Temperature and Time Dependence of Free Volume in Bisphenol A Polycarbonate Studied by Positron Lifetime Spectroscopy

J.-E. Kluin,[†] **Z. Yu,**[†] **S. Vleeshouwers,*** **J. D. McGervey,**[†] **A. M. Jamieson,**[‡] **and R. Simha**[‡]

Departments of Physics and Macromolecular Science, Case Western Reserve University, Cleveland, Ohio 44106, and Center for Polymers and Composites, Eindhoven University of Technology, 5600 MB Eindhoven, The Netherlands

Received March 9, 1992; Revised Manuscript Received May 27, 1992

ABSTRACT: New positron lifetime experiments have been carried out for Bisphenol A polycarbonate. The influence of unavoidable e^+ irradiation on the lifetime and intensity of *o*-Ps annihilation was investigated. Our results obtained using a state of the art lifetime spectrometer (count rate 670 cps with a 30-μCi ^{22}Na source, time resolution 260 ps fwhm for ^{22}Na) are free from potential artifacts due to irradiation damage. Three lifetime components were computed from each spectrum. The temperature dependence of the *o*-Ps lifetime (τ_3) and intensity (I_3) were measured in the range between 20 and 150 °C for the as-received material and between −30 and +180 °C after annealing above T_g. We find that τ_3 is unaffected by annealing but that I_3 is significantly larger for the annealed samples. In addition, the time dependence of τ_3 and I_3 due to physical aging in the glassy state was investigated at 30 and 90 °C, respectively. While τ_3 appeared constant for both temperatures, I_3 decreased significantly with aging time. Anomalies in the absolute τ and I values derived from such fits and the temperature dependence of these values indicate that a distribution of τ_3 lifetimes must be present in the *o*-Ps decay. This is consistent with the presence of a distribution of hole sizes which would be expected from current models of free volume in amorphous polymers. Variations in the distribution, e.g. conversion of larger into smaller holes may result in changes of the apparent I_3. Adopting a simple free volume definition, a comparison of the thermal expansivity of the vacancy fraction and of the macroscopic value yields a free volume fraction f of 8% at T_g = 150 °C.

Introduction

It is well understood that the size and concentration of free volume holes in amorphous polymers determine the polymer chain dynamics and hence play an important role in determining the mechanical properties and in diffusion phenomena. Knowledge of the temperature dependence of the hole free volume, especially of the change of the hole expansion coefficient through the glass transition, is very important as an experimental test of current free volume theories[1,2] and transport theories.[3,4]

Physical aging of an amorphous polymer, which occurs in the nonequilibrium glassy state, has its origin in the gradual approach to equilibrium and affects all material properties whose temperature and pressure coefficients change drastically at T_g.[5] Thermal expansion is related to the magnitude of free volume, and therefore corresponds to a change in the distribution of cavity sizes. Likewise, the physical aging process involves a time-dependent decrease in volume and, consequently, a corresponding change of the distribution of free volume holes.

The positively charged positron (e^+) is the antiparticle to the electron. Because of the repulsive interaction between e^+ and the positive nucleus, e^+ preferentially samples regions of minimal positive charge density. In the last two decades, positron lifetime spectroscopy has turned out to be one of the most powerful tools for the investigation of vacancy formation in metals[6,7] (see ref 8 for a review). The applicability of positrons to free volume studies in polymers is more complicated because, in addition to annihilating as a free positron with a mean lifetime of less than 500 ps, the positron can capture an electron and form a bound state, a so-called positronium atom (Ps).[9,10] Ps has an atomic radius similar to hydrogen. Two states of different lifetime are possible: (a) *para*-positronium (*p*-Ps), consisting of an electron–positron state with antiparallel spins (spin = 0), annihilates after a mean lifetime τ_1 of 125 ps to produce two 0.511-meV γ-rays; (b) *ortho*-positronium (*o*-Ps), an electron–positron state with parallel spins (spin = 1), must generate three γ-rays in order to conserve spin angular momentum and parity. The ratio of *p*-Ps to *o*-Ps formation equals $^1/_3$. Because the three-γ process is much less likely than the two-γ decay, the mean lifetime τ_3 of *o*-Ps in vacuum is 142 ns.

In condensed matter, however, *o*-Ps can pick off an electron with antiparallel spin. The mean lifetime of *o*-Ps shortens to a few nanoseconds, depending on the electron density of the material surrounding *o*-Ps. Because of its polarizability, Ps samples regions of minimal charge density. Therefore the *o*-Ps wavefunction is concentrated in free volume holes. Since the annihilation rate of *o*-Ps is proportional to the overlap of the positron and the pick-off electron wave functions, the *o*-Ps lifetime is a function of the hole size in which this particle resides.

