Macromolecules **1996,** *29,* 4115−4119

Stick−Slip Transition in Capillary Flow of Polyethylene. 2. Molecular Weight Dependence and Low-Temperature Anomaly

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Received October 11, 1995; Revised Manuscript Received February 1, 1996[⊗]

ABSTRACT: The present study focuses on molecular characteristics and temperature dependence of a superfluid-like stick−slip transition in a series of highly entangled high-density polyethylene (PE) resins and their rheological behavior in pressure-driven capillary flow. It is found that at sufficiently high stresses the capillary flow characteristics are largely dictated by the stick−slip transition occurring at the PE/die wall interfaces. The transition magnitude is found to have an explicit and strong molecular weight M_w dependence reminiscent of bulk chain entanglement, i.e., the extrapolation length $b_c \propto M_w^{3.4}$. In addition to its normal temperature dependence for $T \geq 200$ °C as described in paper 1, the critical stress for the stick−slip transition ceases to scale linearly with T from 200 down to 160 °C for all four molecular weights studied. The extrapolation length b_c at the transition also becomes much larger at a lower T. The anomaly is clearly interfacial in nature and may involve a flow-induced ordered mesophase near the PE/wall interfaces.

I. Introduction

Polymers exhibit many interesting physical properties due to their chain-like structures. One of the most intriguing characteristics is for highly entangled polymer melts, especially polyethylene resins, to undergo a flow-induced stick−slip transition[1−6] in pressure-controlled capillary extrusion. This *interfacial* transition is unique because it has no equilibrium counterpart and it strongly depends on *bulk* properties such as the molecular weight and architecture in addition to interface properties such as the surface energy of capillary walls. The transition yields a slip hydrodynamic boundary (HBC) condition in violation of the well-established stick HBC. Under a constant extrusion rate, apparent melt fracture (commonly termed spurt flow instability) occurs on the extrudate.[7−17] Although stick−slip transition and melt fracture has been known and extensively studied since the inception of the field of high flow rheology of polyethylene,[1−2] the molecular nature of these phenomena has remained elusive.

We have recently studied the superfluid-like stick−slip transition of highly entangled high-density polyethylene (PE) in the temperature range from 200 to 260 °C under controlled-pressures.[18] Paper 1 (i.e., ref 18) elucidated experimentally that this stick−slip transition occurs, at interfaces such as those between polyethylene and metallic capillary walls, via stress-induced disentanglement[19] of adsorbed chains at the wall off unbound chains. There arises a general picture linking extrudate irregularities, which may not be a true melt fracture and may not even be a surface instability on the extrudate, to unsteady hydrodynamic boundary conditions. In particular, the bamboo-like extrudate distortion associated with spurt flow instability of linear polyethylene melts is simply due to oscillation of die swell arising from fluctuation of the wall stress/shear rate in the capillary die, as the PE/wall interface undergoes and recovers from the stick−slip transition.

In the present work, i.e., paper 2 in a series of three publications, we explore in detail molecular characteristics of the stick−slip transition and general features of high-stress rheology of linear high-density polyethylene resins. We report some intriguing low-temperature anomalies of the transition observed at temperatures as low as 160 °C. Our preliminary investigation indicates that the anomalous features originate from flow-induced PE nematic mesophase formation at the capillary wall. More study of the influence of surface condition on the stick−slip transition will be presented in paper 3.[20]

