

Slip Transition of a Polymer Melt under Shear Stress

K. B. Migler,^(a) H. Hervet, and L. Leger

*Laboratoire de Physique de la Matière Condensée, Collège de France,
11 Place Marcelin Berthelot, 75231 Paris CEDEX 05, France*

(Received 22 October 1992; revised manuscript received 18 December 1992)

We present the first direct measurements of the local velocity of a sheared polymer melt within the first 100 nm from the solid-liquid interface. For high enough shear rates we observe a sharp transition between weak and strong slip (i.e., a nonzero boundary fluid velocity) in the case of weak polymer-surface interactions [polydimethylsiloxane (PDMS) on silanated silica surfaces]. For strong polymer-surface interactions the slip is strongly reduced. These results are compared to a theoretical model recently proposed by Brochard and de Gennes.

PACS numbers: 47.45.Gx, 47.50.+d, 81.40.Pq

The boundary condition of the fluid velocity at a solid wall of a sheared polymer melt, despite its important practical and fundamental implications, is still under debate. There is experimental evidence that slip (i.e., a nonzero velocity of the fluid at the solid-liquid interface) may occur at high molecular weights and shear rates [1–6]. In fact, except for one direct velocity measurement in a polymer solution using hot film anemometry [5], all the reported experiments infer slip indirectly from macroscopic behavior such as slope discontinuities in curves of global flow rate versus applied pressure. These features do not always show up and the controlling parameters are not yet clearly identified.

From a theoretical point of view it has been conjectured by de Gennes [7] that a high-molecular-weight polymer melt flowing on a smooth, nonadsorbing solid surface should always slip for any shear rate. Then, the “extrapolation length” b , defined as the distance from the wall at which the velocity profile extrapolates to zero, should be proportional to the third power of the molecular weight. It has also been noticed that polymer chains anchored on the surface should strongly reduce the slip-page [8].

In this Letter, we present what we believe to be the first direct measurements of the flow velocity of a high-molecular-weight polymer melt, within the first 100 nm from the solid wall, in a simple shear stress geometry. The experiments were performed using a novel optical technique, combining two methods: evanescent-wave-induced fluorescence (EWIF) [9] and fringe pattern fluorescence recovery after photobleaching (FPFRAP) [10]. This new tool allows the characterization of the dynamic behavior of the fluid both in the immediate vicinity of the solid surface (≈ 70 nm) and in the bulk. Here, we present the basic principles of the experiment necessary to understand the data. A detailed description of the setup will be reported elsewhere [11].

A small drop of fluorescently labeled polymer melt with refractive index n_2 is sandwiched between two planar substrates, with indices $n_1 > n_2$ (see Fig. 1), maintained at a distance d by two Mylar spacers. The melt is

never in contact with the spacers. The top surface can be translated with respect to the bottom one in the X direction at a variable controlled velocity V_t . This provides an apparent shear rate, $\dot{\gamma}_{\text{app}} = V_t/d$, within the range $2 \times 10^{-2} \text{ s}^{-1} \leq \dot{\gamma} \leq 40 \text{ s}^{-1}$. Interference fringes are produced by splitting a laser beam of wavelength λ_0 into two beams and recombining them on the bottom surface. If the adjustable angle of incidence θ_i is greater than the critical angle $\theta_c = \sin^{-1}(n_2/n_1)$, total internal reflection occurs with energy still penetrating into the polymer in the form of an evanescent wave with an exponentially decaying profile along the Z axis. This energy, confined within the penetration depth $\Lambda = \lambda_0/4\pi[n_1^2 \sin^2(\theta_i) - n_2^2]^{1/2}$ from the bottom surface, can locally excite the labeled polymer. In the crossing region of the two beams the mixing of the two evanescent waves creates an interference pattern with a fringe spacing $i = \lambda_0/[2\sin(\alpha/2)]$, where α is the adjustable angle between the two beams. A device, described in Ref. [11], modulates the phase shift between the beams at a frequency f , creating a sinusoidal oscillation of the fringe pattern with

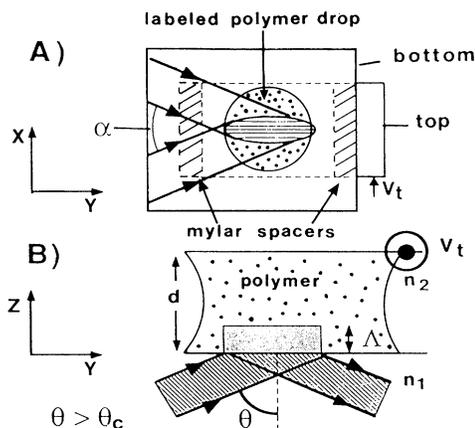


FIG. 1. Schematic representation of the sample cell: (a) view from the bottom of the cell; (b) side view showing the penetration depth Λ of the evanescent waves.

