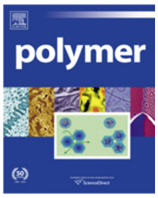
Polymer 51 (2010) 5309–5312

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer



Polymer Communication

Structural relaxation and dynamic fragility of freely standing polymer films

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ARTICLE INFO

Article history:
Received 12 August 2010
Received in revised form
20 September 2010
Accepted 22 September 2010
Available online 29 September 2010

Keywords:
Ultrathin polymer films
Freely standing films
Glass transition

ABSTRACT

In addition to a tremendous reduction in the glass transition temperature, dielectric spectra of freely standing films reveal two other intriguing features: a temperature dependent asymmetric broadening of the structural relaxation peak towards lower temperatures and a reduction of the dynamic fragility down to the monomer limit. We verified that this experimental evidence is a manifestation of a gradient of glass transition temperatures across the film thickness induced by an enhanced molecular mobility at the two free surfaces of the membrane. As a direct implication of the peculiar features just described, the properties of freely suspended membranes neither correspond to those in bulk nor to a simplified scenario where the structural relaxation peak is merely shifted towards lower temperatures.

The excellent processability and the broadly-tunable permeability of macromolecular materials have stimulated a large-scale development of polymer membranes for applications ranging from ultrafiltration to separation of gases and smart packaging [1]. Due to the continuing miniaturization of devices, the production and characterization of thinner membranes are pushed down to the nanometer scale [2–4]. Compared to inorganic materials (failing as sensing elements already in the sub-millimeter range due to an excessive rigidity), polymers, owing to lower processing costs, intrinsical ductility and lower stiffness, are more suitable candidates for future applications of nanomembranes in fields like biomedicine and microelectronics [5]. Although such applications are promising, a more accurate understanding of the physical properties of nanomembranes is a prerequisite for their future improvements. Valuable contributions to this issue come from the ongoing debate on dynamics of ultrathin polymer films, for a Review see Refs. [6–8]. In particular, from purely geometrical considerations, freely standing films, showing depressions of the glass transition temperature (T_g) by more than 70 K [9], are appropriate benchmark systems to test properties of freely suspended polymer nanomembranes. Furthermore, unveiling the molecular origins of the relaxation processes taking place in the presence of free surfaces and their penetration depth is crucial for the comprehension of the behavior of soft matter at the nanoscale and has a huge impact on the development of ultrastable glasses [10]. These investigations are also inline with deGennes's suggestion to perform experiments that probe the distribution in glass transition temperatures [11] within thin polymer films rather than determining just their mean value. Although a large number of investigations focused on the properties of nanometer-thick layers supported on solid substrates, just a limited number of experimental studies has been devoted to the characterization of freely standing films [12–17], due to experimental conditions requiring greater efforts (e.g. longer sample preparation, lower signal/noise ratios, difficulties to apply electric fields and to couple to mechanical stresses).

In this Communication, we show that, in addition to a tremendous reduction in the glass transition temperature [9,16,17], dielectric spectra of freely standing films reveal more intriguing features not present in supported and capped films [18–20]: a temperature-dependent asymmetric broadening of the structural (α-)peak towards lower temperatures and a reduction of the dynamic fragility down to the monomer limit. We compare our experimental results with other work on thin films supporting a strong gradient of T_g's extending inside the film for a few hundreds of nanometers.

Freely standing membranes of atactic polystyrene ($M_w = 932{,}000$ g/mol, $M_w/M_n = 1.2$, $R_g = 28$ nm) were obtained by spincoating dilute solutions of the polymer in chloroform onto freshly cleaved mica sheets. Polymer layers were subsequently floated on ultrapure water and finally allowed to dry in air for several days before being finally transferred and suspended onto interdigitated comb electrodes (IDE) (Xensor Integration). To reduce thermal and mechanical stresses, IDE structures were preheated at $T_g^{BULK} + 10$ K during the transfer of the membrane. Differently to the conventional methods used to investigate ultrathin films, IDE structures permits to apply electric fields to

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doi:10.1016/j.polymer.2010.09.060

