

Direct Visualization of Continuous Simple Shear in Non-Newtonian Polymeric Fluids

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Using a particle tracking velocimetric technique, we show direct evidence of nonlinear velocity profiles during simple-shear flow of an entangled polymer solution, offering new insight into the origins of such characteristics as stress overshoot. Upon a startup shear by imposing a constant velocity on one of the two surfaces that confine the sample, the velocity field evolves from the initial linearity across the gap to a final state with a shear rate gradient. The unexpected deviation from the widely assumed linear variation of the velocity along the gap direction is most plausibly due to the entangled polymer's ability to disentangle in the presence of high shear that can orient the polymer chains leading to anisotropy in their mutual constraint.

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Flow behavior of polymers is of fundamental and practical importance because of the nonlinear physics behind it and the ever expanding use of plastic materials in daily life. Unlike small molecule liquids, the fluids made of chainlike polymeric molecules flow in complicated ways that have drawn decades of efforts. Specifically, non-Newtonian flow behavior of entangled polymers have been investigated extensively over the past four decades [1–3], both experimentally [4–11] and theoretically [12–19]. The objectives have been to (a) determine the relationship between the flow and corresponding stress fields in both transient and steady states and (b) depict the structure of polymeric fluids in terms of the states of chain orientation and entanglement as a function of the flow condition. The constitutive relationship between stress and flow rate dictate how such liquids behave in processing. The resulting fluid structure provides a link in the structure-processing-property relationship.

When undergoing processing in industrial practice, polymeric liquids may be subjected to complicated flow geometries. To explore the constitutive relationship in a fruitful way so as to be able to describe non-Newtonian fluid mechanical behavior of entangled polymers in such practical flow conditions, one resorts to the promising scheme that a homogeneous flow field can be generated for simple geometries. One particularly convenient and clever device used universally by workers in the field is a cone-plate shear cell [20], allowing continuous simple shear to be produced. This device creates uniform simple-shear flow for both Newtonian and non-Newtonian liquids, provided that their constitutive relation is simple, and neither secondary flow nor edge instability would be present to complicate the analysis. Regarding polymeric liquids as simple fluids possessing a one-to-one relationship between stress and shear rate, the cone-plate cell has been the favorite and popular setup for polymer rheologists for many decades.

Employing the cone-plate shear cell to explore a constitutive relationship for various polymers, workers in the

field have consistently adopted the strain-controlled mode for shearing their samples, namely, imposing an angular velocity Ω on one of the two surfaces in a cone-plate flow cell [9–11], in expectation that a uniform shear rate $\dot{\gamma}$ proportional to Ω would be generated across the sample thickness. This mode of imposing a plate velocity has become a standard protocol because of its convenient assumption that the velocity field could be taken as prescribed independently of the constitutive behavior of tested materials. Only the stress fields need to be measured using a force transducer to determine constitutive relationships.

So far, no theoretical reasons have been found for why the constitutive curves for entangled polymeric liquids would be discontinuous despite a continuous 20 yr search [2,12–19]. Thus, there has been little suspicion that any anomaly would occur in simple-shear flow devices such as a cone-plate cell. This situation only underscores the importance to obtain direct experimental verification of the assumption of homogeneous simple shear in a cone plate for entangled polymers.

Research efforts have been made to complement the rheological measurements of complex fluids (particularly polymeric fluids) with structural information that can be obtained by flow birefringence [21], light scattering [22,23], and neutron [24] and x-ray [25] scatterings. These *in situ* structure analyses typically collect spatially averaged (across the gap) information and do not explore structural differences (if any) between different sheared layers in the gap. The more recently developed single molecule techniques [26–29] directly quantify the local chain deformation and alignment in shear without statistical ensemble averaging. They also assumed the information to be independent of the position along the gap direction.

Recent [30,31] and ongoing work in our lab appears to question the validity of the rheometric protocol of imposing strain-controlled shear. Specifically, monodisperse entangled polymer solutions were found to display a yieldlike flow transition under constant applied shear stress. The

controlled-rate measurements produce only a smooth continuous flow curve. Our previous results pose the question of whether a shear rate gradient is present in strain-controlled shear for entangled polymeric liquids. There has never been any attempt at visualizing and determining the velocity field in a cone-plate cell where an entangled polymeric liquid is sheared.

