Macromolecules **2007,** *40,* 7291−7298

Viscoelastic Properties of Ultrathin Polystyrene Films

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Received February 22, 2007; Revised Manuscript Received July 2, 2007

ABSTRACT: The dewetting of ultrathin polystyrene films on a liquid substrate is studied in the vicinity of the glass transition. This technique leads to the measurement of the extensional creep compliance of the film. The results reported in this article show that the rubbery plateau value of the compliance is unchanged for films as thin as 20 nm. Thus, we conclude that the entanglement density is unaffected by the surface at a scale of the coil size. These results are discussed in the context of previous results that report the reduction of the viscosity in the same films. Furthermore, the creep compliance of ultrathin films in the segmental relaxation regime exhibits a small reduction of the characteristic times. For high molecular weight thin films, the time scale reduction in the transition zone is much weaker than the reduction of the terminal relaxation time. This observation shows that the different parts of the time spectrum are not equally sensitive to the confinement. This is consistent with expected effects of the confinement at different length scales.

1. Introduction

Glass-forming materials in confined geometries have been extensively studied during the past decade,[1] with much attention being paid to ultrathin polymer films. In fact, in addition to having major importance in industrial applications, these films are of great fundamental interest. When film thickness is decreased down to thicknesses of a few nanometers or a few tens of nanometers, this dimension of the system becomes of the order of the characteristic length scales of the material itself. One could then expect that the physical properties would deviate from their bulk values when the thickness reaches the length scale that governs the tested property. Investigations on physical properties of such confined systems should therefore help to better characterize these length scales. Polymers exhibit wider length scales and more complex dynamic properties than do small molecules and offer potentially richer experimental conditions for study. The present work is presented in this vein.

The dynamical properties in the vicinity of the glass transition have been the focus of many studies. Following the early observation due to Keddie et al.[2] of a significant decrease of the glass transition temperature (T_g) when the thickness of polystyrene (PS) films becomes smaller than 50 nm, the T_g value of different polymers as a function of film thickness has been studied using a wide variety of technique (for a review see refs 1 and 3). Even though there is a global trend to confirm the observations of Keddie et al., some discrepancies between the different experiments and polymers remain unresolved and some unexpected features rather poorly understood.[4] For the moment, it seems that the experimental studies of ultrathin polymer films remain unable to define completely the length scales that are involved in the glass transition.

One challenge is to dissociate the role of the confined state of the molecules from the role of the surfaces. It has been shown that T_g decreases near a free surface or a nonattractive wall but increases near an attractive one.[5] Deviations from bulk behavior are more dramatic when the film has a free surface.[6] Suspended films should be simpler at least for symmetry reasons, but they reveal nontrivial behaviors.[7−10] The glass transition temperature is found to be more strongly depressed in free-standing films, and this may confirm the strong influence of free surfaces. The T_g reduction in free-standing films also depends on the molecular weight for high molecular weight polymers. This last feature seems difficult to reconcile with the glass transition picture in the bulk, since the molecular weight has no influence on the T_g value when the polymer length is large enough to allow to neglect the influence of chain ends.[11] Furthermore, it is not consistent with present views of the T_g reduction of thin films.[12,13]

The dynamics in a polymeric material cannot be reduced to a single parameter. Indeed, these systems exhibit a very broad time spectrum, which is associated with different length scales. Only a part of this time spectrum is directly involved in the glass transition, while some longer times play a great role in above-T_g properties. In the bulk, the above-T_g dynamics is somewhat better described than the glass transition phenomenon. The Rouse model and the reptation model have been able to successfully account for the polymer properties.[14] The link between time and space scales is, in these theories, rather straightforward. Ultrathin polymer films may offer a way to experimentally bring evidence of this direct correlation between length and time scales in polymer melts.

As compared to T_g measurements, very few experimental techniques have been employed to characterize the whole dynamics in ultrathin films. Concerning the very long time dynamics, chain diffusion measurements have been achieved using a fluorescence technique[15] or secondary-ion mass spectrometry (SIMS) experiments.[16,17] Both techniques lead to the conclusion that chain diffusion is affected on a scale of the order of the coil size, which is consistent with the reptation mechanism that involves this particular length of the polymer material. However, the diffusion is found to be slowed down, which is in apparent contradiction with recent mechanical results near a free surface. The viscosity in ultrathin films and in the vicinity of the surface has been reported to be decreased as compared to that of the bulk.[18,19] Rouse modes have been less studied, but indications have been reported that they might be slower or less efficient in a thin film.[9,20,21] The global picture of the dynamics in ultrathin films is thus still rather confusing, and

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10.1021/ma070460d CCC: $37.00

