Dewetting as a Probe of Polymer Mobility in Thin Films

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ABSTRACT: Spin-coated polystyrene films thinner than the unperturbed size of the molecules on glass substrates were studied by X-ray reflectometry. Detailed knowledge about the dewetting process of these unstable films allowed to probe polymer dynamics in this confined geometry. The film thickness increased upon annealing reaching a stable value before dewetting started. The thickness change translates into a decrease in polymer density. This decrease is larger the thinner the films are. Consequently, the polymer density depends on film thickness and reaches its bulk value only for films thicker than about the size of the unperturbed molecule. A quite distinct dependence of the onset of dewetting on film thickness was observed. For the thinnest films dewetting was completed at temperatures well below the glass transition temperature. As a consequence of the lower polymer density, the mobility of the molecules was increased. A tentative explanation of these effects based on packing considerations leading to inaccessible sites is given.

1. Introduction

Miniature devices and various applications like coatings, lubrication, or electronic packaging demand progressively thinner polymeric films. In some cases the thickness of such films can be smaller than the unperturbed size of the macromolecules (in the following such films are called *thin*). Confinement influences conformation and intertwining of the molecules.[1] Structural changes induced by the interaction with a solid substrate can affect dynamical aspects as well as adhesion and wetting characteristics.[2,3] At present it seems to be widely accepted, based on theoretical considerations[1,4] and computer simulations,[5–10] that static properties like local density differ from bulk values only up to a few segmental layers away from an interface. Such conclusions are drawn for both cases, molecules in semiinfinite systems close to an impenetrable interface, or molecules in thin films. Experimentally observed long range forces[11,12] are attributed to pinning of the molecules at the contact with the wall.[13]

Dynamical properties are strongly affected by adsorptive interactions with the substrate and entropic constraints.[5–10] The mobility of molecules close to a hard wall depends distinctly on the strength of the interaction with the surface. One reason is that segments touching an attractive wall are less mobile (trapped) and thereby slow down the motion of the whole chain.[14,15] Alternatively, strong attraction to the surface might also increase the local density and therefore reduce the mobility. In polymer solution this effect of increased density in adsorbed layers is sometimes related to an increased effective glass transition temperature.[16] Weak interaction, on the other hand, causes a depleted region close to the wall. It should be mentioned that the influence of an interface is negligible a few segmental diameters away from the interface. Confining polymers in a small gap between two walls or within thin films on solid substrates can also affect the degree of interpenetration between the molecules.[1,17,18] This can lead to a reduced number of entanglements which can cause decreased viscosity and increased diffusivity.

Molecules in restricted geometries often show a change in melting or glass transition temperature.[19,20] In most cases the transition temperature is reduced, but there are also reports demonstrating an increase of the melting point.[21] Important parameters seem to be the interaction and commensurability with the wall but also packing considerations.

At present all theoretical treatments[1,4] and computer simulations[5–10] of confined polymer systems (melts) assume that the average density of a thin layer of macromolecules is not deviating from its value in the bulk. This is probably true if one looks at molecules close to an interface within a thick sample. However, if the molecules are confined by two interfaces like in a thin film there is experimental indication that this assumption might not hold under all conditions.[22]

In this study we report how one can use the effect that unstable polymer films dewet the substrate as detected by X-ray reflectometry to learn more about polymer density and corresponding glass transition temperature of thin films and about the mobility of polymers within such films.

2. Experimental Section

Samples and Their Characterization. The investigated samples consist of polystyrene (PS) films on float glass slides (70 × 30 × 4 mm^3). Two different molecular weight materials as purchased from Polymer Laboratories, U.K., have been used. The polymers were characterized by GPC: PS 28k, M_w = 28 000 g/mol, M_w/M_n = 1.05, R_{EE} = 11 nm, T_G = 100 °C; PS 660k, M_w = 660 000 g/mol, M_w/M_n = 1.1, R_{EE} = 54 nm, T_g = 104 °C. M_w and M_n are weight and number average molecular weight, respectively. R_{EE} is the average end-to-end distance.

