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Communications to the Editor

Segmental Mobility and Glass Transition Temperature of Freely Suspended Ultrathin Polymer Membranes

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Extensive investigation of polymer layers confined in nanometer-sized geometries revealed that the presence of an absorbing substrate or a free surface alters properties of polymers such as biaxial creep behavior,[1] flow and intermolecular entanglements,[2] diffusion of small molecules inside the matrix,[3] crystallization kinetics,[4,5] physical aging,[6] the glass transition temperature (T_g),[7] and thus local chain (segmental) mobility.[8−12] In bulk, the local chain mobility can be investigated by means of several experimental approaches.[13] On the contrary, due to obvious instrumental difficulties, a technique probing the local chain dynamics of freely standing ultrathin polymer films was not available so far.

In this Communication, we introduce a novel experimental method taking advantage of the sensitivity of dielectric spectroscopy (DS) and being able to probe the segmental dynamics of freely standing ultrathin polymer layers over a broad frequency range (1 Hz−1 MHz) without altering or eliminating[14] their two free surfaces. The glass transition temperatures assigned by the approach described in this Communication are in excellent agreement with data from the literature.

In our approach, polymer films are suspended over interdigitated comb electrodes, IDE.[15] The electric signal is measured by applying an ac voltage to elevated metallic electrodes made up by the two interdigitated comb structures deposited on a highly insulating substrate (see Figure 1a). For films of thickness D much smaller than the separation between two neighbored electrodes (∼10 μm), the electric field lines penetrate inside the layer with a direction *parallel* to the surface. Consequently, the individual complex electric capacitances of all sublayers (of thickness D_i) constituting the polymer membrane add up to the total capacitance according to $C^*_{\mathrm{TOT}}(\omega,T,D) = \sum_i C^*_i(\omega,T,D_i)$, an expression that holds for any angular frequency ω and temperature T.[16] Under these conditions, the different contributions to the relaxation spectra are linearly superimposed. The comb electrode geometry, in fact, avoids ambiguities arising from spectra of ultrathin films probed by an electric field *orthogonal* to the surface, as in the parallel plates geometry[10] where capacitances enter in a series model, $C^*_{\mathrm{TOT}}(\omega,T,D)^{-1} = \sum_i C^*_i(\omega,T,D_i)$. To prove the feasibility of our technique, we investigated the structural relaxation dynamics of atactic

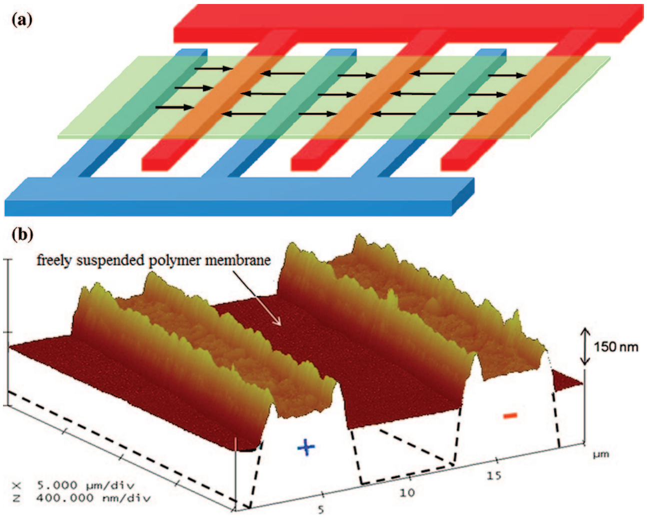

Figure 1. (a) Schematic representation of the IDE chip; the red and blue fingers are at opposite potential. The height of the structures is 0.8 μm, the width of each finger is 5 μm, and the mean distance between two neighbored fingers is 8 μm. The black arrows represent the direction of the E-field inside the film. (b) AFM image 20 μm × 20 μm (topography) of a 65 nm thick film of PS after annealing at 70 °C above its T_g (see text). The white dashed lines reproduce the structure of the empty chip. The peaks at the edge of the electrodes metal build-ups already present in the empty chip.

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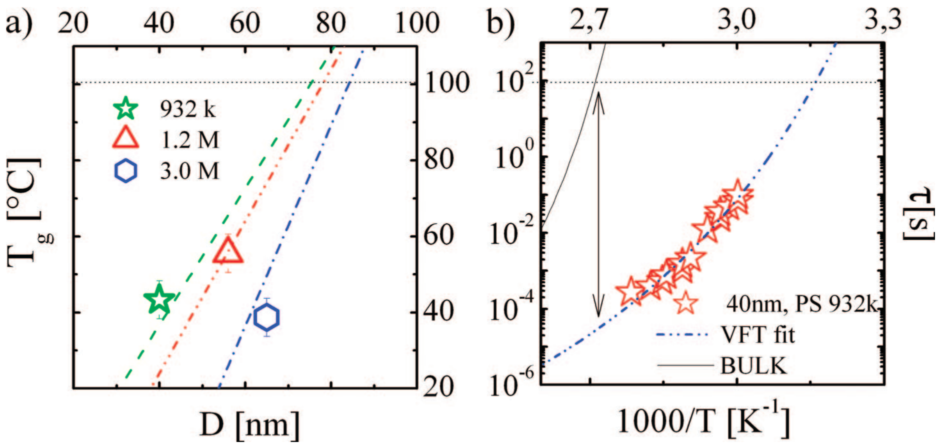

Figure 2. (a) Thickness dependence of T_g of freely standing membranes of high molecular weight PS. The colored lines are readapted from the scaling law proposed in ref 19. (b) Relaxation map of the local chain mobility for a film of PS (932K) of 40 nm. The dashed line is a VFT fit to the experimental points. The solid line is a VFT fit for a PS bulk sample, from ref 20.

polystyrene, PS, a system widely explored in both supported and freely standing geometry.[17−19]

Because of the micrometer spacing between the electrodes, IDE allow the employing of higher voltages compared to the parallel plate geometry, ensuring a better signal/noise ratio. In fact, keeping constant the electric field, the maximum voltage applicable in the IDE is larger than the one in the parallel plate geometry by a factor equal to the ratio between the distance separating the fingers (~10 μm) and the film thickness (~10−100 nm). The low intensity of the applied electric field (~10^5 V/m) does not alter the properties of the investigated materials but acts a perturbation in the linear regime response (approximation valid for field strengths $\leq 10^6$ V/m).