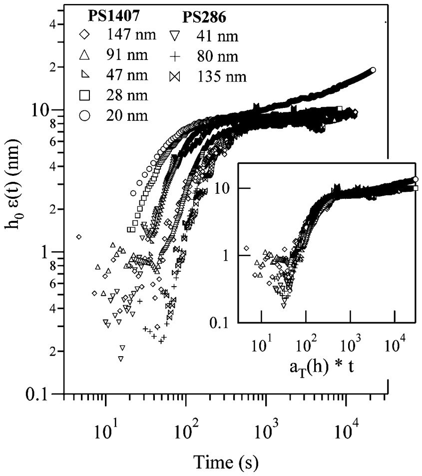

Figure 1. Normalized apparent creep compliance $h_0\tilde{\epsilon}(t)$ for PS1407 and PS286 films of initial thickness ranging from 20 to 150 nm. Temperature is 378.5K (±0.5 K). The inset shows the superposition of the apparent creep compliance curves which is obtained by multiplying the experimental time scale by a shift factor $a_T(h)$, for each thickness.

we may conclude that one needs deeper analysis of the evolution of the global time spectrum when the film thickness is decreased to very small sizes. A complex interplay between length and time scales and temperature may explain some of the discrepancies between the experiments.[22,23]

In a bulk polymer melt, the dynamics is closely linked to the structure of the chains and, more precisely, to the entanglement network.[14] It thus seems necessary to obtain information not only on dynamical properties but also on the polymer structure. If the dynamics is strongly affected either by the confinement or by the presence of a free surface, then one has to take such an effect into account when interpreting the dynamical properties of ultrathin polymer films. It was early proposed that the entanglement density should be slightly decreased near a free surface.[24] This theoretical prediction was recently experimentally checked and refined by Si et al.[25] According to these authors, the entanglement density remains constant in an ultrathin film, while the entanglement nature turns from interchain entanglement in the bulk to intrachain entanglements in a confined polymer film. However, using a fluorescence technique, Itagaki et al.[26] did not see any deviations on the chain overlapping down to a thickness of $2R_g$. The question of the entanglement structure might be an issue of importance for understanding the dynamics of ultrathin films. Indeed, a recent model that accounts for the T_g reduction is based on the distance between entanglements.[27] Ultrafast relaxation observed in glassy films was also attributed to a lack of interchain entanglements.[28]

In the bulk, the entanglement density is usually deduced from mechanical properties in the rubbery regime.[11] It seems thus that mechanical measurement performed in the corresponding time domain would be of great interest to answer the question of the entanglement structure in ultrathin films. To our knowledge, the only mechanical test that has been performed on ultrathin film was reported by O'Connel and McKenna.[9,29] Their nanobubble experiment was designed to measure the time-dependent creep compliance of free-standing films. These authors report a rather unexpected result. In the rubbery regime, ultrathin films seem to be much stiffer than bulk samples. If one interprets these experiments in terms of entanglement structure, it leads to the hardly conceivable conclusion that the entanglement density would be much higher than in the bulk.

In order to bring new insights to this question of the entanglements structure, other mechanical measurements are needed in the rubbery regime. Moreover, transient or dynamic mechanical experiments should allow the investigation of the global time spectrum, since the viscoelastic functions reveal the whole dynamics of the system.

In a previous communication, we have reported a method that allows the measurement of an apparent creep compliance in thin polymer films.[30] The dewetting of a viscoelastic film on a liquid substrate is rather simple to describe, due to the absence of friction between the film and the substrate. For films thicker than 100 nm, it has been shown that the apparent creep compliance measured by this technique is in quantitative agreement with bulk properties. This experiment is thus particularly suitable to answer the two main questions that are detailed above. What are the length scales governing the entanglement structure, and what are the different relaxation times in ultrathin films?

The salient results of our previous communications using this technique concern the very long times of the creep compliance (or at high temperature).[18] At these times a steady-state flow is reached, and the elongational viscosity is measured. For thick films, the viscosity measured follows the bulk temperature dependence and scales approximately as $M_w^{3.4}$, similar to bulk samples. For thinner films, however, the viscosity is found to be reduced as compared to the bulk. The ratio h/R_g where h is the film thickness and R_g is the radius of gyration seems to govern this viscosity reduction.

In the present article, the creep compliance of ultrathin films is investigated in the vicinity of the glass transition. Based on these results, we discussed the nature of entanglements in thin polymer films. Confinement effects on the dynamics in the T_g region are also shown and analyzed with regards to the large viscosity reductions earlier reported.