Thin films of different thicknesses were prepared by spin-coating toluene solutions of various concentrations (1–5 mg/mL) at a speed of 2000 rpm onto the substrate. The resulting films were checked by X-ray reflectrometry[23,24] and interference light microscopy.[25] The polymer density of the thinnest films (after some annealing) was found to be lower than the bulk value. However, the resolution of X-ray reflectometry with respect to polymer density for the present case is rather poor due to the low scattering contrast between substrate and film. The thickness of the film, on the contrary, can be determined with much higher precision (better than 0.1 nm). Interfacial density profiles were described by an error-function (standard deviation: σ) assuming Gaussian roughness. The roughness of the air-polymer interface was similar to the roughness of the substrate ($\sigma \ll 1$ nm) as expected from theoretical considerations[26] and earlier experimental studies.[27]

Electron Density Profile Representing a Dewetting Film. A large number of measurements was performed (more than 50 samples and more than 500 X-ray measurements) to make sure that the observed effects do not dependent on a particular sample. All films were unstable and finally dewetted the substrate. Rupture and dewetting processes have been investigated in detail earlier.[28,29] The samples of the present study showed similar

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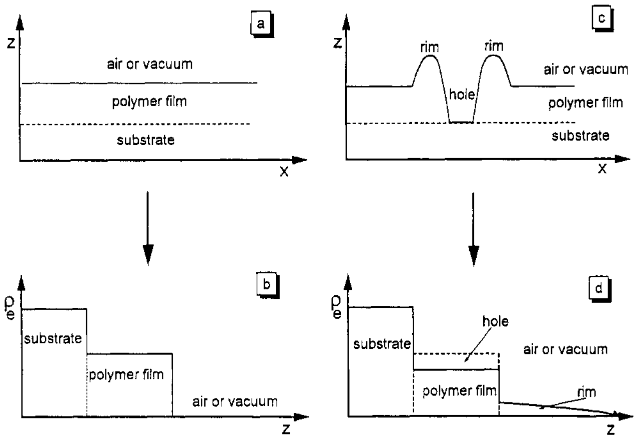

Figure 1. Schematic representation of the investigated systems: (a) a smooth polymer film on a flat substrate, (b) the corresponding electron density (ρ_e) profile averaged laterally as seen by X-ray reflectometry, (c) a polymer film with a typical hole as created by dewetting, and (d) the corresponding ρ_e profile averaged laterally over several μm^2. This implies that X-ray reflectometry averages over many holes. The number of holes/μm^2 is proportional to h^{-4}.

patterns as observed in refs 28 and 29. A completely dewetted sample did not exhibit any interference fringes in the reflectivity curve. When dewetting started the interference fringes of the reflectivity curve got progressively smeared out. The effect is similar to increasing roughness of the film-air interface. At the onset of dewetting the fringes are damped more at lower wavevectors (k) than at higher k.

Specular X-ray reflectometry is averaging laterally over an area of some μm^2.[24] Due to the small angle of incidence, the well collimated beam and the Heisenberg uncertainty relation the coherence length (L) is

$$L = \Delta x/\sin\phi = 2\pi/(\Delta k \sin\phi) \qquad (1)$$

Here $\Delta x \Delta k \geq 2\pi$ is the Heisenberg uncertainty relation with Δx being the maximum resolution for the space coordinate and Δk the divergence of the wavevector of the incident beam, ϕ is the angle of incidence. This gives, for the conditions of the present experiments (divergence of the beam is 0.02°), a coherence length of about 25 μm at an angle of incidence of 1°. Thus, as long as the holes are smaller in diameter than L, this technique resolves the holes created by dewetting as a simple decrease in electron density of an apparently homogeneous film.

The laterally averaged density profiles used to fit the measured reflectivity curves are shown in Figure 1. Dewetting has essentially two effects on the density profile. It reduces the density of the film region because of the creation of holes and adds a tail corresponding to the rims around the holes. The number (Z) of holes per reference area depends on film thickness as described in ref 29. The thicker the film the fewer holes will be created. ($Z = \beta h^{-4}, \beta = 1/25$ Å^2 [30]). The holes have a cylindrical shape and the radial contour of the rim can be described by a section of a circle with radius R. Consequently, the only unknown parameter needed to calculate the density profile of Figure 1d is the diameter (D) of the holes. Holes could be unambiguously detected as soon as they get larger than a few 100 nm.[31] The used electron density profile $\rho_{el}(z)$ is described by the following equations:

$$\rho_{el}(z) = \rho_{air} + \Delta\rho(A_{rim}/A_{max})((R^2 - (R_{\cos}\theta + z - h)^2)^{1/2})/R_{\sin}\theta + \\ + \Delta\rho(A_{film}/A_{max})(1 - \mathrm{erfc}((z-h)/\sigma)) \quad \text{for } h \leq z \leq h + H_{rim} \qquad (2a)$$

$$\rho_{el}(z) = \rho_{air} + \Delta\rho(A_{film}/A_{max})(1 - \mathrm{erfc}((z - \mathrm{h})/\sigma)) \quad \text{for } z \leq \mathrm{h} \qquad (2b)$$