A theoretical model,[11,12] in which the positronium resides in a sperical potential well having an infinite potential barrier of radius R_o with an electron layer in the region $R < r < R_o$, predicts a connection between τ_3 and the (spherical) free volume hole size. Using this semiempirical approach, one can determine the average absolute size of free volume holes from this relation:

$$1/\tau_3 = \lambda_3 = 2[1 - R/R_o + 1/2\pi \sin (2\pi R/R_o)] \quad (1)$$

with $R_o = R + \Delta R$ and the reasonable assumption that the lifetime of *o*-Ps in the electron layer is the spin-averaged Ps lifetime of 0.5 ns. A value ΔR = 0.1656 nm was determined by fitting experimental τ_3 values to data from molecular materials with well-known hole sizes.[13]

While there is no doubt that Ps indeed samples free volume in molecular solids (see ref 14 for a review), its precise behavior is still poorly understood. In particular,

---

* To whom correspondence should be addressed at Eindhoven University of Technology.

[†] Department of Physics, Case Western Reserve University.

[‡] Department of Macromolecular Science, Case Western Reserve University.

0024-9297/92/2225-5089$03.00/0

the effect on *o*-Ps annihilation of a distribution of hole sizes is controversial. To explain the reasonably good fit of their positron lifetime curve to a three-component distribution, Kobayashi et al.[15] assumed that an *o*-Ps atom samples a number of holes during its lifetime, so that all *o*-Ps atoms have approximately the same lifetime, even though the holes are of different sizes. In contrast, Deng et al.[16] observed a distribution of τ_3 values in an epoxy polymer and thus assumed that each *o*-Ps is in a single hole during its lifetime.

In this connection we note that, as described above, a *p*-Ps decay of about 125-ps mean lifetime with a corresponding intensity $I_1 = I_3/3$ is expected on theoretical grounds. In many experiments analyzed by three-component distributions in a free-fitting procedure, experimental values of τ_1 and I_1 are generally found to be larger than 125 ps and $I_3/3$. The origin of this discrepancy is unclear, but one possibility is a contribution from short-lived *o*-Ps annihilation. A second potential problem which has recently become evident[17] in *o*-Ps studies in polymers is the presence of damage due to e$^+$ irradiation. This may result in decreasing values of I_3, proportionate to the source strength and the time of exposure. The effect can be erased by increasing the temperature above T_g.[17]

In the present paper we present results from positron lifetime experiments in Bisphenol A polycarbonate using a spectrometer with a high efficiency which allows us to reduce irradiation damage effects. Measurements were carried out in "as-received" material and also after annealing above T_g. Due to careful thermal treatment of the samples and the use of an improved sample holder, spectra could be accumulated up to temperatures of 30 °C above T_g. In addition, physical aging experiments at 30 and 90 °C have been carried out. Analysis of the extracted absolute τ and I values suggests that there is indeed a distribution of τ_3 lifetimes related to a distribution of hole sizes which is to be expected according to the statistical mechanical theory of Simha and Somcynsky.[1] This formalism contains a free volume parameter h which can be extracted in the melt and in the glass by fitting PVT data to the predicted equation of state.

Experimental Procedure

Disks of 10-mm diameter were machined from a Bisphenol A Polycarbonate sheet of 2-mm thickness, which was kindly provided from Bayer AG, Leverkusen, Germany. The glass transition temperature T_g has been determined to be 150 °C using differential scanning calorimetry (DSC) at a heating rate of 20 °C/min.

For lifetime spectroscopy, about 1 MBq of ^{22}Na deposited in an envelope of aluminum foil (1.7 mg/cm^2) was sandwiched between two sample disks. This sandwich was completely enclosed in a copper sample holder. Heating wires were mounted at two opposite sites of the sample holder, so that a good thermal contact to the sample was guaranteed and temperature gradients could be avoided. Each selected temperature was kept constant within ±0.2 °C during data aquisition by means of two diode sensors, which were connected to a temperature controller (Model DTC 500-SP) supplied by Lake Shore Cryotronics, Westerville, OH. The entire assembly was placed in a vacuum chamber, which provided the capability of sample cooling down to temperatures of liquid nitrogen.

The following sequence of measurements was carried out on samples of different thermal histories in a vacuum of about 10^{-3} mbar:

(a) In order to investigate the influence of e$^+$ irradiation on positronium formation, measurements were performed at 22 °C on the as-received ("old") material immediately after source installation every 90 min for an initial 25.5 h and finally after 75 h.

