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Interfacial Flow Behavior of Highly Entangled Polybutadiene Solutions

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ABSTRACT: Strong flow behavior of entangled polymer solutions is investigated to illustrate a correlation between linear viscoelastic properties and interfacial slip flow behavior. It is found that entangled polybutadiene (PBD) solutions (made of 1,4-PBD and oligomeric BD of varying vinyl contents) exhibit an *interfacial stick−slip transition* at a critical stress about one-third of their plateau modulus. The magnitude of the transition, as quantified by the extrapolation length b, depends strongly on the level of chain entanglement which is determined by the concentration ϕ and reflected in the magnitude of the solution viscosity η. Analogous to the case of polymer melts, the experimental data reveal the same molecular weight dependence for b as that for η measured at a constant stress. The ϕ dependence of b is universal in the sense that its scaling behavior $b \propto \phi^3$ holds independently of temperature and the vinyl content of oligomeric BD solvent. The ϕ dependence of η is however more complicated because it depends on the segmental friction coefficient $\zeta(\phi,T)$ besides the tube diameter $a(\phi)$.

I. Introduction

Linear viscoelastic properties of highly entangled polymer solutions can be understood in terms of the classical reptation theory of de Gennes[1] and Doi and Edwards.[2] The simplification of using a tube to describe the chain entanglement restraint works equally well for solutions and melts. The effect of introducing a diluent into an entangled polymer melt is twofold: (a) dilating the tube so that the tube diameter $a(\phi)$ increases with lowering concentration ϕ; (b) modifying the segmental friction coefficient $\zeta(\phi,T)$ when the diluent has a higher glass transition temperature. The tube dilation can be viewed as the solution having a larger critical molecular weight $M_e(\phi)$ for chain entanglement where M_e increases with decreasing ϕ. The concentration dependence of $\zeta(\phi,T)$ is usually not present for common low molar mass solvents that have very low glass transition and crystallization temperatures. This is not true in the present case.

Fast flow behavior of highly entangled polymer solutions has not been extensively studied. Little is well understood because the nonlinear rheology of entangled melts is not. One particular theoretical difficulty of the conventional reptation theory is its prediction of a stress maximum in the flow curve of stress versus shear rate.[2] No experiments have ever revealed the occurrence of such behavior and corresponding constitutive instability. Instead, a family of *interfacial* stick−slip transition and flow oscillation phenomena has previously been thought to be constitutive in origin.[3,4] A recent experimental study[5] has shown that the flow discontinuity transition of monodisperse 1,4-polybutadiene is actually interfacial in nature, having nothing to do with the tendency of monodisperse entangled melts to behave "elastically" at the stress level of plateau modulus G_N^0.

Recent studies show that the interfacial stick−slip transition observed in capillary flow of various polymer melts can be understood in terms of the level of chain entanglement.[6,7] One effective way to reduce chain entanglement is to enlarge the tube diameter by introducing diluents. Thus, a series of polymer solutions should show a progressively smaller magnitude of the stick−slip transition as the concentration decreases from the pure melt of $\phi = 1.0$ to rather low values of ϕ. The purpose of this study is to establish a relationship between interfacial flow behavior and linear viscoelastic behavior of entangled polymers by varying the concentration and molecular weight of linear 1,4-polybutadiene (PBD) solutions.

We find in the present work that highly entangled polymer solutions indeed also undergo a stick−slip transition beyond a critical stress σ_c that is about one-third of the solution plateau modulus $G_N^0(\phi)$. The interfacial flow transition characteristics can be formulated by applying the same analysis previously employed for pure melts. Similar to the behavior of melts, linear viscoelastic behavior of the solutions plays an essential role in governing various aspects of the interfacial flow phenomena. Unique linear viscoelastic properties of the 1,4-PBD solutions as well as other intriguing interfacial flow behavior such as sharkskin are subjects of interest beyond the present scope and will be presented elsewhere.[8,9] Here we focus on characterizing the stick−slip transition of the PBD solutions as a function of concentration, molecular weight, and vinyl content of the oligomeric butadiene solvents.

