Role of Electrostatic Interactions in Shear Banding of Entangled DNA Solutions

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Whether entangled polymers exhibit shear banding is an issue that has seen a revival of scrutiny.[1−3] An apparently convincing case of steady state shear banding has been reported recently for an entangled DNA solution.[4] Unlike conventional polymer solutions where edge distortion[5] makes it difficult to ascertain whether shear banding is a genuine bulk property, the DNA solution behaved well up to very high shear rates without noticeable edge distortion or rod climbing. In this report we aim to identify the microscopic mechanism for the shear banding in DNA solutions.

The model system consists of a linear double strand DNA (dsDNA) calf thymus with a weight-average molecular weight of 50×10^6 g/mol or 7.5×10^4 base pairs (bp) (USB Co., used as received). The persistence length of this DNA chain was not measured. The persistence length of a double strand T4 DNA ranges from 67 nm at 0.01 M to 41 nm at 0.5 M NaCl.[6] DNA solutions of 1 and 1.5 wt % were prepared by dissolving the DNA in an aqueous buffer containing 10 mM Tris-HCl (pH 7.9), 0.2 mM EDTA, and 0.01−0.5 M NaCl at room temperature. 200 ppm of glass microspheres with a diameter of 10 μm (Whitehouse Scientific, UK) was dispersed in the solution as tracers. Velocity profiles were measured in a Couette setup[7] at $T = 23$ °C.

Some equilibrium properties of the samples derived from the small amplitude oscillatory test are listed in Table 1. The terminal relaxation time τ is taken from the G' and G'' crossover frequency (Figure 1). The plateau modulus G_p is taken from the G' at the frequency where G'' is minimum. The entanglement number Z is calculated using $Z = M_w/M_e(C)$. Here the entanglement molecular weight M_e is estimated using $M_e(C) = CRT/G_p(C)$, where C, R, and T are the concentration, gas constant, and temperature, respectively.

For the 1% DNA solution with 0.01 M NaCl (denoted as 1% DNA/0.01 M NaCl), the velocity profiles in Figure 2a indicate shear banding in both transient and steady states. For a similar solution with the same 1% DNA but with a much higher NaCl concentration of 0.5 M (denoted as 1% DNA/0.5 M NaCl), the velocity profile is also banded at $t < 0.8$ s, but it becomes largely linear after the stress undershoot and remains so as the stress evolves to the steady state. There is no steady state shear banding for this solution despite transient banding. We have ascertained the absence of steady state banding within $0.1 \leq \dot{\gamma}_{app} \leq 1000$ s^{-1} (Figure 2c).

Figure 3 shows global (directly measured by the rheometer) and local (extracted from the local velocity profiles[8]) flow curves for the 1% DNA solutions. For 1% DNA/0.01 M NaCl, the local flow curve is much more accurate since the global curve is compromised by flow inhomogeneity (Figure 2a) and wall slip at low shear rates detected by velocity profiles (not shown). For 1% DNA/0.5 M NaCl, the global curve should be reasonably accurate since there is little wall slip and bulk flow inhomogeneity in steady state (Figure 2c). The flow curve for 1% DNA/0.01 M NaCl is much flatter than that for 1% DNA/0.5 M NaCl.

Similar trends in shear banding behavior with salt concentration are observed for the 1.5% DNA solutions as shown in Figure 4a,b. For the solution with a low salt concentration of 0.01 M NaCl, the velocity profile is banded with a sharp interface between the high and low flow regimes. In sharp contrast, for the solution with 0.5 M NaCl, the velocity profile is smoothly curved without distinctive flow regimes that characterize shear banding. The local flow curve extracted from the velocity profile is flat or discontinuous for the sample with 0.01 M NaCl whereas it is monotonic for that with 0.5 M NaCl solution (not shown). We have also verified that there is no steady state shear banding in the shear rate range $10 \leq \dot{\gamma}_{app} < 1000$ s^{-1} for the latter solution.

One interpretation of steady state shear banding involves a nonmonotonic constitutive relation.[9−11] For entangled polymer chains, the microscopic mechanism causing a flow curve with a nonmonotonic constitutive relation may be the (excessive) chain alignment. Transient banding, on the other hand, does not require a nonmonotonic constitutive relation as observed here for 1% DNA/0.01 M NaCl and elsewhere.[1,3,8] It has been argued as a result of *temporary* excessive chain alignment.[8] (Another proposed mechanism calls for elastic breakdown of chain entanglement network.[12]) Chain alignment can be enhanced by the increase of entanglement number since a larger entanglement number diminishes the effect of chain-end fluctuations. For charged and semiflexible chains such as DNAs and ionic micelles, electrostatic interactions and excluded volume effects may also enhance chain alignment. An important question then is whether sufficiently large entanglement alone can cause a nonpositive stress slope or there must be other alignment enhancing factors.