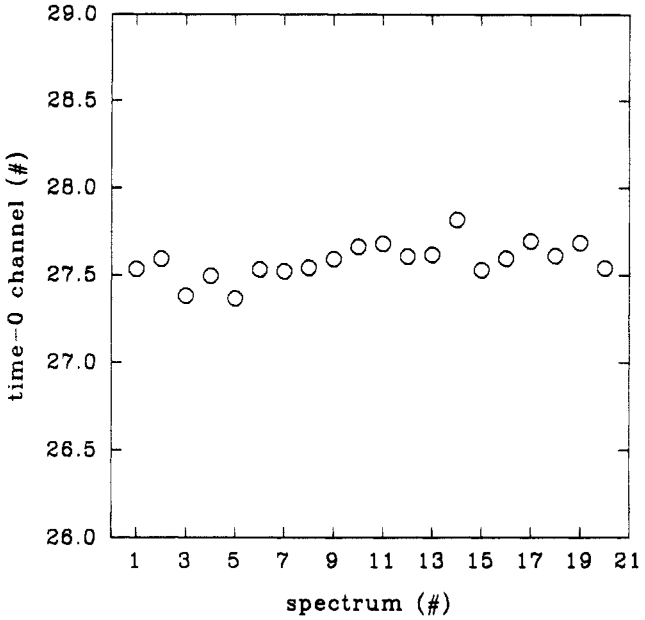

Figure 1. Time-zero channel location of spectra used for determination of the resolution function. One channel equals 10 ps.

(b) Next, the temperature was raised from 20 to 150 °C in steps of 10 deg and lifetime spectra were obtained at each temperature.

(c) Before the subsequent set of measurements the polycarbonate was annealed in the chamber at 154 °C (slightly above T_g) for 18 h to produce well-annealed ("new") glasses. Then spectra were recorded as the temperature was decreased in steps of 10 deg (cooling rate 1 °C/min) down to −30 °C, with a new annealing period at 154 °C for 30 min between each step. Note that this procedure further minimizes possible contributions from irradiation damage which will disappear during each annealing period. Subsequently, in the rubbery state, the temperature was increased stepwise from 154 to 175 °C.

(d) Finally, short-term (60-h) physical aging experiments were carried out at 90 and 30 °C, respectively. Between each isothermal series of measurements, the sample was again annealed at 154 °C for 12 h.

During periods of constant temperature, positron lifetime spectra were collected on a PCA multichannel analyzer (Nucleus Inc., Oak Ridge, TN). A fast-fast lifetime spectrometer was employed, which was based on EG&G Ortec NIM modules [e.g., Model 583 constant-fraction discriminator (CFD) and a Model 566 time-to-amplitude converter (TAC)]. To optimize the resolution as well as the efficiency of the spectrometer, a cylindrical CsF crystal of 1.5-in. length and 1.5-in. diameter (Solon Technologies, Inc.), coupled by glycerol[18] to a photomultiplier tube (Type H2431, Hamamatsu, Japan), was used to detect the 1.275-MeV γ-rays which indicate the "birth" of a positron. In order to detect the 0.511-MeV annihilation γ-ray, a conical BaF$_2$ crystal of 0.8- and 1.0-in. diameters and 1.0-in. length[19] (Solon Technologies, Inc.) likewise mounted to a photomultiplier tube (Type H2431Q, Hamamatsu, Japan) was employed. With an appropriate window setting of both CFD's, spectra which contained about 1.2 million counts were collected within 30 min (count rate 670 cps) with 260-ps fwhm time resolution.

For the analysis of the spectra the fit program PATFIT-88[20] was employed. A two-component source term (0.5651 ns with 1.5%, 0.1883 ns with 7.5%) was subtracted uniformly from each spectrum. In order to determine the resolution function, several spectra were fitted from the left-hand side of the peak into the background on the right-hand side by means of the program RESOLUTION.[20] The resolution function was approximated as a sum of three Gaussians whose statistical weights and fwhm as well as the time-zero channel were determined by the fitting program. To demonstrate the good stability of our system, the fitted time-zero channel location of those spectra is depicted in Figure 1. The resolution function as well as the time-zero channel were found to be identical and fixed during the final three-