II. Experimental Section

A. Materials. Two linear 1,4-polybutadienes (PBD) of different molecular weights with fairly narrow molecular weight distributions are used to make entangled solutions. These samples were synthesized and analyzed in the Goodyear Research Center. The molecular weight information was obtained using a 150C Waters GPC with chloroform as the carrier solvent at a flow rate of 1.0 mL/min at 45 °C for both injector and column compartments. The molecular weight averages were calculated using the Universal calibration method and individual Mark−Houwink parameters, K and a, appropriate to the polybutadienes. The microstructure of the polybutadienes was determined by proton nuclear magnetic resonance spectroscopy (^{1}H NMR). Two oligomeric butadienes (oBD) of different vinyl contents were employed as the solvents of the PBD solutions. They were purchased from Aldrich Chemicals and had molecular weights below chain entangle-

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Table 1. Characteristics of PBD and Oligomeric BD

	M_w ($\times 10^{-3}$)	M_n ($\times 10^{-3}$)	vinyl (%)	cis-1,4 (%)	trans-1,4 (%)	T_g (°C)
PBD1	437	270	10	35	55	−94
PBD2	244	205	10	35	55	−95
oBD1		1.0	45	5	10	−51
oBD2		1.5	25	35	40	−89

ment. The molecular characteristics of these samples are listed in Table 1.

The PBD solutions were prepared by first dissolving PBD at room temperature in toluene. Then an oligomeric butadiene oBD was blended in at different weight fractions to produce final concentrations at $\phi = 0.3$, 0.5, and 0.75. Since the mass densities of PBD1, PBD2, oBD1, and oBD2 are very close, ϕ can be taken to a good approximation as the volume fraction. The mixtures were kept under vacuum at room temperature for about 7 days, and toluene was considered to be removed when the weight loss between two consecutive days was less than 0.1%.

B. Experimental Apparatus. A controlled-pressure Monsanto automatic capillary rheometer (MACR) was used in this study to characterize capillary flow behavior of the PBD melts and their solutions. Two dies of different geometry were employed. One steel die had a tapered 60° entry angle with a length-to-diameter ratio $L/D = 15$ and $D = 1.0$ mm. The second aluminum die had a 180° entry angle with a length-to-diameter ratio $L/D = 80$ and $D = 1.0$ mm. Before use, the dies were cleaned in a flask of THF for at least 3 h, followed by ultrasonic agitation in a bath of THF for 30 min. THF was later removed from the die under vacuum.

In MACR, the piston pressure in the barrel is exerted by a nitrogen tank and controlled by a gas valve. Once a given pressure P is selected, the piston will travel through four identical zones at a speed that depends on the die dimensions and the polymer flow properties. A timer will record the amount of time Δt during which the piston completes a given zone corresponding to a known volume Ω. An average volumetric flow rate Q is obtained as $Q = \Omega/\Delta t$. The nominal wall shear rate $\dot{\gamma}$ is computed from the measured volumetric flow rate Q according to $\dot{\gamma} = 32Q/\pi D^3$ without the Rabinowitsch correction, and the nominal wall share stress σ is computed from the applied pressure P according to $\sigma = (D/4L)P$ without the Bagley correction.

Often viscous heating is suggested to be a pertaining factor in studies of wall slip in the stick−slip transition. Such an effect should not alter the qualitative features of the transition. The effect can be evaluated by using dies of identical aspect ratio L/D and different die diameter D. Since the ratio of viscous heat to heat conduction through the die wall is approximately proportional to D, the apparent flow rate Q or $\dot{\gamma}$ should be higher for a larger D if the viscous heating is not negligible. This is not the case even for PBD melts undergoing capillary flow, as Figure 5 of ref 5 indicated no difference between flow curves obtained with $D = 0.53$ and 1.04 mm dies of $L/D = 15$. Likewise, we did not encounter any noticeable effect due to viscous heating in capillary flow of polyethylenes.[6,7]

III. Theoretical Background

Linear viscoelastic properties of entangled polymer solutions can be described by the molecular tube−reptation model of de Gennes−Doi−Edwards.[1,2] By allowing the tube diameter $a(\phi)$ to be dilated by the solvent and the segmental friction coefficient $\zeta(\phi,T)$ to depend on the concentration ϕ as well as the temperature T, we can write down a generic expression for the disentanglement time τ_d of a chain with length N as

$$\tau_d(\phi) = \frac{\zeta(\phi,T)N^3 a'^4}{\pi^2 k_B T[a(\phi)]^2} \tag{1}$$

where a' is the Rouse segmental length in the reptation theory. Similarly, we can write down the plateau modulus $G_N^0(\phi)$ to be proportional to the polymer weight fraction ϕ and inverse square of the tube diameter a^2

$$G_N^0(\phi)/G_N^0 = \phi[a_0/a(\phi)]^2 \tag{2}$$

where a_0 is the tube diameter in the pure melt and $G_N^0(\phi)$ is the plateau modulus of the melt. In terms of the plateau modulus, the zero-shear or Newtonian viscosity $\eta(\phi)$ of an entangled solution is then given by, according to the Doi−Edwards theory,[2]

$$\eta(\phi) = (\pi^2/12)G_N^0(\phi)\,\tau_d(\phi) \propto \zeta(\phi,T)\phi/[a(\phi)]^4 \tag{3}$$

where the scaling relation follows from inserting eqs 1 and 2 into eq 3.

