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Glass Transition Relaxations in Thin Suspended Polymer Films

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ABSTRACT: Using dielectric spectroscopy, we probe the structural relaxation processes in thin freely suspended polystyrene films. For thin films we observe a relaxation scenario distinctly different from that of bulk polystyrene. The main glass transition relaxation becomes faster with decreasing film thickness, indicating a reduction in the glass transition temperature. For thin films we observe an additional process with an Arrhenius temperature dependence. This process is unique for thin freely suspended films and is not present in bulk polystyrene.

Introduction

Recently, ultrathin polymer films have received ample scientific attention as a route to explore the effects of surfaces and interfaces on the glass transition. Numerous experiments[1−7] and simulations[8−10] report that the glass transition temperature T_g is substantially altered compared to the bulk system and that surface effects extend several tens of nanometers into the film. However, recent experiments challenge these findings by concluding that no change in T_g can be observed even for very thin polymer films.[11,12] Therefore, the reduction of T_g in thin polymer films is presently a controversial issue. The scientific debate is mainly focused on supported films, where the interaction with the substrate is an essential parameter. Using free-standing films, this issue can be circumvented and the inherent properties of the polymer emphasized, resulting in a dramatic reduction in T_g.[4,13−15] Moreover, for high molecular weights, $M_w \geq 575 \times 10^3$, the thickness dependence is quantitatively different compared to supported films, but the physical origin of the phenomena remains elusive.[16] Thus, to scrutinize the existing theoretical models,[16−22] direct observations of the relaxation processes in freely suspended films are required.

Here we report dielectric experiments on thin suspended polystyrene films submerged into a hydrophilic liquid using a specially designed sample holder. We show that the relaxation processes of such thin polymer films indeed are different compared to bulk and supported films. At temperatures below T_g we observe a relaxation process with an Arrhenius temperature dependence. This process might be the missing link to the understanding of the reduced T_g in thin suspended films.

Experimental Section

The films were prepared by spin-coating solutions of polystyrene (PS) ($M_w = 767 \times 10^3$, $M_w/M_n = 1.11$) in toluene onto glass slides and annealed in vacuum at 385 K for 10 h. Thereafter, the film was transferred to a sample holder via floating of a water surface.[4] The thickness of the film was determined using ellipsometry (Optrel Multiskop) at room temperature. The film was then inserted into a sample cell specially designed for thin film dielectric experiments (see Figure 1) and was sealed with grease to prevent leakage. The dielectric experiments were performed over the frequency range from 1 Hz to 1 MHz using a high-resolution spectrometer (Novocontrol, Alpha). In the dielectric experiments the sample was first heated to 353 K and cooled down to 293 K with a heating rate of 2 K/min. This equilibration scan effectively removes wrinkles in the film and improves the reproducibility of the experiments as discussed below. Data were then collected under isothermal conditions from 293 to 383 K in steps of 2 K, yielding a total experimental time of ~5 h.

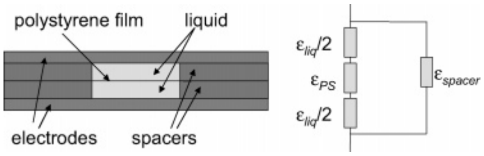

Figure 1. Schematic picture of the sample configuration and its equivalent circuit representation. Note that the drawing is not to scale. The diameter of the suspended part of the film is 4 mm and the total thickness 2 mm.

The dielectric response of the whole sample cell can be represented by the equivalent circuit representation shown in Figure 1 and by the formula

$$\epsilon_{\mathrm{tot}}(\omega) = \frac{\epsilon_{\mathrm{liq}}(\omega)\,\epsilon_{\mathrm{PS}}(\omega)}{\dfrac{h_{\mathrm{tot}}}{h_{\mathrm{PS}}}\epsilon_{\mathrm{liq}}(\omega) + \epsilon_{\mathrm{PS}}(\omega)} + \epsilon_{\mathrm{spacer}}(\omega) \qquad (1)$$

