Positron/Positronium Annihilation as a Probe for the Chemical Environment of Free Volume Holes in Polymers

G. Dlubek,*,†,‡ H. M. Fretwell,†,§ and M. A. Alam†

H.H. Wills Physics Laboratory, University of Bristol, Tyndall Avenue, Bristol BS8 1TL, UK; ITA Institut für Innovative Technologien GmbH Köthen, Aussenstelle Halle, Edvard-Grieg-Weg 8, D-06124 Halle, Germany; and Department of Physics, University of Wales Swansea, Swansea, UK

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ABSTRACT: We assess the nature of the chemical environment of free volume "holes" in polymers of different chemical compositions using positronium annihilation spectroscopy. After the subtraction of a narrow parapositronium component obtained from a three-Gaussian fit from the conventional Doppler broadened annihilation energy line, the remaining broad distribution can be related to the nature and density of the chemical species in the vicinity of the holes. Element specific information on the annihilation site can be expressed in terms of an integral parameter, e.g., the normalized peak height. This method has an advantage in that it can be used as a fast and routine method.

Introduction

The local free volume "holes" in structurally disordered polymers play a crucial role in determining its physical properties, e.g., permeability to gas and liquid.[1] In recent years, positron and positronium annihilation spectroscopy has provided a unique and now a routine probe to study the size and number distributions of these subnanometer cavities.[2−7] In this paper, we show that this technique can also be used to assess the chemical environment in the neighborhood of the holes.

A significant fraction of positrons injected into a polymer migrate to the holes where they preferentially form and annihilate from a bound state positronium (Ps). Ps exists in either a parapositronium (p-Ps: antiparallel electron−positron spins) or orthopositronium (o-Ps: parallel spins) state with a relative formation rate[7] of 1:3. In a vacuum, p-Ps has a lifetime (LT) of 125 ps and annihilates via two photons while o-Ps lives 142 ns and annihilates via three photons. During its lifetime in a hole the o-Ps undergoes numerous collisions with the molecules of the surrounding medium, resulting in a finite probability of the positron annihilating with an electron other than its bound partner (and of opposite spin). This "pick off" process leads to a drastically reduced o-Ps lifetime compared to vacuum and to the production of two photons on annihilation instead of three. In a simple quantum mechanical model the Ps is assumed to be confined in a spherical potential well of radius r and infinite depth. The Ps overlaps with molecules in a thin layer δr at the potential wall. This model provides a relationship between the o-Ps pick-off lifetime and the radius of the hole.[3−6]

$$\tau_{\text{pick-off}} = 0.5ns\left[1 - \frac{r}{r+\delta r} + \frac{1}{2\pi}\sin\left(\frac{2\pi r}{r+\delta r}\right)\right]^{-1} \quad (1)$$

where 0.5 ns is the spin-averaged Ps lifetime and δr is empirically derived to be 0.166 nm.[4−6]

The hole size can also be estimated from the electron−positron momentum distribution as observed via angular correlation of the $2-\gamma$ annihilation radiation (ACAR).[5−8] The momentum density curve is a superposition of a narrow component due to self-annihilation of p-Ps and a much wider distribution arising from the annihilation of free positrons and o-Ps pick-off. The narrow component reflects the localization momentum of the p-Ps inside the holes, and its full width at half-maximum (fwhm) may be related to the hole dimension via the same model used to derive eq 1[5,6]

$$W_n = \frac{1.66}{r+\delta r} \quad (2)$$

W_n is given in mrad, r is in nm, and $\delta r = 0.166$ nm. The same information is also contained in an electron−positron momentum distribution as observed via the Doppler-broadened annihilation energy line (DB spectrum). However, the equivalent momentum resolution of the energy measurement is not adequate enough to extract accurate values of the dimensions of the hole volumes. Both eqs 1 and 2 depend only on the size of the holes which confine the Ps and not on their chemical surroundings. In contrast, the broader components of the momentum distribution (free positron and Ps pick-off annihilation) contain information about the electronic configurations of the surrounding molecules. Since it is believed that free positrons and (as we have already stated) Ps will annihilate within the free volume holes,[9−11] the broad components of the momentum distributions are expected to reflect the chemical surroundings of the annihilation site in the holes.