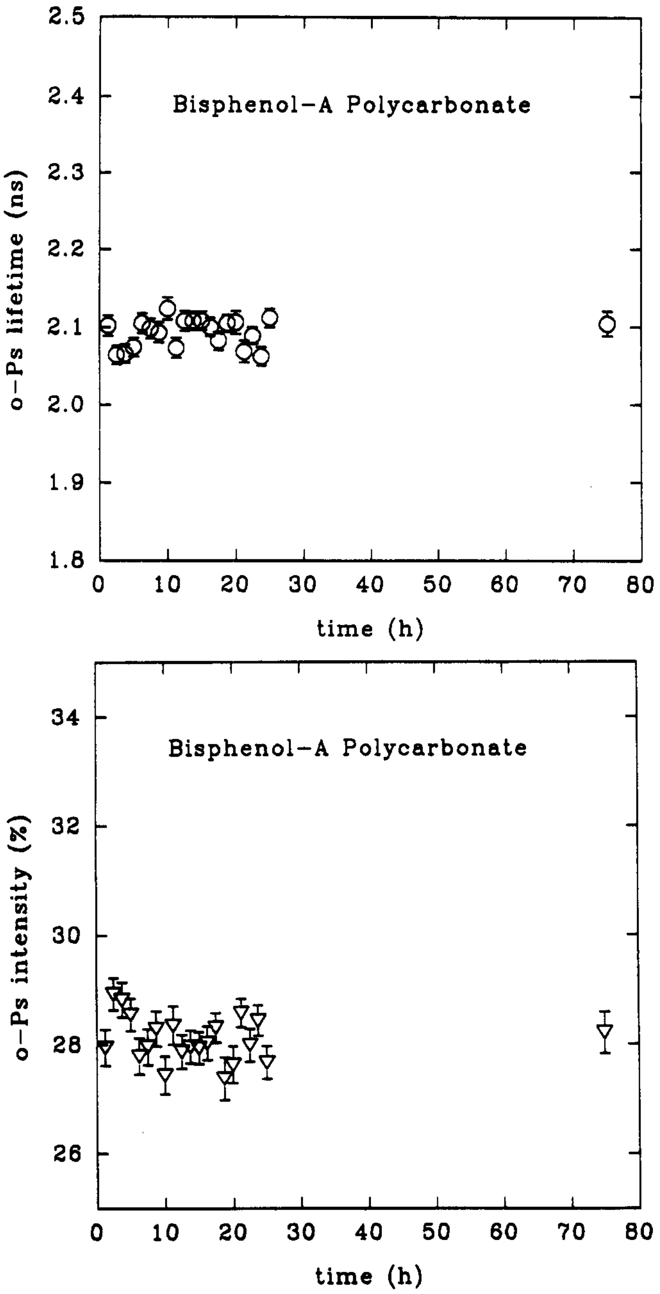

Figure 2. Time dependence of the *o*-Ps lifetime τ_3 (a) and corresponding intensity I_3 (b) in as-received Bisphenol A polycarbonate. Data collected at T = 22 °C.

component analysis. Spectra were analyzed from the peak well into the background on the right side. The X^2/ν values were always between 0.9 and 1.2. There were no constraints for τ_1, τ_2, and τ_3 and corresponding intensities, except $I_1 + I_2 + I_3 = 1$. The background was a free-fit parameter.

Results and Discussion

Positron irradiation effects are explored in Figure 2a,b. In agreement with recent measurements in Bisphenol A polycarbonate,[17] neither τ_3 nor I_3 change significantly over the exposure periods used in our experiments. Therefore, the influence of e^+ irradiation on the current investigations can be excluded.

Parts a and b of Figure 3 compare the results of measurements of the *o*-Ps decay as a function of temperature in the as-received material (filled symbols) and after annealing above T_g (open symbols). Within the scatter of the data no difference in τ_3 can be observed. Values of the average hole size V_{hole} in Bisphenol A polycarbonate, which have been determined from eq 1, are depicted at the right vertical axes of Figure 3a. Apparently, V_{hole} does not depend on the thermal history of the material. From the slopes of $V_{hole}(T)$ two distinct thermal expansion coefficients can be extracted, using linear fits: below T_g 150 °C $\alpha_{hole,g} = 2.5 \times 10^{-3}/K$ describes the thermal expansion of the average hole volume of the glassy polymer state, which increases drastically at above 150 °C to the melt value $\alpha_{hole,m} = 7.2 \times 10^{-3}/K$. In order to calculate the corresponding macroscopic volume expansion coefficients α_g and α_m, the fraction of the free volume in the sample has to be known. Consider a simple definition of a free volume fraction f, namely