$$R = (Dh/(4(\theta - \sin\theta\cos\theta))^{1/2}) \qquad (3)$$

$$H_{rim} = R(1 - \cos\theta) \qquad (4)$$

$$d_{rim} = 2R\sin\theta \qquad (5)$$

$$A_{max} = 1/Z \qquad (6)$$

$$A_{hole} = (D/2)^2\pi \qquad (7)$$

$$A_{rim} = (D/2 + d_{rim})^2\pi - A_{hole} \qquad (8)$$

$$A_{film} = A_{max} - A_{hole} - A_{rim} \qquad (9)$$

$$\Delta\rho = \rho_{poly} - \rho_{air} \cong \rho_{poly} \qquad (10)$$

Here ρ_{poly} and ρ_{air} are the electron densities of the polymer film and air, respectively. H_{rim} and d_{rim} are the height and the diameter of the rim. θ is the dynamic contact angle of the moving rim, here approximated by the equilibrium contact angle of polystyrene on glass. A_{max}, A_{hole}, A_{rim}, and A_{film} are the maximum area of a hole at the end of dewetting, area of a hole, the area of the rim at its base, and the area of the unperturbed film, respectively. erfc is the complementary error function with the parameter σ.

Annealing Procedure. The samples were annealed in a vacuum oven as sets of about 10. Annealing in sets reduces differences between samples caused by annealing. After each annealing step the samples were quenched down to room temperature, measured by X-ray reflectometry, and annealed again. This procedure was repeated until no interference information was detectable in the reflectivity curves. For the main part of this study the annealing time was kept constant (1 h per step), and the temperature was increased in intervals of approximately 5 deg. In general, this study deals with four parameters which affect the dewetting process: time of annealing (t), annealing temperature (T), thickness of the sample (h), and molecular weight (M_w). Mainly, thickness and temperature dependence were investigated. The time and molecular weight dependence were touched only briefly.

3. Results

Relaxations Before the Onset of Dewetting. All appropriate (smooth and homogeneous) samples were first annealed under vacuum at temperatures well below the glass transition temperature of the polymer in bulk samples (T_g). This was done because residual solvent molecules which might have been left in the films should get out of the films. One would have expected a slight decrease of the film thickness. However, such a decrease of h was never observed. On the contrary, in most cases h increased. Some of the PS28k samples were stored at ambient conditions for about 3 months prior to annealing, and the thinnest of them showed a slight expansion after that time. This seems to indicate relaxations within the films happening at temperatures well below T_g. The relative thickness changes depended on h and were more pronounced for the thinnest films. Figure 2 shows reflectivity curves of PS28k and PS660k samples of different thicknesses after annealing for 1 h at 70 and 80 °C, respectively, compared to the results right after preparation.

After annealing the minima shifted to lower k values indicating an increase in film thickness. Besides this shift the reflectivity curves were not altered. In particular there is no damping of the fringes. This means that the film interfaces did not become rough. It should be noted that the 14.9-nm thick PS660k film in Figure 2b still changed its thickness whereas a PS28k film of similar thickness (14.2 nm) in Figure 2a did not.

Thicknesses increased further after annealing at increasingly higher temperatures. In all cases a final thickness value was reached after several annealing steps. The thinner the film the lower the temperature where this value, which is probably an equilibrium value, was reached. However, one has to be careful not to misinterpret this

