Reduced Viscosity in Thin Polymer Films

Hugues Bodiguel and Christian Fretigny*

Laboratoire PPMD, CNRS UMR 7615, ESPCI, 10 rue Vauquelin, 75235 Paris Cedex 05, France
(Received 23 August 2006; published 29 December 2006)

The dewetting of thin polystyrene films (20–500 nm) on a liquid substrate is studied at time scales that are long compared to the reptation time. It is shown that the kinetics correspond to those of purely viscous flow and that the viscosity measured by this technique is, for the thickest films, consistent with bulk measurements. Films on the order of the coil size are then studied. The effective viscosity of these films displays a large decrease when the film thickness h is below several radius of gyration, R_g. This viscosity reduction is found to depend only on the ratio h/R_g.

During the past decade, ultrathin polymer films have been the focus of numerous studies. Most of them have focused on their glass transition (T_g), which has been found to be reduced when the thickness of the film is below several tens of nanometers [1] (see, for a review, Ref. [2,3]). However, the global dynamics in thin polymer films remains an unresolved issue [3]. As recently pointed out, a direct comparison between the experimental techniques is usually not straightforward, since the dynamics appear to be more complex than in the bulk [4]. Time scales involved in the dynamics, from segmental to chain motion, are associated with different length scales and are thus likely to be affected differently by confinement.

Though many authors report enhanced mobility below bulk T_g, all experiments conducted above T_g report either no deviation from bulk properties [5,6] or a slowing down of the dynamics [4,7,8]. Those results may confirm several theoretical considerations, which predict that chain motion (either Rouse modes [9] or reptation [10]) should be slower in ultrathin films than in the bulk.

However, other arguments may lead to opposite conclusions concerning above-T_g dynamics. Considering first a chain lying near the surface, in a layer of thickness the coil size, it should have one ore more contacts with a very thin molten region at the surface. These contacts may have a great mobility and should accelerate the reptation mechanism. This effect is analogous to the sliding motion described by de Gennes [11]. This argument leads to the conclusion that the reptation time of a chain in a layer on the order of the coil size is lowered. Chain motion might be accelerated by such a mechanism.

Second, arguments coming from chain packing theory [12] together with a recent experiment [13] lead to the conclusion that, close to a surface, the nature of entanglement differs from that of the bulk. The pervaded volume of a chain that meets the surface should be less than in the bulk. Thus, other chains are excluded from the pervaded volume, which results in a lack of *interchain* entanglements in a layer of characteristic thickness the radius of gyration R_g, even though the entanglement density remains bulklike. One of the assumptions of the reptation theory is that reptation is the dominant mechanism of the motion [14]. If there is a lack of interchain entanglements in the surface layer, other modes than reptation may be allowed and we would expect the viscosity to be reduced. Under these assumptions, the viscosity would be reduced in a surface layer on the order of the coil size.

Since these two considerations seem to be in conflict with previously mentioned experimental and theoretical studies, it is of great interest to directly access the viscosity of the surface layer, or that of a freestanding film that is on the order of the coil size. In this last case, the measured properties should be somewhat averaged if the surface affects the dynamics.

We take advantage of the surface tensions that act on a thin film lying on a liquid substrate to measure the viscosity [15]. The effect of the surface and interfacial tensions can be accounted for by a normal stress acting on the edges of the film of intensity $\sigma = S/h$, where h is the film thickness and $S = \gamma_f + \gamma_{f/l} - \gamma_l$ is the spreading parameter. γ_f and γ_l are the surface tensions of the film and liquid substrate, respectively, while $\gamma_{f/l}$ is the interfacial tension of the film-liquid interface. If we assume incompressibility, the stress acting on the edge is equivalent to a normal stress acting on the planar faces of the film. The strains are those of an uniaxial stretching [15]. In the case of polystyrene (PS) films floating on glycerol, S is negative [15]; dewetting thus occurs and the film contracts in the planar direction, while its thickness increases as a function of time.

In this Letter, we focus on the long time (or high temperature) regime of viscoelastic dewetting. At long times ($t \gg \tau_d$, τ_d being the reptation time), the elastic contribution to the extensional creep compliance $D(t)$ of melt polymers can be neglected [16]. The creep compliance reaches a linear regime, which corresponds to the flow of a Newtonian liquid: $D(t) \sim t/\bar{\eta}_0$, where $\bar{\eta}_0$ is the steady state extensional viscosity. The stress-strain relation in this regime is thus given by $\sigma = \bar{\eta}_0 \dot{\epsilon}$, where $\dot{\epsilon}$ is the extensional strain rate. In the case of a uniaxial stretching, $\dot{\epsilon} = \dot{h}/h$. Since the applied stress is $-S/h$, the stress-strain relation leads to $\dot{h} = -S/\bar{\eta}_0$. Thus, when S is negative, the film thickness is expected to increase linearly with time.