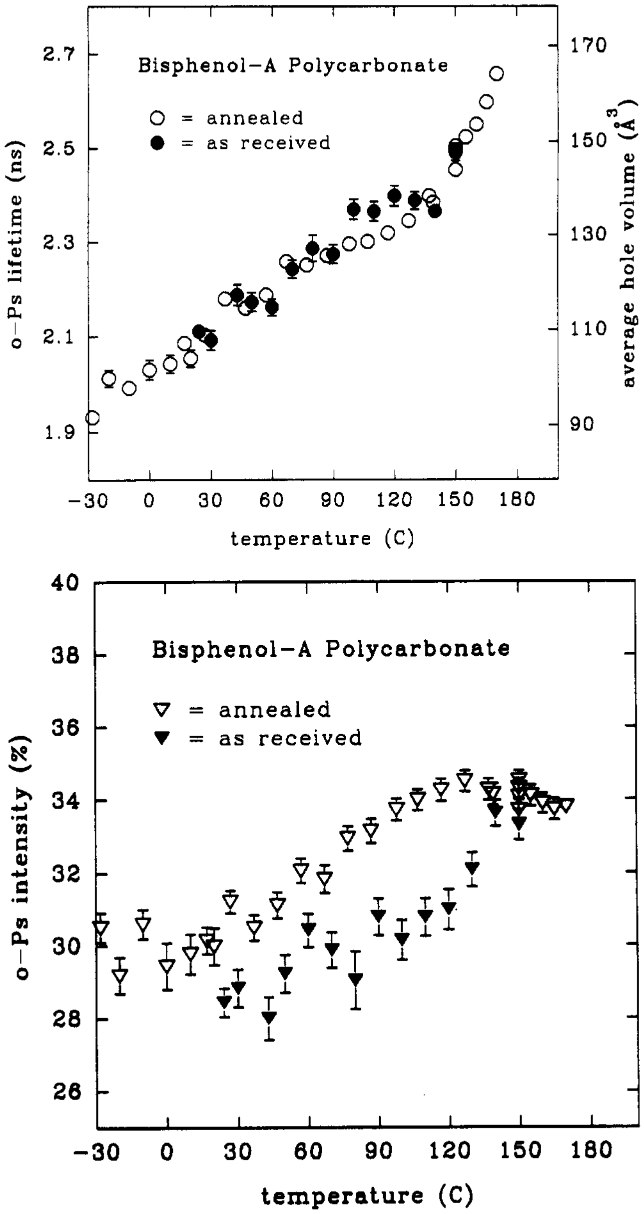

Figure 3. Comparison of the temperature dependence of (a) the *o*-Ps lifetime and (b) corresponding intensities in as-received and annealed material.

$$f = (V - V_o)/V \qquad (2)$$

with V the total and V_o the hard core volume of the sample. The macroscopic expansion coefficient α can be expressed then as

$$\alpha = \alpha_{hole} f/(1 - f) + d \ln V_o/dT \qquad (3)$$

Under the assumption of constant V_o it follows that

$$\alpha/\alpha_{\text{hole}} = f/(1-f) \qquad (4)$$

Using values of $\alpha_g = 2.15 \times 10^{-4}/K$ and $\alpha_m = 6.04 \times 10^{-4}/K$ for the macroscopic thermal expansion coefficients measured by means of dilatometric techniques[21] and the above-mentioned values for $\alpha_{\text{hole,g}}$ and $\alpha_{\text{hole,m}}$ from PAS measurements, a volume fraction $f = 0.08$ at $T_g = 150$ °C is obtained from both data sets. A detailed discussion of the application of the statistical mechanical theory to the free volume distribution in polycarbonate and comparison with these positron data will be given elsewhere.[22] Here we note that application of the equation of state theory yields a parameter $h(T_g) = 0.10$, which represents the hole fraction in this model.

While no deviation in τ_3 between old and new Bisphenol A polycarbonate was measured, I_3 of the as-received sample was found to be significantly lower for temperatures below T_g. In previous analysis,[15] I_3 was assumed to be directly proportional to the number density of free volume holes. In this framework, the deviations observed here can be interpreted as the result of volume relaxation in the old material caused by physical aging during storage. Our observations can be contrasted with an earlier study,[23,24] in which *o*-Ps annihilation in Bisphenol A polycarbonate was compared for specimens as received and subjected to a stepwise thermal cycling to 120 °C. This earlier study was performed with a spectrometer of lower efficiency than that used in our present work. Typically, in the earlier study, it took 9 h to measure a spectrum (10^6 counts) whereas in our work, we obtain a spectrum (1.2×10^6 counts) in 30 min, so that the time of e^+ irradiation, which can affect the apparent I_3,[17] is drastically reduced. Notwithstanding the fact that the samples were never at equilibrium, i.e. above T_g, it was found that τ_3 was unaffected by thermal cycling whereas I_3 increased. The magnitude of the change is substantially larger in our experiments, however. We note further that, in this earlier study, a second set of experiments was performed in specimens aged in the glass over a period of 4 months, after which τ_3 and I_3 had decreased to values below those in the as-received material. Interpretation of this as evidence of free volume decrease[24] must be considered suspect without proof of the absence of e^+ irradiation effects.