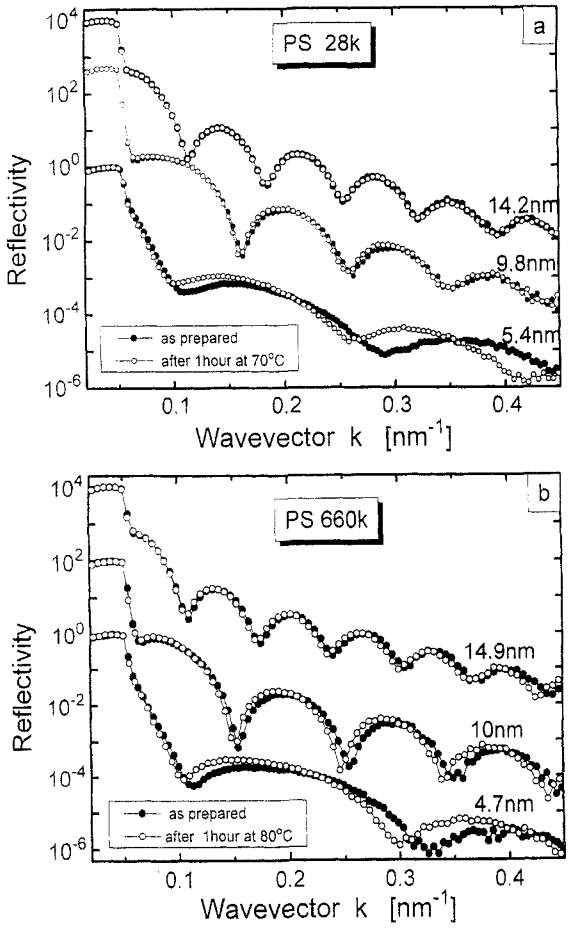

Figure 2. Typical X-ray reflectivity curves versus incident wavevector for various thin films of (a) PS28k and (b) PS660k. Curves measured right after preparation and after annealing for 1 h at 70 and 80 °C, respectively, are compared. Note that the thinner films show more pronounced changes and that the fringes of the thicker PS660k films are shifting to lower k values while the thickest PS28k film is not affected by annealing.

shift of the temperature where the thickness finally reaches a constant value. The annealing time of 1 h at each temperature might *not* have been long enough to allow that equilibrium is attained at this temperature. It seems likely that thicker films would need more time to relax than thinner ones. (This relaxation process was not the main concern of this study and not studied in detail.)

Figure 3 illustrates the relative changes in thickness as a function of temperature. Thickness values at temperatures where dewetting already occurred were obtained from the unperturbed regions of the films only. These values are included in Figure 3. The arrows indicate the temperature at which all interference fringes were lost due to total dewetting. As already indicated by Figure 2, there is a qualitative difference in behavior between the two molecular weight samples for thicknesses larger than about 11 nm. The lower molecular weight films did not change in thickness upon annealing, but films of the higher molecular weight polymer did. This becomes even more visible when plotting the maximum relative change in thickness (Δh_{max}) versus the initial film thickness (h_o) as can be seen in Figure 4.[32] Figure 4a clearly indicates that Δh_{max} for PS28k tends to zero around 11–12 nm, a value which has to be compared with R_{EE} of 11 nm for PS28k.

"Roughening" of the Films by Dewetting. Upon further annealing at progressively increasing temperatures the interface between air and polymer film became more diffuse, eventually leading to a complete loss of all interference structures in the reflectivity curves. Characteristic examples are shown in Figures 5 and 6. Again, the thinner the films are the lower are the temperatures where this loss of the fringes occurs. As an extreme case, Figure 5 shows the thinnest film which could be prepared by spin-coating (PS660k: 3.5 nm)[34] where dewetting can be observed after 1 h annealing at 80 °C and only shadows of interference fringes are seen after 1 h annealing at 90 °C.

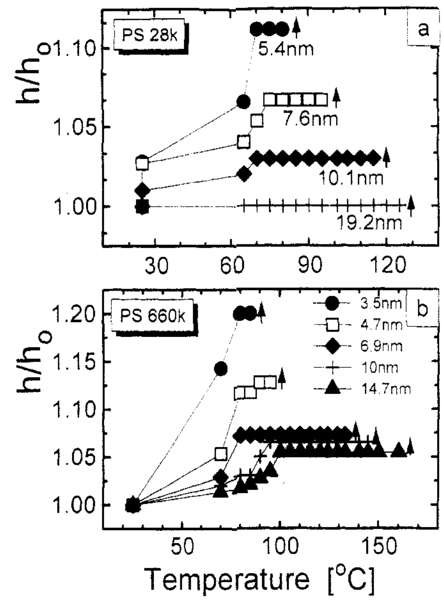

Figure 3. Examples for the increase in film thickness h (normalized by the initial film thickness h_o) as a function of annealing temperature (annealing time at each temperature 1 h) for (a) PS28k and (b) PS660k. The thinner the films are the more pronounced is their relative change in thickness. PS28k films thicker than about 11 nm are stable, whereas PS660k films of similar thickness still change their thickness upon annealing. Arrows indicate the temperature where all interference information is lost. The change in thickness at room temperature in (a) occurred after storing the samples for 3 months at ambient conditions.

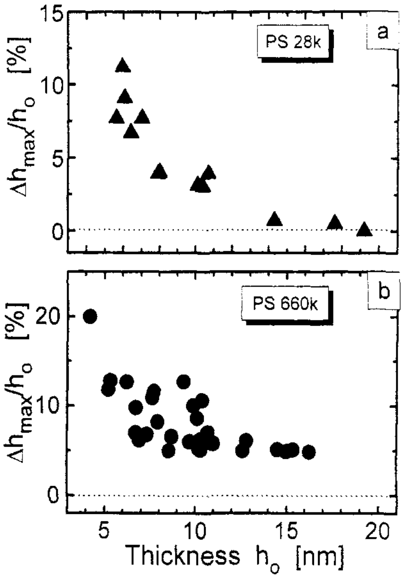

Figure 4. Maximum change in film thickness Δh_{max} normalized by the initial film thickness h_o versus h_o for (a) PS28k and (b) PS660k.

