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Spreading of High Molecular Weight Polymer Melts on High-Energy Surfaces

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ABSTRACT: The spreading behavior of high molecular weight poly(dimethylsiloxane) (PDMS) drops on silica surfaces has been investigated through optical microscopy and ellipsometry. For molecular weights higher than the entanglement molecular weight, both the drop profile and the macroscopic spreading kinetics differ from the well-known low molecular weight behavior: a "bump" appears on the side of the macroscopic drop at thicknesses comparable to the radius of gyration of the chains while the macroscopic spreading slows down and finally stops, departing from the usually observed Tanner's law. The existence of the bump is highly sensitive to the nature of the monomer-substrate interactions. The lateral extension of the bump evolves with time in a diffusive manner, and the molecular weight dependence of the corresponding diffusion coefficient appears compatible with a reptation process for the transport of the chains along the surface. These results will be discussed and compared to recent theoretical predictions which take into account two characteristic features of the hydrodynamics of entangled polymer melts, namely, a finite *slippage* of the chains at the solid wall and an *enhanced friction* of the monomers in contact with the surface due to solid-monomer interactions.

Introduction

The investigation of very thin liquid polymer films is of special interest for a number of practical applications (e.g., lubrication, adhesion, etc.) as well as for more basic concerns on confined polymer systems.

Several molten polymer films confined between two mica plates have recently been studied through force measurements.[1] The most striking result of these experiments is the appearance of a strong repulsive force when the polymer thickness becomes lower than twice the chains' radius of gyration. As pointed out recently by Van Alsten and Granick,[2] this is probably not a thermodynamic effect but, more likely, a dynamical observation. de Gennes[3] has interpreted this repulsive force by a trapping of the chains at the surfaces.

The very long relaxation times described in ref 3 for low molecular weights demonstrate the need to use techniques complementary to force measurements in order to fully characterize high-viscosity entangled liquid polymers.

Recently, wetting experiments have demonstrated their ability to probe solid-liquid interfaces.[4] The principle of such experiments is simple: it consists of analyzing the dynamic behavior as well as the profiles of a drop of the considered liquid spontaneously spreading on the solid surface. A situation of particular interest both theoretically and experimentally[5] is the case of "dry" wetting when the liquid is not volatile (there is no transport of matter via the vapor phase). This is obviously the case with high molecular weight polymeric liquids.

For nonpolymeric liquids or low molecular weight molten polymers, these spreading behaviors begin to be well understood: macroscopically, the drop is a spherical cap which progressively flattens down on the solid surface. Its dynamic radius $R(t)$ and contact angle $\theta(t)$ (Figure 1) follow the so-called Tanner's laws:

$$R(t) \propto t^{0.1}; \quad \theta(t) \propto t^{-0.3}$$

Simultaneously, ahead of this macroscopic drop, a precursor film develops, as has been experimentally observed[7] and theoretically explained.[5] The thickness of this film is controlled by the spreading parameter S ($S = \gamma_{SG} - \gamma_{SL} - \gamma$ where γ_{SG}, γ_{SL}, and γ are the surface tensions at respectively the solid-gas, solid-liquid, and liquid-gas interfaces) and by the effective Hamaker constant[8] of the system.[4,5] For very large surface-energy solids (for which $S > \gamma$), the precursor film becomes flat over large distances and its thickness is molecular.[7a] At the connection between the precursor film and the macroscopic drop a few "steps" of molecular thickness have also been observed.[7b]

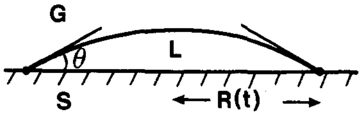

Figure 1. Schematic representation of the macroscopic drop. The dynamic contact angle is θ. At equilibrium $\theta \rightarrow 0$ (total wetting).