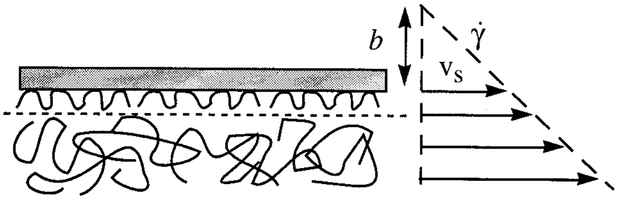

Figure 1. Sketch of the polymer/wall interface and the flow field showing slip upon the stick−slip transition, where there is no chain entanglement across the dashed line between the layer of adsorbed chains and the unbound flow-by chains.

When a surface is introduced in contact with a uniformly entangled polymer solution, it breaks the isotropic symmetry in the sense that a special layer is created between the adsorbed chains and the unbound free chains. In other words, the dynamic interaction between the adsorbed chains and mobile chains is fundamentally different from that between two layers of free chains. Consequently, it is possible for a strong flow to cause disentanglement between the adsorbed and free chains before disentanglement would occur within bulk chains. There have been many examples of such a stress-induced "interfacial" disentanglement that leads to a slip boundary condition.[6,7] Slip due to absence of chain entanglement next to the wall can be quantitatively described in terms of an extrapolation length b that is a natural length scale arising from the very existence of a slip boundary condition. By assuming presence of a finite slip velocity v_s at the wall that is proportional to the wall stress σ, i.e., $v_s = \sigma/\beta$, the Navier−de Gennes extrapolation length b arises as[6−7,10]

$$b = v_s/\dot{\gamma} = \eta(\phi)/\beta(\phi) \tag{4}$$

where the interfacial friction constant $\beta = \eta_1/a_1$, with η_1 being the interfacial viscosity of the layer free of chain entanglement and a_1 the layer thickness.[10] The physical meaning of b is illustrated in Figure 1. At a discontinuous stick−slip transition, the apparent shear rate is double-valued, taking $\dot{\gamma}_A$ and $\dot{\gamma}_C$ respectively below and above the transition. Then the extrapolation length b can be estimated from the relation $\dot{\gamma}_A/\dot{\gamma}_C = 1 + 8b/D$, which is exact for Newtonian fluids.[5] It is expected that η_1 as a Rouse viscosity is proportional to the Rouse segmental friction coefficient $\zeta(\phi,T)$ so that

$$\beta(\phi) \propto (a^2/a_1)\zeta(\phi,T)/a^2 \propto (a^2/a_1)\tau_d(\phi) \tag{5}$$

In terms of eqs 3 and 5, eq 4 can be rewritten as

$$b \propto G_N^0(\phi)(a_1/a^2) \qquad (6)$$

Thus, by measuring either b and $G_N^0(\phi)$ or $\beta(\phi)$ and $\tau_d(\phi)$ as a function of ϕ, we can determine whether the interfacial layer thickness a_1 has the same ϕ dependence as the tube diameter a does. Formula 6 indicates that b depends not on friction dynamics but only on the elastic property and topological structure of the sample.

IV. Results and Discussion

Linear viscoelastic behavior of these entangled polybutadiene solutions has been studied elsewhere[8] to show that the polymer dynamics depend explicitly on the distance from the effective glass transition temperature $T_g(\phi)$ of the solutions. In particular, it was found that at some special temperature (i.e., 40 °C) the solutions possess nearly identical overall reptation time τ_d for almost all values of ϕ between 1.0 and 0.3 because the solution with a lower 1,4-PBD concentration ϕ has a higher $T_g(\phi)$ in the oligomeric BD of higher vinyl content (i.e., oBD1 in Table 1). From the oscillatory shear measurements we also found the scaling relations[8] for the tube diameter $a(\phi)$ as $a(\phi) \propto \phi^{-2/3}$ and for the elastic plateau modulus $G_N^0(\phi) \propto \phi^{7/3}$. These results are summarized in Table 2. All of the information in Table 2 is obtained from oscillatory shear studies of the same solutions.[8] For example, at 40 °C, the pure PBD1 has $\tau_{d0} \cong 5$ s, $G_N^0 = 1.0$ MPa, and $a_0 = 38$ Å. In fact, G_N^0, the critical molecular weight M_e for chain entanglement in the melt, and the value of a_0 are all known for 1,4-PBD as listed in ref 16. In the present work, we focus on the strong steady shear behavior of these solutions using a capillary rheometer. It turns out that an elementary understanding of the capillary flow behavior relies essentially on the information given in Table 2.

