Macromolecules
ARTICLE

Macromolecules **2011**, *44*, 987–992 **987**
DOI: 10.1021/ma200007d

Nanoscale Viscoelastic Behavior of the Surface of Thick Polystyrene Films as a Function of Temperature

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Received January 3, 2011

ABSTRACT: The variation in the glass transition temperature of thin polymeric films represents a phenomenon yet to be fully explained. To date, it is widely agreed that it is linked to the interfaces that the film forms with the air and the supporting substrate. Herein, we address one of the main issues regarding the viscoelastic behavior of the region near the free interface of thick polystyrene films where a reduction in the glass transition temperature is expected to occur. We have measured, as a function of the temperature, the elastic and viscous responses of polystyrene films with molecular weights above and below the critical value for the occurrence of molecular entanglement. The experiments have been carried out by means of scanning probe microscopy in a configuration combining the acquisition of force versus distance and indentation versus time curves. We show that the viscoelastic behavior of polystyrene films with thickness down to 30 nm can be successfully evaluated in the time scale from tenths to tens of seconds. In particular, we observe that the viscoelastic behavior of thick film surfaces has a similar dependence from the temperature as the viscoelastic behavior of the bulk, independently if the molecular weight is above or below the critical value. We estimate that the region at the free interface with a reduced glass transition temperature, if present, has a thickness below 3 nm.

Introduction

In thin polymeric films, confinement effects and interactions with the substrate can lead to modifications of molecular conformation and dynamics affecting the glass transition temperature (T_g). The T_g is arguably one of the most important parameters, as it also defines the temperature range of technological applicability for polymeric materials. Because of the recent major developments in nanotechnology, it is increasingly important to know and, if possible, to control the T_g of ultrathin films, given that it typically varies from the bulk values.

The first observation of a T_g deviation from the bulk value (T_g^{bulk}) was reported back in 1994 by Keddie and co-workers.[1] They studied such a phenomenon for atactic polystyrene (PS) deposited on a silicon substrate and showed that the T_g was lowered when the film thickness was reduced. Subsequently, several studies have confirmed these findings on PS supported[2] and freely standing films.[3−5] Other polymers have also been investigated such as poly(methyl methacrylate) (PMMA)[6−8] and poly(vinyl acetate) (PVAc).[9] The effects of strong or weak interactions with the substrate have been investigated,[10−12] and the relevance of molecular entanglement has been also pointed out.[4,5] At present, there is wide agreement on the importance of the two interfaces that the polymer film forms (see Figure 1): one with air (*free interface*)[3−5,13] and one with the substrate (*support interface*).[14,15] However, a comprehensive explanation of the roles that each interface plays and the mutual interplay between the two is still elusive.

In this paper, we intend to address the issue regarding the thickness (h_C) of the region at the free interface possessing a T_g lower than the T_g^{bulk} for the case of PS. In their first paper,[1] Keddie and co-workers already suggested that the T_g of thin films might not be represented by a single value but that it might be a continuous function of the distance from that interface. The first dedicated investigation, carried out by Xie and co-workers, did not report any detectable change in T_g with the distance from the free interface.[16] On the contrary, Jean et al. measured a big drop in T_g locating it in the first 5 nm from the film surface.[17] Another interesting experiment has been devised by employing nanoparticles as probes and measuring their penetration at the surface as a function of the film temperature (T). The collected data have been variously interpreted: the authors have claimed a depression in T_g in the first 5 nm layer[18,19] and some others none.[20] Indirect evidence of surface molecular mobility below the T_g^{bulk} has been also obtained by studying the charge transport of pentacene films, although it is not possible to quantify to what depth extent the molecules are mobile.[21] However, the most striking study is arguably the one carried out by Ellison and co-workers, in which a thin layer made of PS molecules modified with fluorescent side chains is used as an internal probe.[22] A thin layer of the modified PS was placed on top or underneath a thick unmodified PS film, and it was found that the extent of the top layer with a reduced T_g could be quantified to at least 14 nm.

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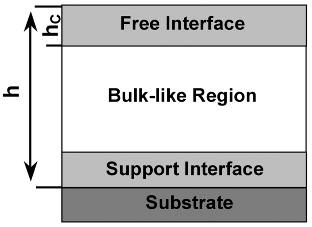

Figure 1. Schematic drawing of the relevant regions of a polymer film with a given thickness (h): "free" and "support" interfaces, bulk-like region. h_C represents the region where a reduction in glass transition temperature might occur.

