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Confinement Effects on the Relaxation Time Distribution of the Dynamic Glass Transition in Ultrathin Polymer Films

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ABSTRACT: The dynamic glass transition in ultrathin films of poly(vinyl acetate) (PVAc) is investigated by broadband dielectric spectroscopy. With decreasing film thickness changes in the relaxation time distribution are detected, leading, for thicknesses below ∼20 nm, to an increase in the average relaxation rate. This is caused by an asymmetric suppression of the relaxation modes—predominantly on the low-frequency side.

One obstacle in understanding the molecular mechanisms of confinement effects on the glassy dynamics of thin polymer films[1−14] is related to the fact that, in most of the studies, the glass transition is characterized by using mean values of physical parameters (i.e., the average relaxation time, the glass transition temperature), while no information about the underlying distributions is available. For instance, an increase in the average relaxation rate, corresponding to a faster dynamics in thin films, can either arise from (i) groups of polymer segments fluctuating faster in confinement than in the bulk or (ii) freezing-out of the slower relaxation modes. In the present study we show that a clear distinction between these two alternatives is only possible when the relaxation time distribution is quantitatively analyzed in dependence on the external confinement. By that, we give evidence that the faster dynamic glass transition detected in ultrathin PVAc films can be traced back to a change in the relaxation time distribution caused by a gradual asymmetric suppression of the slower relaxation modes.

Poly(vinyl acetate) (PVAc) having a molecular weight of M_w = 157 000 g/mol and a polydispersity index of 2.73 was purchased from Scientific Polymer Products. Thin PVAc films were prepared between two aluminum electrodes using the preparation procedure shortly described in the following. Glass plates of 1 cm × 1 cm × 1 mm, cleaned in an ultrasound alkaline bath, rinsed in pure acetone, and dried under nitrogen flow, were used as support substrates. Aluminum electrodes (width of 0.5 mm, height of 60 nm, root-mean-square roughness of 1 nm) were deposited on the glass substrate by thermal evaporation in high vacuum (10^{-7} mbar). Subsequently, thin polymer films were spin-coated from a chloroform solution at 3000 rpm. The film thickness was adjusted by changing the concentration of the polymer in solution. After spin-coating, the samples were annealed at temperatures well above the bulk glass transition (i.e., 86 °C) in an oil-free high vacuum (10^{-7} mbar) for at least 12 h. The final step of the sample preparation was the evaporation of a second aluminum counter electrode on top of the polymer films. This procedure, described in detail in ref 15, ensures an excellent reproducibility and stability of thin polymer films. Prior to the dielectric measurements, the samples were annealed once again several hours above T_g (at 86 °C) in a pure nitrogen atmosphere (in the cryostat of the dielectric spectrometer). After this, the experiments were started, without exposing the samples to ambient air again. The dielectric measurements[16] were performed using a high-resolution Alpha Analyzer (Novocontrol GmbH) in a broad frequency domain (0.1 Hz−10 MHz) and at temperatures between 300 and 360 K. The thermal stability, controlled by heating the samples with a jet of pure nitrogen, was set to be better than 0.1 K. The film thickness was determined by measuring the real part of the sample capacitance in a spectral region not affected by dielectric dispersions (at 300 K and 100 kHz). The value of ϵ' at this frequency ($\epsilon' = 3.06$, in good agreement with other reports[17,18]) was determined by measuring independently the thickness of one sample by means of mechanical nanoprofilometry and was assumed not to depend on the film thickness.

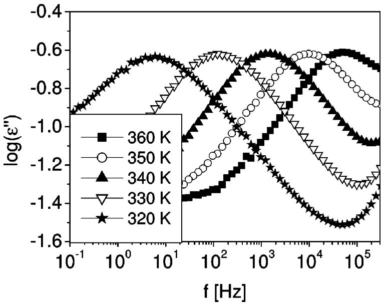

Figure 1. Dielectric loss vs frequency at different temperatures, as indicated, showing the dynamic glass transition for a thin PVAc film of 5.8 nm. The errors are comparable to the size of the symbols is not indicated otherwise.

