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Monte Carlo Calculations of Hole Size Distributions: Simulation of Positron Annihilation Spectroscopy

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SYNOPSIS

Consequences are explored of a hole size distribution in an amorphous polymer for the *ortho*-positronium (o-Ps) lifetime (τ_3) and intensity (I_3), determined by positron annihilation lifetime spectroscopy. The disordered lattice model, with a vacancy fraction h as a central quantity, is used to represent the equation-of-state behavior of the polymer. By means of Monte Carlo simulations, we obtain the cluster size distribution as a function of h and hence temperature. The predicted average cluster size and the cluster concentration are compared to τ_3 and I_3 data, respectively, for bisphenol-a polycarbonate. Furthermore, the influence of an o-Ps lifetime distribution on the experimental mean τ_3 is investigated. By mimicking the computational methods used in experimental analysis, agreement between experiment and theory in respect to τ_3 and to I_3 in the melt ensues. In the glass, however, the experimental I_3 becomes increasingly smaller with decreasing temperature than is computed. These deviations may result from a distortion of the equilibrium free volume. © 1992 John Wiley & Sons, Inc.

Keywords: positron annihilation lifetime spectroscopy • lattice model • Monte Carlo • hole size distribution • bisphenol-a polycarbonate

INTRODUCTION

The concept of free volume is often applied to interpret the behavior of a polymer melt or glass, or to study physical aging effects when configurational thermodynamic quantities like volume and enthalpy or viscoelastic properties are investigated. Comparatively few techniques are available to study the behavior of a polymer directly on a molecular level. Among them are small-angle x-ray scattering, Fourier-transformed infrared spectroscopy, fluorescence spectroscopy, and positron annihilation spectroscopy (PAS).

In the PAS technique, the lifetime τ_3 of *ortho*-positronium (o-Ps) is measured. The value of τ_3 depends on the electron density in the immediate vicinity of the o-Ps particle,¹ which preferentially locates in regions of low electron density, and τ_3 increases with decreasing electron density. Within

the scope of free volume theories, the o-Ps particle is bound inside a free volume region or hole,² and the lifetime τ_3 increases with increasing hole size. Besides the o-Ps lifetime τ_3 , the total fraction of positrons that form o-Ps I_3 is also determined in PAS. The number of o-Ps particles formed is assumed to depend on the preponderance of regions with low electron density in which o-Ps can exist.² Thus, in terms of free volume theories, I_3 is assumed to be related to the concentration of holes and increases with increasing hole concentration. The PAS technique can therefore be used, in principle, to obtain direct information about both hole size and hole concentration in the polymer matrix.

It is known that the distribution of free volume in a polymer, which is a measure of the degree of disorder in the structure factor observed by x-ray scattering methods, and the associated distribution of viscoelastic relaxation times, play an important role in understanding the mechanical properties of polymers,³ the formation of polymer glasses,⁴ and relaxation processes in glasses.^{5,6} However, only very

recently has the concept of free volume distribution been introduced quantitatively into the analysis of PAS experiments.⁷ Specifically, Deng et al.⁷ assume that the lifetimes measured by PAS are not single exponential decays but are the result of Gaussian distributions. In this work, we wish to quantify the free volume distribution concept in a different way by taking as a basis for our investigation the lattice model employed in a previous discussion.⁸ We use the Holey–Huggins (HH) theory,⁹ which is a slightly modified version of the Simha–Somcynsky (SS) theory,¹⁰ to describe the lattice. These theories have proven to be powerful tools to describe equation-of-state behavior, both in melt¹¹ and glass,¹² and in connection with a free volume distribution, the dynamics of physical aging^{5,6} and of glass formation.⁴ The principal concept in these theories is a partly filled lattice with sites filled randomly by repeat units (not necessarily equal to chemical repeat units) of the polymer molecule. The total fraction h of empty sites depends on temperature and pressure. We assume a random distribution of empty sites that form clusters of different sizes.

