Sub-Glass-Transition-Temperature Annealing of Polycarbonate Studied by Positron Annihilation Spectroscopy

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ABSTRACT: Positron annihilation lifetime spectroscopy is used to monitor the sub-glass-transition-temperature (sub-T_g) annealing of a polycarbonate sample. The intensity of ortho-positronium annihilation decreases as a stretched-exponential function of annealing time at $T_g - 121$ K. The data are successfully fitted to a model applied to free-volume relaxation.

Introduction

Over the past several years experimental[1] and theoretical[2] advances have been made in the area of sub-glass-transition-temperature (sub-T_g) annealing of polymers and other glass-forming materials. The occurrence of sub-T_g annealing or physical aging is of practical importance because it generally leads to embrittlement.

Many techniques have been used to study sub-T_g annealing. These fall into two broad areas: (1) those that measure macroscopic properties that change somewhat linearly with the collapse of free volume that typifies physical aging and (2) those that measure microscopic properties that vary more or less exponentially with changing free volume. Observables that fall into the first category include macroscopic thermodynamic changes such as volume relaxation[3] and enthalpy relaxation.[4] Observables that fall into the second category generally include those that are indicative of molecular mobility such as dielectric or dynamic mechanical relaxation times.[5]

In recent years, positron annihilation spectroscopy (PAS) has emerged as a unique and potent probe for characterizing the free-volume properties of polymers.[6] PAS falls into category 2 above. In PAS, one employs the antiparticle of electrons, the positron, as a nuclear probe. Because of its positively charged nature, the positron is repelled by the ion cores and preferentially localized in the atomic-size free-volume holes of a polymeric material. Therefore, positron and positronium (a bound atom which consists of a positron and an electron) annihilation signals are found to be associated mainly with the free-volume holes in a polymer. Currently, for polymeric applications, PAS has been mainly developed for monitoring orthopositronium (o-Ps, the triplet state of Ps) annihilation lifetimes (PAL). In such applications, o-Ps lifetime and its probability are related to the free-volume hole size and fraction, respectively. Free-volume hole sizes, fractions, and distributions in a variety of polymers have been reported in recent years using PAL methods. Also, for the case of sub-T_g annealing, some PAL results have been reported;[7−10] the o-Ps lifetime and intensity were found to decrease as a function of time at temperatures below T_g in polymer samples, such as epoxies,[7] polystyrene,[8] polyvinyl acetate,[9] and polycarbonate.[10] No conclusive approach has been reported for relating the existing volume relaxation theory[2] and the free-volume hole properties probed by PAL. In this work, we measure o-Ps lifetime and its intensity under controlled sub-T_g annealing conditions and report a direct relationship between the relaxation model and the free-volume hole fraction probed by o-Ps in a polycarbonate sample.

Experimental Section

Sample. Polycarbonate (PC) is one of the most popular samples for the study of physical aging in polymers. It was supplied from General Electric Co. with the following properties: MW = 79 000, density = 1.200×10^3 kg/m^3, T_g = 145 °C (DSC). It is the same PC material used in our recent miscibility studies of polymer blends.[11] The PC sample was first heated to 210 °C under vacuum for 4 h in a copper cell and then quickly quenched in a liquid nitrogen bath for 0.5 h. The temperature of the quenched PC sample was then quickly raised to room temperature (24 °C) in a water bath for PAL experiments performed as a function of time at room temperature (24 °C) under vacuum.

Positron Annihilation Lifetime (PAL) Spectroscopy. The positron annihilation lifetimes of polymer blends were determined by detecting the prompt γ-rays (1.28 MeV) from the nuclear decay that accompanies the emission of a positron from the ^{22}Na radioisotope and the subsequent annihilation γ-rays (0.511 MeV). A fast−fast coincidence circuit of PAL spectrometer with a lifetime resolution of 260 ps as monitored by using a ^{60}Co source was used to record all PAL spectra. The counting rate was about 300 cps. Each spectrum was collected to a fixed total count of 1×10^6. Therefore, the reported time of sub-T_g annealing has a deviation of 0.5 h. Detailed descriptions of PAL can be found elsewhere.[12]

Mean Free-Volume Hole Size and Fraction. All of the PAL spectra obtained were analyzed by a finite-term lifetime analysis method using the PATFIT program.[13] The finite-term lifetime decomposes a PAL spectrum into two to five terms of negative exponentials. In these polymers, we found that three lifetime results give the best χ^2 (<1.1) and most reasonable standard deviations. The shortest lifetime ($\tau_1 \approx 0.12$ ns) is the lifetime of p-Ps (singlet Ps), the intermediate lifetime ($\tau_2 \approx 0.4$ ns) is due to positron (unbound) annihilation, and the long lifetime ($\tau_3 \approx 1-3$ ns) is due to o-Ps annihilation. In the current PAL method, we employ the results of o-Ps lifetime to obtain the mean free-volume hole radius by the following semiempirical equation:[14]

$$\tau_3 = \frac{1}{\lambda_3} = \frac{1}{2}\left[1 - \frac{R}{R_0} + \frac{1}{2\pi}\sin\left(\frac{2\pi R}{R_0}\right)\right]^{-1} \qquad (1)$$

where τ_3 (o-Ps lifetime) and R (hole radius) are expressed in ns and Å, respectively. R_0 is equal to $R + \Delta R$, where ΔR is a fitted empirical electron layer thickness (=1.66 Å).

