Molecular Weight Dependence of Spreading Rates of Ultrathin Polymeric Films.

M.P.Valignat¹, G.Oshanin²,³, S.Villette¹, A.M.Cazabat¹ and M.Moreau²
¹ Laboratoire de Physique de la Matière Condensée,
Collège de France, 11 place M.Berthelot, 75252 Paris Cedex 05, France
² Laboratoire de Physique Théorique des Liquides,
Université Paris VI, 4 place Jussieu, 75252 Paris Cedex 05, France
³ Centre de Recherche en Modélisation Moléculaire,
Université de Mons-Hainaut, 20 place du parc, 7000 Mons, Belgium
(Received: December 11, 1997)

PACS No: 68.45.-v, 68.10.Gw, 68.45.G, 83.10.Nn

We study experimentally the molecular weight $M$ dependence of spreading rates of molecularly thin precursor films, growing at the bottom of droplets of polymer liquids. In accord with previous observations, we find that the radial extension $R(t)$ of the film grows with time as $R(t) = (D_{exp} t)^{1/2}$. Our data substantiate the $M$-dependence of $D_{exp}$: we show that it follows $D_{exp} \sim M^{-\gamma}$, where the exponent $\gamma$ is dependent on the chemical composition of the solid surface, determining its frictional properties with respect to the molecular transport. In the specific case of hydrophilic substrates, the frictional properties can be modified by the change of the relative humidity (RH). We find that $\gamma \approx 1$ at low RH and tends to zero when RH gets progressively increased. We propose simple theoretical arguments which explain the observed behavior in the limits of low and high RH.

Experimental studies of non-volatile drops spreading spontaneously on solid surfaces often reveal thin precursor films. For some liquid/solid systems only a single well-defined precursor film develops from the macroscopic droplet. In other cases, the films have a remarkable "terraced" shape being formed by superimposed compact monolayers. For liquids composed of polymers with low molecular weight $M_c$ (i.e. such that $M$ is well below the entanglement threshold $M_c$ in 3D), the experimentally observed thickness of the precursor film or of the "terraces" is typically of order of several angstroms. It is much less than the gyration radius $R_g$ of the same polymers in solution and corresponds to the transverse size of the monomeric units. This implies that contrary to the behavior expected for polymers with high $M$, $M > M_c$, for which the predicted thickness of the precursor film should compare to $R_g$, for low-$M$ polymer liquids the macromolecules in the precursor film (or in the superimposed monolayers) are essentially disentangled and lay flat on the solid substrate or on the lower layers.

Most of available experimental studies were devoted to the analysis of the temporal evolution of precursor films. Meanwhile, there is ample evidence that at sufficiently short times, when the macroscopic droplet still acts as a reservoir, the radial extension $R(t)$ of such films follows a universal time-dependence of the form

$$R(t) = \sqrt{D_{exp} t}$$  (1)

In view of the form of Eq.(1) the prefactor $D_{exp}$ is often referred to as the "diffusion coefficient" of the precursor. Needless to say that $D_{exp}$ is different from the conventional diffusion coefficient describing particles random motion in the bulk liquid phase or on solid substrates; as a matter of fact, $D_{exp}$ also depends on the driving forces which cause the film spreading.

Physical processes underlying the temporal behavior as in Eq.(1) are now rather well understood. Moreover, several theoretical models which explain the $\sqrt{t}$-dependence of $R(t)$ are now available. However, still little is known about the dependence of $D_{exp}$ on different physical and chemical factors, such as, for example, the temperature, relative humidity (RH), chemical composition of the substrate and, for polymer liquids, the molecular weight of polymers. On the other hand, especially the latter point is of essential importance for many practical applications, such as, e.g. coating, gluing or lubrication, - most of liquids used in these material processing operations are either polymer liquids or contain polymeric additives.

