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POSITRON AND POSITRONIUM ANNIHILATION LIFETIME, AND FREE VOLUME IN POLYMERS

by

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Submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy

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January, 1995
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GRADUATE STUDIES

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*We also certify that written approval has been obtained for any proprietary material contained therein.
Abstract

by

ZHIBIN YU

Positron annihilation lifetime measurements were carried out for six polycarbonates of different structures and four polystyrenes of different molecular weight over a wide temperature range covering the glass transition region. The o-Ps mean lifetime is very sensitive to the changes of free volume in those polymers which occur due to change of molecular structure, chain length, and temperature. The influence of the unavoidable \( e^- \) irradiation and physical aging on the mean lifetime and the intensity of o-Ps annihilation were studied by conducting time dependent measurements on both very aged and rejuvenated samples. Both irradiation and physical aging reduce the formation of positronium, but have no effect on the mean lifetime of Ps atoms. The free volume fraction \( h \) obtained from the positron lifetime measurements was compared with the prediction of the statistical mechanical theory of Simha and Somcynsky; good agreement was found in the melt state though clear deviations were observed in the glassy state. A free volume quantity, computed from the bulk volume, which is in a good numerical agreement with the Simha-Somcynsky \( h \)-function in the melt, gives improved
agreement with the $h$ value calculated from the positron lifetime measurements. To investigate certain anomalies observed in the computer analysis of the positron annihilation lifetime spectra on polymers, we developed a computer simulation of the experimental data, which then was used to test the accuracy of the fitting results in the different circumstances. The influence caused by a possible distribution of the o-Ps mean lifetimes and the width of the spectrometer time resolution function were studied. The theoretical connection between the o-Ps mean lifetime and the free volume hole size was reviewed based on a finite spherical potential well model, and the status of the localized Ps atom in polymers was evaluated by calculation of the barrier transmission probability and the escaping probability of the trapped Ps atom. We conclude that there is no justification for a one-to-one correlation of lifetime components with specific hole sizes.
To the Memory of My Father

— iv —
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# Table of Contents

Abstract ii  
Dedication iv  
Acknowledgment v  
Table of Contents vi  
List of Figures ix  
List of Tables xv

Chapter 1. Introduction to Positron and Positronium Annihilation in Polymers 1

1.1 Positron 1  
1.2 Positronium 6  
1.3 Free Volume in Polymer 10  
1.4 Positron and Positronium in Polymer Materials 13

Chapter 2. Experimental Methods and Principal Working Equations 19

2.1 Positron Annihilation Lifetime Spectrometer 19  
2.2 Mathematical Model of Decays and Spectrum Analysis 26  
2.3 Principal Working Equations 29

— vi —
Chapter 6. Positronium Localization in Macromolecule Substances

6.1 Background
6.2 Correlation Between o-Ps Lifetime and Free Volume Size
6.3 Localization of Positronium and Distribution of o-Ps Annihilation Lifetimes
6.4 Conclusions

Chapter 7. Summary and Future Work

7.1 Summary
7.2 Future Work

Bibliography
List of Figures

Chapter 1

Figure 1-1. Schematic comparison of hydrogen atom and positronium atom. 7

Figure 1-2. The qualitative free-volume concept. 12

Figure 1-3. Formation probability of Ps as a function of positron energy in an Ore gap model. 15

Chapter 2

Figure 2-1. Diagram of PAL Spectrometer. 21

Figure 2-2. The nuclear decay scheme of a positron source $^{22}$Na. An intermediate state of decayed $^{22}$Na emits a $\gamma$-ray of energy 1.27 $MeV$ which is used as a "birth" signal of the positron in the lifetime experiments. 23

Figure 2-3. Energy distribution of positrons emitted from $^{22}$Na. 23

Figure 2-4. Energy spectrum from BaF$_2$ detector. $^{22}$Na sandwiched by two pieces of polycarbonate sheet is used as radiation source. The shadows reflect window settings on CFDD. 25

Figure 2-5. Positron annihilation lifetime spectrum of polycarbonate. 25
Figure 2-6. The density distribution of Ps, e+ and e- in lattice model.

Figure 2-7. Square well potentials are used to approximate the lattice interaction.

Figure 2-8. The free-volume hole radius is $R$ with an electron layer of thickness $\Delta R$. The ground state of the Ps wave function is schematically shown. The shaded area represents the overlap between the electron and the positron densities.

Figure 2-9. A correlation curve between the observed o-Ps lifetime and the free volume hole size ($4\pi R^3/3$). The solid line is the best fit using Equation (2-20) with $\Delta R = R_o - R = 1.656 \, \text{Å}$.

Chapter 3

Figure 3-1. Structures of the polycarbonates investigated in this work.

Figure 3-2. The diagram of sample holder. Each selected temperature can be kept constant within ± 0.2 °C during data acquisition.
Figure 3-3. Influence of irradiation time on o-Ps intensity $I_3$ for BPA and TMBPA polycarbonate. Data were collected at 22°C.

Figure 3-4. Comparison of the temperature dependence of (a) the o-Ps lifetime and (b) corresponding intensities in as-received and rejuvenated Bisphenol A polycarbonate.

Figure 3-5. Apparent o-Ps lifetime $\tau_3$ and the corresponding average hole volume $\langle V_{\text{hole}} \rangle$ as a function of temperature for investigated polycarbonates. Each curve can be approximated by two linear functions, whose intersection defines a glass-transition temperature $T_{g,ps}$.

Figure 3-6. Time dependence of (a) o-Ps lifetimes, $\tau_3$, and (b) intensities, $I_3$, after quench from $T_g + 5^\circ C$ to 23°C in TMBPA and BPA compared to irradiation effects.

Chapter 4

Figure 4-1 The o-Ps lifetimes and the corresponding average hole volumes, as a function of temperature for polystyrenes of narrow polydispersities with the indicated weight-average molecular weights.
Figure 4-2. The o-Ps intensities as a function of temperature for polystyrenes of narrow polydispersities with the indicated weight-average molecular weights.

Figure 4-3. Comparison of the p-Ps, free e*, and o-Ps intensities, \( I_1, I_2 \) and \( I_3 \), respectively, for the polystyrene of highest \( M_w \) (400,000).

Figure 4-4. Superposition of the temperature dependencies of (a) \( h_{ps} \) and (b) \( h_{th} \) for polystyrenes of different molar masses.

Figure 4-5. Comparison of the theoretical free volume fraction \( h_{th} \) with the calculated free volume fraction \( h_{ps} \) from o-Ps annihilation. The broken lines indicate that rescaling \( h_{th} \) to lower \( T_g \) does not produce agreement with the experimental \( h_{ps} \).

Figure 4-6. The o-Ps free volume fraction is compared with that computed from Equation (4-5), as a function of temperature.

Chapter 5

Figure 5-1. Comparison of p-Ps and free positron annihilation fitting results, evaluated under the constraint \( \tau_f = 125 \) ps, with input values of the simulation: a) lifetimes \( \tau_f \) and \( \tau_2 \), b) intensities \( I_1 \) and \( I_2 \).
Figure 5-2. Analysis under constraint $\tau_f = 125$ ps: comparison of fitting results with average input values for the multiple o-Ps decay. a) lifetimes and b) intensities.

Figure 5-3. Results of free 3-component analysis as a function of FWHM of time resolution function: a) lifetimes $\tau_1$ and $\tau_2$, b) intensities $I_1$ and $I_2$. Filled symbols depict experimental results.

Figure 5-4. Apparent o-Ps a) lifetimes $\tau_{3,app}$ and b) intensities $I_{3,app}$ as a function of FWHM of time resolution function. Filled symbols depict experimental results.

Chapter 6

Figure 6-1. The finite spherical potential well with radius $R$ and height $V_0$. Also plotted is the schematic Ps wave function.

Figure 6-2. Graphs of $\cot(kR)$ with different $R$ values, and $\sqrt{(\beta^2 - k^2)/k^2}$.

Figure 6-3. The scaled o-Ps lifetime, $\tau' \tau^*$, vs. the scaled free volume hole size, $V/V^*$.

Figure 6-4 The comparison of the Equation (6-1) with the Equations (6-14) and (6-15). We assume that the scaling parameter $\tau^* \sim 0.5$ ns, and the potential barrier $V'_0 \sim 1.4$ eV.
Figure 6-5. Cubic lattice with hole on the lattice sites, $d$ is the distance between the center of one hole to the center of the nearest hole. $R'$ satisfies $4\pi R'^3/3 = d^3$. 
List of Tables

Chapter 1

Table 1-1. Differences in physical properties between the positron and the electron. 3

Chapter 3

Table 3-1. Characteristic data of the investigated polycarbonates. 42

Chapter 4

Table 4-1. The temperature dependence of $I_1$, $I_2$, $I_3$, $\tau_2$ and $\tau_3$ for the polystyrene of highest $M_w$ (400,000) with $\tau_1$ fixed at 125 ps. 62

Table 4-2. The molecular weight dependence of $T_g$ and $C$ constant. 62

Table 4-3. The molecular weight dependence of Parameters $C$ and $V'$ in Equation (4-5). 78
Chapter 1

Introduction to Positron and Positronium Annihilation in Polymers

1.1 POSITRON

The existence of the positron was first predicted theoretically by Dirac\(^1\) in 1931 from the negative solution of electron energy, and then proved experimentally by Anderson\(^2\) a year later from the observation of cosmic ray showers.

Represented as \(e^+\), the positron is an antiparticle of the electron, \(e^-\), carries opposite charge and magnetic moment equal in magnitude to those carried by the electron and has all other properties almost identical to those of the electron. Like its antiparticle, the positron is a member of the lepton group, defined by two characteristics: (1) it obeys Fermi-Dirac statistics, and (2) it does not directly participate in strong interactions.


The Table (1-1) lists the differences of some basic properties between the two particles.

It is rare to find a stable positron naturally due to its very small population and short lifetime compared to its antiparticle. The positron can be generated via nuclear reactions such as decays of neutron deficient radioisotopes, and pair production by γ-rays with energy greater than $2mc^2$.

When the positron encounters an electron, annihilation may take place, and the energy of $2mc^2$ or more is emitted in the form of γ-ray radiation,

$$e^+ + e^- \rightarrow n\gamma,$$

where $n$ is the number of photons created by the annihilation process.

The annihilation behavior of positron and electron is governed by quantum electrodynamics and can be described as singlet ($^1S$) interaction when spins of conjugate particles are antiparallel, and triplet ($^3S$) interaction when spins are parallel. So far there are only three different experimentally observed annihilations, i.e., one-photon, two-photon, and three-photon annihilations.

One-photon annihilation is possible only in the presence of a third body that absorbs the recoil momentum required by momentum conservation. The cross section for one photon annihilation$^3$ between a

---

Table 1-1. Differences in physical properties between the positron and the electron\(^4\).

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Charge</td>
<td>(\frac{</td>
</tr>
<tr>
<td>Mass</td>
<td>(\frac{m^- - m^+}{m^-} &lt; (1.01 \pm 1.85) \times 10^{-4})</td>
</tr>
<tr>
<td>Magnetic moment</td>
<td>(\frac{\mu^- - \mu^+}{\mu^-} &lt; 1.2 \times 10^{-8})</td>
</tr>
<tr>
<td>Charge-to-mass ratio</td>
<td>(\frac{e^+/m^+ -</td>
</tr>
<tr>
<td>Gyromagnetic ratio</td>
<td>(\frac{g^+ - g^-}{g^-} \approx 1.0 \times 10^{-11})</td>
</tr>
</tbody>
</table>

free positron and a $1S$ electron of an atom with atomic number $Z$ is:

$$\sigma_1 = \frac{4\pi r_0^2 Z^5 \alpha^4}{(\gamma + 1)^2 \sqrt{\gamma^2 - 1}} \left[ \gamma^2 + \frac{2}{3} \gamma + \frac{4}{3} \frac{\gamma + 2}{\sqrt{\gamma^2 - 1}} \ln(\gamma + \sqrt{\gamma^2 - 1}) \right]$$  \hspace{1cm} (1-2)

where $\gamma = 1/\sqrt{1-(v/c)^2}$; $r_o$ is the classical radius of the electron; $\alpha = e^2/hc$ is the fine structure constant; and $v$ is the velocity of the annihilating positron.

The most common annihilation events observed are the two-photon annihilations. The associated cross section\(^1\) is found to be:

$$\sigma_2 = \frac{\pi r_0^2}{\gamma + 1} \left[ \frac{\gamma^2 + 4 \gamma + 1}{\gamma^2 - 1} \ln(\gamma + \sqrt{\gamma^2 - 1}) - \frac{\gamma + 3}{\sqrt{\gamma^2 - 1}} \right]$$  \hspace{1cm} (1-3)

and the cross section for three-photon annihilation is:

$$\sigma_3 = \frac{4}{3\pi} (\pi^2 - 9) \alpha \sigma_2 \approx 0.27\% \sigma_2$$  \hspace{1cm} (1-4)

which is negligible compared to the cross section of two-$\gamma$ annihilation. However, three-photon annihilation is important in a spin-correlated state like ortho-positronium discussed below.

For the slow positron, $v/c \ll 1$, $\gamma \rightarrow 1$:

$$\sigma_1 \rightarrow \frac{4}{3} \pi r_0^2 Z^5 \alpha^4 \frac{v}{c}$$  \hspace{1cm} (1-5)
\[ \sigma_2 \rightarrow \pi r_0^2 \frac{c}{v} \] (1-6)

Since \( \sigma_2 >> \sigma_1 \), two-photon events dominate the annihilation. To illustrate this, we use the positron from \(^{22}\text{Na}\) as an example. The typical kinetic energy is about 200 KeV, and the atomic number \( Z \) is on the order of 10 for most polymers, so the ratio \( \sigma_1/\sigma_2 \) is about \( 10^{-6} \).

For the fast positron, \( v/c \rightarrow 1, \gamma \rightarrow \infty \):

\[ \sigma_1 \rightarrow 4\pi r_0^2 Z^5 a^4 / \gamma \] (1-7)

\[ \sigma_2 \rightarrow \pi r_0^2 (\ln \gamma) / \gamma \] (1-8)

All cross sections become very small. Therefore, for free positron annihilation, one has to consider only two-photon annihilation.

The positron annihilation rate \( \lambda_i \) for \( i \)-photon annihilation is simply the product of the relevant cross section \( \sigma_i \), the positron velocity \( v \) and the "available" electron number density \( n \) as follows:

\[ \lambda_i = \sigma_i v n \ , \ i = 1, 2, 3 \] (1-9)

The positrons annihilate faster in an electron-rich region than in an electron-poor one, and this makes positrons an effective probe to sense the electron density in the matter.
1.2 POSITRONIUM

Before annihilating with an electron, it is possible for a positron to capture an electron to form a bound-state called positronium (Ps), the simplest atom. The stability and structure of the Ps atom was first discussed in the work of Pirenne\textsuperscript{5} and Wheeler\textsuperscript{6} in 1944, the first experimental evidence for the existence of Ps atom was demonstrated in 1951 by Deutsch\textsuperscript{7} and after a long time, the 2430 Å, $^2\text{P} \rightarrow ^1\text{S}$ emission line was finally observed by Canter et al.\textsuperscript{8} in 1975.

Ps has a similar structure to that of the hydrogen atom, and the same size since the diameter of Ps is just twice the Bohr radius ($2a_0=1.06$ Å). Figure (1-1) gives a schematic comparison between the hydrogen and the Ps atoms. The formation of Ps atoms occurs mainly in molecular media which usually have a relatively open structure. There exists two ground states of Ps: (i) one-quarter of all Ps atoms are formed in the singlet state $^1\text{S}_0$ or para-positronium (p-Ps), in which the spins of electron and positron are antiparallel, so that the total spin is zero; and (ii) the rest are formed in the triplet state $^3\text{S}_1$ or ortho-positronium (o-Ps), in which the spins are parallel, the total spin equals one. The energy splitting between two states is only $8.4 \times 10^{-4}$ eV with the singlet state being the lower one.

