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# X-ray reflectivity study on the surface and bulk glass transition of polystyrene

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The surfaces of polystyrene (PS) films decorated with gold nanoclusters were investigated by x-ray reflectivity measurements. The thicknesses of the films are much larger than the radii of gyration of the different PS samples. By annealing the films above the glass transition temperature $T_g$ an embedding process of the clusters into the polymer is detected which is accompanied by a substantial increase in the cluster layer thickness due to Brownian motion. These processes start at a sufficiently low viscosity and may be regarded as a probe of the glass transition in the near surface region of the PS films. Simultaneously the thermal expansion of the entire film and hence its approximate bulk behavior were monitored. Two samples of different molecular weight do not show a significant difference between the surface and bulk $T_g$ values.

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## I. INTRODUCTION

During the past few years many works have been published where the glass transition of polymers in confined geometries was investigated. The main focus concentrated on thin films which have been investigated mainly by four different techniques. Ellipsometry [1–3], x-ray reflectivity measurements [4–6], Brillouin light scattering (BLS) [7,8] and positron annihilation lifetime spectroscopy (PALS) [9] were applied to films of different thicknesses. All these experimental techniques are somehow sensitive to properties related to the density change of the polymer at the glass transition temperature $T_g$. Apparently contradictory results obtained in these works could be explained by pointing out the importance of the interaction between the polymer film and the supporting substrate [2,10]. This led to either a decrease or an increase in $T_g$ with decreasing film thickness depending on the strength of the polymer-substrate interaction. In general, the less attractive the substrate the stronger the $T_g$ reduction with decreasing thickness, whereas the strongest reductions were found in freely standing polymer films [7].

The reasons for the scatter in the observed values of $T_g$ are still not clear and have demanded techniques to investigate effects on the surface itself rather than to measure changes that affect the entire polymer layer. A layer model with enhanced mobility at the surface was proposed to explain the deviations from the bulk values [9], but could not be confirmed unambiguously. A technique that is sensitive in a depth from about 5 nm from the surface is PALS. Xie *et al.* [11] did not find a deviation from the bulk value of PS samples at the surface while on the other hand Jean *et al.* [12] could find a decrease using a related method. Besides, mechanical relaxation properties have been probed by scanning force microscopy. At room temperature Kajiyama *et al.* [13] found the surface to be in the glassy state for polystyrene of molecular weight greater than $M_W=40000$ g/mol, and it appeared to be liquidlike for $M_W \leqslant 30000$ g/mol, suggesting a stronger dependence of the surface $T_g$ with $M_W$ than expected in the bulk and hence an increased mobility at the surface. This effect was explained by surface segregation of chain end groups and verified by dynamic secondary ion mass spectroscopic depth profiling [14]. Later the same group reported molecular weight dependent values of the surface glass transition temperature that dropped even below room temperature for $M_n$ lower than 50000 g/mol [15]. In contrast to these works are the shear modulation force microscopy (SMFM) measurements performed by Ge *et al.* [16] that do show the same $M_W$ dependence both at the surface and in the bulk for supported as well as freely standing films. Atomic force microscopy (AFM) adhesion measurements by Tsui *et al.* [17] did not show evidence for an enhancement in the surface relaxation either. Similar results are proposed by the near edge absorption fine structure (NEXAFS) measurements of Liu *et al.* [18] that did not show a higher mobility at the surface as well. Thus, so far the question whether the glass transition is altered at a free surface still is discussed controversially. A comprehensive summary and interpretation of the above-quoted publications and others can be found in Ref. [19].

## II. EXPERIMENT

We present x-ray reflectivity measurements where the embedding of gold clusters on PS surfaces, which form during deposition, is used as a probe of the viscosity of the polymer in the near surface region [20,21]. Simultaneously the change of the thermal expansion coefficient $\alpha_{\mathrm{th}}$ of the polymer at $T_g$ is monitored in order to measure the glass transition integrated over the film thickness $d_P$. It has been shown before that for sufficiently thick PS films on Si/SiO$_x$ ($d_P \gg R_G$, with $R_G$ the radius of gyration) the change of the

