

Real-Time Determination of the Slippage Length in Autophobic Polymer Dewetting

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We investigated the kinetics of autophobic dewetting, caused by differences in entropy, of a polymer melt slipping on a monolayer of end-grafted identical molecules (polymer brush). From simultaneous measures of the dewetted distance and the width of the resulting rim, we obtained in real time and quantitatively the slippage length and the contact angle, a measure of the “incompatibility” between identical molecules. Furthermore, we could directly relate a decrease in the slippage length in the course of the experiments at elevated temperatures to temporal or permanent attachment of polymers from the melt to the brush.

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The retraction of liquids from nonwetable surfaces, e.g., water film on a windscreen or ink on photographic paper, is a commonly observed phenomenon. This *macroscopically* visible process is affected by static and kinetic *molecular* interfacial properties [1,2], key parameters of the interaction between different phases like in wetting, adhesion, or friction. The static interaction between materials is to a large extent characterized by the interfacial tension between them. As already stated in 1805 by Young [3], contact angle measurements provide a simple, fast, and surprisingly precise way to determine such molecular interactions by regarding macroscopic phenomena. However, contact angles do not give direct information about kinetic effects like friction or slippage [4–8] at such an interface. These can be quantified by following the displacement of a contact line in dewetting experiments [9–14] (see Fig. 1). In such experiments capillary driving forces and energy dissipation at the interface are *intrinsic* properties controlled by molecular interactions. Thus, a dewetting system is at all stages of the process *self-adjusting* to any variations of the system.

In a typical dewetting experiment the driving capillary forces (uncompensated Young force, F_d) are balanced by viscous forces F_v (forces per unit length of the three-phase contact line) [2,9]. In a good approximation, F_d is determined by the contact angle (θ) and the surface tension (γ) of the liquid as $F_d = 0.5\gamma\theta^2$. F_v depends on the hydrodynamics of liquid flow. For nonslipping films the energy is dissipated in a small volume located at the contact line [1]. Then, F_v is simply proportional to the viscosity (η) and the velocity (V). In such dewetting experiments, V remains constant in time [9]. However, long polymers on a nonadsorbing substrate have been found to slip [6,15,16]. There the capillary energy is dissipated over the whole moving part of the film proportional to the width (w) of the rim formed by the liquid from the dewetted region [2,5,6]. In this case, $F_v = 3\eta Vw/b$. The parameter b is called the slippage length [4–6] and characterizes the degree of “slippiness.”

Such experiments allow one to determine and even to track θ , without any fitting. For nonvolatile liquids like

polymers, θ is related to w , the dewetted distance (d), and the film thickness (h) by mass conservation, valid at any time t

$$\theta(t) = d(t)h(t)/Cw^2(t). \quad (1)$$

The constant C , accounting for the shape of the rim, has been found [5] to be 0.1 for slipping films. It should be noted that Eq. (1) is valid for any self-similar profile of the rim. In our experiments, the value of $C = 0.1$ was verified by complementary atomic force microscopy measurements.

Such experiments also allow one to determine b for any time interval $t_i - t_{i-1}$, without any fitting.

$$b(t_i) = 3\eta V(t_i)w(t_i)/F_d(t_i). \quad (2a)$$

The velocity $V(t_i)$ can be determined by taking differences, $V(t_i) = [d(t_i) - d(t_{i-1})]/(t_i - t_{i-1})$. This allows us to

