

A direct comparison of surface and bulk chain-relaxation in polystyrene

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Abstract. Near-edge X-ray absorption fine-structure (NEXAFS) spectroscopy was used to measure simultaneously the relaxation rates of polystyrene (PS) molecules at the free surface and in the bulk. The samples were uniaxially stretched and annealed at temperatures below the bulk glass transition temperature of PS. The surface and bulk chain relaxation was monitored by measuring the partial-electron and the fluorescence NEXAFS yields, respectively, both parallel and perpendicular to the stretching direction. The decay of the optical birefringence was also measured to provide an independent measure of the bulk relaxation. Relaxation of PS chains was found to occur faster on the surface relative to the bulk. The magnitude of the surface glass transition temperature suppression over the bulk was estimated based on the information on the temperature dependence of the rates.

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Introduction

Over the last few decades there has been much work in the study of bulk chain relaxation dynamics in a wide variety of bulk amorphous polymers [1,2] including polystyrene [3–5] using dynamic mechanical, rheo-optical, photon correlation spectroscopy [6], dielectric relaxation [7] and nuclear magnetic resonance (NMR) techniques [8]. Chain relaxation dynamics at the free surface of amorphous polymers has been previously studied using surface-sensitive techniques such as atomic-force microscopy (AFM) [9] and sum-frequency generation [10]. However, these techniques lack the sensitivity for the bulk chain relaxation dynamics. Direct and simultaneous measurements of both surface and bulk chain dynamics in the same sample are rare because of the lack of suitable experimental technique. In this work, we use NEXAFS spectroscopy to monitor simultaneously the surface and bulk chain relaxation in polystyrene.

Liu and coworkers first used NEXAFS to measure the segmental relaxation of polystyrene (PS) [11]. Their measurements revealed that the surface and sub-surface relaxation rates, as measured by the partial and total electron yield, were similar to that of PS bulk. More recently, Tsang *et al.* [12] and Schwab *et al.* [13] have investigated the depth dependence of the glass transition temperature

(T_g) using optical birefringence measurements on PS films with different extents of surface rubbing. Based on the notion that only the depth of chain orientation increased with the extent of rubbing while the magnitude of orientation stayed constant, a depth-dependent reduction in the glass transition temperature in the near-surface region was discovered. Their results are highly relevant to the present work and will be discussed later.

We have recently applied NEXAFS to probe the difference in the local chain mobility of the free surface *versus* bulk [14]. PS samples six mm thick were uniaxially deformed; the relaxation of both the surface orientation and the bulk was determined simultaneously from the partial electron yield (PEY) and fluorescence yield (FY) signals, respectively. In contrast to the work of Liu and coworkers, our result revealed an evidence of surface chains outpacing the bulk ones in their relaxation kinetics. In the previous work, the pre-oriented PS samples were annealed at 60 °C for a certain amount of time, removed from the heating chamber and cooled to room temperature, and then placed inside the NEXAFS instrument where the data were collected. The above procedure was repeated for each additional data point. Because of this rather time-consuming process, only a limited number of data points were collected at a single temperature. The present work is a continuation of the previous work with major changes in both sample preparation and data collection. Instead of

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conducting the measurements at one temperature (60 °C), relaxation rate at several temperatures ranging from 60 °C to 105 °C was measured. In addition, NEXAFS experiments were collected *in situ*, *i.e.*, samples were heated and maintained at a preset annealing temperature inside the NEXAFS high vacuum chamber and the data were collected continuously without any interruption. During the annealing and data collection the chain relaxation occurred in a zero strain condition, that is, no annealing-induced deformation or sample shrinkage was allowed. This is in contrast to the previous work where the stress state during the relaxation step was not well controlled. For pre-oriented bulk samples used in the previous work, annealing results in a substantial shrinkage of the sample and it often leaves the sample surface distorted, a condition not suitable for quantitative NEXAFS measurements. For quantitative NEXAFS measurements it is desirable to maintain the flatness of sample surface. As a result, samples were clamped between metal plates during the annealing step in the previous work. Due to the friction and compression forces exerted by the metal plates, the relaxation step was likely not at a stress-free condition. Some dimensional recovery was noticed after annealing, revealing possible strain distribution in the specimens. In the present work the sample thickness was maintained at 2 μm . This thickness is much smaller than that used previously. The solvent cast PS films adhered securely to a thick silver foil, which assured a uniform temperature distribution on the sample. In addition, the silver foil provided mechanical rigidity that prevented the PS film from shrinking.

