

Unusual Deviations from Bulk Behavior in Ultrathin Films of Poly(*tert*-butylstyrene): Can Dead Layers Induce a Reduction of T_g ?

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Interfaces strongly affect the final performance of hybrid materials, a fast growing class of multiphase systems mainly based on the combination of inorganic and organic components at the nanoscale.¹ Regardless the nature of the interfacial interactions between the different components, the proximity of an interface alters molecular conformations responsible for macroscopic quantities like, for example, adhesion, wettability, friction, reactivity, and biocompatibility. As a consequence of the large interest in these composites with improved functionalities, the demand of investigations of inorganic/organic interfaces sharply increased.

The main complication in the characterization of these systems is the presence of buried interfaces, lacking a direct optical access between the two components. In addition to molecular dynamics simulations,^{2,3} several experimental methods can contribute to overcome this issue. The most common approaches use surface techniques with a penetration depth larger than the first accessible layer, contrasts methods, where the sensitivity of the applied excitation is enhanced in the case of one component, and analysis of the trend in the average response of the hybrid barriers upon change of the relative concentration. In particular, these last two methods have been largely used to characterize ultrathin polymer films supported on and capped in between inorganic layers. Because of the versatility in their preparation, thin films have often been considered as bench systems for the development of hybrid materials with more complex molecular architectures. Moreover, the peculiar geometry of the

ABSTRACT The temperature and thickness dependence of the thermal expansivity of ultrathin thin films of poly(*tert*-butylstyrene) capped between aluminum layers revealed an unusual and intriguing confinement scenario. Below 50 nm, both the glass transition temperature and the thermal expansion coefficients decreased. Such a mixed behavior implies an enhancement of the molecular mobility, without the presence of any free surface, but dead layers. On the basis of a careful analysis of averaged quantities measured by capacitive dilatometry, we deduced a profile of thermal expansivity that explains our experimental data and previous observations in polymer nanocomposites. The effect of density-conformation coupling in proximity of a nonattractive interface allows the coexistence of an immobilized fraction in direct contact with the metal and an excess of thermal expansivity, arising from the long-range effects of packing frustration penetrating inside the bulk-like core of the film.

KEYWORDS: ultrathin polymer films · nanocomposites · confinement effects · glass transition · thermal expansivity · dilatometry · free volume

films allows a straightforward modeling of materials performances based on gradients of properties in the layers at different distances from the inorganic phase.

The most common experimental approaches used for thin organic films measure the temperature dependence of thickness-related quantities and can thus provide information on both the thermal expansion coefficients (TECs) and the glass transition temperature, T_g .⁴ Although comparison of data sets collected in different scanning conditions might lead to contradictory results,⁵ intuitive considerations relating a reduction of T_g to enhancement mobility at the free surface^{6–8} and an increase of T_g upon the anchoring of polymer segments on an attractive interface⁹ are experimentally confirmed and widely accepted. In this communication we show evidence for a lower T_g in the proximity of surface layers with almost zero thermal expansion coefficients (dead layers). Results are analyzed considering the unusual conditions

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imposed by the coupling between segmental density and chain conformations¹⁰ in a stiff polymer capped between nonattractive interfaces.

In our previous work we investigated the effect of annealing on the thickness dependence of the glass transition temperature and the thermal expansion coefficients in ultrathin films of polystyrene capped between aluminum layers.¹¹ Films prepared in this geometry are model systems to study phenomena influencing processing (T_g) and lifetime storage (physical aging) of nanometer-confined polymer systems and polymer-based nanocomposites.¹² Measurements were performed by means of capacitive dilatometry,¹³ an approach that permits determining the thermal expansion coefficients in the presence of buried interfaces down to 4 nm.

