# Glassy Dynamics in Thin Polymer Layers Having a Free Upper Interface

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ABSTRACT: The molecular dynamics in thin polymer layers having a free upper interface is investigated by means of Broadband Dielectric Spectroscopy and AC-calorimetry. Down to film thicknesses of ∼10 nm no shifts in the average relaxation time and no broadening of the dynamic glass transition are detected for polystyrene, poly(methyl methacrylate), poly(vinyl acetate), poly($\gamma$-benzyl-L-glutamate) and poly(2-vinyl pyridine). This experimental finding restricts to a few nanometers the length-scale of a possible alteration of the polymer mobility in the vicinity of free interfaces.

One approach to rationalize the confinement effects on the dynamic glass transition in thin polymer films reported in numerous studies[1–12] represents the conjecture that, near free interfaces, polymers exhibit an enhanced mobility. This idea, supported[7–12] but as well questioned[13–19] in recent experiments, is currently the object of an intensive debate. For instance, pronounced gradients of mobility at free polymer surfaces are reported in a study on thin polymer films using fluorescence techniques.[7] Tracking the embedding-process of metal nanocolloids into the surface of polystyrene films, evidence for an enhanced polymer mobility at free interfaces is found in a study employing atomic force microscopy.[8] An identical approach, but using X-ray reflectometry, delivered opposite conclusions, i.e. no "significant difference between the surface and the bulk $T_g$ values".[13] The glass transition temperature near free polymer surfaces was measured by shear modulation force microscopy, and no shifts from the bulk value were found.[14] Similar conclusions were drawn also in refs 15–19 while in other studies[9–12] the contrary was reported. The concept of an enhanced mobility at free polymer surfaces was also adopted in several theoretical models. For instance, in the sliding model of de Gennes,[20] the chain-loops coming in contact with a free interface are supposed to exhibit an enhanced mobility, which is held responsible for the pronounced reductions of the glass transition temperature reported in thin freely standing films.[21]

The focus of our study is to analyze a possible impact of an altered polymer mobility in the vicinity of free surfaces on the glassy dynamics of thin polymer layers. It is out of the scope of the present work to explicitly investigate, in this context, the role of the interfacial interactions between the polymer and the solid substrate.

The following polymeric systems were investigated in the present work: polystyrene (PS, molecular weight $M_w = 700000$ g/mol, polydispersity index PDI = 1.04, purchased from Polymer Standards Service GmbH), poly(2-vinyl pyridine) (P2VP, $M_w = 200000$, PDI = 1.11, purchased from Scientific Polymer Products Inc.), poly(methyl methacrylate) (PMMA-144K, isotactic content 98%, $M_w = 144000$ g/mol, PDI = 1.7; PMMA-300K, isotactic content 95%, $M_w \sim 300000$ g/mol, PDI $\sim 7$; both purchased from Polymer Source), poly(vinyl acetate) (PVAc, $M_w = 157000$ g/mol, PDI = 2.73 purchased from Scientific Polymer Products) and poly($\gamma$-benzyl-L-glutamate) (PBLG, 30000 g/mol $< M_w <$ 70000 g/mol, PDI = 1.15). Chloroform (for P2VP, PMMA, PVAc, and PBLG) and toluene (for PS) were used as solvents.

A recently developed experimental approach[4,22] was refined and employed to measure—in a broad frequency and temperature range—the molecular dynamics of thin polymer films having a free interface (Figure 1). The method is based on the idea of performing dielectric measurements on samples resembling an air-gap capacitor and uses ultraflat highly conductive silicon wafers as electrodes and a small amount of silica colloids as spacers. It is schematically described in Figure 1a: thin films are spin-coated from solution on silicon wafers at 3000 rotations/min. The wafers, having flat surfaces (root-mean square roughness <0.5 nm) and a typical resistivity smaller than 5 mΩ cm, were purchased from www.Universitywafer.com. The film thickness was adjusted by changing the concentration of the polymer in solution and was determined by means of mechanical nanoprofilometry and atomic force microscopy. On a second set of wafers, a small amount of monodisperse silica colloids (1 μm diameter, delivered by Gerlinde Kisker GmbH) was randomly spread. The spin-coated wafers and those with the colloids were brought in contact and slightly pressed against each other. The hard silica colloids, acting as spacers, keep the

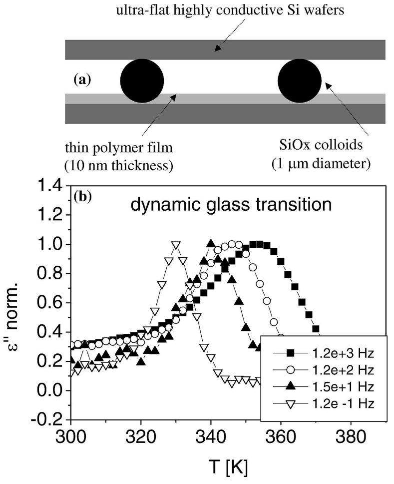

**Figure 1.** (a) Schematic representation of the novel preparation procedure. (b) Dielectric loss vs temperature at different frequencies, as indicated, showing the dynamic glass transition for a thin film of PMMA-300K (7 nm thickness) having the upper interface free. The error bars are comparable to the size of the symbols, unless specified otherwise.

