12-2009

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Recommended Citation

Boukany, Pouyan E. and Wang, Shi-Qing, "Nature of Steady Flow in Entangled Fluids Revealed by Superimposed Small Amplitude Oscillatory Shear" (2009). *College of Polymer Science and Polymer Engineering*. 99.
http://ideaexchange.uakron.edu/polymer_ideas/99

Nature of steady flow in entangled fluids revealed by superimposed small amplitude oscillatory shear

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(Received 28 April 2009; final revision received 17 August 2009)

Synopsis

We carry out a systematic investigation into steady-state shear behavior of six entangled solutions based on a superposition of continuous shear and small amplitude oscillatory shear (SAOS). During steady shear in the shear thinning regime, the superimposed SAOS frequency sweep measurements reveal characteristics of viscous liquids, e.g., terminal dynamics, on the experimental time scale of the reciprocal shear rate. The residual entanglement network retains the same level of elastic stiffness as the equilibrium system does. Consistent with the convective constraint release idea, chains in the network are forced to pass around each other as they must do so to undergo steady flow. When such a sample is examined at significantly short time scales, chains are unable to pass around and the signature of this residual entanglement is that the storage modulus is greater than the loss modulus at higher frequencies than the applied shear rate. The particle-tracking velocimetric observations confirm that whether shear banding is present or not does not affect the basic "terminal flow" character revealed by the superimposed SAOS. © *2009 The Society of Rheology.* [DOI: 10.1122/1.3236523]

I. INTRODUCTION

Continuous shear and oscillatory shear are two commonly employed protocols to investigate rheological properties of complex fluids such as granular matters, suspensions, colloids, emulsions, foams, liquid crystals, surfactant aggregates, and polymers [Larson (1999); Wyss *et al.* (2007)]. One key issue to address in the field of rheology of viscoelastic materials is to understand how these materials arrive at their final steady-state flow. For entangled polymeric liquids, a major task is to explain observed rheological phenomena such as shear thinning in terms of the state of chain entanglement.

Linear viscoelastic (LVE) properties of entangled polymeric liquids appear to be well described by combination of the reptation idea of de Gennes and Doi–Edwards tube model [Doi and Edwards (1986)]. The most common way to measure the LVE properties is to perform small amplitude oscillatory shear (SAOS) and measure storage modulus $G'(\omega)$ and loss modulus $G''(\omega)$ as a function of frequency ω. For monodisperse systems, the reptation time τ can be shown to be within 2% from the inverse of ω_c, for which $G'(\omega_c)=G''(\omega_c)$ [Doi and Edwards (1986)]. It is also useful to superimpose such an SAOS upon a steady shear flow [Ferry (1980)]. Commercial rotational rheometers have an option to enable such a combination. This approach was first applied by Osaki *et al.*

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(1965) on polymer solutions such as polystyrene in toluene, poly-(methyl methacrylate), and poly (n-butyl acryalte) in diethyl phthalate. Similar measurements were subsequently performed of other polymer solutions including ethylene-propylene copolymer [Booij (1966a, 1966b)], polyisobutylene [Tanner and Simmons (1967); Macdonald (1973); Isayev and Wong (1988)], poly-(ethylene oxide) [Laufer *et al.* (1975a, 1975b); Powell and Schwarz (1975)], aqueous polyacrylamide [Vlastos *et al.* (1997)], associative polymers [Tirtaatmadja *et al.* (1997); Mewis *et al.* (2001)], worm-like micellar solutions [Anderson *et al.* (2006)], and polyethylene and isotactic-polypropylene melts [Kataoka and Ueda (1969); Costello (1997); Somma *et al.* (2007)]. All of these studies were made with the implicit assumption that the steady flow involves homogeneous shear.