Annealing the samples at different temperatures allowed tuning the mobility profile of the films, removing a free surface effect, and passing from a reduction to an increase of T_g . We highlighted a striking correlation between the distribution of TECs inside the film and the trend in T_g . Films annealed at low temperatures ($t_{\text{ann}} = 12$ h, $T_{\text{ann}} = T_g$) showed the signature of a free surface, while annealing at higher temperatures ($t_{\text{ann}} = 12$ h, $T_{\text{ann}} = T_g + 25$ K) resulted in samples mimicking a system consisting of a bulk core embedded into two immobilized (dead) layers. T_g decreased in the former series and it increased in the latter, as expected. In both cases, a quantitative analysis confirmed that at each polymer/metal interface the dead layer δ extends over (2.7 ± 0.4) nm. The results were rationalized assuming that in the samples annealed at low temperatures the upper interface was unable to heal and acted as a free surface. This hypothesis is justified by the sharp interfaces created between polymer and aluminum, a metal that, differently from gold and copper, does not

diffuse into the polymer core.¹⁴ Further support for this argument comes from the agreement between the reduction of T_g in this series and those of films with one free surface measured by different other techniques.

To gain information on the nature of the dead layer and its influence on the confinement effects on T_g , we extended our investigation to poly(4-*tert*-butyl styrene), PTBS, a polystyrene derivate, where the 4-position of the aromatic ring is replaced by the apolar *tert*butyl group ($(\text{CH}_3)_3\text{C}-$). Fluorescence spectroscopy on polystyrene derivatives revealed how the introduction of bulky end groups at the para position of the aromatic ring leads to more sterical hindrance that manifests in larger deviations from bulk behavior.¹⁵ At 25 nm, the glass transition temperature of supported films of PS is 15 K lower than the bulk value, a reduction that further increases by 10 K upon addition of a methyl group, and finally approaches almost 50 K for PTBS. For the latter system in particular, the reduction of T_g starts at an extraordinary high value in the order of 300–400 nm, which falls out of the typical range where T_g assumes values different than in bulk (*ca.* 20–100 nm).

The tremendous deviations from bulk behavior of supported films of PTBS were attributed to stiffening of the chains resulting from the addition of the bulky *tert*-butyl group. Chain stiffening, in fact, increases the correlation length of the surface induced changes in the polymer conformations,¹⁰ that is, deviations from bulk behavior can propagate deeper inside the bulklike core of the film. Moreover, such a modification brings to a drop by 9% of the bulk density ($\rho_{\text{PTBS}} = 0.94$ g cm⁻³; $\rho_{\text{PS}} = 1.055$ g cm⁻³), implying a less efficient packing of the chains and an increase of free volume as for the crystalline γ form of syndiotactic polystyrene ($\rho = 0.977$ g cm⁻³).¹⁶ An analysis of the thickness dependence of the TECs of capped films of PTBS revealed an enhancement of segmental mobility together with immobilization of polymer chains at the interface, an unexpected scenario showing mixed features of the two series of PS.

RESULTS AND DISCUSSION

Capacitive Dilatometry. Figure 1 shows the temperature dependence of the capacitance $C(T)$ at 15 kHz, normalized to its value at the reference temperature $T_{\text{ref}} = 303$ K, for films of 78, 15, 7, and 5 nm. Two distinct linear regimes, related to the glass and the melt, respectively, at low and at high temperatures, are easily identified and separated by a contrast proportional to the ratio between the slopes in the different temperature windows. For nonpolar systems, like PS and PTBS, the temperature dependence of the capacitance is exclusively driven by the expansion coefficient in the normal direction to the surface, α_n . This is a direct consequence of the inverse proportionality between capacitance and thickness, valid in the absence of molecular relaxation processes. In the case of a constant interfacial