A small number of birefringence measurements were also performed at elevated temperatures to determine the relaxation rates averaged over the entire sample thickness of 2 μm . A comparison between the relaxation rates obtained from birefringence and the FY data will be provided later in the paper.

The main objective of this work is to determine the temperature dependence of the relaxation rates of PS chains on the free surface and the bulk. The activation energy calculated from the temperature-dependent data is expected to shed light on possible difference in the relaxation mechanisms between the surface and the bulk. In addition, such information will enable one to estimate the magnitude of surface T_g suppression.

Experimental

A 5% mass fraction solution of a narrow molecular-weight polystyrene ($M_w \approx 228000 \text{ g/mol}$, $M_w/M_n = 1.05$) in toluene was prepared. An annealed silver foil of 25 mm \times 25 mm \times 0.1 mm was dip-coated with the PS solution and allowed to dry in air for 24 h, followed by annealing in vacuum at 120 °C for additional 24 h. This process resulted in 8 μm thick PS films. A copper plate of 1 mm thickness was degreased and dipped in dilute nitric acid in order to remove its native surface oxide. The PS film on the silver substrate was then placed between two copper plates and deformed between two steel rollers at room

temperature. As in any cold rolling process, the friction between the steel roller and the copper plate is expected to generate a shear flow at the outer surface of the copper plate. The PS film was situated at the central plane of the copper-silver/PS-copper sandwich. By virtue of symmetry, the deformation of PS/silver is almost 100% uniaxial even though the outer surface of the copper is deformed in a combination of shear and extensional flows. After cold rolling the PS/silver bilayer was removed from the copper sheet and ready for the *in situ* annealing and NEXAFS measurements.

PS was elongated 4 \times ; the resultant film thickness is estimated to be 2 μm . This thickness was sufficient to avoid the effects of substrate that may alter the free surface behavior [12]. The bonding between PS and the silver plate was sufficient to withstand any delamination or debonding during the subsequent annealing and the NEXAFS measurements. The immense thickness difference between the PS film and the silver substrate ensures that sample shrinkage did not occur during the annealing and the NEXAFS experiments. This represents a significant improvement over the samples used in our previous work. Cold rolling has been used extensively over the last three decades to produce oriented semi-crystalline polymers [15] and we now adopt it in this work to orient PS molecules. What is new of this work is that the thin polymer film was placed between two copper sheets in order to achieve a simple extensional flow of the samples. The orientation of the surface chains is expected to be identical to that of the bulk by virtue of a simple extensional flow. Any deformation of glassy polymers could induce chain rupture, hence results in some low-molecular-weight chains. The cold rolling process used in this work is not exempted from this possibility. However, the samples encounter only extensional flow in this work and any ruptured molecules are expected to distribute uniformly across the sample thickness. This will not affect the difference of relaxation rate between surface and bulk—the main objective of this work. In addition, the deformation was conducted at room temperature and the majority of the NEXAFS measurements were carried out at temperature below the bulk T_g of PS, the likelihood of fragmented chains migrating to sample surface is rather low. Furthermore, the presence of low-molecular-weight chains at surface will make the relaxation process somewhat fast. This will make the difference between surface T_g and bulk T_g even smaller than what reported in this work. In addition, sub- T_g relaxation does not have a strong molecular-weight dependence. The size of the PS/silver films after cold rolling was 25 mm \times 100 mm. A sample size of only 2 mm \times 5 mm was needed for both NEXAFS and birefringence measurements. All samples used in this work were cut from the central strip of a single sheet.

The NEXAFS experiments were carried out on the U7A NIST/Dow Chemical Soft X-ray materials characterization facility at the National Synchrotron Light Source at Brookhaven National Laboratory, Upton, NY. The measurement details including the principles NEXAFS in characterizing the PS surface and bulk structure and a