This aspect of the momentum distributions, although of significant relevance in the evaluation of microstructural properties of polymers, is largely overlooked. In contrast, the element specificity of the momentum density distributions is now well-known and is frequently used, *in a variety of forms*, in the studies of lattice defects in metals and semiconductors. A classic example is the case of alloys with a tendency of precipitation of one of the elements. Here, a semiquantitative evaluation of the composition of these nanometer size coherent clusters has been achieved through a simple scaling of the DB line shape parameter, S, of the alloy constituents.[12] (S is a routinely used integral

† University of Bristol.
‡ ITA Institut Köthen.
§ University of Wales Swansea.

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Table 1. Polymers under Investigation

(1) polymers with groups of carbon and hydrogen only	
NR: (*cis*-)polyisoprene	$[-CH_2-CH=C(CH_3)-CH_2-]_n$
BR: (1,4-*trans*-)polybutadiene	$[-CH_2-CH=CH-CH_2-]_n$
SBS: styrene−butadiene−styrene block copolymer	
PS: polystyrene	$[-CH_2-CH(C_6H_5)-]_n$
PE: polyethylene of 18%, 43%, 60%, and 70% crystallinity	$[-CH_2-CH_2-]_n$
PP: polypropylene of 55% and 45% crystallinity	$[-CH_2-CH(CH_3)-]_n$
1-Bu: poly(1-butene)	$[-CH_2-CH(C_2H_5)-]_n$
1-Hd: poly(1-hexadecene)	$[-CH_2-CH(C_{14}H_{29})-]_n$
(2) polymers containing also oxygen, chlorine, or fluorine	
EVA: ethylene copolymers with 3−80 wt % of vinyl acetate	$[-CH_2-CH(OCOCH_3)-]$
PC: polycarbonate	$[-O-C_6H_4-C(CH_3)_2-C_6H_4-O-CO-]_n$
PMMA: poly(methyl methacrylate)	$[-CH_2-C(CH_3)(COOCH_3)-]_n$
POM: polyoxymethylene	$[-CH_2-O-]_n$
PVC: poly(vinyl chloride)	$[-CH_2-CHCl-]_n$
PVDC: poly(vinylidene chloride)	$[-CH_2-CCl_2-]_n$
PVDF: poly(vinylidene fluoride)	$[-CH_2-CF_2-]_n$
PTFE: poly(tetrafluoroethylene)	$[-CF_2-CF_2-]_n$
nafion	

parameter defined as the counts in a given range near the peak normalized to the total counts in the DB spectra.) Such experiments have also led to semiquantitative estimation of the chemical environment of lattice vacancies.[12] In more recent years, DB measurements with two detectors in coincidence have been used which offer the possibilities of more accurate analysis of the core electron contribution to the momentum densities. This, in turn, has led to more accurate estimation of the elemental environment of a defect site.[13−15]