2. Experimental Method

The method consists of measuring the strain response of the whole film to the stress applied by the surface tensions. In the case of a viscoelastic film lying on a liquid substrate, it has been shown[30] that the surface tensions can be accounted for by a normal stress acting on the edge of the film. The intensity of the stress is S/h, where h is the film thickness and S is the spreading parameter, defined as $S = \gamma_l - \gamma_f - \gamma_{f/l}$; γ_f and γ_l are the film and liquid surface tensions, respectively, and $\gamma_{f/l}$ is the interfacial surface tension. The strain has been shown to be uniform inside the film, and the time-dependent strain response is linear to the applied stress.[30]

The PS films where spin coated on a mica substrate at 3500 rpm, from dilute solutions of PS in toluene, having weight fractions ranging from 0.2% to 2.5%. The solutions were prepared using monodisperse polymer purchased from Polymer Source Inc. Two molecular weights were used, $M_w = 1407$ kg/mol, referred in the following as PS1407, and $M_w = 286$ kg/mol, referred as PS286. Both are well entangled since the average molecular weight between entanglements is about 43 kg/mol.[11] Their radii of gyration are 32.6 and 12.7 nm for PS1407 and PS286, respectively.[31] The films were annealed under vacuum at 453 K during 8 days, to remove the residual solvent and the stress induced by the spin coating process. After the annealing, they were cooled at 0.5 K/min, and cut into small pieces of size about 1 mm. The films were floated on distilled water and then transferred successively into two glycerol baths in order to obtain films that lie on a glycerol substrate. Glycerol is a very poor solvent for PS, and plasticization of the films is not expected (see ref 30). If a small penetration did occur, the viscosity measurements reported in ref 18 would have shown a viscosity decrease during the experiment. The initial thickness h_0 of the PS films was then measured by ellipsometry, with an absolute uncertainty of about 1 nm.

The films were deposited inside an home made oven, onto a warm glycerol bath. The temperature was controlled to ±0.5 K (for details see ref 30). At this moment, the time was set to zero. The area $A(t)$ of the film was measured as a function of time using an analysis of the images obtained with a standard color camera. The relative error is estimated to be less than 0.5%.

We have argued that the huge temperature step from the glassy state that the polymer films undergo is, as a first approximation, equivalent to a stress step. Thus an apparent creep compliance is measured. However, it has to be kept in mind that this leads to a rather complex mixing in the very early times of the experiments between equilibrium times and times required to reach equilibrium. The time scale that is probed by this technique is, at short times, dependent on the thermal history of the material. At long times, however, this effect vanishes, and the creep compliance is properly measured. For thick films, time–temperature superposition is similar to that of the bulk at long time,[18] but the comparison is not made at short times where the material is not at equilibrium.[30]

The Hencky definition is used for the strain ϵ,

$$\epsilon(t) = \ln \frac{A_0}{A(t)} = \ln \frac{h(t)}{h_0} \quad (1)$$

where A_0 is the initial area of the film and h is the film thickness. For very thin films, the thickness increment during the dewetting cannot be neglected as compared to the initial thickness. Thus the stress $|S|/h$ slightly decreases during the experiment. Therefore, the apparent extensional creep compliance $D(t)$ is not strictly proportional to the experimental strain. It could be calculated from the strain, using the superposition principle. As detailed in the appendix, the following equation is used to compute a corrected strain $\epsilon(t)$, which is proportional to $D(t)$

$$\tilde{\epsilon}(t) = \epsilon(t) + \int_0^t \tilde{\epsilon}(t - t') \frac{\mathrm{d}\epsilon(t')}{\mathrm{d}t'} \exp[-\epsilon(t')]\, \mathrm{d}t' \quad (2)$$

$$D(t) = \frac{h_0}{|S|} \tilde{\epsilon}(t) \quad (3)$$

Since the spreading parameter is not known with a high accuracy, we report in the following $h_0\tilde{\epsilon}(t)$ curves rather than the apparent creep compliance. These curves will be referred to in the text as the normalized apparent creep compliance. Estimates of the scaled creep compliance could be achieved using a typical value of 5 mJ/m^2 for the spreading parameter.[30] This value accounts for both the rubbery plateau compliance and the viscosity and is in agreement with extrapolations of the spreading parameters deduced from contact angle measurements. Though a typical error on this parameter might be as much as 5 mJ/m^2, the exact value is not of great importance since it is a constant scaling factor and we focus on the relative changes in strain.

3. Results

The method described above was applied for the measurement on PS films of different thicknesses, down to 20 nm. The high molecular weight polymer (PS1407) is the focus of the present communication as it is for this material possible to study films of thickness smaller than the radius of gyration R_g ($R_g = 32.6$ nm). PS286 films were also studied to test the effect of the polymer chain length. The temperature was set at a few degrees above T_g, in order to measure the transition zone and the rubbery plateau of the entangled polymer within a reasonable experimental time.

Figure 1 summarizes the results. The measured apparent creep compliances exhibit two regimes. At short times, it is observed to increase. This regime corresponds to the end of the transition zone from the glassy state to the melt. Within experimental error, this regime is independent of the thickness for films thicker than 90 nm. For thinner films, this regime is faster. The corresponding characteristic times thus decrease when decreasing films thickness. If the time scale is multiplied by a factor $a_T(h)$ that depends on the initial thickness, the curves superpose, as shown in the inset of Figure 1. The second regime, where the creep compliance exhibits a very smooth increase corresponds to the rubbery plateau regime. The plateau compliance remains constant for thicknesses down to 20 nm. Moreover, with a value of $|S| = 5$ mJ/m^2, the rubbery compliance measured is about 1.6×10^{-6} Pa^{-1}, which is in numerical agreement with the bulk value.[32] For the thinnest tested film (20 nm), a third regime is observed. An inflection point at long times is clearly observed. This behavior will be discussed in the following.