description of the beam U7A beamline have been given elsewhere [16,17]. The partial electron yield (PEY) and fluorescence yield (FY) signals with normal incidence were collected simultaneously in all instances. Conductive glue was used to secure two samples of pre-oriented PS/silver film to a copper stud (30 mm diameter) to enhance the thermal and electrical conductivities. The pre-oriented PS/silver films were positioned on the stud parallel and perpendicular to polarization vector of the incident soft X-ray beam. The stud was in turn placed in a NEXAFS sample holder equipped with a resistance heating element and a temperature sensor and all the thermal annealing and orientation measurements were conducted inside the NEXAFS instrument where a vacuum of 10^{-8} torr was maintained throughout the run. Approximately 60 s was required for the temperature to reach set points ranging between 60°C and 105°C . This delay time in heating precludes any measurement of a dynamic process with the relaxation time constant in the range of few minutes. Once the set temperature was reached, NEXAFS data were collected continuously and automatically. A complete spectrum at the carbon K -edge was taken every 120 s, shuttling alternatively between the parallel and perpendicular oriented PS films with most of the sampling points focused at the $1s \rightarrow \pi_{\text{C}=\text{C}}^*$ transition (at 285.5 eV). After 286 eV sufficient data points were collected only for post-edge normalization purpose. This process continued until the change in the magnitude of NEXAFS signal was no longer noticeable. The condition used in the present NEXAFS measurement did not cause any beam damage of the sample, no change in the NEXAFS spectrum was noticed on fully relaxed samples after many scans.

A limited number of birefringence measurements were also conducted to measure the relaxation rate averaged over the entire sample thickness of $2\ \mu\text{m}$. An optical microscope equipped with a tungsten light source and an interference filter (532.0 nm with a half-bandwidth of 8.6 nm) was used to measure the optical birefringence of the PS film on the silver substrate in a reflection mode at normal incidence. The reflected light intensity from the sample at cross polarization condition was recorded with a photon counter (Oriel Photon Counting System model 76915) [18]. This system allows for a data collection time faster than one second.

Results

The PEY (standard uncertainty 1%) and FY (standard uncertainty 5%) signals for each sample were collected with the electric field vector of the incident X-ray beam perpendicular and parallel to the sample orientation direction, respectively. The incident soft X-ray beam was kept normal to the sample surface in all instances. Figure 1 shows typical PEY and FY carbon K -edge NEXAFS spectra taken from a sample annealed at 80°C for 1 min and 89 min. A spectrum of the carbon K -edge including both the pre-edge and post-edge regimes is given in the inset of Figure 1a. The portion of the $1s \rightarrow \pi_{\text{C}=\text{C}}^*$ transition (at 285.5 eV) is expanded for clarity. The area under