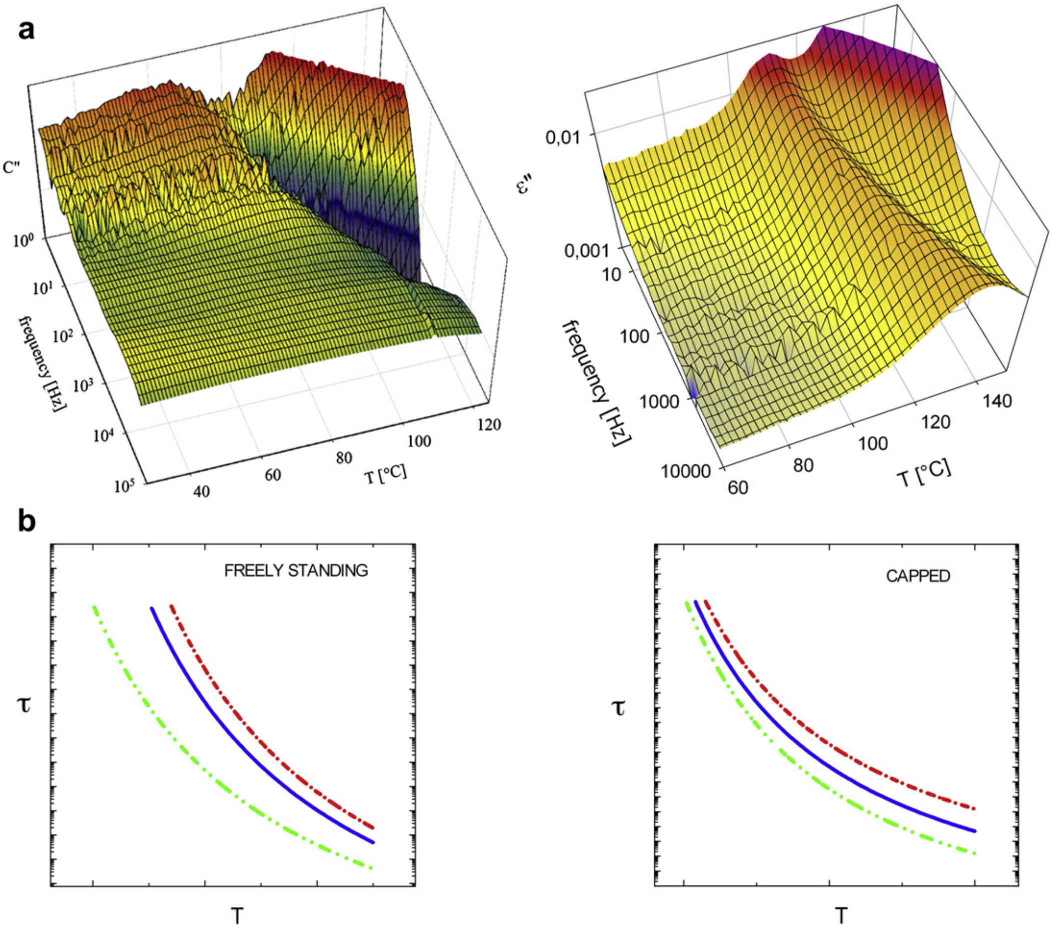

Fig. 1. (a) Comparison between the frequency and temperature dependence of the imaginary part of the complex capacitance of a 40 nm thick freely standing membrane of PS (932,000 g/mol) and the dielectric loss (scaling with the capacitance via a geometrical factor) of a 45 nm thick film of PS (932,000 g/mol) capped between aluminum electrodes. (b) Sketch of the temperature dependence of the structural relaxation time (blue) and of the peak broadening; green and red lines respectively indicate the onset and the offset of the α-peak [For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.].

layers having both surfaces not in contact with a solid substrate. Measurements of the complex electric capacitance were performed using a high-resolution dielectric analyzer (Alpha Analyzer, Novocontrol Technologies) under high vacuum, in the temperature region from above the bulk glass transition down to room temperature and in the frequency domain from 1 Hz to 1 MHz. Integrity of the samples and their freely standing character after several heating cycles above bulk T_g was confirmed by atomic force microscopy. In particular measurements shown in this work are related to the second cooling scan (~ -0.5 K/min) from $T_g^{BULK} + 30$ K down to room temperature. Annealing up to $T_g + 50$ K did not affect the position nor the shape of the structural peak. A full description of the experimental procedure can be found in Ref. [16].