In the glassy polymer state, I_3 in the well-annealed as well as in the old material decreases significantly with decreasing temperature. This behavior would indicate that the number of free volume holes is strongly temperature dependent. However, on theoretical grounds, only a slight decrease is to be expected.[22] In order to investigate this phenomenon, the lifetimes and intensities for *p*-Ps (component 1) and free-positron annihilation (component 2) were examined. The corresponding lifetimes, τ_1 and τ_2, were found to be 220 and 590 ps, respectively, and independent of temperature (Figure 4). Each value is significantly larger than expected. While no definite temperature dependence was observed in I_1 and I_2, we find a direct numerical correlation of both parameters and an absolute value of I_1 that is about 4 times the expected value $I_3/3$. We believe that each effect is an artifact of the fitting procedure, suggesting that there are multiple *o*-Ps lifetimes. Since the fitting program is not able to accurately fit a large number of values, the decrease observed in I_3 with decreasing temperature may be a result of changes in the short-time part of the τ_3 distribution.

The results of physical aging experiments are depicted in Figure 5a,b. In agreement with the previous comparison of $\tau_3(T)$ in the old and new material, no significant effect in τ_3 is observed either at 90 or at 30 °C. However, I_3 decreases slightly with aging time for both temperatures. Due to the rather large scatter of the data, a quantification of the aging function $I_3(t)$ is not possible. As for previous studies in polystyrene,[25] polycarbonate,[23,24] and poly(vinyl acetate),[15] the decrease in I_3 suggests that physical aging reduces only the number of holes, while the apparent change in the average measured hole volume seems to be only of minor importance. Again, however, the effect is likely to be an indirect reflection of changes in the τ_3 distribution.

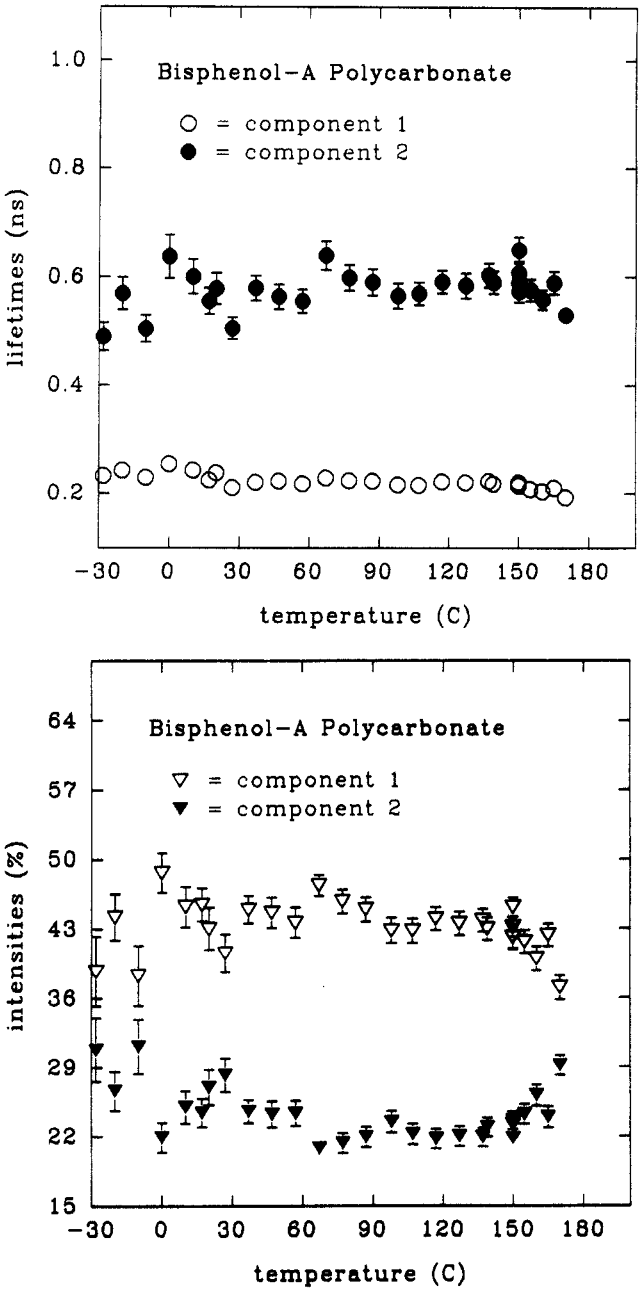

Figure 4. τ_1 and τ_2 (a) and intensities I_1 and I_2 (b) as a function of temperature. A correlation between I_1 and I_2 is clearly evident.