Other authors also observed a roughening of polymer films.[36] They described the interface by an error function profile assuming a Gaussian distribution for the height correlation function. A similar approach was tried but did not yield satisfactory results regarding the quality of the fits. As it is known that this roughening is caused by

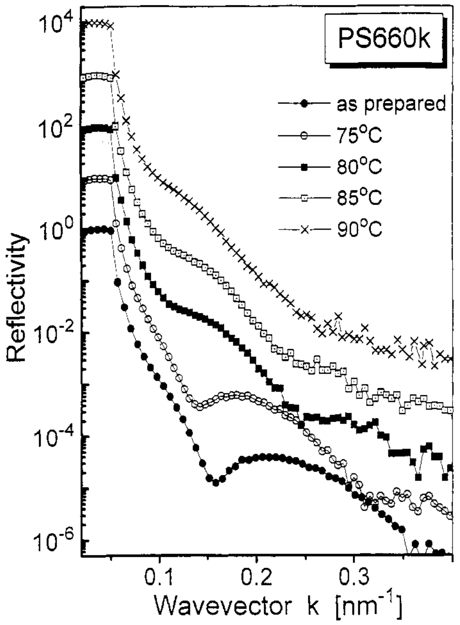

Figure 5. X-ray reflectivity versus incident wavevector for a PS660k film of initial thickness h_o = 3.5 nm after progressive annealing for 1 h at each step. Note that the glass transition temperature for PS660k in the bulk is 104 °C. Vanishing of the interference fringes is caused by dewetting.

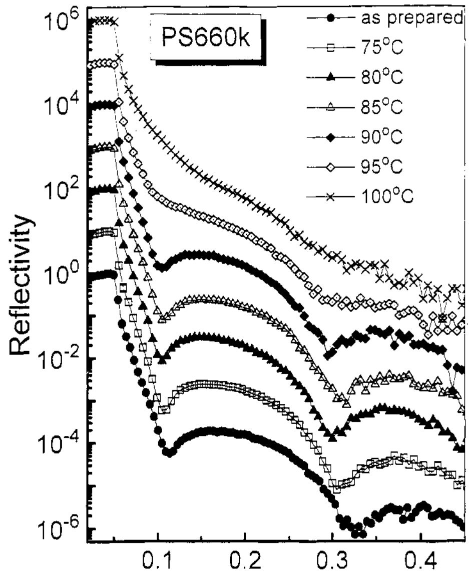

Figure 6. Same as Figure 5 for an h_o = 4.7-nm thick PS660k film. The interference fringes are not damped up to an annealing temperature of T = 85 °C. Dewetting sets in between 85 and 90 °C as the interference pattern of the 90 °C curve is already slightly damped especially at the first minimum at low k values.

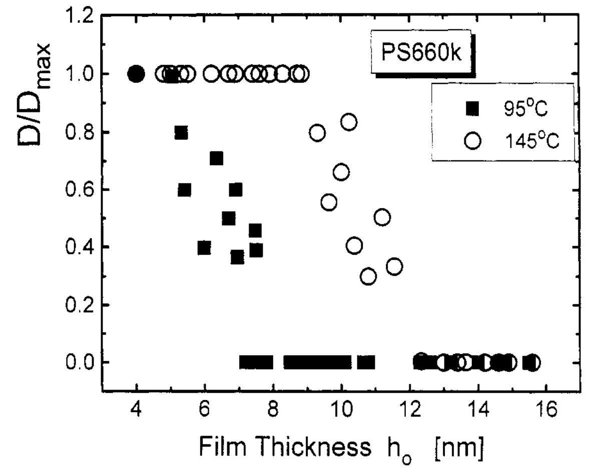

Figure 7. Diameter D of holes created by dewetting normalied by the maximum possible diameter D_{max} (=$\beta^{-1/2}h^2$, β = 1/25 Å^2) for the investigated PS660k films versus their initial thickness h_o for annealing temperatures of up to 95 °C (solid squares) and up to 145 °C (open circles).

