Positronium Formation as a Probe of Polymer Surfaces and Thin Films

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The lifetime, τ_3, and formation fraction, I_3, of triplet positronium decaying in the void volume near a polymer surface are measured versus the positron implantation energy, E. The strong E dependence of I_3 supports a spur-electron capture model of Ps formation with deduced spur sizes ranging from 200 to 660 Å. Thin film measurements indicate that the mean probe depth can be much smaller, given mainly by the average positron implantation distance, $\bar{z}(E)$. Surface-induced changes in the void size and glass transition temperature of polystyrene are searched for at $\bar{z} \approx 40$ Å.

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Studies of polymer surfaces, films, and interfaces are motivated by many applications in coatings, resists, film adhesion and wettability, surface absorption, and wear resistance [1–3]. There is also fundamental interest in polymer surfaces involving, for example, non-bulk-like thermodynamic behavior in thin films, both free and constrained. Detailed predictions of density vs depth [4] and surface-induced reductions in the glass transition temperature, T_g, have been made [5]. Measurements of T_g [6] and anomalous thickness behavior [7] have been reported for very thin polymer films on supporting substrates. There is little corresponding data on free (vacuum-polymer) surfaces, however, simply because there are so few techniques that can depth profile below the surface. Surface selectivity can be achieved with grazing incidence beams (e.g., neutrons [8] or x rays [9]), but depth profiling is limited and there is little hope for also resolving fine lateral features. Spatial resolution in three dimensions is a primary motivation for considering focused, low-energy beams of positrons in the study of polymer surfaces. Although we will concentrate in this paper on depth profiling, such beams should eventually achieve submicron lateral resolution [10] thus extending the utility of this new probe to studies of polymer fatigue, crack propagation, and epitaxial film growth where features are highly localized.

Positron annihilation lifetime spectroscopy (PALS) using radioactive beta-decay positrons has been widely used to study void volume and T_g in *bulk* polymer samples [11]. Such studies detect a relatively long-lived 2 ns component [attributed to triplet positronium (Ps) trapped within 5–10 Å voids] that is considered a direct probe of void volume. Changes in the Ps lifetime during thermal expansion [12], mechanical loading [13], and physical aging, etc., are easily observed. However, the high-energy beta-decay positrons are much too penetrating (~0.3 mm) to be useful for surface studies. Variable implantation energy, keV beams which have been extensively used to study metal and semiconductor surfaces [14] are therefore required, but only a few preliminary PALS studies [15] have been attempted. In this Letter we report the first systematic PALS investigation of the incident-beam energy dependence of Ps formation in the voids near a surface and in thin films of glassy polymers.

The variable energy, UHV positron beam has been described elsewhere [16]. It has been modified for PALS studies using the timing technique of Lynn, Frieze, and Schultz [17]: the beam is directed at a channel plate detector that is tilted 45° with respect to the beam where a retarding electric field deflects the positrons into the sample. Secondary electrons are accelerated to the channel plate to generate a "start" timing signal. The gamma "stop" detector and timing electronics are similar to conventional fast-timing systems [13]. The time resolution of this system is 0.5 ns. The annihilation lifetime spectrum is composed of five lifetime components that are characterized by their respective exponential lifetime τ_i and relative intensity I_i. The shortest two components (corresponding to direct positron annihilation in the polymer) are unresolved and hence are fixed in lifetime ($\tau_1 = 0.2$ ns and $\tau_2 = 0.5$ ns) and constrained in intensity ($I_1 = I_2$) as determined by our bulk PALS studies. The longest two components ($\tau_4 \sim 8$ ns, $\tau_5 \sim 110$ ns) are unique to surface studies and correspond to fast and slow triplet Ps formation by backscattered positrons. Both I_4 and I_5 are less than 10% and scale identically with incident-beam energy as E^{-1}, as expected from backscattering. These two Ps components, which are independent of the polymer, have been carefully studied in recent precision Ps lifetime measurements [18]. It is found that the 8 ns component due to fast (~20 eV) triplet Ps quenching on the channel plate is not exponential at early times owing to the finite time of flight to the quenching surface. By limiting the fitted spectra to the first 12 ns we found that these two components can be very adequately represented by a flat "background" whose intensity, along with τ_3 and I_3, are the fitted parameters in a three lifetime-component fit using PFPOSFIT [19]. I_3 is then the triplet Ps formation fraction for those positrons stopping in the sample.