The situation is far more complex for polymeric liquids in the entangled regime. For poly(dimethylsiloxane) (PDMS) on silica, Tanner's laws are well obeyed at the beginning of the process.[9] The molecular film has been observed by X-ray reflectivity methods showing that the density is not uniform: at the edge of the film, the density is only 60% of the bulk density.[7a] However, it has been reported that a much thicker "bump" (several hundreds of angstroms thick) can appear on the side of the macroscopic drop.[10] The observation of this bump is greatly influenced by the surface contamination and the presence of impurities in the surrounding atmosphere.

In a recent paper,[11] we have shown that, for one molecular weight of PDMS (in the entangled regime) on silica, such a bump can effectively be observed providing that experiments are performed under rigorously controlled conditions. The aim of the present paper is to clarify the behavior of this bump for a variety of molecular weights. Its structure and its dynamic behavior will be compared with a recent theory of Bruinsma[12] which takes into account the possible slippage of the chains on the surface as well as their potentially enhanced friction compared to the bulk.

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Table I

M_W	M_W/M_N	Viscosity, P
33 000	1.12	11.5
50 000	1.13	45
79 000	1.15	205
160 000	1.11	2300
280 000	1.19	14500

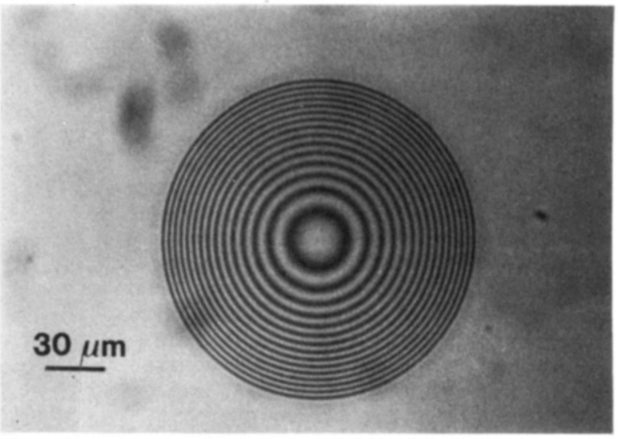

Figure 2. Equal-thickness fringes as they can be observed on the drops by optical microscopy in natural light. The macroscopic radius (R) is defined by the external black fringe and the contact angle by extrapolation of the entire profile.

Experimental Section

A. Material. PDMS was purchased from Rhône-Poulenc Co. (France) and fractionated by us. In Table I, we list the molecular weights and polydispersities of the samples used in this study. All of them are in the entangled regime.[13] The surface tension of these samples is 21 ± 0.5 dyn/cm as measured by the Wilhelmy plate method.

The solids are silicon wafers [111] (Siltronix, France) naturally covered by oxide (amorphous silica, 20 Å thick). Their roughness has already been measured to be about 5 Å.[7a] Before each experiment, they are cleaned by UV irradiation under oxygen,[14] a method which has been proven to efficiently remove traces of organic contamination while preserving the surface quality. These wafers are of very high surface energy: a water drop spontaneously spreads on them giving $S > 50$ dyn/cm for PDMS in air.

B. Drop Deposition. Conservation of the Samples. A drop of a given molecular weight is deposited on each wafer, inside of a glovebox filled with filtered dry nitrogen. Typical deposited volumes are 10^{-8} cm^3. This is performed by slowly approaching to the surface a steel wire previously dipped in PDMS. The droplet at the very end of the wire can then be deposited on the wafer.

From that point the samples were enclosed in air-tight boxes equipped with a glass window to allow observations in optical microscopy. When other techniques have been used, samples were transferred (inside of the glovebox) into other specially designed boxes. With all these precautions, the atmosphere surrounding the spreading drop was clean, dry nitrogen.

