Temperature Dependence of the Deviations from Bulk Behavior in Ultrathin Polymer Films

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The static and thermodynamic properties of liquid layers at the very interface with air or with an attractive substrate differ strongly from those characteristics of the material at much larger length scales.[1−5] Previous studies have proven that the deviations from bulk behavior mainly originate from interfacial layers showing specific molecular conformations and consequently a different mobility.[1,6−13] In fact, for supported ultrathin polymer films, properties like physical aging,[2] self-diffusion and tracer diffusivity,[14,15] segmental mobility[16] and thus the glass transition temperature, T_g,[1,17] show a sensitivity on the sample dimensions already at hundreds of nanometers. On the contrary, finite size effects that could be attributed to the characteristic length of cooperative rearranging regions would play a role when the confining geometry approaches a few nanometers.[18] Moreover, several measurements of T_g in supported thin films revealed a lack of molecular weight dependence,[5] implying that no well-defined molecular size could be related to the changes in these systems.

Therefore, surfaces and interfaces can be treated as boundary conditions perturbing the material properties and generating a mobility gradient inside the sample over a temperature-dependent length scale. At high temperatures, the ordering effects induced by interfacial interactions persist only over a few monomer units, while in the deeply supercooled state the effects induced by a bounding interface can penetrate over length scales larger than several radius of gyration.[19]

Recently, we arrived at analogous conclusions by using two different independent paths.[3,4] From the analysis of the dielectric response of extremely thin films of polystyrene (PS) we suggested[3] that confinement effects depend on the time scale related to the procedure used to assign T_g, and decrease at shorter relaxation times (temperatures well above bulk T_g) or similarly at high cooling rates.[20] The coupling model of Ngai[21,22] offers a theoretical support for this evidence predicting that, despite variations in the intermolecular coupling (different conformations) at the interfaces, the change in the relaxation time is proportional to the relaxation time itself. Similar results were obtained by modeling the thermal evolution of the structural relaxation time of confined polymer layers[4] via the empirical Vogel−Fulcher−Tammann (VFT) equation

$$\tau_\alpha(T) = \tau_\infty \exp\left(\frac{BT_0}{T - T_0}\right) \quad (1)$$

where T_0 is the Vogel temperature, B a positive parameter related to the dynamic fragility of the system, and τ_∞ the pre-exponential factor related to the inverse of the phonon frequency. Though empirical, eq 1 describes the temperature dependence of the α-modes related to the dynamic glass transition over a broad spectrum of relaxation times.[23] Assuming that, compared to the bulk, interfacial layers are characterized by the same fragility parameter but a different T_g (varying under these conditions by an equal amount as T_0), we have proposed[4] that deviations from bulk behavior are temperature dependent and vanish at sufficiently high temperatures.

To prove the experimental validity of our model, we have investigated via broadband dielectric spectroscopy the thickness and the temperature dependence of the structural relaxation time of films of atactic poly(2-vinylpyridine), (a-P2VP) capped between aluminum layers. Because of specific hydrogen bond interactions,[24] the polymer layers at the very interface with the metal have a high number of contacts with the walls. The resulting changes in the chain conformation allow only a restricted segmental mobility.[5] The observed increase in the glass transition temperature by 6 K at 8 nm supports the idea that the interfacial layer can be described as a reduced mobility layer, RML, as found earlier for the systems poly(ethylene terephthalate) (PET)/Al[16] and P2VP/SiO$_2$.[24]