TABLE I. PS samples have been purchased from Polymer Source, Inc. M_w and M_w/M_n data are given by Polymer Source, Inc. Values of the radii of gyration have been calculated according to the following expression: $R_g(nm) = 0.87\sqrt{M}w(kDa)$ [17]. The annealing temperatures have been set in such a way that the reptation time of each sample is approximately several tens of minutes.

Sample	M_w (kDa)	M_w/M_n	R_g (nm)	Annealing temperature
PS54	54.0	1.04	6.4	388 K
PS286	286	1.06	14.7	403 K
PS1407	1407	1.05	32.6	423 K

Films are obtained by spin coating PS solutions from toluene. Monodisperse polystyrene of various molecular weight has been used (see Table I). The films are annealed under vacuum after the spin coating for 8 days above T_g (the annealing temperatures are given in Table I). They are then floated at room temperature and transferred onto a heated glycerol bath, used as the substrate. A standard camera is used to acquire images of the film. The film thickness is calculated from the area of the film, assuming volume conservation. The reader may refer to Ref. [15] for more experimental details.

We first report experiments on thick films ($h > 100$ nm for PS286 and PS54, $h > 300$ nm for PS1407). The viscosity of these films should be bulklike, since the length scale of the surface contribution is expected to be much smaller than the investigated thicknesses. Second, we report results on thinner films, for which deviations from bulk properties are found.

Figure 1 presents results obtained on thick films. The film thickness is seen to increase linearly at long times. The short time response contains an elastic contribution, and is affected by the thermal history of the sample [15]. Good numerical agreement with viscosity values of bulk samples has been found, using $|S| = 5$ mN/m [15]. In the following, we discuss the experimental value of $\bar{\eta}_0/|S|$ since the value of S is only an estimation.

The dependency of the inverse of the slope $\bar{\eta}_0/|S|$ with temperature and molecular weight has been studied. Results are summarized in Fig. 2. In a large temperature range above T_g, the bulk viscosity of polymers follows the Volger-Fuchs-Tamman (VFT) empirical law [16]: $\eta = \eta_0(M_w)\exp[B/(T - T_0)]$. Using values obtained by Plazeck [20] on bulk PS for B and T_0, the experimental points are fitted by the VFT law, η_0 being the only variable parameter. The quality of the fit, as shown in Fig. 2, ensures that the temperature dependence of the viscosity measured in our experiment is similar to that of the bulk. Then, we used the fitted parameter η_0 to check the molecular weight dependence of the viscosity. In the inset in Fig. 2, it is shown that this parameter follows the usual empirical power law variation for entangled polymers [14]: $\eta \sim M_w^{3.4}$.
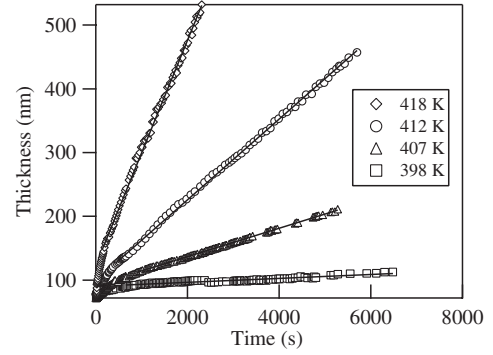

FIG. 1. Film thickness as a function of time at various temperatures for PS286. The initial thickness of all films was 80 nm. At long times, the thickness reaches a linear regime. The straight lines are the best linear fits to the data. The slope of the linear regime is given by $|S|/\bar{\eta}_0$, according to our analysis.

