Interface and Surface Effects on the Glass Transition in Thin Polystyrene Films

G. B. DeMaggio, W. E. Frieze, and D. W. Gidley
Department of Physics, University of Michigan, Ann Arbor, Michigan 48109

Ming Zhu, H. A. Hristov, and A. F. Yee
Department of Materials Science and Engineering, University of Michigan, Ann Arbor, Michigan 48109
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Lifetime analysis of positronium annihilating in nanometer voids is used to study the thermal expansion behavior of thin, Si-supported polystyrene films near the glass transition temperature T_g. A reduction in void volume expansion is correlated with a reduction in the *apparent* T_g as film thickness decreases. Our results can be fitted using a three-layer model incorporating a 50 Å constrained layer at the Si interface and a 20 Å surface region with reduced T_g. [S0031-9007(97)02458-7]

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A fundamental understanding of the surface and interfacial properties of amorphous polymer films is important in many applications, including protective and lubricating coatings, adhesives, high performance composite materials, and microelectronic encapsulants and dielectrics [1,2]. Polymer systems that are particularly relevant and experimentally easy to access, such as substrate supported films, are challenging to theorists since the two interfaces (one solid, one vacuum) and thinness-induced confinement may all play separate and perhaps competitive roles in determining a film's molecular conformation and how it differs from that of a bulk sample [3–5].

In this paper we present the first use of positron lifetime spectroscopy to study the thermal expansion and glass transition of 70–3000 Å thick polystyrene (PS) films spin cast on hydrogen passivated Si(111) crystals. This is an ideal model system since uniform thin films that do not dewet the Si surface can be made and atactic PS does not crystallize. Furthermore, the existing experimental situation for PS is quite controversial. Ellipsometry measurements [6] in air claim that the glass transition temperature (T_g) goes down with decreasing film thickness while the expansion coefficient in the glass phase increases and approaches that of the rubber phase for films as thin as ~100 Å. On the other hand, x-ray reflectometry in vacuum [7] indicates just the opposite trends: T_g is higher than bulk for films thicker than 400 Å (below which no glass transition is observed), and the expansion coefficients in both the glass and rubber phases are less than the respective bulk values. Both methods nominally measure the thickness of the film. Very recently, more intrinsic film properties are being probed with acoustic techniques [8,9] and optical fluorescence [10]. The implementation in this work of positron lifetime spectroscopy using a variable energy positron beam is attractive because the depth profiling capability [11] may permit delineation of the surface, film, and substrate roles. It is also highly complementary to previous techniques since the more intrinsic property of nanovoid thermal expansion (nominally related to the free volume expansion) is probed, and free volume is a fundamental concept in some theories of the glass transition.

The basic technique of positron lifetime spectroscopy in bulk polymers is well known [12]. The extension of this technique to low energy, monoenergetic positron beams of controlled and shallow implantation depth enabling one to probe surfaces and thin films was recently reported [11]. Briefly, a beam of 10^5 positrons/s is implanted into the film at a selected energy (average implantation depth) ranging from 300 eV (50 Å) to 3000 eV (2000 Å). After slowing down to an energy of about 1 eV the positrons capture an electron to form positronium which localizes in the polymer void volume. Interaction of the positronium with surrounding molecular electrons reduces its annihilation lifetime τ from the vacuum value of 140 ns to about 2–2.5 ns. This allows one to relate τ to an average void size using a spherical hole model [13]. (The assumed shape of the void is not important.) The sample is heated by a filament behind the silicon substrate, and temperature is monitored and controlled by use of a thermocouple attached to the silicon. Thermal expansion of the polymer void volume is indicated by an increase in τ.

PS films were prepared by spin casting dilute toluene solutions onto H-passivated Si(111) wafers. A variety of substrate preparation prescriptions were used including oxidation of the Si, but no strong effects were observed. Typically, the cleaning procedures of Ref. [7] were used. The nominal film thicknesses were determined by ellipsometry and several films were cross-checked in detail using spectroscopic ellipsometry. PS samples of three different molecular weights (M) were used: monodispersed 63 000 and 400 000; and polydispersed 260 000. Samples were annealed overnight in ultrahigh vacuum (UHV) at 140–150 °C. After cooling to room temperature, lifetime measurements (at a beam energy selected to maximize positronium formation throughout the film) were acquired in UHV by successively heating the sample to higher temperatures. Several heating cycles were acquired to assure reversibility and reproducibility.