Poly(vinyl acetate) exhibits one relaxation process in the frequency and temperature window of our experiment, i.e., the α relaxation process representing the dynamic glass transition. This is exemplified in Figure 1, showing, in spectra of dielectric loss ϵ'' vs frequency, the α relaxation process for a thin PVAc film of 5.8 nm. The influence of geometrical confinement on the dynamic glass transition of PVAc is illustrated in Figure 2. With decreasing film thickness a pronounced decrease in the dielectric strength and—for thicknesses below ∼20 nm—a shift of the α peak to lower temperatures are observed The latter corresponds to an increase in the average relaxation rate. The mechanism of this effect is unravelled by quantitatively analyzing the changes of the relaxation time distribution (determined using the Tickonov regularization procedure[19]) in dependence on the confinement size (Figure 3). The relaxation modes of the dynamic glass transition are gradually suppressed in confinement, leading to a pronounced decrease in the dielectric strength and—for thicknesses below 20 nm—to a shift in the average relaxation time. All distributions of relaxation times measured in confinement are “included” in the bulk distribution.

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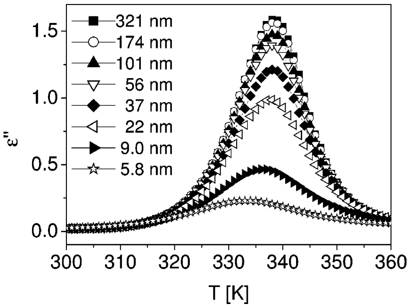

Figure 2. Dielectric loss vs temperature at 300 Hz, showing the dynamic glass transition for thin PVAc films having different thicknesses, as indicated.

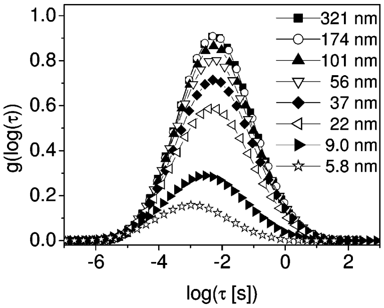

Figure 3. Relaxation time distribution of the dynamic glass transition at 330 K in dependence on the film thickness.

In addition, a monotonic dependence on the film thickness exists; i.e., the relaxation time distribution corresponding to a larger film thickness includes the distribution corresponding to a smaller one. This shows that the origin of the confinement effects in ultrathin PVAc films is related to an asymmetric “freezing-out” of the α relaxation modes—predominantly on the low frequency side. This “immobilization” effect takes presumably place in the vicinity of the confining interfaces, where the slower relaxation modes of the dynamic glass transition are supposed to be suppressed due to the interfacial interactions.

The changes in the relaxation time distribution detected in confinement lead accordingly to shifts in the mean values of parameters like relaxation time, temperature position of the α relaxation peak, etc. This is exemplified in Figure 4, showing the maximum temperature position of the α relaxation peak T_α, the average relaxation time, and the dielectric strength as a function of film thickness. With decreasing film thickness down to 5.8 nm, T_α exhibits a reduction by ~6 K (Figure 4a). Correspondingly, the average relaxation time of the dynamic glass transition decreases by about 1 order of magnitude (Figure 4b). The dielectric strength shows a pronounced decrease as well (Figure 4c). Similar shifts in the mean values of parameters like the glass transition temperature T_g or the relaxation time τ were also reported in refs 1−14. Nevertheless, experimental techniques measuring average values (T_g, T_α, τ) cannot provide a complete picture of the mechanisms underlying the confinement effects since they do not have access to the distributions giving rise to these mean values.

The impact of geometrical confinement on the molecular dynamics of PVAc is summarized in Figure 5, by plotting the average relaxation rate, extracted using the usual fitting procedure,[16] as a function of inverse temperature. Significant shifts in the molecular dynamics are detected starting with film thicknesses of ~20 nm, indicating an increase in the average relaxation rate.