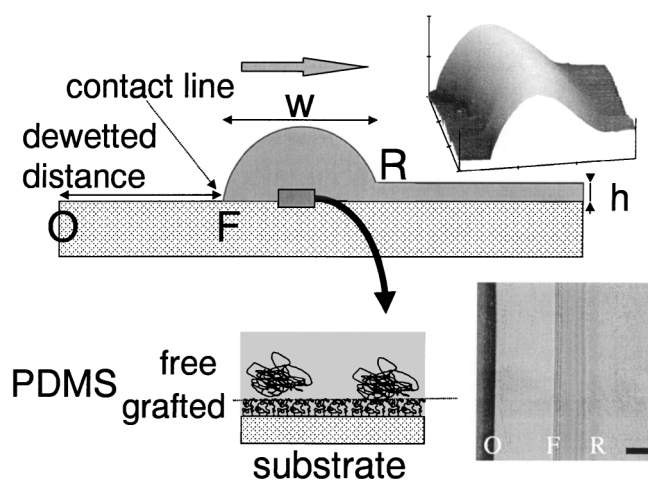


FIG. 1. Schematic representation of the experimental setup. A typical shape of the rim, as measured by atomic force microscopy, is shown in the upper right corner. The size of the image is $60 \times 60 \times 0.4 \mu\text{m}^3$. Note that the lateral scale is about a factor of 100 larger than the vertical scale. In the lower right corner we show an optical micrograph representing the top view corresponding to the scheme. The length of the bar equals $50 \mu\text{m}$.

check for possible changes in b in the course of an experiment, without the assumption of an exponent for a power-law relation between d and t .

Alternatively, b can be obtained by using the prefactors P and Q from the fits to the time dependence of $d = Pt^{2/3}$ and $w = Qt^{-1/3}$, respectively (assuming that θ and b do not depend on time), as predicted by theory [2,5]:

$$b = 2\eta PQ/F_d. \quad (2b)$$

For our experiments we used thin polydimethylsiloxane (PDMS) films supported by silicon wafers which were coated with a layer of end-grafted PDMS molecules [17], as indicated schematically in the “blowup” of Fig. 1. We treated the wafers chemically with chlorodimethylvinylsilane (CDMVS) to avoid adsorption of PDMS. Grafting polymers by one end at a high areal density onto a solid substrate leads to a reduction of the entropy of the grafted with respect to free molecules. This may lead to autophobic behavior [18,19]; i.e., the free molecules will dewet the grafted layer [20–22].

PDMS films [$M_w = 308\,000$ g/mol, $\eta(25^\circ\text{C}) = 1000$ Pa s] of different thicknesses between 20 and 850 nm were put on top of densely grafted layers of end-functionalized PDMS molecules ($M_w = 8800$ g/mol).

Dewetting was followed in real time by optical microscopy at temperatures between room temperature and 130°C . It was initiated at a straight line, denoted O , after a three-phase contact line was created at time t_o by breaking the sample in two parts, a process used previously [23]. At time $t_i > t_o$ the straight contact line has moved to point F and thereby dewetted the distance $d(t_i) = F(t_i) - O(t_o)$. The removed liquid was collected in a rim of width $w(t_i) = R(t_i) - F(t_i)$. h was measured by ellipsometry, η was varied by taking different monodisperse polymer fractions or by performing experiments at different temperatures, the values of γ were tabulated [24] and did not vary much for the molecular weights of the chosen polymer, and θ was determined *in situ* from mass conservation [Eq. (1)] and b from the balance of viscous and capillary forces [Eqs. (2)].

Previous polymer dewetting experiments of slipping films [6,15] have found $d \sim t^{2/3}$. However, it should be noted that such a slowing down of dewetting (i.e., $V \sim t^{-1/3}$) may also be induced by other factors, e.g., by surface modifications in the course of the experiment. Consequently, the value of the exponent may deviate from 1 (nonslipping) or $2/3$ (slipping). Thus, we believe that a more convincing evidence for slippage is the thickness dependence of the prefactor $P \sim h^{-1/3}$ (or $Q \sim h^{1/3}$) [2,5]. Note that for nonslipping films the dewetting velocity is independent of film thickness [2]. Our experimental results at a temperature $T = 50^\circ\text{C}$ (Fig. 2), normalized for differences in θ and b , unambiguously show that thicker films dewet more slowly than thinner films. In addition, we also found the expected $t^{2/3}$ dependence for d . Moreover, Fig. 3 shows that V is proportional to $1/w$, as