4. Discussion

4.1. Entanglements. 4.1.1. Rubbery Plateau. Although the spreading parameter may vary when decreasing film thickness, major change in the surface energy is not expected for films above a few tens of nanometers.[33,34] Moreover, it is unlikely that such a change would be exactly compensated by a change in the rubbery compliance. Thus, the results presented in Figure 1 are a strong indication that the rubbery compliance remains unchanged down to 20 nm.

In the bulk, the rubbery plateau modulus (or the inverse of the compliance D_e) is, in the ideal case, of entropic nature and is proportional to the entanglement density,[14] $D_e^{-1} \sim \nu_e k_B T$, where ν_e is the entanglement density and k_B the Boltzmann constant. Assuming that this still holds in an ultrathin film, an interpretation of the results presented in Figure 1 is straightforward. The total entanglement density is roughly constant down to a fraction of R_g. In the thinnest PS1407 film studied, all the material lies at a distance shorter than 10 nm from the surface, which corresponds to about $R_g/3$.

This result brings some new experimental insights to the debate concerning the entanglement density for a confined polymer chain. It seems clear that a purely two-dimensional (2D) film cannot be entangled[35] and that the entanglement density should recover its bulk value when the chain is far away from the surface. The problem is then to know which distance is the characteristic length governing the transition from a disentangled 2D polymer film to a bulklike melt. Since we do not observe any significant deviation of the rubbery plateau compliance for films as thin as $2/3R_g$, we conclude that R_g is not the length scale governing the disentanglement of the polymer chains close to a free surface. This transition should happen at a smaller length scale, which we might guess to be the tube diameter (~3 nm).

The absence of any deviation of the rubbery plateau compliance is in contradiction with the conclusions of O'Connell and McKenna,[9,29] according to which thin polymer films are much stiffer than a bulk melt. In their experiment, the inflation of the polymer bubbles is limited by the film elasticity but also by the surface tension of the film, which has to be taken into account for very thin films. The relevance of the surface tension in this case is still under discussion,[36] but it may explain the apparent contradiction with the results presented in this article, though they have argued the contrary. It is clear from those results, however, that the surface tension accounts for a large portion of the stiffening but does not account for all of it. Hence, it is still important to further investigate the phenomenon to determine what roles other effects such as residual stresses or changing surface tension in thin films might play. Clearly, reconciliation of those results with those presented in the present work will further our understanding of the thin film behavior.

With the use of some primitive path analysis, recent simulations lead to the conclusion that the entanglement length is significantly higher than in the bulk, at a distance of about R_g

from the surface,[37] or in a film of thickness smaller than R_g.[38] At first sight, these numerical results disagree with our observations. However, the polymers used for both simulations are very small compared to the chains used experimentally. The average number of entanglements is about 2 or 3, and the radius of gyration is thus of the order of the tube diameter. It is therefore unclear in the simulations whether the disentanglement happens in chains that are confined to the tube diameter or to the radius of gyration. Considering the results reported in the present work, where the radius of gyration is more that 10 times longer that the tube diameter, we may conclude that it is the tube diameter and not the radius of gyration that controls chain disentanglement close to a free surface or in an ultrathin film. In order to experimentally prove this effect, rubbery plateau measurements need to be carried out on films with thicknesses on the order the tube diameter (3 nm). This range of thickness is unfortunately hardly accessible with suspended films.

Several authors have argued that the entanglement density should be reduced near a surface.[24] The argument comes from chain packing theories and is based on the hypothesis that the pervaded volume of a chain close to a free surface is smaller than in the bulk. If such a chain is packed in a smaller volume, then other chains are excluded from the pervaded volume, and interchain entanglements should be reduced.[25] Si et al. observed that the elongation ratio of a shear deformation zone increases for very thin films, which could be interpreted as a decrease of the interchain entanglement density when film thickness decreases below the coil size.[25] The model developed by the authors accounts well for the results and assumes a constant entanglement density correlatively with a corresponding reduction of the interchain entanglements. The nature of the entanglements (inter- or intrachain) is a minor consideration in the bulk, since interchain entanglements largely dominate. It might be an issue in ultrathin polymer films, where interchain entanglements are obviously reduced. In a first approximation, we might consider that the nature of the entanglements does not play a great role on the rubbery plateau value, since the existence of this plateau is due to a cut off of the Rouse modes of longer wavelengths than the distance between entanglements. With this in mind, we conclude that the results presented here indicate that the total entanglement density is constant in films confined at the scale of the coil size. The nature of the entanglements may, however, be affected by the proximity to the surface.

The fact that the rubbery plateau value is not affected when the thickness is of the order of R_g may be easily understood by remarking that the thickness of the films remains at least 1 order of magnitude higher than the length scale that governs the rubbery plateau value which is the entanglement length.