Recent studies by a combination of particle tracking velocimetric (PTV) and rheometric measurements revealed that entangled fluids may undergo inhomogeneous shear in the form of either interfacial wall slip or bulk shear banding for Weissenberg number Wi $=\dot{\gamma}\tau > 1$ [Boukany *et al.* (2008); Ravindranath and Wang (2008a, 2008b); Boukany and Wang (2009a, 2009b)]. Such inhomogeneous shear in steady state would make it difficult to interpret the characteristics of the superimposed SAOS. The shear banding occurs apparently because well-entangled polymeric liquids, though initially uniform, are unable to undergo yielding in a homogeneous manner. The signature for yielding shows up in the form of a shear stress overshoot during suddenly started simple shear [Wang *et al.* (2007); Wang and Wang (2009)]. More detailed studies of the scaling characteristics associated with the yield point have been carried out [Ravindranath and Wang (2008c), Boukany *et al.* (2009)]. It was shown that yielding indeed occurs beyond the stress overshoot because the elastic recovery can no longer be 100% beyond the shear stress maximum.

In the present work, we have carried out systematic parallel superposition and PTV measurements on several entangled DNA and polybutadiene (PBD) solutions with different entanglements per chain Z=13–155 in various flow conditions involving either uniform flow or shear banding. Most of SAOS superposition measurements were obtained from the non-shear-banding systems to avoid difficulty in interpretation although the features of SAOS are not even quantitatively different for the same sample that suffers shear banding.

II. EXPERIMENT

A. Materials

Six entangled solutions based on DNA and PBD are investigated in this work. The DNA solutions were made by dissolving 0.5–2.2 wt % of DNA (75 kbp $\sim 50 \times 10^6$ g/mol, USB Co., which is not monodisperse) in a glycerol (Fluka). They are the same materials and prepared in the same way as described previously [Boukany and Wang (2009a, 2009b)]. The PBD based solutions were prepared by dissolving 5 and 10 wt % PBD ($M_w = 0.75 \times 10^6$ g/mol, $M_n = 0.74 \times 10^6$ g/mol, Bridgestone-America) in low molecular-weight PBD of $M_w = 1.8$ K (Aldrich, Cat. No. 20,043-3, which has a significantly higher T_g and thus is rather sluggish) and 9.0 K g/mol (Bridgestone-America) respectively, and 10 wt % PBD ($M_w = 1.052 \times 10^6$ g/mol, $M_n = 1.014 \times 10^6$ g/mol, Quirk's Laboratory, Akron, USA) in a PBD solvent with $M_w = 15.0$ Kg/mol. More details on the sample preparation of these PBD solutions can be found in Ravindranath and Wang (2008a, 2008b).

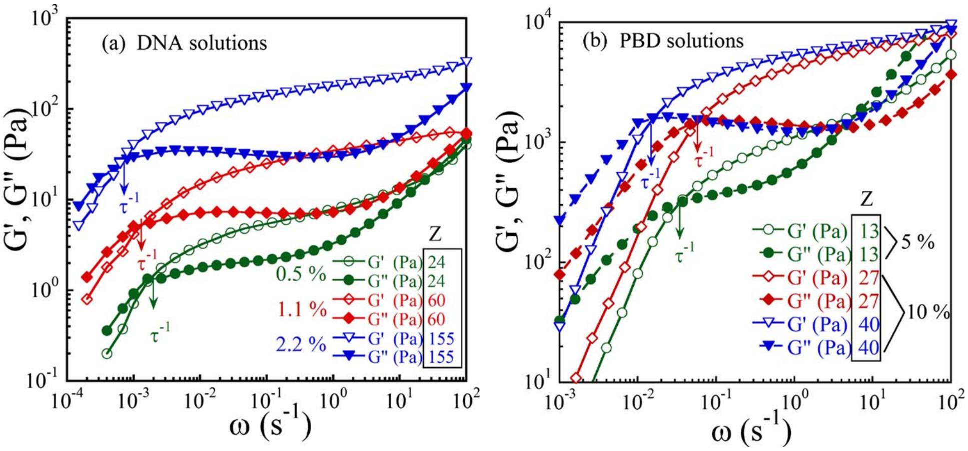

FIG. 1. Storage and loss moduli G' and G'' as a function of frequency ω from SAOS measurements in quiescence. (a) 0.5–2.2 % DNA solutions in glycerol with Z from 24 to 155. (b) PBD solutions: 5.0% PBD(0.7M)-1.8K, 10% PBD (0.7M)-9K, and 10%PBD (1.0M)-15K whose Z are from 13 to 40.