Based on the preceding discussion, we regard it necessary to determine for entangled polymeric fluids whether the velocity gradient would remain uniform in simple-shear apparatuses such as a cone plate. We have developed a specific experimental method toward this aim that is based on analyzing the movement of tracing particles. Below we present our essential findings.

The entangled polymer solution under study is similar to a previously prepared and studied 10 wt% 1,4-polybutadiene (PBD) solution [30], made of a high weight PBD of $M_w = 1.24 \times 10^6$ g/mol and $M_w/M_n = 1.18$ from Polymer Source Inc., dissolved in a phenyl-terminated oligomeric butadiene of $M_n = 1.0$ K (Aldrich 20041-7). However, the sample after two years has turned rather polydisperse as indicated by its linear viscoelastic properties and gel permeation chromatography [32]. For the particle tracking purpose, the sample is seeded with silver-coated particles of 10 μ m diameter (Dantec Dynamics HGS-10) at a low level of several hundred parts per million. A dynamic mechanical spectrometer (Advanced Rheometrics Expansion System-ARES) equipped with a cone-plate assembly of 25 mm diameter was employed to make velocity profile measurements, where the cone angle θ is 5°.

Our particle tracking velocimetry consists of sending a laser beam along the velocity gradient direction through the gap between cone and plate and video recording the illuminated moving particles over time with a CCD camera facing the gap as shown in Fig. 1. A thin film surrounds the meniscus to allow focus of a telemicroscope onto the interior illuminated particles. The negligible perturbation of the confining film on the simple-shear flow inside the cone-plate cell can be estimated and has been experimentally verified [32]. For the determination of the velocity field along the gap, the video movie was played back at 15 frames per second to track the speed of particles in each layer where the positions of a chosen particle were

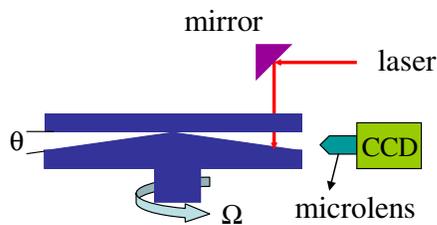


FIG. 1 (color online). The setup of the particle tracking velocimetry, where the upper stationary plate is made of transparent glass, the lower rotating cone made of steel, and $\theta = 5^\circ$.

followed on the different frames to yield the information of displacement over time.

We examine the flow field in the cone-plate cell at three imposed shear rates of 0.05, 0.1, and 5 s^{-1} , corresponding to the Newtonian, just before the stress plateau, and well inside the stress plateau regions, respectively, since the terminal relaxation time, taken as the reciprocal frequency in oscillatory shear where storage and loss moduli equal, is about 10 s at room temperature (25 °C). At the two low values of $\dot{\gamma} = \Omega/\theta$, i.e., two low values of angular velocity Ω , the stresses grow monotonically. But at 5 s^{-1} , Fig. 2(a) shows nonmonotonic behavior in both shear (σ) and normal (N_1) stresses, where σ first grew to its maximum at $t = 0.5$ and then dropped to its steady state value at $t = 2.4$ s; meanwhile, the first normal stress N_1 reached its maximum at $t = 1.7$ s and approached its steady state around $t = 5.5$ s. The feature of overshoots (especially of σ) is well known for entangled polymers under high shear and has been understood for decades to be the flow characteristic of a homogeneously sheared sample.

Our particle track velocimetric (PTV) measurements in Fig. 2(b) show that the velocity gradients were essentially uniform along the gap at the low shear rates. At the high shear rate of 5 s^{-1} , i.e., when the angular velocity of the rotating cone is set to $\Omega = 5\theta = 0.44$ rad/s, the velocity field no longer varied linearly across the gap after an initial transient period as shown in Fig. 2(c). In contrast, when a Newtonian oligomeric butadiene liquid (which was used as the solvent for the 10% PBD solution) is subjected to the same shearing condition at 5 s^{-1} , a constant value equal to the preset value prevails at all times in every layer in the gap, as shown by the plus-filled squares in Fig. 2(c). The actual gap distance H involved in Figs. 2(b) and 2(c) was ca. 0.9 mm (i.e., about 10 mm from the cone center) and was 9 cm on the video monitor where the measurements were taken. Results from positions closer to the cone center yield similar results and are omitted here. The reader can access a movie of the time-dependent velocity profile for $\Omega/\theta = 5 s^{-1}$ on the World Wide Web [33], based on which the measurements were made.

