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Glassy dynamics and glass transition in nanometric layers and films: A silver lining on the horizon

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A B S T R A C T

The long lasting highly controversial discussion on glassy dynamics and the glass transition temperature of polymers in nanometric layers and films seems to be converging based on a multitude of recent experiments: (i) Linear response spectroscopies (e.g. alternating current calorimetry (ACC), broadband dielectric spectroscopy (BDS)) measuring in the liquid state do not observe shifts of the mean relaxation rate in dependence on the 1-dimensional confinement down to layer thicknesses of 8 nm (ACC) and 4 nm (BDS); (ii) Frequency dependent photobleaching techniques working essentially below the bulk glass transition temperature find as well a glassy dynamics in thin (freestanding or supported) films of polystyrene (PS) which is primarily bulk-like and does not depend on the thickness of the layer as demonstrated down to 14 nm. (iii) Evidence exists, that close to the bulk T_g, a layer of strongly enhanced mobility—and having a temperature dependent thickness—is formed on a free polymer surface. This enormously complicates the interpretation of ellipsometric and fluorescent based experiments, and might be the reason for the widely diverging results. In summary the *dynamic* glass transition does not show a confinement effect above *and* below the glass transition temperature in pronounced contrast to the non-equilibrium dynamics in the glassy state, which depend strongly on a variety of parameters including the layer thickness. This decoupling is well described by the free volume hole diffusion (FVHD) model as developed by Cangialosi et al.

1. Introduction

The (dynamic) glass transition (DGT) is a unique physical phenomenon which is characterized (i) by the continuous slowing down of the fluctuations between structural substates (the α-relaxation) according to a Vogel–Fulcher–Tammann (VFT) temperature dependence, (ii) by the rule, that at the calorimetric glass transition temperature T_g the fluctuation rate has reached a value of ~10^{-2} Hz and (iii) by the broadening in the relaxation time distribution function with decreasing temperature. From the nature of the DGT, it follows immediately that it shows up in a variety of different physical quantities measured by the appropriate techniques. They can be separated into *frequency dependent* methods, such as (alternating current) calorimetry (ACC), neutron scattering, broadband dielectric spectroscopy (BDS), nuclear magnetic resonance (NMR), photon correlation spectroscopy (PCS), mechanical spectroscopy and spectroscopies using specific dyes or labels and *static* techniques, like ellipsometry, measurements of thermal expansion or the lifetime of specific fluorescent labels. Naturally the former measure (primarily) in the liquid state ($T > T_g$) and enable one to trace the DGT often over 8 decades or more (ACC, BDS, NMR, PCS) while the latter are usually restricted to the glassy regime ($T < T_g$) in determining typically a kink in a temperature dependence from which *a* glass transition temperature is deduced. The question arises, if the existing and well established interrelationships between the different methods for the bulk are valid as well under conditions of geometrical confinement.

Compiling the data published [1–92] in the last 20 years on the (dynamic) glass transition and the glass transition temperature of polystyrene (PS) confined in nanometric (supported) layers or (free-standing) films delivers a puzzling picture: The published results for the "glass transition temperature" determined by the different methods as indicated in Fig. 1 vary by more than 80 K! To give an example, Ellison et al. [30], employing a fluorescence technique, report for a 13-nm-thick PS layer (M_W = 761 kg/mol, supported on glass) a T_g reduced by 40 K while Keddie et al. [1] find a reduction of only 25 K for a similar thickness (12 nm, M_W = 501 kg/mol, supported on silicon) using ellipsometry. A comparable reduction of T_g, namely 27 K, is obtained by Yang et al. via X-ray reflectivity but for a much thinner layer of only 6 nm (M_W = 853 kg/mol, supported on silicon) [91]. This is contrasted by the ellipsometric results of Fakhraai et al. which show a reduction of only 10 K for a layer of the same thickness (M_W = 641 kg/mol) [31]. On the other hand, Lu et al. [62], by means of ellipsometry, observe a *bulk*-like T_g for a 8-nm-thick PS layer (M_W = 654 kg/mol) floated on an ionic liquid.