B. Methods

1. LVE measurements in quiescence

Rheological measurement was carried out on the controlled-stress rheometer (Physica MCR-301, Anton Paar, USA). This is a multifunctional rheometer that can perform in both controlled-torque (CS) and controlled-displacement (CR) mode. The rheometer is equipped with a cone of 2° angle and diameter of 25 mm. SAOS measurements were first carried out. Figures 1(a) and 1(b) show storage and loss moduli G' and G'' at $\gamma=5\%$ for both the DNA and PBD solutions at different concentrations in absence of continuous shear. The shapes of G' and G'' in Fig. 1(a) reveal that the DNA is not monodisperse. The characteristics of these samples based on the SAOS measurements are listed Tables I and II, where the plateau modulus G_{pl} is estimated from the value of G' at the frequency where G'' shows a minimum and the crossover modulus $G_c=G'(\omega_c)=G''(\omega_c)$. The terminal relaxation time τ is estimated as $1/\omega_c$. The critical entanglement molecular weight $M_e(\phi)$ is estimated from the elastic plateau modulus G_{pl} according to $M_e(\phi)=CRT/G_{\mathrm{pl}}$, where C is the concentration, R the gas constant and, T temperature. Here G_{pl} is obtained as the value of G' at the frequency where G'' shows minimum. When there is no minimum in G'', we apply the well-established scaling law for the concentration dependence of $M_e(\phi)=\phi^{-1.2}M_e(\phi=1)$ to estimate $M_e(\phi)$ for a low concentration from that at a higher concentration, as previously done by Ravindranath and Wang (2008a) for PB solutions and Boukany and Wang (2009a) for DNA solutions. All measurements were carried out at room temperature ($T=24$ °C).

TABLE I. Characteristic properties of DNA solutions.

DNA solutions	G_{pl} (Pa)	G_c (Pa)	$M_e(\phi)$ (g/mol)	Z (ϕ)	τ (s)
0.5 wt % DNA (50M)/glycerol	5.8	1.4	2.1×10^{6}	24	512
1.1 wt % DNA (50M)/glycerol	32	5.3	0.84×10^{6}	60	780
2.2 wt % DNA (50M)/glycerol	169	26.1	0.32×10^{6}	156	1590

TABLE II. Characteristic properties of PBD solutions.

PBD solutions	G_{pl} (Pa)	G_c (Pa)	$M_c(\phi)$ (g/mol)	Z (ϕ)	τ (s)
5.0 wt % PBD (0.7M)/PBD (1.8K)	1766	324	54×10^3	13	29.8
10.0 wt % PBD (0.7M)/PBD (9K)	5490	1530	26×10^3	27	17.7
10.0 wt % PBD (1.0M)/PBD (15K)	6100	1570	27×10^3	40	65.5

2. Parallel superposition measurements

In the CS mode, the Physica rotational rheometer allows us to superimpose an oscillatory shear during a continuous shear. In this study, at first we imposed constant shear rate in CR mode to obtain the steady-state value of the shear stress. Then, the rheometer is switched to the CS mode at the same shear stress to maintain the same steady shear rate meanwhile a SAOS is superimposed. Figure 2 illustrates how Physica is programmed for the 0.5% DNA/glycerol solution to perform the mode switching experiment. For the superimposed oscillatory shear measurements in the CS mode, the peak value of the oscillatory shear stress is chosen to produce a strain amplitudes γ in the range from 1% to 40% as the sweeping frequency decreases from high to low values, so that the superimposed SAOS is not expected to perturb the state of chain configurations produced by the steady continuous shear.