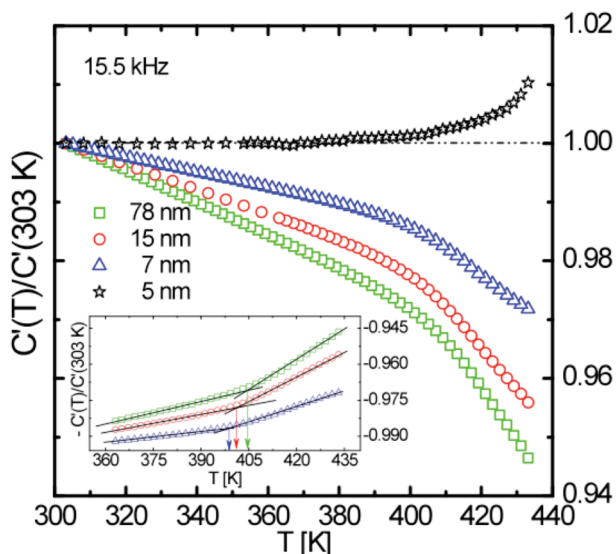


Figure 1. Thermal evolution of the normalized capacity at 15.5 kHz for different film thicknesses; the inset shows examples of the fitting procedure.

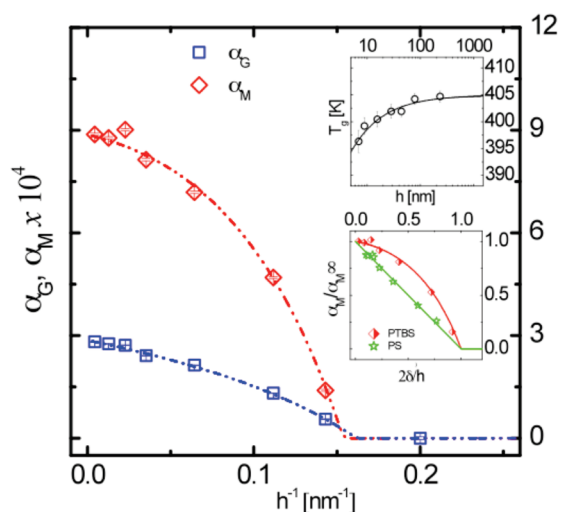


Figure 2. Thermal expansion coefficients of ultrathin films of PTBS, as a function of the inverse of the thickness. The dash dotted lines are fit to the experimental data *via* eq 3. In the upper inset, thickness dependence of the glass transition temperature, the line is a guide for eyes following the equation $T_g(h) = 405(1 - (0.13/h)^{0.6})$ K. In the lower inset, the thickness dependence of the thermal expansion coefficient in the melt for films of PTBS (red diamonds) and PS (green stars) prepared in similar annealing conditions (see text). To facilitate comparison, data were normalized to the bulk value of the thermal expansion coefficient and to the total extension of the dead layer.

area, α_n is given by $-\zeta C(T)/C_0$, where ζ is a temperature independent parameter and C_0 is the value of the geometrical capacitance at the chosen reference temperature.¹³ The glass transition temperature was assigned to the crossover of the two regimes, as the intersection of the two linear fits of the response in the glass and in the liquid. Each cooling scan provided three parameters: α_G , the normal thermal expansion coefficient for $T < T_g$, α_M , the normal thermal expansion coefficient in the liquid state, and T_g . Differences between parameters obtained from consecutive cooling scans, and/or from prolonged annealing steps after metallization of the free surface, were smaller than 3%. This observation suggests that the amount of the immobilized segments at each interface does not further change during the experiment.

The results of this model-free data analysis are reported in Figure 2. Upon reduction of the thickness, a modest decrease of T_g ($\Delta T_g \approx -8$ K, for 7 nm) (see upper inset graph of Figure 2) is accompanied by a drop of both the thermal expansion coefficients ($\alpha_M \approx 15\% \alpha_M^\infty$ and $\alpha_G \approx 20\% \alpha_G^\infty$, where ∞ indicates the bulk value) which do not scale linearly with the inverse of the thickness. For comparison, we added data from PS annealed at high temperatures in the lower inset graph of Figure 2.