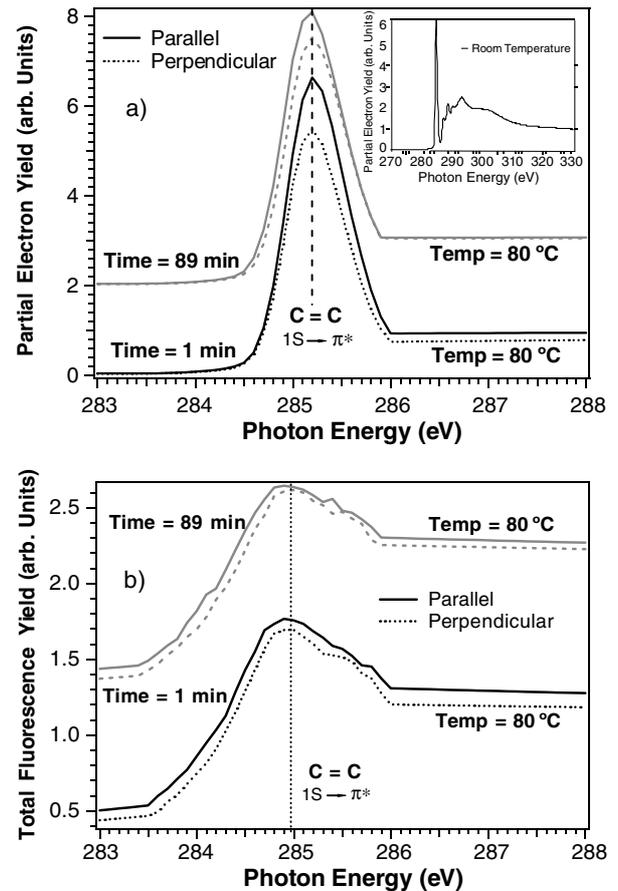


Fig. 1. a) The 285.5 eV peaks ($1s \rightarrow \pi_{\text{C}=\text{C}}^*$) of NEXAFS partial electron yield spectra from polystyrene annealed at 80°C along both the parallel and perpendicular directions. A decrease in the difference in peak height between the parallel and perpendicular ones is clearly visible as the annealing time reaches 89 min. The area under the curve was used in the calculation of dichroic ratio. An example spectrum including both the pre-edge and post-edge regions is given in the inset. b) The 285.5 eV peaks ($1s \rightarrow \pi_{\text{C}=\text{C}}^*$) of NEXAFS fluorescence yield spectra of the polystyrene film annealed at 80°C along both the parallel and perpendicular directions. A decrease in the difference in peak height between the parallel and perpendicular ones is clearly visible as the annealing time reaches 89 min. The area under the curve was used in the calculation of dichroic ratio.

this peak was used to quantify the chain orientation using a dichroic ratio, as described previously [11]. The data in Figure 1 reveal a strong enhancement of the $1s \rightarrow \pi_{\text{C}=\text{C}}^*$ signal intensity when the electric field vector of the incident beam is parallel to the orientation direction. The phenyl π^* orbitals are oriented normal to the phenyl ring and will typically have some components parallel to the chain axis. Hence the intensity of the $1s \rightarrow \pi_{\text{C}=\text{C}}^*$ signal has been used to characterize the backbone orientation [11]. The difference in the $1s \rightarrow \pi_{\text{C}=\text{C}}^*$ signals between the parallel and perpendicular scans decreases with increasing annealing time in both the PEY (Fig. 1a) and

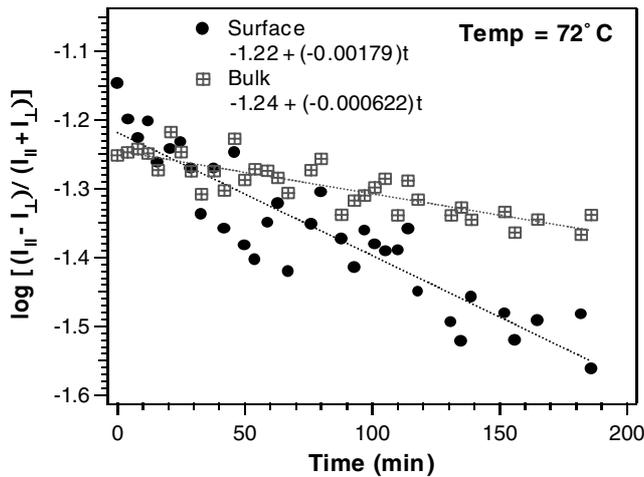


Fig. 2. Decay of dichroic ratio with heating time at 72 °C. The ordinate is on a 10 based logarithm scale.

FY (Fig. 1b) spectra. This behavior indicates the loss of chain orientation during annealing.

In Figure 2 we plot the decay in the dichroic ratio of a sample annealed at 72 °C. The dichroic ratio is defined as

$$R = (I^{\parallel} - I^{\perp}) / (I^{\parallel} + I^{\perp}), \quad (1)$$

where I is the intensity under the $1s \rightarrow \pi_{C=C}^*$ peak taken with the electric field vector perpendicular or parallel to the deformation direction. The dichroic ratio for the surface chains, given by the partial electron yield (PEY), decays faster than that of the bulk, determined from the FY data. A single exponential function, shown as a dotted line in Figure 2, was used to fit the data. More sophisticated functions, *e.g.* a stretched exponential, can be used for data fit. Actually, the data of surface relaxation seem to be a good candidate for a stretched exponential fit, while the bulk data can be fitted reasonably with a single exponential. This apparent difference tends to suggest the existence of different relaxation processes between surface and bulk chains. To dwell further on this point one needs to have experimental data with less scatter and over a more extended time domain.

The decay of optical retardation with time at 90 °C is plotted in Figure 3. The sample heating and data collection times are much shorter in the optical birefringence measurements, relative to those in NEXAFS. The result shows that the first 120 s exhibits a fast decay, which is followed by a rate comparable to that in NEXAFS. A combination of two exponential functions was needed to fit the data; the best fit is given as the solid line in Figure 3. The fast decay in the optical retardation at the onset of relaxation was observed in all the measurements reported in this work. In certain cases with the data collection time going beyond 10^5 s, a third exponential function becomes necessary to fit the latter portion of the data. We note that no NEXAFS data are available within the first two minutes of the sample annealing since the total time needed for each scan is two minutes. The relaxation time constant obtained from the birefringence at short time was