4.1.2. Viscosity. Since the data reported in the present article show that the rubbery plateau of the creep compliance is not affected at a length scale of R_g, we can conclude that the viscosity reduction reported in ref 18 could not be explained by a reduction of the total entanglement density. It is recalled that we observe an important reduction of the viscosity in thin films, using the same technique. The viscosity is found to decrease when $h \sim 7R_g$ and falls down to 10% of the bulk value at $h \sim R_g$. We have verified that this effect only depends on the ratio h/R_g, which strongly indicates that the coil size is the relevant length scale governing the viscosity.

The viscosity reduction phenomenon allows us to comment on the anomalous increase of the creep compliance that is observed for the smallest tested film at long times (see Figure 1). For such a thin film, the terminal relaxation time should be greatly decreased. The onset of the creep compliance at the end of the rubbery plateau should thus occur at shorter times than in the bulk. Thus, the deviation observed at long times in the compliance of a very thin film is consistent with the viscosity reduction measured at higher temperature. It is, however, not possible to quantify the viscosity of this film since the terminal flow regime is not reach during the experiment. We remark further that this deviation is still observed when the compliance curves are rescaled for superposition.

Assuming that, in the Newtonian regime, the viscosity is given by τ_d/D_e, where D_e is the rubbery plateau compliance and τ_d is the terminal relaxation time, the viscosity reduction could be directly transposed to a reduction of the terminal relaxation time of the system. In the bulk and for entangled polymers, this terminal relaxation time is the reptation time.[14] In thin films, however, pure reptation might not occur as detailed below.

In the bulk, the terminal relaxation time is linked to the reptation mechanism and is thus very sensitive to the entanglement length. However, since the mechanism involves the whole chain, the mean field hypothesis that is made when dealing with reptation is probably not valid in a film of thickness of the order of the coil size. As has been often proposed,[39−41] a liquidlike layer may exists at a free surface. Similarly, we have proposed a model that accounts for the reduction viscosity,[18] based on the simple idea that the core of the film is bulklike and that surface regions of thickness R_g are much less viscous. Under this hypothesis, the film is heterogeneous and the measured property averages some more local property. It is important to precisely answer this question of averages in order to compare the results of different experiments. We have argued that in our dewetting experiment, the effective viscosity that is measured is the simple average across the film thickness of the local viscosities. Although it is not very relevant to define a local reptation time at a smaller scale than the coil size, the use of artificial local properties may improve our understanding of the phenomenon. We have proposed[18] that the terminal relaxation time $\tau_d(z)$, at a distance z from the free surface is a unique function of h/R_g, as suggested by the experimental results. This function can be approximated by the arbitrary form

$$\tau_d(z)/\tau_d(\infty) = 1 - \exp[-(z/R_g)^{\beta}] \tag{4}$$

Such a function accounts for the experimental data with a value of 3.4 (±0.2) for the β exponent. According to this scaling, and since $R_g \sim M_w^{1/2}$, the terminal relaxation time at a distance z from the surface scales like $\tau_d(z) \sim M_w^{1.7}$ when z vanishes and recovers the bulk dependence $\tau_d \sim M_w^{3.4}$ far away from the surface. The value of 1.7 mainly means that, in a surface layer, the dependence of the terminal relaxation time on the molecular weight is weaker than in the bulk and than the prediction of the standard reptation theory. Therefore, it has to be concluded that pure reptation does not occur in a surface layer of thickness R_g.

At first sight, one may conclude that because the entanglement density is unaffected, the reduction of the terminal relaxation time is due to an acceleration of the global dynamics of the confined polymer. However, since pure reptation does not occur in such confined films, the acceleration might also be due to a progressive modification of the reptation mechanism. As already noticed, the nature of the entanglements may be affected by the proximity of the surface.[25] Consequently, the reptation mechanism may be modified and accelerated. One possible reason for the terminal relaxation time to be shortened would thus be linked to the lack of interchain entanglements in a surface layer. Indeed, interchain and intrachain entanglements may not be equivalent as far as the reptation mechanism is concerned. If an intrachain entanglement disentangles faster than does an interchain one, then the reduction of the terminal relaxation may be the result of a change of the entanglement nature upon approaching a surface.

Another interpretation of this terminal time reduction could come from the fact that a chain that lies close to the surface explores once or several times a very thin layer of low density and of very fast dynamics. The great mobility of the contact points with the surface would greatly enhance the reptation mechanism and consequently contribute to the reduction of the terminal relaxation time, in a way similar to the sliding motion mechanism proposed by a De Gennes.[13] The center of mass of such a chain is in a surface layer of thickness R_g, which is consistent with the experimental results. Such a phenomenon affects directly the reptation mechanism and may not change the other parts of the dynamics.