This observation is in contrast with the general idea that the reduction of T_g in ultrathin polymer films is solely related to the effect of a free surface. In fact, differently from the series of PS annealed at low temperatures, for the para-modified polymer, we did not ob-

serve a trend in the TECs that would be compatible with a profile of mobility including a free surface at one (or both) of the polymer/metal interface. In these cases, modeling the profile of thermal expansivity with linear combinations of Heaviside functions, α_G should grow with h^{-1} while α_M should decrease or remain thickness independent, depending on either a nonzero or zero value of the size of the dead layer. Moreover, the values of $\Delta T_g(h)$ that we get from the upper inset of Figure 2 are definitely smaller than those extracted by fluorescence spectroscopy¹⁵ and thin-film transistor response.^{17,18} In addition to that, we did not observe any confinement effect on T_g at thicknesses larger than 50 nm, a threshold value 1 order of magnitude lower than in what measured for films with one free surface.

On the other hand, the trend in the expansion coefficients of PTBS resembles the series of PS annealed in the same conditions. Hybrid materials showing such a mixed behavior are as unusual as intriguing. A similar paradox was noticed on supported layers of polycarbonate,¹⁹ another rigid polymer, and seems to be a more common feature for a variegated class of nanocomposites of different matrix/particle nature.^{20,21} But how is it possible to have an enhancement of molecular mobility and simultaneously a reduction of the thermal expansivity? What kind of information about the behavior of polymer chains at the interface can we get from such a trend? The response stays in the nonlinear trend of the thickness dependence of both the thermal expansion coefficients. The analysis of thickness evolution of the average values of the TECs provided strong contour conditions for the solution of the inverse problem related to the thermal expansivity profile of our films.

Deriving a Profile of Thermal Expansivity in Ultrathin Polymer Films Prepared in the Geometry of Model Nanocomposites. From the mean value theorem we obtain an expression for the average value $\langle \alpha(h) \rangle_{G,M}$, related to the profile, $L_\alpha(x)$, from which $\langle \alpha(h) \rangle_{G,M}$ originated, when weighted over $w(x)$, a function of the distance x , measured from a convenient point inside the film, being in our case one of the two interfaces:

$$\langle \alpha(h) \rangle_{G,M} = \frac{\int_0^h L_\alpha(x) w(x) dx}{\int_0^h w(x) dx} \quad (1)$$

We assume the weight function to be a constant ($=1$) as in the previous modeling validated by experimental observations, so that the effects of the changes in thermal expansivity inside the film could be directly incorporated in $L_\alpha(x)$. This last function is intended to be symmetric toward $h/2$, allowing the two interfaces to play an identical role.

To identify the nature of the profile function, we further analyzed the anomaly in the thickness dependence of both TECs. The observed nonlinear trend cannot be

$$L_{\alpha}(x) = \begin{cases} 0 & 0 < x < \delta_{G,M} \cup h - \delta_{G,M} < x < h \\ \alpha_{G,M}^{\infty} \left(1 + \frac{\lambda_{G,M}^2}{x^2} + \frac{\lambda_{G,M}^2}{(h-x)^2} \right) & \delta_{G,M} < x < h - \delta_{G,M} \end{cases} \quad (2)$$

$$\frac{\langle \alpha(h) \rangle_{G,M}}{\alpha_{G,M}^{\infty}} = \begin{cases} 0 & h < 2\delta_{G,M} \\ 1 - 2 \left(\delta_{G,M} - \frac{\lambda_{G,M}^2}{\delta_{G,M}} \right) \frac{1}{h} - 2 \frac{\lambda_{G,M}^2}{h(h - \delta_{G,M})} & h \geq 2\delta_{G,M} \end{cases} \quad (3)$$