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two wafers separated at an interval of 1 $\mu$m. Hence, for samples having thicknesses much smaller than the diameter of the spacers a *free* interface is realized. The contact area between the colloids and the polymer films is typically much smaller than 1% of the total area of the electrodes.[22]

Prior to dielectric experiments, carried-out using a High Resolution Alpha Analyzer assisted by a Quatro Temperature Controller (Novocontrol Technologies), the samples were annealed several hours well above the glass transition temperature in a pure nitrogen atmosphere. During annealing the dielectric signal of the samples was continuously monitored until the equilibrium was reached. Immediately after, the measurements were started without exposing the samples to ambient air again.

The molecular dynamics in thin films of PMMA-300K is shown in Figure 1b, for a film thickness of 7 nm. The relaxation peaks detected in the temperature dependence of the dielectric loss represent the α relaxation process—the dynamic glass transition of the investigated polymer. The relation between the permittivity function (measured employing an air-gap geometry) and the permittivity function of the polymer film was discussed in detail in ref 23. These calculations are based on a serial arrangement of complex impedances and deliver the simple equation

$$\frac{D}{\varepsilon_M{}^*} = d_A + \frac{d_F}{\varepsilon_F{}^*} \tag{1}$$

where $\varepsilon_M$* represents the measured complex permittivity, $\varepsilon_F$* the permittivity function of the polymer film, $D$ the height of the nanospacers, $d_F$ the thickness of the polymer film and $d_A$ the thickness of the air gap (thus, it holds: $D = d_F + d_A$).

The previous equation simplifies to

$$\varepsilon''_M = \varepsilon''_F \frac{x(x+1)}{(x+\varepsilon'_F)^2 + (\varepsilon''_F)^2} \tag{2}$$

where $x = d_F/d_A$.

It can be applied to calculate the measured permittivity function both in the frequency and in the temperature representation. We calculate in the following the measured dielectric loss (for instance, for P2VP) in an air-gap geometry upon decreasing the film thickness and hence increasing the air gap. We chose to perform these calculations in the frequency domain ($\varepsilon''$ vs frequency), because there even small changes in the dielectric spectra are more easily observable. In addition, the shape of the relaxation processes both in $\varepsilon'$ and $\varepsilon''$ vs frequency are described by well-known fit functions given by the Havriliak−Negami formula.

The complex permittivity function corresponding to P2VP in the bulk was determined by measuring a 2-$\mu$m thick P2VP layer using 20 $\mu$m silica colloids as spacers. This dielectric function was used to calculate, using eq 2, the total dielectric response corresponding to thin P2VP films having different thicknesses ranging from 100 to 2 nm (Figure 2). With decreasing film thickness (and hence increasing the air gap) no apparent shifts in the position of the α relaxation peak are observed. Thus, the air gap geometry does not significantly affect, for this particular range of relative thicknesses ($0.002 \le x = d_F/d_A \le 0.1$) the position and the shape of the α relaxation peaks. Therefore, all dielectric losses are presented as measured in the present manuscript, eventually normalized in respect to the maximum amplitude of the relaxation peaks. We mention additionally that pronounced shifts in the position of the α relaxation are indeed expected (especially for materials showing large dielectric losses) but only for relative thicknesses when $x > 1$, which are outside the range of interest in the present work.

Equation 1 can be used as well to determine the dielectric function of the film $\varepsilon^*_F = \varepsilon'_F + i\varepsilon''_F$ from the complex permittivity $\varepsilon^*_M = \varepsilon'_M + i\varepsilon''_M$ measured in a air-gap geometry. It results in

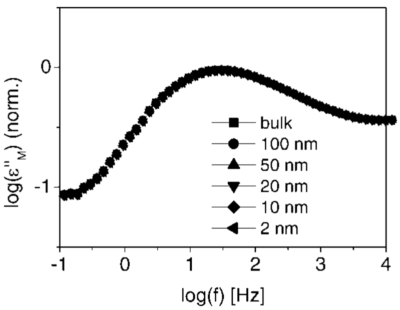

**Figure 2.** (Normalized) dielectric loss vs frequency, showing the α relaxation process of P2VP in the bulk as well as calculated (according to eq 2) for thin films of different thicknesses in an air-gap geometry.