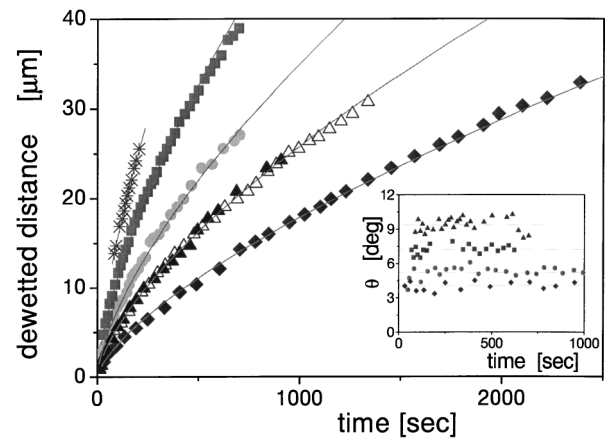


FIG. 2. Typical result for dewetting of a PDMS film [$M_w = 308\,000$ g/mol, $\eta(25^\circ\text{C}) = 1000$ Pa s] on top of a densely grafted layer of end-functionalized PDMS molecules (6.3 nm, $M_w = 8800$ g/mol) for different thicknesses: 27 nm (stars), 47 nm (squares), 52 nm (circles), 92 nm (triangles), and 135 nm (lozenges). The solid lines are best fits to the data using the following equation: $d = P(t - t_o)^\alpha$. We obtained $\alpha = 0.65 \pm 0.05$ for all measurements at low temperatures T (here $T = 50^\circ\text{C}$). Note that two independent measurements using the same sample give the same results (full and open triangles). Note further that films of similar thickness (47 and 52 nm) show rather different prefactors P . The inset shows the contact angle θ , as determined by Eq. (1), which within the experimental error can be taken as constant.

indicated by the full lines. This proves that the dissipation increases linearly with w and implies that the whole rim slips. Note that the capillary driving force (proportional to θ^2) is constant in time (see inset of Fig. 2).

Before normalizing for differences in b and θ , curves of Fig. 3a did not collapse onto a single master curve of V vs w , even if the thickness was the same (see the two curves for $h = 75$ nm in Fig. 3a). Normalizing the velocity by the driving force F_d and b (giving a parameter in units of m/N s) allowed us to obtain a master curve (Fig. 3b) as expected from Eq. (2a). Moreover, experiments performed at different temperatures could also be included if the viscosity was normalized with respect to a reference temperature using the shift factor given by the Williams-Landel-Ferry equation based on a time-temperature superposition principle [25]. Performing numerous experiments [26], we have also verified that the prefactor P (and correspondingly the prefactor Q) depends on θ , b , and h , as expected by the theory [2,5]. We note that we have not observed any systematic dependence of θ or b on h (see inset of Fig. 3b). This corroborates that the theoretical description of our observations takes all relevant parameters into account.

The values obtained for b are of the order of $10\ \mu\text{m}$. The corresponding friction coefficient (per area a^2 of a monomer) $k = \eta/b = 10^8$ Pa s/m compares well to the value of the monomeric friction coefficient [27] $k_o = 3.7 \times 10^7$ Pa s/m. This indicates that only a few (x) monomers at the interface contributed to friction