II. Experimental Section

The materials under investigation are a series of linear high-density polyethylene (HDPE) supplied by BP Chemicals. We will refer to them as MH07, MH20 and MC02, MC60 according to BP Chemicals. The MC series have a small content of hexene comonomers as side groups at the level of 1/1000 C, i.e., 0.3/1000 C for MC02 and 1.2/1000 C for MC60 to be more precise. For the present purpose, we may approximately regard these PE as having the same chemical structure. The weight-average molecular weights are $M_w = 130\,500$, $M_w = 158\,300$, $M_w = 225\,600$, and $M_w = 316\,600$ for MH07, MC02, MC60, and MH20, respectively. In order to study the stress-induced stick−slip transition, a pressure-controlled Monsanto automatic capillary rheometer was used with a die of length-to-diameter ratio $L/D = 15$ and diameter $D = 1.04$ mm, made of case hardened steel. The adjustable pressure on the piston in the barrel is provided by a nitrogen tank. 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 polyethylene under capillary flow. A timer will record the amount of time Δt during which the piston completes a given zone corresponding to a known volume V of PE. An *average* volumetric flow rate Q is obtained as $Q = V/\Delta t$. By design and without modification, the Monsanto capillary rheometer is not able to monitor Q as a continuous function of time. This limitation does cause some errors in determining Q at the stick−slip transition. Nevertheless, sufficiently accurate data can be obtained over many runs. The wall shear stress σ is computed from the *applied* pressure P according to $\sigma = (D/4L)P$ without the Bagley correction, and the 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. Since incorporating these corrections would not alter the nature of our conclusions, we will only present raw data. The experiments on each of MH07, MC02, MC60, and MH20 have been conducted at temperatures 200, 190, 180, 170, and 160 °C in order to elucidate the peculiar temperature dependence

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[⊗] Abstract published in *Advance ACS Abstracts,* May 1, 1996.

S0024-9297(95)01512-9 CCC: $12.00

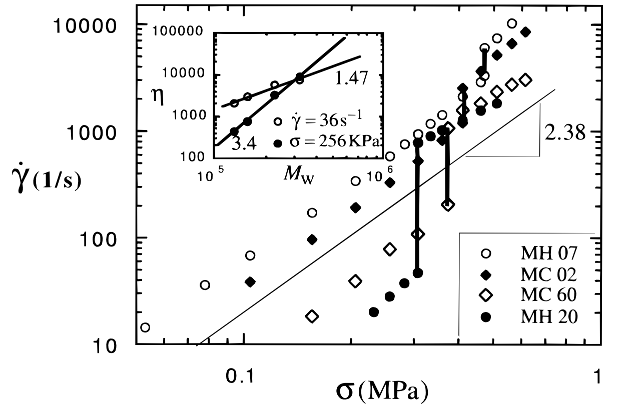

Figure 1. Measured apparent wall shear rate $\dot{\gamma}$ versus the applied stress σ for all four molecular weights at $T = 200$ °C. The straight line indicates the scaling $\dot{\gamma} \propto \sigma^{2.38}$ prior to the stick−slip transition shown by the vertical lines. The inset shows the power-law behavior of the viscosities measured at either a constant stress or a constant rate.

of the flow transition at temperatures not far from the melt point.

III. Results and Discussion

Molecular Weight Dependence of Viscosity before Transition. The HDPE is first studied as a function of molecular weight M_w at both low stresses and around the stick−slip transition. Since the extent γ of chain stretching would be the same and independent of molecular weight at a constant stress according to a generic expression[21a]

$$\sigma \cong G^{(0)} g(\gamma) \tag{1a}$$

where $G^{(0)}$ is the plateau modulus, independent of molecular weight M_w, and g is a universal function of γ, it is more sensible to measure the shear viscosity η_σ at a constant stress σ prior to the stick−slip transition for different molecular weights. At σ, the constant-stress viscosity η_σ is given by

$$\eta_\sigma = \sigma/\dot{\gamma} = \eta_0(M_w) g(\gamma)/\gamma \propto M_w^{\ 3.4} \tag{2}$$