A straightforward method to investigate the structural relaxation is the analysis of the imaginary part of the electric capacitance, C''. This last quantity is proportional to the dielectric loss ε'', via a geometrical factor determined by the cell dimensions. Thermally activated processes, in fact, manifest as peaks both in the frequency (f) and in the temperature (T) dependence of this quantity. The determination of the traces of the structural relaxation as maxima in either isothermal, $f(T)$, or isochronal, $T(f)$, representations is equivalent, but due to the low dipolar activity of PS, a reliable analysis could only be performed in the temperature domain. Moreover, the analysis of isochronal spectra allows a direct comparison with results obtained by techniques such as Brillouin light scattering [21], ellipsometry [9] and fluorescence methods [17], where T_g is determined on the basis of discontinuities in the temperature dependence of appropriate physical quantities in the glass and in the liquid. Fig. 1a shows the comparison between the 3-dimensional plot of $C''(f, T)$ for freely standing (left) and $\varepsilon''(f, T)$ for capped (right) films of PS of the same molecular weight and comparable thickness. In both cases a single relaxation process, attributed to the α-relaxation of PS, is present. Its activation energy (E_a) increases upon cooling, causing a pronounced bend towards lower frequencies. Although this is a common feature of the glassy dynamics, arising from the strong increase in activation energy of the structural process in proximity of the glass transition, what surprises is a tremendous asymmetric broadening of the structural peak in the freely standing films (see also sketch in Fig. 1b). Isochronal representations of the imaginary part of the capacitance revealed, in fact, a relaxation scenario completely different from what observed in bulk and capped samples, see Fig. 2a. In isochronal representations at low frequencies, the low-temperatures tail of the α-peak extends well below room temperature. For a 225 nm thick membrane, at 4.5 Hz the width at half height reaches 56 K see Fig. 2a, a value which reduces to 35 K at 300 Hz. The broadening increases with the film thickness but is always less pronounced at high temperatures. On the contrary, in bulk samples of PS, the structural relaxation appears as a nearly symmetric peak with a full width at half height of 17 K at 4.5 Hz, increasing to 24 K at 300 Hz. The behavior of freely standing films is noteworthy different from what observed in nanolayers of PS confined between solid interfaces [19], where the broadening

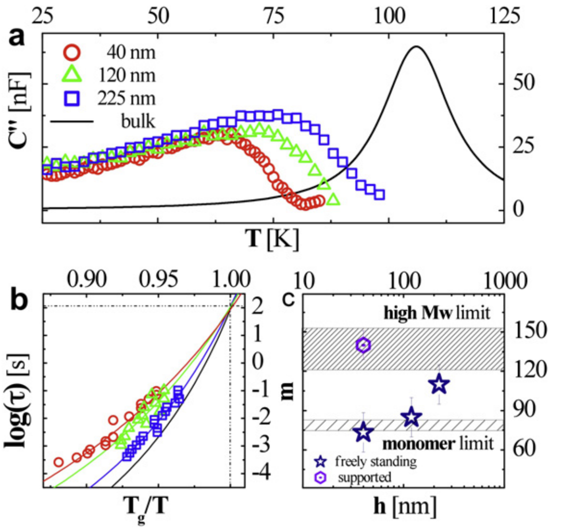

Fig. 2. (a) Isochronal representation ($f = 4.5$ Hz) of the imaginary part of the complex capacitance for freely standing films of PS of different thickness. A peak of arbitrary intensity but the same peak maximum and full width at half height as for bulk samples has been added for comparison. (b) Fragility plot: logarithm of the structural relaxation time as a function of the ratio between T_g and T. Same symbols as in the top panel were used (c) Thickness dependence of the dynamic fragility. Patterned area represents the low and high M_w limiting values for the fragility of polystyrene within the experimental ranges reported in literature.

increases at higher frequencies as in bulk (see sketch in Fig. 1(b)) and at higher surface/volume ratios (reduction of the thickness) [22].

For a given distribution in relaxation times, the width of the α-peak in the isochronal representation is directly linked to the activation energy of the molecular processes involved. Sharper peaks correspond to higher values of E_a, i.e. processes are detectable at a given frequency within smaller temperature windows. In the supercooled regime, a modest reduction of the temperature leads to a progressive increase in the viscosity and thus in the structural relaxation time (τ). As a consequence, E_a increases upon cooling, and the α-peak sharpens in isochronal representations at lower frequencies. The broadening here observed in proximity of T_g cannot be explained on the basis of a drop in the activation energy upon cooling, which would lack of a physical basis. Moreover, this hypothesis would not justify the large asymmetry of the peak.