Scanning probe microscopy (SPM) has been the technique of choice for direct measurements of the viscoelastic properties on the nanoscale. Up to now, most of the reports have not observed any difference in behavior from the bulk at the free interface.[23-27] Some authors have measured the friction force, suggesting the presence of a mobile layer at the top surface, compatible with a reduced T_g.[28,29] Others have locally characterized the thermal properties by using a tip suitably modified so it can be heated.[30,31] It appears that all these SPM experiments have been focused on detecting discontinuities in physical properties of the polymeric film when varying T. However, there have been no specific attempts to quantify the viscoelastic deformation due to the contact between the probe tip and surface. In particular, the tip shape and the cantilever elastic constant have not been carefully calibrated. Therefore, the depth involved in those investigations cannot be clearly defined, and thus controversy still remains about the precise T_g of thin films and subsequent length scales involved.

In our investigation, we employ SPM operating in a configuration specifically dedicated to the purpose. On one side, the elastic response can be obtained by the acquisition of force versus distance curves as reported in the literature.[32] On the other hand, the viscous response can be obtained by the acquisition of indentation versus time curves while keeping a fixed load value. This configuration, recently developed in our group,[33] allows one to fully characterize the viscoelastic properties of polymeric films from hundreds to tens of nanometers as a function of T within a time scale from tenths to tens of seconds. For this work, we have measured the tip radius and calibrated the cantilever elastic constant in order to precisely define the depth of our analysis.

Experimental Section

Our experimental setup consists of a commercial head (NT-MDT, SMENA) with the cantilever moved by a piezo-actuator. The head stands with three micrometric screws on a large metallic base where a Peltier cell is placed under the sample holder in order to vary temperature (T). The Peltier cell is driven by means of an electronic controller, commercially available (Thorlabs, TED-350). This setup, thanks to the reduced number of elements forming the loop between tip and sample, is very stable. It only needs to be thermalized for a few minutes after increasing the sample T. Depending on the external conditions or the thermal coupling, above 100 °C we sometimes notice an oscillatory signal in the z direction with an amplitude from 2 to 3 nm and a temporal periodicity of 6 s. We attribute this to a tiny oscillation in the temperature (< 0.1 °C) due to the electronic feedback. A calibration of the sample T can be carried out by using powdered sulfur and observing with an optical microscope the melting temperature of the powder when placed on a piece of silicon wafer (T_m = 115 °C).

The head is controlled via an custom-developed software that allows one to acquire the relative distance (z) and the lateral force (F_L) during a given "contact" time (t) while the normal force (F_N) is maintained constant for up to a few minutes. The acquisition of z versus t curves is performed for the measurement of the viscous deformation (δ_V), as reported elsewhere.[33] The time of contact can be varied from 1 ms to 180 s. In order to remove the piezo-creep dependence from the history of the voltage applied, several curves are performed before actually starting the data acquisition. This procedure reduces the piezo-creep variability down to less than 1 nm in z-positioning. The acquisition of F_N versus z curves is performed for the evaluation of the elastic deformation (δ_E), as reported elsewhere.[27,32] In our setup, the approach and retraction frequency can be varied from 0.1 to 10 Hz, while the Δz ranges from 100 to 500 nm.

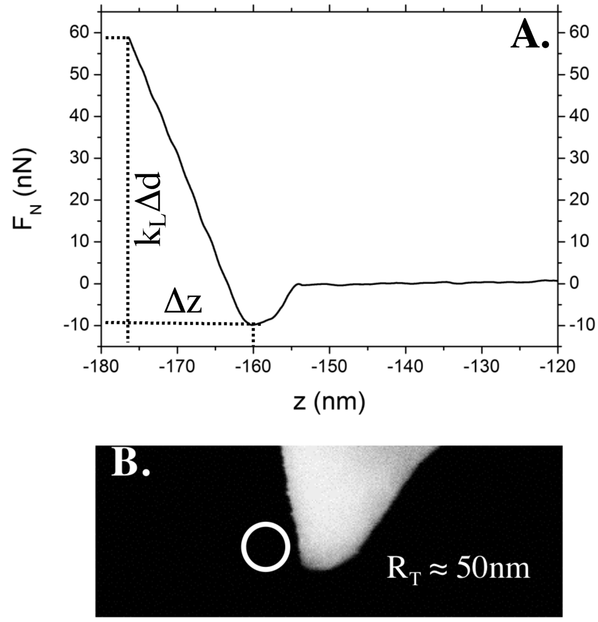

Figure 2. (A) Example of the approach branch of a force (F_N) vs distance (z) curve on a thick 483 kDa film. The elastic deformation (δ_E) can be evaluated from Δd and Δz by means of eq 1. (B) SEM image of the tip (the white circle has a radius of 50 ± 10 nm) used for the elastic and viscous measurements.