an amplitude $i/4$ along the X axis. The experimental sequence is the following: (i) First, a bleaching light pulse (power ≈ 100 mW, duration ≈ 100 ms) is shined on the sample, with neither shear nor modulation of the fringe position. A fraction of the fluorescent polymer is photobleached in the bright fringes. (ii) Immediately thereafter, the shear and the phase modulation are turned on, while the two beams, attenuated by a factor of 10^4 , to suppress further bleaching, read the fluorescence. Since the fluorescence intensity is the result of the product of the bleaching and reading intensities, both proportional to $e^{-Z/\Lambda}$, a region of thickness $\Lambda/2$ is probed. The f and $2f$ components, as well as the dc level of the fluorescence signal, are simultaneously recorded versus time. Without shear stress, due to the spatial distribution of the fluorescent labels and to the diffusion of the polymer, one gets a $2f$ signal which relaxes exponentially to zero, and a zero f component. In the case of pure shear flow and no slip, the $2f$ signal also relaxes monotonically to zero as the initial fringe pattern is tilted by the shear. However, the relaxation time is different from that observed in the absence of flow. If slip occurs, both the f and $2f$ components oscillate, in phase quadrature, at a frequency $\nu = V_s/i$, where V_s is the slip velocity of the polymer at the bottom surface.

In the present experiments the polymer samples are mixtures of high-molecular-weight unlabeled polydimethylsiloxane (PDMS) ($M_w = 962800$, $M_w/M_n = 1.27$, index of refraction $n_2 = 1.410$ at $\lambda_0 = 457$ nm), with 5% by weight of shorter PDMS chains ($M_w = 320700$, $M_w/M_n = 1.18$) end labeled with 4-chloro-7-nitrobenzo-2-oxa-1,3-diazole (NBD, $\lambda_{exc} = 457$ nm, $\lambda_{em} = 510$ nm). The bottom surface under investigation is the polished upper face of a fused quartz prism (index of refraction $n_1 = 1.463$ at λ_0) modified by chemical grafting of a

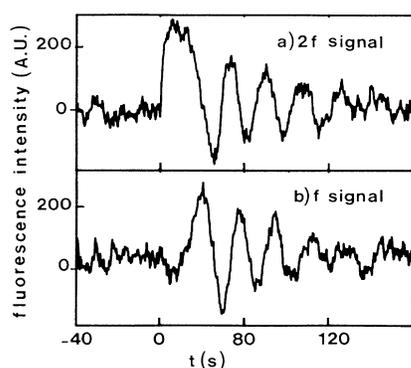


FIG. 2. Typical traces obtained for (a) the $2f$ component and (b) the f component of the fluorescence intensity vs time. The traces at $t < 0$ show the noise of the experiment. At $t = 0$ the bleaching pulse is shined on the sample with neither shear nor phase modulation. Immediately after the pulse, they are both turned on. The frequency of the oscillations gives the flow velocity in the first 70 nm from the surface.

monolayer of octadecyltrichlorosilane (OTS) to reduce the polymer-surface interactions. The top plate is bare fused quartz. Under these conditions, the minimum penetration depth is 94 nm. The data have been collected with a slightly larger value: $\Lambda = 140$ nm.

Figure 2 shows typical traces of the f and $2f$ components of the fluorescence intensity obtained with a polymer sample subjected to an apparent shear rate $\dot{\gamma}_{app} = 0.7$ s $^{-1}$. The oscillations in the two signals are the signature of a finite velocity of the polymer fluid at the polymer-solid wall interface. This establishes unambiguously the existence of slip.

In Fig. 3, the polymer surface velocity V_s is reported versus the top plate velocity V_t . A transition is clearly visible between a regime of weak slip and one of strong slip when V_t increases. Below the transition V_s falls at the lower limit of sensitivity of the technique. Indeed, if the relaxation by shear and diffusion becomes faster than the occurrence of the first oscillation in the f and $2f$ signals, V_s can no longer be determined.