However, in the case of polymers, the presence of the narrow p-Ps self-annihilation component as well as the fact that the conventional DB technique cannot distinguish any possible difference between contributions from free positron annihilation and o-Ps pick-off annihilation in the broader components can pose a serious hindrance to the evaluation of chemically specific information from the momentum density. In ref 16 some of the current authors showed that, in a fitting of the DB spectra by three Gaussians (all centered at the peak), the narrowest component reflects, with sufficient accuracy, the self-annihilation of p-Ps confined in the free volume holes. These authors arrived at this conclusion through (i) a comparison of the DB spectra with high-resolution 2-dimensional angular correlation measurements and (ii) the observed parallelism of the temperature-dependent variation of the intensity of the p-Ps related narrow component in the DB spectra and the intensity of the o-Ps pick-off lifetimes in PE and PTFE. The authors also found that, following the subtraction of the narrow component from the total DB spectra, the normalized peak height of the remaining broader distribution displayed very little temperature dependence despite strong changes in the o-Ps intensity with temperature. From this, one may be tempted to conclude that the momentum densities arising from free positron annihilation and o-Ps pick-off process are very similar. In a naive sense this is not unexpected since in both cases the positrons annihilate with electrons bound to neighboring atoms and molecules. On the other hand, it has to be borne in mind that the repulsive potential between the neighboring atoms and the two "particles" (positron and o-Ps) are of different nature. The positron experiences a Coulomb repulsion from the atomic nuclei while there is an exchange interaction between the electron of the Ps and the electrons bound to the surrounding atoms and molecules. One may thus expect differing overlap between the inner orbitals of the atoms/molecules and the positron and Ps. Nevertheless, Jain et al.[17] concluded from 1-dimensional angular correlation experiments that in ice there is only a small difference between the widths of the pick-off and free positron components, the former being slightly broader than the latter. More recently Hyodo et al.[18] also drew the conclusion that free positron annihilation and o-Ps pick-off processes produce largely similar momentum densities. This was derived from time-dependent Doppler broadening experiments often referred to as age-momentum correlation (AMOC—see ref 19 and references given therein). The discussion above suggests that information about the nature and fraction of the elements that take part in the annihilation process can be obtained from the broader DB components. This also suggests that the o-Ps yield has no or only little influence on such evaluation.

In this paper, we build upon our previous measurements[16] and demonstrate that the estimation and removal of this narrow component from the measured spectra allows the extraction of useful information about the chemical environment in the vicinity of the hole microstructure. For this purpose, we have measured the positron lifetime and electron−positron momentum density in a large number (∼40) of polymer samples containing either pure hydrocarbons or hydrocarbons plus another element (oxygen, chlorine, or fluorine). The momentum densities were measured via the Doppler broadening (DB) of the annihilation radiation distribution, a technique with limited resolution compared to ACAR but with a measurement time 2 orders of magnitude faster and a 3 orders of magnitude less exposure to positron radiation of the polymer. And, the resolution is adequate to assess the chemical environment with sufficient accuracy.

Experimental Section

The samples, obtained from various commercial sources, are presented in Table 1. The lifetime experiments were carried out using a fast−fast system (see for example ref 7) with a time resolution of ∼235 ps. The lifetime spectra (∼20×10^6 counts in each) were analyzed with the MELT (*m*aximum *e*ntropy for *l*ife*t*ime[20]) routine. For the amorphous samples, we observe three characteristic lifetimes: $\tau_1 \sim 120-200$ ps due to p-Ps self-annihilation, $\tau_2 \sim 350-400$ ps due to free positron annihilation, and $\tau_3 \sim 2-3$ ns due to o-Ps pick-off. For the semicrystalline samples we observe two longer lifetimes: τ_3 ∼1.2 ns attributed to o-Ps annihilation in the interstitial free volume between the crystalline lattice planes and $\tau_4 \sim 2-3$ ns in the holes of the amorphous regions.[10] The Doppler-

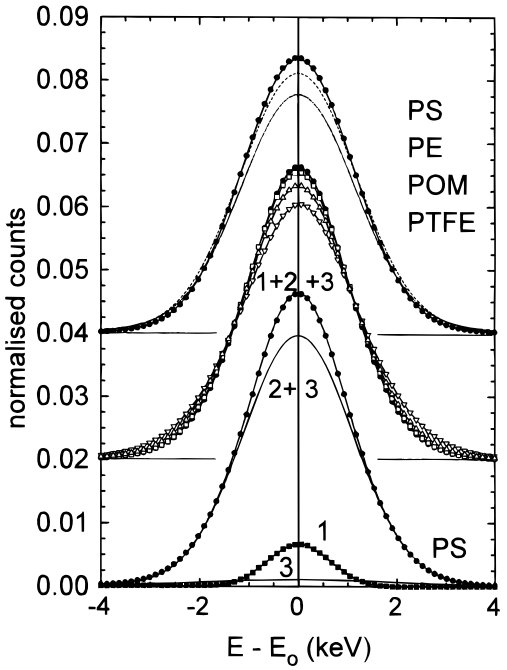

Figure 1. DB spectra in polymers corrected for nonconstant background. Middle: as-measured distributions for two hydrocarbon-based polymers (PS and PE) and for two polymers containing hydrocarbons plus oxygen (POM) and fluorine (PTFE). All curves are normalized to the same area. Bottom: fitting of the distributions with one narrow (1) (p-Ps self-annihilation) and two broad components (3, 2). Top: the broader components for the four polymers (after subtraction of the narrow component and normalization to the same area).