The cantilevers employed are rectangular in shape, as they can be calibrated using Sader's method.[34,35] The elastic constant (k_L) of the cantilever is selected following two criteria: in order to apply an appropriate range of F_N values and to avoid instability during the tip approach (jump-in to contact). For the elastic measurements, it is also important that k_L is comparable to the contact stiffness (k_C).[32] We have found that a k_L with values between 2 and 10 N/m represents a good compromise. The evaluation of the calibration constant of the optical lever system used to detect the cantilever deflection (d) is usually performed on a stiff surface (in our case a piece of silicon wafer).

The tips are cleaned using piranha solution (3:1 of sulfuric acid and hydrogen peroxide 30% for 20 min) to remove organic contaminants due to the packaging employed by the manufacturers, typically made of PDMS.[36] Piranha solution can also be used to remove the PS molecules attached during the investigation of low molecular weight (M_w) films at high T. Scanning electron microscopy (SEM) has been used to characterize the shape of the tips and to measure the tip radius (R_T). This is very important in order to select a tip with a suitable R_T (see Figure 2B) and also to characterize the tip after the experiments.

The films are prepared by spin-coating a PS solution in toluene on the substrate. The concentration has been varied between 1 and 3% (w/v) and the speed between 2000 and 600 rpm. The thickness of the films is determined using a stylus profilometer (VEECO DEKTAKT 8). Thermal annealing is typically performed at $T = T_g + 30$ °C for at least 10 h (unless otherwise stated). The PS standards (Polymer Laboratories) employed have the following molecular weight (M_w) and polydispersity (M_w/M_n) values: 13.1 kDa (1.03) and 483 kDa (1.05), one above and one below the critical M_w above which molecular entanglement occurs ($M_C \approx 30$ kDa).[37]

Silicon wafers with a native oxide have been used as substrates. The silicon wafers are ultrasonically cleaned in a series of solvents (acetone, isopropyl alcohol, and deionized water) for 30 s each and then blown dry with nitrogen. We have not observed dewetting of thick films even after thermal annealing at $T = T_g + 30$ °C. The surface can also be cleaned in other ways, for instance, O_2 plasma cleaning. The T_g values obtained for thick films do not differ from those obtained with the cleaning procedure herein described. It was our intention to avoid substrate treatments that might induce a strong interaction with the PS molecules and alter the T_g values of thin films.

Results

In the literature, it is reported that the indentation depth (δ_E) can be measured from the analysis of "approach" force (F_N) versus distance (z) curves (Figure 2A): d represents the cantilever deflection value. Provided that d and z are calibrated, δ_E is equal to

$$\delta_E = \Delta z - \Delta d \qquad (1)$$

where Δz and Δd are determined from the initial point of contact (where F_N starts to increase after initial negative values) to the point of maximum F_N.[32] Figure 2A shows an approach curve obtained at room temperature with the tip shown in Figure 2B. k_L is equal to 6 N/m (±5%), which is sufficient to avoid instability during the tip approach (see Experimental Section).

The maximum attractive force value measured at the initial point of contact is in agreement in the amplitude (and the z range) to the expected values of van der Waals force between a surface and a tip with R_T of 50 nm:

$$F_{vdW} = -AR_T/z^2 \qquad (2)$$

where A is the Hamaker constant.[38]

If one wants to define what "the surface" means in the case of an SPM experiment, it is important to consider the mechanics of the contact between the tip and the surface. Elastic deformation is unavoidable, and limiting it to a shallow depth is desirable. In order to estimate theoretically this deformation, we have considered models that are modified versions of the Hertzian model for a sphere on a flat surface in order to account for an adhesion force (F_{ad}).[39,40] The Derjaguin, Muller, and Toporov model (DMT)[41] is valid for the case of a surface with low adhesion energy and high Young's modulus (E_Y), while the Johnson, Kendall, and Roberts model (JKR)[42] is valid for high adhesion energy and low E_Y.