\textsuperscript{5}J. Pirenne, Ph. D. Thesis, University of Paris (1944); Arch. Sci. Phys. Nat. 28. 273 (1946); ibid., 29. 121. 207. and 265 (1947)


\textsuperscript{7}M. Deutsch, Phys. Rev. 82, 455 (1951)

Figure 1-1. Schematic comparison of hydrogen atom and positronium atom.
The positron in Ps atom can annihilate with an electron. The self-annihilation of the ground state Ps in vacuum must obey the angular momentum conservation law, hence, one-photon annihilation is forbidden, two-photon is allowed only for the singlet state $1^1S_0$ or $p$-Ps and three-photon annihilation for the triplet state $1^3S_1$ or $o$-Ps respectively.

The ground state wave function of Ps atom can be easily obtained from the analog between Ps and the hydrogen atom:

$$\phi_{100}(r) = \pi^{-1/2} (2a_o)^{-3/2} e^{-\frac{r}{2a_o}}$$

where $a_o = \hbar^2 / m_e e^2$ is the Bohr radius. Therefore the probability density of an electron appearing at a positron site is:

$$P_e = |\phi_{100}^2(0)| = \frac{1}{\pi (2a_o)^3}$$

By replacing the "available" electron number density $n$ with the probability density $P_e$ in Equation (1-9), under the limitation of slow positron (Equation (1-6)), which is true for the positron in Ps atom, the theoretic rate of the self-annihilation of ground state Ps in vacuum can be calculated as:

$$\lambda_2 = \sigma_2 v P_e = \frac{r_o c}{(2a_o)^3} = 2.008 \times 10^9 \text{ (s}^{-1})$$

---

\[
\lambda_3 = \sigma_3 \nu p_c = 0.27\% \lambda_2 = 5.408 \times 10^6 \text{ (s}^{-1})
\]  

(1-13)

for two-photon and three-photon annihilation respectively. This includes the contribution from both p-Ps and o-Ps. Using \( \lambda_i(p-Ps) \) to present the annihilation rate of para-positronium and \( \lambda_i(o-Ps) \) for the ortho-positronium, we have

\[
\lambda_i = \frac{1}{4} \lambda_i(p - Ps) + \frac{3}{4} \lambda_i(o - Ps)
\]  

(1-14)

with \( \lambda_2(o-Ps) = 0 \), and \( \lambda_3(p-Ps) = 0 \). Therefore,

\[
\lambda_2(p - Ps) = 4 \lambda_2 = 8.032 \times 10^9 \text{ (s}^{-1})
\]  

(1-15)

\[
\lambda_3(o - Ps) = \frac{4}{3} \lambda_3 = 7.211 \times 10^6 \text{ (s}^{-1})
\]  

(1-16)

The reciprocal of the annihilation rate is the intrinsic lifetime:

\[
\tau(p - Ps) = \frac{1}{\lambda_2(p - Ps)} = 0.1245 \text{ (ns)}
\]  

(1-17)

\[
\tau(o - Ps) = \frac{1}{\lambda_3(o - Ps)} = 138.7 \text{ (ns)}
\]  

(1-18)

The radiative corrections\(^{10,11}\) modify the above lifetimes to

\[ \tau(p - Ps) = 0.1252 \text{ (ns)} \]  

(1-19)

\[ \tau(o - Ps) = 142.1 \text{ (ns)} \]  

(1-20)

The best experimental value\textsuperscript{12,13} for p-Ps lifetime \( \tau(p-Ps) \) is 0.1251 ns, or annihilation rate \( \lambda(p-Ps) = 7990.9 \pm 1.7 \text{ } \mu s^{-1} \), and for o-Ps, \( \tau(o-Ps) \) is 141.8 ns, or \( \lambda(o-Ps) = 7.0516 \pm 0.0013 \text{ } \mu s^{-1} \).

1.3 FREE VOLUME IN POLYMER

Polymers are molecules that are very long and chainlike, usually extending over several thousand angstroms. Because of their great length these molecules are referred to as macromolecules. The structural arrangement of a single macromolecule is composed of a repetition of building blocks, called a monomer. The binding forces holding the monomers together are covalent, and consequently very strong. But two neighboring macromolecules are held together by weak lateral van der Waals forces. Therefore a relatively open structure due to the loose packing among the macromolecules is a typical mark of polymer substances in the amorphous state.

The free volume concept was introduced qualitatively in the study


of the transport mobility of amorphous polymers, to describe the degree of packing\textsuperscript{14}. As the degree of packing increases, or in other words, as the free volume decreases, the mobility, $M$, decreases rapidly to very small value at a critical degree of packing (see Figure (1-2)) which depends on the size of the diffusing species.

In quantitative free volume models\textsuperscript{15}, the free volume is defined as:

$$V_f = V - V_o(T) \quad (1-21)$$

where $V$ is the specific volume, and $V_o$, the occupied volume, is a function of temperature. The free volume fraction, $h$, is defined by:

$$h = \frac{V_f}{V} \quad (1-22)$$

The relationship between mobility, free volume and temperature is of the following general form\textsuperscript{14}:

$$\ln M = A - \frac{B(T)}{h^\gamma} + \phi(T) \quad (1-23)$$

where $A$ is a constant; $\gamma$ is a positive exponent; $B(T)$ and $\phi(T)$ are functions of temperature.

\textsuperscript{14}L. C. E. Struik, "Physical Aging in Amorphous Polymers and Other Materials" Elseviev Scientific, (1978)

\textsuperscript{15}A. J. Kovacs, Fotschr. Hochpolm. Forsch. 3, 394 (1964)
Figure 1-2. The qualitative free-volume concept.
This simple but useful "free volume" concept has been extensively used to interpret transport phenomena\textsuperscript{14, 16, 17} in macromolecular materials both above and below the glass transition temperature $T_g$. Theoretical models based on free volume prove to be convenient in attempting connections between macroscopic properties and the microstructural features of amorphous polymers. Of particular interest here is a statistical thermodynamic description of amorphous polymer developed by Simha-Somcynsky\textsuperscript{18, 19}, which is based on a lattice model with disorder introduced by vacancies while the other sites are occupied by molecular chain segments. In this model the free volume is computed as the fraction of empty lattice sites, i.e., the fraction of "holes".

1.4 Positron and Positronium in Polymer Materials

When energetic positrons are injected into a polymer substance, they interact with molecules through inelastic collisions including ionization and excitation, and slow down to thermal energies within a very short time of the order of $10^{-12}$ second\textsuperscript{20}. Those initial ionizations and excited states are not formed homogeneously throughout the substance but instead are concentrated in relatively small volumes, which are called


\textsuperscript{17}J. D. Ferry, "Viscoelastic Properties of Polymers", J. Wiley \\& sons (1980)


\textsuperscript{19}J. E. McKinney, R. Simha, \textit{Macromolecules}, 7, 894 (1974); 9, 430 (1976)

\textsuperscript{20}P. Hautojärvi, ed., "Positrons in Solid", Springer-Verlag Berlin Heidelberg (1979)
"radiation spurs".

Some of the thermalized positrons are annihilated as "free positrons" by electrons in the bulk polymer, and the emission of two 0.511 MeV γ-rays dominates in those annihilations. The mean lifetime of such annihilations is determined by the local electron density and found to be in the range 0.1-0.9 ns\(^{21}\). Alternatively the open structure and loose packing of the macromolecules, provide positrons with the opportunity to capture an electron from the surrounding medium and to form a Ps atom in regions of low electron density, i.e., in the free volume holes, before annihilation can take place\(^{22}\).

The formation of positronium in macromolecules is complicated, and not clearly understood. Two major theoretical models, are widely used to explain the Ps formation probability in molecular solids.

( i ) The Ore gap model\(^{23}\) states that Ps formation is most probable when the energy of the slowing positron lies within a gap where no other electronic energy transfer process is possible. The probability of Ps formation as a function of the kinetic energy of the moderating positron is schematically illustrated in Figure (1-3). To capture an electron from a molecule of the medium with ionization energy \(E_i\), the kinetic energy \(E\) of the positron must be greater than \(E_i - E_{ps}\), which is labeled as the


Figure 1-3. Formation probability of Ps as a function of positron energy in an Ore gap model.
threshold energy \( T \) in Figure (1-3). Here \( E_{ps} \) is the binding energy of Ps atom. In a vacuum, \( E_{ps} \) is 6.8 eV but may be smaller in the medium. When \( E > E_i \), the Ps atom is formed with a kinetic energy greater than its binding energy and it will rapidly break up in collisions. Furthermore inelastic collisions will compete with Ps formation until the positron kinetic energy is less then \( E_{ex} \), the lowest electronic excitation energy. Thus Ps atom formation is most probable where the energy in the range

\[
E_i - E_{ps} < E < E_{ex}
\]  

(1-24)

which is called the Ore gap. If we assume that a high-energy positron has an equal probability of deexciting to any energy level below \( E_{ex} \) so that the distribution of \( E \) below \( E_{ex} \) is constant, the probability \( P \) of Ps formation should be in the range

\[
\frac{E_{ex} - T}{E_{ex}} < P < \frac{E_i - T}{E_i}.
\]  

(1-25)

(ii) The spur model\(^{24}\) describes Ps formation as a two-step process. Behaving like an electron, a positron slows down in a medium and creates a radiation track. This is punctuated by spurs and other localized regions which are created when the positron deposits its energy in discrete quantities, nominally about a hundred electron volts. This energy goes mostly into ionization of molecules of the medium, producing ion pairs.

The last spur on the positron track is where the positron finally thermalizes. After that, a Ps atom is formed when the positron succeeds in finding a secondary electron before the latter recombines with its parent molecular cation. According to this model, Ps formation is confined to the terminal spur, and its probability is expressed as the fraction of positrons which do not escape the spur

\[ P = 1 - \exp(-r_c / r_i) \]  \hspace{1cm} (1-26)

where \( r_c = e^2 / \epsilon kT \), the distance at which the potential energy of the electron-positron pair equals the thermal energy \( kT \), and \( r_i \) is the mean thermalization distance of the positron in the medium with dielectric constant \( \epsilon \). Therefore in the spur model, Ps formation is related to the radiation effect induced by the positron, and to the electromagnetic and chemical properties of molecules.

Due to the strong repulsive potential between the ions and the positively charged positron and the high polarizability of Ps, positronium is much more stable in vacuum than in bulk. It is localized mainly to open spaces present in the medium of the polymer. In the free volume model proposed and developed by Brandt, et al.\textsuperscript{25}, it was assumed that Ps forms only in a free volume site.

The lifetime of p-Ps self-annihilation in polymer substance is not affected by the medium, and is still 125 ps, the same as in vacuum. The

three-photon self-annihilation of o-Ps in vacuum has a lifetime of $142 \ ns$, which is more than three orders of magnitude longer than the p-Ps lifetime. However, a "pick-off" annihilation mechanism reduces dramatically the lifetime of o-Ps in a molecular substance to a few nanoseconds, and hence the pick-off events dominate the o-Ps annihilation.

In the pick-off process, the positron of o-Ps suffers two-photon annihilation in collision with a surrounding electron which has opposite spin. Its lifetime is determined by the overlap of wave functions of the o-Ps and the surrounding electrons of the medium. Since the Ps atoms are localized in regions of low electron density, the lifetime of the o-Ps pick-off annihilation, therefore, reflects the information on the free volume holes.
Chapter 2

Experimental Methods and Principal Working Equations

2.1 Positron Annihilation Lifetime Spectrometer

In the last three decades, positron annihilation lifetime (PAL) spectroscopy has become one of the most powerful tools for the investigation of vacancies in metals and semiconductors (see reference 1 for a review). More recently, experimental\(^2\) and theoretical efforts\(^3\) suggest\(^4,5\) that PAL spectroscopy is a unique probe to directly measure free volume hole sizes in amorphous polymers.

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\(^1\) P. Hautojärvi, ed., "Positrons in Solids". Springer-Verlag Berlin Heidelberg (1979)


\(^3\) S. Tao, J. Chem. Phys., 56, 5499 (1972)


The fundamental task of a PAL spectrometer is to measure the time interval between a "birth" signal accompanied by the emission of a positron from a positron source, and a "death" signal created by the annihilation event. A typical setup of PAL spectrometer, shown in Figure (2-1), consists of positron source, two γ-ray detectors, a fast-fast coincidence system which includes two Constant Fraction Differential Discriminators (CFDD), a Time to Amplitude Converter (TAC), and a PC-based Multi-Channel Analyzer (MCA).

Positron sources are usually artificially produced from nuclear decays of neutron deficient radioisotopes. The conventional positron source in the lifetime measurements requires a prompt γ-ray coincident with positron emission to serve as the start signal for timing purposes, as well as a high fraction of positron decays to reduce background counts. The most common choice is the radioisotope sodium-22 ($^{22}\text{Na}$), which is commercially available as aqueous solution of NaCl. It emits a positron through a nuclear decay to neon-22 ($^{22}\text{Ne}$) accompanied by the emission of a γ-ray (1.27 MeV), which is used as "birth" signal of positron, within a time interval of $3 \times 10^{-12}$ sec:

\[ _{11}\text{Na}^{22} \rightarrow _{10}\text{Ne}^{22} + \nu + \beta^+ + \gamma \]  

The fraction of positron from $^{22}\text{Na}$ source is above 90%, and the half-lifetime of decay is about 2.6 year\(^6\), which is important to maintain

\[^6\text{P. M. Endt, C. Van der Leun, Nuclear Physics: A, 310, 42, (1978)}\]
CFDD: Constant Fraction Differential Discriminator
TAC: Time to Amplitude Converter
MCA: Multi-Channel Analyzer

Figure 2-1. Diagram of PAL Spectrometer
a constant source strength during the lifetime spectrum collection. The nuclear decay scheme of $^{22}$Na is shown\(^7\) in Figure (2-2). The energy distribution of positrons from such source is shown in Figure (2-3).

The positron source, usually prepared to be reusable, is folded in very thin metallic foil, such as aluminum foil with a thickness less than 0.004 \textit{mm} or nickel foil thinner than 0.001 \textit{mm}, then sandwiched between two pieces of the sample material in order to have as many positrons as possible annihilate in the sample. The 0.511 \textit{MeV} \(\gamma\)-ray created in the positron annihilation is used as the "death" signal. The source strength used in PAL spectrometer is between 1 to 50 \(\mu\text{Ci}\) depending on the detector efficiency and the distance between source and detectors. A 50 \(\mu\text{Ci}\) source produces about $2\times10^6$ positrons per second, i.e., the average time interval between two positrons is about $5\times10^{-7}$ second. The o-Ps pick-off annihilation mean lifetime in polymer materials is about $10^{-9}$ second. Therefore, the probability of correlating the birth signal from one positron and the death signal from another is negligible.

The \(\gamma\)-ray detector consists of a photo-multiplier tube and a scintillator. Typical scintillators used in PAL spectrometer are single crystal barium fluoride (BaF$_2$), cesium fluoride (CsF) or plastic. The scintillator converts \(\gamma\)-rays into ultraviolet or visible photons, which are amplified by the photo-multiplier and then sent to Constant Fraction Differential Discriminators (CFDD). The signal from each detector has a wide energy range including both birth signal (1.27 \textit{MeV} \(\gamma\)-ray) and death

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\(^7\)C. M. Lederer, V. S. Shirley. "Table of Isotopes". Wiley. (1978)
$\beta^+, \text{E.C.}$

![Diagram of nuclear decay scheme of $^{22}\text{Na}$]

E.C. = Electron Capture

**Figure 2-2.** The nuclear decay scheme of a positron source $^{22}\text{Na}$. An intermediate state of decayed $^{22}\text{Na}$ emits a $\gamma$-ray of energy 1.27 MeV which is used as "birth" signal of the positron in the lifetime experiments.