This first set of particle tracking velocimetric observations reveals that the entangled polymeric liquid is in a state of frustration when subjected to an average shear rate in the stress plateau region. When the imposed angular velocity Ω is such that $\Omega/\theta = 5 s^{-1}$ well beyond the Newtonian branch into the plateau, the system apparently satisfied this boundary condition by sampling a spectrum of shear rates. The local shear rate at the top stationary plate was smaller than 1/6 of the prescribed value of 5 s^{-1} , whereas the local shear rate at the rotating cone essentially doubled from 5 to 10 s^{-1} .

Equally interesting and important, the velocity profile evolved over time. Corresponding to the characteristic times indicated in Fig. 2(a), we found that the velocity gradient was initially constant across the gap up to the

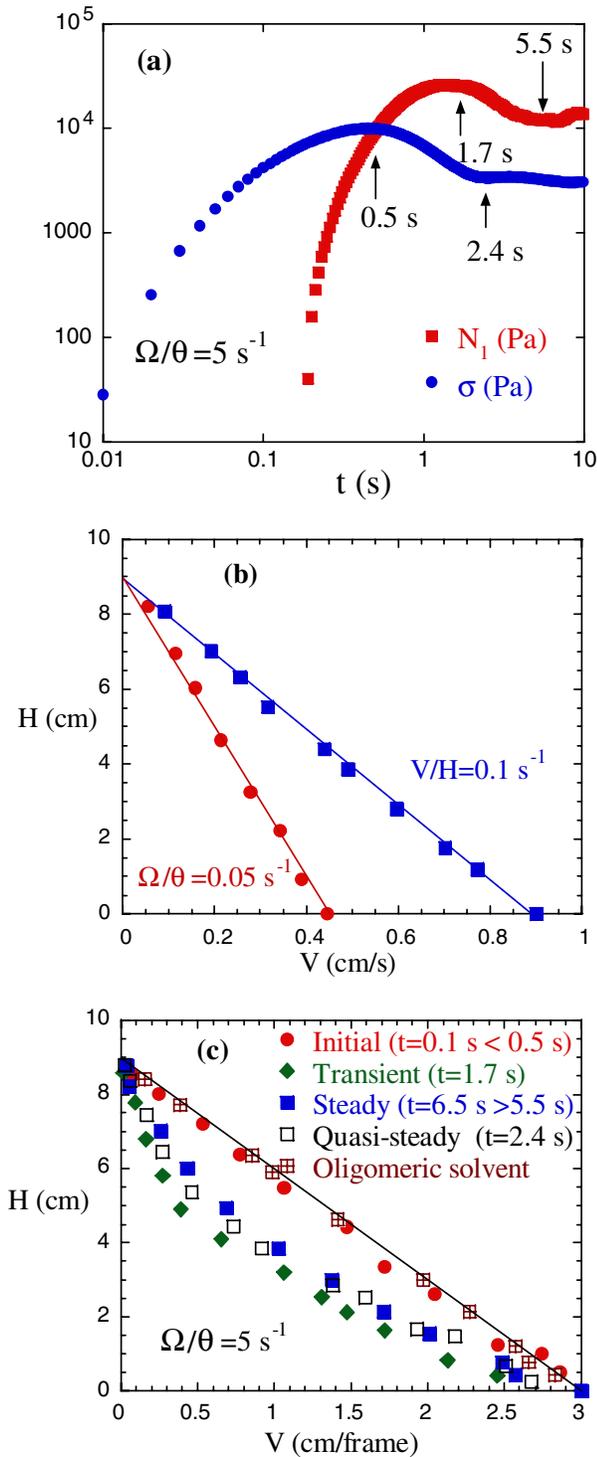


FIG. 2 (color online). (a) Growth upon startup shear at shear rate 5 s^{-1} of both shear and normal stresses (σ and N_1 , respectively). The velocity profiles of the well-entangled 10% PBD solution (b) for shear rates 0.05 and 0.1 s^{-1} at any time, where the straight lines indicate linear profiles, and (c) for shear rate 5 s^{-1} , at initial (circles), transient (diamonds), quasisteady state (open squares), and steady state (squares), as measured on the video monitor where the frame rate is 15 frames per second. The velocity profile for the pure oligomeric solvent, which is a Newtonian liquid, was also depicted in the plus-filled squares.