For 10 wt % PBD (0.7 M)-9.0 K and 10 wt % PBD (1.0 M)-15 K solutions, a stationary plastic film is wrapped around the meniscus to prevent edge instability and sample loss during steady shearing. Oscillatory frequency sweep tests from $\omega=100$ to 0.1 s^{-1} are performed after each steady-shear experiment to evaluate whether appreciable edge fracture had occurred or not. If a noticeable decrease of storage and loss moduli G' and G'' is observed after prolonged shearing, a fresh sample is loaded. Without wrapping a film, it is impossible to approach steady state for the 10 wt % entangled PBD solutions. In

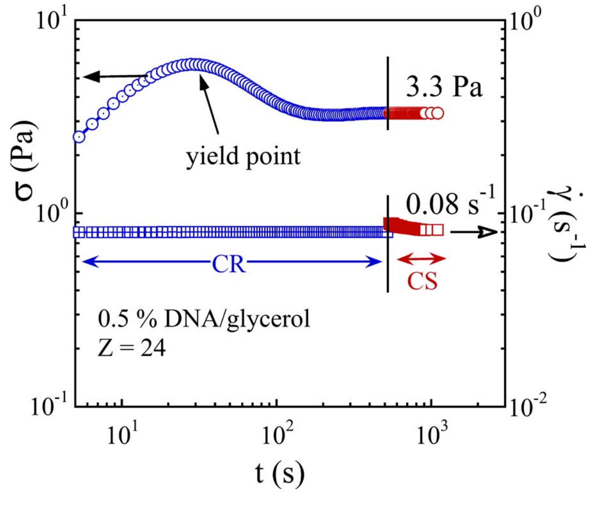

FIG. 2. Non-stop switching from CR measurements at $\dot{\gamma}=0.08$ s^{-1} to CS measurements at $\sigma=3.3$ Pa for the 0.5% DNA/glycerol solution.

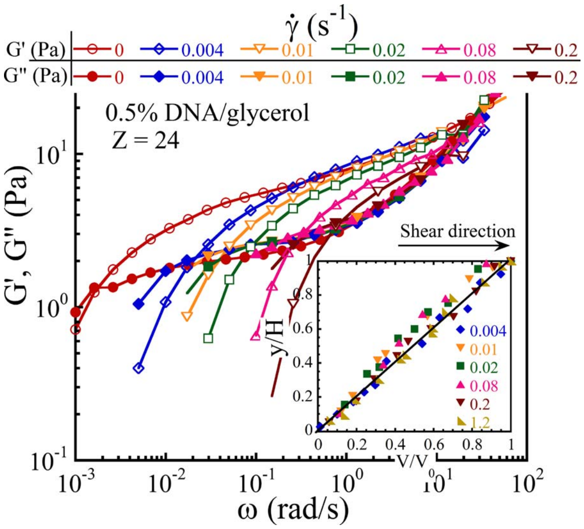

FIG. 3. The frequency dependences of G' and G'' from superimposed SAOS at different shear rates $\dot{\gamma}=0.004\sim0.2$ s^{-1}. Inset shows the PTV measurements of the normalized steady-state velocity profiles during startup shear at these applied shear rates.

DNA-based solutions and 5% PBD (0.7 M)-1.8 K, all rheometric measurements were performed without the plastic film since negligible edge instability occurs during prolonged shear.

3. PTV

For PTV measurements, a cone and plate geometry with a 4° cone angle and diameter of 25 mm is employed. About 300–500 ppm wt % of silver-coated particles (Dantec Dynamic HGS-10 having a size range from 1 to 20 μm) are uniformly dispersed in the samples. The PTV observation plane is 3–4 mm from the meniscus. The details of PTV setup have been provided elsewhere [Boukany and Wang (2009a, 2009b)].