This plethora of contradicting results evidently cannot represent the *molecular* quantity "glass transition temperature" of PS. It reflects rather

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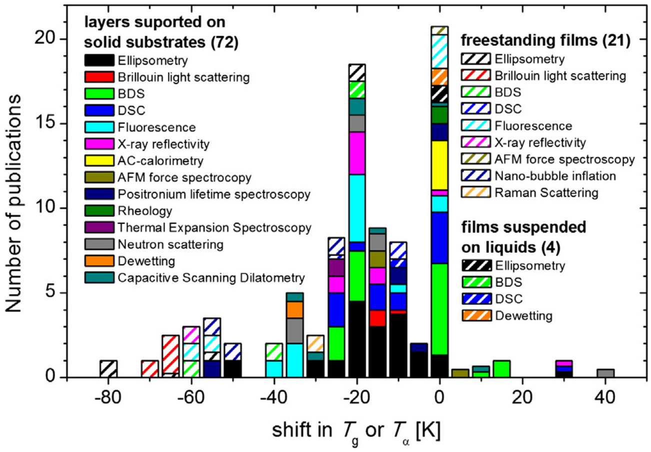

Fig. 1. Number of publications vs. shift in T_g or T_α reported therein for the thinnest studied layer of polystyrene [1–92]. The collection is restricted to molecular weights in the range of 10^2–10^4 kg/mol and thicknesses between 5 and 50 nm; the employed experimental method and type of support are indicated. In total 92 publications are included. The number of publications on each type of support is indicated in brackets after the type of support; 5 papers employing more than one type of support are recorded in each corresponding category. The increment in the y-axis representing one publication is always one which means that for a publication covering several methods the representative area is split into as many parts.

the fact that in geometrical confinement the well established relationships between different molecular methods to determine glassy dynamics and the glass transition temperature are no longer necessarily valid.

2. Results and discussion

2.1. Segmental and chain dynamics poly(cis-1,4-isoprene) in nanometric confinement

Being a Type A polymer, poly(*cis*-1,4-isoprene) (PI) is an ideal candidate for studying both segmental and chain dynamics in confinement. The use of the nanostructured electrode arrangement, on the other hand, avails the experimental possibility of probing ultra-thin layers by BDS. It has been shown [93]—for several molecular weights of PI lying in the range 11.6 to 75 kg/mol—that while the structural (segmental) relaxation remains largely unaffected by changes in layer thickness (down to 7 nm), molecular weight and the polymer concentration of the spin-cast solution, the chain dynamics are drastically altered in dependence on these parameters. For $M_W \cong M_c$, where M_c ($=10^4$ g/mol) is the critical molecular below which Rouse dynamics dominate, the normal mode (which represents the fluctuation of the end-to-end vector of the whole chain) remains bulk-like in its mean relaxation rate even when the layer thickness is reduced to about $3/2R_g$ (Fig. 2a). On the other hand, for $M_W >> M_c$, a decrease in film thickness causes an interference of the normal mode. Its relaxation rate increases with reducing layer thickness, approaching that of the segmental mode (Fig. 2b). We refer to this modified normal mode as the terminal subchain (TSC) mode. These observations intuitively lead to the view that entanglements play a significant role in influencing the chain dynamics. This thought was further experimentally probed by varying the concentration of the spin-cast solution from semi-dilute to dilute regimes in such a way that the thickness of the resulting films was kept constant (Fig. 2c). It is observed that the films prepared from dilute solutions portray an almost fully suppressed TSC mode. As the concentration is gradually increased, the TSC mode gains its strength, but its relaxation rate remains faster than that of the bulk by about 3 orders of magnitude.

