Free Volumes in Polystyrene Probed by Positron Annihilation

A. Uedono, T. Kawano, Lumei Wei, S. Tanigawa, M. Ban, M. Kyoto

► To cite this version:

A. Uedono, T. Kawano, Lumei Wei, S. Tanigawa, M. Ban, et al.. Free Volumes in Polystyrene Probed by Positron Annihilation. *Journal de Physique IV Proceedings*, 1995, 05 (C1), pp.C1-199-C1-203. 10.1051/jp4:1995123 . jpa-00253559

HAL Id: jpa-00253559

<https://hal.science/jpa-00253559>

Submitted on 1 Jan 1995

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Free Volumes in Polystyrene Probed by Positron Annihilation

A. Uedono, T. Kawano*, L. Wei, S. Tanigawa, M. Ban** and M. Kyoto**

Institute of Materials Science, University of Tsukuba, Ibaraki 305, Japan

** Radioisotope Center, University of Tsukuba, Tsukuba, Ibaraki 305, Japan*

*** Analytical Characterization Center, R&D Group, Sumitomo Electric Industries Ltd., 1 Taya-cho, Sakae-ku, Yokohama 244, Japan*

Polystyrene specimens with different molecular weights were characterized by the positron annihilation technique. Lifetime spectra of positrons were measured in the temperature range between room temperature and $\sim 150^\circ\text{C}$. The observed lifetime spectra were resolved into three components, where the longest lifetime, τ_3 , was associated with pick-off annihilation of ortho-positronium (o-Ps) trapped by free-volumes. Above the glass transition temperature (T_g), the temperature coefficient of τ_3 was found to be about 4 times larger than that below T_g , while no drastic change in the intensity corresponding to the annihilation of o-Ps was observed at T_g . These facts suggest that the glass transition mainly affects the expansion rate of the free volumes in polystyrene specimens.

1. INTRODUCTION

The application of the positron annihilation technique to studies of lattice defects in solids has contributed a substantial amount of valuable information. Previous studies using the positron annihilation technique have demonstrated that positrons can be utilized as a nondestructive and sensitive probe for vacancy-type defects in metals and semiconductors [1]. This technique gives direct information about sizes of open spaces and their concentrations in amorphous polymers [2]. A positron implanted into the specimen eventually annihilates with an electron producing annihilation γ -rays. The lifetime of positrons in materials reflects the density of electrons in region where the positron annihilates. Since a positron is positively charged, it is repelled from ion cores by Coulomb interaction. Thus, if a specimen contains vacancy-type defects, there is a finite probability of positrons being trapped in these regions. Due to reduced electron density in vacancy-type defects, the lifetime of trapped positrons increases. For metals and semiconductors, the relationship between the lifetime of positrons and the species of defects has been established. By using this technique, the concentration of defects for a detectable response is about 0.1 ppm, and there are no restrictions regarding specimen conductivity nor specimen temperature.

It is well known that positronium (Ps) atoms may form in molecular solids [2]. Ps exhibits two spin states which are called "ortho" (o-) and "para" (p-) for the triplet state and the singlet state, respectively [3]. The intrinsic lifetime of p-Ps is calculated as ~ 0.125 ns and that of o-Ps is ~ 140 ns. In very dilute gases or in powders, one may observe lifetimes of o-Ps very close to those given above. In condensed materials, however, the lifetime of o-Ps is only 1–3 ns because the positron involved in o-Ps can annihilate with one of the surrounding electrons rather than its own partner. This process is called "pick-off" annihilation [4]. Ps can not form in materials with high electron densities such as metals or semiconductors. Unlike metals or semiconductors, amorphous polymers always contain a large fraction of imperfect regions. Many of these regions serve as free-volumes for the formation of Ps. Because of the relatively small size of Ps (~ 0.106 nm), the positron annihilation technique is particularly sensitive to small holes and free volumes of sub-nm in size. Despite many studies which have been carried out, the

annihilation characteristics of positrons in amorphous polymers are not yet so clear. This may be due to complicated annihilation modes of positrons in amorphous polymers, and resultant difficulties in the data analysis. Because of the difficulty of the deconvolution of lifetime spectra, previous studies have mainly discussed the behavior of o-Ps in amorphous polymers. Information about other annihilation modes, however, is also important for a full understanding of the annihilation characteristics of positrons in amorphous polymers. In the present paper, therefore, we report high precision measurements of lifetime spectra of positrons for polystyrene specimens with different molecular weights in order to obtain detailed information not only about the annihilation of Ps but also that of positrons.