According to these models, one can control two parameters: R_T and F_N. We have thus characterized the tip shape by means of SEM and opted for a tip with a R_T of 50 ± 10 nm (Figure 2B). It is generally agreed that E_Y for bulk PS is around 3 GPa.[43] This value has also been reported for thin films down to tens of nanometers by means of nanoindentation measurements,[44-46] and it is not M_w-dependent.[47] Therefore, considering a F_{ad} of 40 nN (as measured for the tip employed and shown in Figure 2B) and a F_N of 50 nN (typically used for our experiments), δ_E can be estimated to be 2.2 ± 0.3 nm for both DMT and JKR models: the larger R_T, the smaller δ_E. The use of a tip with a larger R_T value would be beneficial in order to reduce the initial elastic deformation, but it would also affect the sensitivity to viscous yield around the T_g.

Finally, a crucial issue is the fact that around the T_g both E_Y and the viscous modulus (η) dramatically vary. For instance, the bulk E_Y diminishes by several orders of magnitude with a ΔT increase of 10 °C.[43] There is no experimental study that has accurately quantified such variations on the nanoscale. It is however been proven that these variations are large enough to be detected.[26] Their detection depends strongly on the values of R_T and F_N.[24]

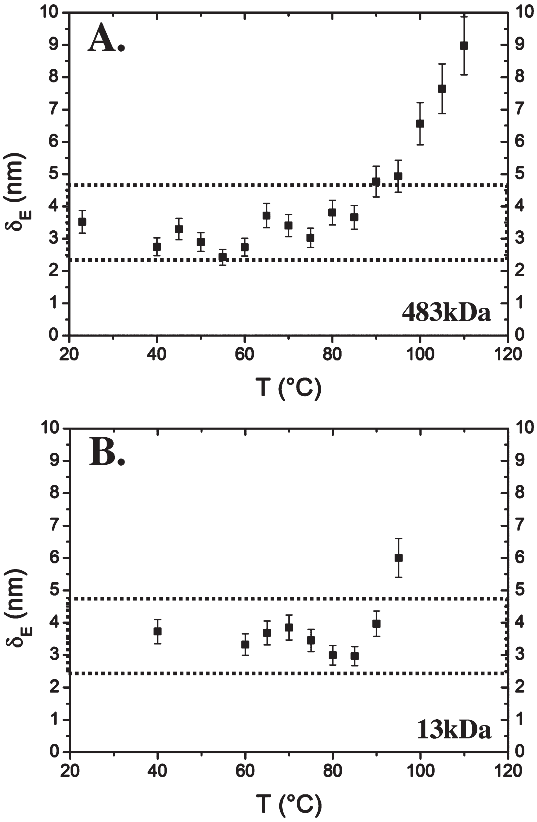

Figure 3. (A) Plot of the elastic deformation (δ_E) vs temperature (T) data obtained for a thick 483 kDa film (280 nm). (B) Plot of δ_E vs T obtained for a thick 13 kDa film (220 nm).

Table 1. Summary of the T_g Values Evaluated from the Elastic Deformation Data, for PS Films Varying the Molecular Weight (M_w) and Thickness (h)[a]

	T_g (°C)	
h (nm)	M_w = 483 kDa	M_w = 13 kDa
bulk	100	93
>200	95−100	90−95
≈30	85−90	

[a] The higher value represents the lowest T at which a significant increase in the elastic deformation can be observed. For T_g bulk values, see for instance refs 25 and 37.

In Figure 3A, we show the δ_E data as a function of T obtained for a thick 483 kDa film (280 nm). It appears that δ_E is around 3−4 nm for $T < 90$ °C. It increases slightly at 90−95 °C and then more dramatically for $T \geq 100$ °C. In Figure 3B, data recorded for a thick 13 kDa film (220 nm) show a similar behavior with δ_E around 3−4 nm for $T < 90$ °C. In this case δ_E represents a discontinuity for $T \geq 95$ °C. This M_w-dependent observation for E_Y vs T is in agreement with the T_g values of the bulk (T_g^{bulk}) reported in the literature.[48]

In Table 1, we summarize values for T_g of thick and thin films estimated from data of the elastic measurements versus T. In particular, T_g is defined not as a single value but a range of values: the higher value represents the lowest T at which a significant increase in the elastic deformation can be observed. For a thin 483 kDa film (≈ 30 nm), δ_E presents a discontinuity at $T \geq 90$ °C. This value is in agreement with those ones reported in the literature for