A few available by now studies of polymeric films spreading on solid surfaces concern the molecular weight dependence of $D_{exp}$. Early experimental analysis of spreading rates of mesoscopically thin films of perfluorocarbon polymers suggest that $D_{exp}$ decreases algebraically with an increase of $M$, i.e. $D_{exp}$ obeys

$$D_{exp} \sim \frac{1}{M^{\gamma}}$$  (2)

where the experimentally observed value of the exponent $\gamma$ is close to 1.7. The same behavior was recently recovered in [10] (see also [11]) for low-$M$ perfluoropolyalkylether polymers, used in the computer industry for lubricating the hard discs in order to reduce wear. Studies of low-$M$ polydimethylsiloxane (hereafter abbreviated as PDMS) molecules spreading on bare oxidized silicon wafers, used without cleaning, or on wafers bearing loose grafted trimethyl layers demonstrate that $D_{exp}$ is with good accuracy inversely proportional to the PDMS bulk viscosity $\eta(M)$. Here, since for the range of
polymer weights studied in Ref.5 the best fit for the viscosity (Petrarch data for the PDMS) is given by the algebraic law $\eta(M) \sim M^{1.7}$, the observations of Ref.5 appear to agree quite well with the results reported in Refs.9 and 10. We note also that the dependence $D_{\text{exp}} \sim 1/\eta(M)$ is consistent with the theoretical prediction of the hydrodynamical model of mesoscopically thin films spreading [4]. Such a model, however, is not justified for films whose thickness amounts to only a few angstroms.

On the other hand, recent ellipsometric studies [6] show that the $M$-dependence of $D_{\text{exp}}$ fades out at high RH in case of PDMS molecules spreading on cleaned hydrophilic substrates. This contradicts apparently to the results of Refs.9 and 10 and suggests that the exponent $\gamma$ is not necessarily a constant, but may vary with the RH. As a matter of fact, the observation made in Ref.6 is in favor of the theoretical model of Ref.13, which predicts that dewetting dynamics of polymeric monolayers is governed by the law in Eq.(1) with $M$-independent $D_{\text{exp}}$.

In this Letter we report the results of first systematic analysis of the $M$-dependence of $D_{\text{exp}}$, deduced from the experimental studies of rates of molecularly thin PDMS films spreading on cleaned bare silicon wafers, exposed to an atmosphere with controllable, variable RH. Our experimental data substantiate the $M$-dependence of $D_{\text{exp}}$ at different physical and chemical conditions. We show that it is actually consistent with the algebraic law in Eq.(2), but the exponent $\gamma$ appears to be non-universal and depends, in general, on many different factors: For instance, it is very sensitive to the chemical composition of the solid surface, which determines the frictional properties of the surface with respect to the molecular transport. Moreover, we find that $\gamma$ may attain different values depending whether only a single precursor film develops from the macroscopic droplet, or in the terraced wetting case, when the precursor is formed by a succession of superimposed monolayers. In the former case, $\gamma$ is typically less than unity, while for the latter case it may actually reach under certain conditions the value 1.7, as reported previously in Refs.9 and 10.

Here we summarize the results obtained for the situation with a single precursor film of monomolecular thickness. The parameters which are varied in our experimental studies are the polymer weight $M$ and the chemical composition of the substrate. For the substrates used in this set of experiments, namely, for the hydrophilic oxidized wafers, the frictional properties can be modified by changing the RH. We perform our experiments at different RH and calculate the corresponding values of the exponent $\gamma$. "Terraced" profiles are observed at very low RH ($\lesssim 20\%$), while a single monolayer is observed for RH $\geq 35\%$. For such RH, which corresponds to the limit of maximal friction in the single precursor film case, $\gamma$ is maximal, but is substantially less than the value reported in Refs.5,9 and 10. We find that here $\gamma \approx 1$. With an increase of RH, which lowers friction with the substrate, $\gamma$ drops off monotonously to zero. Note that $\gamma \approx 1$ is also found for compact hydrophobic grafted trimethyl layers, on which the profile again exhibits a single step. For two extreme cases of low ($\approx 35\%$) and very high RH we propose simple arguments which explain the observed values $\gamma \approx 1$ and $\gamma \approx 0$. Results of systematic experimental studies of the behavior in the terraced wetting case, for which we actually recover the value $\gamma \approx 1.7$ either at very low RH or on loose grafted trimethyl layers, will be presented in the complete paper [4].