broadened annihilation energy lines[7] were measured simultaneously with the lifetime spectra using a high-resolution intrinsic Ge detector system. Following the correction for a nonlinear background using the routine SPARAM[22] (for details see ref 17; and also 7, p 44) the energy distributions were fitted to a sum of three superposed Gaussians of intensities J_i and fwhm$_i$ = $2(2 \ln 2)^{1/2}\sigma_i$ (σ_i = standard deviation) centered at zero momentum (E_0 = 511 keV),

$$F(E) = J_i[1/\sigma_i(2\pi)^{1/2})] \exp[-(E - E_0)^2/2\sigma_i^2) \quad (i = 1, ..., 3) \tag{3}$$

using the program ACARFIT of the PATFIT-88 package.[22] The intensities are normalized *as* $J_1 + J_2 + J_3 = 1$.

Results and Discussion

Shape of the DB Energy Distribution. An example of such a fit to a DB energy distribution for polystyrene (PS) is shown in the bottom section of Figure 1. All DB curves could be adequately fitted with three Gaussians of fwhm = W_i. The fitting process yields a wide Gaussian (W_3 = 5.1−5.4 keV) of low intensity (J_3 = 3−10%), a medium width Gaussian (W_2 = 2.6−3.0 keV) of high intensity (J_2 = 84−91%), and a small width Gaussian (W_1 = 1.45−1.65 keV; J_1 = 1.4−11.4%). We attributed the Gaussian with the smallest width to p-Ps self-annihilation in the free volume holes and in keeping with the common term in the literature denote it as the "narrow component" and index both the width and intensity with subscript n ($W_1 = W_n$; $J_1 = I_n$).

In the middle section of Figure 1 we show four selected as-measured distributions. Two of the samples are pure hydrocarbons (PS and PE), and the others contain oxygen (POM) or fluorine (PTFE). The shape of these momentum distributions already demonstrates

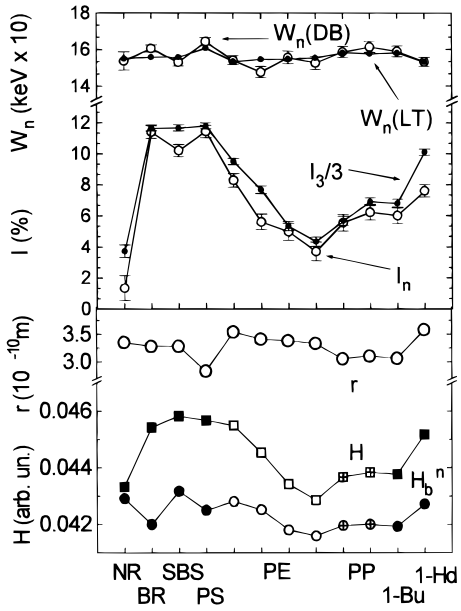

Figure 2. (a, upper) The fwhm of the narrow component derived from the DB spectrum (W_n(DB)) and calculated from the average hole size obtained from positron lifetime data (W_n(LT)) for a set of *pure* hydrocarbons. Also shown is the comparison between the intensities of the narrow component I_n and $I_1 = I_3/3$ (both related to p-Ps yields). (b, lower) Normalized peak height of the full DB curve, H, compared with the normalized peak height, H_b, of the broader components in the hydrocarbon polymers. (The same symbols for the PP and PE polymers signify varying crystallinity.) The average hole radii r in the same polymers, obtained from positron lifetime, are also shown. Where no error bars are specifically indicated in the figure, such errors are no greater than the symbols used. This is also the case in the following figures.