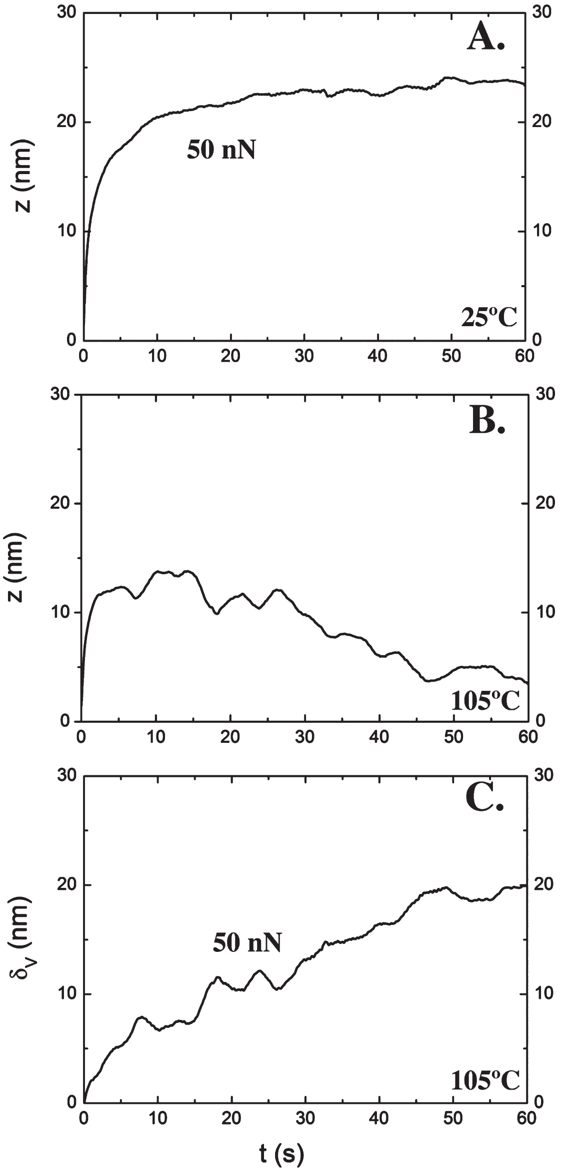

Figure 4. (A) Plot of a distance (z) vs time (t) while maintaining constant the normal force (F_N) on a silicon surface at room temperature. The creep of the piezo determines an increase of z with t. (B) Plot of z vs t while maintaining constant F_N on a thick 483 kDa film (280 nm) at 105 °C. The viscous yield is superimposed to the piezo-creep and has an opposite sign. (C) Plot resulting from subtracting the curve reported in (A) from the curve reported in (B).

such a film thickness.[25] Unfortunately, we have not been able to accurately measure the T_g of thin 13 kDa films. We believe that this is imputable to the fact that the molecules are not entangled and can attach to the tip when the film is at a T close to T_g. This hinders a correct evaluation of δ_E as the effective R_T can vary during the experiment and in particular from measurement to measurement.

In previous studies, the viscous yield was qualitatively evaluated from the hysteresis between the approach and retraction regions of F_N versus z curves.[26] In order to better measure it, we have implemented a new operating mode in which the tip and the surface are maintained in contact under a given F_N for a given length of time (t).[33] In Figure 4A, we show the case of a tip in contact with a silicon substrate at 50 nN for 60 s at room temperature. It is first important to notice that, in these experiments, z is never constant but tends to increase immediately after the feedback is switched on. Then it flattens out at a value of around 25 nm, depending on the history of the applied voltage to the piezoactuator but almost independent by T. This is due to the so-called "creep effect" of the piezoactuator. In Figure 4B we show the same experiment carried out on a thick 483 kDa film (280 nm) at $T > T_g$. Viscous yield (δ_V) occurs, and there is a penetration of the tip into the film. d is thus reduced, and the feedback extends the piezoactuator in order to maintain a constant F_N, therefore changing z. δ_V is superimposed to the piezo-creep, but its contribution to z variations can be easily discriminated as it has an opposite sign. Plots of δ_V versus t can be obtained by subtracting the creep contribution to the z versus t data (Figure 4C). In the following all data obtained will be thus reported in this way (see Figures 5 and 6).