![Energy distribution of positrons emitted from $^{22}\text{Na}$]

**Figure 2-3.** Energy distribution of positrons emitted from $^{22}\text{Na}$. 

kinetic energy $E$, in MeV
signal (0.511 MeV γ-ray). As an example, a typical energy spectrum of γ-ray from a detector with single crystal BaF₂ is shown in Figure (2-4), in which, ²²Na sandwiched by two pieces of polycarbonate sheet is used as radiation source.

The Constant Fraction Differential Discriminators (CFDD) single out the birth signal and death signal from the energy spectrum of the detectors by appropriate energy window settings (the shadow part of energy spectrum in Figure (2-4)), and convert them simultaneously to fast logic signals which serve as "start" input signal and "stop" input signal for the Time to Amplitude Converter (TAC). The latter converts the time interval between start and stop signals to a voltage amplitude which is finally recorded by a PC-based Multi-Channel Analyzer (MCA). A sample positron annihilation spectrum of polycarbonate is shown in Figure (2-5).

The two major concerns in designing a PAL spectrometer are system time resolution and data acquisition efficiency. The plastic scintillator offers a very fast timing response, which contributes about 0.14 ns to the system time resolution function, but has a very poor energy resolution and low efficiency to stop γ-rays due to its low density. Cesium fluoride (CsF) is efficient in stopping γ-rays, but the time resolution function is not good (usually wider than 260 ps). Single crystal barium fluoride (BaF₂) gives both high counting efficiency and good timing response; time resolution under 180 ps can be achieved with careful adjustment. In addition to the scintillators, the photo-multiplier tubes and discriminators contribute a great deal to the time resolution function, and
Figure 2-4. Energy spectrum from BaF$_2$ detector. $^{22}$Na sandwiched by two pieces of polycarbonate sheet is used as radiation source. The shadows reflect window settings on CFDD.

Figure 2-5. Positron annihilation lifetime spectrum of polycarbonate.
the discriminator affects data acquisition efficiency through the width of the energy windows.

2.2 **Mathematical Model of Decays and Spectrum Analysis**

Positrons annihilate with electrons in polymers in different ways, i.e., free positron annihilation, para-positronium self-annihilation, ortho-positronium pick-off annihilation, etc. Each process contributes, in the lifetime spectrum, a specific decay component which can be represented as an exponential function of time. For the decay component \( j \), the decay function can be formulated as:

\[
\alpha_j(t) = \begin{cases} 
A_j \exp(-t / \tau_j), & t > 0 \\
0, & t < 0 
\end{cases} \tag{2-2}
\]

where \( A_j \) is constant, \( \tau_j \) is the mean lifetime of the \( j \)th decay component. The total number of annihilation events contributed by the decay component \( j \) is simply

\[
N_j = \int_0^\infty \alpha_j(t) dt = A_j \tau_j \tag{2-3}
\]

Therefore, the relative number intensities of annihilation events for the \( j \)th decay component is found to be of the form:

\[
I_j = A_j \tau_j / \sum_{j=1}^{J_0} A_j \tau_j \tag{2-4}
\]
In the experimental positron annihilation lifetime spectrum, the
decay function \( f(t) \) consists of a sum of \( j_0 \) decaying exponentials \( a_j(t) \)
convoluted with the resolution function \( R \) of the lifetime spectrometer, plus
a constant noise background \( B \):

\[
f(t) = \sum_{j=1}^{j_0} (a_j \ast R)(t) + B \quad (2-5)
\]

The symbol \( \ast \) is used to represent a convolution operation which can be
evaluated as an integral

\[
(a_j \ast R)(t) = \int_{-\infty}^{\infty} a_j(v)R(t-v)dv \quad (2-6)
\]

We assume that the resolution function \( R(t) \) is a sum of \( k_0 \) Gaussians
which may be displaced with respect to each other:

\[
R(t) = \sum_{k=1}^{k_0} \omega_k G_k(t) \quad (2-7)
\]

where \( \omega_k \) is a weighting factor: \( \sum_{k=1}^{k_0} \omega_k = 1 \), and

\[
G_k(t) = \frac{1}{\sqrt{2\pi}\sigma_k} \exp \left[ -\frac{(t-t_k)^2}{2\sigma_k^2} \right] \quad (2-8)
\]

Each Gaussian in the above equation is centered at \( t_k \). The standard
devation \( \sigma_k \) of the Gaussian is related to its Full Width at Half Maximum
\[ FWHM_k = 2(2 \ln 2)^{1/2} \sigma_k \]  
\hspace{1cm} (2-9)

The decay function in Equation (2-5) is a continuous function of time, while the lifetime spectra are recorded in channels of a multi-channel analyzer. If we use the channel width as the unit of time, the \( n \)th channel number is of the form:

\[ N_n = \sum_{j=1}^{l_n} F_{jn} + B \]  
\hspace{1cm} (2-10)

with

\[ F_{jn} = \int_{t_{jn-1}}^{t_{jn}} (\alpha_j \ast R)(t) dt \]
\[ \int_{t_{jn-1}}^{t_n} \frac{k_j}{t_j} \sum_{k=1}^{k_n} \omega_j \int_{x-z}^{x} A_j \exp(-\frac{v}{t_j})G(t-v)dvdt \]
\[ = \sum_{k=1}^{k_n} \frac{\omega_j A_j}{\sqrt{2\pi}\sigma_k} \int_{t_{jn-1}}^{t_n} \int_{-\infty}^{\infty} \exp(-\frac{v}{t_j} - \frac{(t-v-t_k)^2}{2\sigma_k^2})dvdt \]  
\hspace{1cm} (2-11)

The least squares technique is used to fit the above model to experimental spectra. By changing the constant parameters \( l_j, \tau_j, FWHM_k \) and predefined \( \alpha_j \), the weighted error function

\[ \Phi = \sum_{n=1}^{n_n} w_n (y_n - N_n)^2 \]  
\hspace{1cm} (2-12)
can be minimized, where \( y_n \) is the observed value for channel \( n \) in experimental spectrum, and \( w_n = 1/(N_n)^2 \) is the positive statistical weight attached to channel \( n \).

A sophisticated program code named PATFIT-88\(^8\), which is specifically designed for deconvolution of positron annihilation spectra, is based on the above model with limited components. Experience shows that a spectrum with more than 1 million counts is essential to get a reliable and stable result. With certain constraints, up to six components including the source correction terms, which are decay components caused by annihilation of positrons in the source and source cover materials, can be derived reliably. The system time resolution can be a fitting parameter or a sum of predefined Gaussian functions.

An alternative is to use a Laplace inversion method to obtain a continuous distribution of intensities as a function of mean lifetime, using a program such as CONTIN\(^9\). In this method, a reference spectrum with single lifetime is used to derive the system resolution function, and spectra having more than \( 10 \times 10^6 \) counts are usually required to get fitting convergence. Therefore, maintaining a high electronic stability over a long period of measurement is very essential.

### 2.3 Principal Working Equations

Here, we summarize the pertinent working equations for the

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evaluation of the positron data. As a convention in the community of
positron annihilation lifetime studies, p-Ps self-annihilation mean lifetime
is referred to as $\tau_f$, o-Ps pick-off annihilation mean lifetime referred as $\tau_3$,
and $\tau_2$ is specified to be the lifetime of free positrons. The corresponding
number fractions of annihilation events for each species are the intensities
$I_1, I_2$ and $I_3$. Of particular interest is the o-Ps lifetime $\tau_3$ which is sensitive
to the free volume hole sizes in polymer materials.

Since the de Broglie wave length of thermalized Ps is about an
order of magnitude larger than the dimension (several Å) of free volume
in a typical molecular lattice, the Ps wave function may be considered to
be delocalized as illustrated in Figure (2-6)\(^{10}\). The "available" electron
number density for the positron bound in the o-Ps may be symbolically
expressed as the overlap integral between the wave function of the lattice
electron $\psi_L$ and of the positron in o-Ps $\psi_+$ as:

$$n = \int_L \psi^*_L(F) \psi^*_+(F) \psi_+(F) \psi_L(F) dF$$  \hspace{1cm} (2-13)

By neglecting the internal structure of Ps and by approximating the lattice
interactions by square well potentials (see Figure (2-7)) and the electron
density by a constant $\rho_o$ between the wells, the Equation (2-13) is
simplified as:

$$n = \rho_o \int_{\psi} \psi^*_P \psi_P dF$$  \hspace{1cm} (2-14)

\(^{10}\)W. Brandt, S. Berko, and W. W. Walker, Phys. Rev., 120, 1289 (1960); erratum,
ibid., 121, 1864 (1961)
Figure 2-6. The density distribution of Ps, e+ and e− in lattice model.

Figure 2-7. Square well potentials are used to approximate the lattice interaction.
Where $v_o$ is the volume excluding the wells, and $\psi_{Ps}$ is the wave function for the center-of-mass motion of Ps in the wells.

Combining Equations (1-6), (1-9) and (2-14), we have the pick-off annihilation rate of the o-Ps as:

$$\lambda_{pick-off} = \pi v_o^2 c \rho_o \int_{v_o} \psi_{Ps}^* \psi_{Ps} dP$$

(2-15)

To evaluate the above integral, we use a simple model in which a positronium atom resides in a spherical well with radius $R_o$ having an infinite potential barrier, to derive the wave function of Ps. The Schrödinger equation for the center-of-mass motion of Ps can be written in spherical polar coordinates as:

$$\left[ -\frac{\hbar^2}{2m} \left( \frac{d^2}{dr^2} + \frac{2d}{dr} - \frac{l(l + 1)}{r^2} + V(r) - E_n \right) \right] \psi_{Ps}(r) = 0$$

(2-16)

with

$$V(r) = 0 \quad \text{for} \quad 0 < r < R_o$$

$$V(r) = \infty \quad \text{for} \quad r > R_o$$

The solution of ground state wave function is as follows:

$$\psi_{Ps} = \frac{\sin(\pi r / R_o)}{(2\pi R_o)^{1/2} r} \quad 0 < r < R_o$$

(2-17)

$$= 0 \quad r > R_o$$
with energy eigenvalues for the $n$th state of Ps as

$$E_n = \frac{n^2 \hbar^2 \pi^2}{2mR_o^2}$$  \hspace{1cm} (2-18)

The calculation of the annihilation rate requires the electron density $\rho_o$. Instead of pursuing a calculation of $\rho_o$, we use a semiempirical approach\(^{11}\) which further assumes that there is a homogeneous electron cloud layered on the wall of the rigid sphere with thickness $\Delta R = R_o - R$ (see Figure (2-8)), and the o-Ps annihilation rate in this electron cloud is $2.0 \text{ ns}^{-1}$. Therefore, the pick-off rate can be represented as

$$\lambda_{\text{pick-off}} (\text{ns}^{-1}) = 2 \int_{0}^{r_o} |\psi_{Ps}^* \psi_{Ps}|^2 r^2 dr = 2 \times 4 \pi \int_{R}^{r_o} \psi_{Ps}^2 (r) r^2 dr$$ \hspace{1cm} (2-19)

Applying the wave function obtained before (Equation (2-17)), we have

$$\lambda_{\text{pick-off}} (\text{ns}^{-1}) = 2 \left[ 1 - \frac{R}{R_o} + \frac{1}{2\pi} \sin \left( \frac{2\pi R}{R_o} \right) \right]$$ \hspace{1cm} (2-20)

The empirical parameter $\Delta R$ is determined by fitting the observed o-Ps lifetime $\tau_3(=1/\lambda_{\text{pick-off}})$ with the known hole and cavity sizes in molecular substance. The best fit value of $\Delta R$ for all known data is found to be $1.656 \text{ Å}$.

The Equation (2-20) gives a quantitative way to bridge the o-Ps

Ps Wave Function

Radius

Figure 2-8. The free-volume hole radius is $R$ with an electron layer of thickness $\Delta R$. The ground state of the Ps wave function is schematically shown. The shaded area represents the overlap between the electron and the positron densities.
pick-off annihilation rate and the free volume hole radius, and becomes the
foundation of the positron annihilation lifetime method since, if we can
experimentally measure o-Ps lifetime in polymer materials by positron
lifetime spectroscopy, we can use this equation to convert lifetime to free
volume hole radius. The average hole "volume" is then computed as:

\[ <v_f(r_3)> = \frac{4 \pi R^3}{3} \]  \hspace{1cm} (2-21)

The correlation between \( r_3 \) and free-volume is shown in Figure (2-9)\(^{12}\).

While there is no doubt that Ps indeed samples free volume in
molecular solids, its precise behavior is still poorly understood. In
particular, 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.\(^{2}\) 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.\(^{13}\) observed a distribution of \( r_3 \)
values in an epoxy polymer and thus assumed that each o-Ps is in a single
hole during its lifetime. ( The detailed discussion about lifetime
distribution will be found in chapter 5 and chapter 6 ). Except where
indicated, in the following work, we use single o-Ps lifetime model, in
which the relation between p-Ps decay intensity \( I_1 \) and o-Ps decay


Figure 2-9. A correlation curve between the observed o-Ps lifetime and the free volume hole size \(4\pi R^3/3\). The solid line is the best fit using Equation (2-20) with \(\Delta R = R_o - R = 1.656 \text{ Å}.\)
intensity $I_3$ is expected to be $I_1 = I_3/3$ on theoretical grounds.

To describe and predict the thermodynamic behavior of polymer materials, Simha and Somcynsky developed a statistical theory\textsuperscript{14, 15}, by means of which the fractional free volume $h_{th}$ can be extracted from experimental $P$-$V$-$T$ data. Physically, we may define this quantity as:

$$h_{th} = \int n(v_f)dv_f = N <v_f>$$  \hspace{1cm} (2-22)

where $n(v_f)dv_f$ is the number density of holes whose volume is between $v_f$ and $v_f + dv_f$, $N = \int n(v_f)dv_f$ is the number of holes per unit volume, and $<v_f>$ is the average free volume hole size.

Positron experiments of Kobayashi et al.\textsuperscript{2} on PVAc suggested that $<\tau_3>$ can be related to $<v_f>$ and that $I_3$ can be taken as proportional to the free volume hole density $N$, and therefore a quantity $h_{ps}$ can be defined as:

$$h_{ps} = C'I_3 <v_f(\tau_3)>$$  \hspace{1cm} (2-23)

where $C'$ is a constant relating the o-Ps intensity $I_3$ to the hole density. Clearly, $C'$ can be determined through the equality $h_{ps} = h_{th}$, provided that $<v_f(\tau_3)>$ is proportional to the thermodynamic average hole size $<v_f>$ in Equation (2-21).

\textsuperscript{14}R. Simha, T. Somcynsky, Macromolecules, 2, 342 (1969)

\textsuperscript{15}J. E. McKinney, R. Simha, Macromolecules, 7, 894 (1974); ibid., 9, 430 (1976)
Chapter 3

Positron Lifetime Studies of Free Volume in Polycarbonates of Different Structures

3.1 Background

It is well understood that the size and concentration of free-volume holes in amorphous polymers influence the chain dynamics and hence play an important role in determining mechanical properties and diffusion phenomena. Thermal expansion implies an increase in the level of free volume, and therefore corresponds to a change in the distribution of cavity sizes. In order to predict the properties of amorphous polymers, several theoretical models, based on the free volume concept, have been developed. Knowledge of the temperature dependence of the free volume size, especially of the change of the hole expansion coefficient through the glass transition, is therefore very important as a experimental test of current free volume theories\textsuperscript{1, 2} and transport theories\textsuperscript{3, 4, 5} of the polymer melt and glass.