It may be argued that the placement of occupied and empty sites does not necessarily occur in a random manner. The underlying equation-of-state theory, however, is based on this assumption. Hence it must be consistently employed here. We note that the theory has recently been modified to include nonrandomness (E. Nies and H. Xie, to be published). A new analysis of the polycarbonate equation of state above and below T_g would be required for the present purposes. In the light of current PVT results, however, we do not expect significant differences, especially in the melt. Monte Carlo (MC) simulations are used to analyze the cluster size distribution as a function of the occupied fraction $1 - h$ of the lattice. The effect of the resulting site cluster distribution on hole concentration and hole size, quantities that are measured by PAS, are examined, taking into account certain properties of the PAS-analysis process. Finally, calculations of hole size and distribution are compared to experimental PAS data on bisphenol-a polycarbonate.¹³

FREE VOLUME CALCULATIONS

To calculate the free volume fraction h , experimental PVT data on bisphenol-a polycarbonate by Zoller¹⁴ are employed. In the HH theory, the mass of a repeat unit m_o has to be chosen.⁹ Usually the monomeric unit ($m_o = 254$ g/mol in the case of polycarbonate) is taken, but in this paper we use m_o

$= 50$ g/mol, for reasons to be explained later. As has been shown before,¹⁵ the value of h is not sensitive to the value of m_o . Changing m_o from 254 g/mol to 50 g/mol alters the value of h at 420 K from 0.1024 to 0.1005, a difference of 2%. Using Zoller's PVT data for the melt, the characteristic parameters $e^* = 4027.9$ J/mol, $v^* = 0.40339 \cdot 10^{-4}$ m³/mol, and $c/s = 0.51226$ are obtained, employing a fitting procedure described elsewhere.⁹ To determine h below the glass transition temperature T_g , the glass was treated by the "adjustable parameter" procedure¹² with the use of the values for e^* , v^* , and c/s determined in the melt.

The temperature dependence of h is almost linear both above and below the T_g ($T_g = 416.5$ K) and can be represented in the melt by

$$h = 0.0985 + 0.000488(T - 416.5) \quad \text{for } T_g < T < 500 \text{ K} \quad (1)$$

and in the glassy state by

$$h = 0.0985 + 0.00013(T - 416.5) \quad \text{for } 300 \text{ K} < T < T_g \quad (2)$$

with the temperature T in K. Maximum deviations from the exact solution never exceed 0.0003 within the given validity ranges of eqs. (1) and (2), which are limited by the availability of PVT data at both low and high temperatures. For estimation of the theoretical equilibrium behavior of h below T_g and of h in the glass at temperatures below 300 K, eqs. (1) and (2), respectively, can be used, albeit with some uncertainty.

MC CALCULATIONS

The lattice used in the HH or SS theories to describe the polymer is a partly filled fcc lattice with coordination number $z = 12$. Assuming randomness in the placement of holes, only the degree of occupancy $y = 1 - h$ determines the clustering of empty lattice sites. It may be recognized that the problem of determining the distribution of clusters is closely related to a percolation problem.¹⁶ However, no analytical solution is available for a three-dimensional lattice with $z = 12$.^{16,17} Furthermore, the use of percolation results for our problem is restricted because most of the literature is focused on processes close to the percolation threshold h_{thr} , which in this instance equals 0.198.^{16,17} Our region of concern turns

out to be $0.08 < h < 0.14$, with particular interest in the smaller clusters.

We define i as the number of sites forming a single cluster, $i = 1, 2, 3, \dots$, and p_i as the probability that any empty site is part of a cluster of size i . The quantity p_i is by definition equal to the fraction of free volume present in clusters of size i . For $i = 1$, $p_i = p_1$ can easily be calculated:

$$p_1 = y^{12} \quad (3)$$

with y the fraction of occupied lattice sites. The exponent in eq. (3) represents the perimeter t (the number of surrounding sites that are occupied), and is $t = 12$ for an isolated empty lattice site. Similarly, we find for p_2 , taking into account all possible configurations,

$$p_2 = 2(1 - y)6y^{18} \quad (4)$$

For $i = 2$, six different configurations of the cluster are possible, each having a perimeter $t = 18$. The prefactor 2 arises from the size of the cluster. For $i = 3$, not all possible configurations have the same perimeter t . For example, for three empty sites in a straight line, $t = 24$, and for an equilateral triangle, $t = 22$. We find

$$p_3 = 3(1 - y)^2(28y^{24} + 12y^{23} + 8y^{22}) \quad (5)$$

Analytical calculations for p_i when $i > 3$ involve a large number of possible configurations. Using MC calculations, it is possible to obtain p_i for values $i > 3$.