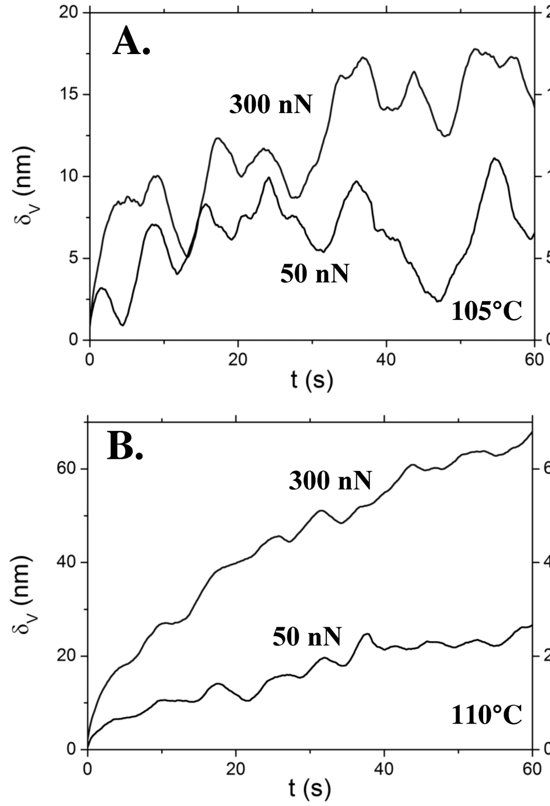

Figure 5. Plots of viscous indentation (δ_V) vs time (t) for a thick 483 kDa film (280 nm) on native silicon oxide. F_N is equal to 50 and 300 nN. T is equal to 105 °C (A) and 110 °C (B) on native silicon oxide.

Figure 5 shows the δ_V data obtained on the same sample as in Figure 3A (i.e., a thick 483 kDa film). For $T \leq 100$ °C, we observe no δ_V taking place with t, independently of the F_N values. At $T = 105$ °C, δ_V starts to appear with a dependence on F_N. At $T \geq 110$ °C, the δ_V dependence on F_N is more evident. Figure 6 shows the δ_V data obtained on the same sample as in Figure 3B (i.e., a thick 13 kDa film). For this film δ_V starts to appear for $T \geq 95$ °C. Generally, the z versus t curves on 13 kDa films are noisier. As discussed above, we interpret this with the fact that the molecules are not entangled and can stick to the tip surface at $T \geq T_g$.

In Table 2, we summarize values for T_g of thick and thin films estimated from data of the viscous measurements versus T. As for the case of elastic deformation, we do not indicate a single value but a range of T: the lower value represents the highest T at which no viscous yield can be observed, the higher value is the lowest T at which viscous yield can be observed. For a thin 483 kDa film (≈ 30 nm), δ_V begins to occur at $T \geq 90$ °C. In this case we have been able to measure also the thin 13 kDa film (≈ 30 nm): δ_V starts to increase for $T \geq 85$ °C. This value is in agreement with the T_g values reported in the literature for such a film thickness.

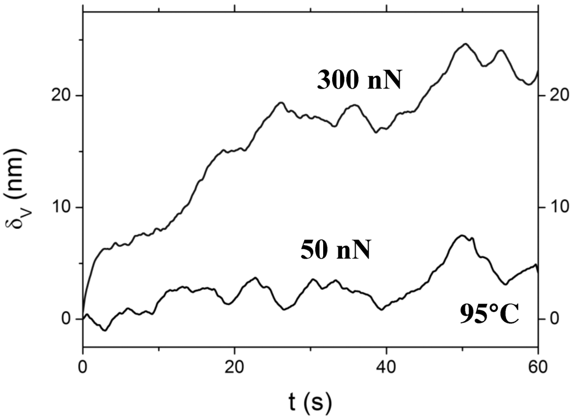

Figure 6. Plot of viscous indentation (δ_V) vs time (t) for a thick 13 kDa film (220 nm) on native silicon oxide. F_N is equal to 50 nN and 300 nN, whereas T = 95 °C.

Table 2. Summary of the T_g Values Evaluated from the Viscous Deformation Data, for PS Films Varying the Molecular Weight (M_w) and Thickness (h)[a]

	T_g (°C)	
h (nm)	M_w = 483 kDa	M_w = 13 kDa
bulk	100	93
> 200	100−105	90−95
≈30	85−90	80−85

[a] The lower value represents the highest T at which no viscous yield can be observed and the higher value the lowest T at which viscous yield can be observed. For T_g bulk values, see for instance refs 25 and 37.