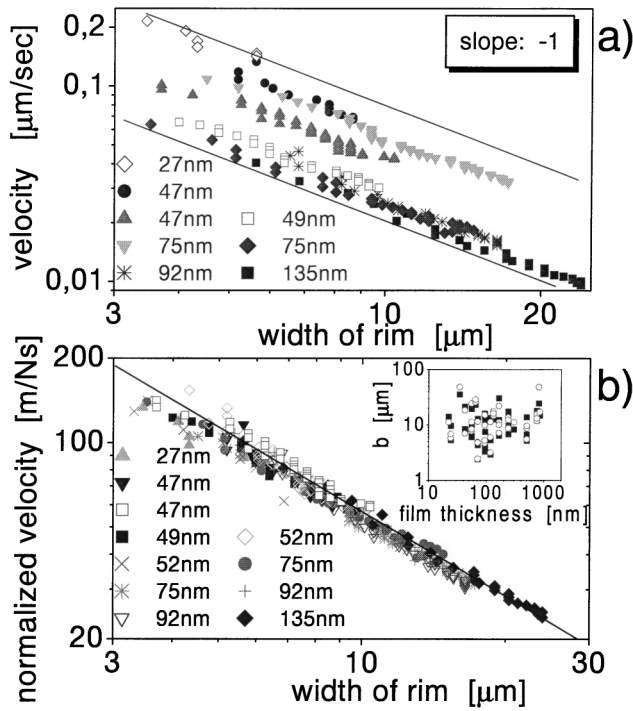


FIG. 3. (a) Dewetting velocity and (b) normalized velocity (multiplied by b/F_d) as a function of the width of the rim (w) for various film thicknesses. The slippage length b (inset of Fig. 3b) was determined by using Eqs. (2a) and (2b) shown by full and open symbols, respectively.

($k = xk_o$), thereby implying that the free molecules penetrated only a little into the brush [27]. This conclusion is corroborated by the experimentally found observation that b was rather independent of velocity, for V varying between 10 nm/s and 1 μ m/s (this holds only for experiments at 50 $^{\circ}$ C on densely grafted brushes). The friction coefficient k is controlled only by the entropy loss of the grafted molecules and not by the flow velocity of the free molecules [7].

In summary, our experiments show that our results can be described perfectly well by theory [2,9]. Consequently, we are able to determine, without any assumptions, θ and b directly during the dewetting process. Furthermore, the kinetics of different samples can be compared only when θ and b have been determined. At 50 $^{\circ}$ C and for brushes of high grafting density, both θ and b proved to be independent of time.

However, in contrast to the above statement, less perfect brushes of lower grafting density showed lower θ and much lower b , i.e., deeper interpenetration between melt and brush, and, in addition, significant deviations from the expected $d \sim t^{\alpha} = t^{2/3}$ behavior. Furthermore, at elevated temperatures higher than about 100 $^{\circ}$ C, most samples showed exponents $\alpha < 2/3$. Figure 4 shows a typical example obtained at 130 $^{\circ}$ C.

In search for the origin for such deviations we note that the slippage length is very sensitive to even tiny changes of interfacial properties which may occur in the course of