In the MC calculations we have selected a lattice of size $20 \times 20 \times 20$. It is filled 400 times randomly, with a prescribed value for y . This is sufficient to render the results independent of further trials. The procedure is carried out for 10 different values of y , $0.8 \leq y \leq 0.99$. After the filling procedure, the lattice is analyzed by counting the number of clusters of different sizes. For all clusters present, the size i and the perimeter t are determined. To minimize the effect of boundaries, periodic boundary conditions are used. In agreement with percolation theory, the perimeter t is found to be proportional to the cluster size i , except for small values of i .

In Figure 1 the volume fraction of clusters of size i , p_i , is plotted versus the size of the cluster i for different values of y , $0.84 < y \leq 0.99$. For this range of y the MC results are supported quantitatively by the analytical calculations. However, for $0.8 \leq y \leq 0.84$ we find some deviations between the two methods. This is due to the fact that for values of y

Figure 1. Volume fraction distribution of cluster sizes versus cluster size for different values of occupied lattice fraction y . MC calculations (solid symbols) and analytical calculations (open symbols). $\bullet$, 0.99; $\blacktriangle$, 0.95; $\blacksquare$, 0.92; $\blacklozenge$, 0.88; $\circ$, 0.84; $\triangle$, 0.80. Solid lines represent the stretched exponential of eq. (6).

≤ 0.84 the occurrence of holes connecting two opposite sides of the $20 \times 20 \times 20$ lattice begins to play a role in the counting process in the MC calculation. Therefore for $0.8 < y < 0.85$ some deviations between MC and analytical calculations may be expected. Considering $y = 0.85$ as the lowest pertinent value for our application, this then implies that the lattice used in the MC calculations has to be chosen large enough to accurately describe cluster sizes for $y = 0.85$. The size $20 \times 20 \times 20$ fulfills this requirement. Also plotted in Figure 1 are the results of analytical calculations using eqs. (3)–(5) for values $i = 1, 2, 3$.

To use the MC results for further calculations, distributions for intermediate values of y must be available. These can be represented by the empirical function

$$p_i = p_n \exp(-(i/l(y))^{\beta(y)}) \quad \text{for } 0.8 \leq y \leq 0.99 \quad (6)$$

where $l(y)$ and $\beta(y)$ are polynomial functions of y , and p_n is a normalization factor, so that $\sum p_i = 1$. Of course, eq. (6) is only meaningful for integer values of i . To determine p_n and the coefficients in the polynomials $l(y)$ and $\beta(y)$, eq. (6) was fitted to the MC results for $0.84 < y \leq 0.99$ and to the analytical results for $0.8 \leq y \leq 0.84$. The p_n and the polynomial coefficients were determined to give the best fit of eq. (6) to the calculated values. The analytical results were included to enable extension of eq. (6) to values of y for which MC showed deviations, although these values of y and also values of $y \approx 1$ are not necessary for applications in this paper. Strictly $l(y)$ has to obey the following boundary condition:

$$l(y) \rightarrow 0 \quad \text{if } y \rightarrow 1 \quad (7)$$

to force the distribution to become a δ function. Probably due to the choice of polynomial expressions for $l(y)$ and $\beta(y)$, this boundary condition cannot be satisfied without drastically decreasing the quality of the fit of eq. (6). Because the region of interest of y does not include values y close to 1, the boundary condition is not used in the fitting procedure. The final result is

$$l(y) = 12.347 - 12.035y \quad (8)$$

$$\beta(y) = 0.4088 - 2.5242y + 3.1156y^2 \quad (9)$$

Together with eq. (6), eqs. (8) and (9) represent the results of both MC and analytical calculations with a maximum deviation for p_i of 0.004 in the range $0.84 < y \leq 0.99$ and 0.013 in the range $0.8 \leq y \leq 0.84$. Typical results are depicted in Figure 1.