(most clearly seen at the peak height) that the two pure hydrocarbon DB spectra are very similar whereas those containing additional elements are quite different. The upper picture in Figure 1 shows the same four distributions with the narrow component subtracted and the remainder normalized to the same area. We find that these broad distributions for the pure hydrocarbons are nearly identical (as anticipated, given their similar chemical environment). Equally, this close correspondence supports the validity of our method for subtracting the narrow component.

Polymers with Groups of Carbon and Hydrogen Only. First, we discuss the results for the polymers based only on hydrocarbons. In the upper box in Figure 2 we plot the intensity of the narrow component (I_n = J_1, (DB)) and compare these with the equivalent parapositronium intensity[7] $I_1 = I_3/3$ (or $I_4/3$, if two o-Ps lifetimes appear) from LT measurement. In this figure, we also compare the fwhm of the narrow component in the DB, W_n(DB) (=W_1), with those derived from the hole radius associated with the o-Ps-lifetime τ_3 (or τ_4), W_n-(LT). The latter were calculated via eqs 1 and 2 and convoluted with the DB resolution. The good agreement between parameters derived from DB and LT, particularly between the intensities I_n and $I_3/3$, is taken as a strong indication that, despite the relatively poor energy (and therefore momentum) resolution of the DB technique, the narrowest Gaussian provides a realistic description of the self-annihilation of p-Ps within the holes in these samples.

In the lower box of Figure 2, we plot the normalized peak height parameter H, which is the counts in the central channel divided by the total number of counts

below the Doppler curve. H can be calculated from the parameters of the three Gaussian fits

$$H = F(E=E_0) = J_1/\sigma_1(2\pi)^{1/2} + J_2/\sigma_2(2\pi)^{1/2} + J_3/\sigma_3(2\pi)^{1/2}$$

Because of the fitting related smoothing of the data, the integral parameter H has a high statistical accuracy. The use of such an integral parameter (H has the same characteristics as the line shape parameter S) facilitates a simple characterization of the DB spectra. In addition, this allows one to quantify the effects of the variation in the distribution of the chemical elements in the vicinity of the hole volumes on the DB spectra. Remarkably, the peak height of the full spectrum mirrors the intensity of the narrow component I_n (and $I_3/3$), indicating that, here, the Ps yield dominates the variation in the momentum density. *This is exactly true only for different but chemically similar polymers. Some of the current authors have already shown in a temperature-dependent study of the PE and PTFE that the temperature dependence of the DB spectra is governed by the Ps yield reflected in the narrow component.*

In polymers with different chemical compositions, the electronic configuration of the different elements must also play a dominant role in determining the momentum densities. However, in light of the discussion above, the role of the different chemical species is likely to be masked by the Ps yield. If the narrow component is subtracted from the full DB curve, the resulting momentum distribution consisting of the two broad Gaussians is a combination of free positron annihilation and o-Ps pick-off events with electrons bound to molecules. We, however, see no a priori way to attribute the broad Gaussians to the two possible individual channels of annihilation. We only assume that the broad DB component, that is, the superposition of both broad Gaussians, describes the integral effect of free positron and Ps (mainly o-Ps) pick-off annihilation well. We characterize the shape of the broader distribution via the peak height of the broad DB component, H_b^n, normalized to the total counts in this new distribution. The peak height can be calculated from the fitting parameters as