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thermal expansion coefficient $\alpha_{\mathrm{th}}$ occurs at the bulk glass transition temperature of the polymer [22]. Thus, in order to minimize substrate effects, only thick samples which fulfill this condition were used in the present study. Films with almost monodisperse PS of two different molecular weights $M_W = 3800$ g/mol (PS1) and $M_W = 220\,000$ g/mol (PS2) were prepared on silicon wafers with a native oxide layer by spin coating and by casting from solution, respectively. The samples were annealed at $p \approx 10^{-6}$ mbar for 12 h (PS1) and 1 h (PS2) at 30 K above $T_g$ before being cooled down to room temperature at slow rates of about 0.3 K/min (PS1) and 1 K/min (PS2), respectively. This guarantees that the polymer is as much relaxed as possible before the gold is evaporated. The evaporation was done in an ultrahigh vacuum (UHV) chamber at a deposition rate of 0.8 Å/min. Gold layers of nominal thicknesses of 10 Å (PS1) and 20 Å (PS2) were prepared on the PS films with thicknesses of $d_{\mathrm{PS1}} = 800$ Å and $d_{\mathrm{PS2}} = 1.2$ $\mu$m, respectively. The polymer was kept at a constant temperature with $\Delta T = 50$ K below $T_g$ during preparation of the samples.

It is known that the evaporation of noble metals such as gold or silver onto polymer surfaces in UHV generally leads to the formation of clusters because the polymer-metal interaction is much weaker than that among the metal atoms. Therefore an atom impinging onto the surface retains a high mobility and thus diffuses until it sticks at a nucleation site or will desorb again [23]. Provided that the evaporation rate is sufficiently low, relatively few spherically shaped clusters grow [24]. If the relation $T < T_g$ holds as well, the clusters are confined to a narrow surface region [20,25,26]. These were the preparation conditions for the examined samples PS1 and PS2.

An upper limit for the thermal energy of a gold atom hitting the polymer surface during the preparation is estimated by $E_{k,\mathrm{Au}} = \frac{3}{2} k_B T_{b,Au}$ with $T_{b,Au} = 3130$ K being the boiling temperature of gold [27] (at atmospheric pressure). From this one gets $E_{k,Au} = 0.4$ eV. This is only about 10% of the energy needed to alter the chemical composition of the polystyrene, since the energies of the C–C bonds [28] are about 3.6 eV and those of the C–H bonds about 4.3 eV. Thus the polymer hardly can be damaged at the surface by the evaporation of the metal.

Kovacs and Vincett [29] calculated with purely thermodynamic arguments that clusters on a polymer surface become embedded provided that $\gamma_c > \gamma_p$. In addition, as long as the relation $\gamma_c > \gamma_{cp} + \gamma_p$ is valid they are expected to become completely covered by the polymer. Here $\gamma_c$, $\gamma_p$, and $\gamma_{cp}$ are the surface and interfacial tensions of the clusters, the polymer, and the polymer-cluster interface, respectively. For kinetic reasons the embedding process only starts at temperatures above $T_g$. Hence the onset of this process can be used as a probe of the glass transition and in particular for the determination of $T_g$ in a narrow surface region which is given by the extent of the height distribution of the gold clusters [30]. At temperatures above $T_g$, where the viscosity decreases drastically, the polymer chains have the possibility of covering the top of the clusters and hence forming a top layer of PS with increasing thickness. Besides one expects a change in the cluster height distribution due to an enhanced movement of smaller clusters into the bulk polymer material by Brownian motion [31,32,26].

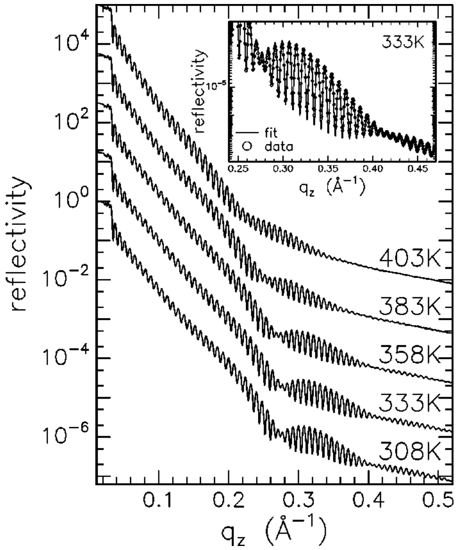

FIG. 1. X-ray reflectivity data of PS1 at different temperatures shifted with respect to each other. The inset shows as a typical example the virtual indistinguishability between data and fit at 333 K.

The x-ray measurements were performed at the Hamburger Synchrotronstrahlungslabor (HASYLAB at DESY) at the beamlines W1.1 and BW2 with wavelengths $\lambda = 1.18$ Å and 1.55 Å, respectively. The samples were mounted in a vacuum cell ($p \approx 10^{-6}$ mbar) in order to provide good temperature stability, and to prevent dewetting of the PS films with higher temperatures [33]. After reaching a desired temperature using a heating rate of 1 K/min, for a waiting time of 30 min relaxation of the metal-polymer system was allowed. It turns out that at temperatures $T > T_g$ no equilibrium state is reached, but even after many hours only a very small increase of the cluster layer thickness was detected. However, all fast relaxation processes have ceased and only slight changes occur during the x-ray measurements which took approximately 1 h for each temperature.

