

Residual stresses in thin polymer films cause rupture and dominate early stages of dewetting

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In attempting to reduce the size of functional devices, the thickness of polymer films has reached values even smaller than the diameter of the unperturbed molecule. However, despite enormous efforts for more than a decade¹, our understanding of the origin of some puzzling properties of such thin films is still not satisfactory and several peculiar observations remain mysterious. For example, under certain conditions, such films show negative expansion coefficients^{2–6} or show undesirable rupture although energetically they are expected to be stable⁷. Here, we demonstrate that many of these extraordinary effects can be related to residual stresses within the film, resulting from the preparation of these films from solution by fast evaporation of the solvent⁸. Consequently, depending on thermal history and ageing time, such films show significant changes even in the glassy state^{9,10}, which we quantify by dewetting experiments and corresponding theoretical studies. Identifying the relevance of frozen-in polymer conformations gives us a handle for manipulating and controlling properties of nanometric thin polymer films.

A longstanding ‘mystery’ of thin polystyrene (PS) films, which has been extensively investigated for more than a decade¹, is the cause of rupture of these films when heated above the glass-transition temperature. Rupture is surprising because, in equilibrium, intermolecular forces should stabilize such films and holes should only form by means of nucleation⁷. However, it has been realized that the conditions of film preparation play a crucial role⁸. Thus, it may be anticipated that the polymers in such thin films, even above the glass-transition temperature, are not in their equilibrium state and physical properties such as density may change over time^{4,5}. However, it is unclear whether film preparation has direct consequences with respect to the stability of such films. To find a connection between film preparation and film stability, we have investigated whether the probability of film rupture, defined as

the maximum number N_{\max} of circular holes per unit area formed in a film of given thickness, depends on ageing time t_{ageing} , the time the film was stored at temperatures below the glass-transition temperature. Such physical ageing may be caused by molecular relaxations of non-equilibrium amorphous states frozen-in during the vitrification of the material and therefore sensitive to the history of the sample, that is, how fast the sample has passed the glass-transition temperature and how long it was stored below this transition temperature.

For the corresponding experimental studies we used 40–65-nm-thin PS films on smooth silicon substrates coated with thin (non-wettable) polydimethylsiloxane (PDMS) layers^{11,12}. In a first attempt, we examined films stored for more than 100 days at room temperature, that is, about 80 °C below the glass-transition temperature. A significant reduction in the number of holes by more than a factor of five was observed. For a more systematic study, we chose to store the films at 50 °C, which allowed us to accelerate the influence of ageing. Independent of the age, all holes formed in a rather short initial period of about 100 s (Fig. 1a). In contrast, N_{\max} decreased with age (t_{ageing}), following an exponential decay (Fig. 1b) with a characteristic decay time $\kappa(N_{\max})$:

$$N_{\max}(t_{\text{ageing}}) = N_{\max}(\infty) + N_{\max}(0) \exp[-t_{\text{ageing}}/\kappa(N_{\max})],$$

yielding $N_{\max}(\infty) = 3 \pm 1$ (holes per $10^4 \mu\text{m}^2$) and $\kappa(N_{\max}) = 47 \pm 6$ h. This suggests that after sufficiently long periods of ageing of the films ($t_{\text{ageing}} \gg \kappa$) no holes, except those nucleated by non-polymeric defects, will be formed.

From our experiments on film stability it becomes clear that significant changes take place in spin-coated thin polymer films even at temperatures well below the glass-transition temperature. As a possible cause for these changes, we assume that the fast evaporation of the solvent during spin-coating inevitably leads to frozen-in non-equilibrated chain conformations of the