The fractional free volume (%) is expressed as an empirically fitted equation:[15]

$$F_v = AV_fI_3 \qquad (2)$$

where V_f (in Å^3) is the volume of free-volume holes calculated by using the spherical radius (R) of eq 1 from τ_3 (in ns), I_3 (in %) is the intensity of the exponential term associated with τ_3,

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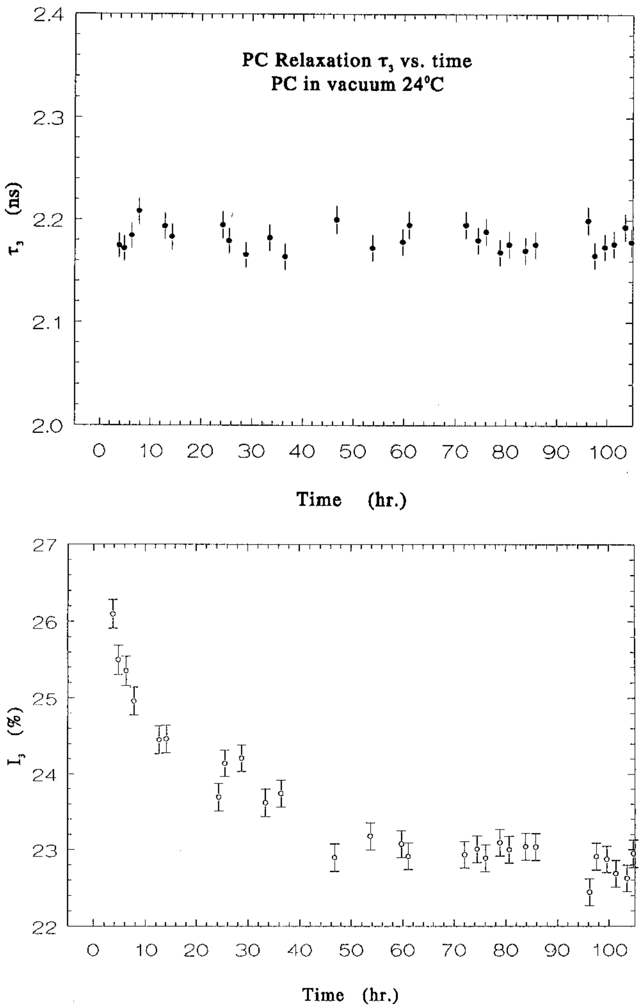

Figure 1. o-Ps lifetime, τ_3, and intensity, I_3, in PC as a function of annealing time at 297 K = T_g − 121 K. The sample was quenched at 77 K after it was heated at 483 K (see text). The PAL experiments were performed at 297 K under vacuum.