\textsuperscript{1}R. Simha, T. Somcynsky, \textit{Macromolecules}, 2, 342 (1969)
Physical aging of an amorphous polymer, which occurs in the non-equilibrium glassy state, has its origin in the gradual approach to equilibrium and affects all material properties whose temperature and pressure coefficients change drastically at $T_g$. 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 free volume and, like thermal expansion, a corresponding change of the distribution of free volume hole size.

In the first section of this work, the effects of the unavoidable positron irradiation of the samples are discussed. Then we report results of an investigation of the temperature dependence of free volume in glass and melt for six structurally-distinct polycarbonates of different $T_g$. In addition to experiments on "as-received" bisphenol A polycarbonate, measurements were carried out on rejuvenated samples between 20°C and 200°C for all six samples. Differences in the extracted o-Ps lifetime $\tau_3$ and intensity $I_3$ values between rejuvenated and aged materials will be

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discussed. The last section will focus on positron annihilation during physical aging. The time dependent measurements are performed at room temperature.

3.2 Experimental Procedure

The polycarbonate samples used in this work were kindly provided in the form of sheets of thickness about 2 mm by Bayer AG, Leverkusen, Germany. There were six structurally-distinct polycarbonates, including two based on bisphenol-A, denoted BPA and TMBPA and two based on bisphenol-Z, denoted BPZ and TMC, as well as two statistical copolymers TMBPA (50%)-BPA (50%) and TMC (35%)-BPA (65%). The structures of these polymers are shown in Figure (3-1). The glass transition temperatures $T_g$ (listed in Table (3-1)) have been determined using Differential Scanning Calorimetry (DSC) at a heating rate of 20°C/min.

The polycarbonate sheets were cut into discs of 10 mm diameter. About 1 MBq of $^{22}$NaCl was deposited in an envelope of aluminum foil (1.7 mg/cm) and then sandwiched between two pieces of the sample. The source-sample sandwich was then completely enclosed in a copper sample holder (see Figure (3-2) for a diagram of 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 acquisition by means of two silicon diode sensors (model DT-470, Lake Shore Cryotronics, Westerville, Ohio), which were connected to a temperature controller (model 805, Lake Shore
Figure 3-1. Structures of the polycarbonates investigated in this work.
Table 3-1. Characteristic data of the investigated polycarbonates.

<table>
<thead>
<tr>
<th>composition</th>
<th>$T_{g.ps}(^\circ C)$</th>
<th>$T_{g, dsc}(^\circ C)$*</th>
<th>$V_g(A^3)$</th>
<th>$V_g/T_g.ps$</th>
<th>$\rho(g/cm^3)$*</th>
</tr>
</thead>
<tbody>
<tr>
<td>BPA</td>
<td>145±4</td>
<td>150</td>
<td>127±3</td>
<td>0.88±0.03</td>
<td>1.189</td>
</tr>
<tr>
<td>TMBPA-BPA 50/50</td>
<td>163±4</td>
<td>178</td>
<td>140±3</td>
<td>0.86±0.03</td>
<td>1.130</td>
</tr>
<tr>
<td>TMBPA</td>
<td>18±4</td>
<td>192</td>
<td>158±3</td>
<td>0.85±0.03</td>
<td>1.086</td>
</tr>
<tr>
<td>BPZ</td>
<td>138±4</td>
<td>174</td>
<td>112±3</td>
<td>0.81±0.04</td>
<td>1.205</td>
</tr>
<tr>
<td>TMC-BPA 35/65</td>
<td>160±4</td>
<td>187</td>
<td>149±3</td>
<td>0.91±0.04</td>
<td></td>
</tr>
<tr>
<td>TMC</td>
<td></td>
<td>234</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Data provided by Bayer AG, Leverkusen, Germany. Density $\rho$ is at room temperature.
Figure 3-2. The diagram of sample holder. Each selected temperature can be kept constant within ±0.2°C during data acquisition.
Cryotronics ). The entire assembly was placed in a vacuum chamber, which permitted the sample to reach temperatures up to 200°C.

To optimize the resolution as well as the efficiency of the spectrometer, a cylindrical CsF-crystal of 1.5" length and 1.5" diameter (Solon Technologies, Inc., Ohio), coupled by glycerol 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 crystal of 0.8" and 1.0" in diameter and 1.0" in length (Solon Technologies, Inc.) likewise mounted to a photomultiplier tube (type H2431Q, Hamamatsu) was employed. A fast-fast coincidence system was employed, which consisted of two Constant Fraction Differential Discriminators (CFDD) (NIM module model 583, EG&G Ortec, Oak Ridge, Tennessee) and a Time-to-Amplitude Converter (TAC) (NIM module model 566, EG&G Ortec). With an appropriate window setting of both CFDD's, spectra which contained about 1.2 million counts were collected within 30 minutes (count rate 670 per sec.) with 260 ps FWHM time resolution. Positron lifetime spectra were collected on a PC-based Multi-Channel analyzer (PCA-II, Nucleus Inc., Oak Ridge, Tennessee) which has a channel time 10.03 ps/channel.


The following sequence of measurements was carried out on the polycarbonates in a vacuum of about 10^{-3} mbar:

(i) First we investigate the time-dependent influence of e^{+} irradiation on positronium formation. The measurements were performed at room temperature (23°C) on the as-received ("very aged") BPA and TMBPA samples immediately after source installation. Spectra were continually recorded up to 60 hours.

(ii) The temperature dependent measurement on as-received Bisphenol A polycarbonate was carried out from room temperature to above glass phase transition temperature $T_g$. Then, the measurements on all six rejuvenated samples were performed between room temperature and 200°C, each temperature-dependent spectrum being recorded after annealing at $T_g+5^\circ C$ for 30 minutes to remove prior thermal history and then cooling at a rate of $2^\circ C/min$ to the measurement temperature.

(iii) The time dependence of free volume relaxation (physical aging) was measured at room temperature after a quench from annealing temperature $T_g+5^\circ C$ (cooling rate $2^\circ C/min$). To compare with irradiation damage effects, the measurements were carried on the same BPA and TMBPA samples used in the investigation of irradiation influence.

For the analysis of the spectra, the program PATFIT-88⁹ was employed. A two-component source term (0.5651 ns with 1.5%, and 0.1883 ns with 7.5%) was subtracted uniformly from each spectrum. In order to determine the resolution function, several spectra were fitted from

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the left-hand side of the peak into the background on the right-hand side by means of the program RESOLUTION. 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. The resolution function was found to be identical and fixed during the final 3-component analysis. Spectra were analyzed from the peak well into the background on the right side. The $\chi^2/n$ values were always between 0.9 and 1.2. There were no constraints for lifetimes and corresponding intensities, except $\tau_1 = 125$ ps and $I_1 + I_2 + I_3 = 1$. The background as well as the time zero channel were free-fit parameters.

### 3.3 Results and Discussion

**Effects of $e^+$-Irradiation**

Recently it has become clear\(^1\) that positron irradiation can cause damage in molecular samples which influences the positron annihilation behavior and thus modifies measured spectral parameters. Precise investigations of this effect are very important to establish credibility of free-volume measurements by positron annihilation. Therefore, we first evaluated the dependence on exposure time of the key parameters $\tau_3$ and $I_3$. Figure (3-3) gives an illustration on the variation of $I_3$ with exposure time for as-received polycarbonate BPA and TMBPA samples. In agreement with recent measurements of Welander and Maurer\(^1\), no effect of irradiation time on $\tau_3$ is observed, independent of the material.

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Figure 3-3. Influence of irradiation time on o-Ps intensity $I_3$ for BPA and TMBPA polycarbonate. Data were collected at 22°C.
However, $I_3$ always decreases with time, although the magnitude of this effect is dependent on the particular material and varies, for example, among the polycarbonates investigated in this study.

Since these as-received samples are very "old", the physical aging process is very slow. The observed 2% drop in o-Ps intensity $I_3$ for BPA and 6% drop for TMBPA during a time interval of 60 hours is not contributed by a physical aging effect but by irradiation damage. Similar results were reported recently by Li and Boyce\textsuperscript{11} on polycarbonate and polystyrene. The stronger the radiation source used in the experiment, the more irradiation damage will be produced. The electric field created by annihilation events is apparently the source of the decrease in $I_3$. Hence, in all following free volume studies, $I_3$ is unavoidably influenced to different extents by irradiation damage, or in other words, $I_3$ is always reduced from the true intensity in cases where irradiation damage exists.

\textit{Temperature Dependence of Free Volume}

The temperature dependencies of the o-Ps decay parameters are plotted in Figure (3-4). Figure(3-4a) shows the o-Ps lifetime $\tau_3$, and Figure(3-4b) shows the o-Ps intensity $I_3$ both for as-received samples (open symbols) and after rejuvenation (filled symbols) for BPA polycarbonate. Within the scatter of the data, no difference in $\tau_3$ can be observed. Apparently, $\tau_3$ does not depend on the thermal history of the material, whereas $I_3$ of the as-received sample was found to be

\textsuperscript{11}X. S. Li, M. C. Boyce, \textit{J. of Polymer Sci.: B Polymer Phys.}, \textit{31}, 869 (1993)
Figure 3-4. Comparison of the temperature dependence of (a) the o-Ps lifetime and (b) corresponding intensities in as-received and rejuvenated Bisphenol A polycarbonate.
significantly lower for temperatures below $T_g$. Since we measured the as-received sample first, and rejuvenated sample later, the difference in $I_3$ can not be caused by irradiation damage which always reduces o-Ps intensity. We therefore deduce that the smaller $I_3$ of the as-received sample is due to physical aging.

In previous analysis$^{12}$, $I_3$ 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. In the glassy polymer state, $I_3$ in the well-annealed as well as in the "old" sample 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$^{13}$. We interpret this discrepancy as due to the fact that, when the temperature is decreased, the free volume hole size distribution shifts. With definite probe size, positronium has different sensitivity on the free volume with different hole size, the threshold of the smallest hole which can be probed by positronium, contributed to the decrease in number of "visible" free volume holes.

Figure (3-5) compares the experimental values of the average o-Ps lifetimes $\tau_3$ as a function of temperature in all six investigated

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Figure 3-5. Apparent o-Ps lifetime $r_3$ and the corresponding average hole volume $<V_{\text{hole}}>$ as a function of temperature for investigated polycarbonates. Each curve can be approximated by two linear functions, whose intersection defines a glass-transition temperature $T_{g,ps}$. 
polycarbonates. The free volume units on the right hand side vertical axis are computed from the $\tau_3$ via Equation (2-20). Clearly, the average hole sizes $V_{\text{hole}}$ at a particular temperature vary significantly among these materials. In the glassy state, the slopes of $V_{\text{hole}}(T)$ (i.e. the thermal expansion coefficients of the holes $\alpha_{\text{hole},g}$) in all polycarbonates measured in this work, can be approximated by a single value $\alpha_{\text{hole},g} = 1.7 \times 10^{-3}/K$. In the melt, $\alpha_{\text{hole},m}$ varies between $7 \times 10^{-3}/K$ and $10 \times 10^{-3}/K$.

The intersection of both linear functions defines a glass transition temperature $T_{g,ps}$, with values listed in Table (3-1). Likewise, corresponding $T_g$'s determined by means of DSC at a heating rate of $20^\circ C/min$ are given. $T_{g,ps}$ was found to be always lower than $T_{g,DSC}$.

While a difference of 5-10$^\circ C$ could be plausibly assigned to the slower cooling rate ($2^\circ C/min$) in the positron experiment, the reason for discrepancies of as much as 30$^\circ C$ in BPZ and TMC/BPA 35%/65% is presently unclear. This would not be inconsistent with the idea that, because of its small size, o-Ps is sensitive to smaller holes which remain unfrozen for some temperature range below the $T_g$ observed by DSC.

It is interesting to note, that the experimental hole volumes at $T_{g,ps}$, viz. $V_g(T_{g,ps})$, exhibit an increasing trend with $T_{g,ps}$, as shown in Table (3-1), where the ratios $V_g/T_{g,ps}$ are seen to be rather similar. This is qualitatively consistent with the deductions of the statistical theory and with physical intuition, i.e. that "low $T_g$ systems should require relatively few holes to pass into the liquid state"$^{14}$. A more detailed comparison

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with theory must await determination of PVT data for these polymers. It is pertinent to note, however, that the average hole volume of each polycarbonate (Figure (3-5)) shows an inverse correlation with bulk densities at room temperature (cf. \( \gamma \) and \( \rho \) in Table (3-1)).

**Physical Aging**

The gradual approach of the glassy state to equilibrium is investigated in BPA and TMBPA. Since only a small change in the distribution is expected on physical aging, as compared to temperature effects, we will focus here on lifetimes and intensities of the o-Ps annihilation. Figure (3-6) shows the time behavior of the o-Ps lifetime (a) and the corresponding intensity (b) for samples after quench from \( T_g + 5^\circ C \) to \( 23^\circ C \) with a cooling rate of \( 2^\circ C/min \) in comparison to measurements in as-received material. While no aging effect is visible in the o-Ps lifetime within the scatter of the data, a significant difference is evident in the intensity between the rejuvenated and the as-received samples approximately for the first 10 hours after quench. The decrease of \( I_3 \) suggests that physical aging reduces the free volume fraction in both samples, while the change of \( \tau_3 \) seems to be only of minor importance. However, note that (especially for TMBPA) \( I_3 \) in the as-received material decreases with \( e^+ \) exposure time. Therefore, the magnitude of the change due solely to aging effects may have been overestimated in previous positron studies. We conclude that only a comparison of positron measurements in polymers after quench with those in the "old" material can give evidence about the time dependence of free volume
Figure 3-6. Time dependence of (a) o-Ps lifetimes, $\tau_3$, and (b) intensities, $I_3$, after quench from $T_g+5^\circ C$ to $23^\circ C$ in TMBPA and BPA compared to irradiation effects.
relaxation in polymers after quench.

As for previous studies in polystyrene\textsuperscript{15}, polycarbonate\textsuperscript{16, 17} and poly(vinyl acetate)\textsuperscript{12}, 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 distribution of hole sizes.

\subsection*{3.4 Conclusions}

The irradiation influence on the result of positron annihilation lifetime measurement was found only on free volume intensity, which is always reduced from the "true" value, and depends on the material. The time dependency of o-Ps decay in BPA and TMBPA after an annealing at $T_{g}+5{^\circ C}$ was compared with measurement result of the as-received samples, distinct physical aging effects were monitored for approximately 10 hours after quench in both samples. An investigation of the temperature dependence of the o-Ps decay was performed from room temperature to about $200{^\circ C}$ in six polycarbonates of different $T_g$. We found an increasing

\begin{itemize}
\end{itemize}
trend of $<v_{hole}>$ with increasing $T_g$, which is qualitatively consistent with deductions of the statistical theory of Simha and Somcynsky. The comparison of the temperature dependence of free volume in as-received and rejuvenated bisphenol A polycarbonate suggested physical aging only reduces the "visible" free volume intensity, possibly by moving the distribution of free volume hole sizes.
Chapter 4

Molecular Weight Dependence of Free Volume in Polystyrenes and Correlation Between PAL Measurements and SS Theory

4.1 BACKGROUND

The free-volume concept has been extensively used to interpret transport phenomena in macromolecular materials\(^1\), \(^2\), \(^3\). Theoretical models based on free volume are a convenient vehicle with which to attempt connections between such macroscopic properties and the microstructural features of amorphous polymers.

A fundamental aspect of studies utilizing positron annihilation


spectroscopy is the search for connections between the derived structural information and bulk properties such as thermal expansion and viscoelastic behavior. Correlations of this nature have been extensively presented by Kobayashi for both low molar mass fluids and high polymers, typically, however, at a single temperature. In that work, a particular feature was the introduction of a free volume quantity defined by Bondi's well-known scheme for computing van der Waals volumes.