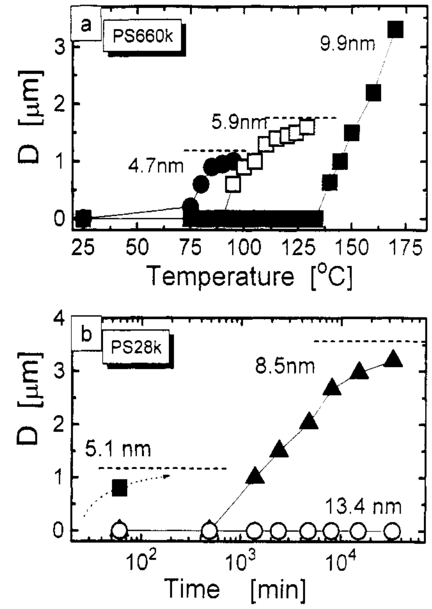

Figure 8. (a) Diameter D of holes caused by dewetting versus annealing temperature (annealing time 1 h per point) for three different PS660k films. The broken lines indicate the maximum value D can reach. (b) D as a function of annealing time (annealing time 90 °C) for three different PS28k films. The broken lines indicate D_{max}.

dewetting, the more appropriate analysis using a profile schematically depicted in Figure 1d was performed. Figure 7 shows the hole diameter normalized by its maximum possible value for PS660k samples as a function of film thickness after annealing at two different temperatures. Qualitatively, a roughness interpretation of the damped reflectivity curves would yield a similar trend. However, besides the fact that the used profile is based on the physical origin of the apparent "roughening" of the films, the reflectivity curves can be fitted much better using the dewetting profile. The big advantage of the profile of Figure 1d is that it provides direct information on the dynamics of dewetting. Using an error function profile neglects the fact that the number of holes depends significantly on film thickness ($Z \sim h^{-4}$). This means that thicker films seem to be stable for a longer period of time simply because there are fewer holes which have to grow much larger to produce the same change in the density profile.

Rate of Dewetting. In order to decide how fast the dewetting process takes place the hole diameter D was plotted versus temperature keeping the time constant (Figure 8a) and versus time keeping the annealing temperature constant (Figure 8b). The dewetting velocity v is not constant during the whole dewetting process. (Note that the time in Figure 8a is plotted on a logarithmic scale.) v slows down as the height of the rim increases in the course of dewetting. This implies that dewetting at a constant temperature is faster the thinner the film is. As the average hole diameter reaches its maximum possible value the hole growth slows down drastically and finally stops. Constant temperature experiments demand to vary the time over many orders of magnitude. For the thinnest films dewetting occurs already below T_g. In order to resolve the dewetting process in time one has to anneal these

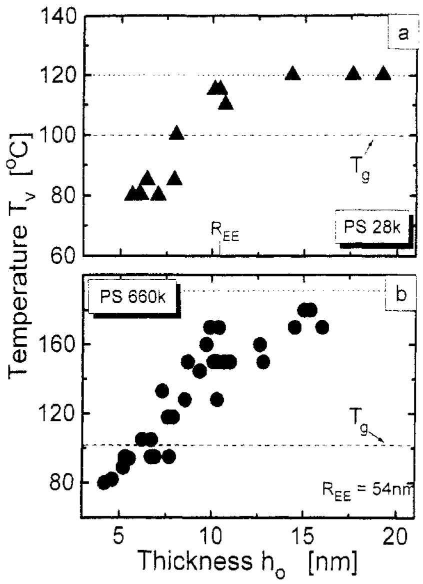

Figure 9. The dewetting velocity reaches a value of 500 nm/h at a temperature T_v. The dependence of T_v on the initial thickness (h_o) of the films is plotted for (a) PS28k and (b) PS660k. Values expected for bulk-like behavior are indicated by dotted lines. The glass transition temperatures (T_g) for bulk samples are marked by broken lines. R_{EE} is the end-to-end distance of the molecules.

samples below T_g.[37] However, at such a temperature thicker films seem to be stable for extremely long times. In fact, the time is certainly longer than several days making constant temperature experiments very difficult.

It is not clear if time-temperature superposition applies to our case. We preferred to keep the annealing time constant and interpolate between adjacent temperatures to determine the temperature T_v where the dewetting velocity ($v = \Delta D/\Delta t$) has reached a value of 500 nm/h. These temperatures versus initial film thickness are plotted in Figure 9.