Having an expression for the volume fraction p_i as a function of i , it is also possible to calculate the number distribution of clusters. Let n_i be the number fraction of holes of size i , then

$$n_i = (p_i/i) / \sum (p_i/i) \quad (10)$$

ANALYSIS OF EXPERIMENTAL RESULTS

To analyze experimental τ_3 and I_3 data, expressions for the cluster concentration and the average cluster size have to be developed. Adopting the assumption that the probability for a positron to become trapped in a hole and to form o-Ps is independent of the size of the hole, the total amount of o-Ps formed is proportional to the number of holes. For this case the intensity I_3 is proportional to the cluster concentration in the lattice model. Tao¹⁸ has shown that for spherical holes the lifetime τ_3 of o-Ps is related to the radius of the hole by

$$\tau_3 = 0.5[1 - (r/r_0) + 0.159(\sin(2\pi r/r_0))]^{-1} \quad (11)$$

with τ_3 in nanoseconds, r the hole radius, and $r_0 = r + \delta r$. The assignment $\delta r = 0.1656$ nm yields good agreement with experimental τ_3 values.¹ To calculate τ_3 for a nonspherical hole, we employ an equivalent spherical cavity. That holes formed by clustering of lattice sites are generally not spherical is shown clearly by the perimeter t , which is proportional to i for large holes, rather than proportional to $i^{2/3}$ as would be the case for spheres.

At this point the question of cavity geometry and τ_3 may be raised, e.g., a generalization of eq. (11) to ellipsoids. Such extensions are not available, and in any case the issue of a cluster geometry would still remain. On the other hand, the prediction of τ_3 as a function of temperature involves a scaling factor related to the segment mass m_0 (see below and the discussion of Figure 5). A change in geometry should affect this factor. It should not change the temperature dependence, unless detailed considerations regarding the effect of temperature on the internal geometry of clusters, for example orientation effects, were to be introduced. This certainly goes for several reasons beyond what can be expected from current positron theory.

For a specified temperature and hence $h = 1 - y$, eq. (6) provides the distribution p . In the case of polycarbonate, h is obtained from eq. (1) or eq. (2). The number-averaged cluster size $\langle n \rangle$ can be calculated by

$$\langle n \rangle = \sum p_i / \sum (p_i/i) \quad (12)$$

and the total cluster concentration N_{cl} by

$$N_{cl} = h/\langle v \rangle = h/\langle n \rangle v_1 \quad (\text{nm}^{-3}) \quad (13)$$

with v_1 the size of one lattice site,

$$v_1 = y \cdot V \cdot m_0 \cdot 10^{21} / N_a \quad (\text{nm}^3) \quad (14)$$

and V the specific volume of the polymer in cm^3/g , m_0 the mass of the repeat unit used in the lattice theory in g/mol , and N_a Avogadro's number. For the average cluster volume $\langle v \rangle = \langle n \rangle \cdot v_1$, the o-Ps lifetime can be calculated using eq. (11) with r the radius of a spherical hole with volume $\langle v \rangle$. Focusing now on polycarbonate (PC) at a temperature T , the only adjustable parameter in the description of cluster size and cluster concentration is m_0 , which scales the size of the lattice. A value for m_0 is chosen to give best agreement between predicted and experimental τ_3 values. Because h is a very weak function of m_0 , as pointed out before, recalculation of the lattice free volume fraction h does not have to be considered as long as m_0 is close to 50 g/mol . Such values can therefore directly be used in eq. (14).

Finally, the analysis has to deal with the fact that experiment provides a single lifetime $\tau_{3,\text{exp}}$, whereas the theory leads to a spectrum $\tau_{3,i}$, $i = 1, 2, \dots$. Thus some averaging operation must be performed. In the simplest approximation $\tau_{3,\text{exp}}$ can be compared to the lifetime τ_3 computed from the average cavity volume $\langle v \rangle$. In Figure 2 experimental τ_3 values for

Figure 2. The o-Ps lifetime for polycarbonate¹³ (●) versus temperature, compared with o-Ps lifetime calculated from the number-average hole size (solid line).