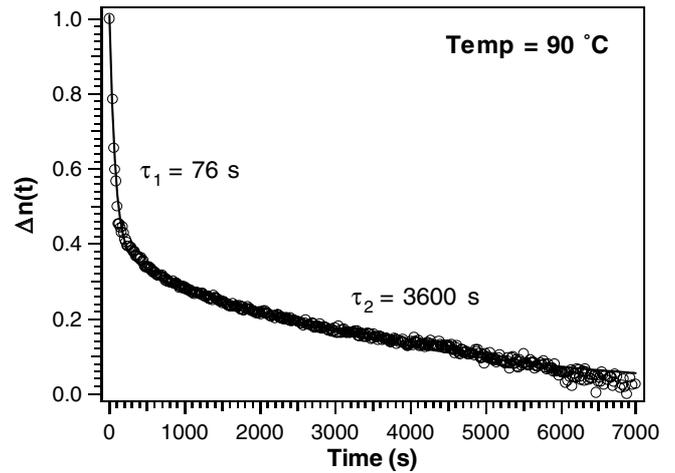


Fig. 3. Decay of optical birefringence with heating time at 90 °C. The data were normalized and fitted with two exponential functions (solid line) and the relaxation times are given in the plot.

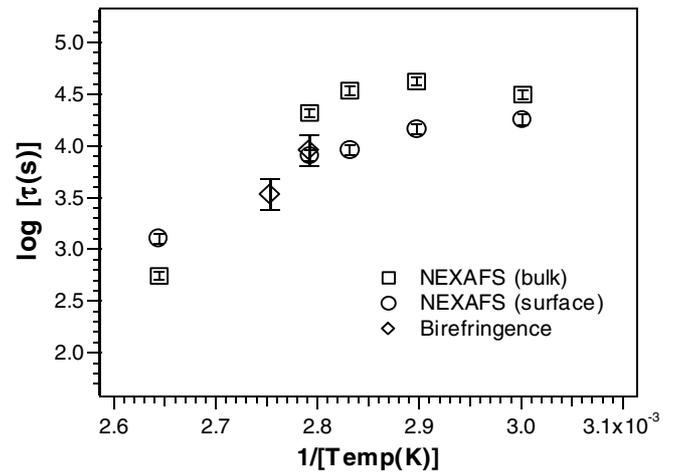


Fig. 4. Relaxation time τ at various temperatures of the surface and bulk from both the NEXAFS and optical birefringence measurements. Only the NEXAFS data between 60 °C and 85 °C were used to calculate the activation energy.

therefore disregarded when comparison was made with the NEXAFS results.

In Figure 4 we compare the relaxation time constant obtained from the PEY, FY and birefringence data as a function of temperature (standard uncertainty is presented as the error bar). NEXAFS results collected from samples annealed at 105 °C are also given. At this temperature, the orientation relaxation took place rapidly and NEXAFS was not capable of capturing such a fast process. These high-temperature data are included in Figure 4 only to provide the magnitude of the relaxation time of 300 s to 1000 s, a range close to what was measured by others in PS using second-harmonic generation [19].

Discussion

The type of deformation used in this work, a simple extensional flow by compression, is expected to induce equal amount of uniaxial orientation of both the surface and bulk chains. Since cold rolling is a procedure rarely used to orient glassy polymers, it merits some discussions. It is a process widely used in metallurgy to prepare metal sheets with desirable thickness and modulus. Copper is a good candidate for cold rolling because of its work hardening characteristics and others. Typically, the friction between the roller and metal results in a large shear deformation at both sides of sample surface while the central portion of the rolled sheet is deformed uniaxially. Cold rolling has been applied to orient semi-crystalline polymers [15] which often have a natural drawing ratio or necking strain. A mismatch of the rolling ratio and the material's natural drawing ratio often results in instability which in turn gives rise to irregular surface and internal cracks. In this work we took advantage of the rolling stability of copper to ensure an even and stable process. By placing the PS thin film near the central plane we promoted pure extensional deformation of the PS film, hence a sample with the surface chains and bulk chains equally oriented. The oriented PS films are smooth without voids as evaluated with optical microscope at a $200\times$ magnification. We were able to detach a small piece of the oriented film from the silver substrate. It stayed at the bottom of a beaker containing water with 3.5% wt. table salt after being immersed. At a salt concentration of 4% wt, the film floated to the top. This indicates that the density of the oriented PS film is between 1.023 and 1.027 [20]. Given the literature value of PS is 1.03, the density value measured precludes the presence of any significant amount of cracking or crazing. To measure the density of polymer thin films supported on solid substrate is a challenging task. Progress has been made with the use of energy disperse X-ray reflectivity [21] and twin angle neutron reflectivity [22]; however, the precision is still far less than what needed for T_g -related discussion.