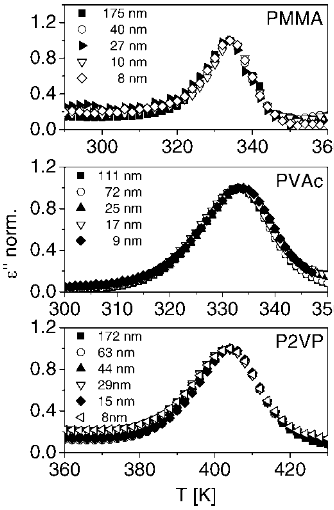

**Figure 3.** Normalized dielectric loss vs temperature showing the dynamic glass transition in thin films: (a) PMMA-144K (0.12 Hz); (b) PVAc (120 Hz); (c) P2VP (1.3 kHz).

$$\varepsilon''_F = \varepsilon''_M \frac{d_F}{D} \frac{(\varepsilon'_M)^2 + (\varepsilon''_M)^2}{\left[\varepsilon'_M - \frac{D-d_F}{D}[(\varepsilon'_M)^2 + (\varepsilon''_M)^2]\right]^2 + (\varepsilon''_M)^2} \tag{3}$$

and

$$\varepsilon'_F = [(\varepsilon'_M)^2 + (\varepsilon''_M)^2] \frac{d_F}{D} \frac{\varepsilon'_M - \frac{D-d_F}{D}[(\varepsilon'_M)^2 + (\varepsilon''_M)^2]}{\left[\varepsilon'_M - \frac{D-d_F}{D}[(\varepsilon'_M)^2 + (\varepsilon''_M)^2]\right]^2 + (\varepsilon''_M)^2} \tag{4}$$

The thickness dependence of the dynamic glass transition is shown in Figure 3, for PMMA-144K, PVAc, and P2VP. Down to a film thickness of 7 nm for the case of PMMA-144K, 9 nm for PVAc, and 8 nm for P2VP, no shifts in the dynamic glass transition are detected. Additionally, no significant broadening of the α relaxation process is observed. Similar findings are found for thin PS layers measured down to a film thickness of 12 nm (Figure 4).

The experimental results for all five investigated polymers are summarized in Figure 5, showing for different film thicknesses the temperature dependence of the mean relaxation time measured in a frequency range covering 5–6 orders of magnitude. No shifts in the average relaxation time of the glassy dynamics are detected down to film thicknesses smaller than

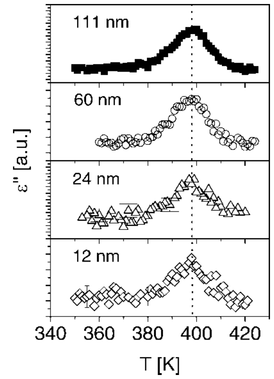

**Figure 4.** Dielectric loss vs temperature at 380 Hz, showing for different thicknesses the dynamic glass transition of thin PS films having a free upper interface.

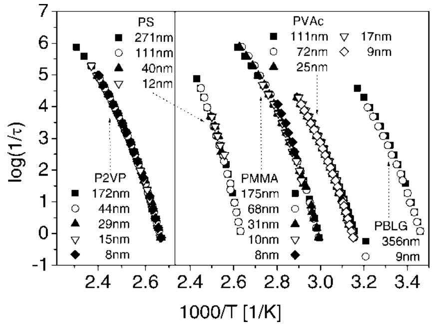

**Figure 5.** Average relaxation rate of the dynamic glass transition as a function of inverse temperature for thin films of PMMA-144K, PVAc, PS, P2VP, and PBLG.

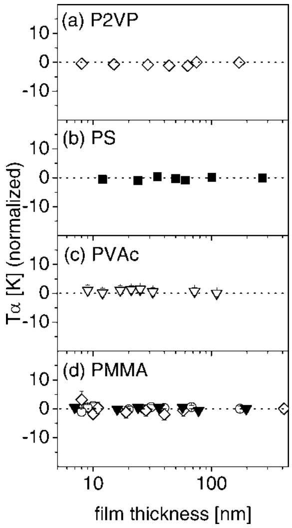

**Figure 6.** Temperature position of the α relaxation peak (normalized with respect to the value corresponding to the maximum film thickness) in dependence on the film thickness: (a) P2VP (0.75 Hz); (b) PS (380 Hz); (c) PVAC (0.75 Hz); (d) (○) PMMA-144K (0.12 Hz), (▼) PMMA-300K (0.12 Hz), and (◇) calorimetric measurements on PMMA-144K (80 Hz).