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The amorphous polymer samples used in this study are (with average molecular weight in g/mole): polystyrene (PS) (260 000), polycarbonate (PC) (58 000), polymethylmethacrylate (PMMA) (280 000), polyethylene terephthalate (PET) (43 000), and two monodispersed samples of PS (30 000 and 600 000). Cross-linked samples of DGEBA epoxy and silicone rubber were also used to systematically vary the sample material. Samples were typically cut to size (about 1.5 cm × 1.5 cm × 0.2 cm), cleaned, dried, and/or vacuum annealed above their respective T_g. A special sample holder with a radiant heater permitted data acquisition at elevated temperatures. With a beam rate of 10^4 positrons/sec a lifetime spectrum is typically acquired in 1–2 h. Between runs the chamber is briefly flooded with electrons from a hot filament to prevent sample charge-up.

The fitted values of $I_3 = f$ are shown in Fig. 1 as a function of the beam energy E. For all of the polymers studied, the corresponding values of τ_3 are independent of E and consistent with bulk values. In bulk studies [11], I_3 is considered to be a relative measure of the density of voids in the polymer. Naively, the trend in f at low E implies that the void density approaches zero near the polymer surface (without change in the average void size). In other words, the polymer chains which have greater mobility near the surface are able to fully relax to equilibrium. As interesting as this surface relaxation interpretation may be, it is not consistent with the more detailed measurements. As can be seen in Fig. 1 there is no dependence of the PS depth profile on molecular weight or temperature. In particular, above T_g where the bulk is in equilibrium there is no significant change in the depth profile—a result that is difficult to reconcile with relaxation. A similar argument holds for silicone rubber which is well above its T_g at room temperature and for DGEBA epoxy which is rigidly cross-linked and hence unable to relax. Furthermore, one would expect a drastically lower surface T_g, and (as will be discussed later) there is no evidence for such a reduction.

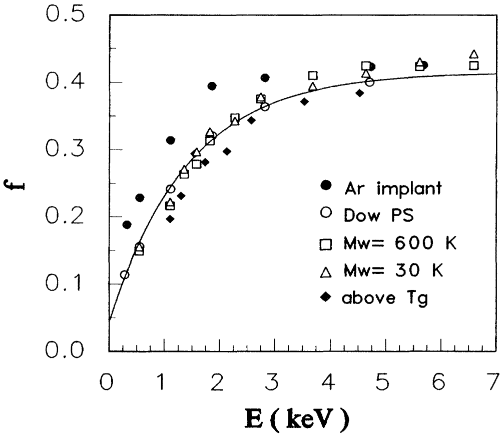

FIG. 1. The fraction f of positrons stopping in PS that form triplet positronium vs the positron beam energy. The solid line is a fit of Eq. (1) to the commercial (Dow) PS data (open circles). This sample was also used for the Ar ion implantation test (solid circles) and for the data acquired above T_g (solid diamonds). Monodispersed samples are identified by their molecular weight M_w. The statistical fitting error is represented by the size of the plotting symbol.

Our interpretation is that the $f(E)$ profile is direct confirmation of the *spur* model of Ps formation in polymers [20]. In this model positrons that have slowed to several eV and are energetically incapable of capturing a bound electron can form Ps with electrons in the ionized "spur" of the slowing positron. Bulk studies [20] with electron scavenging impurities and a depth profiling experiment in crystalline ice [21] suggest that the spur process successfully competes with the so-called *Ore* model of Ps formation (fast positron capture of bound, molecular electrons). However, there has been a longstanding debate (see, for example, Ref. [22]) over the relative roles of each Ps formation process in amorphous materials. Our results for $f(E)$ in glassy PS, PC, PET, and silicone rubber indicate that the spur process is dominant. In the Ore model, electron capture occurs after the positron has slowed to tens of eV. There would be no further increase in $f(E)$ for $E > 100$ eV, a prediction that is clearly inconsistent with our results. Further support for the spur model is found in the low fluence (10^{13} cm^{-2}), low implantation depth (200 Å), Ar ion results in Fig. 1. Our interpretation of the almost uniform increase in $f(E)$ is that Ar bombardment generates additional trapped spur electrons far below the 200 Å Ar ion stopping range. Moreover, the entire increase in $f(E)$ can be neutralized by exposure to UV light which presumably photodetraps the spur electrons (without any rearrangement of void volume). We see no way to account for these results based on the Ore model.