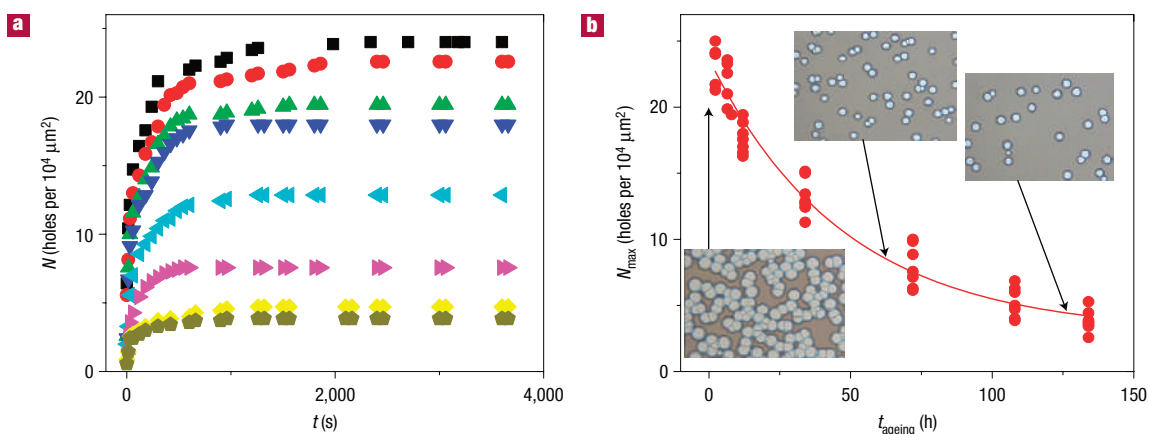


Figure 1 Influence of ageing on the probability of film rupture, expressed by means of the areal density of holes. **a**, The areal density of holes (N) as a function of time at 125 °C for PS films ($h_0 = 40$ nm, $M_w = 4,840$ kg mol $^{-1}$) after being aged at 50 °C for increasing times (from top to bottom: 2.25, 6.5, 8, 12, 34, 72, 108 and 134 h). The maximum value N_{\max} (per $10^4 \mu\text{m}^2$) for each sample is reached in about 100 s. **b**, A systematic study of N_{\max} for the same type of films as in panel **a**, stored at 50 °C for various times. The insets show some typical corresponding optical micrographs ($310 \times 230 \mu\text{m}^2$; Metallux 3, Leitz, Germany). The solid line represents the fit to the exponential equation described in the text.