We first chose to conduct capillary flow experiments at the special temperature of 40 °C on three solutions of $\phi = 0.3$, 0.5, and 0.75 as well as the pure PBD1. Figure 2 shows that all four samples exhibit an interfacial stick–slip transition at about the same critical shear rate as indicated by the dashed line. Analogous to the behavior of the pure PBD1, the flow transition in the solutions occurs essentially in the Newtonian region away from their elastic plateau.

The critical stress σ_c strongly varies with the concentration ϕ. Figure 3 reveals that $\sigma_c(\phi) \cong G_N^0(\phi)/3$ for all values of ϕ, where $G_N^0(\phi)$ has previously been obtained on the basis of eq 2 and scaling behavior of the tube diameter $a(\phi)$ obtained from the oscillatory shear experiments.[8] Using eq 3 to write $\sigma_c(\phi) = \eta\dot{\gamma}_c = (\pi^2/12) G_N^0(\phi)\, \tau_d(\phi)\dot{\gamma}_c$, $\sigma_c(\phi) \cong G_N^0(\phi)/3$ implies that the product $\tau_d(\phi)\dot{\gamma}_c \cong 0.4$, which is typically called the Deborah number, remains constant independent of the concentration ϕ. More specifically, we obtain approximately the same $\tau_d(\phi) \cong 4$ s at 40 °C for ϕ ranging from 1.0 to 0.3 since the critical shear rate $\dot{\gamma}_c$ for the stick–slip transition is almost constant equal to 0.13 s^{-1}. This result is in agreement with the previous discovery[8] that $\tau_d(\phi)$ remains invariant with respect to ϕ, at 40 °C.

This observation underscores the unique role of the special interfacial structure that is not present in the bulk: a layer of "tethered" chains due to polymer adsorption. The shear flow is bound to be much more effective in stretching the layer of tethered chains to cause disentanglement with the unbound chains and to produce cohesive wall slip upon the transition. This is expected and can be understood by recognizing that the "tethered" chains execute much slower dynamic motion and possess much longer relaxation times because they act like branched chains. Furthermore, because of their inability to leave the surface, the shear flow near the wall is as effective as extensional flow to stretch the layer of immobile chains.

Table 2 describes how the vinyl content of the oligomeric solvent and temperature affect the reduced reptation time as a function of concentration ϕ, where the subscript zero denotes quantities of the pure PBD melt. It shows that $\tau_d(\phi)$ is no longer invariant with respect to ϕ for the PBD1/oBD1 solution at a higher $T = 80$ °C and for the PBD1/oBD2 solution at 40 °C. Since $\tau_d(\phi)$ varies with ϕ as shown in Table 2 under these conditions, the critical shear rate $\dot{\gamma}_c$ for the stick–slip

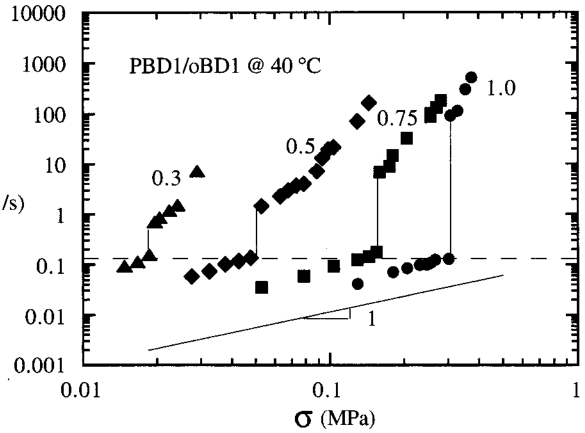

Figure 2. Flow curves of the PBD1/oBD1 solutions and pure PBD1 at 40 °C showing a distinctive interfacial stick–slip transition at a nearly identical critical shear rate that drastically decreases in its amplitude with lowering ϕ from 1.0 to 0.3.