imputed to experimental errors. The accuracy of the data is limited only by the sensitivity of the instrument, which brings to errors one to 2 orders of magnitude below the mean value. We checked that this effect was not related to a broader interfacial region. The widely used Heaviside function is justified in the case of very sharp profiles, or even at large differences between the weight coefficients of the different layers in the total average, that is, being dilatometric analysis sensitive to molecular mobility, a less mobile fraction occupies a virtually lower volume. The broadening of the interface between the bulk and the dead layer, obtained for example by calculating the response to $L_{\alpha}(x) \approx \text{erf}(x - \delta)$, would manifest as a smooth shift of $\langle \alpha(h) \rangle_{G,M}$ toward higher values of h^{-1} . Figure 2 shows the opposite trend. Differently from other experimental works, where a linear correlation was observed for the full thickness range investigated,^{11,22} we notice a saturation of α_M and α_G at low values of h^{-1} corresponding to thicknesses smaller than 50 nm. Moreover, especially for $\alpha_M(h)$, the reduction rate of the TECs is not constant with the inverse of the thickness, but it increases in the thinnest films. Consequently, even a superposition of Heaviside functions would not allow a description of the requested profile function. In comparison with films of PS annealed above T_g (see Figure 2 and its lower inset graph) α_G and α_M decrease until reaching a constant value below the instrument sensitivity, suggesting the presence of interfacial layers with thermal expansivity orders of magnitude below the bulk value. Thus $L_{\alpha}(x)$ become zero when x or $h - x$ get smaller than a given length scale which we will assume as the dead layer. Furthermore, we do not observe any broadening of the transition region where the capacitance is not linear with the temperature in the thinnest films, as instead usually observed in our previous work and by ellipsometry.²³ For PTBS, the opposite trend is present: the non-linear temperature region simply scales with $|\alpha_M(h) - \alpha_G(h)|\alpha$, that is, it decreases upon thickness reduction. The broadening is related to an increase of the heterogeneous character of the films, or similarly to an increase of difference between the responses in the two regimes above and below T_g . This fact, although indirectly, further implies a symmetric form of $L_{\alpha}(x)$ toward the core of the film. Finally, in contrast to PS and other polymers, here we find an excess of thermal expansivity (see the area in between the two data sets in the lower panel of Figure 2), which is probably related to the origin of the reduction of T_g .

To facilitate an analytical derivation of $L_{\alpha}(x)$, we noticed that the values of $\langle \alpha(h^{-1}) \rangle_{G,M}$ could be interpolated by a sum of power laws limited to the second order. The choice of this function does not influence the observations on the nature of this intriguing phenomenon but could be directly related to existing models on polymer melts in proximity of an interface.²⁴ Under the assumptions just discussed, we obtain eq 2 and consequently eq 3, where λ is a length scale whose role will be more clear in the following discussion. The form of $L_{\alpha}(x)$ in the equations incorporates the influence of mutual interactions between the perturbations exerted by the two opposing interfaces. Profiles where the global effects were calculated by doubling the weight of one single interface showed similar analytical trends and comparable fit parameters.

Considering the boundary conditions of eq 2, eq 3 assumes nonzero values only for film thickness larger than 2δ , this being the total extension of the layers at zero expansivity. The profile, whose average values correspond to the experimental results of Figure 2, is drawn in Figure 3. The analytical form of eq 2 is the superposition of two Heaviside functions (dash lines) and two power law branches (dash dotted lines) governed by λ , symmetric toward the core of the film. For the melt we find $\delta_G = 3.1 \pm 0.5$, $\lambda_G = 2.0 \pm 0.2$ and $\delta_M = 3.2 \pm 0.5$, $\lambda_M = 3.0 \pm 0.2$; all parameters are expressed

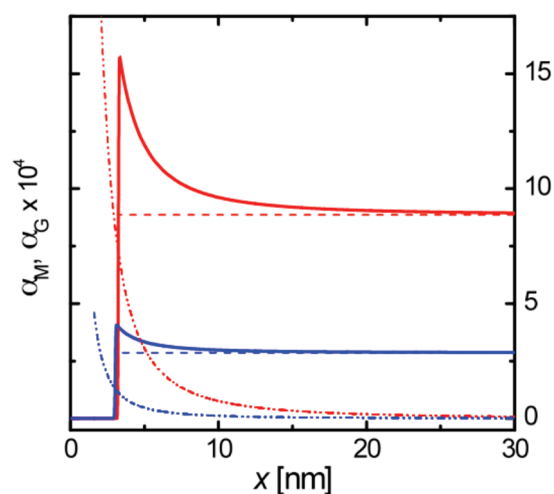


Figure 3. Reconstructed profile of the thermal expansivity in the melt (red) and in the glass (blue), referring to the data plotted in Figure 2. Single contributions from the Heaviside step due to the dead layer (dash line) and to the decay of interfacial conformation correlation function (dash dot dot line) are also given. Only half of the profile is plotted, this being symmetric with respect to the middle of the film.

in nm. Similarly to previous models that successfully captured the confinement scenarios in other polymer systems, the fitting parameters have the meaning of characteristic lengths.