The observation that permanent banding occurs in 1% DNA/0.01 M NaCl having a smaller entanglement number of 65 but

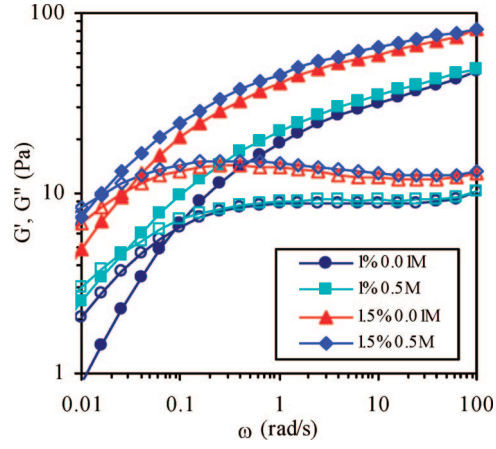

Figure 1. Storage and loss moduli G' and G'' vs angular frequency for the DNA samples measured by the small-amplitude oscillatory test. The strain is fixed at 5%. Closed and open symbols represent G' and G'', respectively.

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Table 1. Equilibrium Properties of the DNA Solutions

C_{DNA} (wt %)	C_{NaCl} (M)	τ (s)	G_p (Pa)	M_e (kg/mol)	Z
1	0.01	11	31.8	774	65
1	0.5	38	35.2	699	72
1.5	0.01	36	65.7	562	89
1.5	0.5	67	71.7	515	97

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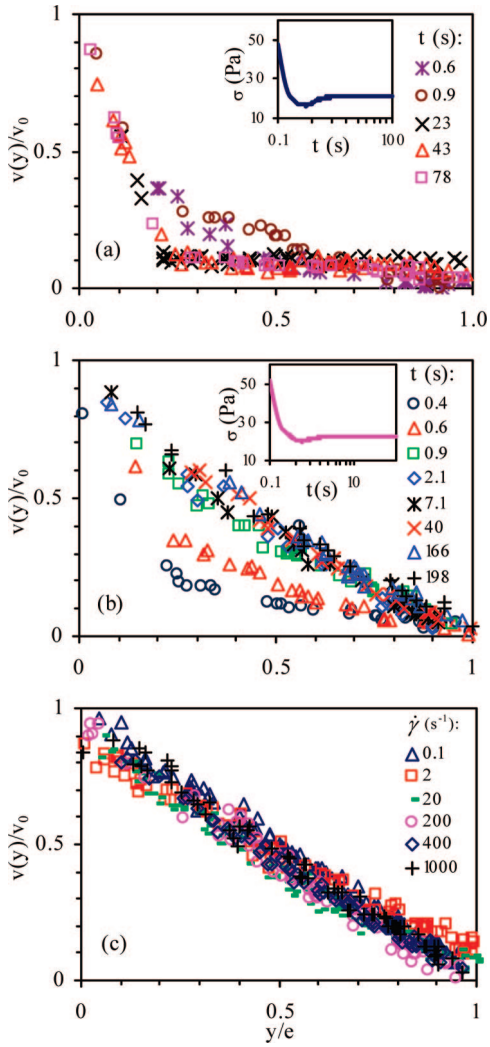

Figure 2. (a) Velocity profiles across the Couette flow cell gap for 1% DNA /0.01 M NaCl at $\dot{\gamma}_{app} = 100\ s^{-1}$. The inset shows the stress curve. (b) Velocity profiles for 1% DNA/0.5 M NaCl at $\dot{\gamma}_{app} = 100\ s^{-1}$. The inset shows the transient stress curve. (c) Steady state profiles for 1% DNA/0.5 M NaCl in the shear rate range $0.1 \leq \dot{\gamma}_{app} \leq 1000\ s^{-1}$.

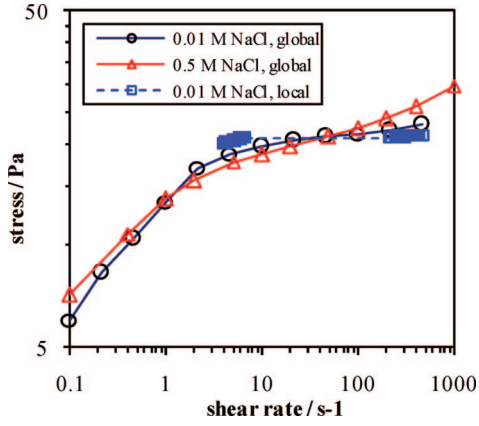

Figure 3. Global and local flow curves for the 1% DNA solutions with 0.01 and 0.5 M NaCl.

not in 1.5% DNA/0.5 M NaCl having a much larger entanglement number of 97 suggests that the large entanglement alone is not sufficient to cause the shear banding. The Debye screening length for the former solution is 3 nm, which is much larger than the Bjerrum length (distance at which the electrostatic interaction is comparable to thermal energy, k_BT) of 0.7 nm,