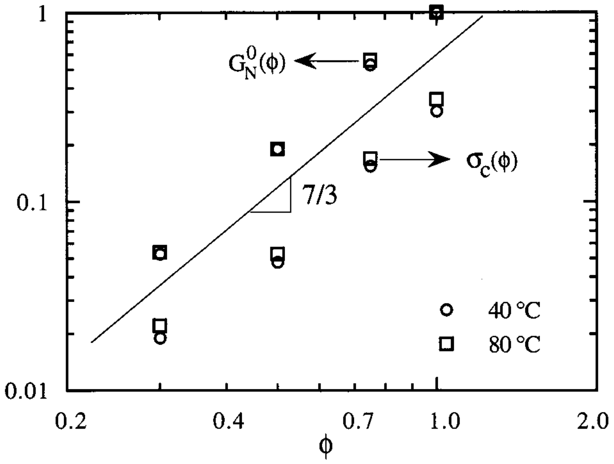

Figure 3. Critical stress σ_c for the stick–slip transition and the plateau modulus $G_N^0(\phi)$ as a function of the concentration ϕ, both in the unit of MPa at two temperatures. Note that the range of ϕ is physically bounded by unity and the choice of 0.2–2.0 is a mere convenience.

Table 2. Viscoelastic Properties of PBD Solutions

	$\tau_d(\phi)/\tau_{d0}$				
ϕ	40 °C PBD1/oBD1	40 °C PBD1/oBD2	80 °C PBD1/oBD1	$a(\phi)/a_0$	$G_N^0(\phi)/G_N^0$
0.75	1	0.9	0.9	1.2	0.5
0.5	1	0.7	0.8	1.6	0.2
0.3	0.8	0.4	0.5	2.2	0.06

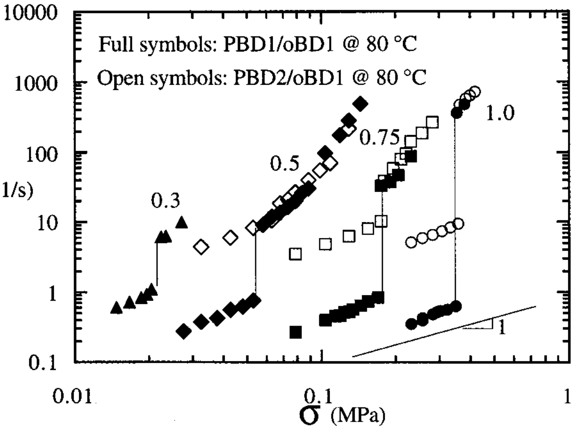

Figure 4. Flow curves showing the stick−slip transition of the PBD1/oBD1 and PBD2/oBD1 solutions at 80 °C.

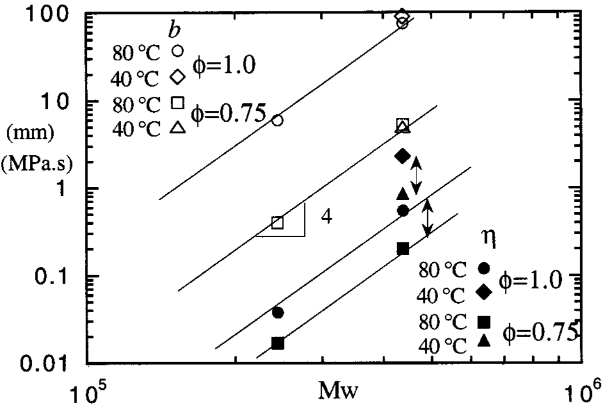

Figure 5. Extrapolation length b and viscosity η as a function of molecular weight M_w at 80 °C for $\phi = 1.0$ and 0.75, as well as b and η at 40 °C for pure PBD1 and its solution at $\phi = 0.75$.

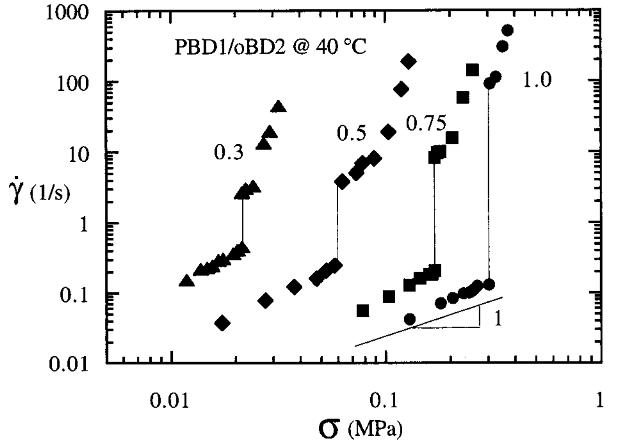

Figure 6. Flow curves of PBD1/oBD2 solution at 40 °C showing the stick−slip transition at different critical shear rates, where the magnitudes are similar to those in Figure 2.