Here h and ϵ are the thickness and the complex permittivity of the different layers. The signal from the spacers, including the supported part of a polymer film, was measured separately and subtracted from the experimental data before the data analysis, $\tilde{\epsilon}_{\mathrm{tot}}(\omega) = \epsilon_{\mathrm{tot}}(\omega) - \epsilon_{\mathrm{spacer}}(\omega)$. At the lowest frequencies, typically 5 Hz or less, the response of the spacer is not negligible, and those data points were excluded from the analysis. As the surrounding liquid, we primarily used ethylene glycol (EG). EG is a suitable choice since it is hydrophilic and has no observable dielectric processes in the temperature and frequency range of interest here. Moreover, both the real and imaginary parts of the permittivity are much larger for EG than polystyrene. By separating the static and the dynamic part of the permittivity for the film, $\epsilon_{\mathrm{PS}}(\omega) = \epsilon_{\mathrm{PS}}^{\infty} + \epsilon_{\mathrm{PS}}^{\mathrm{D}}(\omega)$, eq 1 can be approximated with two terms

$$\tilde{\epsilon}_{\mathrm{tot}}(\omega) \approx \frac{\epsilon_{\mathrm{liq}}(\omega)\epsilon_{\mathrm{PS}}^{\infty}}{\dfrac{h_{\mathrm{tot}}}{h_{\mathrm{PS}}}\epsilon_{\mathrm{liq}}(\omega) + \epsilon_{\mathrm{PS}}^{\infty}} + \frac{h_{\mathrm{PS}}}{h_{\mathrm{T}}}\,\epsilon_{\mathrm{PS}}^{\mathrm{D}}(\omega) \qquad (2)$$

The first term is the so-called Maxwell−Wagner (MW) peak, which is a direct consequence of the layered configuration of the sample cell.[23] It is important to note that the MW peak is of purely static origin, i.e., not related to any re-orientation of dipoles neither in the liquid nor in the film. The second term in eq 2, on the other hand, is the frequency-dependent dielectric response of the polystyrene film. Thus, the dielectric signal of the whole sample cell is approximately a superposition of a MW peak and the dynamical response of the polymer film.

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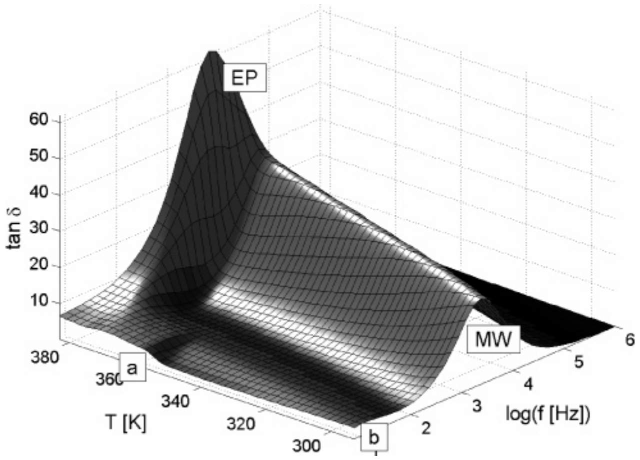

Figure 2. tan δ of a 450 Å polystyrene film after subtraction of the spacer response as a function of temperature and frequency. The peaks denoted *a*, *b*, MW, and EP are discussed in the text.

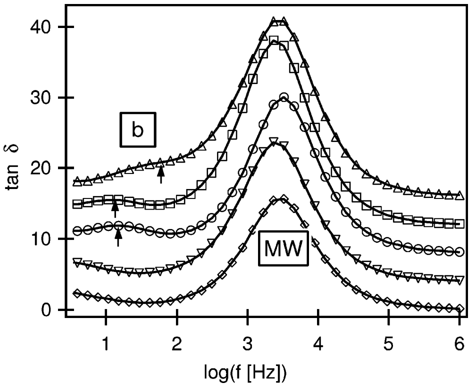

Figure 3. tan δ at 293 K for films with thicknesses 360 (△), 450 (□), 590 (○), 700 (▽), and 980 Å (◇). The data are shifted vertically for clarity. The arrows indicate the peak position of tan δ for the *b*-process.

Results

In Figure 2, the dielectric response of a 450 Å film is shown using the tan $\delta = \epsilon''(\omega)/\epsilon'(\omega)$ representation. The data reveal a complex pattern with several processes. Using bulk values for PS and EG, the peak position of the first term in eq 2 can be estimated to $\sim 10^3$ Hz for a 500 Å thick film at room temperature. We therefore attribute the high-frequency loss peak (marked MW in Figure 2) to a Maxwell−Wagner process. The shift of the peak to higher frequencies with increasing temperature is primarily an effect of higher ionic conductivity of EG at elevated temperatures.