C. Observations. The different parts of the drops were probed using complementary techniques.

Optical reflection microscopy (Microscope Polyvar, Reichert Young, Austria) was used to obtain accurate profiles of the macroscopic drop through equal-thickness fringes formed with unpolarized monochromatic light (Figure 2). By using several wavelengths, the accuracy of the method can be increased (getting more points on the drop profile). The smallest thickness that can be probed this way corresponds to the first black fringe, i.e., $h = \lambda/4n$ where λ is the considered wavelength and n the refractive index of the silica + PDMS always considered as a homogeneous layer whose index is that of PDMS. For each wavelength, refractive indices of PDMS have been measured using the limit refraction method. When using blue light, thicknesses as small as about 770 Å can then be probed ($n \simeq 1.416$ at $\lambda \simeq 404.7$ nm). Still, in optical microscopy, much thinner parts of the drop (down to about 50 Å) can be observed between crossed polarizers using the ellipsocontrast method.[9] The thickness determination is then only qualitative, but evolution of thin films can be easily followed.

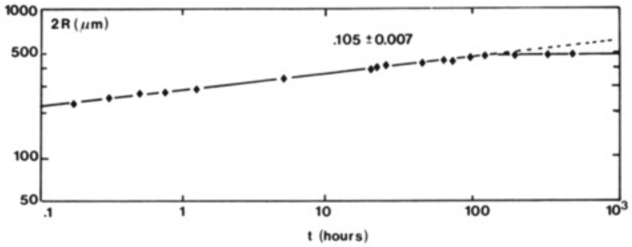

Figure 3. Evolution of the radius $R(t)$ of a spreading drop ($M_W \simeq 33\,000$). The solid diamonds indicate the experimental points, and the line is the best fit with a scaling law, giving the theoretical Tanner's exponent. After 4 days, the spreading stops.

The last technique used was ellipsometry. It has been widely used for thickness measurements of thin films and more recently applied to several wetting experiments.[7b,15,16] The main obstacle encountered with this technique is the nonplanarity of the considered surfaces due to the natural curvature of the drop profiles. However, when the thickness does not change "too abruptly" (as can be checked using the procedure described in ref 5), a remarkably good profile determination can be obtained. The ellipsometer used here has already been described elsewhere.[17] Thicknesses as low as 1 Å can be studied with an accuracy of about 1 Å and a particularly good lateral resolution (~20 μm).

Results

A. Kinetic Observations. Observations in microscopy in natural light show that, within experimental error, the profiles of the macroscopic drops are spherical. At the beginning of their evolution, they follow the classical Tanner's laws.

However, after a certain time (depending on the molecular weight), the macroscopic spreading seems to slow down until its definitive stop (Figure 3). The higher the molecular weight, the sooner this happens.

When observed in ellipsocontrast, a thick film develops all around the macroscopic drop (Figure 4b). This is what we call the bump, as schematically represented on Figure 4c. It cannot be mistaken for the molecular precursor film already reported for similar systems through X-ray reflectivity experiments.[7a] This bump is not visible in nonpolarized light (Figure 4a) and, for the particular example on Figure 4, its thickness is estimated to be about 200 Å. Qualitatively, the higher the molecular weight, the thicker the bump.

A qualitative analysis of the profile can be performed through the photograph on Figure 4. The connection between the bump and the macroscopic drop is steep: the gray level of the extreme black fringe does not decrease continuously toward the film. On the contrary, the edge of the film is more diffuse: the thickness decreases slowly toward the edge of the wafer.

We have studied the dynamic behavior of this bump and, more precisely, its extension $l(t)$. This is represented on Figure 5 on a l vs $t^{1/2}$ plot. A diffusive law

$$l(t) = (Dt)^{1/2} \tag{1}$$

well-describes the data over a long period of time (up to several months for the higher molecular weights).