PC¹³ are compared to values for τ_3 calculated from $\langle v \rangle$ with $m_o = 51$ g/mol, a value selected to give a good fit at the glass transition temperature T_g . In the glass an equilibrium cluster distribution is assumed, depending only on h . In Figure 3 experimental data of I_3 for PC¹³ are compared to the cluster concentration N_{cl} . The numbers on the ordinate correspond to a proportionality between $I_{3,exp}$ and N_{cl} .

Whereas $\tau_{3,exp}$ and $\tau_{3,calc}$ are in good agreement, as seen in Figure 2, significant discrepancies between $I_{3,exp}$ and $N_{cl} \propto I_{3,calc}$ are clear from Figure 3. In particular, the calculated maximum in I_3 in the melt is not found experimentally. This maximum in cluster concentration arises from the fact that at high temperatures the average cluster size $\langle n \rangle$ increases faster with temperature than the total amount of free volume h , and hence, according to eq. (13), N_{cl} decreases. In addition, below T_g , $I_{3,exp}$ decreases rapidly with decreasing temperature, whereas N_{cl} remains almost constant.

Figure 3. The o-Ps intensity for polycarbonate¹³ (●) versus temperature, compared with calculated number-average cluster concentration (solid line).

Instead of relating $\tau_{3,exp}$ directly to a volume $\langle v \rangle$, alternative possibilities can be considered. It has been proposed⁸ that an o-Ps can sample several holes during its lifetime. Sampling only a small number of holes very effectively averages the lifetime of the sampling o-Ps particle. However, the idea that o-Ps can visit different holes but also be trapped in a hole requires a tunneling process that may not occur with a high probability.

If o-Ps spends its whole lifetime in the same hole, a distribution of hole sizes gives rise to a spectrum of lifetimes $\tau_{3,1}, \tau_{3,2}, \tau_{3,3}, \dots$, each with a corresponding intensity. In the analysis of many PAS experiments, however, the spectrum is fitted to only three lifetimes— τ_1, τ_2 and τ_3 —where τ_1 and τ_2 represent annihilation of parapositronium (p-Ps) and free positrons, respectively. Thus in the mathematical process of spectrum analysis an averaging of $\tau_{3,1}, \tau_{3,2}, \tau_{3,3}, \dots$ to a single τ_3 takes place. To establish a connection between experiment and theory, we must mimic the fitting procedure used in the PAS experiment. In this procedure the statistical weight of the content of a channel is proportional to the square root of the number of counts in that channel.¹⁹ Hence in the fitting of a single exponential decay to a spectrum of such decays the same weighting factor is to be used. Taking this constraint into account, we can now obtain a mean value for τ_3 based on the distribution of hole sizes for a specified y and thus temperature. The values of both $\tau_{3,calc}$ and $I_{3,calc}$ depend strongly on the width of the distribution. This can be seen from Figure 4. The intercept of the curve formed by the sum of exponential decays and the ordinate is proportional to the number of positrons that have formed o-Ps, which is proportional

Figure 4. Schematic representation of the decay spectrum of o-Ps. Plotted is the fraction of initial positrons still present as o-Ps versus time. The solid curve is the result of the o-Ps decay assuming a hole size distribution. The dotted curve represents a single exponential decay fitted to the solid curve.

Figure 5. The o-Positronium lifetime for polycarbonate¹³ (●) versus temperature, compared with o-Ps lifetime calculated following the procedure illustrated in Figure 4 (solid line).

to I_3 . It is evident that the fitted single exponential decay has a lower intercept, so the apparent value of I_3 will be lower than the true $I_3 = \sum I_{3i}$, which is proportional to the hole concentration. The difference increases with increasing width of the distribution.

In Figure 5 $\tau_{3,\text{calc}}$ is compared to the experimental τ_3 for PC; $m_0 = 42.5$ g/mol is used to scale the calculation to experimental values at T_g . Improved agreement between theory and experiment is observed. The small deviation seen in the glass could be caused by differences in T_g between the present PC sample¹³ and that used to determine h ¹⁴. In Figure 6 $I_{3,\text{calc}}$ and experimental I_3 data are compared. There is a proportionality factor between the calculated and experimental I_3 values; this factor is determined by scaling $I_{3,\text{calc}}$ to $I_{3,\text{exp}}$ at T_g . In the melt both experiment and calculation indicate a decrease of I_3 with increasing temperature. Below T_g , however, $I_{3,\text{calc}}$ is almost temperature independent, whereas $I_{3,\text{exp}}$ decreases by about 10% over a temperature range of 100 K.