For thin films a broad peak, which is denoted *b*, is observed at frequencies below the MW peak. In Figure 3, the response at room temperature for different thicknesses is shown. The graph shows that the trend is that the *b*-process becomes faster for thinner films, although the scattering in position and amplitude is significant. Moreover, for film thicker than roughly 700 Å the *b*-process is either too slow or too weak to be observable. This coincides with the critical thickness of 710 Å where T_g starts to deviate from the bulk value for free-standing films.[16] This indicates that PS films submerged in a hydrophilic liquid resemble free-standing films. This is expected since the dynamics of the surrounding liquid is many orders of magnitude faster than the segmental motion of the polymer as for example discussed in ref 24. Since bulk polystyrene does not have any detectable dielectric process in this range,[25,26] this prevents an attribution of the *b*-process to a classical Johari−Goldstein β-process. Thus, the *b*-process appears to be a dynamical process characteristic for very thin polymer films.

At temperatures around bulk T_g another process, which is denoted *a*, enters at low frequencies. For thick films this can be attributed to the α-relaxation of bulk polystyrene. However, major structural rearrangement inevitably leads to holes through the film. With such holes the sample geometry is fundamentally different, resulting in electrode polarization effects (EP) of the surrounding liquid. Such EP effects can be observed directly for the pure liquid. Subsequent lowering of the temperature also shows that the hole formation process is irreversible. Thus, the *a*- and EP-processes are closely coupled, but for thin films they are separated by more than 10 K (see Figure 2), which justifies the distinction between the *a*- and EP-processes. Also note that the EP-peak does not start to dominate the spectra until the temperature has reached bulk T_g. This implies that thin suspended polystyrene films are stable up to bulk T_g, in accordance with previous suggestions[17] and findings.[16]

The standard thermal treatment in this study is to cycle the temperature up to 353 K, i.e., somewhat below bulk T_g, before the data are collected. During this equilibration scan the *b*-process remains practically unaffected. However, at intermediate temperatures a quite sharp, irreversible step can often be observed at low frequencies. This typically occurs at or above the T_g reported for thin free-standing films.[16] Tentatively, this irreversible step can be attributed to the removal of wrinkles.[14] This equilibration scan also results in that the MW peak becomes narrower and shift to higher frequencies. The amplitude of the *b*-peak is large compared to the low dielectric response of bulk polystyrene. This can partly be explained by that under the present experimental conditions the *b*-process is a perturbation of the low-frequency slope of the pronounced MW peak; i.e., the values of tan δ measured here are not directly comparable to those of bulk PS. Another very plausible explanation is that a thin surface layer of the solvent tracks the dynamics of the PS film; i.e., the polar solvent molecules act as probe molecules for the film dynamics. To investigate the influence of the liquid, we therefore performed complementary measurements using water and glycerol as the surrounding liquids. Because of different ionic conductivity and dielectric constant, the MW peak shifts in frequency and amplitude for different surrounding liquids. However, the *b*-peak remains at roughly the same frequency for the different surrounding liquids although the experimental uncertainty is considerable, especially for glycerol where the overlap with the MW peak is substantial. This is a strong indication in favor of that the *b*-process indeed is originating from the polystyrene film, even if it is indirectly probed via the surrounding liquid. We have also repeated the experiments for a film that was submerged in water for more than 6 days before the experiment and a film that was placed under vacuum for more than 1 day. The response from neither of these films deviates from films with standard treatment more than expected from the typical reproducibility. This shows that observed relaxation scenario is not caused by residual water from the floating procedures. In total, more than 50 thin polystyrene films, of which more than 20 is included here, have been investigated under varying experimental conditions, giving results that are consistent with the observations described here.

To quantify the findings, we used a sum of three Havriliak−Negami expressions

$$\epsilon(\omega) = \epsilon_0 + \frac{\Delta\epsilon}{[1 + (j\omega\tau)^{\alpha}]^{\beta}} \tag{3}$$

and curve-fitted it to the experimental data using the serial admittance representation. The temperature dependence of the *a*-relaxation time for a thick film is shown in Figure 4. The