III. RESULTS AND DISCUSSSIONS

A. Viscoelastic state in non-shear-banding DNA solution (Z=24)

Our PTV observations have confirmed, consistent with a previous report of Boukany and Wang (2009a), that the 0.5% DNA/glycerol solution does not undergo shear banding because of its low concentration. So this sample serves as an ideal system to probe the state of viscoelasticity during steady shear in the shear thinning regime. Figure 3 shows that the crossover frequency $\omega_c(\dot{\gamma})$ systematically shifts with the imposed steady shear rate in the range from 0.004 to 0.2 s^{-1}. In particular, $\omega_c(\dot{\gamma}) < \dot{\gamma}$ implying that in the steady shear at any rate $\dot{\gamma}$, the system is flowing as if it is undergoing terminal flow. For example, at $\dot{\gamma}$=0.08 s^{-1}, the system has clearly transformed from its initial, equilibrium state of a fully entangled elastic network to an eventual homogeneously flowing liquid. At a Weissenberg number of 41, the entanglement network would have undergone 41 shear strain units of quasi-elastic deformation had the network not been forced to yield. In reality, the system yields as shown by the shear stress overshoot around γ_y=2.4 in Fig. 2. Beyond the yield point, flow (irrecoverable deformation) takes place. In other words, it is necessarily true that the condition of $\omega_c(\dot{\gamma}) < \dot{\gamma}$ emerges during steady-state homogeneous

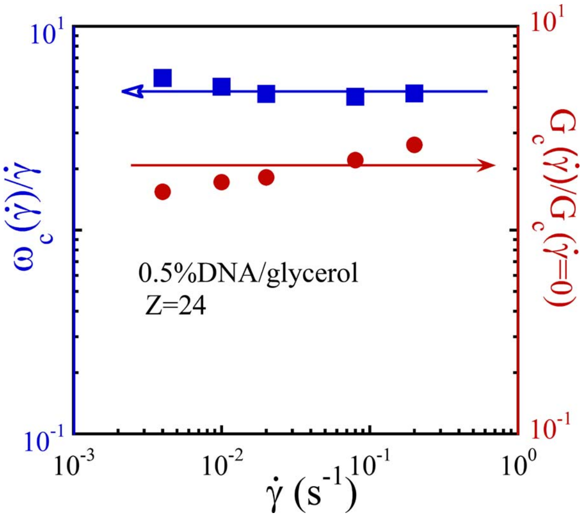

FIG. 4. The ratio $\omega_c(\dot{\gamma})/\dot{\gamma}$ is nearly a constant around 5 and $G_c(\dot{\gamma})$ only increases slightly with $\dot{\gamma}$.

shear. This condition is what we mean by *flow*. The inset of Fig. 3 indicates that the steady shear is essentially homogeneous.

Figure 4 confirms that $\omega_c(\dot{\gamma})$ increases approximately linearly with $\dot{\gamma}$ to make the ratio $\omega_c(\dot{\gamma})/\dot{\gamma}$ nearly a constant around 5 and $G_c(\dot{\gamma})$ hardly changes with $\dot{\gamma}$. The phenomenon is fully consistent with, and offers support for the idea of convective constraint release (CCR) [Marrucci (1996); Somma *et al.* (2007)]. It is of great significance that the level of $G_c(\dot{\gamma})$ remains approximately unaltered. This fact gives us penetrating insight into the essence of chain disentanglement. For example, it is inappropriate to think about chain disentanglement in terms of an increase in the critical molecular weight M_e such that $Z = M/M_e$ would be reduced. Z is at best a useful concept to depict the level of chain entanglement in quiescence.

There must not be chain entanglement during steady flow in the following sense. Entanglement is a concept to depict the fact that chains do not pass around one another until the molecular diffusion brings them out of each other's way. Loss of entanglement is simply a statement that chains are now able to pass around one another on some experimental time scale. When there is steady flow, the chains necessarily are being forced by external continuous deformation to pass around one another on the experimental time scale of the reciprocal $\dot{\gamma}$ as if their effective relaxation time $\tau_{\text{eff}}(\dot{\gamma}) \sim 1/\omega_c(\dot{\gamma})$ is shorter than $\dot{\gamma}$. Figure 4 shows that the effective Weissenberg number $\dot{\gamma}\tau_{\text{eff}}(\dot{\gamma})$ is around 1/5. On the other hand, when the steady-sheared sample is probed on time scales significantly shorter than the experimental time scale, it exhibits a similar level of elasticity, i.e., a magnitude of G' comparable to that of the equilibrium plateau modulus G_{pl}. In the other words, the stiffness of network remains the same when examined on a time scale, on which the chains are unable to move past one another.