What mechanism could originate this broadening? We think that both trends found for the maximum of the τ relaxation and its peak shape are clear manifestations of a gradient of glass transition temperatures [23,24] across the film thickness induced by an enhanced molecular mobility at the two free surfaces [25] of the membrane. The existence of a similar asymmetric broadening towards lower temperatures was already observed by Kawana and Jones [26] by means of ellipsometric measurements in films of PS with one free surface and recently revisited by Kim et al. [27] We could rationalize the phenomena observed in the spectra of freely standing films translating recent experimental and theoretical observations into an equivalent dielectric response.

The motion of polymer chains at the very interface with air (or vacuum) is facilitated by different molecular configurations arising from an intuitive increase of free volume. Moreover, it is noteworthy mentioning that a growing number of experimental works suggests that the origin of similar deviations from bulk behavior (reduction of T_g) are related to nonequilibrium chain conformations arising from sample preparation, for a Review see Ref. [8]. Comparison with supported films [28] suggests that, given the particularly high M_w of the polymer, the observed invariance of the α-peak during different thermal cycles might be related to a metastable state with a tremendously long lifetime, probably exceeding several weeks. Regardless their nature, the perturbation in the chain configurations propagate towards the core of the film and die out gradually with the distance from the polymer/air interface, giving rise to a smooth gradient of relaxation times, or equivalently to a distribution of glass transition temperatures, as in the profiles sketched in Fig. 3a. We modeled free surfaces as potential barriers imposing an exponential decay of the relaxation temperature as proposed by several molecular dynamics simulations [29–31], see Fig. 3a, and verified the equivalence of such profile with our experimental results. In particular, we considered the dielectric response of a membrane with a depth profile of the maxima of the structural peak in isochronal representations, T_α, see Fig. 3b. Note that $T_g \equiv T_\alpha (f = (2\pi 100\ \mathrm{s})^{-1}) = 1.6$ mHz. Sampling the relaxation temperatures $T_\alpha{}^i$ with a fixed step ΔT_α, i.e. considering the thickness range satisfying the condition $|T - T_\alpha{}^i| \leq T_\alpha$, yielded the thickness contribution Δx^i of each sub-layer, which we used as weight coefficients. We used a symmetric function to reproduce the response of each sub-layer [19], and obtained the dielectric response of the equivalent dielectric circuit summing up the different contributions as capacitances in parallel [31] via:

$$C''(T) = C_0 \sum_i \frac{\Delta x^i}{1 + \left[b^{-1}\left(T - T_\alpha^i\right)\right]^2} \tag{1}$$

where C_0 is the value of the geometrical capacitance of the measurement cell per unit of thickness, b is the half width at half height of the structural process in bulk, and Δx^i and $\overline{T}_\alpha^i$ are here the respective thickness and the average relaxation temperature of the i-th layer.

Why is the broadening smaller in the thinner films and at higher temperatures? Experimental evidence by Torkelson et al. suggests that supported films thinner than the perturbation length scale introduced by a free surface ~40–70 nm at the upper interface of a supported film) cannot sustain the full gradient of glass transition temperatures [17,23,27]. Consequently, because of the presence of even two facing free surfaces, freely standing films thinner than a threshold thickness should not contain any bulk component. The resulting smaller range of glass transition temperatures reachable in these membranes limits the broadening of the α-peak. We reproduced this trend in films thinner than 2λ, where λ is the length scale over which surface effects extend, see Fig. 3b. From our

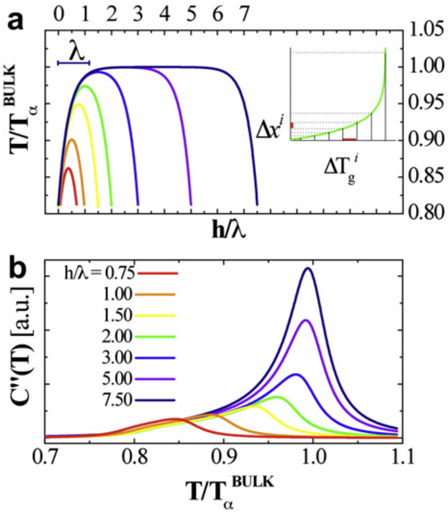

Fig. 3. Profiles of glass transition temperatures along the membranes of different thicknesses normalized to the length scale necessary to recover the bulk behavior (a) and corresponding isochronal representations (b).