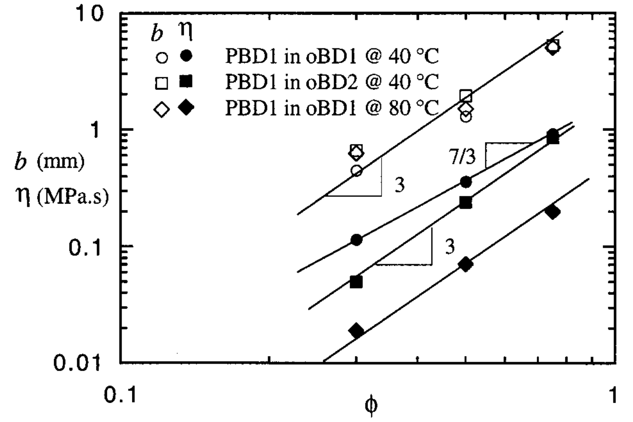

Figure 7. Concentration dependence of b and η evaluated at the transition for both PBD1/oBD1 and PBD1/oBD2 solutions at two temperatures.

transition is no longer constant with respect to ϕ as shown in Figures 4 and 6 although $\sigma_c(\phi)$ is still approximately $G_N^0(\phi)/3$ for all values of ϕ.

Plotted in Figure 4 are also the flow curves of the PBD2/oBD1 solutions at 80 °C, showing for both pure PBD and their solutions that the magnitude of the transition, i.e., the extrapolation length b, scales strongly the molecular weight of the PBD. This is explicitly shown in Figure 5, where the open symbols denote b and filled symbols designate η evaluated just below the transition for both $\phi = 1.0$ and $\phi = 0.75$ at two temperatures 40 and 80 °C. It is interesting to note that η drops significantly from 40 to 80 °C whereas b remains constant. The strong molecular weight dependence of the extrapolation length b has been previously reported for the PBD melts[5] and linear polyethylene melts.[11] It is also worth noting that the independence of σ_c on the molecular weight shown in Figure 4 agrees with the previous study on the stick−slip transition of pure PBD melts.[5]

It is most striking to note that although η only decreases by a factor of less than 3 as indicated by the vertical double arrows in Figure 5, b drops by a factor of 15 upon diluting the pure PBD1 of $\phi = 1.0$ to $\phi = 0.75$. In other words, $\beta(\phi{=}0.75) > 5\beta_0$ according to (4), regardless of the molecular weight M_w, where the subscript "0" refers to $\phi = 1.0$. Since this conclusion is also true for the PBD solutions involving oBD2 as the solvent as shown in Figure 6 and is independent of the experimental temperature T, it does not arise from any surface segregation effect, i.e., enrichment of the oligomers at the wall. Because β is the ratio η_1/a_1 and neither η_1 nor a_1 is independently measured experimentally, we are not able to determine which of the two factors causes β to increase many times for a 75% solution in comparison to that of the pure melt.

The solution of PBD1 in oBD2 offers another way to illustrate how the interfacial flow behavior depends on the bulk polymer entanglement. Figure 6 once more shows that $\sigma_c(\phi) \cong G_N^0(\phi)/3$. Since $\tau_d(\phi)$ increases considerably with ϕ as shown in Table 2, $\sigma_c(\phi) \propto G_N^0(\phi)$ implies that the stick−slip transition occurs at a lower critical shear rate for a higher ϕ. The data in Figure 6 consistently depict this trend.

We can summarize the characteristics of the interfacial stick−slip transition and rheological behavior as described by Figures 2, 4, and 6, involving the PBD1/oBD1 solution at 40 and 80 °C and PBD1/oBD2 solution at 40 °C. In terms of the extrapolation length b (in open symbols) and viscosity η (in full symbols) just below the transition, Figure 7 illustrates the interfacial and rheological behavior of the PBD solutions as a function of concentration ϕ. The straight lines are not the fit to the data but rather the expected scaling behavior. For instance, η of PBD1/oBD1 at 40 °C should have approximately the same ϕ dependence as $G_N^0(\phi) \propto \phi^{7/3}$ according to (3) since $\tau_d(\phi)$ is essentially invariant with ϕ. In the other two cases, η should behave as $\eta \propto$