point of the stress maximum, i.e., up to $t = 0.5 \text{ s}$. The maximum deviation from this linear velocity profile occurred around the maximum of N_1 , i.e., at around $t = 1.7 \text{ s}$. The eventual steady state possessed a weaker non-linear profile, as shown in Fig. 2(c), which was not reached until after N_1 had stabilized at 5.5 s . In other words, the profile was still evolving at $t = 2.4 \text{ s}$ when the shear stress σ had already stabilized.

Apart from these explicit rheological and PTV measurements in Fig. 2, it is helpful to get a direct visual impression of the variations of the velocity profile across the gap with time. Figure 3 shows three snapshots of the particle movements for a shear rate of $\Omega/\theta = 10 \text{ s}^{-1}$ as seen from the gap at three characteristic times corresponding to initial, transient, and steady states. The exposure time of our CCD camera is $\Delta t = 1/60 \text{ s}$. From the length Δx of the streak generated by the moving light-scattering particle, we can compute the speed of the particle according to $V = \Delta x/\Delta t$. Thus, the streak length is directly proportional to the particle speed V since Δt is fixed during the video recording. The three pictures clearly show different streak length variations along the gap, indicating different velocity profiles similar to those measured in Fig. 2 for 5 s^{-1} at the different times. In real time, it is easy to watch the particle motion at a lower shear rate of $\Omega/\theta = 2.5 \text{ s}^{-1}$ as Movie 1 on our website [33].

In summary, we applied an in-house-developed particle tracking velocimetric method along with the standard rheometric techniques to elucidate the flow responses of entangled polymer solutions in a commonly employed shear device of a cone plate. Specifically, the particle tracking velocimetric observations directly indicate that the velocity profile was nonlinear in the gap between the cone and plate when sheared in the stress plateau region. In contrast, there was no shear rate gradient in the initial state of high shear, when sheared in the Newtonian region and for a Newtonian fluid. While this result is consistent with the earlier report of a chain entanglement-disentanglement transition [30] in shear flow of the same materials [34], it cannot be explained by simply invoking the abandoned feature [12] of the Doi-Edwards theory, because a non-

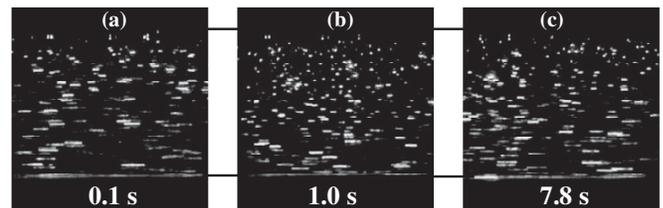


FIG. 3. Still pictures from video recording of the illuminated moving particles at (a) initial ($t = 0.1 \text{ s}$), (b) transient ($t = 1.0 \text{ s}$), and (c) steady ($t = 7.8 \text{ s}$) states for an imposed apparent shear rate of $\Omega/\theta = 10 \text{ s}^{-1}$, where the distance between the two horizontal lines H is again about 0.9 mm . Only the particles in focus yield the brightest spots and streaks.

monotonic constitutive curve could allow only two values of shear rate to coexist across the gap. The smooth distribution of a spectrum of shear rates observed in the imposed velocity mode reflects the fact that our sample is now rather polydisperse in terms of the molecular weight distribution of long PBD chains.