measurements we obtain $\lambda \sim$ 150–200 nm $\sim$6–7 R_g), a value larger than what found in supported films of PS, i.e. 2 nm via Atomic force microscopy and 40–70 nm via fluorescence spectroscopy [23,32]. In addition to technique-specific averaging issues inducing different transition breaths [27], the presence of two interfaces with air (or vacuum, as in our case) might allow the propagation of smoother gradients of molecular mobility, otherwise inhibited by interfacial interactions with solid interfaces. The penetration depth induced by substrate interactions can affect distances exceeding several tens of nm, as experimentally verified for the relaxation time of free surfaces of isotactic poly(methyl methacrylate) on silicon and aluminum oxide, where $\lambda \sim$ 180 nm, regardless the molecular weight of the chains [33].

Furthermore, in analogy to our idea on supported films [20,22], we expect that the gradient in mobility generates a position dependent perturbation of the high temperatures limit of E_a ($T >$ 1.2–1.3 T_g). Similarly to bulk samples, the apparent activation energy of each single sub-layer decreases upon heating. On the contrary, due to the intrinsic form of the temperature dependence of τ, the differences between the E_a of each sub-layer increase upon cooling leading to the characteristic diverging shape as shown in the 3D representation of the loss spectra. This effect expresses itself as a reduction of λ at higher temperatures, justified by molecular dynamics simulations [29,30] and by the experimental evidence of Fakhraai and Forrest showing that the enhancement of mobility [25] in the presence of a free surface vanish in the temperature region where the surface relaxation time equals the bulk value.

Embedding gold nanoparticles on surfaces of PS revealed molecular processes taking place in the first $\sim$2–4 nm of material with an almost temperature independent activation energy [25], i.e. free surfaces should have a dynamic fragility lower than the value assumed by the bulk layers of the same material. On the contrary, pinning of polymer chains on attractive interfaces does not affect the dynamic fragility [22,34]. To check the impact of surface chains on the structural process of the whole membrane, we extracted the temperature dependence of the structural relaxation time out of 3D-representations like in Fig. 1. We assigned the traces of the process to those couples of values of frequency and temperature ($f_{\max}$, $T_{\max}$) identifying the maximum of the structural relaxation peak; frequencies were finally converted to times via the relation τ, and the temperature dependence of τ was fitted by the Vogel-Fulcher-Tammann equation [35]. Dynamic fragility, m, was related to the rate of increase of τ upon temperature reduction, as $\frac{\partial \log\tau(T)}{\partial(T_g/T)}\big|_{T=T_g}$, with T_g operationally defined as $T(\tau = 100\ \mathrm{s})$ [35], see Fig. 2b. The expected thickness dependent reduction of the fragility is reported in Fig. 2c. Surprisingly, the value of the fragility of 40 nm thick membranes crosses the monomer limit [36,37]. This evidence suggests that the surface dynamics of polystyrene does not share the same cooperative nature of its structural relaxation in bulk and its impact on the properties averaged over the whole membrane is enormous.

As a direct implication of the peculiar features just described, the properties of freely suspended membranes neither correspond to those in bulk nor to a simplified scenario where the structural relaxation peak is merely shifted towards lower temperatures. In particular, we expect a decoupling between observables related to rotational and translational motion stronger than in bulk. The enrichment of mobile fractions, given by the reduction of T_g and the long extension of the α-peak tail towards lower temperatures, in fact, affects mostly those quantities, like tracer diffusivity, being proportional to the inverse of τ. The resulting enhancement of diffusion at the free surfaces will provoke a virtual thinning of the membrane, and thus enhanced gas permeability. Models on transport and elastic properties of polymer nanomembranes and theoretical consideration on the effect of free surfaces will take advantage from the experimental evidence here reported on the peculiar aspects of the segmental chain mobility in freely standing films.

Acknowledgments

SN acknowledges FWO (Fonds Wetenschappelijk Onderzoeks – Vlaanderen) for a postdoctoral scholarship and Cinzia Rotella (Dept. Physics and Astronomy, KULeuven) for preparation of the membranes.

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