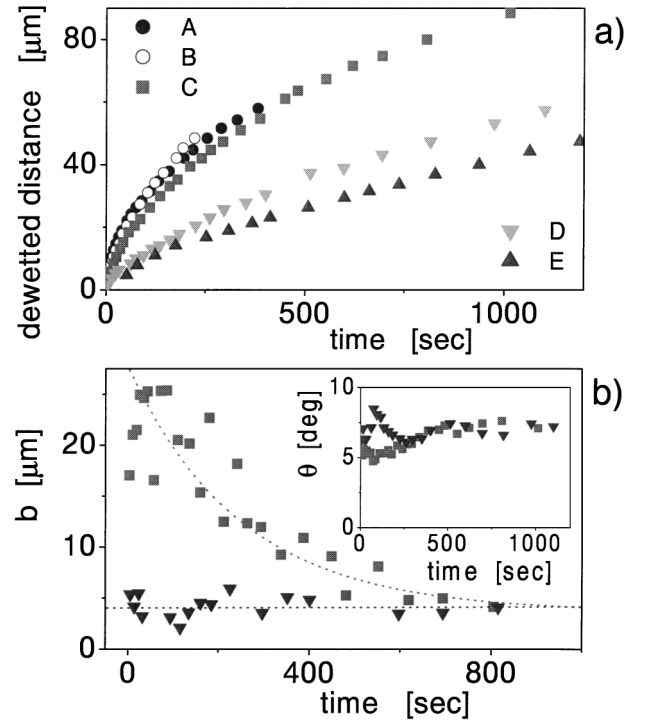


FIG. 4. Temporal changes of the slippage length. Dewetting of a 106 nm thick PDMS film measured at 130 $^{\circ}$ C after different thermal treatments of the supporting grafted PDMS layer (a). A: as prepared, B: after 3 h at 130 $^{\circ}$ C in vacuum, C: after 24 h at 130 $^{\circ}$ C in vacuum, D: after being coated with a 106 nm thick PDMS film and 3 h at 130 $^{\circ}$ C in vacuum, E: after being coated with a 106 nm thick PDMS film and 24 h at 130 $^{\circ}$ C in vacuum. The inset shows that the contact angles θ for cases C and D were similar and rather independent of time. It should be noted that by fitting $d = P(t - t_o)^{\alpha}$ to the data we obtained $\alpha = 0.55 \pm 0.05$ for curves A–C and 0.66 ± 0.02 for D and E, respectively. In contrast to θ the slippage length b [see (b)] shows a pronounced decay for case C reaching the rather constant value of case D after several hundred seconds. The dotted lines serve as guides to the eye.

an experiment. In order to exclude the possibility that such changes were due to thermal degradation of the brush, we checked the thermal stability of the brush by ellipsometry. Annealing the brush without a film on top for 24 h at 130 $^{\circ}$ C in vacuum yielded almost the same dewetting behavior of $d \sim t^{1/2}$ as without prior annealing of the brush (compare curves A, B, and C in Fig. 4a). However, if the brush was annealed with a film on top for 3 or 24 h at 130 $^{\circ}$ C (also under vacuum), the retraction of the contact line was much slower (see curves D and E in Fig. 4a). In addition, in contrast to curves A, B, and C, we obtained the $d \sim t^{2/3}$ behavior also observed for samples at 50 $^{\circ}$ C (see Fig. 2).

Figure 4b provides an explanation. In contact with the long polymers of the film the interface is modified, expressed by a time-dependent reduction of b [28]. This observation can be explained if some of the long polymers of the film have been trapped within the brush or if such molecules have been temporarily or permanently attached

onto “defects” in the CDMVS layer, possibly caused by annealing at elevated temperatures. These polymers can act as “connectors” [23] and thereby reduce the slippage length [7]. Once the interface was “saturated,” b stabilized at a constant but now lower value. For the observed reduction of b only very few connectors are necessary [23]. Thus, such surface modifications are not detectable by static measurements of the thickness of the brush, e.g., by ellipsometry. Before the actual dewetting experiments, but after the different thermal treatments, the brush was washed in a good solvent (heptane). The thickness of the grafted layer was constant within the resolution of ellipsometry (0.2 nm).

It should be noted that the capillary driving force F_d represented by θ (see inset of Fig. 4b) stayed more or less constant, consistent with the experiments on bimodal polymer brushes [23]. However, the dissipative counterforce F_v increased. From the increase of the friction coefficient k by a factor of about 5 we estimate that a fraction (y) of about $y = 0.001$ of the interfacial sites of monomer size a^2 were occupied by attached or trapped long polymers. Here we assumed that the increase in k is only due to Rouse friction of all N monomers of the long adsorbed polymers [4,7] ($k = yNk_o$). If these molecules were, however, entangled with the melt (which is likely regarding the molecular weight) much fewer molecules would be responsible for this reduction [4,7].