Contrary to the elastic ones, the viscous measurements are less sensitive to tip contamination occurring for 13 kDa films, as we are interested in the occurrence of viscous yield and not in a quantitative evaluation. Similar results on the viscous properties have been obtained with other tips. However, in these measurements, R_T had not been calibrated, and therefore it was not possible to define the initial δ_E.

On the other side, the viscous measurements have been carried out for a period of time which is necessarily long in order to observe tip penetration. Typically, we operate on a time scale of 1 min. It is expected that during this lapse of time the relative position between tip and surface changes. First of all, the thermal drift due to the heating of the sample cannot be fully eliminated although, after varying the sample temperature, we wait for a while in order to thermalize the system (see Experimental Section). Second, the cantilever is tilted, and there is a force component parallel to the surface that acts during the tip penetration. Finally, the viscosity might locally fluctuate especially when T is close to T_g (see Figures 5A and 6). As a result, the δ_V plots do not always show smooth curves but present fluctuations of a few nanometers. The measurements reported in Figures 5 and 6 are representative examples of data taken in different regions of a given film at a given T and for a given force value (F_N). They are shown in order to prove that the tip always penetrates into the film to a different extent depending on T and F_N. This represent clear evidence that a film is in a viscous regime.

Discussion

A first point of discussion regards data reported in Tables 1 and 2. It is worth stressing that the T_g values estimated from elastic and viscous measurements are in good agreement. A small difference has been observed only for the case of a thick 483 kDa film, where the elastic transition occurs at a smaller T compared to the viscous one, but within the experimental error. Second, both elastic and viscous methods have been able to evaluate the T_g values of thin films. These values are lower than those ones of thick films and of the bulk. They are also in good agreement with what is reported in the literature for thin films on noninteractive substrates, such as the case of silicon oxide.

The major issue of this paper however regards the determination of the viscoelastic properties of the top surface as a function of the temperature. Our experimental data (see Figure 3) show that during the tip approach the total deformation for the 483 kDa films is between around 3 and 4 nm at $T < 90$ °C and below 5 nm at 90 °C < T < 100 °C. For the 13 kDa films, the total deformation is between 3 and 4 nm at T < 95 °C. This total deformation can be due to either the elastic response, or to a possible viscous yield, or to both. The possible viscous yield can be attributed to a layer with a T_g lower than the T_g of the whole film. By using the theoretical models of contact mechanics, the elastic deformation can be estimated (vide supra) and hence the thickness of the viscous region deduced. For the tip employed, the calculated deformation is 2.2 ± 0.3 nm, assuming E_Y equal to the bulk value (3 GPa). The presence of a thin layer at the very top surface with a different T_g that is instantaneously penetrated at the contact formation can be thus estimated to be less than 3 nm. One might also put forward the hypothesis that E_Y has a reduced value at the surface compared to the bulk. Concerning this hypothesis, Zaitseva et al. have reported that E_Y is equal to 1 GPa within a few nanometers from the surface.[49] In this case, the calculated value for the elastic deformation would be of 4.4 ± 0.5 nm. This would suggest that the region with a lower T_g can be even shallower. At present, we can safely state that if a region with a reduced T_g is present its thickness is below 3 nm.

Another important point of our work is in regard to the comparison between films made of molecules with different M_w. In particular, we have employed two values: one above and one below M_C, the critical M_w value above which molecular entanglement occurs. From the δ_E data, we can notice that there is no M_w dependence for thick films at $T < T_g$. This suggests that molecular entanglement is not a relevant parameter in determining E_Y of PS films. This is in agreement with what reported by Kalliapan et al.[47] but not by Zaitseva et al.[49]

Conclusions

The viscoelastic behavior of thick and thin polystyrene films as a function of temperature can be successfully studied on the nanoscale by means of scanning probe microscopy operating in a configuration that combines the acquisition of force versus distance and indentation versus time curves. In particular, the viscoelastic behavior of thick film surfaces versus temperature has been found to be similar to the viscoelastic behavior of the bulk. Additionally, no difference has been noticed for molecular weight values below and above the critical value for the occurrence of molecular entanglement. Finally, we estimate that a region near the free interface with a reduced glass transition temperature, if present, should have a thickness below 3 nm. This limit can be set from the evaluation of the initial viscoelastic deformation occurring at the contact formation.

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