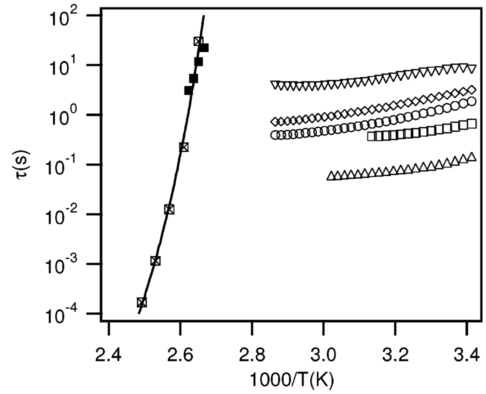

Figure 4. Arrhenius plot of the peak relaxation times. The crossed squares are the relaxation times for the α-process in bulk PS ($M_w = 1387 \times 10^3$), which is well described by the VFT equation (full line), $\tau = \tau_0 \exp[DT_0/(T - T_0)]$, with $\tau_0 = 10^{-13}$ s, $D = 4.2$, and $T_0 = 334$ K. The filled squares are for the *a*-process of a 975 Å thick film. The *b*-process are shown for 700 (▽), 500 (◇), 450 (○), 540 (□), and 350 Å (△) thick films.

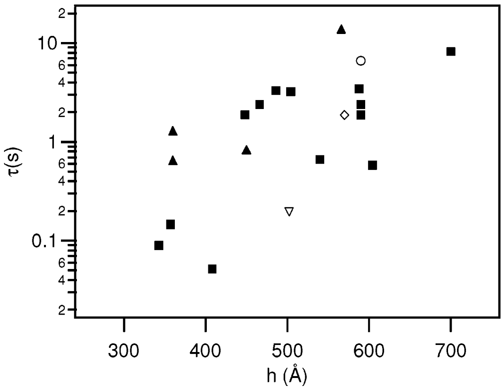

Figure 5. Relaxation time of the *b*-process at 293 K as a function of films thickness. The filled symbols are for EG (squares) and water (triangles) as surrounding liquid. The open symbols correspond to films that were submerged in water for 6 days (circle), floating 1 day (triangle), and exposed to vacuum for 2 days (diamond).

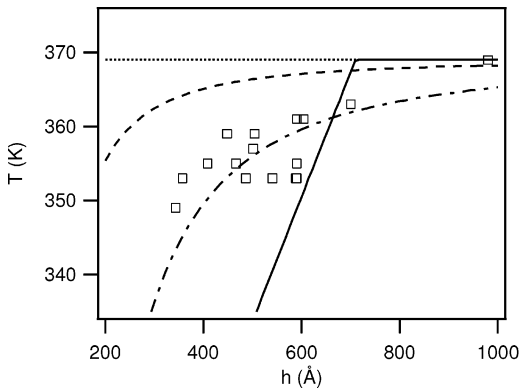

Figure 6. $T_g^{(a)} = T(\tau_a = 100\ \text{s})$ as a function of film thickness. The solid line is the literature value for T_g for free-standing films with $M_w = 767 \times 10^3$ and the dashed-dotted line T_g for low molecular weight free-standing films.[16] The dashed line is T_g reported for supported films and the dotted line the bulk value for polystyrene.[16]

similarities to the α-relaxation times for bulk polystyrene show that *a*-process can be identified as the α-relaxation, at least for thick films. For thinner films the presence of the broad *b*-process prevents extraction of the temperature dependence of the *a*-relaxation, but generally the *a*-process appears at lower temperatures for thinner films as further discussed below. The *b*-relaxation time is included in Figure 4, revealing an Arrhenius-like temperature dependence. Curve-fitting the data to

$$\tau = \tau_0 \exp\left[\frac{E_a}{RT}\right] \tag{4}$$

yields a low activation energy, typically 15−25 kJ/mol, and a thickness-dependent τ_0. Figure 5 shows the *b*-relaxation time at room temperature as a function of film thickness. The graph indicates the tendency of faster dynamics for thinner film for the *b*-relaxation time but also shows that the spread of the extracted relaxation times is considerable. Note that the uncertainty from the curve fit of each film is small, and thus the spread arises from the difficulties to exactly reproduce the properties of the films and the experimental conditions. Concerning the shape of the peaks, the data analysis shows that the MW process is well described by the Debye expression, $\alpha = \beta = 1$. The *b*-relaxation is significantly broader, $\alpha\beta = 1$ and $\alpha \simeq 0.3-0.5$; i.e., the high-frequency slope exponent is equal to unity while the broadening occurs at the low-frequency slope. In terms of distribution of relaxation times this corresponds to an asymmetric broadening toward long relaxation times.