Atactic polystyrene of three different molecular weights ($M_w = 932$, 1200, and 3000 kg/mol, PDI < 1.3) was used as received from Polymer Source Inc. Because of the low value of the intrinsic dipole moment of PS, the polymer was doped with a small fraction (0.5 wt %) of 4,4′-(*N*,*N*-dibutylamino)-(*E*)-nitrostilbene, (DBANS), an organic molecule with a high dipole moment acting as "dielectric probe". The feasibility of this approach has been already tested successfully in bulk and confined polymer layers by means of both dielectric[20,21] and fluorescent probes.[6,22−24] Here, the addition of DBANS solely increases the sensitivity of our measurements and does not alter the segmental mobility. Exact amounts of the polymer and the probe were mixed together and dissolved in chloroform; ultrathin films of PS with different thicknesses were prepared by spin-coating drops of solutions of different concentrations on freshly cleaved mica. Film thicknesses were determined by ellipsometry on reference samples prepared under the same spin-coating conditions (same concentration, spin speed, and time) and deposited on Si wafer. Freely standing films were obtained by a standard water transfer technique.[19] Well-dried and equilibrated films were transferred to the top of the IDE comb electrodes for the dielectric measurements. Consecutively repeated thermal ramps in heating and cooling resulted in annealing of the film for a minimum of 3 up to 6 h above bulk T_g (see Supporting Information).

Measurements of the complex electric capacitance of PS were performed under high vacuum in the temperature region from above the bulk glass transition down to room temperature using a high-resolution dielectric analyzer (Alpha Analyzer, Novocontrol Technologies). The response of the material originates from the correlated fluctuations of permanent dipole moments which provide the physical link between the molecular motion and the interactions with an external electric field.

IDE structures were purchased from Xensor Integration. Each metal comb structure (finger) is 5 μm wide and 0.8 μm high, and the mean distance between two consecutive oppositely charged finger is 8 μm (see Figure 1a). Contributions of the empty chip to the dielectric response were subtracted. A detailed report on the dielectric characterization of the IDE chips and on the related issues regarding to the measurements is in preparation.

Atomic force microscopy was used in order to verify the stability of the freely standing ultrathin layers after repeated dielectric measurements cycles. Samples were imaged using a MultiMode (Digital Instruments) operating in tapping mode at room temperature with high aspect ratio silicon tips. Figure 1b displays a 20 μm × 20 μm AFM topographic image of a 65 nm thick film of PS ($M_w = 3 \times 10^6$ g/mol) deposited on the top of IDE after a complete thermal measurement cycle where the sample was brought up to 70 °C above the film T_g. The polymer membrane was found to be suspended over the substrate, laying 150 nm from the top of the electrodes and its root-mean-square roughness was on the order of 1 nm. This proves that the film, even after the measurement, remains intact and freely standing. Refer to the Supporting Information for an image at a larger scanning area (50 μm × 50 μm).

The response of the film is dominated by a peak which shifts in temperature and frequency following a super-Arrhenius activation law. The peak is attributed to the structural (or α-) relaxation of polystyrene, the dielectric manifestation of the glass transition dynamics, which is usually assigned to the correlated motion of several repeating units belonging to the same or different macromolecules. The experimental data were analyzed by means of model-independent parameters, relating the traces of the α-modes to those couples of values of frequency and temperature (f_{max}, T_{max}) identifying the maximum of the structural relaxation peak.[13]

The α-relaxation time, τ_α, was calculated from f_{max}, via the relation $2\pi f_{max}\tau_\alpha = 1$, and its temperature dependence was fitted by means of the Vogel−Fulcher−Tammann (VFT) equation

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

which describes a thermally activated process with an apparent activation energy $E_{app}(T) = k_B T B T_0 (T - T_0)^{-1}$ that increases upon cooling.[25] Following a common convention, the glass transition temperatures of the samples were obtained by extrapolating eq 1 to $T_g = T(\tau_\alpha = 100\ \mathrm{s})$. In Figure 2a we compare the T_g values of films of different thickness and different molecular weight with the scaling law proposed by Dalnoki-Veress et al.[19] for freely standing ultrathin films of high molecular weight PS ($M_w \geq 514$ kg/mol). The data obtained via our new experimental approach are in excellent agreement with those obtained by Brillouin light scattering,[18,26] ellipsometry,[19,26] and recently also by fluorescent methods.[24]

This new finding proves that the tremendous T_g reductions in freely standing films of PS as previously observed on the basis of discontinuities in the volume thermal expansivity are truly related to a correspondingly huge shift in the time scale of the structural relaxation. This shift, expressed by the ratio between the relaxation time of the film and the one in bulk at a given temperature, approaches the value of 10^{-7} (i.e, the relaxation peaks are separated by 7 decades in frequency) at bulk T_g and further increases upon cooling (see Figure 2b). Such temperature dependence is in agreement with our previous work on supported films[10,27,28] and with several other experimental observations[6,29] and computer simulations.[30]

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Supporting Information Available: AFM image over a larger scanning area and scheme of a typical measurement cycle. This material is available free of charge via the Internet at http://pubs.acs.org.

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