where the second equality follows from definition for the zero-shear viscosity $\eta_0(M_w) = G^{(0)}\tau$ and the constant γ is related to the shear rate $\dot{\gamma}$ and disentanglement relaxation time τ as $\gamma = \tau\dot{\gamma}$. The expression in eq 2 indicates that η_σ should scale with M_w in the same way as $\eta_0(M_w)$ does, providing a basis for the empirically established master curves in the literature.[21b] Our experiments at low stresses at $T = 200$ °C, as shown in Figure 1, support this scaling law. In particular, it is shown in inset of Figure 1 that η_σ, evaluated at $\sigma = 256$ kPa, scales with M_w with an exponent approximately equal to 3.4. On the other hand, if one measures $\eta_{\dot{\gamma}}$ at a constant shear rate as a function of M_w, he will find a scaling law distorted by the shear thinning behavior of the polymer, with $\eta_{\dot{\gamma}} \propto M_w^{1.47}$ at $\dot{\gamma} = 36$ s^{-1}. This scaling exponent is consistent with the shear thinning exponent found from Figure 1: The function $g(\tau\dot{\gamma})$ in eq 1a assumes a power law in the shear thinning regime

$$\sigma \cong G^{(0)} (\tau\dot{\gamma})^\beta \tag{1b}$$

According to Figure 1, $\beta = 1/2.38$. On the other hand, eq 1b predicts the following scaling law for the constant-rate viscosity $\eta_{\dot{\gamma}}$

$$\eta_{\dot{\gamma}} = \sigma/\dot{\gamma} = G^{(0)} \dot{\gamma}^{\beta-1} \tau^\beta \propto M_w^{\ \alpha} \tag{3}$$

with $\alpha = 3.4\beta = 1.43$ since $\tau \propto \eta_0(M_w) \propto M_w^{3.4}$. The predicted exponent $\alpha = 1.43$ in eq 3 is in very close agreement with the experimentally determined exponent 1.47 shown in the inset of Figure 1. Therefore our data lend strong support for the scaling relation eq 1b for shear thinning and for the universal formula eq 2. The usefulness of the relation $\alpha = 3.4\beta$ is rooted in its prediction for the scaling exponent α in eq 3 once β is known. Thus one only needs to determine β of eq 1b for one molecular weight in order to describe $\eta_{\dot{\gamma}}$ for different molecular weights at the same shear rate $\dot{\gamma}$.

Molecular Weight Dependence of Stick−Slip Transition. Our experimental results in paper 1 appear to back the recent theory of Brochard and de Gennes[19] semiquantitatively. For example, we found[18] that the critical shear stress σ_c for the stick−slip transition scales linearly with temperature T ranging from 200 to 260 °C in agreement with the expression derived by Brochard and de Gennes:[19]

$$\sigma_c = \nu k_B T/D^* \tag{4}$$

where the entanglement distance $D^* = N_e^{1/2} a$, with N_e being the number of segments between adjacent entanglements and a the Kuhn length. Interfacial slip is most appropriately characterized by an extrapolation length b, defined as the distance away from the polymer/wall interface where the velocity of the bulk melt would be extrapolated to zero.[19,22] Contrary to slip velocity v_s, a kinematic variable which has been invoked to describe wall slip ever since Mooney's time, the extrapolation length b is an intrinsic material property. The extrapolation length b depends only on molecular properties of the polymer melt and its interfacial properties with the wall. A simple analysis gives the following explicit formula for the extrapolation length b[19,22]

$$b = (\eta/\eta_i) a \tag{5}$$

where η_i is an effective viscosity for the interfacial layer. Actually, this expression applies both before and after the stick−slip transition: η_i may be as large as η and b is of a molecular length a before the transition; upon the transition, η_i may become extremely small in comparison to η due to the disentanglement between adsorbed and free chains or due to chain debonding[20] such that b may attain a macroscopic magnitude. Equation 5 clearly indicates a strong molecular weight dependence since η/η_i may scale with M_w with an exponent as large as 3.4 at a constant stress.