DISCUSSION

It has been shown that the relationship between $I_{3,\text{exp}}$ and $\tau_{3,\text{exp}}$ on one hand, and cluster concentration and hole size on the other, is not straightforward. Taking into account a lifetime distribution and the consequences of the experimental procedures used in PAS analysis has made it possible to explore this complex relationship. We show that, with the assumption of a hole distribution, PAS results for PC above T_g can be described satisfactorily. Below T_g there are discrepancies: $I_{3,\text{calc}}$ remains essentially

constant with temperature, whereas $I_{3,\text{exp}}$ shows a pronounced temperature dependence. This deviation indicates too large a calculated hole concentration. This might be caused by the use of an equilibrium cluster distribution in the nonequilibrium glass, and indicate a distortion of this distribution. At high temperatures all volume elements will have sufficient mobility to maintain equilibrium during imposed temperature changes. Close to and below T_g relaxation times become comparable to the experimental time scale, which can give rise to local nonequilibrium situations and therefore may lead to a distortion of the equilibrium distribution. Such ideas have been used successfully in the interpretation of volume changes during isothermal aging^{5,6} and cooling.⁴ If regions with a low free volume fraction contain small holes, and regions with a high free volume fraction contain large holes, then during a cooling experiment the latter will maintain equilibrium longer than the former. This will give rise to a nonequilibrium hole distribution, in contrast to the assumptions made in analysis of the glass presented in Figures 5 and 6. Preliminary calculations based on formation of nonequilibrium distributions in the glass show that $I_{3,\text{calc}}$ decreases substantially, while τ_3 decreases to a lesser extent, which is consistent with the experimental observations.

Similar computations to those presented in this paper for PC have been applied to polystyrene²⁰ and polyvinylacetate,²⁰ with comparable results. Moreover, the access to a wider temperature range in the melt for these polymers further supports the kind of agreement between theory and experiment seen in Figures 5 and 6.

Finally a comment is in order with regard to the deviation in Figure 4 between the sum of exponential

Figure 6. The o-Positronium intensity for polycarbonate¹³ (●) versus temperature, compared with o-Ps intensity calculated following the procedure illustrated in Figure 4 (solid line).

decays and the fitted single exponential decay at times shorter than 2 ns. This discrepancy corresponds to the part of the o-Ps decay that in the PAS fitting procedure is assigned to species other than o-Ps, i.e., free positrons and p-Ps. The fitted values of $I_{1,\text{exp}}$ and $I_{2,\text{exp}}$ are larger than the true fraction of positrons that annihilate as p-Ps and as free positrons, respectively. In addition, $\tau_{1,\text{exp}}$ and $\tau_{2,\text{exp}}$ are larger than the true values, because part of the relatively long o-Ps components are interpreted as contributing to τ_1 and τ_2 . In PAS experiments on polymers it is found^{7,8,13,21,23} that the ratio $I_{1,\text{exp}}/I_{3,\text{exp}}$ is indeed larger than the value $\frac{1}{3}$, which is expected on a quantum mechanical basis. Values for $\tau_{1,\text{exp}}$ and $\tau_{2,\text{exp}}$, larger than the expected 125 ps and 0.4–0.5 ns, respectively, have been reported.^{7,8,13,22} All these observations support the relevance and validity of the fitting procedure presented in this paper, and the presence of a o-Ps lifetime distribution. Clearly it is only an approximation to fit a distribution of τ_3 to a single value for τ_3 separately from the fitting of τ_1 and τ_2 . A logical next step in the study of the influence of a hole size distribution on PAS results is the generation of spectra with calculated distributions, including assumptions for τ_1 and τ_2 , noise, a source term and a time resolution function, and the subsequent analysis of these spectra by the conventional PAS spectral analysis software.¹⁹ In a forthcoming paper²⁴ the results of this approach will be presented.

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