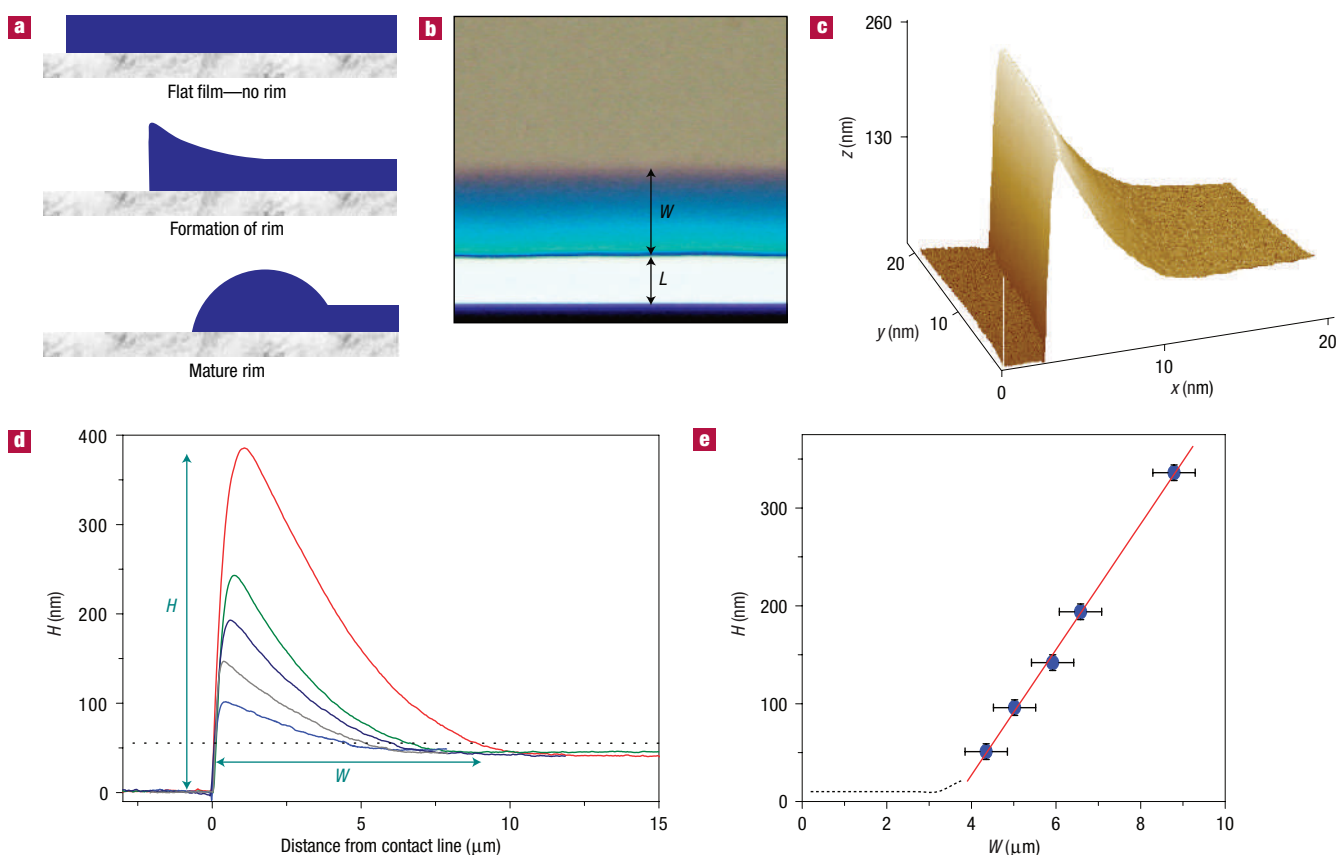


Figure 2 The shape of the rim during early stages of dewetting of thin polymer films on non-adsorbing substrates. **a**, The sequence of three fundamentally different shapes of the rim found experimentally. **b**, A typical optical micrograph ($50 \times 50 \mu\text{m}^2$) taken at the edge of the sample obtained after partial dewetting. The dewetted distance (L) and the width of the rim (W) are indicated. The colours can be directly related to the thicknesses, for example the brighter the blue, the thicker the film. **c**, A typical rim profile as determined by atomic force microscopy (Nanoscope 3a-Dimension3000, Digital Instruments, USA). **d**, Rim profiles for a 45-nm-thick PS film ($M_w = 110$ kg mol $^{-1}$) taken after progressively longer dewetting times (from bottom to top: 66, 455, 1,215, 2,000 and 4,300 s) at 125 °C. H is determined by the distance between the substrate and the apex of the rim. **e**, H versus W for the profiles shown in **d**. The dotted line represents a possible continuation for the experimentally inaccessible region. The error bars reflect the variance of the repeated measurements.