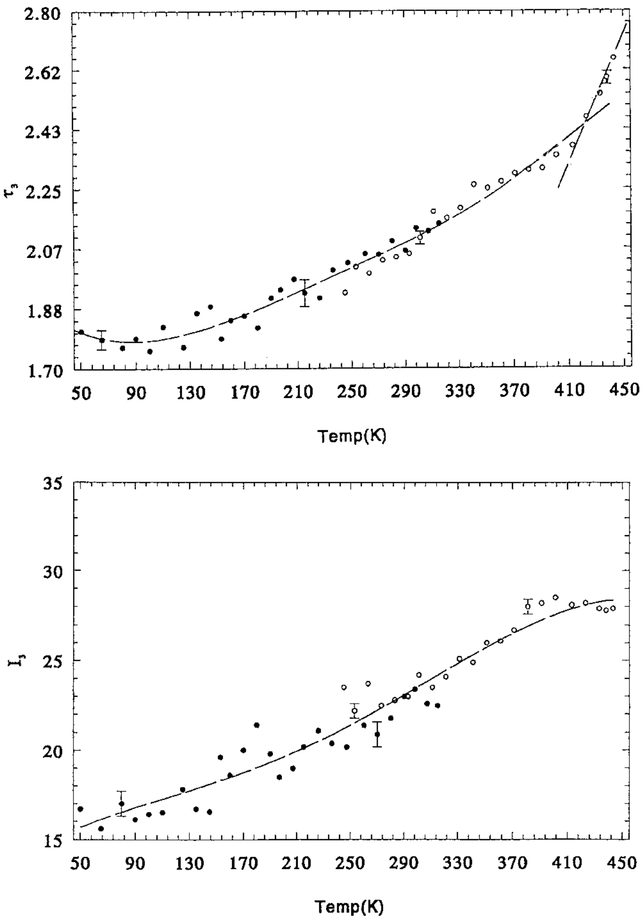

Figure 2. o-Ps lifetime, τ_3, and intensity, I_3, as a function of equilibrium temperature in PC. These data were taken from refs 16 and 14 after appropriate normalization for data between 250 and 300 K. Lines were drawn through data for clarity. The apparent T_g (DSC) = 418 K as seen by the break between drawn lines.

and *A* is empirically determined to be 0.0018 from the specific volume data.[15]

Results and Discussion

Plots of o-Ps lifetime (τ_3) and its intensity (I_3, %) as a function of sub-T_g annealing time at 24 °C for the PC samples are shown in Figure 1. τ_3 (2.2 ns) in our sample is consistent with reported values.[16−19] Existing I_3 results vary from 12% to 32% and depend on the sample conditions, such as MW, chemical composition, and aging. In Figure 2, we plot τ_3 and I_3 values at equilibrium temperatures (50−450 K) from two research groups[16,19] after a slight normalization of their data between 250 and 300 K. It is seen that both τ_3 and I_3 show a large variation with respect to temperature. Our I_3 and τ_3 results (Figure 1) for the nearly equilibrium state (time > 100 h) are consistent with those reported data (Figure 2) at 297 K (24 °C).

It is interesting that a constant value of τ_3 is observed as a function of annealing time. This indicates that the free-volume hole size in PC does not change as a function of sub-T_g annealing. When the PC is quenched from 483 to 77 K, the hole size contracts from 3.7 to 2.7 Å as calculated from eq 1 and the τ_3 data. And when the sample is raised to 297 K, the hole size immediately expands to 3.0 Å. The rate of volume relaxation is so rapid that we do not observe any change in its size (radius) or volume in a time scale on the order of 1 h, as shown in Figure 3. However, the intensity of o-Ps (I_3) shows a systematic decrease as a function of annealing time (Figure 1).

The o-Ps intensities I_3 = 30%, 16%, and 23% for PC at equilibrium temperatures of 483, 77, and 297 K, respectively, agree with the existing data (Figure 2). As shown in Figure 1, the extrapolated value of I_3 (29%) from the first four data points at the initial stage of annealing is nearly the same as I_3 at 483 K. The decrease of I_3 with annealing time thus indicates that the number of free-volume holes decreases as a function of annealing. We then calculate the fractional free volume (F_v, %) from eq 2 and plot F_v vs time in Figure 4 on both linear and log scales. These data were reproducible when we repeated the treatments in the same sample after it reached an equilibrium state (>100 h).

The data in Figure 4 were analyzed more quantitatively by comparing them to data generated by a simple free-volume relaxation model.[1] This model assumes that the free-volume relaxation rate is proportional to both the deviation of the glassy polymer from thermodynamic equilibrium and a relaxation parameter, T^{-1}:

$$\frac{d\delta}{dt} = -\frac{\delta}{T} \qquad (3)$$

Here δ is the difference between the actual free-volume fraction F_v and the equilibrium free-volume fraction F_e,