Figure 1 shows a clear molecular weight dependence of the essential features of the stick−slip transition. It is important to notice the shift of the critical stress σ_c to higher values for a lower M_w polyethylene. When σ_c is plotted against the molecular weight M_w, we find an approximate scaling law $\sigma_c \propto M_w^{-1/2}$, as Figure 2 indicates. Also shown in Figure 2 is the result obtained at $T = 160$ °C. We suspect this molecular weight scaling manifests the relationship in eq 4 and reflects the molecular weight dependence of ν, since the number of chains per unit area is $\nu \propto N^{-1/2} \propto M_w^{-1/2}$, where N is the number of monomers per chain.[23] Thus the agreement between Figure 2 and eq 4 may be understood in terms of the proposed molecular disentanglement mechanism.[18,19]

One of the key results of this paper is the observed molecular weight dependence of the extrapolation length b. b at the transition can be calculated from a modified Mooney relation $b_c = (D/8)(\dot{\gamma}_A/\dot{\gamma}_C - 1)$, where $\dot{\gamma}_C$ and $\dot{\gamma}_A$

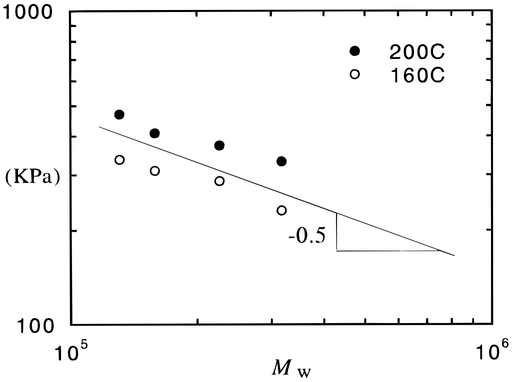

Figure 2. Correlation between the critical stress σ_c for the stick–slip transition and molecular weight M_w at both 200 and 160 °C.

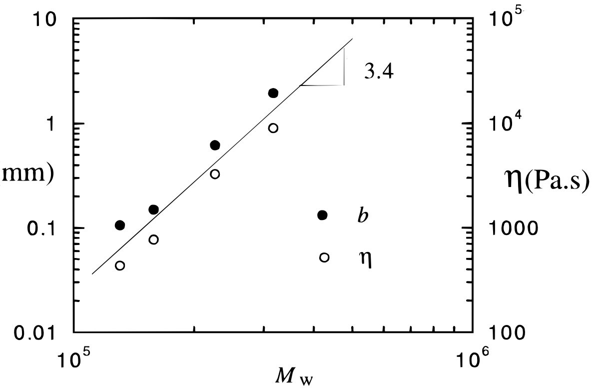

Figure 3. Extrapolation length b_c at the transition and viscosity η versus the molecular weight M_w at $T = 200$ °C. The straight line indicates the scaling $b_c \propto M_w^{3.4}$ and $\eta \propto M_w^{3.4}$, which was measured at $\sigma = 0.256$ MPa for all four polyethylene resins MH20, MC60, MC02, and MH07.

are the shear rates respectively just before and just after the transition corresponding to the same critical stress. Figure 3 shows that the extrapolation length b_c at the stick–slip transition at 200 °C actually scales with M_w as $b_c \propto M_w^{3.4}$. This is an extremely useful and instructive relationship and can be understood through the combination of eq 2 and eq 5. First of all, eq 5 indicates that b_c is proportional to the shear viscosity η near the wall at stress σ_c. Since σ_c is a rather weak function of M_w as shown above and since all the four values of b_c were evaluated on the same-order-of-magnitude stress, η involved in eq 5 for b_c is close to η_σ computed at a constant stress. Second, b_c depends not only on η but also on η_i which, like η, decreases with increasing stress σ, due to stretching of interfacial chains. Thus it is reasonable to expect $b_c = \eta/\eta_i$ to depend on M_w in the same way as the constant-stress viscosity η_σ does.