B. Comparison between homogeneous vs. inhomogeneous shear

The DNA solution at 1.1 wt % concentration is more entangled than the 0.5 wt % solution studied in the preceding Sec. III A. In comparison, at a shear rate of 0.5 s^{-1}, strong shear banding occurs even in steady state as shown in the inset of Fig. 5(a). We have recently demonstrated [Boukany and Wang (2009c)] that with a gradual ramping-up

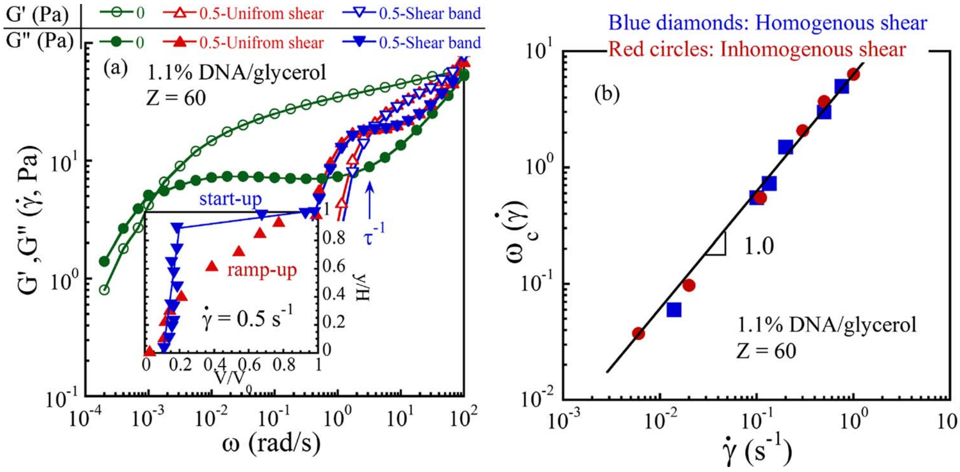

FIG. 5. (a) The frequency dependences of G' and G'' from superimposed SAOS onto a final shear rate $\dot{\gamma} = 0.5\ \mathrm{s}^{-1}$, which is produced by either a startup shear or a gradual rate ramp-up. Inset shows the PTV measurements of the normalized steady-state velocity profiles obtained either during startup shear or ramp-up shear. (b) The dependence of the crossover frequency $\omega_c(\dot{\gamma})$ as a function of $\dot{\gamma}$.

in the applied shear rate, a state of much reduced shear banding can be attained as shown in the inset of Fig. 5(a). For the different velocity profiles, the superimposed SAOS reveals identical characteristics as shown in Fig. 5(a). In other words, it is not possible to infer from Fig. 5(a) whether homogeneous shear prevails. Figure 5(b) summarizes similar superimposed SAOS results at other applied shear rates. Clearly, rheological characterizations alone are insufficient to delineate the state of flow in these entangled DNA solutions.

The results of Figs. 5(a) and 5(b) appear surprising at first sight. It seems reasonable that the apparent rheological response, as measured by the superimposed SAOS, may be dictated by the response of the high shear band. The more entangled portion of the sample, i.e., the low shear band, however, does still influence the overall rheological characteristics of the SAOS measurements. Actually, a model made of two Maxwell elements in series can be used to account for the insensitivity of ω_c to the state of shear deformation.

At sufficiently high shear rates close to the end of the stress plateau, uniform velocity profiles re-emerge across the gap after transient banding even in startup shear mode [Ravindranath and Wang (2008a); Boukany and Wang (2009a)]. This can be understood because at high enough rates, the system is no longer trapped in entanglement. The superimposed SAOS reveals in Fig. 6 for the 1.1 wt % DNA solution that at an applied shear rate of $3.5\ \mathrm{s}^{-1}$, the SAOS frequency sweep data no longer indicate any crossover between G' and G'', where the inset shows the normalized velocity profile that has a uniform velocity gradient in contrast to the inset of Fig. 5(a).