The good agreement between our experimental results and well-known bulk results for the dependence of viscosity on both the temperature and the molecular weight confirms our analysis. Furthermore, it strongly indicates that the viscosity lies in the linear regime. In fact, if rheofluidification was occurring, variations of the measured viscosity with temperature and molecular weight would have been smaller than the expected ones. When the stress is imposed, non-Newtonian behavior occurs when the applied stress is greater than the rubbery modulus [21]. Considering a value of 5 mN/m for the spreading coefficient [15], the applied stress is on the order of
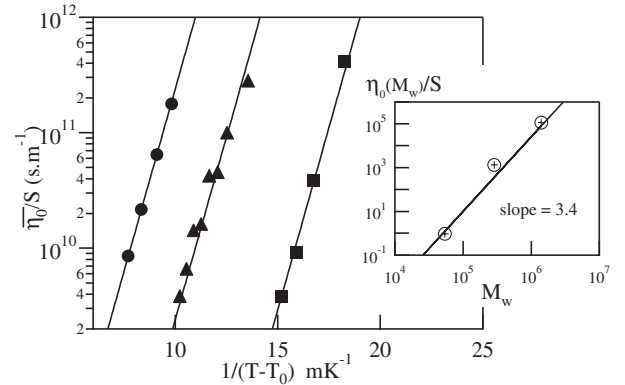

FIG. 2. Steady state extensional viscosity normalized by the spreading coefficient ($\bar{\eta}_0/|S|$) as a function of the reduced temperature $1/(T - T_0)$, for three different molecular weights: PS54 (■), PS286 (▲), PS1407 (●). The temperature range is 383 K to 453 K. Experimental points are fitted by VTF law ($\eta = \eta_0(M_w)\exp[B/(T - T_0)]$), with fixed value for the parameters B and T_0 (1456.3 K and 323.4 K, respectively, taken from Ref. [20]). The inset shows the three parameters $\eta_0/|S|$ that produce the best fits to the experimental data, plotted as a function of the molecular weight. The straight line represents the expected power law variation for the viscosity as a function of the molecular weight: $\eta_0 \sim M_w^{3.4}$.

0.5 MPa for a 10 nm film. Therefore, the stress is always lower than the rubbery plateau modulus for the investigated thickness range. We can conclude that the linear extensional viscosity of polymer films can be measured with this dewetting experiment.

Figure 3 shows results obtained on PS1407 films in a large range of thickness. The thickness is found to increase nonlinearly and faster for the thinnest films. It is reasonable to assume that, in the steady flow regime, the instantaneous viscosity only depends on the thickness value. At a given thickness, encountered during the dewetting process, the thickness increase rate depends on the thickness only, but not on the dewetting time nor on the initial thickness. This hypothesis is verified in inset of Fig. 3, where the inverse of the derivative of the thickness versus time [which is equal to $\eta(h)/|S|$] is computed for each set of experimental points [24] and is plotted as a function of the film thickness: All data nearly lay on a same curve. Thus, η/S only depends on the film thickness, and not on its initial value. As the thickness is higher than 40 nm, the variations of the spreading parameter could be neglected [25,26]. In the following, it is thus assumed that the variations of η/S with the thickness correspond to viscosity variations.

As recalled in the introduction, a chain in a surface layer of thickness R_g should be more mobile for at least two reasons. First, a chain lying in this layer makes contact with the soft region of thickness the monomer size. At these contact points the motion should be easier [11] and the reptation time for this chain should be lower. Second, a lack of interchain entanglement should decrease the reptation time. It has been argued [13] that this effect occurs once again in a layer on the order of R_g. Then, to compare the results obtained on polymers with different lengths, it seems relevant to normalize the films thicknesses to the gyration radii. This is made in insert of Fig. 4. The viscosity curves start to decrease at similar h/R_g values for the two tested polymers, and seems to only differ by a vertical numerical factor. This is verified in Fig. 4, where the

viscosities are normalized to their bulk value $\bar{\eta}_0$ (see below). The good superposition obtained allows to state that the observed viscosity reduction only depends on the h/R_g ratio.

It was not possible to verify this scaling over a wider range of molecular weight. The very small radii of gyration of smaller chains would require experiments on films so thin that the experiment would be difficult to perform. The very high viscosity of films made of longer chains would require either too high temperatures or too long times to conduct the experiment. However, the radius of gyration of PS1407 is more than twice higher than that of PS286. Thus, the observed scaling in h/R_g cannot be due to any experimental error and should properly describe the observed viscosity reduction.

One can expect that the dynamical properties of the segments vary according to their distance to the interfaces. Then it seems difficult to define a single viscosity parameter for the chains. As the experimental results give access to an averaged property, one can define a "local viscosity" $\eta(z)$ parameter [27]. Although this local parameter is certainly meaningless at length scales below R_g, it allows us to discuss the effective viscosity that is measured. Experimental observations (uniform thickness, homothetic shape) indicate that the shear that may occur due the viscosity inhomogeneities is very small. The typical variations of the radial velocity $\Delta v/v$ should be on the order h/R, where R is a typical planar dimension of the film. Thus, $\Delta v/v \ll 1$ and plug flow still occurs in such inhomogeneous films. For a plug flow, the effective viscosity that is measured is the average viscosity along the thickness, $\eta(h) = 2/h \int_0^{h/2} \eta(z)dz$.