Ellipsometry is a well-known optical technique which is sensitive to the presence of films of molecular or sub-molecular thickness, deposited at the solid surface with a different refractive index [15]. It thus allows to measure the thickness of a film and correspondingly, its radial extension, by analyzing the change of polarization of an optical beam at reflection.

The present study was performed with a spatially resolved [2], polarization modulated ellipsometer working at a single wavelength (6328 Å, He-Ne laser) and at the Brewster angle. The setup has been extensively described elsewhere [2]. The liquids used in our experiments were low-$M$ polydimethylsiloxanes. Specifically, the PDMS are neutral, highly flexible chain-like molecules with the transverse size of a monomer being approximately 7Å; PDMS are liquids at ambient temperatures and glassify below $-123^\circ C$. The entanglement threshold $M_c$ in 3D for PDMS is around 25000 g/mol. In our experiments, the molecular weight (viscosity) range between 2000 g/mol (20 cP) and 28400 g/mol (10^3 cP). The polydispersity index is 1.7 for the 20 cP (non fractionated oil) and between 1.05 and 1.29 for the heavier ones (fractionated) [14]. The molecular weight distributions are monomodal, as checked by GPC [3], which ensures that the polydispersity effects are insignificant [2][17]. The substrates used in our measurements were oxidized silicon wafers from electronic industry, polished on one side and covered with a natural oxide. The wafers were cleaned by an oxygen flow under UV illumination, and then placed (for 24 hours) in a measurement chamber with an atmosphere with controlled RH. The purpose of the latter procedure was to obtain on the wafer an equilibrated submonolayer (of controlled coverage, dependent on RH) of water [17]. As we have already mentioned, the presence of the water on top of our hydrophilic wafer is essential and allows us to modify the frictional properties of the substrate by changing the chemical composition of the surface.

Experimentally obtained values of $D_{\text{exp}}$ are summarized in Fig.1, where $D_{\text{exp}}$ is depicted as a function of the number of monomers $N$, which is proportional to the molecular weight $M$. We present here four sets of data: Two sets are deduced from spreading rates of the PDMS monolayers at low RH, (RH $\approx 40\%$), when only a very small portion of the surface is covered by water molecules, which all cluster in isolated, molecularly thin islands. Two other sets are obtained from the data corresponding to the intermediate, (RH $\approx 82\%$), and high, (RH $\approx 98\%$), relative humidities, when water covers progressively higher and higher areas of the surface. The data for the case RH $= 98\%$ shows that the $M$-dependence of
$D_{\text{exp}}$ fades out completely. As an illustration of such a behavior, we depict in Fig.2 the dynamical thickness profiles of different PDMS droplets, spreading on the same wafer exposed to the atmosphere with RH = 98%. Fig.2 shows that the radial extension of precursor films is absolutely independent of the molecular weight at such high values of RH.

To explain the experimentally observed behavior we make use of the so-called "stratified droplet" model, developed in Ref.7, and the microscopic dynamical model of Ref.8. In these theoretical works it was shown that, in essence, the behavior as in Eq.(1) results from the competition of two different factors - the constant driving force, which stems from the presence of attractive liquid-solid interactions, and viscous-type dissipation for molecular motion on solid substrate; $D_{\text{exp}}$ is given by

$$D_{\text{exp}} \approx \frac{W_2 - W_1}{\zeta},$$

where $\zeta$ is the friction coefficient for molecular motion on solid substrate, while the terms $W_1$ and $W_2$ describe the energy of the liquid-solid and the liquid-liquid interactions of a molecule being directly on the top and at the height of one molecular size above the substrate.

For low-$M$ disentangled polymers, as it appears in our case, one evidently has that

$$W_2 - W_1 \sim M \triangle w,$$

where $\triangle w$ is the corresponding gain of the interaction energy due to moving of a monomeric unit from the second layer to the first one. Consequently, the comparison between the experimentally observed behavior for low and high RH against Eqs.(3) and (4) suggests that

$$\zeta \sim \begin{cases} M^2, & \text{for low RH}, \\ M, & \text{for high RH}. \end{cases}$$

which is reminiscent of the chain friction in melts (repulsion) and in the Rouse regime, respectively [15].