Ultrathin films of a-P2VP (M_w = 159 kg/mol, M_w/M_n < 1.05, from Aldrich) in the geometry of model nanocomposites[17] were prepared by spincoating dilute solutions of the polymer in *n*-butanol directly on aluminum coated glass slides providing the lower electrode for the dielectric measurements. After a first annealing step (12 h at 400 K) necessary to remove residual solvent and reduce mechanical stress induced during film formation, a second Al electrode was evaporated on top of the
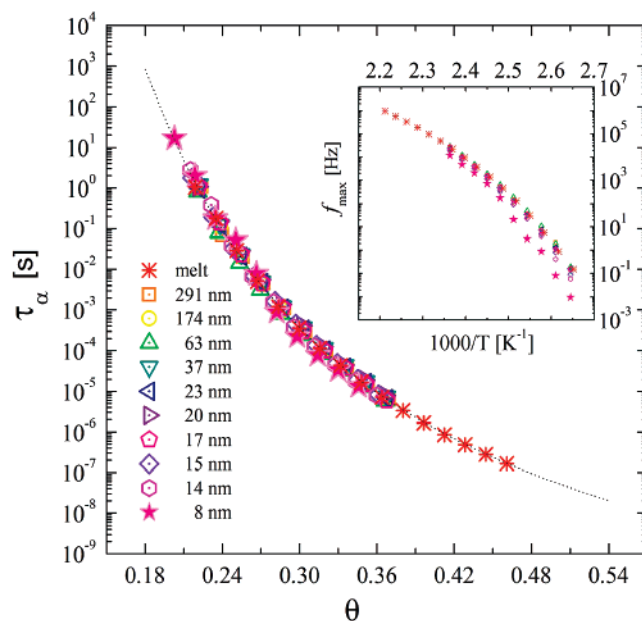
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Figure 1. In the inset: frequency of the maximum of the structural relaxation process of the different film thicknesses, as a function of 1000/*T*. The same curves were superimposed by rescaling the temperature by the dimensionless parameter θ, described in the text.

films. Before measurements, samples were again annealed (2 h at 423 K) to allow healing of the upper interface. The film thickness was varied by changing the polymer concentration and determined by measuring the dielectric constant at high frequencies and low temperatures, ϵ_∞, where molecular relaxations are not present. Measurements of the complex dielectric function $\epsilon(\omega) = \epsilon'(\omega) + i\epsilon''(\omega)$ were performed in the frequency range from 10 mHz to 10 MHz by means of a high-resolution dielectric analyzer, under isothermal conditions in a dry N_2.

Values for the structural relaxation times were extracted in the frequency domain by analyzing isothermal dielectric spectra in terms of the empirical Havriliak−Negami (HN) function. For the different thicknesses, $\tau_\alpha(T)$ followed typical non-Arrhenius behavior, see inset of Figure 1. The relaxation times were fitted by the VFT equation and the glass transition temperature was evaluated using the common convention $\tau_\alpha(T_g) = 100$ s. As observed from the results of the fits, τ_∞ and B were independent of the film thickness while T_0 sharply increased for samples thinner than 20 nm.

The data thus validated our model, and it was possible to superimpose all the experimental curves by rescaling the temperature over the dimensionless parameter $\theta(h,T) = T/T_0(h) - 1$, h being the thickness of the sample. The obtained master curve is displayed in Figure 1. Such a rescaling suggest the introduction of a thickness dependence in the VFT equation

$$\tau_\alpha(h,T) = \tau_\infty \exp\left[\frac{BT_0(h)}{T - T_0(h)}\right] = \tau_\infty \exp\left(\frac{B}{\theta}\right) \qquad (2)$$

The physical meaning of our assumptions is evident considering the exponential term of the VFT as the temperature dependence of the activation energy of the relaxation modes involved in the structural process.[25] This is possible by simply writing $E(T)/k_BT = B/\theta$. It follows that a higher value of the Vogel temperature implies a higher effective activation energy for the structural relaxation. Consequently the increase of T_0 observed upon thickness reduction for ultrathin films of P2VP can be related to an increase in the average potential barrier of the process. Such a higher barrier is the effect of a relative enrichment in the population of relaxing units (dipole moment) associated with slower relaxation modes. As a reduction of the film thickness corresponds to an increase of the ratio between the interfacial layer and the bulk like layer, the augment of T_g is related to a higher value of T_0 of the RML at the interface.[4] Analogously, simulations have shown how the potential energy minima connected to the different relaxation modes are deeper for the molecules in proximity of an attractive interface.[26]