$$H_b^n = [J_2/\sigma_2(2\pi)^{1/2} + J_3/\sigma_3(2\pi)^{1/2}]/(J_2 + J_3)$$

The normalized peak height of the broad DB component for various hydrocarbon polymers is shown in the lower box of Figure 2. We observe that the dynamic range of H_b^n is smaller (by a factor of 2) than in H. The residual small variations for H_b^n follow the trends in H and I_n to some extent. From this observation, we can conclude that the influence of the Ps yield in the extracted broad components is largely although not completely absent. Two possible reasons for this residue are the following: (i) The first is an incomplete subtraction of the narrow component from the DB distribution. If we fix the width of the narrow component during subtraction to the value calculated from τ_3 via eqs 1 and 2 and, in addition, fix the intensity to 0.95 ($I_3/3$) (a small reduction of $I_3/3$ to reflect the p-Ps pick-off annihilation),[7,17] the residual variation is reduced to $\sim^1/_3$ of that seen in H. (ii) The residual variation may also be a consequence of a difference between the free positron and o-Ps pick-off momentum densities which is apparently not too large. Notwithstanding this, our results show that the influence of the Ps yield and the size (r in Figure 2b, estimated via eq 1) of free-volume holes on the parameters H_b^n is highly supressed.

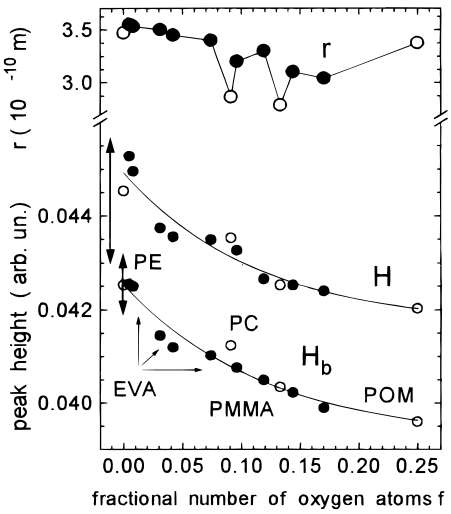

Figure 3. Normalized peak height of the full DB curve, H, compared with the normalized peak height, H_b^n, of the broader components in polymers containing hydrocarbon plus varying oxygen fraction. The average hole radii in the same polymers are also shown.

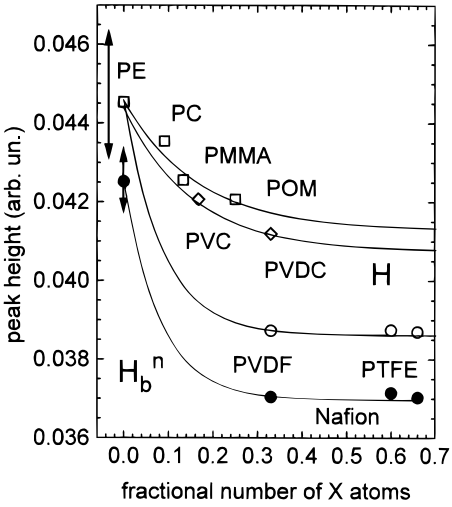

Figure 4. As in Figure 3, for polymers containing oxygen, chlorine (PVC, PVDC), and fluorine (PVDF, Nafion, PTFE).

Polymers Containing Also Oxygen, Chlorine, or Fluorine. In Figures 3 and 4 we examine the behavior of the uncorrected H and corrected H_b^n peak heights when other atoms (besides carbon or hydrogen) are incorporated into the polymer. Figure 3 shows these parameters for a series of polymers with different fractional number of oxygen atoms (f) per chemically repeating unit. The value of PE is shown for the pure hydrocarbon as $f = 0$. Although H is affected by the narrow component and its variation with the different polymers, it already displays a distinct exponential-like dependency on the oxygen fraction. The peak height also shows no correlation with the hole size, r (derived from the lifetime data). The hole radius in these materials varies in a similar range as in the pure hydrocarbons. If one compares the decrease in H and H_b^n with the total spread of values in H for the pure hydrocarbons (illustrated by the vertical arrows), H falls below this region at an oxygen fraction of $\sim$0.12. After subtracting the narrow component, H_b^n falls out of the pure hydro-