The unique feature of this *interfacial* stick–slip transition phenomenon is that its characteristics (e.g., its critical stress σ_c and magnitude b_c) are functions of the *bulk* properties such as molecular weight M_w of polyethylene. Equations 4 and 5 explicitly depict this behavior, with eq 4 showing $\sigma_c \propto \nu(M_w)$ and eq 5 indicating $b_c \propto \eta/\eta_i \propto M_w^{3.4}$. However, these seemingly universal features of the superfluid-like stick–slip transition are not invariant at all temperatures. Below we will explore the anomalous temperature dependence of this flow transition.

Low-Temperature Anomaly. The quantity σ_c/T is found to systematically decrease with temperature T below 200 °C for all four molecular weights: MH07, MC02, MC60, and MH20, as shown in Figure 4a. Since the adsorbed chain density ν in eq 4 is only expected to increase with lowering temperature at a constant stress, Figure 4a forces us to conclude that the disentanglement took place more easily; i.e., D^* in eq 4, as an entanglement distance, begins to increase with decreasing T at lower temperatures. Because the deviation of σ_c/T from a constant value (i.e., its value at 200 °C) is systematic for all of the four polyethylene resins and is very large (ca. 25%) compared to the experimental error (ca. 5%), we must take it seriously. We tentatively suggest that this low temperature anomaly arises from a flow-induced ordered phase[24] (e.g., a nematic phase) at the wall at these lower temperatures when the wall shear stress is as high as σ_c. Such a mesophase would introduce local chain orientation at the PE/wall interface, so that it is now *easier* for the tethered chains to disentangle from free chains. In other words, the interfacial chains need not be stretched (shear deformed) as much as when they are in the isotropic liquid phase, and the stick–slip transition would only require a lower critical stress.

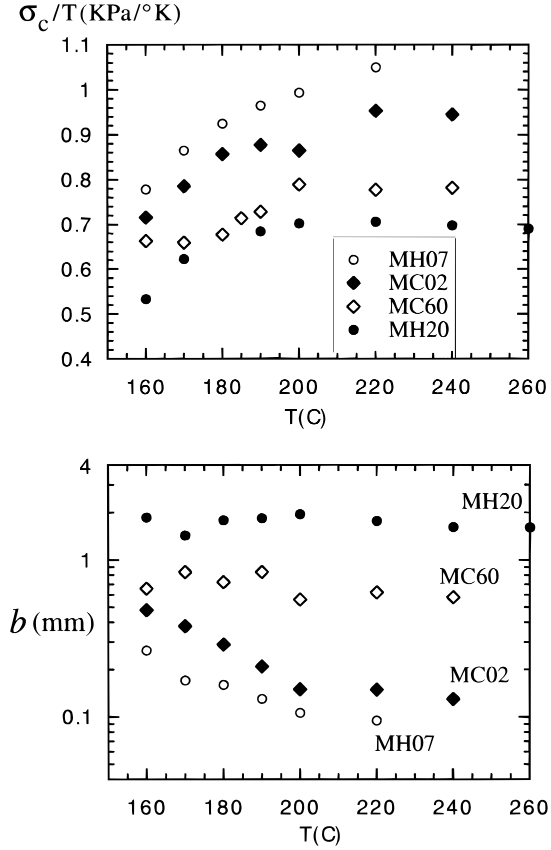

Figure 4. (a, top) Temperature dependence of the critical stress σ_c for all four polyethylene resins from 160 to 260 °C. (b, bottom) Temperature dependence of the extrapolation length b_c at the transition for all four polyethylene resins from 160 to 260 °C.

Other critical quantities also show anomalous temperature dependence for $T < 200$ °C. Especially the measured extrapolation length b_c at the transition increased with decreasing temperature for MH07 and MC02 which are the two lower molecular weight PE resins, while b_c of MH20 and MC60 remains nearly constant throughout the temperature range from 160 to 260 °C, as shown in Figure 4b. This molecular weight effect is rather perplexing. We have further verified the trend observed in Figures 4a,b by using a capillary die of much smaller diameter: $L/D = 25$ and $D = 0.625$ mm, and found results similar to those in Figure 4b: for