Independent determinations of V_s are also displayed in Fig. 3 (squares). They have been obtained by using a bulk method where a single beam with an angle of incidence $\theta_i < \theta_c$ is used to photobleach a thin line through the bulk of the sample before applying the shear stress. Slip at the bottom surface will tend to translate this line whereas shear will tend to rotate it. After turning off the shear, a uniform translation of the entire sample (no shear) brings the reading beam into coincidence with a portion of the bleached line. This leads to a decrease of the fluorescence intensity. The first appearance of this decrease yields the position of the bottom of the bleached line. The translated distance divided by the duration of shear gives V_s values in good quantitative agreement with those of the evanescent fringe technique. This bulk method has a vertical resolution not better than 1 μm and only works for high enough V_s . However, it can give in-

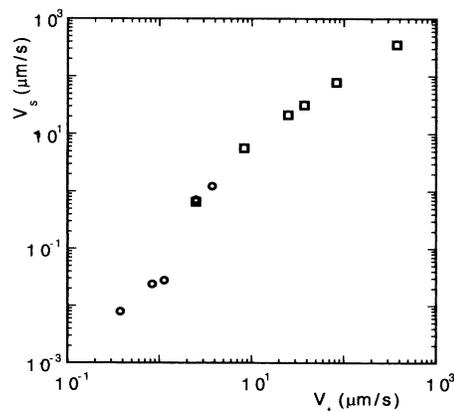


FIG. 3. Log-log plot of slip velocity of the polymer V_s vs the velocity of the top plate V_t . Circles and squares correspond to evanescent and bulk determinations, respectively.

formation on possible slip at the top surface (top slip velocity V_t). Such a tendency has indeed been detected in the present experiments for the four higher top velocities. It remains a weak effect, smaller than 5%, but has to be taken into account in evaluating the real shear rate applied to the polymer $\dot{\gamma}_p = (V_t' - V_s)/d$, where $V_t' = V_t - V_t$. In Fig. 4, V_s is reported as a function of the intrinsic variable $\dot{\gamma}_p$, a representation more convenient for comparison with models than that of Fig. 3.

Brochard-Wyart and de Gennes [12] have recently suggested that the presence of polymer chains end grafted onto a solid surface in a nondense packing (i.e., in the "mushroom regime" where the average distance between the grafted monomers is larger than the coil size R_g) can induce a transition between weak and strong slip above a critical shear rate. Their main prediction is the existence of a "marginal state" in which the grafted chains keep a constant elongation over a wide range of V_s . In the tube picture, each grafted chain may be considered as made of blobs (N_c monomers per blob, with N_c the critical number of monomers between entanglements) and progressively elongates under the action of the shear. When the chain of blobs is fully elongated, any further elongation would strongly reduce the friction (disentanglement). The balance between elastic and friction forces then tends to restore a more coiled structure. The chain of blobs then keeps a constant elongation as long as the shear rate is not large enough to further stretch the blobs. The onset of the marginal state corresponds to the onset of strong slip. As a consequence of the model, the extrapolation length b (see inset in Fig. 5) should display three regimes as a function of V_s . At low slip velocity, b is small and roughly constant. In the marginal state, b should increase linearly with V_s , and then saturate when the grafted chains are totally disentangled from the bulk polymer.

In Fig. 5, the b values deduced from the data of Fig. 3 are plotted as a function of V_s . There are indeed indica-

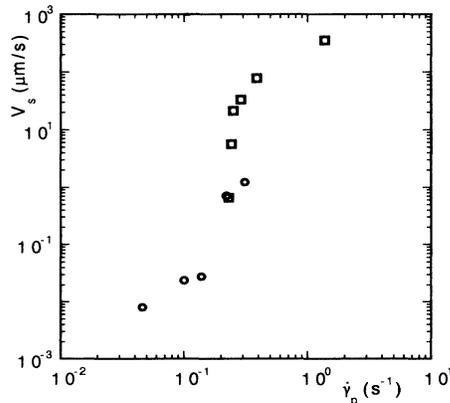


FIG. 4. Log-log plot of the slip velocity of the polymer V_s vs the shear rate $\dot{\gamma}_p$. Circles and squares correspond to evanescent and bulk determinations, respectively.

tions for the existence of three regimes. At low shear, b is small and roughly constant; above $V_s \cong 0.3 \times 10^{-2} \mu\text{m/s}$, b increases, following a simple power law with an exponent 0.87 ± 0.05 , and for V_s larger than $10^2 \mu\text{m/s}$ a tendency to saturation appears. All these features are in qualitative agreement with Brochard-Wyart and de Gennes's predictions, a result which may seem surprising since in the experimental system no chains have been grafted on the surface. However, additional experiments at long times show that the $2f$ signal, which should go to zero, remains at about 10% of its initial value. This indicates that a small fraction of the chains at the surface are immobile. They may play a role analogous to the grafted chains of the model.