C. Superimposed SAOS results for non-shear-banding PBD solutions

To test the universality of the findings based on DNA solutions, we carry out similar experiments on three entangled PBD solutions: 5% PBD (0.7 M)-1.8 K, 10% PBD (0.7 M)-9 K, and 10% PBD (1.0 M)-15 K, where the level of entanglement Z ranges from 13 to 40. It has been reported previously that there is no wall slip and shear banding across the gap for these samples during steady shear due to the low level of entanglement and

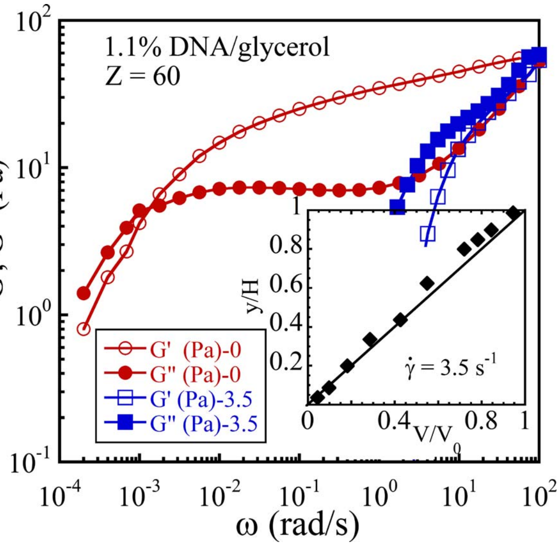

FIG. 6. $G'(\dot{\gamma})$ and $G''(\dot{\gamma})$ from the superimposed SAOS onto a sufficiently high shear rate of 3.5 s^{-1}, where all chain entanglements are lost and the system displays homogeneous shear as shown in the inset.

use of polymeric solvents [Ravindranath and Wang (2008a, 2008b)]. Figures 7(a) and 7(b) show the storage and loss moduli measured from the superimposed SAOS as a function of frequency at different imposed $\dot{\gamma}$ for 5% PBD (0.7M) and 10% PBD (0.7M), respectively. The insets confirm that uniform shear prevails across the sample thickness during steady shear for these entangled solutions.

Finally, the characteristics of these superimposed SAOS, e.g., the coordinates at the crossover point, $\omega_c(\dot{\gamma})$ and $G_c(\dot{\gamma})$, can be summarized in universal master curves for all entangled DNA and PBD solutions at different levels of chain entanglement. Specifically,

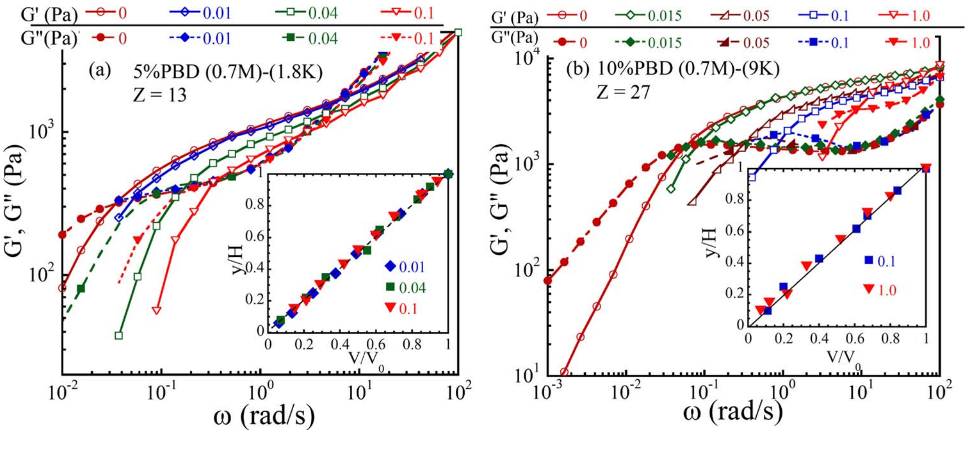

FIG. 7. The frequency dependences of G' and G'' from superimposed SAOS experiments for (a) 5.0% PBD(0.7M)-1.8K and (b) 10% PBD (0.7M)-9K. Insets show the normalized linear velocity profiles across the gap during shear at various representative shear rates of 0.1 and 1.0 s^{-1}.