In our investigations, the link between probe spectroscopy and macroscopic properties was provided by the free volume hole fraction \( h(v,T) \) defined in the Simha-Somcynsky (SS) theory. This temperature- and volume-dependent function is extracted from the equation of state surface. In the equilibrium melt, \( h(v,T) \) satisfies the minimum condition on the configurational free energy. Above \( T_g \), the probe-derived free volume fraction \( h_{ps}(T) \) is found to be proportional to \( h(T) \) at atmospheric pressure for several high polymer systems. Below \( T_g \), deviations occur which remain unresolved. We note, however, that the free volume function in the glass is a non-equilibrium quantity and must be specified for a

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6A. Bondi, *J. Phys. Chem.*, 68, 441 (1964)


well-defined formation history.

In this work, we first report positron lifetimes and intensities in several polystyrenes of different molecular weights and narrow polydispersities as a function of temperature at atmospheric pressure. It is of particular interest to evaluate the contributions of the enhanced free volume, typically associated with the chain ends, to the thermodynamic and o-Ps free volume functions. From the temperature dependence of the o-Ps lifetime, we aim to directly observe the effects of the chain ends on the average free volume hole size. Then, the relation of positron annihilation lifetime and intensity to the thermal properties in the melt is described. We calculate the free volume hole size $\langle \gamma(r_3) \rangle$ and the fractional free volume $h_{ps}$ via Equations (2-20) to (2-23). The theoretical free volume fraction $h_{th}$ was determined from experimental $P$-$V$-$T$ data on low molecular weight polystyrenes in the literature via the SS theory. Comparing $h_{ps}$ and $h_{th}$ for the different polystyrenes in the equilibrium melt, we find excellent agreement. The deviations between $h_{ps}$ and $h_{th}$ occur in the glassy state and are discussed in detail. A simple free volume expression employing the bulk volume which is consistent with the SS theory in the melt, gives good agreement with $h_{ps}$ in the glass.

4.2 Experimental

The polystyrene (PS) samples used in this work were obtained from Polysciences, Inc. The reported molecular weights $M_w$, are 4,000; 9,200; 25,000; and 400,000. All of the materials were received as white powders. The $T_g$ values of these samples were determined by Differential
Scanning Calorimetry (DSC) to be 75 °C, 90 °C, 96 °C, and 102 °C, consistent with the literature relationship between \( T_g \) and molecular weight\(^9\). These powders were molded at \( T_g + 20 \, ^\circ \text{C} \) to form bubble-free transparent discs of 10 mm diameter and 2 mm thickness suitable for the sample holder of the positron annihilation lifetime spectrometer.

The positron lifetime spectrometer, which is described in detail in Chapter 3, consists of a \(^{22}\text{Na} \) positron source, two \( \gamma \)-ray detectors, a fast-fast coincidence system, and a PC-based multichannel analyzer. The positron source used in this work is about 1 MBq of \(^{22}\text{Na} \) deposited in an envelope of aluminum foil and sandwiched between two identical polystyrene sample discs. Each positron lifetime spectrum was collected with more than 1 million counts in about one hour.

The polystyrene samples were rejuvenated in the sample holder at a temperature of \( T_g + 10 \, ^\circ \text{C} \) for one hour before positron annihilation measurements, to erase any thermal history. Subsequently, a set of spectra was recorded, in a temperature range from 5°C to \( T_g + 30 \, ^\circ \text{C} \) in steps of 10°C. After each measurement below \( T_g \), we rejuvenated the sample for 15 minutes at \( T_g + 10 \, ^\circ \text{C} \). This procedure is identical to that utilized in our earlier o-Ps studies of polymers in the glassy state, and is designed to minimize possible anomalous decreases in o-Ps intensity resulting from prolonged exposure to e\(^+\) radiation.

The program PATFIT-88\(^{10}\) was employed to determine the positron

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\(^{10}\)P. Kirkegaard, N. J. Pedersen, M. Eldrup, Riso National Laboratory, Denmark (1989)
annihilation lifetimes and intensities. A two-component source correction term was assumed. The time resolution function of the spectrometer was constructed via a fit to a sum of three Gaussians. The full width at half-height of the time resolution function was 260 ps. The positron annihilation spectra were fitted to three exponentially decaying lifetime components: p-Ps, free-positron and o-Ps. The p-Ps lifetime $\tau_1$ was constrained to the theoretical value of 125 ps and the sum of the intensities to be equal to 100%.

4.3 RESULTS AND DISCUSSION

Molecular Weight Dependence of Free Volume

In Table (4-1), we list values of $l_1$, $l_2$, $l_3$, $\tau_2$ and $\tau_3$ for the polystyrene of highest $M_w$ (400,000) at different temperature, the p-Ps lifetime $\tau_1$ being held constant at the theoretical value of 125 ps in fitting procedure. No significant differences were found when comparing the four specimens with different chain lengths in the free positron decays. Figure (4-1) shows the ortho-positronium lifetimes, $\tau_3$, for the four monodisperse polystyrenes as a function of temperature. For each sample, a distinct increase in temperature coefficient is observed at a certain temperature designated, $T_{g,ps}$, corresponding to the location of the glass transition. The $T_{g,ps}$ values for each sample are shown in Table (4-2). Interestingly, these values are systematically lower than the bulk $T_g$ values measured by DSC. A similar difference has been noted and discussed previously in a series of structurally distinct polycarbonates in Chapter 3. We note that, below $T_{g,ps}$, the o-Ps lifetimes for all four polystyrenes are
Table 4-1. The temperature dependence of $l_1$, $l_2$, $l_3$, $\tau_2$ and $\tau_3$ for the polystyrene of highest $M_w$ (400,000) with $\tau_f$ fixed at 125 ps

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>$l_1$(%)±0.49</th>
<th>$l_2$(%)±0.42</th>
<th>$l_3$(%)±0.16</th>
<th>$\tau_2$(ns)±0.004</th>
<th>$\tau_3$(ns)±0.008</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>24.55</td>
<td>40.77</td>
<td>34.67</td>
<td>0.358</td>
<td>2.037</td>
</tr>
<tr>
<td>20</td>
<td>23.99</td>
<td>40.47</td>
<td>35.53</td>
<td>0.353</td>
<td>2.052</td>
</tr>
<tr>
<td>30</td>
<td>24.84</td>
<td>39.33</td>
<td>35.82</td>
<td>0.357</td>
<td>2.072</td>
</tr>
<tr>
<td>40</td>
<td>25.05</td>
<td>38.36</td>
<td>36.58</td>
<td>0.355</td>
<td>2.075</td>
</tr>
<tr>
<td>50</td>
<td>25.71</td>
<td>38.30</td>
<td>35.97</td>
<td>0.364</td>
<td>2.132</td>
</tr>
<tr>
<td>60</td>
<td>24.06</td>
<td>39.54</td>
<td>36.38</td>
<td>0.352</td>
<td>2.109</td>
</tr>
<tr>
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<td>24.37</td>
<td>39.23</td>
<td>36.39</td>
<td>0.353</td>
<td>2.148</td>
</tr>
<tr>
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<td>25.86</td>
<td>38.02</td>
<td>36.11</td>
<td>0.367</td>
<td>2.170</td>
</tr>
<tr>
<td>90</td>
<td>25.85</td>
<td>37.85</td>
<td>36.29</td>
<td>0.366</td>
<td>2.193</td>
</tr>
<tr>
<td>100</td>
<td>25.18</td>
<td>38.45</td>
<td>36.36</td>
<td>0.362</td>
<td>2.249</td>
</tr>
<tr>
<td>110</td>
<td>26.22</td>
<td>37.62</td>
<td>36.14</td>
<td>0.374</td>
<td>2.342</td>
</tr>
<tr>
<td>115</td>
<td>26.16</td>
<td>37.45</td>
<td>36.38</td>
<td>0.370</td>
<td>2.382</td>
</tr>
<tr>
<td>120</td>
<td>26.72</td>
<td>36.95</td>
<td>36.31</td>
<td>0.377</td>
<td>2.430</td>
</tr>
<tr>
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<td>26.31</td>
<td>37.18</td>
<td>36.50</td>
<td>0.373</td>
<td>2.465</td>
</tr>
<tr>
<td>130</td>
<td>26.26</td>
<td>36.91</td>
<td>36.82</td>
<td>0.368</td>
<td>2.482</td>
</tr>
</tbody>
</table>

Table 4-2. The molecular weight dependence of $T_g$ and $C$ constant

<table>
<thead>
<tr>
<th>$M_w \times 10^{4}$</th>
<th>$T_g$(°C)*</th>
<th>$T_g(DS)$(°C)</th>
<th>$T_g$(°C)**</th>
<th>$C \times 10^{3}$(Å⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.4</td>
<td>75</td>
<td>73</td>
<td>77</td>
<td>1.52</td>
</tr>
<tr>
<td>0.92</td>
<td>90</td>
<td>75</td>
<td>87</td>
<td>1.55</td>
</tr>
<tr>
<td>2.5</td>
<td>96</td>
<td>91</td>
<td>92</td>
<td>1.61</td>
</tr>
<tr>
<td>40</td>
<td>102</td>
<td>95</td>
<td>94</td>
<td>1.67</td>
</tr>
</tbody>
</table>

* Determined by DSC. ** Calculated from Equation (4-3)¹⁹
Figure 4-1. The o-Ps lifetimes and the corresponding average hole volumes, as a function of temperature for polystyrenes of narrow polydispersities with the indicated weight-average molecular weights.
numerically very similar at the same temperature, but differ substantially above $T_{g,ps}$. It is pertinent to note here that several previous positron lifetime studies of polystyrene have been described in the literature\textsuperscript{11, 12, 13, 14, 15, 16, 17}. Our $I_3$ and $\tau_3$ values are in good numerical agreement with these studies, both in the glass and in the melt. Of particular interest is the investigation of West et al\textsuperscript{11}, who measured $I_3$ and $\tau_3$ for a series of polystyrenes of differing molecular weights at room temperature. These authors found that $\tau_3$ remains essentially constant as $M$ decreases until $M \sim 1000$, when the glass transition occurs at room temperature. At lower $M$, $\tau_3$ increases, reflecting the further decrease in $T_g$. Our observations provide a more comprehensive demonstration of the sensitivity of the o-Ps lifetime to the free volume contributions, attributed to the presence of chain ends in these low-molecular weight polystyrenes.

\textsuperscript{11}D. H. D. West, V. J. McBrierty, F. G. Delaney, \textit{Appl. Phys.}, 7, 171 (1975)


\textsuperscript{17}J. -E. Kluin, F. Faupel, \textit{Material Sci. Forum}, 105-110, 1613 (1992)
We further point out that our $\tau_3$ data for the highest molecular weight, which falls in the asymptotic regime where $T_g$ becomes independent of $M$, are essentially superimposable on previous data for high molecular weight polystyrenes$^{11-17}$.

The average free volume hole sizes, $\langle \nu(\tau_3) \rangle$ were calculated from Equation (2-20) and (2-21), and are depicted on the right vertical axis of Figure (4-1). Comparing the temperature dependence of the free volume hole sizes for different samples above $T_{g,ps}$, we find that the molecular chain length does not affect the temperature coefficient $(\partial \langle \nu(\tau_3) \rangle / \partial T)_M$ but does strongly influence the absolute magnitude of $\langle \nu(\tau_3) \rangle$ at a given temperature in the liquid state, viz. the shorter the chain, the larger is $\langle \nu(\tau_3) \rangle$. This result is consistent with the viewpoint that polymers with shorter chains have larger average free volumes due to the contribution from the chain ends. Below $T_{g,ps}$, there are much smaller variations in the free volume sizes among the different specimens. Within experimental error, there appears to be a slight tendency for the polystyrene with shorter chain length to have larger holes at a given temperature. For each polymer, the average hole volume at $T_g$ is essentially constant, $\langle \nu(\tau_3) \rangle \approx 115 \, \text{Å}^3$. This corresponds to an effective spherical hole radius of $\sim 3 \, \text{Å}$.

The temperature dependence of the relative intensities of ortho-positronium annihilation ($I_3$) are presented in Figure (4-2). While our use of $I_3$ in Equation (2-23) assumes a proportionality to the number density of free volume holes, our recent computer simulation studies (to be discussed in Chapter 5) indicate that the experimental $I_3$ may underestimate the contribution of small holes, whose $\tau_3$ values may be
Figure 4-2. The o-Ps intensities as a function of temperature for polystyrenes of narrow polydispersities with the indicated weight-average molecular weights.
comparable to $r_2$. To illustrate this phenomenon, we give a comparison of $I_2$ and $I_3$ for the polystyrene of highest $M_w$ (400,000) in Figure (4-3). At low temperatures, there is a significant increase in $I_2$ which accompanies the sharp decrease in $I_3$, whereas $I_1$ shows no such change. This could reflect an increase in numbers of small holes at low temperature. Also, however, the value of $I_3$ in the glass can be influenced by chemical effects due to prolonged exposure to $e^+$, as described by Welander and Maurer\textsuperscript{18} which could further obscure the relationship to the free volume hole density. Bearing in mind these considerations, the $I_3$ values suggest that the change of hole density is insignificant except, perhaps, at very low temperatures ($T \leq 50^\circ C$ ). Comparing $I_3$ vs. temperature curves for the different samples suggests that the polystyrenes with shorter chains contain either more free volume holes or a larger proportion of the bigger holes. Interestingly, the hole density does not show any significant change at $T_{g,ps}$.

*Correlation Between PAL Measurement And The Statistical Mechanical Theory of Sinha and Somcynsky*

Next we evaluate the theoretical free volume fraction from the SS theory, requiring the volume-temperature relations of the polystyrene fractions. Here, we have made use of extensive earlier measurements by Ueberreiter and Kanig\textsuperscript{19}. These concerned degrees of polymerization


\textsuperscript{19}K. Ueberreiter, G. Kanig, Z. Naturforschg. 6a, 551 (1951)
Figure 4-3. Comparison of the p-Ps, free $e^+$, and o-Ps intensities, $I_1$, $I_2$ and $I_3$, respectively, for the polystyrene of highest $M_w$ (400,000)
ranging from unity to about 900 for fractions of thermally-polymerized samples. Moreover the authors provided convenient expressions for the molar mass and temperature dependencies of the volume in both the melt and the glassy states, and the mass dependence of the glass transition temperature. The pertinent equations are 19:

\[ V' = (5.50 + 339 / M) \times 10^{-4} T + 0.7674 \quad T > T_g \quad (4-1) \]

\[ V = (1.84 + 224 / M) \times 10^{-4} T + (3.66 + 115 / M) \times 10^{-4} T_g + 0.7674 \quad T < T_g \quad (4-2) \]

with

\[ T_g = \frac{1}{(2.720 \times 10^{-3} + 0.540 / M)} \quad (4-3) \]

and \( V' \) denoting the specific volume. Note that the \( T_g-M \) relation of Ueberreiter and Kanig 19 is different from the currently-accepted experimental relation, c.f. Reding et al 19. We list in Table (4-2) the \( T_g \)'s calculated from Equation (4-3) as well as our DSC values which agree with the later more accurate relation. The combination of Equations (4-1) - (4-3) with the formalism of the SS theory 7, and using procedures described previously 8, 9, then yields the free volume fraction \( h_{th} \).