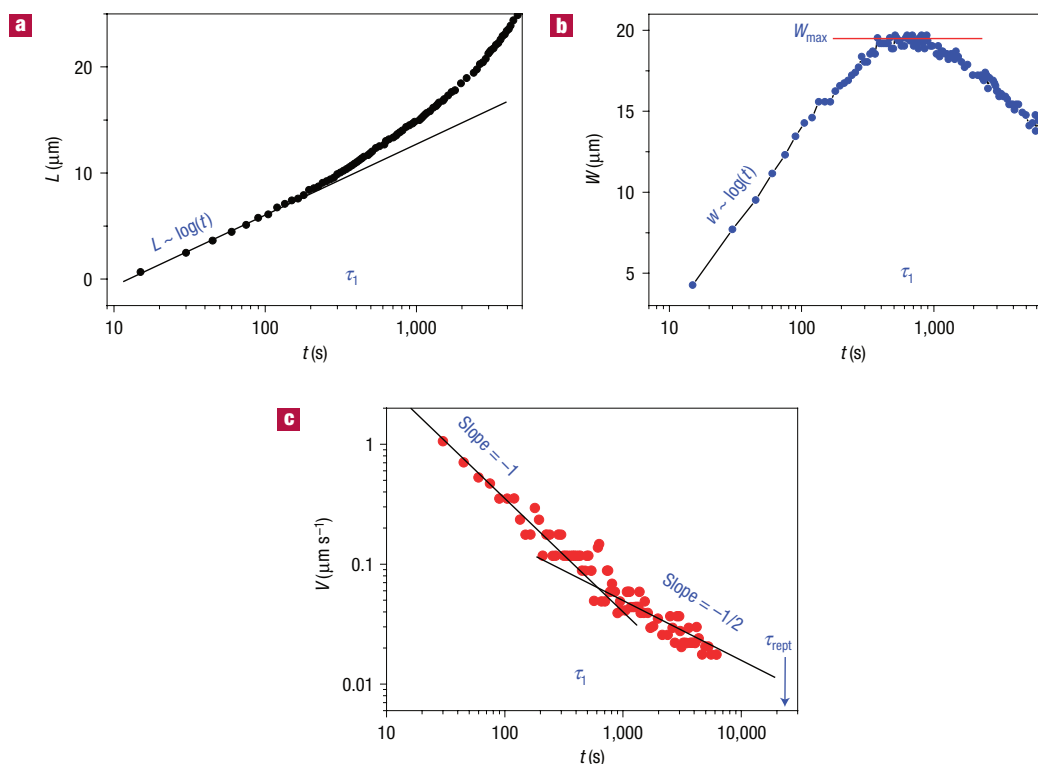


Figure 3 Typical results for dewetting of PS thin films on a non-adsorbing substrate. **a**, Dewetted distance L from the edge versus t . **b**, Width of the rim W versus t . **c**, Dewetting velocity V versus t . The data were obtained for a 65-nm-thick PS ($M_w = 390 \text{ kg mol}^{-1}$) film at 140°C . The characteristic time τ_1 is indicated. Under the conditions of the experiment, τ_{rept} of the polymer is about 25,000 s. The lines in **c** represent expectations from theory, that is $V \sim t^{-1}$ for $t < \tau_1$ and $V \sim t^{-1/2}$ for $t > \tau_1$.

polymers. During this evaporation process the polymer chains have to undergo a marked change in conformations, from isolated individual coils to an entangled polymer melt. In this way, at a still rather high solvent concentration of about 20%, long before the end of the evaporation process, the chains will be frozen-in as the solvent–polymer mixture passes through its glass transition. The key postulation is that such non-equilibrated polymer chains generate residual stresses within the film. Several complementary observations have been published in the literature that support this conclusion. For example, the existence of negative expansion coefficients^{2–5} or ultra-slow relaxations of several days^{5,6}, corroborated by investigations of the ageing process based on fluorescence⁹ or ellipsometric¹⁰ studies, also indicate non-equilibrated states in nanometric polymer films.

To shed more light on what kinds of changes took place during storing of the films, we performed detailed dewetting studies. Dewetting experiments represent an attractive, that is, simple and fast, possibility for linking molecular and interfacial properties with macroscopically observable parameters such as the shape of the part collecting the removed material, that is, the rim^{13–19}. Such has been demonstrated very clearly in refs 11,12,19–22. Here, we concentrate on the early stages of the dewetting process and how they were influenced by the time the films were stored at a temperature below the glass-transition temperature.