2. EXPERIMENT

The polystyrene specimens used in the present experiment were reagent grade. The average molecular weights, M_n , of the specimens were $M_n=5,730$ ($M_w/M_n=1.02$) and $M_n=1,520,000$ ($M_w/M_n=1.26$), respectively. The specimen with $M_n=5,730$ was casted from a melt at 150 °C under a nitrogen atmosphere, and it was slowly cooled to room temperature. The specimen with $M_n=1,520,000$ was casted by using 10 wt% chloroform solvent, and annealed at 150 °C for 48 hours under vacuum. In order to know the effects of chloroform on the formation of Ps, lifetime spectra for polystyrene specimens with different chloroform concentrations were measured. From these measurements it was found that chloroform decreased the intensity corresponding to pick-off annihilation of o-Ps, while no drastic change in the lifetime of o-Ps was observed. For the specimen with $M_n=1,520,000$, the concentration of residual chloroform is considered to be very low because of the severe thermal treatment. However, the effect of the residual chloroform was not confirmed in this specimen.

The lifetime spectra of positrons were measured while lowering the specimen temperature at a rate of ~ 0.5 °C/h in a vacuum of 10^{-4} Pa. The temperature of the specimen was automatically stabilized by a temperature controller. A two-parameter multichannel analyzer was designed in order to measure both lifetime spectra of positrons and the specimen temperature. By using this system, the lifetime spectra and the specimen temperature were automatically stored into 1024 channels (lifetime spectra) $\times$ 64 channels (temperature). The lifetime spectra were measured by a fast-fast system with BaF₂ scintillators attached to XP2020Q photomultiplier tubes. A ^{22}Na source with an activity of about 7×10^5 Bq deposited on a Kapton foil with a thickness of 7.5 μm , was sandwiched between two specimens. The full width at half-maximum (FWHM) of the time resolution of the system was ~ 220 ps. At each temperature, the observed lifetime spectrum contained about 1×10^6 counts.

The lifetime spectrum of positrons, $I(t)$, is expressed by,

$$I(t) = \sum I_i \exp(-t/\tau_i), \quad (\sum I_i = 1) \quad (1)$$

where τ_i and I_i are the lifetime of the i -th component and its intensity, respectively. The lifetime of positrons annihilated in the Kapton films, τ_{source} , was estimated from measurements of the lifetime spectrum for a well-annealed Ni specimen. This lifetime spectrum was decomposed into two components by a computer code "RESOLUTION" [5], and the obtained value of τ_{source} was 393 ps and its intensity, I_{source} , was 16.0%, where the lifetime of positrons in the Ni specimen was 110 ps. The derived value of τ_{source} was in good agreement with the value reported in previous experiments [6]. For the polystyrene specimens, the lifetime spectra of positrons were successfully decomposed into three components by using the value of I_{source} and that of τ_{source} obtained for the Ni specimen.

3. RESULTS AND DISCUSSION

Figure 1 shows the mean lifetime, τ_m , for the polystyrene specimens with different molecular weights as a function of temperature, where τ_m was calculated by the relation; $\tau_m = \sum \tau_i I_i$. In Fig. 1, the glass transition temperature, T_g , was clearly seen for both specimens, where the values of T_g for the specimens with $M_n=5,730$ and 1,520,000 were 75 °C and 89 °C, respectively. This suggests that the value of T_g increases with increasing molecular weight. Kasbekar *et al.* [7] have reported measurements of lifetime spectra of positrons for polystyrene specimens with different molecular weights. They reported that the values of T_g for specimens with $M_n=96,000$ and 130,000 were 82 °C and 86 °C, respectively. Figure 2 shows the results reported by them and those obtained in the present experiment. The decrease in the value of T_g observed for the specimen with low molecular weight can be attributed an increased segmental mobility of molecules associated with the small molecular weight in the polystyrene specimens.