We showed that dewetting experiments present extremely sensitive measures of molecular interfacial parameters, like the friction coefficient, depth of interpenetration, or slippage length. The high sensitivity comes from the fact that even small modifications of the interface have a huge effect on the dewetting kinetics which can easily be detected in real time and related to interfacial parameters. The biggest advantage of this approach is its simplicity in allowing one to obtain complementary information (see b and θ) in a single experiment, a feature missing in other techniques. Now that the theory has been experimentally verified and applied to understand the time-dependent behavior of basic cases, one can extend this approach to more complex systems of mixed materials and elucidate the relation between the molecular scale interfacial properties and macroscopic behavior, both static and kinetic.

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- [1] P.G. De Gennes, *Rev. Mod. Phys.* **57**, 827 (1985).
- [2] F. Brochard-Wyart, P. Martin, and C. Redon, *Langmuir* **9**, 3682 (1993).
- [3] T. Young, *Philos. Trans. R. Soc. London* **95**, 65 (1805).
- [4] F. Brochard-Wyart and P.G. de Gennes, *Langmuir* **8**, 3033 (1992).
- [5] F. Brochard-Wyart, P.G. de Gennes, H. Hervet, and C. Redon, *Langmuir* **10**, 1566 (1994).
- [6] C. Redon, J.B. Brzoska, and F. Brochard-Wyart, *Macromolecules* **27**, 468 (1994).
- [7] F. Brochard-Wyart, C. Gay, and P.G. de Gennes, *Macromolecules* **29**, 377 (1996).
- [8] P.A. Thompson and S.M. Troian, *Nature (London)* **389**, 360 (1997).
- [9] C. Redon, F. Brochard-Wyart, and F. Rondelez, *Phys. Rev. Lett.* **66**, 715 (1991).
- [10] P. Martin and F. Brochard-Wyart, *Phys. Rev. Lett.* **80**, 3296 (1998).
- [11] A. Buguin, L. Vovelle, and F. Brochard-Wyart, *Phys. Rev. Lett.* **83**, 1183 (1999).
- [12] P. Lambooy, K.C. Phelan, O. Haugg, and G. Krausch, *Phys. Rev. Lett.* **76**, 1110 (1996).
- [13] Q. Pan, K.I. Winey, H.H. Hu, and R.J. Composto, *Langmuir* **13**, 1758 (1997).
- [14] R.A. Segalman and P.F. Green, *Macromolecules* **32**, 801 (1999).
- [15] G. Reiter, P. Auroy, and L. Auvray, *Macromolecules* **29**, 2150 (1996).
- [16] E. Durliat, H. Hervet, and L. Leger, *Europhys. Lett.* **38**, 383 (1997).
- [17] G. Reiter *et al.*, *Europhys. Lett.* **46**, 512 (1999).
- [18] S. Sheiko, E. Lermann, and M. Möller, *Langmuir* **12**, 4015 (1996).
- [19] M.W.J. Van der Wielen, M.A. Cohen Stuart, and G.J. Fleer, *Langmuir* **14**, 7065 (1998).
- [20] Y. Liu *et al.*, *Phys. Rev. Lett.* **73**, 440 (1994).
- [21] G. Henn, D.G. Bucknall, M. Stamm, P. Vanhoorne, and R. Jérôme, *Macromolecules* **29**, 4305 (1996).
- [22] L. Leibler, A. Ajdari, A. Mourran, G. Coulon, and D. Chatenay, in *Ordering in Macromolecular Systems*, edited by A. Teramoto, M. Kobayashi, and T. Norisuje (Springer-Verlag, Berlin, 1994), pp. 301–311.
- [23] G. Reiter, J. Schultz, P. Auroy, and L. Auvray, *Europhys. Lett.* **33**, 29 (1996).
- [24] B.B. Sauer and G.T. Dee, *Macromolecules* **24**, 2124 (1991).
- [25] J.D. Ferry, *Viscoelastic Properties of Polymers* (Wiley, New York, 1980), 3rd ed.
- [26] G. Reiter and R. Khanna, *Langmuir* **16**, 6351 (2000).
- [27] H.R. Brown, *Science* **263**, 1411 (1994).
- [28] The time for the decay of b was found to vary between samples.