Discussion

The generic idea to explain shifts in T_g in thin film is that free surfaces enhance the dynamics. However, if the *b*-process would be a simple surface process, it should also be observable for in our experiment on a 1000 Å thick film. Thus, in agreement with recent findings,[5,6] it appears that the generic model with mobile surface layers is an oversimplification. Instead, we need models that address the dynamics of the complete film. Two such models are the "sliding motion" by de Gennes[17,18] and the coupling model (CM) approach by Ngai.[19−21] The CM is based on the idea that the α-relaxation originates from dynamical coupling of entities performing a primitive process. It is argued that the coupling is reduced in a free-standing film, which results in a lower T_g.[19−21] The proposed sliding motion, on the other hand, is a completely different relaxation process originating from a polymer sliding along its own contour. Such a process is very inefficient in bulk but would reduce T_g of free-standing films.[17,18] Since both the CM and the sliding motion are based on the idea that a simple or primitive dynamical process acts as a precursor to the glass transition, this provides a possible explanation of the *b*-relaxation. Such an attribution implies that the *b*-relaxation is a secondary relaxation process consistent with the observed Arrhenius temperature dependence. There is also a remarkable resemblance of the *b*-relaxation and ordinary secondary relaxations in bulk glass-formers (see Figure 4), despite that the physical origin of the dynamical processes apparently is different. Moreover, a secondary relaxation was recently reported for a very thin PS-film capped between Al layers,[27] which was discussed as a surface process although there are no free surfaces. The reported activation energy ($E_a \sim 72$ kJ/mol) and the film thickness ($h = 87$ Å) are, however, distinctly different from the present observation for the *b*-relaxation.

To estimate the glass transition temperature corresponding to the *a*-relaxation, $T_g^{(a)} = T(\tau_a = 100\ \text{s})$, we determined the temperature where $\tau_a \simeq 1$ s and extrapolated using bulk VFT parameters. Figure 6 shows that $T_g^{(a)}$ is decreasing with decreasing film thickness, but much less than the T_g reported for free-standing films of the molecular weight investigated here.[16] This discrepancy cannot be attributed to the heating rate dependence of T_g demonstrated for supported films,[29] since our data were collected under isothermal conditions, i.e., lower heating rate than in previous ellipsometric experiments on free-standing films.[14,16] Note also that at $T_g^{(a)}$ the *a*-relaxation time is, by definition, very slow and thus consistent with the observation that reduced T_g can only be observed with low probe frequencies.[29] Therefore, an intriguing observation is that $T_g^{(a)}$ is well described by the expression proposed for low-M_w free-standing PS films. This remarkable result implies that the enhanced dynamics resulting in the reduction of T_g for low-M_w films is present also in high-M_w films, as previously suggested by Long et al.[30] In the model by Long and co-workers the glass transition is described as a percolating skeleton of slow domains.[22,30,31] For thin free-standing films the percolation threshold is larger than in bulk, and the model predicts a reduced T_g in quantitative agreement with the observations for low molecular weight free-standing films and consequently with $T_g^{(a)}$.[16,22] An attractive feature of the model is that it addresses potential differences and similarities between different confinement geometries, such as nanocomposites, spheres, and supported and free-standing films.[6,16,24] The model cannot, however, explain the much more pronounced reduction in T_g observed for high-M_w free-standing films (see Figure 6). Long et al. therefore suggested that their modified α-relaxation can coexist with for example the sliding motion.[30] Note that in the sliding motion model the kink in the thermal expansion occurs when the mobile layers penetrate the entire film. Thus, the sliding motion description does not require any dramatic change of the local dynamics at T_g of free-standing films, in agreement with our observations. This is in distinct contrast to the traditional glass transition dynamics where the α-relaxation appears at experimental time scales, typically 100 s, at T_g. A tentative attribution of the relaxation processes observed here is therefore that the *a*-relaxation is a modified α-relaxation and the *b*-process is the primitive precursor, subsequently leading to the sliding motion of larger polymer segments. This interpretation infers that the reduced T_g reported for free-standing films is indeed due to a relaxation process not present in bulk PS or in supported films. The present observations could therefore provide new insights into the present controversy of the glass transition in thin polymer films.

Conclusions

In summary, we have shown that suspended polystyrene films with a thickness less than 700 Å exhibit a dynamical process not observed in bulk. The typical relaxation time of this novel process is of the order of seconds at room temperature with a slight decrease with decreasing film thickness. Our findings also indicate that the main structural relaxation process becomes faster for thinner films, but less than expected from previous observation of T_g for free-standing films.

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