## III. RESULTS AND DISCUSSION

Figure 1 shows as an example a set of x-ray reflectivity data for the sample PS1. $q_z = (4\pi/\lambda)\sin\alpha_i$ denotes the vertical wave vector transfer, where $\alpha_i$ is the incidence angle with respect to the surface. From the maximum electron density of the cluster layer (see Fig. 2) we estimated that the coverage of the surface by gold clusters is about 30%. Since the cluster layer thickness is less than 40 Å the penetration depth of the x rays is sufficiently large so that only the critical angles of total reflection of the silicon substrate and of the thick PS layer can be seen at very small $q_z$. The rapid oscillations correspond to the thick PS layer. From the period $\Delta q_z$ a thickness of $d_{\mathrm{PS1}} \approx 800$ Å is obtained. The low frequency beating is due to the presence of the gold cluster layer. From this period a thickness of $d_c \approx 35$–40 Å is estimated. The detailed shape of the curves is explained by ver-

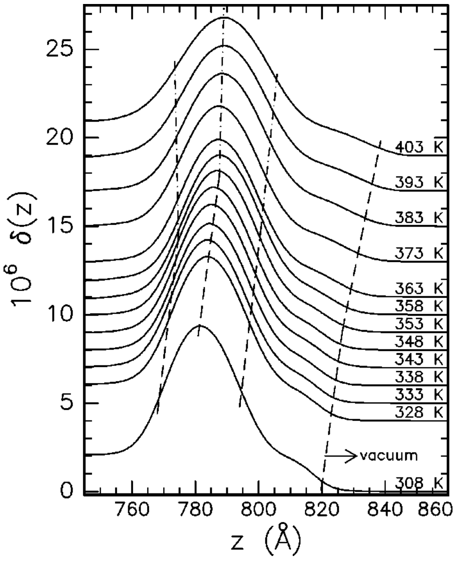

FIG. 2. Electron density profiles obtained from the refinements of the reflectivity data of PS1. The curves are shifted under consideration of the temperature differences. The zero of the $z$ axis is located at the polymer/substrate interface. The dashed lines reflect the thermal expansion of the sample while the dash-dotted lines are guides to the eye to clearly mark the appearing changes.

tical electron density profiles. The refinement of the model which leads to the profiles shown in Fig. 2 was done in two steps: First a layer model with the conventional Parratt algorithm [34] was used in order to obtain the mean electron density profile which is able to explain the major features of the reflectivity data. The second step was a further refinement performed by an inversion algorithm which produces a close to perfect explanation of the data, which allows quite accurate conclusions. This inversion technique has been described in detail in Ref. [35]. Applying this technique leads to fits of the x-ray reflectivities which are virtually indistinguishable from the data shown in Fig. 1 (see inset).

In Fig. 2 only the important part of the electron density profiles is shown, i.e., the upper 110 Å below the surface. The origin of the $z$ axis is given by the substrate/polymer interface. Since gold has a much larger electron density than PS the contribution of the gold clusters to the overall electron density around $z=780$ Å is clearly visible. The PS film is emerging into the region $z<760$ Å. The additional shoulder at $z\approx 810$ Å above the gold cluster layer suggests that even at temperatures below $T_g$ there is already some polymer on top of a non-negligible fraction of the clusters.

The profiles in Fig. 2 show that below a certain temperature no significant change of the interface structure is visible. There is only a slight increase of the total thickness due to the thermal expansion of the PS layer as highlighted by the dashed lines.

With increasing temperature three major changes of the profiles become visible, all of them starting at the same temperatures above $T\approx 348$ K. These changes are emphasized by the dash-dotted and dashed lines in Fig. 2.

(i) The cluster layer starts to become thicker while the related maximum electron density decreases. This indicates a movement of the gold clusters deeper into the PS film, taking into account that it is favorable for smaller clusters to move faster into deeper regions than for larger ones, since the mean square displacement for spheres in a medium after a time $t$ due to Brownian motion is given by the Stokes-Einstein equation [31,32] according to the relation $\langle z^2\rangle =(k_BT/2\pi\eta r)t\sim t/r$. Here $\eta$ denotes the viscosity of the polymer and $r$ the radius of the clusters. In addition a possible growth of the clusters (coalescence) for temperatures above $T_g$ has also been reported [26]. However, for the preparation parameters used in the present study this effect is expected to be small.