Figures 3 and 4 show the lifetimes and the intensities for the specimen with $M_n=5,730$. The observed temperature dependencies of the lifetimes and the intensities were in good agreement with those reported by Kluin and Faupel [8]. In Fig. 3, the value of the longest lifetime, τ_3 , was found to be shorter than the intrinsic lifetime of o-Ps (~ 140 ns). However, this value is longer than the typical lifetime of positrons in crystalline solids. Thus, this annihilation mode can be associated with pick-off

annihilation of o-Ps trapped by the free volumes. In Fig. 3, the value of τ_3 was found to increase with increasing specimen temperature, where the temperature coefficient of τ_3 below T_g was smaller than that above T_g . In Fig. 4, the value of I_3 monotonically increased with increasing specimen temperature. At T_g , no drastic change in the value of I_3 was observed. This means that the concentration of the free volumes was not changed by the glass transition. Thus, it can be concluded that the glass transition in the polystyrene specimen mainly affects the expansion rate of the free volumes.

Figures 5 and 6 show the lifetimes and the intensities for the specimen with $M_n=1,520,000$. The temperature dependences of the lifetimes and the intensities were found to be similar to those for the specimen with $M_n=5,730$. Figure 7 shows the temperature dependence of τ_3 for the specimens with $M_n=5,730$ and 1,520,000. From Fig. 7, it was found that each expansion rate of the free volumes below and above T_g was almost the same for both specimens. The temperature coefficients of τ_3 were derived

Fig. 1 The mean lifetime, τ_m , for the polystyrene specimens with different molecular weights as a function of temperature.

Fig. 2 The glass transition temperature, T_g , as a function of the average molecular weight, M_n . The values of T_g reported by Kasbekar *et al.* [7] are also shown.

Fig. 3 The lifetimes for the polystyrene specimen with $M_n=5,730$ as a function of temperature. The longest lifetime, τ_3 , corresponds to the lifetime of o-Ps annihilated by pick-off process in the free volumes.

Fig. 4 The intensities for the polystyrene specimen with $M_n=5,730$ as a function of temperature.

from the observed τ_3 - T relationships. The ratio of the temperature coefficient above T_g to that below T_g was calculated as 4 for both specimens. This means that the expansion rate of the free volumes above T_g was about 4 times higher than that below T_g .

In Figs. 3 and 5, no temperature dependence of τ_1 and τ_2 was observed. Thus, average values of τ_1 and τ_2 in the measured temperature range were calculated and they are summarized in Table I. In Table I, the value of τ_1 was longer than the intrinsic lifetime of p-Ps (0.125 ns). Since the ratio of the formation probability of o-Ps to that of p-Ps is 3, the intensity corresponding to the annihilation of p-Ps can be estimated as $I_3/3$. As shown in Figs. 4 and 6, however, the derived values of I_1 were larger than $I_3/3$. These facts mean that the first component is the superposition of the annihilation of p-Ps and that of positrons. Thus, the lifetime of positrons convoluted in the first component was estimated by using the intensity and the intrinsic lifetime of p-Ps and the observed value of τ_1 . Figure 8 shows the estimated lifetime of positrons, $\tau_{2(cal)}$, for the polystyrene specimens with different molecular weights. In Fig. 8, for both specimens, no temperature dependence of $\tau_{2(cal)}$ was observed. Thus, average values of $\tau_{2(cal)}$ were calculated and they are summarized in Table I. The origin of the annihilation mode incorporated into the first component and that of the second component are not clear at this stage. The behavior of the free volumes defined in computer simulations [9,10] is known to agree reasonably well with that detected by pick-off annihilation of o-Ps [2]. By using the definition of free volumes in the computer simulations, therefore, the size of the open spaces detected by the annihilation of positrons is considered to be smaller than "free volumes". Since the lower limit of the size of the open spaces for a detectable response by Ps is ~ 0.1 nm, these annihilation modes could be associated with positron annihilation in open spaces with size of < 0.1 nm. The value of $\tau_{2(cal)}$ is close to the lifetime of positrons annihilating from the free state in semiconductors. However, these annihilation modes cannot be simply attributed to the annihilation of positrons in the bulk because a detrapping of positrons from open spaces decreases the lifetime of positrons trapped by such regions. For metals or semiconductors, the detrapping of positrons from vacancy clusters is negligible, because of the deep trapping potential of such defects for positrons. For amorphous polymers, however, since open spaces are considered to be