In Fig. 2a, we show the sequence of the three main regimes in the opening of holes, characterized by changing shapes of the rim. Initially, the energy resulting from capillary forces is mainly dissipated by means of viscous losses in the vicinity of the hole edge. Under such conditions, no rim is formed¹⁵. However, as the radius of the hole becomes larger than a decay length $\Delta = (h_0 b)^{1/2}$ (with

h_0 the film thickness and b the slippage length related to friction coefficient ζ and viscosity η , $b \sim \eta/\zeta$; refs 15,16,18), friction at the substrate–film interface gains importance. As a consequence, the velocity decays within the film, which results in the appearance of a highly asymmetric rim (Fig. 2b,c), with a steep side reaching a height H next to the three-phase contact line and an approximately exponential decay on the other side, with a decay length Δ (refs 15, 22). The width W of the rim is defined as the distance between the contact line and the position where the height H of the rim has decayed to a value close to the initial film thickness h_0 , designated by the dotted line in Fig. 2d. The extrapolated value of $W \approx 4 \mu\text{m}$ (for $H = 0$) indicates that from the beginning $\Delta = 4 \mu\text{m}$ is contributing to energy dissipation (Fig. 2e). At long times, the surface tension of the liquid will eventually lead to a rounded shape of the rim¹⁵, with a dewetting velocity V , defined at the contact line, decaying with time according to a power law $t^{-1/3}$.

In the following we focus on the evolution of the asymmetric rim in the intermediate regime, which is rather pronounced for thin, highly viscous films close to the glass transition. This regime is most interesting as the shape of the rim is controlled by both interfacial friction and rheological properties of the film. Time-resolved experiments (Fig. 3) showed that, during the early stages of rim build-up, both the dewetted distance L and W increased in a logarithmic fashion in time, up to a time τ_1 when W reached a maximum. Correspondingly, V decreased continuously according to $V \sim t^{-\nu}$. Interestingly, around τ_1 the exponent ($-\nu$) changed from -1 to $-1/2$. We want to emphasize that a logarithmic time dependence of L and the corresponding t^{-1} decrease of V are not expected for a newtonian liquid^{15,22}, and that our results cover times shorter than the relaxation time in equilibrated bulk samples, that