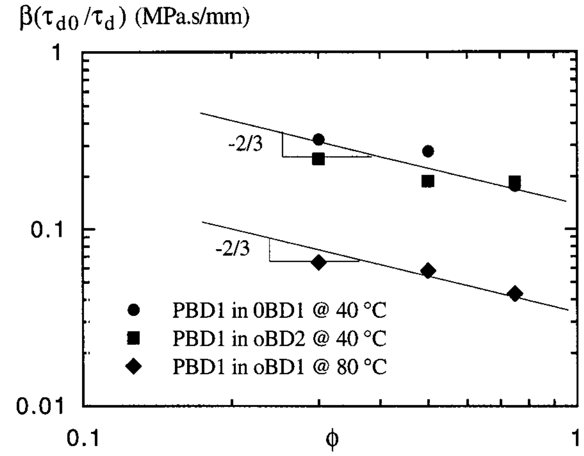

Figure 8. Reduced interfacial friction constant $\beta(\tau_{d0}/\tau_d)$ as a function of concentration ϕ for different solutions and temperatures.

$G_N^0(\phi)/a(\phi) \propto \phi^3$ since $\tau_d(\phi) \propto \phi^{2/3}$ as approximately shown in Table 2. Furthermore, if b scales as $b \propto \phi^3$, then (6) implies that a_1/a^2 behaves as $1/a(\phi) \propto \phi^{2/3}$ or $a_1 \propto a(\phi)$. The data in Figure 7 appear to suggest that $a_1 \propto a(\phi)$ is roughly true.

An independent way to determine how the interfacial friction constant β depends on the interfacial thickness $a_1(\phi)$ is to evaluate $\beta(\phi) = \eta/b$ and the reptation time $\tau_d(\phi)$ separately and plot $\beta(\phi)/\tau_d(\phi)$. According to (5), this ratio of β/τ_d should depend explicitly on a^2/a_1. In other words, for $a_1 \propto a(\phi)$ we have $\beta/\tau_d \propto a(\phi) \propto \phi^{-2/3}$. Figure 8 shows that β/τ_d indeed behaves approximately as $\phi^{-2/3}$ independent of the polymer dynamics that depend on the solvent vinyl content and temperature.

V. Further Discussion

The finding of $\sigma_c(\phi) \cong G_N^0(\phi)/3$ and $\sigma_c(\phi) \propto M_w{}^0$ at all values of ϕ including the case of $\phi = 1.0$ studied previously[5] shows an intriguing relation between the characteristics of the interfacial stick–slip transition and the bulk properties of these PBD samples. It appears that this interfacial failure, involving a breakdown, i.e., disentanglement between the adsorbed and unbound chains, is intimately related to a potential bulk rupture that would presumably occur at the higher stress level of the elastic plateau modulus $G_N^0(\phi)$. It suggests that there may be a *saturated* layer of adsorbed chains that form small loops in both the pure melt and solutions, such that the onset condition for the transition is not determined by the adsorbed chain density ν, which seems to be the case for linear polyethylenes.[11] The coil–stretch transition of bound chains leading to disentanglement probably involves chains that are entrapped by the adsorbed chains. Upon the stick–slip transition, these "bound" chains may free themselves from the adsorbed chains after their disentanglement with the unbound chains. Figure 1 only depicts the steady interfacial state above the transition where the flowing-by chains slide over the layer of adsorbed chains without an opportunity to penetrate and reentangle into the adsorbed chains.

There are hardly any reports on wall slip of entangled polymer solutions with three exceptions. The pioneering work of Vinogradov and co-workers[12] examined the capillary flow behavior of entangled monodisperse PBD solutions and found the critical shear rate for spurt or stick–slip transition is proportional to the overall molecular relaxation rate, which is equivalent to our finding that $\sigma_c(\phi) \propto G_N^0(\phi)$. Like their work on PBD melts, however, the origin of the stick–slip (spurt) transition in these solutions was thought to be constitutive and related to a transition "from the fluid to the high-elastic state". We have shown elsewhere that the spurt transition in PBD melts and solutions are entirely interfacial in nature.[5,9]

The work of Pomar et al.[13] on polyethylene solutions seems to suggest that σ_c for the stick–slip transition is independent of the concentration ϕ (see Figure 7 of ref 13). This is actually possible since σ_c appears to be proportional to the adsorbed chain density ν for PE materials[11] which has a rather weak dependence, $\nu \propto \phi^{2/3}$. In other words, there does not appear to be a correlation between σ_c and G_N^0 for polyethylenes (PE) in contrast to that revealed in ref 5 for PBD. There appear to be some errors, however, in ref 13: (a) Figure 4 of ref 13 indicates $G_N^0(\phi) \propto \phi$, in contradiction with all reported results for entangled solutions in the literature.[8,14] This discrepancy presumably arises from the difficulty in determining the plateau modulus $G_N^0(\phi)$ of a commercial (from Union Carbide) linear low-density polyethylene with a *broad* molecular weight distribution. (b) Thus, for example, G_N^0 was reported[13,15] to be more than 1 order of magnitude lower than that listed in ref 16, which gives $G_N^0 = 2.6$ MPa for pure PE melts.