FIG. 4. Viscosity of polymer films as a function of the thickness, for PS286 (410 K) and PS1407 films (433 K and 443 K). The thickness is normalized by R_g (see Table I). The inset displays the scaled experimental data, whereas the figure shows the same data, normalized by the bulk value. For each condition, the effective viscosity $\eta(h)$ was first fitted by $2/h \int_0^{h/2} \bar{\eta}_0\{1 - \exp[-(z/R_g)^\beta]\}dz$ (see text), with β and $\bar{\eta}_0$ as adjustable parameters, and then normalized by the best fit value of $\bar{\eta}_0$. This parameter was found to be, within experimental error, in agreement with the data shown in Fig. 2. The best fit shown (solid line) is obtained with $\beta = 3.4$.
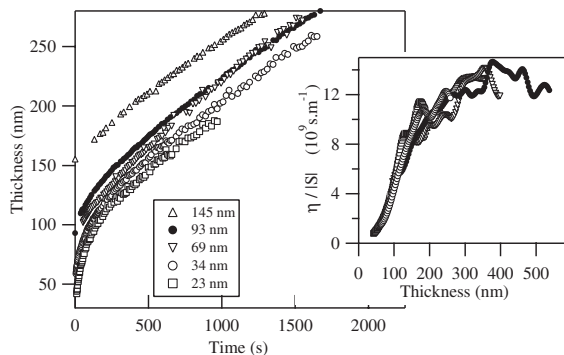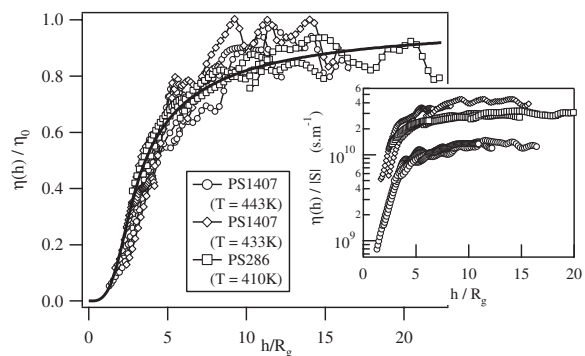
FIG. 3. Thickness as a function of time for PS1407 films (only the shorter times are shown for clarity), at 443 K. The inset displays $\eta/|S|$, the inverse of the derivative of thickness, vs time. Its calculation is performed as detailed in [24].

Let us assume that $\eta(z)$ increases from zero towards $\bar{\eta}_0$, with a characteristic length R_g, and that the cooperativity between the two surfaces is negligible. Independently on the exact form of $\eta(z)$, the effective viscosity reaches an hyperbolic asymptotic form. It could be accounted by the bulk viscosity acting on an effective thickness $h - 2R_g$. At $z \lesssim R_g$, $\eta(z)$ should be negligible as compared to $\bar{\eta}_0$. An arbitrary example of $\eta(z)$ is obtained with a stretched exponential function $\eta(z)/\bar{\eta}_0 = 1 - \exp[-(z/R_g)^\beta]$. The effective viscosity, calculated using this equation, is plotted in the Fig. 4, using the best fit value for β: 3.4. The global shape of the viscosity variation is well reproduced, which strongly indicates that the essential hypotheses of this tentative model are verified. The local viscosity increased from the surface to the bulk with a characteristic length on the order of the coil size. The high value of the β exponent indicates that the viscosity in a layer of thickness R_g is well below the bulk value.

One could discuss the observed viscosity reduction in the background of the Tg reductions found for ultrathin PS films. The viscosity involves time scales that are very long as compared to those of T_g. Then, it seems difficult to extrapolate our results to T_g without any hazardous hypothesis on the global time spectrum. It seems clear that the M_w-independent T_g reductions observed in many supported films are of different nature to that of the viscosity reduction which scales with R_g. In the case of freestanding films, Dalnoki-Veress *et al.* showed that the T_g reduction depends on M_w [28]. However, contrary to our results, no direct link to the coil size was found. Moreover, no effect on T_g is reported in the literature for films of thickness greater than 100 nm, even for very long chains. In this Letter, we show that viscosity is reduced when the film thickness is below 7–8 R_g, which corresponds, for the longer polymers tested, to a thickness of more than 200 nm. Therefore, we might conclude that T_g shifts and the viscosity reductions are two distinct phenomena. It confirms that the dynamics of polymers in thin films is rather complex and that the time spectrum of the material is not simply shifted.

