

1 Samples Preparation

Linear polystyrene (PS) from Polymer Source Inc. with the following molecular weights was employed: $M_w = 1408$ kg/mol, $M_w/M_n = 1.17$ and $M_w = 572$ kg/mol, $M_w/M_n = 1.1$. Toluene (99.8 %; Sigma-Aldrich) was used to dissolve PS.

Freestanding PS films with thicknesses $h \geq 1\mu m$ were prepared by solvent casting PS solutions into freshly cleaned Petri dishes of varying sizes (Duran Group), placed on a horizontal bench under the fume hood. After casting of the PS solution, the samples were left at room temperature under the fume hood during at least 12 hrs before being transferred to an oil free vacuum oven at 433 K, where they were dried during 4 days. After annealing, the solvent casted films were removed from the Petri dishes by the floating on water method. The thickness of the so-prepared samples was verified by Scanning Electron Microscopy (SEM).

Freestanding PS films with thicknesses $h < 1\mu m$ were prepared by spin coating PS solutions onto ultraflat glass slips (18x24 mm; Menzel-Glaser), previously rinsed in acetone. Spin-coating was realized with a speed of 50 rpm, during 30 s, under the fume hood. The thickness of the films was controlled by varying polymer concentration. As-deposited PS films were annealed in vacuum at 433 K for 4 days in oil free vacuum oven at 433 K, where they were dried during 4 days. After annealing, the solvent casted films were removed from the Petri dishes by the floating on water method. The thickness of the so-prepared samples was verified by Scanning Electron Microscopy (SEM).

PS films were also prepared between two aluminium electrodes. Glass slides of 25x25x1 mm were used as substrate. The slides were cleaned in a first step in an ultrasound alkaline bath at 333 K for 15 min followed by a second ultrasound bath with ultrahigh purified water (Millipore, resistivity > 18 MΩ/cm). Then the glass plates were first rinsed in acetone and then in toluene. After that, the substrates were dried in a nitrogen flow. An aluminium electrode (width 2 mm, height ca. 60 nm) was deposited onto the glass substrate by thermal evaporation in an ultrahigh vacuum (10^{-6} bar). After the evaporation of this first electrode, the plates were again rinsed in acetone and toluene. Subsequently, a thin polymer film was spin coated from a filtered toluene solution at 3000 rpm. After spin coating, the sample was annealed at a temperature well above the bulk glass transition (433 K for 4 days under vacuum). The preparation was finalized by the evaporation of the counter-electrode on the top of the polymer film. Further detail on Al-capped films preparation can be found elsewhere.

2 Standard Differential scanning calorimetry

For the preparation of differential scanning calorimetry (DSC) pans, the thin films were repeatedly stacked until the weight of the sample was high enough (> 2 mg) to get a reasonable signal. Thus, for the thinnest films, about 100 ultrathin films had to be stacked. The so-prepared DSC pans were subsequently dried at 343 K under vacuum during one day, in order to eliminate the water used to remove the films from the glass substrates.

The DSC measurements were carried out on a DSC-Q2000 calorimeter from TA-Instruments, calibrated with melting indium. The measurements of $T_g$ were performed under nitrogen atmosphere on samples placed in aluminium pans at a cooling rate of 20 K/min. To do so, all samples were first heated to 443 K, a temperature substantially higher than the $T_g$ of bulk PS to ensure that the specified cooling rate is reached when crossing $T_g$, stabilized for 1 min to erase their previous thermal history, and subsequently cooled down to room temperature, at 20 K/min for data collection. To prevent chain interdiffusion.
of the stacked thin films, the samples were kept at temperatures higher than the PS bulk $T_g$ for times as short as possible. However, as estimated in Ref. $^3$, the time scale for interdiffusion for a very high molecular weight PS, is extremely long, which ensures to avoid interdiffusion of the layers in the time scale of the DSC experiments and at the highest achieved temperature. The experimental conditions adopted to measure the $T_g$ of stacked films, included PS molecular weight, are very similar to those employed by Koh and Simon. $^4$ Thus, in our case each film behaves as a single film and not like the total stack. $^5$ The absence of interdiffusion of the stacked PS layers was also verified by the reproducibility of the $T_g$ measurements on the same sample after several temperature cycles.