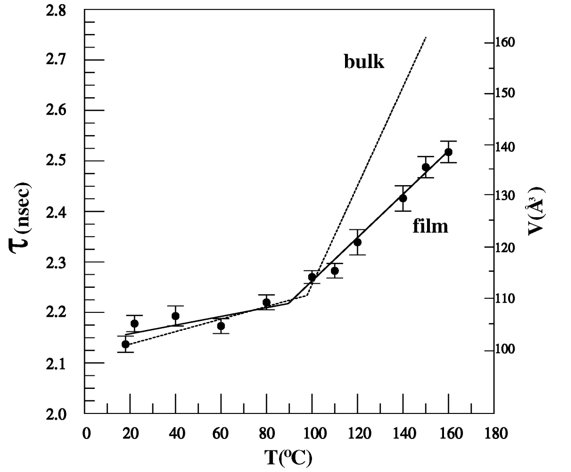

FIG. 1. The measured positronium lifetime τ, and the corresponding spherical hole volume V, for a 115 Å thick PS film at various temperatures T. The solid (dashed) line is a fit of the film (bulk) data to two lines intersecting at the point (T_g, τ_g) that minimizes the chi-square of the fit.

Figure 1 shows the fitted value of τ and the deduced spherical void volume as a function of temperature for a film of thickness 115 Å. Each point is an average of 2–3 runs, and each run is 4–12 hours in duration. Superimposed on the graph is the fitted result for a bulk sample. The trends evident in this figure are typical of all the films studied. The thermal expansion coefficients $\frac{1}{V}\frac{\partial V}{\partial T}$ of the *void* volume in the glass and rubber phases, β_g and β_R, respectively, are less than the corresponding bulk values (β_g and β_R are the respective slopes in Fig. 1). The apparent glass transition temperature T_g, where the expansion coefficient changes, is also typically 0–3 standard deviations *less* than the bulk value of 96 °C determined using positron lifetime spectroscopy (this trend will become clear in Fig. 3). Thus, to the extent that nanometer void volume and film thickness measurements can be compared, we find that our expansion coefficient results are consistent with Ref. [7] (but not with Ref. [6]) while the decrease in apparent T_g is consistent with Ref. [6] (but not with Ref. [7]). With these intriguing differences in mind, we turn to a more detailed consideration of the trends summarized above.

For all films, β_g shows no trend with thickness and is typically $(0.08 \pm 0.3)\%/°\mathrm{C}$ compared to the bulk (glass) void volume expansion coefficient of $(0.14 \pm 0.02)\%/°\mathrm{C}$. This result is expected from simple contact of the film with the substrate which constrains in-plane expansion to the relatively negligible value of Si. Combining this effect with the linear expansion normal to the film plane (which is enhanced according to Poisson's ratio [7]) the film's volume expansion coefficient is then β_g (film) $\sim\frac{2}{3}\beta_g$ (bulk). It should be noted that since we deduce a specific void *volume* directly from τ (rather than measuring film *thickness*) our determinations of β_g and β_R do not require any knowledge of how Poisson's ratio changes near T_g for a thin film. If there are additional interfacial and/or thin film effects in the glassy film, our measurements are not sensitive enough to resolve them.

The observed reduction in β_R and the reduction of T_g are considered more fundamental manifestations of interfacial effects. Our determination of $\beta_R(h)$ for various film thicknesses h is shown in Fig. 2. For comparison a two-layer model fit is plotted in which $\beta_R(h) = \beta_R(\mathrm{bulk})(1 - \delta/h)$, where δ is the equivalent thickness of an interfacial "dead" layer. The expansion coefficient of this layer is taken to be zero, but could be the negligibly small value measured for the film's glassy phase. The remainder of the film is assumed to expand with β_R(bulk). We find that $\delta = 50 \pm 5$ Å and is independent of the sample's molecular weight. Use of an equivalent dead layer is appropriate if all of the z-dependent suppression of thermal expansion occurs within $\sim$100 Å of the interface (z is the perpendicular distance from the interface). Since we nominally measure the average void volume expansion of the entire film, $\beta_R(h) = 1/h \int_0^h \beta_R(z)\, dz$, for films with $h \geq 100$ Å we are not sensitive to the details of $\beta_R(z)$, but instead are sensitive to an integrated effect that can be expressed in terms of a nonexpanding layer of thickness δ. It is also interesting to note that there is independent evidence for a constrained or "rigid" layer of this nominal size. In the amorphous phase of some semicrystalline polymers it is found [14,15] that the glass transition can be suppressed when the crystalline lamellae confine the amorphous phase. Our previous measurements [16] show that this confined region is approximately 100 Å thick (i.e., within 50 Å of a crystalline domain). Studies of diffusion and rheological properties of polymer melts also indicate the presence of an immobile polymer network of chains stuck to a confining wall [17].