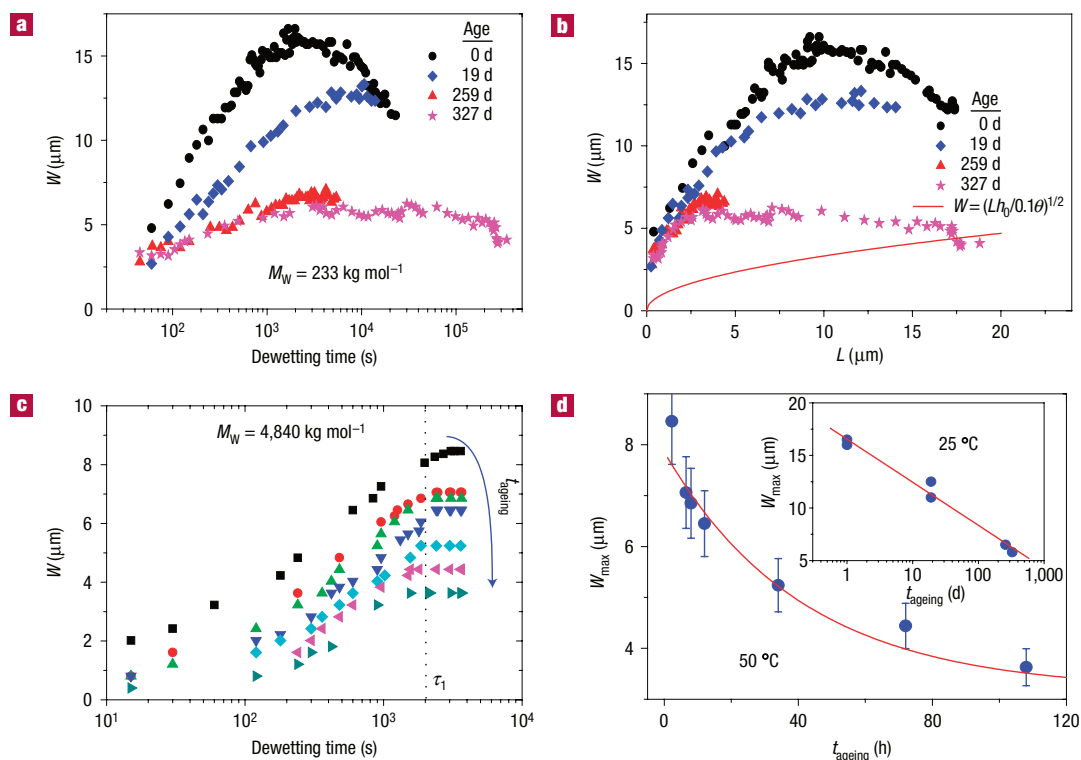


Figure 4 The influence on dewetting of storing (ageing) PS films for increasing times below the glass-transition temperature. **a**, The width of the rim (for dewetting from the edge of the sample) as a function of dewetting time for films ($h_0 = 57$ nm, $M_w = 233$ kg mol $^{-1}$) that have been aged at room temperature for different times indicated in the figure. **b**, The same data as in **a**, but presented as a function of the dewetted distance. The full red line indicates the expected width for a rim rounded by surface tension, related to L by volume conservation (assuming a contact angle θ of 30°). **c**, The width of the rim around a dewetting hole as a function of dewetting time for films ($h_0 = 40$ nm, $M_w = 4,840$ kg mol $^{-1}$) that have been aged at 50°C for increasing times (from top to bottom: 2.25, 6.5, 8, 12, 34, 72, and 108 h). **d**, W_{\max} taken from **c** as a function of ageing time. The error bars indicate the scatter observed for repeated measurements. The inset shows the corresponding data on semi-logarithmic scales for the samples of in **a**. All dewetting experiments were performed at 125°C .

is, the reptation time τ_{rept} (refs 23–25). Thus, viscoelastic properties of PS are assumed to be important in our experiments.

Assuming plug flow, we developed a model²² based on the mechanical balance between friction forces at the substrate interface and both viscous and elastic forces within the volume for every slice of the film between x and $x + dx$, where x represents the direction of the moving dewetting front. Capillary forces act as the driving force at the contact line. This model predicts a high initial dewetting velocity (independent of polymer molecular weight M_w) and a decrease of the velocity proportional to $t^{-1/2}$ for times shorter than the relaxation time of residual (elastic) stresses. Assuming a shear-thinning behaviour of PS would bring about an even softer decrease of the velocity²² ($V \sim t^{-n/2}$, with $0 \leq n < 1$ being the shear thinning exponent time²⁰). Consequently, the t^{-1} power law of the dewetting velocity cannot be understood by only considering the above rheological properties of the polymer film. We note that the characteristic time τ_1 was found to be an extremely reliable and reproducible measure that we link to relaxation processes of constrained polymers. Interestingly, τ_1 did not depend much on M_w (for high M_w) and was significantly shorter than τ_{rept} .

In contrast to the behaviour of τ_1 , the value of the maximum width (W_{\max}) of the rim showed considerable differences between samples that were nominally identical and differed only in age. Whereas τ_1 was almost constant (see, for example, Fig. 4c, for all data sets W_{\max} was reached at about the same time τ_1 , indicated by the dotted line), W_{\max} differed by more than a factor of three. Systematic studies on the temporal evolution of W , shown in

Fig. 4d, indicated an exponential decay of W_{\max} with t_{ageing} , similar to the behaviour of N_{\max} :

$$W_{\max}(t_{\text{ageing}}) = W_{\max}(\infty) + W_{\max}(0) \exp(-t_{\text{ageing}}/\kappa(W_{\max})),$$

yielding the characteristic decay time $\kappa(W_{\max}) = 41 \pm 7$ h.