From \( l_3 \) and \( r_3 \), using Equations (2-20) and (2-23), we then obtained \( h_{ps}/C' \). Selecting a reference point at temperatures near \( T_{g,ps} + 10 \) °C for each polystyrene sample, and comparing the values of \( h_{ps} \) and \( h_{th} \),
we determine the constants $C'$ for each polystyrene (see Table (4-2)). These results show a small systematic increase in $C'$ with increasing molecular weight, but this is within the range of experimental errors. The temperature dependencies of $h_{ps}$ and $h_{th}$ are exhibited for all four polystyrene samples in Figure (4-4), which clearly demonstrates the strong $M$-dependence of $h_{ps}$ and $h_{th}$ in the melt. In the glass there is a considerable reduction in the variation with molar mass. There appears to be a weak residual $M$-dependence in both $h_{ps}$ and $h_{th}$. However, in the former, the differences are comparable to the experimental errors, and furthermore reflect an $M$-dependence of the calibration constant $C'$ (see Table (4-2)). The variation in $h_{th}$ depends on two opposing contributions (see Equations (4-2) and (4-3)), one a chain-end effect and the other the $T_g$-dependent term.

In Figure (4-5) the temperature dependencies of $h_{ps}$ and $h_{th}$ are compared individually for each sample. We see that, for all samples, the positron results agree very well with the theoretical values at temperatures above $T_g$, i.e. in the liquid state. However, systematic deviations between the two sets of values are clearly evident below $T_g$, $h_{ps}$ falling increasingly below $h_{th}$ with decreasing temperature. A similar discrepancy was observed in earlier studies on polyvinylacetate and polycarbonate. As indicated by the broken lines, the discrepancy can be reduced, but not entirely removed by rescaling $h_{th}$ to a lower $T_g$. This is equivalent to proposing that $h_{ps}$ is sensitive to larger holes which have a lower $T_g$ but the same thermal expansion coefficient in the melt and glass. Evidently, from Figure (4-5), $dh_{ps}/dT > dh_{th}/dT$ in the glass for all four samples. The
Figure 4-4. Superposition of the temperature dependencies of (a) $h_{ps}$ and (b) $h_{th}$ for polystyrenes of different molar masses.
Figure 4-5. Comparison of the theoretical free volume fraction $h_{th}$ with the calculated free volume fraction $h_{ps}$ from o-Ps annihilation. The broken lines indicate that rescaling $h_{th}$ to lower $T_g$ does not produce agreement with the experimental $h_{ps}$.
origin of this effect is not clear, but several contributions can be proposed.

One possibility arises because of differences in the thermal histories involved in the o-Ps and P-V-T measurements. Specifically, each positron lifetime measurement involves a rapid quench at \( \sim 5^\circ/min \) from the melt to the measurement temperature followed by an annealing period of 20 - 30 mins and a measurement time of \( \sim 1 \) hour. In contrast, determinations of the bulk volume, from which \( h_{th} \) is computed, were conducted via sequential small temperature decrements, and following an annealing period at each temperature of \( \sim 30 \) mins to several hours. With increasing quench rate, one expects a more rapid relaxation to the equilibrium volume\(^{20,21}\). However, at lower temperature, the amount of annealing in the volume for a specified annealing time will be smaller. We have directly compared the o-Ps lifetime parameters \( l_3 \) and \( r_3 \) in high molecular weight polystyrene at room temperature following rapid and slow cooling histories, the latter comparable to that utilized in the quenched specimen. The results do not support differences in thermal treatment as the source of the discrepancy between \( h_{ps} \) and \( h_{th} \).

Alternatively, based on Monte Carlo simulations of the influence of a distribution of hole sizes on the o-Ps lifetime spectrum, it has been recently suggested\(^{22}\) that the deviations between \( h_{ps} \) and \( h_{th} \) may be partly


due to a distortion of the equilibrium free volume distribution in the glassy state. Specifically, on cooling into the glass, larger holes, which are emphasized in the o-Ps intensity, maintain their equilibrium character longer than small holes, i.e. their relative contribution continues to decrease below $T_g$. Finally, we point out that, necessarily, even with a rapid quench, the exposure of glassy polymer specimens to $\text{e}^+$ radiation is longer at lower temperatures. This could lead to anomalous decreases in $I_3$ and hence in $h_{ps}$ relative to $h_{th}$, as first reported by Welander and Maurer\textsuperscript{18}.

To gain further insight into the discrepancy between o-Ps and thermodynamic free volume quantities in the glass, it is useful to consider that we have assigned to the $h$ function the role of an (excess) free volume quantity. Are there other expressions of free volume which may allow us to establish connections in both melt and glass between the o-Ps cavity volumes and a measure of free volume, obtained from thermal expansion data? Relevant to this question we recall that the hole theory leads to the following expression for $h$ as a function of temperature\textsuperscript{23} valid for the equilibrium melt at atmospheric pressure:

$$h = [V' - K(T / T^*)V'^*] / V$$  \hspace{1cm} (4-4)

Here $V^*$ and $T^*$ are scaling parameters. The most accurately-determined values for polystyrene are\textsuperscript{24} $V^* = 0.9626 \text{ cm}^3/\text{g}$ and $T^* = 12781 \text{ K}$, or\textsuperscript{25}

\textsuperscript{23}R. Simha, \textit{Macromolecules}, 10, 1025 (1977)
\( l^* = 0.9634 \, cm^3/g, \quad T^* = 12840 \, K. \) Both sets were derived from the complete \( P-V-T \) surfaces up to pressures of 2000 \( bar \) for high molar masses. The small differences between each set are essentially irrelevant. The quantity \( K \) is a very slowly varying function of temperature. Over the experimental range of less than 50\(^\circ\) in the melt the argument of \( K \) varies by about \( 3.9 \times 10^{-3} \). Table II in Ref.26 indicates a variation of \( K \) from 0.954 to 0.955, that is \( K \) is practically constant. Thus \( h \) in Equation (4-4) may indeed be interpreted in the melt as a free volume quantity with an effectively excluded volume of \( KL^* \approx 0.9190 \, cm^3/g. \) We note that this is approximately equal to \( 1.38 \, l_w^* \), with \( l_w^* \), the Bondi van der Waals volume, since \( l^* \approx 1.45 \, l_w^* \).

Since we have seen that this \( h \)-function is closely related to the positron free volume quantity, it appears that \( KL^* \) may be also viewed as a positronium excluded volume at least above \( T_g \). In the glassy state, the approach has been to extract the \( h \)-function from the experimental \( P-V-T \) surface\(^8\). This \( h \) does not satisfy Equation (4-4). If \( h \), so computed, is still to be viewed as a simple free volume quantity, then we must formally allow \( K \) to become a more strongly varying function of \( T \), increasing with \( T \) for \( T < T_g \).

Coming now from the other side, consider the o-Ps free volume

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26R. Simha, P. S. Wilson, Macromolecules, 6, 908 (1973)

fraction $h_{ps}$ from Equation (4-4) and assume that this may be written in terms of an excluded volume $V_s$ as

$$h_{ps} = C'I_3 <V_f> = (V' - V_s) / V'$$

(4-5)

The numerical evaluation of the $V_s$ and $C'$ parameters, using 2 data points, selected at different temperature in the melt, allows us to show a test of Equation (4-5) in Figure (4-6). Clearly Equation (4-5) is very consistent with the experimental data for all four polymers in melt and glass. Table (4-3) shows the numerical values of the constants $C'$ and $V_s$, employed in Figure (4-6). The results for $V_s$ are close to the theoretical value of 0.919, for large molecular weights (see above). This reflects the good agreement between the predictions of the SS theory, the positron measurements in the melt and the free volume expression Equation (4-5).

### 4.4 CONCLUSIONS

Positron annihilation lifetime measurements are reported for four monodisperse polystyrenes with molar mass $M = 4,000; 9,200; 25,000;$ and 400,000. The temperature dependencies of ortho-positronium (o-Ps) lifetime ($\tau_3$) and intensity ($I_3$) were measured from 5°C to $T_g + 30°C$ for each sample. From these data, the free volume hole size, $<\nu_f(\tau_3)>$, and fractional free volume $h_{ps} = C'I_3 <\nu_f(\tau_3)>$ were calculated. The temperature dependencies of $\tau_3$, $<\nu_f(\tau_3)>$ and $h_{ps}$ show a discrete change in slope at an effective glass transition temperature, $T_g, ps$, which is measurably below the conventional bulk $T_g$. This suggests that $\tau_3$ is
Figure 4-6. The o-Ps free volume fraction is compared with that computed from Equation (4-5), as a function of temperature.
Table 4-3. The molecular weight dependence of Parameters $C$ and $V_{S}$ in Equation (4-5)

<table>
<thead>
<tr>
<th>$M_w \times 10^4$</th>
<th>$C' \times 10^3$ (Å$^{-3}$)</th>
<th>$V_{S}$ (cc/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.4</td>
<td>1.54</td>
<td>0.896</td>
</tr>
<tr>
<td>0.92</td>
<td>1.49</td>
<td>0.901</td>
</tr>
<tr>
<td>2.5</td>
<td>1.58</td>
<td>0.902</td>
</tr>
<tr>
<td>40</td>
<td>1.70</td>
<td>0.900</td>
</tr>
</tbody>
</table>
sensitive to large holes which retain their liquid-like mobility in the glassy state. The end group contributions to free volume in these polystyrene samples are clearly evident in the o-Ps annihilation results. The molecular chain length affects not only the glass transition temperature, $T_{g,ps}$, but also the o-Ps intensity and lifetime and the associated cavity size. As expected, the polystyrene with longer molecular chain length has higher $T_{g,ps}$ and smaller average cavity sizes in the melt.

The SS theory has been compared with the o-Ps results, and good agreement is found between $h_{ih}$ and $h_{ps}$ in the liquid state. In the glassy state, a systematic deviation between $h_{ps}$ and $h_{ih}$ is observed, $h_{ps}$ falling increasingly below $h_{ih}$ as temperature decreases. Possible reasons for this discrepancy have been discussed. Whereas $h_{ps}$ and $h_{ih}$ depend strongly on $M$ in the melt, each are essentially independent of $M$ in the glass. A free volume quantity, computed from the bulk volume, which is in good numerical agreement with the Simha-Somcynsky $h$-function in the melt, gives improved agreement with $h_{ps}$ in the glassy state.
Chapter 5

Computer Simulation Studies of Positron Lifetime Spectrum: Influence of Free Volume Hole Size Distribution

5.1 BACKGROUND

The formation of Positronium\(^1\) and interaction\(^2\) between positronium and its surrounding medium in polymer materials complicated the application of positron annihilation method in molecular solids. It is clear that positroniums are mainly localized at open spaces present in the molecular structure, and the pick-off annihilation rate of ortho-positronium is determined by the overlap with the surrounding molecules. However, there are many open questions on the formation and localization of positroniums in molecular solids, as well as the interaction between positronium and molecular chain.

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Experimentally, the degree of accuracy and reliability of measurement result from the positron annihilation lifetime method are largely dependent on the time resolution function of spectroscopy and correct assumption of decay components in the matter. In our previous investigation on polycarbonates, polystyrenes and other polymers, we have observed certain anomalies in computer-fitting of data from positron annihilation lifetime spectra. The fitted lifetime for p-Ps is always longer than the theoretical value of 125 ps; the corresponding decay intensity $I_1$ is much bigger than the theoretical one, i.e., one third of o-Ps decay intensity $I_3$; and there is a systematic deviation among fitted o-Ps lifetimes on the same sample but measured with different spectrometers, to cite a few examples.

A further complication has been developed as a result of recent positron lifetime studies. These studies, involving free volume Monte Carlo simulations in bisphenol-A polycarbonate $^3$, have suggested the presence of multiple o-Ps mean lifetimes originating from a distribution of hole sizes. If this is correct, then o-Ps annihilation in such polymers, must be described by an apparent lifetime $t_{3,app}$, which is a mean value averaged over all o-Ps components, with corresponding intensity $I_{3,app}$.

These points suggest to us that some reported ortho-positronium (o-Ps) lifetimes and intensities in the polymers could be artifacts of the computer fitting procedure. In order to evaluate this hypothesis, we have developed a computer simulation of experimental data, which can then be

used to test the accuracy of the fitting program and the effect of system time resolution on fitting results. In this work, we use bisphenol-A polycarbonate as an example to generate a series of positron lifetime spectra containing $\tau_3$ distributions which are the result of the above mentioned Monte Carlo free volume simulations. We will specify consequences in results of the conventional spectra fitting procedure.

The input to the simulation consists of the lifetimes and intensities of any number of positron populations (including para-positronium, ortho-positronium, and free positron decays), plus the spectrometer resolution function, a contribution from annihilation in the positron source, and random background. The simulation uses the computer's random number generator to make the output spectrum resemble an actual experimental curve. The output spectrum is then used as input to the conventional fitting program PATFIT-88, which determines the best-fitting values of lifetime and intensity for three positron lifetime components.

5.2 COMPUTER SIMULATIONS

If the $\alpha$-Ps lifetime in a polymer does indeed consist of multiple exponential components with various mean lifetimes, finding the mean lifetime and intensity of each component becomes a serious problem. With an experimental curve involving possibly dozens of variable parameters, the best fit to a presumed theoretical curve is highly suspect. The best that one can hope for is a situation in which the $\alpha$-Ps components

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are all considerably longer-lived than the para-Ps or free-positron components. In such a case, it can be possible to find the best fit to a curve that consists of only four distinguishable components, which are: (1) para-Ps, (2) free positrons, (3) ortho-Ps, (4) positrons annihilated in the source material.

An important aspect of positron experiments in polymers is the influence of hole size distributions and hence of possible multiple o-Ps lifetimes on the results of data fitting procedures\textsuperscript{3, 5, 6}. In order to investigate possible consequences, we developed a computer program to simulate positron decay in molecular materials. Events, which are generated randomly, are accumulated to spectra of $1.4 \times 10^6$ counts. In addition to any number $i$ of o-Ps components ($\tau_{3i}$ and corresponding $l_{3i}$), the p-Ps ($\tau_1 = 125$ ps with $l_1 = l_3 / 3$) and free positron decays ($\tau_2 = 450$-ps with $l_2 = 1 - l_1 - l_3$) are input parameters for each simulation. To ensure conformity with our experiments, a two-component source term ($0.565$ ns with 1.5%, $0.188$ ns with 7.5%) as well as an average statistical background of 60 counts per channel are included. The finite time resolution of 260 ps FWHM (the Full Width at Half Maximum) of the experiment was synthesized by a convolution of the spectra with a corresponding Gaussian function.

In order to generate distributions of o-Ps lifetimes for the simulation procedure, we use results of the recent Monte Carlo simulations for


\textsuperscript{6}See Chapters 3, 4
bisphenol-A polycarbonate (\(T_g = 143.4^\circ C\)) (see reference 3 for details). The equation-of-state behavior of the amorphous polymer was represented by a partly-filled, disordered lattice model with the temperature dependent free volume fraction \(h(T)\) as a central quantity. Using experimental \(P17\)-data on bisphenol-A polycarbonate\(^7\), \(h(T)\) has been calculated to be\(^3\)

\[
h(T) = 0.0985 + 4.88 \times 10^{-4}(T - 416.5) \\
\quad \text{for } T_g < T < 500K \tag{5-1}
\]

and

\[
h(T) = 0.0985 + 1.30 \times 10^{-4}(T - 416.5) \\
\quad \text{for } 300K < T < T_g \tag{5-2}
\]

in the melt and in the glass, respectively. Therefore, \(h(T_g)\) is approximately 0.1. With these \(h(T)\) values, Monte Carlo simulations (in which free volume in the polymer was computed by randomly filling a fcc-lattice with coordination number 12) generated a connection between the degree of occupancy \(y = 1 - h\) and hole size distributions in units of the single-hole volume \(v_f\). The volume fraction of holes \(p_i\) with cluster size \(iv_f\) could be fitted as a function of \(y\) by the expression\(^3\)

\[
p_i = p_n \exp\left[-(i / l(y))^\beta(y)\right] \quad \text{for } 0.8 \leq y \leq 0.99, \tag{5-3}
\]

\(^7\)P. Zoller, *J. Polymer Sci.: Polymer Physics*, 20, 1453 (1982)
where the polynomial functions of \( y \), \( l(y) \) and \( \beta(y) \) are calculated to be

\[
l(y) = 12.347 - 12.035y
\]  \hspace{1cm} (5-4)

\[
\beta(y) = 0.4088 - 2.5242y + 3.1156y^2
\]  \hspace{1cm} (5-5)

and \( p_i \) is a normalization factor, so that \( \sum_i p_i = 1 \).