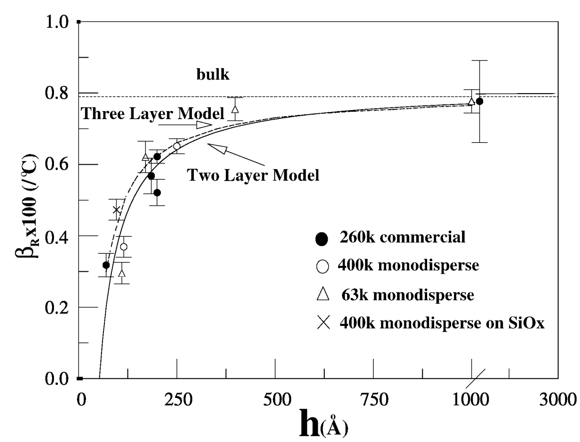

FIG. 2. The thermal expansion coefficient β_R of H-passivated PS films above T_g are shown versus film thickness h for various sample molecular weights. One film had an oxidized Si surface. The horizontal line denotes the bulk value of β_R. Fitting a two-layer model to the data yields $\delta = 50 \pm$ Å. The three-layer model results using this value of δ are also included (see text for discussion).

The observation of a concommitant reduction in T_g (usually associated with increased chain mobility) with the above reduction in β_R (presumably due to reduced expansivity/mobility due to substrate attachment) seems contradictory. However, it should be noted that if a strongly confined dead layer does indeed exist *with no* T_g *within the measurement range,* then the apparent T_g detected is related to those regions above the dead layer and near the vacuum interface. In other words, the entire film may not be characterized as having only one value of T_g. The observed correlation of apparent $T_g(h)$ with $\beta_R(h)$ is summarized in Fig. 3. The straight line in the figure indicates a good fit to the following relation:

$$T_g(h) = T' - \frac{\Delta V/V_g}{\beta_R(h)}, \qquad (1)$$

where $T' \sim 101$ °C is 5 °C above T_g(bulk) and $\Delta V/V_g = 0.05$ is the fractional increase in void volume at T' relative to T_g(bulk). T' is not an observable glass transition temperature. Instead, a direct implication of the above relation is that at T' all of the films (regardless of thickness) have the same specific void volume $V' = V_g + \Delta V$. Thus, we conclude that the fundamental observations of void volume expansion derived from this experiment are that β_R decreases with decreasing PS film thickness in accordance with a molecular weight-independent, 50 Å dead-layer model; and there exists a temperature T' in the rubber phase where all films have the same average specific hole size V'.

There are a number of plausible explanations of the universality of T' and V', some of which include details of the solvent evaporation process in spin casting the films. However, one explanation that has much broader implications is based on a three-layer model of the film which incorporates a 50 Å dead layer ($\beta_R \approx 0$) near the substrate, a surface layer with reduced T_g and $\beta_R \sim \beta_R$(bulk), and a bulklike layer between these interfaces. This model is attractive because it begins (crudely) to address the inhomogeneities that inevitably exist in such supported thin films. There is also evidence that unsupported PS films do have a reduced T_g because of the vacuum interfaces [8]. We find that if we set the surface layer to have an equivalent thickness of 20 Å with a $T_g \simeq 75$ °C, then this three-layer model reproduces rather nicely the observed results as shown in Figs. 2 and 3. This model actually has slope discontinuities at $T = 75$ and 96 °C, but such details are lost in the statistics when the model is fitted to two lines intersecting at a single T_g in the range 75–96 °C. Above 96 °C this model formally reduces to a two-layer model since we have assumed that the surface layer has a bulk-like value for β_R. The slight difference between the two and three-layer fits for β_R in Fig. 2 is related to shifts in the three-layer model fits due to the slope discontinuities mentioned above.