Partial electron yield was used to quantify the chain relaxation within the top 1 nm of the free surface, similar to the experiments of Liu *et al.* [11] and Wallace *et al.* [14]. The X-ray fluorescence yield was used to measure chain alignment within the top 200 nm of the free surface and the optical birefringence provided a measure of chain alignment throughout the entire sample thickness of $2\ \mu\text{m}$. Combination of all probes allows for a direct comparison of surface and bulk chain relaxation dynamics under well-defined, zero strain conditions. The results given in Figure 4 indicate that relaxation of the surface orientation is faster than that in the bulk. The results from the birefringence measurement seem to be in qualitative agreement with the FY data. This indicates that the FY is a viable tool for measuring chain orientation; the concern of re-absorption by the film issue could severely hamper the use of FY for this purpose. The initial dichroic ratio or chain orientation of the deformed film is not included at time zero or before any heating since the temperature history during the initial heating step makes this data

difficult to use. To know the initial value of dichroic ratio is useful to determine the early phase (0 to 120 s) of the relaxation process. However, as in most stress relaxation measurements, stress at time zero is not needed to determine relaxation time as long as the time window is specified.

The accuracy of the relaxation time obtained is less than desirable, most noticeably is the bulk chain relaxation time measured at 60°C . The results in Figure 4 indicate that the relaxation time at 60°C is shorter than that of 72°C and this just cannot be true. Nevertheless, we went ahead to estimate the activation energies of relaxation using the NEXAFS data from 60°C to 85°C and the results are $(33 \pm 5)\ \text{kJ/mol}$ and $(52 \pm 15)\ \text{kJ/mol}$ for the surface and bulk, respectively. These values are far less than the range of $188\ \text{kJ/mol}$ to $209\ \text{kJ/mol}$ reported by Dhinojwala *et al.* [19] for PS at temperatures below its bulk T_g . Our results are close to those reported by Tsang *et al.* [12], who deduced the activation energy values from the birefringence decay of surface-rubbed PS films. The magnitudes of the activation energies and relaxation time constants estimated in this work suggest that the relaxation process observed with both NEXAFS and optical birefringence involve mainly the local segmental motion. We note that a similar conclusion was reached also by Tsang *et al.* [12].

The ratio of the surface relaxation rate over the bulk rate averaged over temperatures ranging from 60°C to 85°C is 2.6 and the activation energy averaged with the eight data points of both the surface and the bulk is $42.5\ \text{kJ/mol}$. One can estimate the effective temperature of the surface, or equivalently the surface T_g suppression, with the above information of enhanced surface dynamics and activation energy. For PS at 27°C the effective surface temperature enhancement or surface T_g suppression was estimated to be $\sim 18^\circ\text{C}$. This value is close to that reported by Schwab *et al.* [13] who studied the birefringence decay of PS films with different extent of surface rubbing. It is noteworthy that the above-estimated surface T_g suppression is based on the value of the activation energy obtained herein and this value seems to be rather low. If one chooses to use a nominal value of $\sim 200\ \text{kJ/mol}$ for PS relaxation at temperatures below bulk T_g , the equivalent value of surface T_g suppression will be far less than 18°C .

Conclusion

The surface and bulk relaxation rates were measured simultaneously on uniaxially deformed polystyrene films using NEXAFS. Our results indicate that the surface relaxation is approximately 2.6 times faster relative to the bulk over a temperature range 60°C to 85°C . Based on the difference in the relaxation rates and its measured temperature dependence, the effective temperature enhancement (or the surface T_g suppression) of the PS free surface is estimated to be 18°C . The temperature dependence of the relaxation time measured in this work is rather weak but consistent with a recent work by others [12]. The data

quality might be just at the limit to make a firm determination of the difference between surface and bulk T_g . If one chooses to a literature value of stress relaxation time of PS in glassy state the apparent difference between surface and bulk T_g will be far less than what reported above.

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