The diffusion coefficients deduced from these measurements seem independent of the drop volumes except when the drops are so small that the volume of liquid contained in the film becomes an appreciable fraction of the total volume. They appear to be about 10 times smaller than the bulk self-diffusion coefficients.[18]

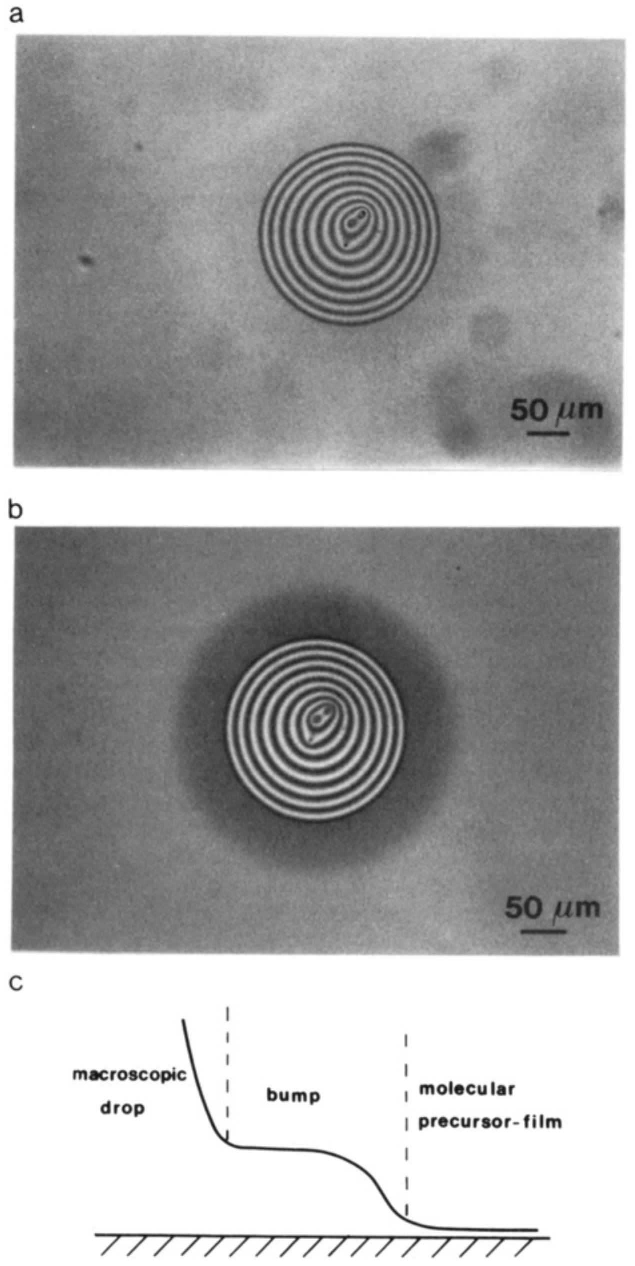

Figure 4. Observation of a PDMS droplet ($M_W \simeq 79\,000$) in optical microscopy in natural (a) and polarized (b) light. While invisible on a, the bump is clearly visible on b. (Here, its thickness is $\simeq$200 Å). A qualitative description of the profile can be performed through this photograph (see text for details). The profile of this bump is schematically represented on c.

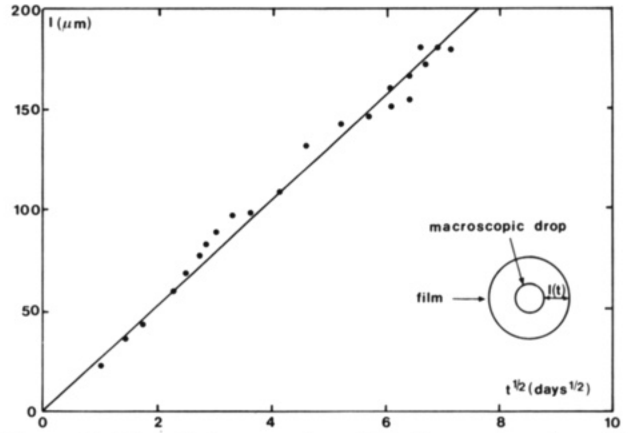

Figure 5. Plot of the extension of the bump, l, against $t^{1/2}$ demonstrating the diffusive behavior of the bump ($M_W \simeq 79\,000$).