With the given volume fraction in reference 3, the number fraction of the holes of size \( i \) can be calculated as

\[
n_i = \left( \frac{p_i}{i} \right) / \sum_i \left( \frac{p_i}{i} \right)
\]  \hspace{1cm} (5-6)

and the number-average hole size \( \langle v_f \rangle \) is

\[
\langle v_f \rangle = \sum_i n_i v_i = \sum_i p_i / \sum_i \left( \frac{p_i}{i} \right)
\]  \hspace{1cm} (5-7)

Therefore, the multiple o-Ps spectrum can be described by

\[
n_3(t) = \sum_i q_{3i} \exp\left(-t / \tau_{3i}\right)
\]  \hspace{1cm} (5-8)

The constants \( q_{3i} \) are related to the number fractions \( n_i \) by

\[
n_i = q_{3i} \tau_{3i} / \sum_i q_{3i} \tau_{3i}
\]  \hspace{1cm} (5-9)
where $t$ is the lifetime (responding channel number) and $n_3(t)dt$ the corresponding number density of annihilation events with lifetimes between $t$ and $t + dt$. The dependence of $\tau_{3i}$ on $v_i$ is given by Equation (2-20).

In the analysis of positron annihilation lifetime spectra, the multiple o-Ps decay is fitted by a single exponential function. As shown in the appendix at the end of this chapter, if we introduce the apparent o-Ps mean lifetime $\tau_{3,\text{app}}$ as the fitted value of the long-lived components, we obtain

$$\tau_{3,\text{app}} \approx \sum n_i \tau_{3i} \tag{5-10}$$

which is simply the number averaged lifetime $<\tau_3>$, and can be calculated with Equations (2-20) and (5-7) from the input parameters of the simulation.

For the multiple o-Ps component simulation we must define the lifetime distribution for each particular value of $h$. Hole sizes are taken into account up to $\sum p_i = 0.99$. In order to generate absolute $\tau_{3i}$ and $I_{3i}$ values, $v_I$ as well as $I_3(h)$ have to be known. Adjusting fitting results to measurements at $T_g$, we obtain $v_I = 65 \, \text{Å}^3$ (equal to $\tau_{3I} = 1.64 \, \text{ns}$) and $I_3(0.1) = 43\%$, respectively. While the model parameter $v_I$ is constant, $I_3(h)$ is given by Equation (2-23). We use these values as input parameters for all following simulations. Spectra are generated for $7.5\% < h < 12.5\%$ in steps of $0.25\%$ corresponding to a temperature range between $-40^\circ C$ and $200^\circ C$. 
5.3 RESULTS AND DISCUSSION

Subsequently, the programs RESOLUTION of PATFIT-88⁴ are employed to analyze simulated spectra. First, spectra were fitted in a free 3-component analysis. We found very large deviations in lifetimes as well as in intensities, these are dependent on \( h(T) \) i.e. on the width of the \( \tau_3 \) distribution. As in most positron experiments on polymers⁸, ⁹, the apparent values \( \tau_{1,\text{app}}, \tau_{2,\text{app}} \) and \( l_{1,\text{app}} \) were significantly higher than expected.

To provide a more appropriate test, we fitted the same simulated spectra with the p-Ps lifetime constrained to the theoretical value of 125 ps. The results are shown in Figures (5-1) and (5-2). The values of \( l_{1,\text{app}}, \tau_{2,\text{app}} \) and \( l_{2,\text{app}} \) are much closer to the input values than for the free 3-component. Also, as shown in Figure (5-2a), \( \tau_{3,\text{app}} \) matches nearly perfectly with \( \langle \tau_3 \rangle \). In the analysis of experimental positron lifetime spectra in Chapter 3 and 4, we have already applied this result. Unfortunately, however, \( l_{3,\text{app}} \) still departs strongly from the input value \( l_3 \), as seen in Figure (5-2b). The presence of a \( \tau_3 \) distribution appears to have a substantial effect on the fitted value \( l_{3,\text{app}} \). This can result from the overlap of the shorter o-Ps lifetimes with the shorter-lived components \( \tau_1 \) and \( \tau_2 \) when the computer fitting is done, causing the fitted values of \( l_1 \) and \( l_2 \) to be higher than their actual values, and thus \( l_{3,\text{app}} \) to be too small.

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Figure 5-1. Comparison of p-Ps and free positron annihilation fitting results, evaluated under the constraint $\tau_1 = 125\,\text{ps}$, with input values of the simulation: a) lifetimes $\tau_1$ and $\tau_2$, b) intensities $I_1$ and $I_2$. 
Figure 5-2. Analysis under constraint $\tau_l = 125 \mu s$: comparison of fitting results with average input values for the multiple o-Ps decay. a) lifetimes and b) intensities.
The same tendency was found in all positron annihilation lifetime measurements, in which, the fitted values of p-Ps decay intensity were always much bigger than the theoretical values of one third of o-Ps decay intensity. If this is true, then changes in the time resolution of the spectrometer should affect the fitted values.

In order to check the influence of the time resolution of the spectrometer on the fitted results, we generated a set of spectra which all contain the same hole size distribution ( \( h = 10\% \) ), but are convoluted with different resolution functions of FWHM between 160 \( ps \) and 340 \( ps \). Results of a free 3-component procedure are depicted in Figures (5-3) and (5-4). All values are found to be dependent on the resolution. It is highly significant that observed deviations from the input values increase drastically if FWHM exceeds 280 \( ps \). In the literature, one finds positron experiments with quite different time resolutions (often larger than 300 \( ps \) FWHM) applied to polymers. This may explain certain numerical inconsistencies when comparing results on a particular material obtained with different spectrometers. We need to confirm this important result experimentally. Therefore, spectrometers with different time resolutions have been designed by using different combination of CsF and BaF\(_2\) single crystals with different size and shape as \( \gamma \)-ray scintillators. Using each set-up, we have measured a well aged BPA-polycarbonate sample at room temperature (the experimental procedure is the same as described in Chapter 3). In agreement with our simulations, the results, which are also depicted in Figures (5-3) and (5-4), depend significantly on the precision of the equipment, and all analyzed values show the predicted tendencies.
Figure 5-3. Results of free 3-component analysis as a function of FWHM of time resolution function: a) lifetimes $\tau_1$ and $\tau_2$, b) intensities $I_1$ and $I_2$. Filled symbols depict experimental results.
Figure 5-4. Apparent o-Ps a) lifetimes $\tau_{3,app}$ and b) intensities $I_{3,app}$ as a function of FWHM of time resolution function. Filled symbols depict experimental results.
5.4 Conclusions

We developed a computer simulation of positron annihilation in Bisphenol-A polycarbonate using a random-number generator. The influence of hole size distributions on the conventional spectroscopic fitting procedures was investigated. As found in most positron experiments on polymers, fitted p-Ps lifetime parameters $\tau_{l.app}$ and $l_{1.app}$ showed significantly higher values than expected. Furthermore, the analyzed o-Ps lifetime $\tau_{3.app}$ with $l_{3.app}$ deviated significantly from the input $<\tau_3>$ and $l_3$. In a second analysis, the fitting procedure was constrained by fixing $\tau_l$ at the theoretical value of 125 ps, which is also the input value in simulated spectra. When this is done, $\tau_{3.app}$ matches nearly perfectly with the input $<\tau_3>$. $l_{3.app}$, however, still departs significantly from $l_3$, the deviation of $l_{1.app}$ and $l_{3.app}$ from the input values has the same tendency as that of fitted values of real lifetime spectra from theoretical values. Apparently, the distribution of o-Ps components resulted in artifacts of the fitting procedure, the magnitude of which are found to be strongly dependent on the FWHM of the system time resolution function. This result, which has then been confirmed experimentally by a set of lifetime measurements on the system with different FWHM, may explain certain numerical inconsistencies when comparing results on a particular material obtained with different spectrometers.

5.5 Appendix

Introducing the apparent o-Ps lifetime $\tau_{3.app}$, we can write
\[ n_i^u(t) = q_3^u \exp(-t / \tau_{3,app}). \] (5a-1)

Then the difference between the input multiple o-Ps spectrum and the fit is given by

\[ \Delta n = n_3 - n_3^u = \sum_i q_{3i} \exp(-t / \tau_{3i}) - q_3^u \exp(-t / \tau_{3,app}) \] (5a-2)

or

\[ \Delta^2 = \int_0^\infty \left[ \sum_i q_{3i} \exp(-t / \tau_{3i}) - q_3^u \exp(-t / \tau_{3,app}) \right]^2 dt \] (5a-3)

The best fit is determined by the minimization of \( \Delta^2 \), i.e.

\[ \frac{\partial \Delta^2}{\partial q_3^u} = 0 \] (5a-4)

and

\[ \frac{\partial \Delta^2}{\partial \tau_{3,app}} = 0 \] (5a-5)

It follows that

\[ q_3^u \tau_{3,app} - 2 \sum_i q_{3i} \frac{\tau_{3,app} \tau_{3i}}{\tau_{3i} + \tau_{3,app}} = 0 \] (5a-6)
as well as

\[ \frac{(q_3^o)^2}{2} - 2q_3^o \sum_i q_{3i} \left( \frac{\tau_{3i}}{r_{3i} + \tau_{3,app}} - \frac{\tau_{3,app}}{(r_{3i} + \tau_{3,app})^2} \right) = 0 \]  

\[ \text{(5a-7)} \]

Combination of Equations (5a-6) and (5a-7) yields

\[ \sum_i q_{3i} r_{3i} \frac{\tau_{3,app} - \tau_{3i}}{(r_{3i} + \tau_{3,app})^2} = 0 \]  

\[ \text{(5a-8)} \]

Since the intensity \( I_{3i} \) in the analysis program is defined as

\[ I_{3i} = q_{3i} \frac{r_{3i} I_3}{\sum_i q_{3i} r_{3i}} \]  

\[ \text{(5a-9)} \]

we obtain with \( I_3 / \sum_i q_{3i} r_{3i} = \text{const.} \)

\[ \sum_i I_{3i} \frac{\tau_{3,app} - \tau_{3i}}{(r_{3,app} + \tau_{3i})^2} = 0 \]  

\[ \text{(5a-10)} \]

and with \( \tau_{3i} = \tau_{3,app} + \Delta \tau_{3i} \)

\[ \sum_i I_{3i} \frac{\tau_{3,app} - \tau_{3i}}{(2 \tau_{3,app} + \Delta \tau_{3i})^2} = 0 \]  

\[ \text{(5a-11)} \]

Since \( \sum_i I_{3i} = I_3 \) and under the assumption \( \Delta \tau_{3i} \ll \tau_{3,app} \), a single
exponential fit of the multiple o-Ps annihilation yields a numerical value of \( \tau_{3,\text{app}} \) which can be approximated by the arithmetical average over all o-Ps components, i.e.

\[
\tau_{3,\text{app}} = \sum_i l_{3i} \tau_{3i} / l_3.
\]  

(5a-12)

Because \( n_i \) describes the number fraction of free volume holes of size \( v_i \), it follows that

\[
n_i = l_{3i} / l_3.
\]  

(5a-13)

Therefore, we identify \( \tau_{3,\text{app}} \) with the number average lifetime \( \langle \tau_3 \rangle \), which can be calculated with Equations (2-20) and (5-3) from the input parameters of the simulation.

\[
\langle \tau_3 \rangle = \sum_i n_i \tau_{3i}.
\]  

(5a-14)
Chapter 6

Positronium Localization in Macromolecule Substances

6.1 BACKGROUND

Positron annihilation provides a unique way of obtaining information about the internal structure of molecular materials. When a positron from a radioactive source reaches thermal energy in a very short time (the order of $1\text{ps}$) in molecular material, it may diffuse through the material as a free particle or capture an electron to form an atom of positronium. The free volume model, proposed and developed by Brandt, et al.\textsuperscript{1}, assumes that positronium is formed only in a free volume which is larger than a certain critical value. Unlike metals, molecular materials always contain a large fraction of imperfect sites, such as impurities, defects, voids grain boundaries, etc. Many of these sites serve as free volumes for positronium formation.

\textsuperscript{1}W. Brandt, S. Berko, and W. W. Walker, Phys. Rev. 120, 1289 (1960)
The positronium (Ps) atoms are favored to stay in low electron density areas in macromolecular substances, or in other words, localized in free-volume holes. This behavior is described as a self-trapping state of Ps, which is a bound state with an induced local potential.\(^2\)\(^3\) Thus the information about free volume hole size and density is carried out of the material through the annihilation \(\gamma\)-rays. A carefully established relation between \(\alpha\)-Ps lifetime and free-volume hole size is the basis for obtaining accurate information with positron annihilation lifetime techniques. Several models have been developed to interpret the Ps behavior in molecular liquids\(^4\), such as the "bubble" model\(^5\)\(^6\). For molecular solids, however, the question remains essentially unsolved. Because of the relative rigid structure of molecular solids, the Ps atom does not create additional spaces in glassy polymers, the bubble model is no longer valid.

A new challenge to the positron annihilation lifetime method is the distribution of free volume hole sizes in the polymer materials, which have been theoretically predicted by molecular dynamics and kinetic theory\(^7\).


Experimentally, a computer code called CONTIN\textsuperscript{8}, which uses a numerical Laplace inversion method, can fit the positron annihilation lifetime spectrum to a continuous distribution of intensities as a function of mean lifetime, and such a distribution of mean lifetime has been reported on numbers of polymers\textsuperscript{9}. However the so obtained free volume hole size distribution does not match that predicted by molecular dynamics and kinetic theory\textsuperscript{10}.

In agreement with the work of Gregory and Zhu\textsuperscript{8}, we find that it is difficult to separate discrete lifetime components when two of the lifetimes differ by less than a factor of two. We are not convinced that the lifetime distributions extracted from CONTIN can accurately reveal the distribution of hole sizes in polymers from our experience on computer simulated spectra, unless experimental resolution is greatly improved as well as counting efficiency. However the problem goes beyond experimental techniques to basic quantum mechanics.

Whether a hole size distribution can cause a distribution of ortho-positronium lifetimes depends on how the positronium atoms are localized in free volume holes. If each ortho-positronium atom remains in a single hole for the entire lifetime, its mean lifetime would reflect the hole size of


that particular hole. If it does not, then one can only determine average hole sizes rather than hole-size distributions.

In the following work, we first review the relation between o-Ps decay mean lifetime and free volume hole size, then take a close look on how closely a Ps atom is located in a free volume hole, by calculating the one-dimensional transmission probability of quantum barrier tunneling and three dimensional escaping probability of Ps atom from one hole to others.

6.2 Correlation Between o-Ps Lifetime and Free Volume Hole Size

The experimental correlation of o-Ps lifetime with molecular volume was reported by Eldrup et al. on solid pivalic acid, with pore radius by Nakanishi et al. on zeolites, with the total free volume by Kobayashi et al. on both molecular liquids and polymers, and with bubble radius by Ujihira et al. on several organic molecular liquids. The theoretical attempts were based on the bubble model and the polaron concept for molecular liquids.