Let us speculate now about the origin of the behavior described by Eq.(5). A physically plausible explanation, which parallels in many aspects the earlier discussion of slow spreading of polymer melts [19-20] and slow desorption of polymer chains through an overlayer of strongly adsorbed chains [21-22], may be as follows: The substrates used in our experimental studies, i.e. bare oxidized silicon wafers, are chemically heterogeneous and contain different types of surface sites; these are, namely, low energy siloxane bridges and high energy, chemically active silanol sites. The silanol sites, which are present at a density $n_s \approx 1 \text{ nm}^{-2}$, (i.e. typically one such a site per each 10 angstroms for our wafers), may form a hydrogen bond with any of monomers of the PDMS molecules and thus represent the "hot spots" of attachment to the surface. Consequently, the disentangled PDMS molecules, which emerge on the wafer and form the precursor, get trapped by the silanol sites. Since the density of these sites is rather high, many of the PDMS monomers have a chance to form bonds, which means, first, that in accord with experimental observations the polymers will not have pronounced "loops" between the attached monomers and will lay almost flat on the substrate. Second, it implies that the effective time $\tau_{fr}(M)$, which a given PDMS molecule spends being trapped by many silanol sites simultaneously, can be significantly larger than the life-time of a hydrogen bond for a single monomer.

Now, following Refs.19 to 22, we suppose that in such a situation the transport of "mass" in the precursor proceeds mainly by tortuous diffusion of a small portion of non-adsorbed molecules, (for instance, those which emerge on the substrate already occupied by many other polymers), through a two-dimensional array of immobilized polymers, which serve for the latter as obstacles. Motion of non-adsorbed macromolecules on solid surfaces among immobilized, adsorbed polymers was first discussed in Ref.19. Assuming essentially reptative type of motion of non-adsorbed molecules, it has been shown that apart of non-significant logarithmic factor $\ln(M)$ resulting from the presence of "loops" in adsorbed polymers, which is not the case here, the friction coefficient follows the dependence described by Eq.(5.a). We also remark that the behavior as in Eq.(5.a) has been recently deduced from experimental studies of polymer adsorption on substrates, grafted with other polymers [22]. Lastly, we note that this reptation-like picture does not require the adsorbed chains to be irreversibly trapped. However, the trapping time $\tau_{fr}(M)$ must be larger than some characteristic time involved in the non-adsorbed chain dynamics (possibly, the time needed for one molecule to progress over its own length) [23].

Consider next how the situation can be changed, if prior to the deposition of a drop the substrate was exposed to an atmosphere with high RH. As a matter of fact, the water molecules also have a strong affinity to the silanol sites and effectively screen them, forming molecularly thin islands of water [17]. Consequently, increasing the RH prior to the deposition of the droplet, we decrease substantially the number of the silanol sites which can trap the PDMS molecules and thus make the substrate more chemically homogeneous. On the other hand, the presence of interconnected clusters of water, appearing at high RH, enhances the PDMS surface mobility and facilitates mass transfer. Accordingly, at high RH one encounters an effectively ideal surface with low friction, which seemingly explains the Rouse-type behavior described by Eq.(5.b).

In conclusion, we have presented here the results of systematic ellipsometric studies of the polymer weight dependence of spreading rates of single monomolecular precursor films, emitted by droplets of low-$M$ polydimethylsiloxane molecules. We have shown that the "diffusion coefficient" $D_{\text{exp}}$ of the precursor follows an algebraic dependence on the molecular weight, $D_{\text{exp}} \sim M^{-\gamma}$, where the exponent $\gamma$ depends on the frictional properties of the
solid substrate. In case of hydrophilic substrates used in our studies, such properties are most conveniently modified by the change of the RH. Our experiments have shown that for high friction $\gamma$ is maximal, $\gamma \approx 1$, and that it tends to zero when friction gets decreased. For two extreme cases of high and very low friction we propose simple arguments which explain the experimentally observed behavior.