The f vs E data for all of the polymers studied can be adequately fitted to an equation of the form

$$f(E) = f(0) + [f(\infty) - f(0)](1 - e^{-E/E_0}), \qquad (1)$$

where $f(0)$ and $f(\infty)$ are the fitted low and high E limits. $f(\infty)$ is always consistent with bulk PALS results. At low energy, where the spur-electron density should approach zero, a sizable $f(0)$ (as found in PMMA and DGEBA epoxy) could represent Ps formed in an Ore process. The increase in $f(E)$ is, however, assumed to be due to spur electron capture. The fitted parameter E_0 is taken to be a characteristic energy (called the "terminal spur energy" [20]) at which the positron stopping range becomes so large that spur electrons generated near the surface can no longer participate in Ps formation. To our knowledge, this is the first direct determination of the terminal spur energy, and it is surprisingly large [20], ranging from 740 eV in PC to 1400 eV in PS.

The strong energy dependence of $I_3(E)$ in the spur model complicates the detection of any real changes in the void density with depth. However, τ_3 is considered a more useful parameter, and its interpretation in terms of average void size is more reliable [11–13]. In order to know the surface specificity or depth resolution of τ_3 vs E, it is necessary to know the average depth at which Ps is formed for a given positron beam energy. Nominally, the average positron implantation depth [14] is given by $\bar{z}(E) = [(400\ \text{Å})/\rho]E^{1.6}$ for E in keV and density ρ in g/cm^3. This is the average depth over which the positron generates spur electrons in slowing down to about 20–30 eV. However, the spur electrons (which also have 20–30 eV of kinetic energy) and the positron will diffuse some distances, l_- and l_+, respectively, in slowing down to near-thermal energy where Ps formation can occur. Thus the probe depth will be greater than $\bar{z}$. Ultimately, a complete understanding of where and how Ps forms will be complicated, requiring knowledge of positron scattering and energy loss processes, electron-ion production and recombination, hot electron and positron mobilities, etc. At this point we assume $\bar{z}(E_0)$ is a measure of the average terminal spur size [23], with values listed in Table I.

The spur size represents some combination of l_-, l_+, and a correlation length, r_c, for electron-positron attraction to form Ps. r_c has an upper limit of about 200 Å [20] and could be much shorter if the particles trap or screen the interaction. We therefore conclude that l_- and/or l_+ must be of order $\bar{z}(E_0)$. If the spur size is primarily determined by l_+ (and not l_-) then the Ps probe depth cannot be much less than several hundred Å (Table I), despite the fact that $\bar{z}$ of the positron at low implantation energies is only tens of Å. Conversely, if l_+ is small then Ps forms at an average depth of $\bar{z}$ determined by the positron beam energy.

In an attempt to distinguish the relative sizes of l_- and l_+ we depth profiled several thin PS films on single crystal Si(111) wafers. The films were spin cast from a toluene solution and the thickness determined by ellipsometry and profilometry. The results at low E in Fig. 2 indicate that as long as the positron is *implanted* in the film Ps is also *formed* in the film without any interaction with the substrate (presumably f would be reduced by interaction with the Si substrate since Si has no 2 ns Ps lifetime component). Although not definitive [24], the film results suggest that l_+ in PS is small compared with the 170 Å film thickness and thus l_- primarily determines $\bar{z}(E_0)$. This tentative conclusion for PS ($l_- \sim 600$ Å, $l_+ \ll 170$ Å) predicts that the spur electron and positron mobilities are, respectively, $\mu_- > 1$ cm^2/V sec and $\mu_+ < 0.1$ cm^2/V sec. Further measurements of l_- may be useful in understanding radiation-induced conductivity in these nearly perfect insulators [25]. Bulk measurements of μ_+ are not sufficiently sensitive [26] to detect such a low mobility, although a beam measurement in Kapton [27] found $\mu_+ \approx 10^{-3}$ cm^2/V sec.

TABLE I. Fitted values of E_0 [from Eq. (1)] and the deduced terminal spur size for positronium formation, $\bar{z}(E_0)$. The statistical fitting error is shown in parentheses.