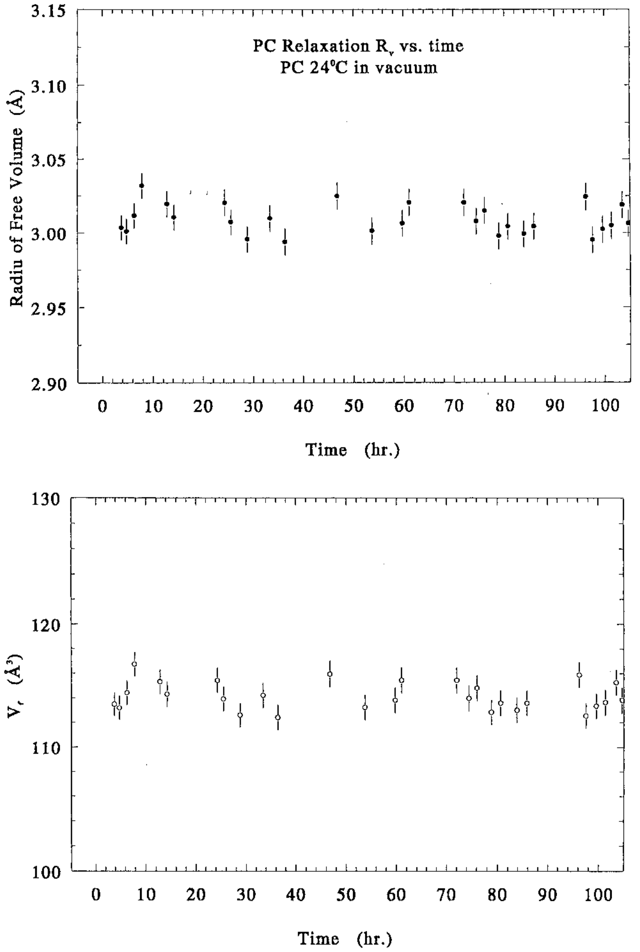

Figure 3. Mean radii (R) and volume (V_f) of holes in PC as a function of sub-T_g annealing time. These were calculated according to eq 1 with a spherical hole model.

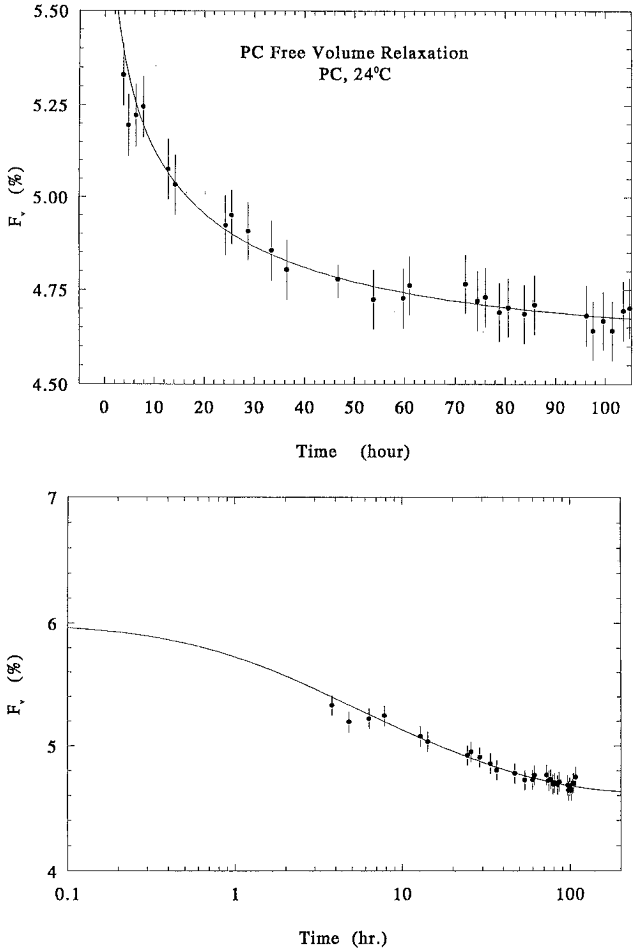

Figure 4. Fractional free volume (F_v) as a function of annealing time at 297 K = T_g − 121 K. The lines are fitted curves to eq 5 of one-parameter Doolittle model of volume relaxation (T_0 = 3.5 h, B = 0.60, F_0 = 6.0%, and F_e = 4.6%).

which is a function of sample temperature. The relaxation parameter T is assumed to be dependent on the fractional free volume F_v in a manner described by the following Doolittle-type[20] equation:

$$T = T_0 \exp\left(B\left[\frac{1}{F_v} - \frac{1}{F_0}\right]\right) \qquad (4)$$

where B is the Doolittle parameter, which corresponds to an “activation free volume” and generally has values near unity. Combining eqs 3 and 4 yields the following equation, which describes elapsed annealing time as a single-valued function of F_v (and vice versa):

$$\frac{t}{T_0} = -e^{(-B/F_0)} \int_{F_0}^{F_v(t=t)\geq F_e} \left(\frac{e^{[B/F_v]}}{[F_v - F_e]}\right) dF_v \qquad (5)$$

From the above equation F_v is expected to decrease approximately with $\log(t/T_0)$ if B is not too far from 1. Typical values of B range between 0.5 and 1.0, so F_v should vary smoothly with $\log(t)$. This is indeed the case, as shown in Figure 4 where we find the best-fitted B = 0.60, T_0 = 3.5 h, F_0 = 6.0%, and F_e = 4.6%. The fitted curves (with a correlation coefficient of fit = 0.95) according to eq 5 are shown as the solid lines in Figure 4.

Conclusion

The phenomenon of physical aging as monitored by sub-T_g annealing has been observed by using positron annihilation lifetime spectroscopy, which enables the direct observation of free-volume relaxation on a microscopic scale. The stretched-exponential plot between the observed fractional free-volume holes F_v and the annealing time can be nicely described by the familiar Doolittle model often used to describe volume relaxation.

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