Other experiments that have focused on the terminal relaxation time, by the means of chain diffusion study,[15−17] have reached the conclusion that this diffusion is slower in an ultrathin film. In contrast, other mechanical results indicate similar to our experiments that the viscosity is lowered near a free surface.[19] The last interpretation given above may reconcile these apparent contradictions. Indeed, the first studies concern supported films, whereas we observe a viscosity reduction in a floating film. Considering a chain that lies in layer of thickness of the coil size near a hard surface, then the contact points that are made would be less mobile than on a free surface. Such an anchoring of parts of a chain might considerably slow down the reptation mechanism. Such an effect is likely to explain the very slow relaxation of the residual stress observed in thin films[30] or some anomalous slow modes that have been reported.[42] The terminal relaxation time is thus very sensitive to the nature of the surface or interface. A solid surface has in that respect an effect opposite to a free or a liquid surface.

Considering the two possible interpretations given above, it is possible for the terminal relaxation to be lowered by a modification of the reptation mechanism even though the global dynamics of the system remains bulklike. This point will help in the discussion concerning the evolution of the global time spectrum in ultrathin films, which will be made in the following sections.

Improvements in the theoretical approaches of the reptation mechanism in a confined and heterogeneous medium seem to be needed to better characterize the long time dynamics of ultrathin polymer films and to account for the observed reduction of the terminal relaxation time.

4.2. Dynamical Properties. 4.2.1. Short Times Dynamics in This Dewetting Experiment. The results presented in Figure 1 involve time scales which are much smaller than those involved in the viscosity measurements. The characteristic times that govern the compliance before it reaches the rubbery plateau are those of the glass transition. Figure 1 clearly shows a small reduction of this transition time scale when film thickness is below several tens of nanometers.

Before comparing the time scale reduction to the reported phenomenon of T_g reductions, some restrictions on the experimental data have to be emphasized.

The range of strain accessible by our experiment limits the measurement of the creep compliance to the end of the transition zone. Only the longest times involved in the glass transition are thus tested in the short times of the measured creep compliance.

A second restriction arises from the fact that the system is not at structural equilibrium at the beginning of the experiment. In fact, a large temperature step (from room temperature to 378 K) is applied to the polymer film. If the time required for the temperature to equilibrate is very small—typically less than 1s, thanks to the very small size of the samples—the time required to reach the equilibrium structure may be quite long, since the polymer is initially in the glassy state. As a consequence of this effect, the rate of change of the creep compliance in this short time region depends on the thermal histories of the glass as reported in a previous communication.[30] It has been experimentally shown that different thermal histories lead to variations of the creep rate that are similar to variations due to a temperature change of a few degrees in this region. For a given thermal history, variations of the creep rate with the thickness thus reflect either a change in the characteristic times of the glass transition or a change in the initial glassy state properties.

The results reported in Figure 1 show that the characteristic time of the compliance in the transition zone is lowered for very thin films. This observation may thus be the consequence of an acceleration of the glass transition dynamics or of a change of the initial glassy state. In order to dissociate the roles of physical aging properties and of the equilibrium ones, we refer to the experimental results obtained by Priestley et al.,[43] who show that, near a free surface, the physical aging rate is a little lower than in the bulk. It is, however, difficult to extrapolate this result in order to predict the time required to reach equilibrium. In fact, a lower aging rate may be due to a reduction of the characteristic time or to a reduction of the departure from equilibrium. One thus needs more experimental results on physical aging in confined states in order to comment further on the effects of confinement on the time required to reach equilibrium. However, since the factor of 2 reported by Priestley et al. is rather small compared to the variations of the characteristic time, variations of the nonequilibrium properties only partially account for the our results.

4.2.2. T_g Shifts? It is important to realize that the observed reduction of the time scale is rather small. Only a factor of 4 to 5 in the time scale is observed for a 20 nm film. Since most experiments performed on thin polymer films follow the variations of a property with the temperature, the deviations from bulklike behavior have usually been reported in terms of T_g reduction. In order to compare the time scale reduction with the T_g reductions reported by several different groups, a time−temperature correspondence has to be used. Whether or not this procedure applies and what are the corresponding parameters is still an open question in ultrathin films. However, we use it below as a hypothesis. We assume that the mean characteristic time τ of the system follows a temperature variation given by the Volger−Tamman−Fuchs law, modified with a shift in the T_g value of $\Delta T(h, T)$

$$\tau(T, h) \sim \exp \frac{B}{T + \Delta T(h, T) - T_0} \tag{5}$$

where B and T_0 are parameters that are, respectively, 1456 and 323.4 K for bulk PS.[32] By inverting this expression, the temperature shift ΔT can be computed as a function of film thickness, knowing the shift factor $a_T(h)$ coming from the short time creep compliance superposition (see Figure 1). ΔT is thus given by