Sample	E_0 (eV)	$\bar{z}(E_0)$ (Å)
PS	1400 (110)	660 (80)
PC	740 (100)	200 (40)
PMMA	900 (110)	290 (55)
PET	925 (240)	270 (110)
DGEBA	1040 (110)	350 (60)
Silicone	980 (110)	375 (70)

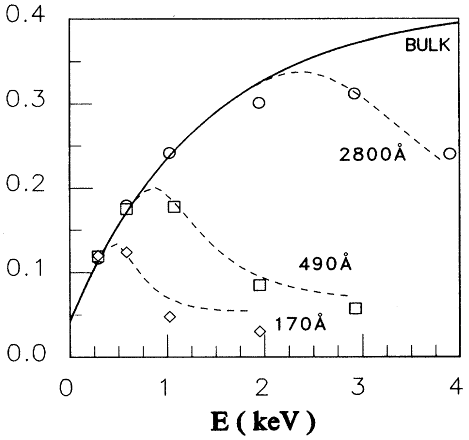

FIG. 2. Depth profiles (as per Fig. 1) for three PS films spin cast on Si(111) substrates. The solid line is a fit of the bulk sample profile from Fig. 1. For each film thickness indicated the dashed curve is a prediction for f using the bulk value multiplied by the calculated fraction of positrons implanted in the film. Without any fitted parameters, this fraction is calculated with the standard positron implantation profile [14] and $\bar{z}(E)$ as given in the text (15% backscattering is assumed at the Si interface).

Assuming l_+ is small we can fix the beam energy at a low value, 0.25 keV where $\bar{z} \sim 40$ Å, and search for surface shifts in T_g and void size relative to the bulk. As shown in Fig. 3, no reduction in T_g is observed

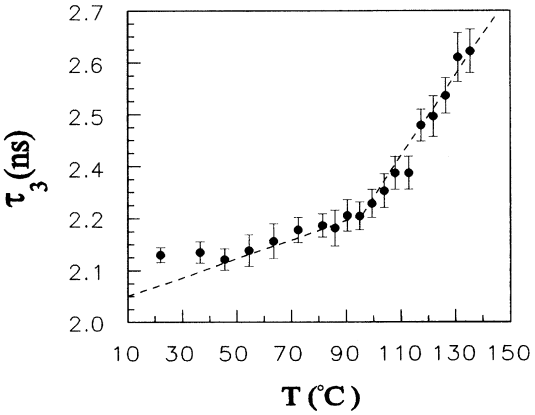

FIG. 3. The fitted values of τ_3 for a heated PS sample. All data were acquired with the beam energy fixed at 0.25 keV ($\bar{z} \sim 40$ Å). The dashed line represents bulk τ_3 data that were acquired with deeply implanted, beta-decay positrons.

for PS. Consistent with this result, τ_3, and hence the average void size, shows no indication of surface-enhanced relaxation. With $\bar{z} = 40$ Å we are nominally probing no deeper than 100 Å. This is less than the 140 Å radius of gyration for this sample, but there is little theoretical guidance [5] on the length scale for surface effects. We know of no other measurements of T_g at a vacuum-polymer surface, although an observed reduction in T_g for thin PS films on silicon [6] is interpreted in terms of a relaxed "liquid" layer on each surface of the film. Based on this model we would expect at least a 25 °C reduction in T_g for the top 100 Å layer. The apparent disparity between our results and the Si-supported film measurements [6,7] could be accounted for if the substrate interaction dominates a relatively small surface effect. Observations of PS film dewetting [1] demonstrate the importance of this Si substrate interaction. Alternatively, our probe depth (and hence l_+) may be much larger than expected. We should eventually be able to measure T_g with PALS in Si-supported films for a direct comparison with Ref. [6].

We conclude that PALS with variable energy beams of positrons (and eventually microbeams) is a promising, depth-sensitive probe of polymer surfaces, thin films, and interfaces. After accounting for surface backscattering effects (I_4, I_5), the exponentially asymptotic beam energy dependence of I_3 is attributed to Ps formation by spur-electron capture. Primarily due to l_-, deduced spur sizes are 200–660 Å. The mean probe depth is, however, not much larger than the average positron implantation distance, $\bar{z}(E)$, for $E \geq 0.25$ keV. Measurements of τ_3 vs temperature in PS at $\bar{z} \approx 40$ Å show no surface-induced reduction in T_g or in the average void size.

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