Interplay between Absorption of Polymer Segments and Packing Frustration. The peculiar form of $L_\alpha(x)$ as deduced from the experimental data of PTBS shows a clear physical picture: an increase of the thermal expansivity (connected to a reduction of density) is present at the interface between bulk and dead layer. Although counterintuitive, an enhancement of molecular mobility in proximity of an immobilized layer is justified by long-range effects of the reduction of density of segments at the interface with a weakly interacting coating. The nonmonotonous trend of $L_\alpha(x)$ is due to the competition of two effects acting on the reorganization of polymer chains in contact with the substrate: at short scales, the pinning of polymer segments at the very interface with Al and, at longer distances, the residual influence of packing frustration. While the former inhibits chain reorientation over large angles and thus reduces thermal expansivity, the latter, obeying a density-conformation coupling, acts as a source of extra free volume and participates in the reduction of T_g .

Considering eq 2, it is straightforward to assign a characteristic length scale to each of the two effects, δ being the immobilization and λ being the perturbation to the chain configuration responsible for the reduction of density. On the basis of simple thermodynamic considerations, the observed reductions of glass transition temperature ($\Delta T_g \approx 8$ K) can be related to a reasonable change of density by 0.5%, a number coherent with investigations by neutron scattering.^{25,26}

The dead layer of PTBS on Al appears temperature independent and assumes values similar to those of PS on Al and silicon oxide. Replacing the 2-position of the aromatic ring with an electron donor element (N) sharply increases the chain immobilization: in poly(2-vinylpyridine) δ extends over 5.5 nm on Al (the value was extrapolated to the thickness where the dipolar orientation of the structural relaxation can no longer be detected)²⁷ and over 20 nm on silicon oxide (the interfacial layer having a constant reduction of thermal expansivity by 70%).²⁸ In these last cases, a dead layer is expected, due to the strong hydrogen bonding between hydroxyl groups present on the metal surface and the nitrogen electron pairs on the polymer chains. An efficient packing of macromolecules onto a substrate in fact, requires a chemical affinity between the two media and/or flexible chains able to self-organize in a structure with a lower density, that is, a reduced free volume environment. On the other hand, the nature of the interactions between PS and Al or SiO₂, considered as weakly interacting or repulsive interfaces, is not yet clear. Nonetheless, the presence of absorbed layers at those metal/polymer pairs was confirmed by recent work⁵ reproposing the experiment of Guiselin.²⁹

Severe washing in a good solvent was not able to completely remove annealed films of PS from Si or SiO₂. The thickness of the residual holes-free layers, which increased and finally reached a plateau with annealing time, scaled with the gyration radius as expected by Guiselin in a dry regime, that is, solvent molecules were no longer present and polymer chains were not cross-linked but irreversibly bonded to the interface. The value of the equilibrium thickness of the residual layers, reaching 25 nm for well-annealed films of PS by 940 kg/mol, is not surprising considering the small number of entanglements necessary to tether the more mobile chains in the core of the film to those frozen at the interface.