Presented data support the picture of a surface layer of thickness on the order of the coil size, in which the chain motion would be enhanced. They seem contradictory with some of the experimental and theoretical work that focus on dynamics above T_g. It had been predicted that the Rouse modes of a polymer chain close to the surface should be slower [9]. Assuming that Rouse modes are slower in an ultrathin film, our results imply that there is another competing phenomenon concerning the longest relaxation time involved in the viscosity. If the nature of entanglements differs from that of the bulk, it is possible to shorten the longest relaxation times together while increasing the Rouse mode times. This may also explain the disagreement between our experimental results and the theory developed by Semenov [10], which predicts a viscosity increase when the film thickness is on the order of the coil size. Indeed, this result was obtained assuming a bulklike entanglement nature.

---

*Electronic address: christian.fretigny@espci.fr
[1] J. L. Keddie, R. A. L. Jones, and R. A. Cory, Europhys. Lett. **27**, 59 (1994).
[2] J. A. Forrest, Eur. Phys. J. E **8**, 261 (2002).
[3] M. Alcoutlabi and G. B. McKenna, J. Phys. Condens. Matter **17**, R461 (2005).
[4] Z. Fakhraai, S. Valadkhan, and J. A. Forrest, Eur. Phys. J. E **18**, 143 (2005).
[5] H. Kim *et al.*, Phys. Rev. Lett. **90**, 068302 (2003).
[6] J. S. Sharp, J. H. Teichroeb, and J. A. Forrest, Eur. Phys. J. E **15**, 473 (2004).
[7] Y. Pu *et al.*, Phys. Rev. Lett. **87**, 206101 (2001).
[8] B. Frank *et al.*, Macromolecules **29**, 6531 (1996).
[9] K. L. Ngai, Eur. Phys. J. E **12**, 93 (2003).
[10] A. N. Semenov, Phys. Rev. Lett. **80**, 1908 (1998).
[11] P. G. de Gennes, Eur. Phys. J. E **2**, 201 (2000).
[12] H. R. Brown and T. P. Russell, Macromolecules **29**, 798 (1996).
[13] L. Si *et al.*, Phys. Rev. Lett. **94**, 127801 (2005).
[14] M. Doi and S. F. Edwards, *The Theory of Polymer Dynamics* (Clarendon, Oxford, 1986).
[15] H. Bodiguel and C. Fretigny, Eur. Phys. J. E **19**, 185 (2006).
[16] J. D. Ferry, *Viscoleastic Properties of Polymers* (Wiley, New York, 1980), 3rd ed.
[17] This expression has been developed by Tujeta *et al.* [18], from the data of Cotton *et al.* [19].
[18] A. Tuteja *et al.*, Macromolecules **38**, 8000 (2005).
[19] J. Cotton *et al.*, Macromolecules **7**, 863 (1974).
[20] D. J. Plazek, J. Phys. Chem. **69**, 3480 (1965).
[21] The transition from Newtonian to non-Newtonian behavior occurs for shear rates greater than the inverse of the longest relaxation times of the system [22,23]: $\tau_d \dot{\epsilon} > 1$.
[22] W. W. Graessley, Adv. Polym. Sci. **16**, 1 (1974).
[23] A. Bach *et al.*, Macromolecules **36**, 5174 (2003).
[24] Experimental data are interpolated to obtain equally spaced points in thickness, $t = \phi(h)$. The function ϕ is convolved with a Gaussian function of standard deviation 12 nm and is then differentiated to obtain the effective viscosity: $\eta(h) = \phi'(h)$. Since the very short times contain an elastic contribution to the thickness increment, the derivation is calculated only for experimental points for which the strain is greater that twice the strain at the rubbery plateau (corresponding to a thickness increase of about 20 nm [15]).
[25] D. Y. Ryu *et al.*, Science **308**, 236 (2005).
[26] K. M. Ashley *et al.*, Langmuir **21**, 9518 (2005).
[27] M. Vladkov and J.-L. Barrat, Macromol. Theory Sim. **15**, 252 (2006).
[28] K. Dalnoki-Veress *et al.*, Phys. Rev. E **63**, 031801 (2001).