Conclusions

We have presented results of positron lifetime measurements in Bisphenol A polycarbonate, carried out to compare the temperature dependence of free volume in as-received (old) specimens (temperature range 20–150 °C) and well-annealed material (new) (temperature range −28 to +180 °C). Positron lifetime spectra were analyzed

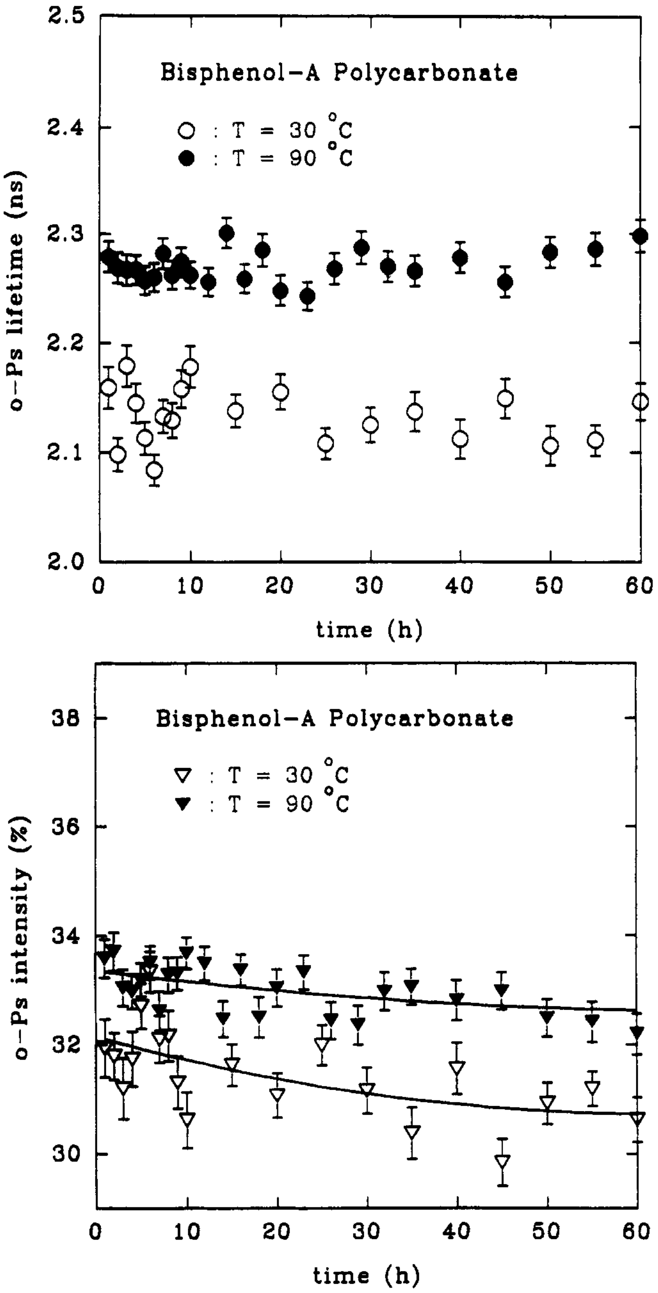

Figure 5. Physical aging at 30 and 90 °C. While no time dependence is found in τ_3 (a), I_3 decreases slightly with aging time.

by means of PATFIT-88 in a free three-component analysis. While no deviation between the old and new samples could be observed in the o-Ps lifetimes, the corresponding intensities were strongly dependent on the thermal history of the sample, being higher in the annealed sample. Volume relaxations due to physical aging during storage of the material may be responsible for this effect. Using the model of Tao, average free hole sizes V_{hole} were determined from measured τ_3 values. By adoption of a simple free volume definition, a comparison of the thermal expansivities of cavity sizes extracted from o-Ps lifetimes and of the macroscopic volume expansion yields a free volume fraction at T_g of 0.08. In the glassy state the intensity I_3 increases more rapidly with increasing temperature than expected on theoretical grounds.[22]

These and similar observations for other polymers raise questions regarding the numerical analysis of the positron experiment. The lifetimes τ_1 and τ_2 were found to be 220 and 590 ps, respectively, and independent of temperature. Both values are significantly higher than expected. While no temperature dependence was found for the corresponding intensities, a direct correlation of both parameters and an unexpectedly high value of I_1 was obvious. This and the above-mentioned temperature dependence of I_3 suggest the possibility that artifacts of the fitting procedure originating from the presence of multiple o-Ps mean lifetimes are present. Further investigations are underway to confirm this interpretation. Specifically, the application of the three-component fitting procedure to interpret simulated positron lifetime spectra which contain τ_3 distributions based on free volume Monte Carlo simulations will be a rigorous test and will be the topic of a forthcoming paper.