carbon "uncertainty" range at a much smaller oxygen fraction of 0.05. The normalized peak height of the broad components (H_b^n) shows an exponential behavior as a function of oxygen fraction $y(f) = y_0 + \Delta y \exp(-f/c)$ with $y_0 = 0.0392$, $\Delta y = 0.0033$, and $c = 0.122$. *If such behavior is generic, at least for "doping" with the same element, this behavior may well act as a calibration curve for at least a semiquantitative chemical analysis around polymer hole volumes.* We tested the sensitivity of such an analysis during the reversible increase in oxygen fraction, through water uptake, in the polyamides (nylons) PA6 and PA66. The corrected peak height for the dry specimen corresponded to a value of $f = 0.09$ according to the "calibration curve" of Figure 3, in excellent agreement with the combined relative contents of oxygen and nitrogen in the polyamides. After the uptake of water, the measured H_b^n relates to $f = 0.14$ according to Figure 3, again in good agreement with the total oxygen plus nitrogen fraction in the polyamides following the estimated water uptake of ~9 wt %.

In Figure 4 we plot H for a few polymers containing chlorine and fluorine and include the oxygen for comparison. The chlorine polymers behave in a similar *exponential* fashion as those containing oxygen, while the overall changes in H and H_b^n for the fluorine polymers are substantially greater. We are unable to resolve a narrow component in PVC and PVDC, i.e., $H_b^n = H$. This is compatible with the very small Ps yield in these materials (o-Ps intensity $I_3 < 3\%$) and again confirms the validity of a general three-Gaussian fitting analysis. The varying sensitivity of the positron/positronium to the chemical environment may be understood in terms of the different electronic configurations of the atoms: H: $1s^1$; C: $2s^22p^2$; F: $2s^22p^5$; Cl: $3s^22p^5$. The higher kinetic energy of the p-electrons leads to a broader momentum distribution compared to the s-electrons. Although Cl and F contains equal numbers of outer shell p-electrons, the DB spectrum for the fluorine containing polymer is demonstrably broader (lower peak height) than that of the chlorine-containing sample. Via 1-d ACAR studies, Mogensen[7] has demonstrated that the momentum distribution for [e^+, F^-] is significantly broader than that for [e^+, Cl^-]. It is conceivable that the origin of the broader momentum density in the fluorine polymers is the same as that in [e^+, F^-].

The nonlinear dependency of H_b^n with fractional atomic composition f points to preferential annihilations in the presence of these atom types. Whether this influences the positron or o-Ps lifetime is yet to be assessed. In the analysis of such information one also needs to keep in mind that the o-Ps pick-off annihilation as well as the annihilation of free positrons takes place predominantly within the "holes" that comprise the free volume and that these regions may have either enhanced or depleted population of some atom types. It has also to be taken into consideration that the polar nature of some bonding can lead to attraction or repulsion of the positrons.

Conclusion

Through a comprehensive and careful study, we have demonstrated that the measurement and evaluation of positron/positronium DB (or ACAR) momentum densities may potentially act as a probe of the chemical environment in the vicinity of the free volume holes in polymers and other molecular materials. Through the fitting of three Gaussians, a narrow component arising from p-Ps self-annihilation can be identified and subtracted. The remaining broader distribution shows little or no correlation to the spatial dimensions of the holes or the positronium formation probability and shows an enhanced sensitivity to the presence and number densities of various types of atoms in the material.

This presentation that this DB technique based simple method can be used for such analysis has the advantage that it requires relatively short measurement times and therefore results in a lesser radiation exposure to the polymers and that this can be pursued simultaneously with the positron lifetime measurements. Admittedly, the momentum density distribution contains far more information about the bound electrons than we utilize. However, such an exercise in describing the element specific sensitivity through an empirical integral parameter has the advantage in that its interpretation does not require theoretical calculations of the contributions from the individual electron shells to the momentum density. Thus, this method is particularly suited for routine monitoring of the changes in the chemical composition of the environment of the hole volumes due to growth conditions and/or post-growth treatment of polymers.

Obviously, the information content of this method can be further enhanced through the use of DB measurements in coincidence which leads to more precise information about the core electron annihilation.[13−15] In the same way it would also be very interesting to use age-momentum correlation (AMOC)[18,19] for such studies. The measurement of the DB spectra triggered by o-Ps pick-off annihilation will enable the separation of this component from the rest of the annihilation channels and would allow a more detailed interpretation of the spectra. Nevertheless, such measurements require substantially more equipment and more importantly time investment. The main essence of this technique lies in its ability to be used as a routine probe where a vast number of such measurements are necessary.