It should be finally noted that the value of δ is technique dependent:¹⁹ approaches based on localized segmental motions, as rotations and vibrations of the different chemical species, “see” smaller dead layers compared to techniques averaging over larger angular fluctuations. In our case, using electric capacitance as a probe of thermal expansivity, dead layers are regions where the electric polarization is unable to sense any density dependence. This happens both in the case of very low thermal expansivity ($\ll 10^{-5}$) as well as for strong reduction of the polarizability, which could be possible in the presence of $\pi-\pi$ stacking or loss of aromaticity upon substrate interactions. Considering the large steric hindrance of the *tert*-butyl group, we can easily exclude the second mechanism and assume that the measured trend in α_n depends only on mere thermal expansivity. Films of PTBS thinner than 2δ revealed a constant value of the capacitance, which slightly increased only at higher temperatures. As the raise of capacitance augmented at lower frequencies, the feature should not be attributed to a negative expansion coefficient, but rather to an orientational (dipolar) polarization process related gradual defreezing of immobilized chains.¹¹ On the basis of the new insights provided by PTBS, the mechanism of defreezing could be associated to an increase of free volume. The build-up of this extra capacitive contribution further proves that even in the dead layer, some residual molecular mobility is still present. The T_g of these films would probably fall out of the measuring window at temperatures where the just described polarization process is not negligible and does not allow determination of any discontinuity in $C(T)$. On the other hand, the severe restriction on segmental mobility strongly limits the weighting contributions of dead layers on the average T_g of the film. The mechanical coupling between immobilized layers and the neighboring segments with a higher mobility allows the propagation of chain conformation related to non-bulk T_g values.

To provide new insight into the impact of dead layers on the deviations from bulk behavior, we have further analyzed the role of the parameter λ , governing the transition zone between bulk and layers at zero ex-

pansivity. At distances from each interface larger than δ , the density ($\sim 1/\alpha(x)$) increases quadratically with the distance from the wall, a scaling behavior expected from mean-field calculations for equilibrium profiles of polymers in the presence of weakly interacting media.²⁴ Profiles scaling with the square of the distance were already observed *via* neutron scattering at the interface between the two components of isotopic blends of PS.³⁰ Under this framework, λ assumes a physical meaning in accordance with our previous definition, being the double of the correlation length for the concentration fluctuations.²⁴ Larger values of λ are expected for stiffer chains and other cases showing a pronounced density reduction at the interface. The higher value of λ found in the melt suggests that molecular mobility, on the time and length scale of the glass transition temperature, further interferes on chain packing, leading to a larger drop of density.

Depending on the macromolecular architecture and the nature of the substrate, different confinement scenarios are possible. In our picture, the nature of the possible interfaces simply translates in different values of the ratio λ/δ . Regardless the value of λ , in the case of $\delta/\lambda > \sqrt{3}$ the memory of interfacial configuration effects is completely erased;³¹ that is, the chains recover their bulk expansivity before gaining enough mobility allowing large scale reorientations. This last situation cannot be experimentally distinguished from the trivial case $\lambda = 0$ where, as for the annealed series of PS, the profile of a bulk layer capped between two dead layers is recovered.

Similarly, a nonlinear character cannot be excluded for data sets covering thickness range limited to values larger than 4δ , where $\langle\alpha(h)\rangle_{G,M}$ shows the maximum deviation from the Heaviside form. As a direct consequence of the fitting, a lower value of the dead layer would be estimated.

The unusual trend observed for PTBS occurs at a value of $\lambda \approx \delta$ a condition which requires semiflexible or rigid chains on weakly interacting or repulsive substrates. In this case, the reduction of thermal expansivity is retarded by the residual low-density component correlated to packing frustration. The effects of packing frustration are in fact not limited to $x > \delta$, but start immediately after pinning at the interface. However, being not possible to disentangle mere immobilization from a reduction of mobility resulting in a lower intensity of the measured signal, it is not possible to follow the first stages of the decay $\sim (x/\lambda)^{-2}$. The sharp transition in $L_\alpha(x)$ at δ , is justified by these considerations. Hence, in case of packing frustration, dead layers might assume the unusual self-accelerating character that we observed for PTBS. This enhancement of the molecular mobility, not driven by free surfaces but by a severe perturbation generated by a bonding of polymer segments, is not only limited to the case of stiff para-modified PS. This mixed regime resembles in fact