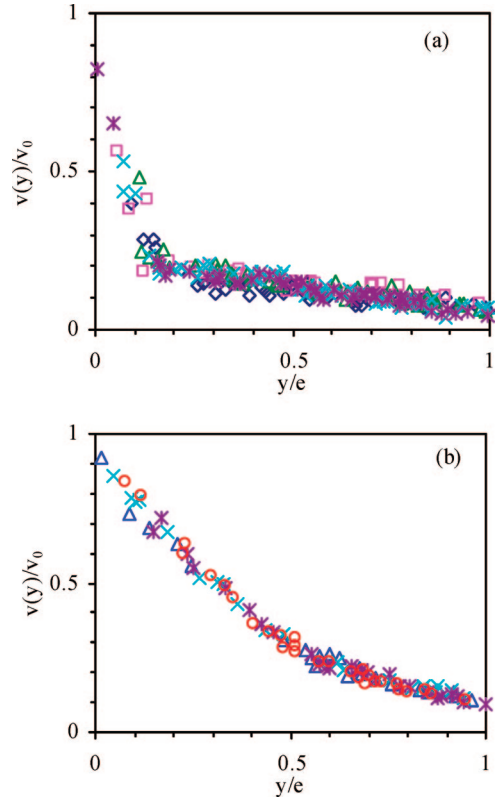

Figure 4. Long time velocity profiles for the 1.5% DNA solutions with (a) 0.01 M NaCl and (b) 0.5 M NaCl at $\dot{\gamma}_{app} = 200\ s^{-1}$.

suggesting electrostatic interactions are significant compared with thermal diffusion. On the contrary, the Debye length for 1.5% DNA/0.5 M NaCl is only 0.4 nm, being smaller than the Bjerrum length. Thus, we speculate that the electrostatic interaction in 1% DNA/0.01 M NaCl enhances chain alignment and is more critical to the shear banding. The very small viscosity of 0.05 Pa·s in the high shear band suggests some nematic order, which is perhaps made possible by the electrostatic repulsions and chain stiffness. The role played by the electrostatic interactions might explain why steady state banding has been often reported in charged and/or rigid chain systems such as micelles,[7,8,13−18] semiflexible polymers,[19] and liquid crystals.[20]

In conclusion, for the first time we have assessed the effects of entanglement and electrostatic interactions by studying systems with different entanglement numbers and electrostatic interactions for DNA systems. Our key observation that the system with a much smaller entanglement number Z but significant electrostatic interactions exhibits steady shear banding whereas the sample with a much larger Z but screened electrostatic interactions does not suggests that the chain alignment enhanced by the electrostatic interactions as the critical mechanism for the steady shear banding observed in our DNA solutions.

References and Notes

(1) Tapadia, P.; Ravindranath, S.; Wang, S. Q. *Phys. Rev. Lett.* **2006**, *96*, 016001.
(2) Ravindranath, S.; Wang, S. Q.; Ofechnowicz, M.; Quirk, R. P. *Macromolecules* **2008**, *41*, 2663.
(3) Hu, Y. T.; Wilen, L.; Philips, A.; Lips, A. *J. Rheol.* **2007**, *51*, 275.
(4) Boukany, P. E.; Hu, Y. T.; Wang, S. Q. *Macromolecules* **2008**, *41*, 2644.
(5) Schweizer, T.; Stockli, M. *J. Rheol.* **2008**, *52*, 713.
(6) Makita, N.; Ullner, M.; Yoshikawa, K. *Macromolecules* **2006**, *39*, 6200.
(7) Hu, Y. T.; Lips, A. *J. Rheol.* **2005**, *49*, 1001.

(8) Hu, Y. T.; Palla, C.; Lips, A. *J. Rheol.* **2008**, *52*, 379.
(9) Spenley, N. A.; Cates, M. E.; McLeish, T. C. B. *Phys. Rev. Lett.* **1993**, *71*, 939.
(10) McLeish, T. C. B.; Ball, R. C. *J. Polym. Sci., Part B: Polym. Phys.* **1986**, *24*, 1735.
(11) Olmsted, P. D.; Radulescu, O.; Lu, C. Y. D. *J. Rheol.* **2000**, *44*, 257.
(12) Wang, S. Q.; Ravindranath, S.; Wang, Y. Y.; Boukany, P. Y. *J. Chem. Phys.* **2007**, *127*, 064903.
(13) Becu, L.; Manneville, S.; Colin, A. *Phys. Rev. Lett.* **2004**, *93*, 018301.
(14) Fischer, E.; Callaghan, P. T. *Phys. Rev. E* **2001**, *64*, 011501.
(15) Mair, R. W.; Callaghan, P. T. *Europhys. Lett.* **1996**, *36*, 719.
(16) Makhloufi, R.; Decruppe, J. P.; Ait-Ali, A.; Cressely, R. *Europhys. Lett.* **1995**, *32*, 253.
(17) Miller, E.; Rothstein, J. P. *J. Non-Newtonian Fluid Mech.* **2007**, *143*, 22.
(18) Salmon, J. B.; Colin, A.; Manneville, S.; Molino, F. *Phys. Rev. Lett.* **2003**, *90*, 228303.
(19) van der Gucht, J.; Lemmers, M.; Knoben, W.; Besseling, N. A. M.; Lettinga, M. P. *Phys. Rev. Lett.* **2006**, *97*, 108301.
(20) Pujolle-Robic, C.; Noirez, L. *Nature (London)* **2001**, *409*, 167.

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