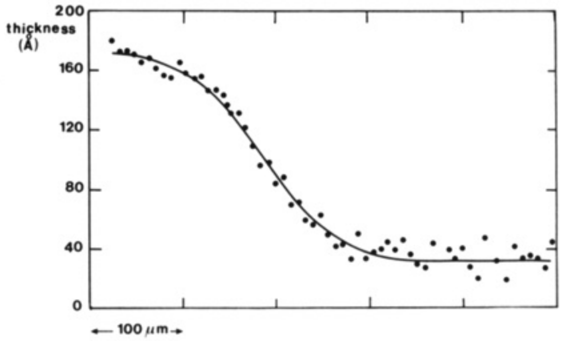

Figure 6. Ellipsometric profile of the bump ($M_W \simeq 50\,000$). The solid circles indicate the experimental points. The solid line is the best fit with an error function (see text for details). Note the base line at a 30-Å thickness which represents the 20-Å-thick silica layer on which the molecular film ($\simeq$10 Å thick) had spread out.

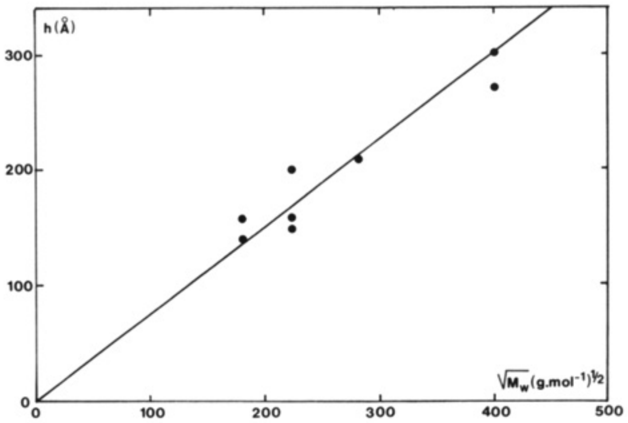

Figure 7. Evolution of the bump thickness, h, vs $M_W^{1/2}$. The linear shape of the curve and the experimental value of the slope ($\simeq$0.75) are strong evidence that h can be described by the radius of gyration of the chains.

B. Profiles of the Edges of the Films. We have determined profiles of these bumps by ellipsometry. One of these is represented on Figure 6. The experimental points are well-described by a law of the type

$$h = A\left[1 - \operatorname{erf}\left(\frac{x - x_0}{(4Dt)^{1/2}}\right)\right] + B \qquad (2)$$

characteristic of diffusive profiles when they are invariant along one dimension.[19] In the fits, A, x_0, and D are the adjustable parameters. B is fixed at 30 Å: it represents the 20-Å-thick silica layer on which the molecular film had spread out ($e \sim 10$ Å[7a]).

The good agreement between the error function and the experimental profiles is another argument which supports the analysis in terms of a diffusive process. Qualitatively, the orders of magnitude of the diffusion coefficients obtained from relations 1 and 2 are consistent. Quantitatively, however, there is a discrepancy (for instance, $D \sim 1.7 \times 10^{-15}$ m²/s from (1) compared to 4.5 $\times 10^{-15}$ m²/s from (2) for $M_W \sim 50\,000$) which has been attributed to the geometry of the drop (circular and not invariant along the transverse direction).

C. Molecular Weight Dependence. Through the ellipsometric profiles, the thickness h of the bump has been determined for each molecular weight. The experimental data represented on Figure 7 show that this bump thickness is well described by a $M_W^{1/2}$ dependence. More precisely, when translated in terms of polymerization indices N, we obtain $h(N) \simeq aN^{1/2}$ where $a \sim 6$ Å. h is thus comparable to the chains' radius of gyration (or twice this value).