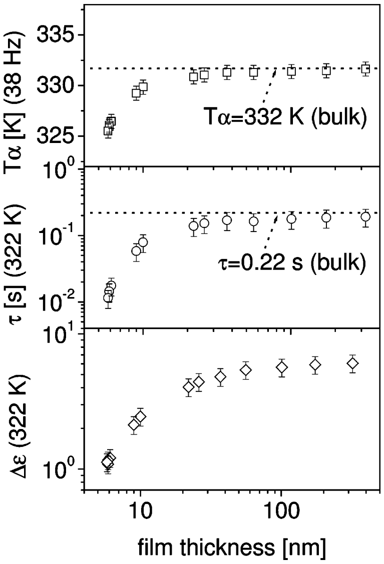

Figure 4. Maximum temperature position of the α relaxation peak T_α at 38 Hz, relaxation time at 322 K, and dielectric strength at 322 K as a function of film thickness.

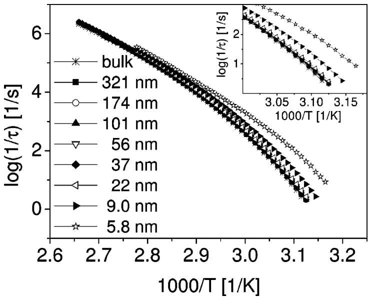

Figure 5. Mean relaxation rate vs inverse temperature for thin PVAc films having different thicknesses, as indicated. In the inset the activation curves are presented enlarged for clarity.

Studies on the glass transition of confined PVAc have been also reported previously. Freely standing films of PVAc were investigated,[20] and in good agreement with our results, no significant T_g shifts down to a film thickness of 27 nm have been detected. Thin PVAc films confined in a sandwich geometry between two Al electrodes were studied[21] as well by means of broadband dielectric spectroscopy and using a similar procedure to ours for the sample preparation. Confinement effects at thicknesses much larger (i.e., 62 nm) than those reported in the present study (<20 nm) have been reported. A reason for this discrepancy might be the pronounced difference in the values of ϵ'_∞ used for the determination of the film thickness.[22]

Investigations on thin polymer films in which the relaxation time distribution is analyzed in dependence on the confinement size are scarce. Nevertheless, similar “freezing-out” effects giving rise to a faster dynamics in thin films were recently reported for other polymer systems (hyperbranched polyesters[23]). The relevance of these experimental findings for understanding the molecular mechanisms of the confinement effects is schematically depicted in Figure 6. Shifts in the average relaxation time or in the glass transition temperature are consequences of the changes in the relaxation time distribution arising in confinement. These can take place in two ways. Either groups of polymer segments may fluctuate faster (or slower) in confinement than in the bulk or the relaxation modes of the dynamic glass transition might be (asymmetrically) suppressed. An unambiguous distinction between these two alternatives—both leading to shifts in the molecular dynamics but having fundamentally different molecular origins—is only possible when

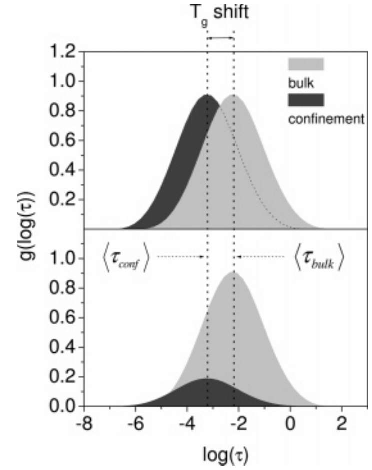

Figure 6. Schematic representation of two possible mechanisms leading to a shift of the mean relaxation time: (a) shifts of the relaxation time distribution as a whole due to the fact the polymer segments fluctuate faster in confinement than in the bulk or (b) freezing-out of the slower relaxation modes.

the relaxation time distribution is analyzed in dependence on the confinement size.

This concept is used in the current paper to get insights into the mechanism of the confinement effects in ultrathin films of poly(vinyl acetate). It turns out that the increase in the average relaxation rate observed in confinement is caused by an asymmetric suppression of the α relaxation modes—predominantly on the low-frequency side.

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