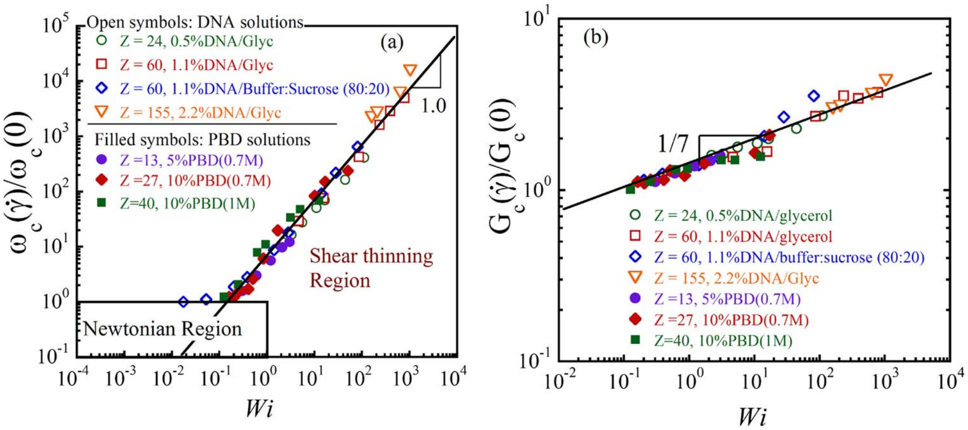

FIG. 8. Master curves depicting how the coordinates of the crossover point change in a universal way for all the entangled DNA and PBD solutions. (a) The linear increase of $\omega_c(\dot{\gamma})/\omega_c(0)$ as a function of Wi in shear thinning regime. (b) The gradual rise of $G_c(\dot{\gamma})/G_c(0)$ as a function of Wi with a slope of 1/7.

Fig. 8(a) shows the normalized crossover frequency $\omega_c(\dot{\gamma})/\omega_c(0)$ increases linearly with the Weissenberg number Wi. Moreover, $G_c(\dot{\gamma}\tau)/G_c(0)$ very gradually increases with Wi with a small slope of 1/7 as shown in Fig. 8(b).

IV. SUMMARY

The main purpose of this work is to gain insight into the nature of steady shear flow in entangled polymeric liquids. Apparently, the effect of the applied shear rate is simply to force chains to pass around one another without altering the stiffness of the residual entanglement network. When chains in one layer pass around each other at a different rate from chains in another layer, shear banding occurs. However, strikingly, the parallel superposition of SAOS was unable to reveal noticeable difference between a sample homogeneously sheared and the same sample that undergoes shear banding.

The frequency sweep of a SAOS superimposed upon steady homogeneous shear of both DNA and PBD solutions (with the number of entanglement per chain ranging from 13 to 156) shows that the equilibrium chain entanglement does not survive during steady shear. In other words, the state of flow is similar to a steady shear in the Newtonian regime, where the effective polymer relaxation time is shorter by a factor of 5 than the reciprocal shear rate. The feature is favorably consistent with the CCR idea advocated by Marrucci (1996) and Marrucci and Ianniruberto (2003).

For an entangled polymer liquid with an overall relaxation time τ, at a Weissenberg number Wi$=\dot{\gamma}\tau \gg 1$, a sudden startup shear must cause it deform elastically at the beginning when no chains can pass around one another, i.e., chain entanglement is initially intact. In other words, in response to the externally imposed fast shear, the "liquid" initially undergoes deformation elastically, i.e., without chains passing by each other. Eventually, the dynamic strength of the entanglement network is overcome and the system yields. The signature of yielding is the shear stress overshoot, beyond which the chains are forced, during the continuing external deformation, to move past one another [Wang and Wang (2009)]. It is in this sense that the chains have lost entanglement due to CCR and flow has occurred. In other words, some entanglement is lost whenever the chains spend less time passing around one another than they do in equilibrium. The less time they spend, the more disentanglement occurs relative to the full entanglement seen in equilibrium.

ACKNOWLEDGMENT

This work is supported, in part, by a grant (Grant No. DMR-0821697) from the National Science Foundation.

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