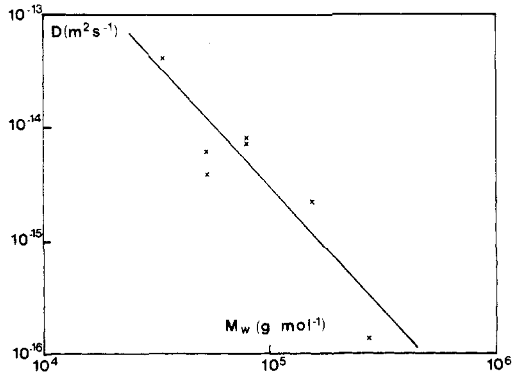

Figure 8. Logarithmic plot of D vs M_W. The crosses indicate the experimental points. The solid line is the best fit of a scaling law, giving $D \propto M^{-2.3\pm0.3}$.

It must be pointed out that, below the entanglement molecular weight, no bump has ever been observed either by us or by other authors on the same system or on different ones.[7b,16]

We have also studied the molecular weight dependence of the diffusion coefficient (here, we have used the diffusion coefficients obtained through relation 1). Its evolution is shown on Figure 8 on a logarithmic plot. The important dispersion of the points as well as the restricted range of molecular weights experimentally accessible does not allow a really quantitative analysis. Nevertheless, one can interpret these results by a power law: $D(M) \propto M^a$ where $a \cong -2.3 \pm 0.3$.

Discussion

The spreading of polymer melts has been recently theoretically treated and has shown behaviors quite different from that of simple liquids presented in the Introduction.

Two contributions specific of polymeric liquids have to be taken into account: the first one is the possible finite *slippage* of the chains close to the surface.[20] For molecular weights higher than the entanglement weight, the entanglements in the bulk oppose shear and it becomes energetically favorable to concentrate the dissipation at the surface: the result is a finite velocity of the chains close to the surface. This effect is characterized by the extrapolation length $b = aN^3N_e^{-2}$ where a is the monomer length, N the polymerization index, and N_e the polymerization index at the entanglement weight (see Figure 9). For PDMS, for, say, M_W = 100 000, $b \sim 20$ μm.

The second effect that has to be taken into account is the possible *reduction of mobility* of the monomers close to the surface compared to the bulk: the chains may develop interactions (for instance, hydrogen bonding) with the surface. In the following, we will call f the ratio of the monomers' mobility on the surface and in the volume.

The slippage effect has been included in the description of wetting processes by Brochard and de Gennes[21] and should lead to a change in the curvature of the precursor film profiles (a "foot" of height b). As we said, for entangled chains, b is very high and the resulting foot should be easily visible by interferometry or ellipsometry. We do not observe such a foot but rather the bump at a thickness R_g.

Bruinsma[12] has discussed the profiles of spreading drops when taking into account both the slippage and the friction effects. The different following regimes can then be identified:

(1) If $f < N^{3/2}N_e$, the friction can be neglected and the profile is described by the foot of Brochard and de Gennes. Its height however is b/f instead of b and can thus be severely reduced.

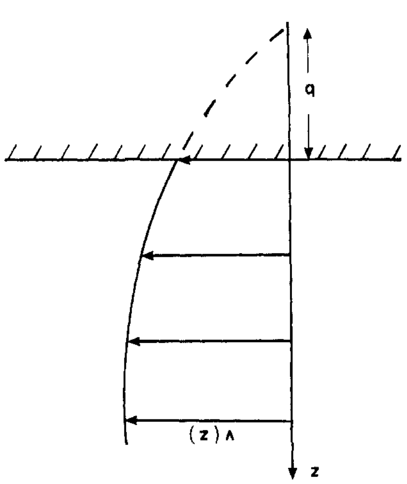

Figure 9. Velocity profile of a polymer melt near a solid surface. b is the extrapolation length.

(2) When $N^{3/2}N_e < f < (N/\theta N_e)^{3/2}$, the monomer–surface interactions become quite important. For thicknesses smaller than R_g, most of the chains have one or more contact points with the solid surface; their mobility is thus very much reduced. However, there remains statistically a small fraction of the chains with no attachment. In this two-fluid model, these, although very scarce, are at the origin of the mass transport. The sticked chains form a porous medium through which the Laplace pressure in the macroscopic drop pushes the mobile chains. For this process, the reptation mechanism can be referred to.[22] The most striking result of this calculation is then the existence of a bump whose thickness is R_g and whose extension should vary linearly with time.