The constant value of τ_∞ and B together with the relatively small variation of T_0 (1.7% at 8 nm) allow the rescaling over θ and suggest that the substrate interactions do not particularly affect the energy landscape scenario. Instead, the variation of the energy barriers results in a shift of T_0 and consequently of T_g. On the first order, the substrate interactions can be treated as a small perturbation on the value of Vogel temperature, δT_0, resulting in a correction factor in the activation energy, $E^{(1)}(T)$.

Although derived from simple energetic considerations, our model is consistent with the observation on deviations from bulk behavior in ultrathin polymer films.[20] The confinement effects quantifiable via a model independent parameter

$$\Delta(h,T) \equiv \log\left|\frac{\tau_\alpha(h,T)}{\tau_\alpha(\infty,T)}\right| = \frac{|E(h,T) - E(\infty,T)|}{k_BT} \simeq \frac{E^{(1)}(h,T)}{k_BT} \qquad (3)$$

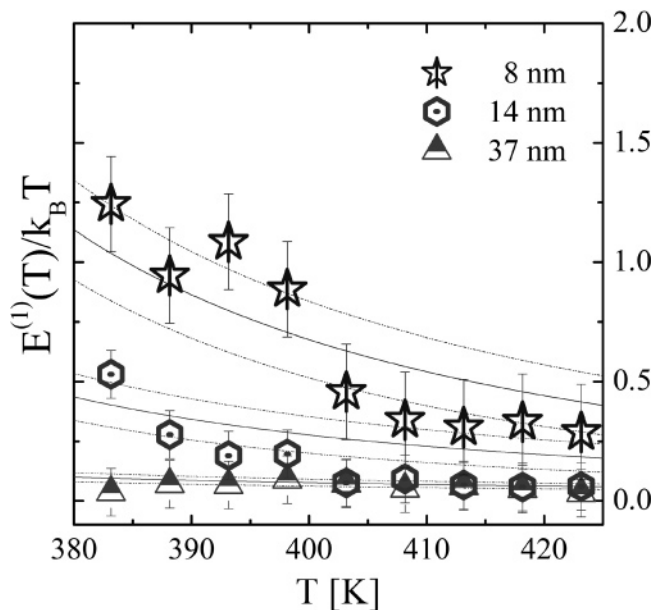with ∞ indicating the unperturbed response of a bulk system,

Figure 2. Temperature dependence of the deviations from bulk behavior for different thicknesses. The ratio between the first order correction to the activation energy of the dynamic glass transition and k_BT was calculated from the relaxation time of the structural process, as described in the text. The continuous line indicate the value obtained for $E^{(1)}(T)/k_BT$ from the VFT fits, within the experimental uncertainties (dashed lines) of 1.5%, 0.5%, and 0.2% on the fragility parameter B, respectively for films of 8, 14, and 37 nm.

are temperature dependent and disappear at temperature sufficiently high where Δ equals zero or assumes values smaller than the technique sensitivity.

This trend is reflected in the data of Figure 2 where the structural relaxation time normalized to its bulk value is plotted toward the temperature at different thicknesses. Thinner films, in which the nonbulk component is more relevant, show higher values of $\Delta(h,T)$, but regardless of the film thickness the confinement effects reduce upon heating, as expected.[4,20]

The results of the model, here experimentally verified, are technique and geometry independent. A similar trend (constant value of the fragility related parameter) was reported for the influence of a bounding interface on the layer resolved diffusion of deuterated PS in various matrices of hydrogenated PS, probed by secondary ion mass spectroscopy.[14] At a distance of 7.6 nm from the interface, the reference temperature[27] T_0 increased of 5%, suggesting that our considerations are still valid at higher values of $E^{(1)}(T)/k_BT$.