We chose this particular value of v for several reasons. D has to be large enough to be detectable even for low hole concentrations. D should be small in order to resolve the onset of dewetting as closely as possible. In the limit $v \rightarrow 0$ T_v is expected to represent the effective glass transition temperture of the films. As it turns out a value of $D = 500$ nm is small enough to minimize the uncertainty of the onset temperature to a few degrees. Increasing the annealing temperature by a step of 5 deg changes D from zero to several 100 nm within 1 h (one annealing step). Using linear interpolation thus can yield T_v better than one annealing step. As can be seen from Figure 9a, T_v became independent of h for h larger than about 11 nm for PS28k samples. This thickness compares well to the h_o value above which films of PS28k do not change their thickness upon annealing. The PS660k samples do not show such leveling off for T_v vs h_o. For both molecular weights dewetting was observed below T_g if the film thickness is small enough (< ca. 8 nm).

4. Discussion

Effective Glass Transition Temperature of Thin Films. The results of this study clearly show the following tendency. In marked contrast to thicker films the temperature at which dewetting starts depends significantly on film thickness. For films thinner than about 8 nm dewetting at a velocity of 500 nm/h occurs even below T_g. Consequently, as dewetting cannot happen when the molecules are in the glassy state, the effective glass transition temperature of polystyrene in thin films is lower than in the bulk. The reduction of this transition temperature depends on film thickness, most likely on the ratio of R_{EE}/h for $h < R_{EE}$. The results indicate a crossover to bulk behavior happening at a film thickness which is much more proportional to R_{EE} than to the size of a single segment.

Comparison to Bulk. One may quantify the deviation from bulk behavior by comparing the viscosity the polymers of this study show in bulk samples with the value one can estimate from the measured dewetting velocity. According to theoretical considerations[38] and recent dewetting experiments[39] with thick films the dewetting velocity v is related to the viscosity η in the following way.

$$v = \alpha \cdot \gamma \cdot \eta^{-1} \cdot \theta^3 \qquad (11)$$

α is a constant of order 1, γ is the surface tension of polystyrene, and θ is the contact angle polystyrene forms on glass. From eq 11 follows that for the chosen velocity (v = 500 nm/h) the viscosity of polystyrene in the film must be approximately 10^7 Poise. PS660k and PS28k reach such a value in the bulk at about 180–190 and 120–125 °C, respectively.[40] Most of the investigated films, however, show this particular value of the viscosity at much lower temperatures. As an example, PS660k in a 5-nm thick film can reach such a value at about 90 °C which is about 100 deg below the bulk value.

Influence of Molecular Weight. Using two very different molecular weight samples allows to compare the influence of the length of the molecule (or degree of polymerization N) on viscosity in the bulk and in thin films. For the used samples the viscosity of bulk samples is proportional to $N^{3.4}$.[41] At a fixed temperature, the viscosity of PS660k is about 5×10^4 larger than that of PS28k. Therefore PS660k reaches the same viscosity as PS28k only at an about 60–70 °C higher temperature. At T_v the viscosity is constant. Figure 9 shows that the difference between the T_v values of the two molecular weight samples depends on thickness and only for the thickest films approaches the difference in temperature expected for bulk samples. This difference gets very small for the thinnest films. This means that the viscosity of these films becomes less pronounced dependent on N as h decreases. One might explain this behavior by relating it to a decreasing number of entanglements.

Density of Thin Polymer Films. The other major result of this study is that the density of thin polymer films decreases with decreasing h. For the thinnest films the reduced density has been detected directly by X-ray reflectometry. However, due to the rather low scattering contrast, the change in density could not be resolved very accurately. In all cases, however, the decrease in density could be calculated from the increase in film thickness. Recent neutron reflectometry measurements which have a much better resolution than the corresponding X-ray measurements, confirmed the relation between thickness increase and density reduction.[22]

It is worthwhile to note that for PS28k films larger than ca. 11 nm properties like density or dewetting velocity become independent of h. Their thickness does not change upon annealing, and, at the same time, T_v becomes constant at a value close to what is expected for bulk samples. This indicates the correlation between the reduced density and the increased mobility which, in turn, can be attributed to an effectively lower glass transition temperature. It is well-known that reducing the polymer density by adding a few percent of solvent molecules shifts the glass transition temperature some tens of deg.[41] Therefore, explaining why the density of thin polymer films can be lower than in the bulk automatically explains the change in mobility.

Improbable Explanations. Two possible explanations of these effects are ruled out. It is known that attractive interactions with the substrate can decrease the mobility of the molecules close to the substrate.[14,15] Weak interaction between polymer and substrate might cause a slightly depleted region close to the wall and therefore increase the mobility. However, as the influence of the interface is of short range only, one expects that this effect depends simply on the ratio of surface to volume and therefore should not depend on the length of the molecules. The observed influence of molecular weight thus cannot be explained.