The most recent work on slip of entangled polymer solutions of Mhetar and Archer[17] attempted to evaluate the possibility of wall slip in entangled polystyrene solutions in a planar Couette geometry. Using tracer particle to measure the velocity field near the wall, they did not observe any sharp stick–slip transition in the entangled PS solutions. The amount of the gradual slip reported was so small that it could not be verified rheologically by determining a gap dependence of the measurements. At sufficiently high shear rates, they reached the stress plateau region where the stress level σ^* is approximately constant, comparable to the plateau modulus. For PS melts, G_N^0 is around 0.2 MPa. Thus, according to the established scaling[8,14] of $G_N^0(\phi) \propto \phi^{7/3}$, one has $\sigma^* \cong 200$, 900, and 4700 Pa for $\phi = 0.05$, 0.1, and 0.2, respectively. At these stresses, the different monodisperse PS solutions respectively begin to show extreme shear thinning or plateaulike behavior in the sense that the shear rate increases rapidly with shear stress. Reference 17 apparently interpreted this constitutive bulk behavior as due to interfacial wall slip.

Finally, it is useful to further comment on the molecular weight dependence of the magnitude of the stick–slip transition. We have repeatedly shown previously for polyethylene[11] and polybutadiene melts[5] and in the present paper in Figure 5 for PBD solutions that the extrapolation length b depends on M_w in the same way as the shear viscosity does at a constant stress, i.e., $b \propto M_w{}^{3.4-4.0}$. In all cases, a controlled stress mode has been used to determine the critical point where the apparent shear rate is double-valued. If the stick–slip transition is evaluated using a rheometer that is inherently rate-controlled, the hysteresis behavior associated with the transition always produces considerable uncertainty. It is for this reason we believe that other determinations of b as a function of M_w for monodisperse PBD melts have yielded inconsistent scaling relations.[18,19] In the first case, a controlled rate capillary rheometer (Goettfert Rheo-Tester 1000) was used,[18] which might not access low enough shear rates to determine the no-slip branch for PBD of high M_w. There is also uncertainty in using the controlled pressure mode through an electronic feedback loop in the Goettfert rheometer. In the second case,[19] b was calculated from (4) by first measuring the tracer particle velocity at the walls which was taken as v_s and then computing the true shear rate $\dot{\gamma}$ from $\dot{\gamma} = \dot{\gamma}_n/(1 + 2b/H)$, where the nominal shear rate $\dot{\gamma}_n = V/H$ may partially involve v_s in the controlled rate mode, with V being the velocity of the moving plate and H the gap distance between the two parallel plates.

VI. Conclusions

We have studied the strong flow behavior of entangled monodisperse linear polybutadiene PBD solutions. An interfacial stick−slip transition is observed for all the solutions to occur at a stress level of approximately one-third of the plateau modulus $G_N^0(\phi)$. Since $G_N^0(\phi) \propto \phi^{7/3}$, the critical stress for the transition is found to depend on the concentration as $\sigma_c \cong G_N^0(\phi)/3 \propto \phi^{7/3}$. The magnitude of the transition, as characterized by the extrapolation length b, varies with the molecular weight M_w as strongly as it does in the melts. More interestingly, b depends strongly on the concentration as $b \propto \phi^3$, which is consistent with the suggestion that the interfacial layer of disentanglement has a thickness $a_1(\phi)$ comparable to the tube diameter $a(\phi)$ and has the same ϕ dependence as $a(\phi)$ does.

It is worth noting that the ϕ dependence of the extrapolation length b is independent of temperature and vinyl content of the oligomeric BD solvent. This is straightforward to understand because b does not involve any dynamic quantities as shown in (6). In contrast, the ϕ dependence of the solution viscosity η is not universal because part of the ϕ dependence arises from the segmental friction coefficient $\zeta(\phi,T)$ which itself varies strongly with the experimental temperature T.[8]

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