Rouse and reptation theories, respectively, predict M^2 and M^3 dependencies of the mean relaxation times of the normal mode below and above M_c. In Fig. 2c, a plot of the mean relaxation times versus molecular weight is presented as a function of PI layer thickness. It must be clarified here that, for the thin layers, the molecular weights presented are those of the mother (starting) sample before dissolution in chloroform. The relation $\tau \propto M^{(3.5\,\pm\,0.1)}$ is found for the bulk samples, quite in quantitative agreement with reported results in literature [94, 95]. For the case of spin-cast samples, a gradual reduction in the gradient of the log (τ) versus log (M_W) plots is noted as the layer thickness is decreased (Fig. 2d). It is therefore directly deduced that the dynamics of the TSC modes approach Rouse dynamics with reducing layer thickness, even though the mother chains are entangled. This trend is confirmed by the activation plot presented in Fig. 2e; it is observed here that the TSC mode of the thinnest films studied (~7 nm) is faster than that of the normal mode of a chain having $M_W = 10^4$ g/mol.

A possible molecular picture to account for these observations is provided in Fig. 2f. It is known that the unperturbed chain in bulk has a Gaussian distribution of the distances of one chain end from the other, and hence its dynamics is that of the end-to-end distance. However, this conformation of the chain is modified when it comes in contact with a solid substrate, as is the case with supported thin layers. As a result of interactions with the substrate, some segments of the chain become immobilized. Only the free tail ends—the terminal subchains—are dielectrically active, and hence the observed faster chain dynamics in confinement. In summary the DGT in thin layers (≥5 nm) of the type-A polymer poly(*cis*-1,4,-isoprene) does not show a confinement effect, while the dynamics of the end-to-end vector of the chain as a whole changes strongly with decreasing thickness.

2.2. Glassy dynamics of condensed (semi)-isolated polymer chains of poly(2-vinylpyridine).

A challenge of highest rank is the question, if single condensed polymer coils perform a glassy dynamics, and if yes, how it does compare with that of the bulk. To answer this, a recently developed setup using nano-structured electrodes to employ BDS for samples with one free interface [96] has been refined. For this particular experiment, the height of the insulating nano-structures acting as spacers between two highly conductive silicon electrodes is reduced to only 35 nm. While these spacers are attached to the upper electrode, the lower electrode carries the polymer chains. The latter are spin-coated from a highly dilute solution onto the silicon electrode resulting in randomly distributed isolated polymer nano-droplets. Their conformational state can be checked by AFM before and after the BDS measurements and it turns out that it resembles a condensed coil. Further, the volume of these coils is determined from the AFM images and compared to the expected value as calculated from the molecular weight and the mass density of the bulk. The assumption of the latter in coils of individual polymer chains was verified by earlier AFM studies of e.g. block copolymers [97]. As sample material poly(2-vinylpyridine) (P2VP) has been chosen due to its large segmental dipole moment which ensures a stronger signal. Fig. 3a and b depicts dielectric loss spectra of bulk P2VP ($M_W = 2250$ kg/mol) and semi-isolated and isolated chains of the same material, respectively. For all three cases the segmental relaxation is present which shows for the first time, that even isolated polymer chains in a condensed coil conformation still exhibit a dynamic glass transition. Plotting the logarithm of the mean relaxation rate as indicated by the peak position in the loss spectra vs. inverse temperature (Fig. 3c) unravels the super-Arrhenius temperature dependence typical for glassy systems. Furthermore, even the isolated polymer chains exhibit a bulk-like dynamic glass transition. The molecular origin of this observation is the fact that the underlying structural relaxation of the dynamic glass transition is the segmental motion which takes place on the length scale of 2–3 segments or ~0.5 nm [98,99]. As schemed in Fig. 3d, this is considerably smaller compared to the extension of the whole condensed chain with a diameter measuring ~50 nm and a height of at least 2–3 nm.

However, a close look at the spectra shown in Fig. 3a and b reveals a broadening of the relaxation peak in the semi-isolated and isolated

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