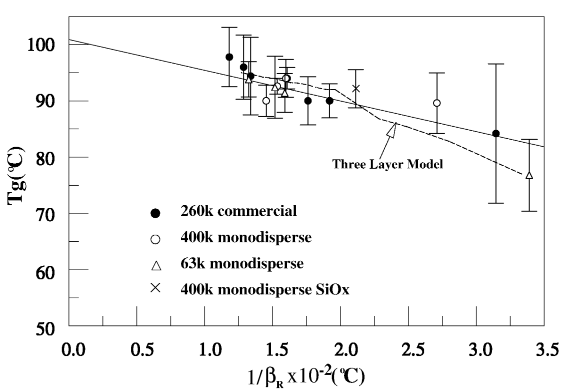

FIG. 3. The fitted values of T_g are plotted versus the corresponding fitted values of $1/\beta_R$ for each PS film. The straight line is a fit to Eq. (1), and the dashed curve shows the simulated results using the three-layer model described in the text.

We conclude that the three-layer model, as the simplest reduction of a multilayer model, sufficiently accounts for all of our results. δ is determined by the $\beta_R(h)$ data in Fig. 2, while the more tentative surface layer characteristics are inferred from Fig. 3. Unfortunately, we cannot directly probe such a thin 20 Å surface layer on a bulk sample because at our minimum implantation energy (300 eV) only about 10% of the positrons will stop in the first 20 Å. This would produce a negligible 2 °C shift in the fitted T_g, which explains why we reported in Ref. [11] no shift of T_g in the top 100 Å of a bulk PS sample.

Can a three-layer model and, in particular, an equivalent dead layer that is independent of molecular weight and with δ as large as 50 Å be understood from theory? For comparison, a typical measure of the bulk polymer coil size is given by the radius of gyration, $R_g = 0.28\sqrt{M}$ (Å) for glassy PS, and ranges from 70 to 180 Å for our samples. Presumably, suppression of β_R is the result of some form of polymer chain attachment to the Si substrate. If we make the extreme assumption that expansion of an entire chain is curtailed by a *single* point of attachment to the substrate, then δ should be equal to the equivalent attachment layer [5] (defined as the integrated thickness of all polymer chains with at least one segment attached to the substrate). Not surprisingly, the deduced values of δ would then be too large (of order R_g) and have the same strong dependence on molecular weight [18]. A value of $\delta \approx R_g$ would, however, be consistent with the polymer melt rheology experiments discussed in Ref. [17]. A more physical approach is to consider loops of polymer chain segments between *two* attachment points. Random walk calculations [5] indicate that the length distributions of such loops are effectively independent of M up to the total chain length. Based on the idea that excitation of cooperative motion over some 25–50 carbon main-chain atoms (about 25 repeat units for PS) produces the glass transition, it seems reasonable to postulate a loop-length cutoff l_c below which expansion of the loop is curtailed to the small glass value. Our estimated values [18] of δ are indeed independent of M but are much too small for any reasonable values of l_c ranging up to 100 repeat units ($l_c \sim 300$ Å). The simple reason is that even loops as long as 300 Å occur almost completely within 20 Å of the interface.

We conclude that we are not able, at this time, to simultaneously account for both the magnitude of δ and its lack of dependence on M based on a detailed microscopic theory of chain-substrate attachment. Nonetheless, the fact that the above estimates for δ bracket 50 Å lends some plausibility to this value, as do the observations of a 100 Å thick "rigid" amorphous phase in semicrystalline polymers [14–16]. The lack of agreement among the various experiments on this system is somewhat disconcerting. However, void volume measurements, wherein the average size of nanometer, positronium-occupied, voids is deduced, may have a fundamentally different (or perhaps more intrinsic) sensitivity to the glass transition than do the measurements [6,7] of average film thickness. It will be interesting to see if the acoustic probes [8,9] can help resolve this situation with PS films. Further measurements with positron lifetime spectroscopy on systematically different polymer-substrate systems are warranted, as are more detailed theoretical calculations of substrate-supported thin polymer films.

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[18] We have performed self-avoiding, cubic lattice, random walk computer simulations that reproduce the attachment layer results and loop length distributions in Ref. [5]. Theoretical values of δ and its dependence on M are deduced from these simulations.