Residual stresses represent an extra driving force for dewetting that adds up to the capillary forces acting at the contact line. In the course of ageing, or when heated above the glass-transition temperature, these stresses tend to disappear as the chain-like molecules will adopt conformations closer to their equilibrium. Including such stresses in our mechanical model²² enabled us to reproduce the experimentally observed decay of $V \sim t^{-1}$. The faster decay of V ($V \sim t^{-1}$ rather than $V \sim t^{-1/2}$ expected for an equilibrated system) can be explained by a progressively decreasing contribution of residual stresses to the driving force.

The most pronounced effect of ageing is probably its influence on the rupture probability. The exponential decay of $N_{\max}(t_{\text{ageing}})$ allows for the possibility that, after a sufficiently long period of ageing, no holes will be formed. This implies that fully equilibrated films would be stable, assuming that no other sources for rupture, such as dust particles, exist. It is remarkable that the decays of $W_{\max}(t_{\text{ageing}})$ and $N_{\max}(t_{\text{ageing}})$ follow the same exponential law. Intriguingly, we observed that t_{ageing} has no measurable influence on the characteristic time τ_1 characterizing the relaxation of such stresses. It seems that τ_1 does not significantly depend on the degree of frozen-in non-equilibrated conformations. However, neither this behaviour nor the unexpected independence of τ_1 on molecular

weight for long chains can cast doubts on the existence and relevance of residual stresses.

We would like to mention that, in contrast to many other systems, our silicon wafers with PDMS coatings are characterized by a rather weak interaction between the film and the substrate. For adsorbed polymers, even if adsorption is weak, we expect significantly longer relaxation times and a rather unusual temperature dependence. These, in turn, may be responsible for negative expansion coefficients, which can be taken as indicators for residual stresses⁸. From the change in W_{\max} with t_{ageing} we can estimate that the residual stresses are at least of the same order of magnitude as the acting capillary forces. Whereas in most cases residual stresses of such high magnitudes may be undesirable, in particular if they are causing the damage to the film, one can also think of instances where they might be advantageous. For example, if non-equilibrium chain conformations can be fixed by chemically crosslinking the polymers in the glassy state, the highly metastable form of matter caused by residual stresses may be transformed into materials having new properties such as a 'permanent' negative thermal expansion coefficient. At this point, we are not yet able to specify a potential influence of residual stresses, and their possibly slow relaxations, on thickness measurements in the context of the glass-transition temperature of thin polymer films. It seems, however, appropriate to be cautious when comparing the observed thin-film behaviour of spin-coated films to equilibrated systems. Along this line, the ageing behaviour of the investigated thin polymer films is probably of different origin compared with systems cooled below the glass-transition temperature, starting from an equilibrated melt state. However, even if this is so, a detailed comparison of ageing effects observed under different conditions may shed light on fundamental relaxation processes possible in polymeric glasses and on the nature of the glass transition itself.

METHODS

Our results are based on experiments performed on thin PS films of molecular weights (M_w) ranging from 35 to 4,840 kg mol⁻¹ with a low index of polydispersity (I_p) between 1.04 and 1.15 and of thicknesses (h_s) varying between 20 and 100 nm (as measured by ellipsometry; Multiscope, Optrel, Germany). The glass-transition temperature of PS in the bulk is about 103 °C. The films were obtained by spin-coating toluene solutions directly onto silicon substrates that were coated with a layer of adsorbed PDMS ($M_w = 26$ or 90 kg mol⁻¹, layer thickness about 4–6 nm). The irreversibly adsorbed PDMS layers resulted from spin-coated films on hydroxylated silicon wafers (cleaned by ultraviolet-ozone, plasma or using so-called Piranha solutions), which were then annealed at 150 °C for 5 h under vacuum.

Isothermal dewetting of thin PS films, that is, the retraction of a straight contact line or the formation of holes and their opening, was followed in real time by optical microscopy. Images were captured with a charge-coupled-device camera. To determine the shape of the rim somewhat more precisely, further measurements were performed by atomic force microscopy (Nanoscope 3a-Dimension3000, Digital Instruments, USA) in the tapping mode.

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Competing financial interests

The authors declare that they have no competing financial interests.

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