.; et al. *Phys. Rev. Lett.* **2007**, *98*, 198304.
- Wen, Q.; et al. *New J. Phys.* **2007**, *9*, 428.
- Britton, M. M.; Callaghan, P. T. *J. Rheol.* **1997**, *41*, 1365.
- Callaghan, P. T.; Gil, A. M. *Macromolecules* **2000**, *33*, 4116. 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”. Other polymer (PS and PEO) solutions and poly(dimethylsiloxane) melt were not found to display shear banding: Callaghan, P. T., private communication.
- Tapadia, P.; Wang, S. Q. *Phys. Rev. Lett.* **2006**, *96*, 016001. A subsequent paper from our lab (*J. Rheol.* **2007**, *51*, 217) recognized that the sample used in the 2006 study was not monodisperse due to aging and therefore did not show sharp shear banding. With broad MWD, there is no sharp shear banding in entangled polymer solutions. Sharp banding occurs in monodisperse solutions as shown in ref 25.
- Ravindranath, S.; Wang, S. Q. *Macromolecules* **2008**, *41*, 2663.
- Boukany, P. E.; Wang, S. Q. *Macromolecules* **2009**, *42*, 6261.
- (a) Wang, S. Q.; Ravindranath, S.; Wang, Y. Y.; Boukany, P. E. *J. Chem. Phys.* **2007**, *127*, 064903. (b) Wang, Y. Y.; Wang, S. Q. *J. Rheol.* **2009**, *53*, 1389.
- Doi, M.; Edwards, S. F. *The Theory of Polymer Dynamics*, 2nd ed.; Clarendon Press: Oxford, 1988.
- Doi, M.; Edwards, S. F. *J. Chem. Soc., Faraday Trans. 2* **1979**, *75*, 38.
- Graham, R. S.; Likhtman, A. E.; McLeish, T. C. B.; Milner, S. T. *J. Rheol.* **2003**, *47*, 1171.
- Adams, J. M.; Olmsted, P. D. *Phys. Rev. Lett.* **2009**, *102*, 067801. We raised questions on this study in: Wang, S. Q. *Phys. Rev. Lett.* **2009**, *103*, 219801. Note that in their reply they still had to invoke a nonhomogeneous deformation profile to produce nonquiescent relaxation after shear cessation. In experiment, a homogeneous step shear produces localized elastic yielding and macroscopic motions during “relaxation” as shown in ref 26.
- Boukany, P. E.; Wang, S. Q. *J. Rheol.* **2009**, *53*, 617.
- (a) Boukany, P. E.; Hu, Y. T.; Wang, S. Q. *Macromolecules* **2008**, *41*, 2644. (b) Boukany, P. E.; Wang, S. Q. *J. Rheol.* **2009**, *53*, 73. (c) Boukany, P. E.; Wang, S. Q. *Soft Matter* **2009**, *5*, 780. These papers show that the linear viscoelastic properties of these entangled DNA solutions are indistinguishable from those of synthetic polymer solutions according to the small-amplitude oscillatory shear frequency sweep. They also exhibit shear banding as entangled polymer solutions do. Moreover, their stress overshoot characteristics obey the same scaling as found for entangled solutions and melts, as shown in ref 32.
- Hu, Y. T.; et al. *J. Rheol.* **2007**, *51*, 275. We cannot agree with the conclusions of this paper because both the existence of an intrinsic stress gradient in the Couette and use of a less than strongly entangled polybutadiene solution made it possible to avoid shear banding at high strains. We have also subsequently seen examples in refs 25 and 33b where moderately entangled samples do not show shear banding in steady state.
- See two PTV movies made from a customer-made counter-rotating shear device. The difference is indeed striking: <http://www3.uakron.edu/rheology/band-or-not>.
- See Figure 4 in: Boukany, P. E.; Wang, S. Q. *J. Rheol.* **2009**, *53*, 1425. See Figure 5 in: Li, X.; Wang, S. Q. *Macromolecules* **2010**, *43*, 5904.
- Grand, C.; Arrault, J.; Cates, M. E. *J. Phys. II* **1997**, *7*, 1071.
- Berret, J. F. *Langmuir* **1997**, *13*, 2227.
- Radulescu, O.; et al. *Europhys. Lett.* **2003**, *62*, 230.