Acknowledgment. We thank Dr. Y. Kobayashi and M. Y. Ruan for useful discussions. This research was supported by the U.S. Army Research Office, Contract No. DAAL03-90-G-0023 and a research award from Miles, Inc., Pittsburgh, PA.

References and Notes

(1) Simha, R.; Somcynsky, T. *Macromolecules* **1969**, *2*, 342.
(2) McKinney, J. E.; Simha, R. *Macromolecules* **1976**, *9*, 430.
(3) Crank, J., Park, G. S., Eds. *Diffusion of Polymers*; Academic Press: New York, 1986.
(4) Vrentas, J. S.; Duda, J. L. *J. Polym. Sci.* **1977**, *15*, 403.
(5) Struik, L. C. E. *Physical Aging in Amorphous Polymers and other Materials*; Elsevier: Amsterdam, 1978.
(6) Hehenkamp, Th.; Kurschat, Th.; Luehr-Tanck, W. *J. Phys. F* **1986**, *F16*, 981.
(7) Kluin, J.-E.; Hehenkamp, Th. *Phys. Rev. B* **1991**, *44*, 11597.
(8) Hautojaervi, P., Ed. *Positrons in Solids*; Springer Press: New York, 1979.
(9) McGervey, J. D.; Walters, V. F. *Phys. Rev. Lett.* **1964**, *13*, 408.
(10) McGervey, J. D.; Walters, V. F. *Phys. Rev. B: Solid State* **1970**, *B2*, 2421.
(11) Tao, S. J. *J. Chem. Phys.* **1972**, *56*, 5499.
(12) Nakanishi, H.; Jean, Y. C. In *Positron and Positronium Chemistry*; Schrader, D. M., Jean, Y. C., Eds.; Elsevier: Amsterdam, 1988; p 159.
(13) Nakanishi, H.; Wang, S. J.; Jean, Y. C. In *Proceedings of the International Conference on Positron Annihilation in Fluids*, Arlington, TX; Sharma, S. C., Ed.; World Scientific Publishing: Singapore, 1987; p 292.
(14) Schrader, D. M., Jean, Y. C., Eds. *Positron and Positronium Chemistry*; Elsevier: Amsterdam, 1988.
(15) Kobayashi, Y.; Zheng, W.; Meyer, E. F.; McGervey, J. D.; Jamieson, A. M.; Simha, R. *Macromolecules* **1989**, *22* (5), 2302.
(16) Deng, Q.; Zandiehnadem, F.; Jean, Y. C. *Macromolecules*, in press.
(17) Welander, M.; Maurer, F. H. J. *Positron Annihilation*; Proceedings of the 9th International Conference on Positron Annihilation, Sombathely, in press.
(18) Bauer, W.; Major, J.; Weiler, W.; Schaefer, H. E. In *Positron Annihilation*; Proceedings of the 7th International Conference on Positron Annihilation, New Delhi; Jain, P. C., Singru, R. M., Gopinathan, K. P., Eds.; World Scientific Publishing: Singapore, 1985; p 82.
(19) McGervey, J. D.; Vogel, J.; Sen, P.; Knox, C. *Nucl. Instrum. Methods* **1977**, *143*, 435.
(20) Kirkegaard, P.; Pedersen, N. J.; Eldrup, M. Riso National Laboratory, Denmark, 1989.
(21) Greiner, R.; Schwarzl, F. R. *Rheol. Acta* **1984**, *23*, 378.
(22) Vleeshouwers, S.; Kluin, J.-E.; McGervey, J. D.; Jamieson, A. M.; Simha, R. *J. Polymer Sci.: Polym. Phys.* Submitted for publication.
(23) Hill, A. J.; Jones, P. L.; Lind, J. H.; Pearsall, G. W. *J. Polym. Sci. A: Polym. Chem.* **1988**, *26*, 1541.
(24) Hill, A. J.; Heater, K. J.; Agrawal, C. M. *J. Polym. Sci.: Polym. Phys.* **1990**, *28*, 387.
(25) McGervey, J. D.; Panigrahi, N.; Simha, R.; Jamieson, A. M. In *Positron Annihilation*; Proceedings of the 7th International Conference on Positron Annihilation, New Delhi; Jain, P. C., Singru, R. M., Gopinathan, K. P., Eds.; World Scientific Publishing: Singapore, 1985; p 690.

Registry No. PC (copolymer), 25037-45-0; PC (SRU), 24936-68-3.