$$\Delta T(h, T) = \frac{(T - T_0)^2}{T - T_0 + B/\ln a_T(h)} \tag{6}$$

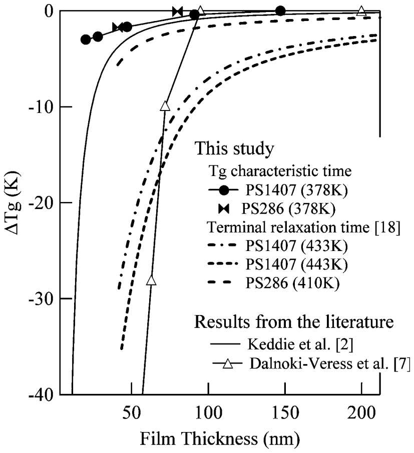

Figure 2. Temperature shifts $\Delta T(T, h)$ as a function of film thickness that accounts from the time reduction. Temperature shifts corresponding to the glass transition zone (circles) are calculated using eq 6 and from the shift factors $a_T(h)$ determined from the superposition procedure of the apparent creep compliance at short times (see Figure 1). Those corresponding to the terminal relaxation time (dashed lines) are also calculated using eq 6 where $a_T(h) = \eta(T, h)/\eta(T, \infty)$ reported in ref 18. In order to compare these apparent T_g reductions to direct measurements, data from the literature have been plotted. For supported PS films, the experimental result from Keddie et al. (ref 2) is plotted (solid line), and for PS free-standing films, results from the work of Dalnoki-Veress et al. (ref 7) are reported (triangles). Only the results obtained with a sample of molecular weight that is the closest to our PS1407 samples, 1250 kg/mol, are reported.

The results of the calculations of the apparent temperature shifts are presented in Figure 2. For the thinnest film (20 nm), the time scale reduction corresponds to an apparent temperature shift of the order of 3 K. This is less than the data reported on supported films[2,4] and much less than studies on free-standing films.[7,9] Since the variations of the aging properties may partially account for the reduction, the discrepancy between the data of Keddie et al.[2] and the present ones may be explained by a thermal history effect on our measurements. However, the huge difference with the data reported on PS free-standing films is not likely to be attributed to thermal history effects. According to the results from Dalnoki-Veress et al.,[7] a 20 nm film would be above T_g at room temperature. If this was the case, then the films would not be easily transferred onto a liquid substrate, and the creep observed in our experiment should have been orders of magnitude faster than what was observed. Finally, we recall that hole growth in ultrathin films has not been observed below the bulk T_g,[44] which is rather consistent with the very small T_g reduction that we observe.

Another qualitative discrepancy remains between the result reported by Dalnoki-Veress et al. and ours. These authors reported that the T_g reductions are molecular weight dependent,[7] which has been also confirmed on poly(methyl methacrylate) (PMMA).[10] On the other hand, our time-dependent dewetting results exhibit no differences between two rather different molecular weights. In the bulk, when the polymer chains are well entangled, chain end effects can be neglected and the glass transition is independent of the molecular weight. Our results are thus consistent with a picture of the glass transition in thin films that is slightly shifted relative to the bulk. The above-cited results ask for a more complex interpretation that remains unclear. The major difference between our samples and those used in refs 7 and 9 seems to be the fact that, in our experiment, the films are not suspended, but lie on a liquid substrate. As a consequence, the film is free mechanically, whereas some tensions might appear in suspended films due to the anchor points at the edge of the hole of the sample holder. The annealing procedure is also of great importance since residual stress is only removed after very long annealing times for very long chains.[30] Finally, it has to be noted that the change from a free surface to a PS/glycerol interface is not expected to influence that much the results, since the glycerol interface is very repulsive, similar to the “hard-wall” of the air−film surface in the free-standing films. As a conclusion, none of these differences are likely to explain the contradictory results in T_g dynamics of free-standing thin films.

Other considerations may, however, help to understand the discrepancies. As discussed in the beginning of this section, only the long time part of the time spectrum of the transition is measured in our experiment. These times might be less affected by confinement than shorter times. Since most of the previous studies on this subject report temperature measurement and not time-resolved experiments, it is not clear which part of the dynamics is tested. Such an explanation is thus difficult to support at present. However, some broadening of the glass transition has been reported,[45,46] which may be an indication of the fact that the transition dynamics is not simply globally shifted. Another interpretation may arise from the temperature dependence of the characteristic times with temperature. Our experiments take place a few degrees above the bulk T_g and reveal the dynamics at this temperature. The extrapolation of the thin film dynamics at the transition might be very different than in the bulk. If the time variation with temperature is much weaker than in the bulk, then it would be possible to observe a small time scale reduction together with a great T_g decrease. These two considerations call for more time-resolved experiments. In particular, the determination of the evolution of the global time spectrum with temperature may be a clue to understand the complex dynamics of ultrathin polymer films in the glass transition region.

As a conclusion on T_g dynamics, one may sum up our observation by saying that our floating films exhibit a reduction of the time scale involved in the glass transition that is rather consistent with the T_g variations reported on supported films but not in agreement with previous experiments on free-standing films of high molecular weight.