(3) At last, if $f > (N/\theta N_e)^{3/2}$, the behavior of the polymer includes many nonequilibrium effects. This last regime is thus quite complex and has only been succinctly discussed by Bruinsma[12] and by de Gennes.[3a]

Of course, the experimental profiles we have observed show strong similarities with the profiles predicted by Bruinsma in the intermediate regime ($N^{3/2}/N_e < f < (N/\theta N_e)^{3/2}$, "reptation + slip" regime). The bump of thickness R_g is indeed observed.

The value of f in our experiments is unfortunately quite difficult to measure. There is some evidence through fluorescence recovery measurements that the mobility of the chains is indeed very much reduced close to the surface.[23] Moreover, we have performed a control experiment for which a droplet of PDMS has been deposited on a silicon wafer grafted with long aliphatic chains whose terminal group is unsaturated.[24,25] On such a surface, PDMS is in total wetting ($S \sim 10$ dyn/cm[24]), but one can expect the monomer–substrate interactions to be strongly reduced compared to the bare silica surface (in particular, hydrogen bonding becomes impossible). No bump developed itself on this surface, confirming the above interpretation.

Dynamically, however, the predicted behavior of the bump evolving linearly with time is clearly not verified here. The fact that the macroscopic spreading stops quite rapidly and the diffusive evolution of the bump rather seem to reveal that the Laplace pressure inside the macroscopic drop is not sufficient to push the free chains through the immobilized ones or, at least, that the characteristic time for the diffusion of the edge of the bump becomes rapidly much smaller than the one associated with the flow induced by the pressure difference between the macroscopic drop and the film. This results in the diffusive evolution of the extension of the bump, the macroscopic drop acting then like a reservoir. At a completely different scale of thickness, this regime has numerous common characteristics with the diffusive regime predicted by Joanny and de Gennes[26] for the precursor film of simple liquids.

Assuming that diffusion at the edge of the bump drives the process and keeping for the microscopic mechanism of mass transport through the bump, the Bruinsma hypothesis (reptation of the mobile chains through the porous medium formed by the immobile ones) yields $D(M) \sim M^{-2}$, indeed close to the experimental -2.3 exponent.[27]

Actually, none of the above assumptions is clearly verified and several other contributions may have to be taken into account. For instance, instead of considering only two populations of chains (one fixed and the other mobile), recent experiments[23] on the dynamics of chains close to the surface suggest that a complete distribution has to be taken into account. This would be expressed here by considering a distribution of mobilities and thus of the friction coefficient f. Moreover, when the chains are confined, one can expect a diminution of the number of entanglements and thus a reduced viscosity at small thicknesses.[28]

Complementary experiments are clearly necessary to fully clarify these points. In particular, the connection between the bump and the molecular precursor film may be of special interest. It may also be instructive to systematically vary the nature of the surface. For example, decreasing the monomer–substrate friction can help us to understand previous observations of macroscopic drops spreading faster than predicted by Tanner's laws.[29]

Conclusion

The present experiments have revealed that the spreading of entangled polymer melts is quite different from that of low molecular weight liquids.

The most striking result we have obtained is the existence of a bump on the edge of the macroscopic drop. Dynamic measurements as well as detailed profile determinations reveal a diffusive behavior of this bump.

These observations can be partly interpreted with the two-fluid description proposed by Bruinsma which takes into account both slippage effects and a reduced mobility of the monomers close to the surface.

It has to be pointed out that experiments as simple as wetting experiments can be quite useful for the determination of the relative importances of the slippage and the friction the chains experience close to the surface. These experiments can then become a powerful alternative to the force measurements which have proven to be particularly ticklish with polymer melts.

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