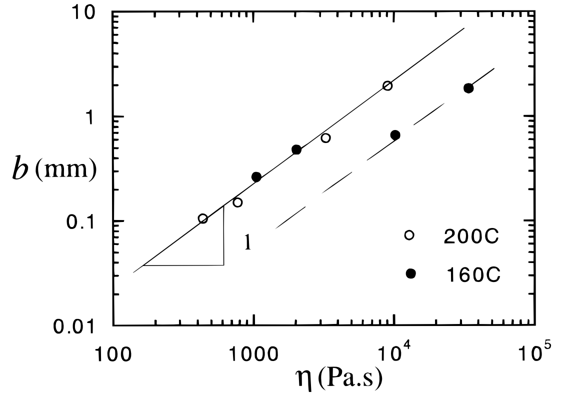

Figure 5. Extrapolation length b against the shear viscosity η which is measured at stresses 0.256 MPa at $T = 200$ °C and 0.205 MPa at $T = 160$ °C.

MC02, $b_c = 0.15$ mm at $T = 200$ °C and $b_c = 0.56$ mm at $T = 160$ °C.

To be consistent with the idea of shear-induced mesophase formation, we assume η_i in eq 5 to correspond to that of an orientationally ordered state for all the four PEs. On one hand, b_c remains constant for MH20 and MC60 because the mesophase presumably developed well into the bulk away from the capillary wall and η in eq 5 is that of the mesophase, so that the viscosity ratio in eq 5 stays essentially constant with respect to temperature T. On the other hand, if MH07 and MC02 are mostly in the normal liquid state away from the die wall, the interfacial slip would be measured against a more viscous bulk fluid, with η in eq 5 corresponding to that of the ordinary disordered PE. Thus for MH07 and MC02, the viscosity ratio in eq 5 reflects that of the disordered melt to that of the ordered interfacial layer and is therefore larger than its value at high temperatures. To go beyond this point, one must ask a basic question of what governs the disentanglement process at PE/wall interfaces as it relates to the molecular interfacial condition. We will defer this investigation to future work.

There is further indication that the formula eq 5 for the extrapolation length b, although extraordinarily simplistic, may have profoundly captured the essence of melt/solid interfacial interactions and corresponding hydrodynamic slip. Equation 5 shows that the magnitude of interfacial slip, as characterized by b and not by the slip velocity v_s, is directly determined by the viscosity ratio of the bulk to the interface. Figure 5 shows the correlation between b_c and the measured melt viscosity η_σ at both $T = 200$ °C and $T = 160$ °C for all four polyethylene resins. In support of eq 5, at $T = 200$ °C b_c scales linearly with η_σ which is measured at a constant stress of 0.256 MPa for each of MH07, MC02, MC60, and MH20. The anomalous behavior is once again seen at $T = 160$ °C, as indicated by the *nonlinear* relationship between b_c and η_σ which is measured at $\sigma = 0.205$ MPa. The two data points for MH07 and MC02 clearly jump up away from the dashed line. While landing on the solid line is simply coincidental, these two points indicate that different physics are operating at the interface at 160 °C depending on the molecular weight.

The interfacial origin of the low-temperature anomaly can be further interrogated by modifying the die wall condition. Instead of a smooth metallic wall, consider a rippled surface which we produce by tapping a smooth die with screw thread. Since melt in the thread valleys is stagnant, a threaded die has a great deal of effective slip interface that is a PE/PE interface. See paper 3 for a detailed study of the surface effects.[20] Figure 6 shows the temperature dependence of the stick–slip transition of MC02 in a threaded die with $L/D = 16$ and minor diameter $D = 1.5$ mm. It is very revealing to notice that the temperature anomaly at 160 °C completely disappears in a threaded die. The master curve in the inset of Figure 6 shows that the transition now satisfies the time–temperature superposition relationship as it always does[18] above 200 °C: the critical stress σ_c shifts linearly with T and the extrapolation length b_c is invariant with respect to T. Introduction of the PE/PE interface at the slip boundary apparently eliminates the mesophase formation and restores the normal features of the stick–slip transition. It is worth noting that this change in the interfacial condition is found to be insufficient to bring back the normal transition behavior for MH20 and MC60 for which the mesophase formation seems to be more pervasive and less prone to be disrupted by the presence of irregular interfacial shear flow.