Using the same polymer, we have performed similar experiments on two different surfaces: (1) bare silica, cleaned by UV irradiation under oxygen flow [13]; (2) silanated silica with an OTS monolayer less densely packed than in the previously reported experiments (advancing contact angle of dodecane $\theta_a = 24^\circ$ instead of 31° before, to be compared to 34° obtained for a fully dense monolayer [14]). For both conditions, bare silica or low-coverage OTS monolayer, the high slip regime has not been observed within the range of shear rates investigated. On bare silica, PDMS can create hydrogen bonds between the surface silanols and the oxygen atoms of the chain backbone. As a result, a dense layer of immobilized molecules builds up at the surface and is indeed detected by EWIF plus FFRAP [11]. Such a layer, which has the structure of a pseudobrush [15] with many loops anchored on the surface and entangled with the polymer liquid, is less deformable than a "mushroom" layer and may well prevent slip.

In conclusion, using a novel optical technique which combines EWIF and FFRAP, we have directly mea-

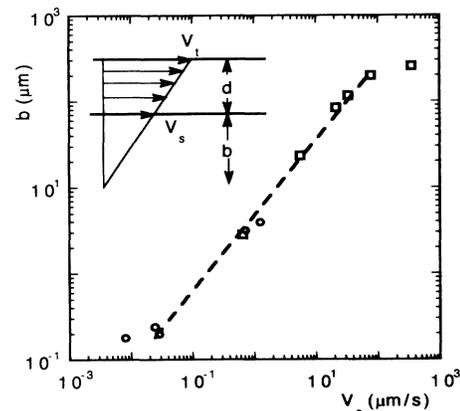


FIG. 5. Log-log plot of the extrapolation length of the velocity profile b , as defined in the inset, vs the slip velocity V_s . The dashed line represents the best fit of the data by a power law, with an exponent 0.87 ± 0.05 in qualitative agreement with the expected behavior of the "marginal state" recently predicted by Brochard-Wyart and de Gennes.

sured the velocity of a polymer melt in the immediate vicinity (≈ 70 nm) of a solid wall, in a simple shear stress geometry. We have thus clearly established that strong slip occurs at the interface for high enough shear rates in the case of weak polymer-surface interactions. The transition between weak and strong slip, rather abrupt in terms of shear rates, is characterized by a simple power-law dependence of the extrapolation length of the velocity profile b versus the slip velocity over three decades. This behavior is consistent with a recent model where the slippage is induced by a few chains bounded to the surface which undergo a coil-stretch transition under the shear stress. In the case of densely bounded chains slippage is strongly reduced. Additional systematic experiments are now under way in order to characterize in detail both the structure of the bounded polymer layer and the molecular weight dependence of the critical shear rate for the onset of slip.

We are deeply indebted to Dr. P. Auroy who finalized the synthesis of the labeled polymer and kindly gave us both the labeled and unlabeled PDMS samples. We also thank Dr. F. Brochard, H. Ji, and Dr. P. G. de Gennes for fruitful discussions. Physique de la Matière Condensée is unité associée No. 792 au Centre National de la Recherche Scientifique.

^(a)Present address: Exxon Research and Engineering Com-

pany, Clinton Township, Route 22 East, Annandale, NJ 08801.

- [1] G. V. Vinogradov, V. P. Protasov, and V. E. Dreval, *Rheologica Acta* **23**, 46 (1984).
- [2] R. H. Burton, M. J. Folkes, K. A. Narh, and A. Keller, *J. Mater. Sci.* **18**, 315 (1983).
- [3] A. V. Ramamurphy, *J. Rheol.* **30**, 337 (1986).
- [4] N. El Kissi and J. M. Piau, *C. R. Acad. Sci. Ser. 2* **309**, 7 (1989).
- [5] A. M. Kraynik and W. R. Schowalter, *J. Rheol.* **25**, 95 (1981).
- [6] S. G. Hatzikiriakos and J. M. Dealy, *J. Rheol.* **36**, 703 (1992).
- [7] P. G. de Gennes, *C. R. Seances Acad. Sci. Ser. B* **288**, 219 (1979).
- [8] F. Brochard-Wyart, P. G. de Gennes, and P. Pincus, *C. R. Acad. Sci. Ser. 2* **314**, 873 (1992).
- [9] D. Ausserré, H. Hervet, and F. Rondelez, *J. Phys. (Paris) Lett.* **46**, L-929 (1985).
- [10] J. Davoust, P. Devaux, and L. Léger, *EMBO Journal* **1**, 1233 (1982).
- [11] D. Frot, H. Hervet, L. Léger, and P. Auroy (to be published).
- [12] F. Brochard-Wyart and P. G. de Gennes (to be published).
- [13] *Treatise on Clean Surface Technology*, edited by K. L. Mittal (Plenum, New York, 1987), Vol. 1.
- [14] P. Silberzan, L. Léger, D. Ausserré, and J. J. Benattar, *Langmuir* **7**, 1647 (1991); P. Silberzan, thesis, Université Paris VI, 1990 (unpublished).
- [15] O. Guizelin, *Europhys. Lett.* **17**, 225 (1992).