Table I. The glass transition temperature, T_g , the averaged value of τ_1 , that of τ_2 and the lifetime of positrons estimated from the first components, $\tau_{2(cal)}$.

M_n	T_g ($^{\circ}\text{C}$)	τ_1 (ns)	τ_2 (ns)	$\tau_{2(cal)}$ (ns)
5,730	75	0.17(1)	0.50(2)	0.22
1,520,000	89	0.17(1)	0.48(1)	0.19

Fig. 5 The lifetimes for the polystyrene specimen with $M_n=1,520,000$ as a function of temperature.

Fig. 6 The intensities for the polystyrene specimen with $M_n=1,520,000$ as a function of temperature.

Fig. 7 The lifetimes of o-Ps for the polystyrene specimens with $M_n=5,730$ and $1,520,000$ as a function of temperature.

Fig. 8 The lifetime of positrons estimated from the observed value of $\tau_1, \tau_2(\text{cal})$.

not isolated from nearby open spaces, detrapping of positrons from such once trapped regions to nearby open spaces might be possible.

4. CONCLUSIONS

We have studied the annihilation characteristics of positrons in two polystyrene specimens with different molecular weights. In addition to the formation of Ps, two different annihilation modes of positrons were observed in the polystyrene specimens. For the specimen with low molecular weight, a decrease in the value of T_g was observed. This was attributed to the increased segmental mobility of molecules associated with the small molecular weight in the polystyrene specimens. The expansion rate of the free volumes above T_g was about 4 times higher than that below T_g . These expansion rates were almost the same for both specimens. At T_g , no drastic change in the value of I_3 was observed. These facts suggest that the glass transition of the polystyrene specimens mainly affects the thermal expansion of the free volumes.

REFERENCES

- [1] Hautojärvi P. and Vehanen A., Positrons in Solids, edited by P. Hautojärvi (Springer-Verlag, Berlin, 1979) pp. 1-23.
- [2] Jean Y.C., Positron and Positronium Chemistry, edited by Y.C. Jean (World Scientific, Singapore, 1990) pp. 1-29.
- [3] Schrader D.M. and Jean Y.C., Positron and Positronium Chemistry, edited by D.M. Schrader and Y.C. Jean (Elsevier Science, Amsterdam, 1988) pp. 1-26.
- [4] Ito Y., Positron and Positronium Chemistry, edited by D.M. Schrader and Y.C. Jean (Elsevier Science, Amsterdam, 1988) pp. 120-158.
- [5] Kirkegaard P., Eldrup M., Mogensen O.E. and Pedersen N.J., *Comput. Phys. Commun.* **23** (1981) 307-335.
- [6] Zhou G.M., Sung S., Sundar C.S., Mahmood T. and Jean Y.C., Positron and Positronium Chemistry (World Scientific, Singapore, 1990) pp. 180-185.
- [7] Kasbekar A.D., Jones P.L. and Crowson A., *J. Polym. Sci. A* **27** (1989) 1373-1382.
- [8] Kluin J.-E. and Faupel F., *Materials Science Forum* **105-110** (1992) pp.1613-1616.
- [9] Theodorou D.N. and Suter U.W., *Macromol.* **18** (1985) 1467-1478.
- [10] Rigby D. and Roe R.J., *Macromol.* **23** (1990) 5312-5319.