(ii) The already mentioned "PS layer" above the gold clusters starts to grow significantly. This is an indication for polymer material covering the upper part of the clusters which can be explained by the embedding process of the metal clusters as described by Kovacs and Vincett [29]. X-ray photoelectron (XPS) measurements for several different polymer substrates are in qualitative agreement with this explanation [20,26]. Here a decrease of the XPS signal from the metal in relation to the signal from the polymer (C atoms) was found. The density profiles from the refinements of the x-ray reflectivity data directly explain these results by the start of the embedding process.

(iii) The total thickness of the sample continues to increase with temperature, but at a much larger rate than before. The coefficient of thermal expansion $\alpha_{\mathrm{th}}$ changes abruptly. This change serves as an indication of the bulk $T_g$ value [22]. It shall be noted again that this value corresponds to the bulk $T_g$, including possible interface effects, because the entire film contributes to the effect. Additionally, differential scanning calorimetry (DSC) measurements at 1 K/min showed a similar value of $T_g\approx 348$ K which closely agrees with our x-ray data ($T_g\approx 345$ K).

The above-mentioned three key changes of the density profiles lead us to suspect that at temperatures above $T\approx 348$ K *both* the viscosity of the bulk *and* the viscosity in the region between the upper surface (see the "shoulder" in Fig. 2) and a depth of about 80 Å starts to decrease abruptly, indicating the onset of the embedding process.

The same series of measurements was performed for sample PS2. Since this sample has a higher molecular weight, $T_g\approx 373$ K is higher also. The same findings have been measured in several studies before. Again a significant movement of the clusters is detected only for temperatures $T>T_g$. However, the error bars for this sample are larger than those for PS1, since the thickness of $d_{\mathrm{PS2}}=1.2\ \mu$m prevents a direct observation of the thickness oscillations. This makes the fit less sensitive with respect to small changes in the corresponding density profile. Besides, small changes below $T_g$ cannot be detected in this case.

Figure 3 shows the major result of this work illustrated by the change of the cluster layer thickness. It can be seen that a significant thickness change starts at temperatures around the respective bulk $T_g$ values for the two samples PS1 and PS2. This effect is a direct consequence of the movement of the gold clusters due to a sufficiently low viscosity and may be regarded as the onset of the glass transition. The error bars were obtained by modifying the electron density profiles sev-

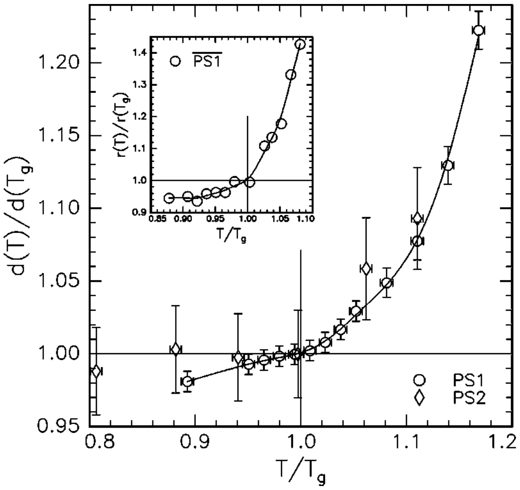

FIG. 3. Changes with temperature in the cluster layer thickness $d(T)$ normalized to the thickness at the glass transition temperature $d(T_g)$ for both PS1 and PS2. The glass transition temperatures were obtained by the change in the coefficient of thermal expansion for PS1 and by DSC measurements of polystyrene bulk material for PS2. The inset shows the normalized ratio $r(T) = I_{C1s}(T)/I_{\mathrm{Cu2p}_{3/2}}(T)$ of the XPS intensity of a sample equivalent to PS1. The lines through the data points are guides to the eye only.

eral times in the near surface region and thereafter applying the data inversion algorithm to get a reasonable fit.

As a complementary method which is sensitive to the region *above* the clusters, the inset highlights the results from x-ray photoelectron spectroscopy (XPS) measurements performed on a sample equivalent to PS1 but with Cu clusters with a mean radius of 5 Å on the surface instead of Au clusters. The ratio of the intensities of C $1s$ and Cu $2p_{3/2}$ as a function of temperature $r(T) = I_{\mathrm{C}1s}(T)/I_{\mathrm{Cu}2p_{3/2}}(T)$ is shown after background correction. As photon energy Al K$\alpha$ radiation ($E = 1486.6$ eV) was chosen. Since the kinetic energy of the Cu $2p_{3/2}$ electrons (the binding energy $E_b$ is 932 eV) is quite low, the mean free path of the detected electrons is small, thus making this method surface sensitive. The inset shows the increasing predominance with the temperature of the carbon signal from the polymer chains over that from the metal clusters indicating an increasing coverage of the clusters by the polymer which becomes significant at $T_g$.