10 nm. A thickness dependence for the temperature position of the α relaxation peak $T_\alpha$ as measured by broadband dielectric spectroscopy and ac-calorimetry (for the case of PMMA) is explicitly given in Figure 6. From the bulk down to film thicknesses smaller than 10 nm, no changes in the position of $T_\alpha$ are detected. The ac-calorimetric measurements on thin films of PMMA-144K (spin-coated on a SiN membrane and having the upper interface free) were carried out at a frequency of 80 Hz. Details about the calorimetric measurements on ultrathin polymer films, performed using a recently developed chip-calorimeter, can be found elsewhere.[24,25] Down to a thickness of 8 nm, no shifts in the calorimetric glass transition are detected.

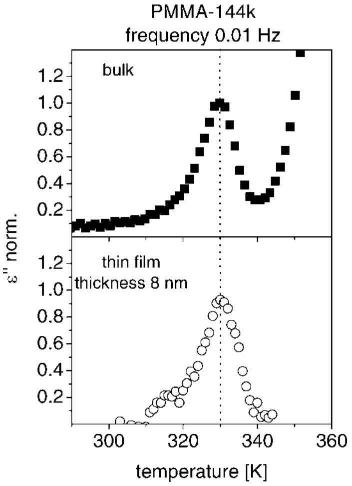

**Figure 7.** Dielectric loss vs temperature at 0.01 Hz, showing the dynamic glass transition of PMMA-144K in the bulk and in a 8 nm-thick film having the upper interface free.

Given a recent study[26] suggesting that confinement effects can be observable only at very low frequencies, the present dielectric investigations have been extended down to 0.01 Hz for the case of polymethylmethacrylate (Figure 7). No shifts in the position of the α relaxation peak are detected down to a film thickness of 8 nm. Measurements at low frequencies on thin PS films—the most investigated system in this field—are not possible due to the high glass transition temperature and the weak permanent dipole moment of this polymer.

Only one dielectric study (investigating polymethylmethacrylate at one single frequency of 1 kHz) on the molecular dynamics of thin films with a free upper interface have been previously reported in the literature.[4] Down to a film thickness of 7 nm, no shifts in the dynamic glass transition were found at 1 kHz. Dielectric investigations on the glassy dynamics of thin polymer films are predominantly carried-out on samples being capped with a thin layer of aluminum, which is deposited by thermal evaporation in high vacuum on top of the polymer films. At thicknesses of 10 nm and smaller, shifts in the dynamic glass transition are usually detected.[27–29] This might be attributed to the presence of solid layers at both interfaces, where relaxation modes of the glassy dynamics are suppressed due to the interfacial interactions.[27] Recently, it has been also shown[30] that evaporation of ountelectrodes on top of ultrathin polymer films can lead to metastable states of the glassy dynamics, which–similarly to confinement effects—exhibit pronounced shifts in the mean relaxation rate of the dynamic glass transition.

The phenomenon of the (dynamic) glass transition is reflected in a variety of microscopic (i.e., structural relaxation time) or macroscopic physical parameters (thermal expansion, heat capacity, density). The pronounced discrepancy between the experimental results presented here and many recent studies reporting $T_g$ shifts in thin polymer films having a free upper interface may originate from the fact that microscopic and macroscopic methods do not necessarily deliver similar results when applied to confined systems. This has been already shown for thin films of hyper-branched polymers,[31] where simultaneous dilatometric and dielectric investigations of the glassy dynamics revealed diverging thickness dependencies for the glass transition. Such effects—initially supposed to originate from the special architecture of the investigated hyper-branched polymers–appear to have a more general character and represent a challenging new topic in the field of confinement effects.

Another possible scenario to explain the present experimental findings must be discussed. The faster mobility which is expected at the free interface might be compensated by a lower mobility which is usually supposed at solid interfaces. This would lead in average to a mean-relaxation time which does not change with decreasing film thickness, as found in our experiments. On the other hand, it is obvious that such a scenario must lead to a broadening of the relaxation time distribution, but this is not observed experimentally.

In conclusion, using a recently developed experimental approach in combination with broadband dielectric spectroscopy, the dynamics of the glass transition is investigated in thin polymer films having a free upper interface. No shifts and no broadening in the dynamic glass transition are detected down to film thicknesses of ~10 nm. This finding indicates that an altered interfacial mobility expected in the vicinity of free interfaces is manifested on a length scale of a few nanometers, with no effects on the dynamic glass transition down to film thicknesses of ~10 nm.

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