Enlightening discussions with P.G.de Gennes are gratefully acknowledged. This research was supported by the European Community with the grant CHRX-CT94-0448.

[1] D.Ausserré, A.M.Picard and L.Leger, Phys. Rev. Lett. 57, 2671 (1986); L.Leger et al., ibid 60, 2390 (1988)
[2] F.Heslot, N.Fraysse and A.M.Cazabat, Nature (London) 338, 640 (1989); F.Heslot, A.M.Cazabat and P.Levinson, Phys. Rev. Lett. 62, 1286 (1989)
[3] P.G.de Gennes, Scaling Concepts in Polymer Physics (Cornell University Press, Ithaca, 1985)
[4] J.F.Joanny and L.Leger, Repts. Prog. Phys. 72, 431 (1992)
[5] N.Frayss, M.P.Valignat, A.M.Cazabat, F.Heslot and P.Levinson, J. Colloid Inter. Sci. 158, 27 (1993)
[6] S.Villette, PhD Thesis, University of Paris VI, 1996, unpublished
[7] P.G.de Gennes and A.M.Cazabat, C. R. Acad. Sci. (Paris) 310, 1601 (1990)
[8] S.F.Burlatsky, G.Oshanin, A.M.Cazabat and M.Moreau, Phys. Rev. Lett. 76, 86 (1996)
[9] V.J.Novotny, J. Chem. Phys. 92, 3189 (1990)
[10] B.Marchon, lecture at the Collège de France, September 1997, unpublished
[11] T.M.O’Connor, M.S.Jhon, C.L.Bauer, B.G.Min, D.Y.Yoon and T.E.Karis, J. Tribol., in press
[12] J.F.Joanny and P.G.de Gennes, J. Phys. Paris 47, 121 (1986)
[13] D.Ausserré, F.Brochard-Wyart and P.G.de Gennes, C. R. Acad. Sci. (Paris) 320, 131 (1995)
[14] M.P.Valignat, G.Oshanin, S.Villette, A.M.Cazabat and M.Moreau, in progress
[15] R.M.A.Azzam and N.M.Bashara, Ellipsometry and Polarized Light, (North-Holland, Amsterdam, 1977)
[16] N.Frayss, PhD Thesis, University of Paris VI, 1991, unpublished
[17] S.Villette, M.P.Valignat, A.M.Cazabat, L.Jullien and F.Tiberg, Langmuir 12, 825 (1996)
[18] P.G.de Gennes, J. Chem. Phys. 55, 572 (1971)
[19] P.G.de Gennes, in: Liquids at Interfaces, eds.: J. Chavvolin, J.F.Joanny and J. Zinn-Justin, (Elsevier Science Publishers B.V., 1990)
[20] R.Bruinsma, Macromolecules 23, 276 (1990)
[21] H.E.Johnson and S.Granick, Science 255, 966 (1992)
[22] H.E.Johnson, J.F.Douglas and S.Granick, Phys. Rev. Lett. 70, 3267 (1993)
[23] P.G.de Gennes, private discussion
Fig. 1. Experimental diffusion coefficient $D_{exp}$ for the $\approx 7\AA$ thick precursor film of the PDMS molecules versus the inverse number of monomers $N$. Crosses and diamonds correspond to RH = 40%, squares - to RH = 82% and the triangles - to RH = 98% respectively. The dashed line has the slope 1; the dash-dotted line - the slope 0.6; the dash-dashed line - constant slope.

Fig. 2. Experimental thickness profiles of several PDMS droplets spreading on the same silicon wafer. RH = 98%. (a) Profiles recorded at 25mn after deposition: solid line - $M = 2000$ g/mol ($I_p = 1.7$) and dashed line - $M = 7300$ g/mol ($I_p = 1.10$). (b) After 40mn: solid line - $M = 28400$ g/mol ($I_p = 1.29$), dashed line - $M = 13000$ g/mol ($I_p = 1.15$). The baseline (silica plus adsorbed water) is at $\approx 21\AA$. 