3 AC calorimetry

Thin films supported by the sensor (XEN 39390, Xensor integrations, NI), with one free surface, were prepared for the measurements with differential alternating current (AC)-chip calorimeter. Firstly, the sensor was cleaned by dropping a droplet of toluene to its centre in order to remove the dust and organic contaminants on the surface by spinning. This procedure was repeated twice, followed by annealing under vacuum at 473 K for 2 h. The annealing process is necessary to cure the epoxy resin completely, which was used to glue the chip to the housing.

Calorimetric measurements on ultra-thin polymer films has been made possible with the development of the ultrasensitive differential AC-chip calorimeter. Smaller-area calorimeter chips were used as a measuring cell for the measurements. The heater is located in the centre of the free standing thin silicon nitride membrane of about 1 $\mu$m thickness supported by a Si frame. Such a nanocalorimeter chip has a hot spot area of about 30x30 $\mu$m, featuring a 6-couple thermopile within two 4-wire heaters (bias and guard heater). The heater and thermopile are covered by a thin silicon oxide layer with the thickness of 0.5-1 $\mu$m for the protection of the membrane. Temperature-scan-mode was used in the measurement. The temperature was changing continuously over a temperature range from 333 K to 453 K for each single frequency. During the measurement the heating power is kept constant at about 25 $\mu$W. Details can be found elsewhere. $^6$

The underlying heating/cooling rate is 2.0 K/min under protecting nitrogen atmosphere. In this measurement, the amplitude of the complex differential voltage as a function of measuring temperature can be obtained. The dynamic glass transition temperature is determined as the half step temperature of the amplitude and/or the peak of its phase angle.

4 Broadband dielectric spectroscopy

A high resolution Novocontrol Alpha analyzer, was used to measure the complex dielectric function $\varepsilon^{\prime\prime}(\omega) = \varepsilon^{\prime}(\omega) - i \varepsilon^{\prime'}(\omega)$, in the frequency range from $10^{-1}$ to $10^6$ Hz. The capacitor assembly was kept in a nitrogen stream of the cryostat, with a temperature stability better than $\pm$ 0.1 K over the duration of the experiments (Novocontrol Quatro). The measurements were carried out as isothermal frequency scans recording $\varepsilon^{\prime\prime}(\omega)$ every 2.5 K on cooling over a temperature range between 313–403 K for freestanding films and 313–453 K for Al-capped films. For freestanding films, the highest measured temperature was limited to 403 K in order to avoid any possible interdiffusion of the PS thin layers during the BDS measurements. $^3$ The absence of interdiffusion between the stacked thin films was verified by the good superposition of the BDS spectra subsequently obtained on heating and cooling.

The preparation of Al-capped samples has been already discussed. Regarding the measurements on freestanding films, the samples were prepared by transferring the single thin films, floating on water, onto a gold electrode, one thin film onto the other, until reaching a total sample thickness of about 2 $\mu$m. Such thickness permits avoiding the occurrence of short cuts during the BDS measurements when using a traditional capacitor assembly consisting of two parallel gold electrodes containing the sample. Apart from the information on the polymer segmental dynamics, BDS measurements also deliver the thermal $T_g$. This is obtained from the discontinuity of the real part of the dielectric permittivity ($\varepsilon^{\prime}$) at relatively high frequency (in this case 10$^5$ Hz), where this magnitude is associated with the number of dipoles per unit volume and, therefore, the density. $^7-9$ It is worth noticing that the possible effect on $\varepsilon^{\prime}$ of films packing during the measurement can be ruled out, since repeated scans alternatively on heating and cooling on the same samples provided exactly the same discontinuity of $\varepsilon^{\prime}$ at the $T_g$.

The conductivity, the electrode polarization and other contributions were generally encountered in all spectra. Therefore, these contributions were removed from the raw spectra for the determination of $\tau$ of the $\alpha$ process, and the evaluation of its relaxation width. To do so, for each spectrum of $\varepsilon^{\prime\prime}(\omega)$ plotted in the temperature domain, a polynomial function was used to fit the data obtained at relatively high and at low temperatures - which do not contain any contribution from PS $\alpha$ process. These contributions were subsequently taken off from the whole spectrum to obtain the neat contribution of the $\alpha$ process.

To summarize, in the same measurement one can simultaneously extract the behavior of $\varepsilon^{\prime\prime}$ as a function of temperature and at different frequencies and the temperature dependence of $\varepsilon^{\prime}$ at relatively high frequency (10$^5$ Hz in the present work). The former delivers information on the spontaneous fluctua-
tions underlying the α relaxation, whereas the latter delivers information on the density of the material. Thus, this kind of analysis provides the thermal glass transition as a discontinuity in \( \varepsilon' \).

References