One might also assume that the way the films were prepared is responsible for the deviation from bulk behavior. Spin-coating might cause nonequilibrium conformations of the molecules. Recent diffusion experiments indicate that molecules in spin-coated films are less entangled.[42] However, after some annealing the molecules will reach equilibrium. Dewetting demands that the molecules move over distances many times their size. Thus, during dewetting the molecules have sufficient time to relax. If their equilibrium properties would be bulk-like, dewetting would have to stop below T_g after the molecules relaxed. The present experiments, however, show that dewetting continues. For the thinnest films the complete dewetting process occurs below T_g. Therefore one has to conclude that polymers in thin films have different equilibrium properties, e.g., lower density, than in bulk samples.

Segregation of Polymers in Thin Films and Possible Consequences. A comparison of what one knows of polymers in the bulk (we call this the three-dimensional case, assuming $h > R_{EE}$) and what one expects for two-dimensional polymers[1,43] might help to understand the observed behavior of thin films. Theory[1] and computer simulations[43] predict that polymers are highly segregated in two dimensions. An ideal random walk in two dimensions occupies all sites within its perimeter. The square of the end-to-end distance R_{EE} is equal to the area of the molecule ($R_{EE}^2 = Na^2$, a is the length of a segment). Consequently, there is only negligible interpenetration for ideal random walks in two dimensions. We may define the concentration of a particular chain within its envelope volume as the internal concentration ϕ. For random walks $\phi = N^{-1/2}$ and $\phi = 1$ in three and two dimensions, respectively. Real polymers cannot cut through themselves, and de Gennes expects that they are slightly swollen in two dimensions.[1]

This is in contrast to the three-dimensional case. As pointed out by Flory,[44] polymer melts in three dimensions behave like ideal random walks. This is because long range interferences between segments of a particular chain cannot be diluted without simultaneously increasing the number of interferences with other molecules. A swelling (or stretching) of the molecules would cost energy that one would not regain from the reduced segmental interferences within a particular chain. One can say that there is effectively no excluded volume for the three-dimensional case. Such a compensation of effects or screening of intramolecular interferences is only possible if the chains are interpenetrating.

Confining polymers in films of $h < R_{EE}$ leads to a reduction of the interpenetration of molecules. The larger ϕ gets the lower is the number of possible paths for other chains through the envelope volume of a particular chain. Interpenetration will cost progressively more entropy the higher ϕ is, because the penetrating chains have to take conformations which are dictated by the chain they penetrate. If ϕ is larger than $1 - p_c$ (p_c is the percolation threshold for empty sites) there is no continuous path through the envelope volume of a chain.[45] Thus there have to be sites which cannot be reached by a chain of connected segments. Only with the help of thermal fluctuations such sites may be reached. This should lead to an even lower interpenetration to polymers. As a consequence not all of the intramolecular interferences can be screened leading to an increase of the excluded volume. It should be noted that in this context the excluded volume is equal (or at least proportional) to a free or inaccessible volume as it follows from the deficiency of chain interpenetration. The number of inaccessible sites increases with decreasing h, and the overall density of polymers in thin films consequently decreases. This decrease in density is in accordance with the results of this study.

5. Conclusions

The purpose of these experiments was to investigate the influence of confinement on static and dynamic behavior of polymers within thin films. It was found that the polymer density of films thinner than their average end-to-end distance is lower than in the bulk in accordance with other studies.[22] For thicknesses $h < R_{EE}$ the density decreased with decreasing h. As one might expect, such a reduced density enables molecules to move more easily which can be detected by the onset of dewetting at temperatures much lower than in bulk samples.

Dewetting was detected even below the glass transition temperature in the bulk (T_g). One can conclude that the effective glass transition temperature of such thin films is lower than T_g. A tentative explanation of the reduced density in thin films is based on packing considerations. Confining polymers in films thinner than R_{EE} leads to segregation of the molecules increasing the internal density of each molecule. This increase in internal density, in turn, makes it more difficult for other chains to penetrate into the volume described by the perimeter of the molecules. As a consequence there are inaccessible sites which will stay empty. While such an explanation seems plausible some more elaborate theoretical work is necessary to prove this idea or, alternatively, to explain the experimental results of this study somehow else.

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(31) Detectability by X-ray reflectrometry depends on film thickness as the necessary change in electron density is proportional to the number of holes $Z \sim \beta h^{-4}$.

(32) From experiments with much thicker films (20–200 nm for PS28k,[28,29] 35–200 nm for PS660k[33]) of the same molecules it is known that the thickness of such films does not change by more than 0.1–0.2 nm upon annealing. In many cases h slightly decreased ($\sim$0.1 nm) which might be attributed to evaporation of residual solvent.

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