4.2.3. Global Time Spectrum. In this last part, we come back to the terminal relaxation time reduction that has been discussed above. As noted, the reduction of this terminal relaxation time is probably due to a modification in the reptation mechanism and is not directly linked to the time scale reduction observed in the vicinity of T_g. In order to verify this interpretation, we calculated the apparent temperature shift that would account for the viscosity reduction using eq 6, where the coefficient $a_T(h)$ is now given by the viscosity ratio $\eta(T, h)/\eta(T, \infty)$. The results are plotted in Figure 2. The temperature shift that is needed at these high temperatures to account for the terminal relaxation time reduction is much higher than the temperature shift in the transition zone. This means that, at a given thickness and a given temperature, the terminal relaxation time is much more reduced than the times involved in the transition zone. Since the viscosity reduction scales like the coil size, the difference between these two reductions of the time scales is higher for high molecular weight polymers.

The apparent creep compliance of the 20 nm film shown in Figure 1 gives an illustration of this observation. When superposing the short times, the long times do not superpose and the terminal relaxation time is more reduced than the transition times.

It thus becomes clear that viscosity reduction and T_g reduction are two distinct phenomena. The former is governed by the coil size and is thus a purely polymer effect. The latter, independent of the coil size, involves shorter length scales, since no significant deviations occurs for films thicker than 50 nm. The discrepancies that are found in the literature on T_g shifts, especially concerning the free-standing films, should, however, be resolved before stating on this particular length scale.

This issue underlines the necessity to clearly identify in each experiment which relaxation modes are probed or, equivalently, which part of the time spectrum is tested.

5. Conclusion

The apparent creep compliance in the vicinity of T_g of ultrathin polymer films brings some insights to both debates on entanglement structure close to a surface and on the acceleration of the dynamics in a confined medium.

The fact that the rubbery plateau value remains unchanged even for thicknesses slightly smaller than the radius of gyration has been interpreted as the consequence of an entanglement density that is not affected at these length scales. With the help of simulation results reported in the literature, we propose that the entanglement density is affected by confinement only at a characteristic distance of a few nanometers from the surface, which might correspond to the tube diameter.

The creep compliance in the transition region also provides some information about the transition dynamics. Even though our results could not be directly interpreted in terms of equilibrium relaxation times, they are in disagreement with the few experiments that have been conducted until now on ultrathin free-standing polymer films of high molecular weight. In contrast, they support the order of magnitude of the T_g reductions reported many times for supported films.

When comparing the reduction of the time scales involved in the glass transition zone with the terminal relaxation of the system, evidence has been presented and discussed that the global time spectrum is not simply shifted. Indeed, the reduction of the terminal relaxation time is much more important for very long polymers.

Appendix A

For thin films, the stress S/h that is applied by the surface and interfacial energy is on the order of the rubbery modulus and leads to strains that are on the order of unity. For these films the thickness variation during the experiment has to be taken into account, because the stress depends directly on the thickness. Since it decreases during the experiment, the strain is not proportional to the creep compliance $D(t)$. However, the creep compliance could be derived thanks to the Boltzmann superposition principle, knowing time variation of the stress. The strain response for an arbitrary stress $\sigma(t)$ is, in the linear regime, given by[11]

$$\epsilon(t) = \int_{-\infty}^{t} D(t-t')\,\frac{\mathrm{d}\sigma(t')}{\mathrm{d}t'}\,\mathrm{d}t' \qquad (7)$$

where (for a Hencky strain):

$$\sigma(t) = H(t)\,\frac{S}{h(t)} = H(t)\sigma_0 \exp[-\epsilon(t)] \qquad (8)$$

Here, $H(t)$ is the Heavyside function and σ_0 is the initial stress ($\sigma_0 = |S|/h_0$). Since σ_0 is not known with a great precision, it is convenient to define a corrected strain $\tilde{\epsilon} = \sigma_0 D(t)$ that is proportional to the creep compliance. Then eqs 7 and 8 lead to the following implicit expression for $\tilde{\epsilon}$,

$$\tilde{\epsilon}(t) = \epsilon(t) + \int_0^t \tilde{\epsilon}(t-t')\,\frac{\mathrm{d}\epsilon(t')}{\mathrm{d}t'}\,\exp[-\epsilon(t')]\,\mathrm{d}t' \qquad (9)$$

This equation is numerically inverted, using the discrete set of experimental points $\epsilon[i]$ and its derivative $\Delta\epsilon[i]$. The calculation is computed according to the following:

$$\tilde{\epsilon}[i] = \epsilon[i] + \sum_{0<j<i} \tilde{\epsilon}[i-j]\Delta\epsilon[j]\exp(-\epsilon[j]) \qquad (10)$$

This procedure is used on the data presented in Figure 1. In practice, the correction is very small for films thicker than 100 nm.

Acknowledgment. We thank K. Danolki-Veress and G. B. McKenna for interesting discussions. G. B. McKenna is also thanked for having carefully read the manuscript.

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MA070460D