A final remark should be given on the observed trend of $T_0(h)$. As regarding ultrathin films, the value of T_0 should be intended as an average of the Vogel temperatures characterizing the layers in the mobility gradient induced by the interfacial interactions. It should be anyway noted that the thickness dependence of T_0 from data of this and several other works[9,16,28] performed with different techniques, does not scale with h^{-1}, see Figure 3. This is an indication that the technique does not weight the layer contributions over their volume percentage.

Regarding our experimental technique, the strength of a dielectric relaxation process, $\Delta\epsilon$, i.e., the area below the dispersion peak, is related to the static correlation function of polarization fluctuations.[29] As here found and as general trend, the relaxation strength strongly drops upon thickness reduction.[16,28,30] In fact, in an RML, the restrictions of molecular mobility bring to a lesser extent of dissipation of energy and thus to a lower value of $\Delta\epsilon$.[16]
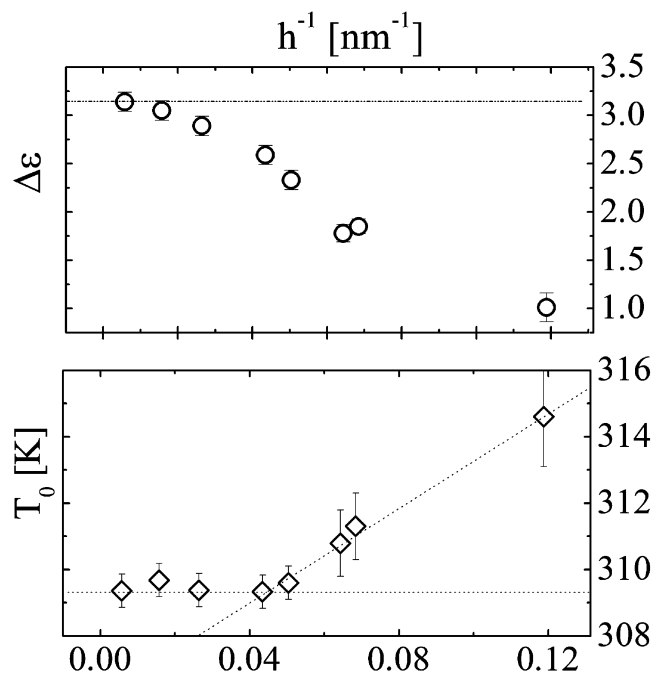
Figure 3. Variation of the dielectric strength, $\Delta\epsilon$, and the Vogel temperature, T_0, with the inverse of the thickness h.

Consequently, the signal arising from the interfacial layers, related to the ensemble of dipoles affected by confinement effects and introducing the energy correction factor $E^{(1)}(T)$, assumes a lower weight on averaging the dielectric signal. For thicknesses bigger than the double of the interfacial layer, the aspect of the spectra is governed by the bulk fraction. This results in a dual transition of the static and dynamic properties, observed in several other systems, and recently rationalized for ultrathin film of PET capped between aluminum layers;[16] see Figure 3. By comparison with the trend of $T_g(h)$ reported for PET, a value of 5 ± 1 nm for the RML at the interface a-P2VP/Al is found.[31]

In conclusion, we have experimentally verified the validity of a model aiming to rationalize the influence of interfacial interactions on the structural relaxation of polymers. The influence of an absorbing substrate has been treated as a small perturbation in the activation energy of the α-modes related to the dynamic glass transition, without affecting the energy landscape scenario. The deviations from bulk behavior are derived from the balance of such a perturbation and the energy of the thermal bath. The model results, supported by experimental evidence, show how these effects are related to the time scale of the experiment and increase upon cooling.

Supporting Information Available: Text discussing and figures showing the broadening of the α-peak upon reduction of the film thickness and isothermal spectra at different thicknesses and temperatures. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

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MA702081W