several experimental observations in polymer matrix nanocomposites, where an acceleration of the structural relaxation time (reduction of T_g) coexists with an immobilized layer over the nanoparticles's core. The nonlinear character of $\langle\alpha(h^{-1})\rangle_{G,M}$ increases at higher values of λ and a maximum appears at intermediate thicknesses on the order of a few δ values. This extreme situation shows also a strong analogy to the deep minimum in density observed for nanocomposites of polyhedral oligomeric phenethylsilsequi-oxanes (POSS) dispersed in a matrix of PC at low content of the inorganic phase.³² The expected trend linear with the nanoparticle concentration (scaling as h^{-1}) is recovered when the same filler was dispersed in PS,³³ where the aromatic moieties increases the affinity with POSS and thus yields higher values of δ/λ . In this kind of samples the direct use of equations analogous to eq 2 permit the extraction of reasonable length scales. Differently from thin films, where the well-defined geometry allowed us a univocal path to recover the form of $L_\alpha(x)$, treatment of data from nanocomposites present some limitations: distribution of particle sizes and distances, as well as possibility of particle aggregation complicate the nature of the weighting function.

CONCLUSIONS

We investigated *via* capacitive dilatometry the confinement effects on thermal expansivity and glass transition temperature of ultrathin thin films of poly(*tert*-butylstyrene) capped between aluminum layers. A decrease of the thermal expansion coefficients in the thinnest films in both the glassy and the liquid state was attributed to the presence of an immobilized layer extending over 3 nm from both polymer/metal interfaces into the film's interior. Because of a long annealing procedure and the geometrical constraints, no liquidlike layer acting as a free surface was present. Opposed to PS, the reduction of thermal expansivity was not constant with the inverse of the thickness, that is, a simple steplike multilayer model cannot describe the experimental results. Unexpectedly, the films with lowest thermal expansion coefficients showed a reduction of T_g , suggesting an enhancement of molecular mobility in the presence of a dead layer.

The analysis of the nonlinear trend in the TECs allowed the rebuilding of a profile that rationalizes the measured average quantities and revealed an excess thermal expansivity at the transition zone from the immobilized layers to the bulk core. We discussed the trend in terms of a conformation-density coupling at the interface between a rigid polymer and a not-strongly interacting medium. We highlighted the similarities between this trend in ultrathin films of PTBS and polymer-based nanocomposites. Moreover, in case of supported films, the excess of free volume at the organic-inorganic interface could further participate in the reduction of T_g driven by free surfaces effects.

Models aiming at unveiling the interplay between structural conformations, interfacial interactions, and

performance of polymer chains at the nanoscale should take into account this intriguing, nonintuitive behavior.

METHODS

Model Nanocomposites Preparation. Ultrathin samples of poly(4-*tert*-butyl styrene), PTBS, ($M_w = 115\text{k}$, $M_w/M_n = 3.6$, from Aldrich), were prepared in the geometry of model nanocomposites.¹² To remove a residual fraction of *tert*-butylstyrene monomer from the material as purchased, prior to any further usage, the polymer was purified by repeated (10 \times) dissolution in toluene and precipitation in methanol. Dilute solutions of the polymer in toluene were filtered and spin-coated on freshly flash-evaporated layers of aluminum (~ 50 nm). Thinner films were obtained by further diluting the same polymer solution. After spin-coating, films were annealed ($t_{\text{ann}} = 12$ h, $T_{\text{ann}} = T_g + 30$ K) in vacuum ($\sim 10^{-3}$ mbar). The bulk dry T_g determined by differential scanning calorimetry was (404 ± 3) K. Evaporation of the upper electrode was operated in the same conditions as for the lower metallic layer, holding samples, at room temperature, under high vacuum ($< 10^{-5}$ mbar) for at least 20 min. The long annealing procedures were performed to promote healing of the polymer/metal interface and remove any effect of the free surface, as well as to avoid or reduce confinement effects imputable to nonrelaxed states of the polymer connected to residual solvent³⁴ and/or nonbulk viscosities due to metastable states in spincoated films.^{35–37}

Capacitive Dilatometry Measurements. Dielectric spectra of the samples were acquired under a continuous nitrogen flow, in isothermal steps of a cooling program, from the melt to the deep glassy state (433 \rightarrow 303 K), resulting in an effective scanning rate of -0.2 K/min.

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