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- [1] J. D. Ferry, *Viscoelastic Properties of Polymers* (Wiley, New York, 1980), 3rd ed.
- [2] M. Doi and S. F. Edwards, *The Theory of Polymer Dynamics* (Clarendon, Oxford, 1988), 2nd ed.
- [3] W. W. Graessley, *Adv. Polym. Sci.* **16**, 1 (1974).
- [4] R. A. Stratton, *J. Colloid Interface Sci.* **22**, 517 (1966).
- [5] M. H. Wagner and J. Meissner, *Macromol. Chem. Phys.* **181**, 1533 (1980).
- [6] C. L. Lee, K. E. Polmanteer, and E. G. King, *J. Polym. Sci., A-2, Polym. Phys.* **8**, 1909 (1970).
- [7] J. D. Huppler *et al.*, *Trans. Soc. Rheol.* **11**, 181 (1967).
- [8] R. L. Crawley and W. W. Graessley, *Trans. Soc. Rheol.* **21**, 19 (1977).
- [9] E. V. Menezes and W. W. Graessley, *J. Polym. Sci., Polym. Phys. Ed.* **20**, 1817 (1982).
- [10] M. Bercea, C. Peiti, B. Simionescu, and P. Navard, *Macromolecules* **26**, 7095 (1993). The 2% solution in this paper appears to be off by a factor of 10 in terms of its viscosity in comparison with that of the 6% solution. Since the plateau stress values are reasonable for both solutions, it seems that the molecular weight in the 2% solution is only half of that in the 6% solution.
- [11] C. Pattamaprom and R. G. Larson, *Macromolecules* **34**, 5229 (2001).
- [12] M. Doi and S. F. Edwards, *J. Chem. Soc. Faraday Trans. II* **75**, 38 (1979), where the first proposal was made to relate the predicted stress maximum to the capillary flow instability (often known as spurt flow).
- [13] T. C. B. McLeish and R. C. Ball, *J. Polym. Sci., Part B: Polym. Phys.* **24**, 1735 (1986). This work followed the idea put forward in Ref. [12] to offer a constitutive explanation for the spurt effect that was later proved to be interfacial in origin [see X. Yang *et al.*, *Rheol. Acta* **37**, 415 (1998)], which was the only flow discontinuity observed in polymers up until our previous work described in Ref. [30].
- [14] M. E. Cates, T. C. B. McLeish, and G. Marrucci, *Europhys. Lett.* **21**, 451 (1993).
- [15] G. Marrucci, *J. Non-Newtonian Fluid Mech.* **62**, 279 (1996).
- [16] D. W. Mead, R. G. Larson, and M. Doi, *Macromolecules* **31**, 7895 (1998).
- [17] S. T. Milner, T. C. B. McLeish, and A. E. Likhtman, *J. Rheol. (N.Y.)* **45**, 539 (2001).
- [18] G. Marrucci and G. Ianniruberto, *Phil. Trans. R. Soc. A* **361**, 677 (2003).
- [19] R. S. Graham, A. E. Likhtman, T. C. B. McLeish, and S. T. Milner, *J. Rheol. (N.Y.)* **47**, 1171 (2003), and references therein.
- [20] Mooney appeared to be the inventor of this cone-plate geometry: M. Mooney and R. H. Ewart, *Physics (N.Y.)* **5**, 350 (1932).
- [21] G. G. Fuller, *Optical Rheometry of Complex Fluids* (Oxford University Press, New York, 1995).
- [22] M. K. Endoh, S. Saito, and T. Hashimoto, *Macromolecules* **35**, 7692 (2002).
- [23] K. Krishnan *et al.*, *Langmuir* **18**, 9676 (2002).
- [24] J. Bent *et al.*, *Science* **301**, 1691 (2003).
- [25] R. H. Somani *et al.*, *Macromolecules* **35**, 9096 (2002).
- [26] D. E. Smith, H. P. Babcock, and S. Chu, *Science* **283**, 1724 (1999).
- [27] C. M. Schroeder *et al.*, *Science* **301**, 1515 (2003).
- [28] D. E. Smith and S. Chu, *Science* **281**, 1335 (1998).
- [29] T. T. Perkins, D. E. Smith, and S. Chu, *Science* **276**, 2016 (1997).
- [30] P. Tapadia and S. Q. Wang, *Phys. Rev. Lett.* **91**, 198301 (2003); *Macromolecules* **37**, 9083 (2004).
- [31] A. Philips and S. Q. Wang, *J. Polym. Sci., Part B: Polym. Phys.* **42**, 4132 (2004).
- [32] P. Tapadia and S. Q. Wang (to be published).
- [33] Click Movie 2 at URL: <http://www3.uakron.edu/rheology/>. Both Movies 1 and 2 show that the top third layer of particles initially moved faster in the left-hand-side direction and then slowed down. This visual impression is explicitly demonstrated in Fig. 2(c).
- [34] Thomas Y. Hu (private communication). We have not ruled out whether there is a sufficient shear stress gradient in a cone-plate cell to produce the observed inhomogeneous shear in a highly shear thinning sample.