It should be noted that recent XPS measurements on *high*-molecular-weight PS revealed a decrease of the glass transition at the surface of the order of 10 K [21]. We would like to emphasize, while there is no obvious effect, that the x-ray reflectivity measurements for the high-molecular-weight polystyrene do not exclude the possibility of such a decrease, since the error bars for this comparatively thick sample are rather large. Obviously the sensitivity for the much thinner sample PS1 is considerably higher.

Figure 3 shows a slight change for sample PS1 in both the x-ray and the XPS data already below $T_g$ which exceeds the calculated error bars. In the XPS measurements which more directly present the mobility of the *polymer* a very strong change at $T_g$ is shown compared to that below $T_g$. This demonstrates that any motion at the surface below the bulk glass transition temperature if present at all must be very slow. This behavior is in agreement with the SMFM results of Ge *et al.* [16] who found a slight increase in their AFM tip amplitude for their lowest molecular weights of $M_W = 3000$ g/mol and $M_W = 7000$ g/mol as well.

It has to be kept in mind that the free surface of the sample has been modified by the presence of the Au clusters. The respective pairwise interaction energies of van der Waals type between the clusters, the polystyrene, and the silicon substrate can be estimated by the material-dependent Hamaker constant $A$ for a certain geometry [36]. Nonretarded Hamaker constants have been calculated from optical data according to the Lifshitz theory [37]. The data obtained are $A_{Au,Au} = 45 \times 10^{-20}$ J, $A_{Cu,Cu} = 28 \times 10^{-20}$ J, and $A_{PS,PS} = 6.5 \times 10^{-20}$ J. The constants for two different media 1 and 2 can be approximately calculated by [36] $A_{12} = \sqrt{A_1 A_2}$, and with a medium 3 in between by $A_{132} = \sqrt{A_{131} A_{232}}$. Hence $A_{Au,PS} = 17.1 \times 10^{-20}$ J, $A_{Cu,PS} = 13.5 \times 10^{-20}$ J, $A_{Au,PS,Si} = 17.4 \times 10^{-20}$ J, and $A_{Au,PS,Au} = 30.8 \times 10^{-20}$ J. Since $A_{Au,PS}$ and $A_{Au,PS,Si}$ are almost identical and the energy between the Au clusters and the underlying polymer and silicon half space obey the same distance behavior, the clusters do not ''feel'' directly, whether the Si substrate starts in a depth of 80 nm or 1000 nm.

The interaction among the Au clusters in the layer is relatively strong. Thus there is a stabilizing tendency, that is, the clusters tend to stay in a layer while there is a net force downwards, of course. This effect competes with the entropic forces that emerge from the reduction in chain conformations when a cluster moves into deeper regions, and it competes with a broadening of the cluster layer due to the Brownian motion as well [29,31]. Besides there is a difference in $A_{Au,PS}$ and $A_{PS,PS}$ and for the XPS measurements in $A_{Cu,PS}$ and $A_{PS,PS}$ for all temperatures. Nevertheless, the interaction between the polymer and the gold should be dominated by the entropy of the polymer, since the proximity of a cluster should lead to a substantial reduction in the number of possible chain conformations if the cluster size is larger than the persistence length of the polymer. Since the results in Fig. 3 show that the main change happens at the bulk glass transition temperature, it is unlikely that the metal polymer interaction exactly compensates a possible reduction in $T_g$ at the surface. This argument is supported by the fact that the XPS measurements were performed with a lower metal coverage and hence smaller cluster size and nevertheless yield virtually the same behavior for the low-$M_W$ polystyrene.

## IV. CONCLUSIONS

In summary, we have presented x-ray reflectivity measurements of PS films decorated with gold clusters as a function of temperature, which monitor an embedding process. At the same time the clusters are a probe of the glass transition in the surface region. The lowering of the viscosity at the surface yields an increasing coverage of the clusters by the polymer which is driven by the differences in the surface and interfacial energies of the involved materials. Besides the cluster layer starts to broaden by the movement of smaller clusters into the polymer bulk. Simultaneously the thermal expansion over the entire sample thickness was measured in order to compare the surface and bulk behavior. No remarkable difference between the glass transition temperature $T_g$ at the surface and that in the bulk was found.

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