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References and Notes

(1) Goldstein, M.; Simha, R. *The Glass Transition and the Nature of the Glassy State*; Academy of Science: NewYork, 1976.
(2) Brandt, W.; Berko, W.; Walker, W. W. *Phys. Rev.* **1960,** *15*, 1289. Brandt, W.; Fahs, J. H. *Phys. Rev.* **1970,** *17*, 1425.
(3) Tao, S. J. *J. Chem. Phys.* **1972,** *56*, 5499.
(4) Eldrup, M.; Lightbody, D.; Sherwood, J. N. *J. Chem. Phys.* **1981**, *63*, 51.
(5) Nakahishi, N.; Jean, Y. C. In *Positron and Positronium Chemistry, Studies in Physical and Theoretical Chemistry*, No. 57; Schrader, D. M., Jean, Y. C., Eds.; Elsevier: Amsterdam, 1988; p 159.
(6) Jean, Y. C. *Microchem. J.* **1990,** *42*, 72; *Mater. Sci. Forum* **1995**, *175−178*, 59.
(7) Mogensen, O. E. *Positron Annihilation in Chemistry*; Springer-Verlag: Berlin, 1995.
(8) Jean, Y. C.; Nakanishi, H.; Hao, I. Y.; Sandreczki, T. C. *Phys. Rev. B* **1990**, *42*, 9705.

(9) Deng, Q.; Sung, S.; Mahmood, T.; Zhou, G. M.; Lu, X.; Shen, S. Y.; Cheng, K. L.; Hellwuth, E. W.; Tsai, C. F.; Jean, Y. C.; Lou, M. F. *Mater. Sci. Forum* **1992,** *105*−*110*, 1541.
(10) Dlubek, G.; Saarinen, K.; Fretwell, H. M. *J. Polym. Sci., Part B: Polym. Phys.* **1998,** *36*,1513.
(11) Dlubek, G.; Eichler, S.; Hubner, Ch.; Nagel, Ch. *Nucl. Instrum. Methods B* **1999**, *149*, 50.
(12) Dlubek, G. *Mater. Sci. Forum* **1987**, *13/14*, 11. Dlubek, G.; Gerber, W. *Phys. Status Solidi B* **1991**, *163*, 83.
(13) Alatalo, M.; Kauppinen, H.; Saarinen, K.; Puska, M. J.; Makinen, J.; Hautojarvi, P.; Nieminen, R. M. *Phys. Rev. B* **1995**, *51*, 4176.
(14) Asoka-Kumar, P.; Alatalo, M.; Ghosh, V. J.; Krusemann, A. C.; Nielsen, B.; Lynn, K. G. *Phys. Rev. Lett.* **1996**, *77*, 2097.
(15) van Veen, A.; Kruseman, A. C.; Schut, H.; Mijnaremds, P. E.; Kooj, B. J.; De Hosson, J. Tj. M. *Mater. Sci. Forum* **1997**, *255*−*257*, 76.
(16) Dlubek, G.; Saarinen, K.; Fretwell, H. M. *Nucl. Instrum. Methods B* **1998,** *142*, 139.
(17) Jain, P. C.; Eldrup, M.; Pederson, N. J.; Sherwood, J. N. *Chem. Phys.* **1986**, *106*, 303.
(18) Hyodo, T. Information presented during the 6th International Workshop on Positron and Positronium Chemistry, Tsukuba, Japan, June 6−10, 1999.
(19) Seeger, A. *Mater. Sci. Forum* **1997**, *255*−*257*, 1.
(20) Shukla, A.; Peter, M.; Hoffmann, L. *Nucl. Instrum. Methods A* **1993,** *335*, 310.
(21) SPARAM: Laboratory of Physics, Technical University of Helsinki, 1989.
(22) PATFIT-88: Kirkegaard, P.; Pedersen, N. J.; Eldrup, M. Report RISO-M-2740, 1989.

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