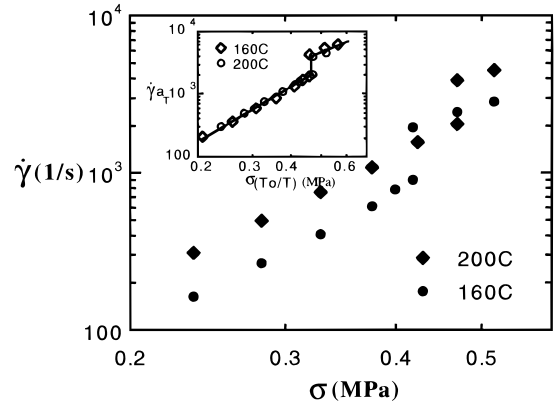

Figure 6. Measured wall shear rate $\dot{\gamma}$ versus the applied stress σ of MC02 at temperatures $T = 160$ and 200 °C obtained using a threaded die with saw-teeth like wall surface. The master curve in Inset indicates that the transition would occur at a constant σ_c/T throughout the entire temperature range above 160 °C and its magnitude is invariant with respect to T.

IV. Conclusion

We have studied the molecular characteristics of a stress-induced stick–slip transition in capillary flow of a series of high-density polyethylene resins. Contrary to slip velocity, a kinematic variable employed by most of the previous studies of wall slip and flow instabilities, we show for the first time that the extrapolation length b, as an intrinsic material property, possesses an explicit molecular weight dependence: $b_c \propto M_w^{3.4}$ at the transition. The critical stress σ_c for the stick–slip transition scales systematically with the molecular weight as $\sigma_c \propto M_w^{-0.5}$. At and above 200 °C the temperature dependence of the characteristics (e.g., σ_c and b_c) of the stick–slip transition can be understood in terms of a recent model[19] for interfacial disentanglement. At lower temperatures, temperature dependence of the transition becomes anomalous. In particular, the critical stress σ_c decreases with lowering T more strongly than linearly for all four polyethylene resins and the extrapolation length b_c at transition of MH07 and MC02 starts to increase with lowering temperature for $T < 200$ °C. It appears that some flow-induced mesophase formation may have taken place near the PE/die wall interface at low temperatures. We showed that this anomaly itself is also interfacial in nature. Although our suggestion of flow-induced nematic phase formation as the origin of the abnormal temperature dependence is tentative, the general physical picture[18] remains unchanged: the interfacial disentanglement between the adsorbed chains and surrounding free chains is the molecular origin of the stick−slip transition observed in pressure-controlled capillary flow of polyethylene resins.

Finally, it is important to remark that for an interfacial slip to be observable at a polymer/wall boundary it is required that the corresponding extrapolation length b not be negligibly small compared to the characteristic dimension such as the die diameter D or gap H between parallel plates. According to the reptation theory,[21] b of eq 5 is given by $n(N/N_e)^2a$, assuming that, in the complete slip limit, the interfacial viscosity is simply related to the monomer friction ζ as $\eta_i = \zeta/a$ where n is the degree of polymerization. Thus the magnitude of b of such polymers as polystyrene and poly(dimethylsiloxane) (PDMS) should only be about a thousandth of that of a linear polyethylene, given the same molecular weight. One key result of the present study is that b indeed scales strongly with the degree of entanglement as given by the product of the number n of monomers and square of the number N/N_e of entanglement points per chain. This explains why we can hardly detect a measurable stick−slip transition in PS and PDMS melts.

Acknowledgment. This work is supported by a fellowship award from BP Chemicals.

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