For molecular solids, the result on the bubble model of liquids has


been borrowed. A very simple model\textsuperscript{11, 16, 17}, in which the positronium resides in a spherical potential well of radius $R_o$ having an infinite potential barrier with an electron layer in the region $R < r < R_o$, gives a connection between o-Ps lifetime $\tau_3$ and free volume hole size. Using this semiempirical approach, one can determine the absolute size of free volume holes from the following equation (see Chapter 2 for details):

$$\tau_3 = \frac{1}{\pi r_o^2 c \rho_o} \left[ 1 - \frac{R}{R_o} + \frac{1}{2\pi} \sin\left(\frac{2\pi R}{R_o}\right) \right]^{-1} \quad (6-1)$$

Instead of pursuing a calculation of $\rho_o$, the o-Ps annihilation rate in the electron cloud was assumed to be 2.0 $ns^{-1}$, i.e. $\pi r_o^2 c \rho_o = 2.0$ ($ns^{-1}$). With $R_o = R + \Delta R$, the value of $\Delta R$ was determined by fitting the Equation (6-1) to experimental $\tau_3$-values and free volume hole sizes obtained from other methods for molecular solids.

However, several problems remained unsolved from above model:

(i). To derive Equation (6-1), an infinite spherical potential was used to calculate the positronium wave function in free volume hole. Then, in order to have an overlap of positronium density and electron density, an electron cloud shell was placed inside of the infinite potential well without considering any effect on the positronium wave function.

(ii). As a fitting parameter, the thickness of the electron layer, $\Delta R$

\textsuperscript{16}S. J. Tao, J. Chem. Phys. 56, 5499, (1972)

is on the same order of, perhaps even bigger than, the potential well radius, and may differ from one material to another. The free volume radius \( R \) can change continuously to zero to satisfy the assumption that the annihilation rate of o-Ps in the electron layer is 2 per ns. The condition for a bound state of positronium is completely ignored.

(iii). So far as we know, there are no techniques other than positron annihilation lifetime spectroscopy capable to measure free volume hole size directly, therefore, we are lacking data on free volume hole sizes to determine the fitting parameter \( \Delta R \).

Strictly speaking, Equation (6-1) is an empirical equation which fits only the bubble model for molecular liquids, but for molecular solids, the bubble model is no longer valid, because of the relative rigidity of macromolecular chains.

Since the de Broglie wavelength of a thermalized positronium is much larger than the mean interatomic distance in most molecular solids, a Ps atom indeed interacts simultaneously with many atoms and such interaction can be simplified as the lattice potentials as shown earlier in Figure (2-6). To derive a quantitative relation between o-Ps lifetime and the free volume hole size in molecular solids, we further describe the lattice potentials as square well potentials. We consider a finite spherical potential well, illustrated in Figure (6-1), with potential barrier \( V_o \), and well radius \( R \), which is defined as the free volume hole radius. By neglecting the internal structure of positronium, i.e., treating positronium as a single particle, and by approximating the electron density as a constant \( \rho_o \) outside of potential wells, the pick-off annihilation rate of the
Figure 6-1. The finite spherical potential well with radius $R$ and height $V_o$. Also plotted is the schematic Ps wave function.
o-Ps can be represented as (see Equation (2-15)):

\[
\lambda = \pi r_o^2 c \rho_o \int_{V_o} \psi_{Ps}^* \psi_{Ps} d\mathbf{r}
\]  

(6-2)

where \( V_o \) is the volume excluding the wells, and \( \psi_{Ps} \) is the wave function for the center-of-mass motion of Ps atom in the wells.

The Schrödinger equation in the spherical polar coordinates for the Ps can be written as:

\[
\left[ -\frac{\hbar^2}{2m} \left( \frac{d^2}{dr^2} + \frac{2d}{r dr} \right) - \frac{l(l+1)}{r^2} + V(r) - E \right] \psi_{Ps} = 0
\]  

(6-3)

with

\[
V(r) = 0 \quad 0 < r < R \\
V(r) = V_o \quad r > R
\]

Let us define

\[
k = \sqrt{2mE / \hbar^2} \\
\alpha = \sqrt{2m(V_o - E) / \hbar^2} \\
\beta = \sqrt{2mV_o / \hbar^2}
\]

then we have

\[
k^2 + \alpha^2 = \beta^2
\]  

(6-4)
For a bound state, \((E - l^2)\) is negative. The solution for the ground state wave function is

\[
\psi_{p_s} = \frac{B \sin(kr)}{r}, \quad 0 < r < R
\]

\[
\psi_{p_s} = \frac{C e^{-\alpha r}}{r}, \quad r > R
\]

(6-5)

where \(B\) and \(C\) are constants, \(E\) is the kinetic energy of positronium. After applying the boundary condition, which requires both wave function \(\psi_{p_s}\) and its first derivative \(d\psi_{p_s}/dr\) to be continuous at \(r = R\), and the normalization of the wave function, which is \(\int_0^\infty |\psi_{p_s}|^2 \, dr = 1\), we obtain:

\[
B \sin(kR) = C e^{-\alpha R}
\]

(6-6)

\[
Bk \cos(kR) = -C \alpha e^{-\alpha R}
\]

(6-7)

and

\[
\frac{B^2}{4k} (2kR \sin(2kR)) + \frac{C^2}{2\alpha} e^{-2\alpha R} = \frac{1}{4\pi}
\]

(6-8)

From Equations (6-6) and (6-7), the positronium ground state energy can be determined by

---

\(^{18}\)It can be found in most Quantum Mechanics text book, as an example, see J. D. McGervey's "Introduction to Modern Physics". Academic Press, (1983)
\[ \cot(kR) = -\frac{\alpha}{k} = -\sqrt{\frac{\beta^2 - k^2}{k^2}} \]  \hspace{1cm} (6-9)

Figure (6-2) shows the graphical solution of the above equation. To have a bound state solution for positronium, we must have

\[ R > R_o = \frac{\pi}{2\beta} = \frac{\pi}{2} \sqrt{\frac{\hbar^2}{2m\lambda'}} \]  \hspace{1cm} (6-10)

The above condition sets a threshold, \( R_o \), of free volume hole size for the localization of positronium, i.e., the positronium can be localized only in these free volume holes with radii bigger than \( R_o \). This result is in agreement with our experimental data discussed earlier in Chapter 4 (Figure 4-2). The sharp decrease in o-Ps intensities at low temperature is evidence of probing such a threshold of positronium radius.

Combining Equations (6-6), (6-7) and (6-8), we have:

\[ \frac{C^2}{\alpha} e^{-2\alpha R} = \frac{1}{2\pi} \int \left[ 1 - kR \cot(kR) + \cot^2(kR) - kR \cot^3(kR) \right]^{-1} \]  \hspace{1cm} (6-11)

The o-Ps pick-off annihilation rate, therefore, can be obtained from Equations (6-2) and (6-11) as:

\[ \lambda = 4\pi^2 r_o^2 c \rho_o \int_R^{\infty} \frac{C^2 e^{-2\alpha r}}{r^2} r^2 dr = 2\pi^2 r_o^2 c \rho_o \frac{C^2}{\alpha} e^{-2\alpha R} \]

\[ = \pi \frac{r_o^2}{2} c \rho_o \left[ 1 - kR \cot(kR) + \cot^2(kR) - kR \cot^3(kR) \right]^{-1} \]
Figure 6-2. Graphs of $\cot(kR)$ with different $R$ values, and
$$\frac{\sqrt{\beta^2 - k^2}}{k^2}$$
Or in the form of the o-Ps lifetime as:

\[ \tau = \frac{1}{\pi r_0^2 c \rho_o} \left[ 1 - kR \cot(kR) + \cot^2(kR) - kR \cot^3(kR) \right] \quad (6-12) \]

The electron density in molecular bulk, \( \rho_o \), can be estimated as:

\[ \rho_o \sim \frac{1}{4} \frac{Zd}{M} N_A \quad (6-13) \]

where \( Z \) is the number of available electrons in one molecule, \( d \) the density of molecular solids, \( N_A \) the Avogadro's number, and \( M \) the molecular weight. The factor 1/4 is present because only one fourth of the total electron population can annihilate with the positron in Ps through singlet interaction. The binding energy of positronium in free volume holes, \( (V_o-E) \) is unknown for molecular solids, but should be on the same order as for molecular liquids\(^{14} \) in which it is about 1 eV.

With Equations (6-9) and (6-12), we have established a relation between o-Ps pick-off annihilation mean lifetime and free volume hole size. To make this relation more clear, we define

\[ \Omega = kR \]

\[ \tau^* = \frac{1}{\pi r_0^2 c \rho_o} \]

\[ R^* = \sqrt{\frac{\hbar^2}{2mV_o}} \]
The Equations (6-12) and (6-9) can be rewritten as

$$\tau = \tau^* (1 - \Omega \cot \Omega + \cot^2 \Omega - \Omega \cot^3 \Omega)$$

(6-14)

$$R = R^* \frac{\Omega}{\sin \Omega}$$

(6-15)

with the condition:

$$\pi/2 < \Omega < \pi$$

(6-16)

The scaled o-Ps lifetime, $\tau^*$, vs. the scaled free volume hole size, $V/V^* = (4\pi R^3/3)/(4\pi R^*^3/3)$, is plotted in Figure (6-3). The exact values of bulk electron density and positronium binding energy should be adjusted by fitting equations to known experimental results. After that, Equations (6-14) and (6-15) can serve as the working equations to correlate o-Ps annihilation lifetime to free volume hole size for molecular solids, and for molecular liquids as well.

Unfortunately, there are no appropriate experimental data on the free volume hole size available at this stage, except those calculated under the bubble model for molecular liquids\(^{14}\). The comparison of Equation (6-1) with Equations (6-14) and (6-15) can be made only qualitatively for the molecular solids in Figure (6-4), where, we set the scaling parameter $\tau^*$ to 0.5 ns, which is the mean lifetime of free positron, and the potential barrier $V_o$ to 1.4 $eV$, having two sets of equations agree in the region of interest (hole sizes around 200 Å\(^3\)).
Figure 6-3. The scaled o-Ps lifetime, $\tilde{\tau}^{*}$, vs. the scaled free volume hole size, $l/l^{*}$.

**Figure 6-4.** The comparison of the Equation (6-1) with the Equations (6-14) and (6-15). We set the scaling parameter $r^{*}$ to 0.5 ns, and the potential barrier $V_o$ to $1.4\, eV$. 
6.3 Localization of Positronium and Distribution of o-Ps Annihilation Lifetimes

Clearly we can use the value of a single component, $r_3$, to determine an average hole size, and then can observe how that average size changes with changes in pressure, temperature, or tensile stress, and this information has some practical value. But when we analyze the o-Ps component to obtain a distribution of o-Ps lifetime components, discrete as in POSITRONFIT or continuous as in CONTIN, we still do not know if we measured the true distribution of hole sizes. The question of whether the distribution of free volume hole sizes causes a distribution of o-Ps pick-off annihilation lifetimes depends on whether positronium is localized in free volume holes.

We consider two extreme cases. First, Ps is favored to stay in lower positive density areas, i.e. in free volume holes, but not in a particular hole. This means o-Ps samples a number of holes with different sizes. We assign $P_i$ as probability and $\lambda_i$ as pick-off annihilation rate of an o-Ps atom which stays in a hole with size $V_i$. The decay of the o-Ps can be presented as

$$dN \propto -\sum_i N_i \lambda_i dt = -N \sum_i P_i \lambda_i dt$$

so that

$$N = N_0 e^{-\sum_i P_i \lambda_i t} = N_0 e^{-\lambda t}$$

(6-17)
where \( N \) is the total number of o-Ps, \( N_i \) is the number of o-Ps in the holes with size \( I_i \) and \( \lambda = \sum_i P_i \lambda_i \). Then the decay can be presented as a single mean lifetime (\( \tau = 1/\lambda \)) exponential function.

Second, if a positronium atom is restricted to a particular hole in its entire lifetime after being thermalized, then the distribution of o-Ps lifetimes would be presented as

\[
dN = \sum_i dN_i
\]

(6-19)

and

\[
dN_i \propto -N_i \lambda_i dt
\]

(6-20)

Therefore

\[
N_i = N_o P_i e^{-\lambda_i t}
\]

(6-21)

and

\[
N = \sum_i N_i = N_o \sum_i P_i e^{-\lambda_i t}
\]

(6-22)

In this case, each hole with certain size gives an annihilation rate \( \lambda_i \), and the decay function would contain a distribution of o-Ps pick-off annihilation lifetimes.
In principle, if the o-Ps atom remains in a single hole after it is trapped, we could determine the hole size distribution by measuring the lifetime distribution, knowing the relation between o-Ps lifetime and free volume hole size. In the nonrelativistic approximation, a thermalized positronium atom with a diameter of 1.06 Å at room temperature 300 K has thermal energy

\[ E \sim \frac{3}{2} kT \sim 3.88 \times 10^{-2} \text{eV} \quad (6-23) \]

and momentum

\[ P = \sqrt{2mE} = \sqrt{3mkT} \quad (6-24) \]

where \( m \), the mass of Ps, equals twice the electron mass. The de Broglie wave length of such a Ps atom is

\[ L = \frac{\hbar}{P} = \frac{\hbar}{\sqrt{3mkT}} \sim 44 \text{Å} \quad (6-25) \]

The typical radius of free volume holes in polymer materials is about 4 Å, and the typical distance between free volume holes is about 10 Å based on a simple lattice model. (This would not be unusual if the free volume fraction were 5% or more.) Both these lengths are much shorter than de Broglie wave length.

The associated de Broglie wave frequency for such thermalized Ps atoms is
which is about $2 \times 10^4$ times the o-Ps annihilation rate \( \frac{1}{\tau_3} \sim 0.5 \times 10^9 \text{ sec}^{-1} \). The above numbers suggest that Ps is very likely to travel among free volume holes instead of staying in a particular hole before annihilating.

In previous reports\(^9\) of free volume hole size distributions measured by the positron annihilation lifetime method, it is assumed that, because of "the large Ps-binding energies with holes (in the order of 0.5 \( eV \))...the chance of the Ps escaping from a hole or diffusing to another before it annihilates is almost zero."\(^{19}\). But escape probability and diffusion rate cannot be analyzed without taking account of quantum mechanical barrier penetration. This is known to occur for hydrogen atoms in polymers, and for o-Ps with its smaller mass, in polymers with a typical free volume distribution, it can not be negligible. Let's examine this process with some typical numbers. Consider a hole of typical radius, 4 Å, and let its surface be 10 Å from the surface of another hole of any size. Although this is not a one-dimensional problem, we can estimate the probability of barrier penetration to the other hole by using the standard equation for the transmission probability \( T \) through a barrier\(^{20}\), and using the zero-point energy of the o-Ps atom (about 0.6 \( eV \) in a hole of this size) and the binding energy of 0.5 \( eV \) quoted above. The equation is

\[ \text{(6-26)} \]

---


\(^{20}\)For example, J. D. McGervey, "*Introduction to Modern Physics*", 2nd ed., 167 (1983)
\[ T = \left[ 1 + \frac{V_o^2 \sinh^2(\alpha a)}{4E(V_o - E)} \right]^{-1} \]  

(6-27)

where \( \alpha = \sqrt{2m(V_o - E)/\hbar^2} \).

In this case, \( a \) is the barrier width of 10 Å, \( m \) is the o-Ps mass, \( V_o \) is the barrier height (1.1 eV), \(( \text{the reason of using this number will be given later})\), \( E \) is the kinetic energy (0.6 eV), and \( V_o - E \) is therefore the binding energy of 0.5 eV. The resulting value of \( T \) is about \( 1.2 \times 10^{-4} \).

To find the probability of escape, we must now estimate the number of times that an o-Ps would strike this barrier during its lifetime of about 1 nanosecond, considering its kinetic energy of 0.6 eV. Setting \( mv^2/2 = 0.6 \) eV, with \( mc^2 = 1 \text{ MeV} \), we find that \( v \approx 3 \times 10^{15} \text{ Å/sec} \). Thus by this semiclassical computation\(^{21}\), o-Ps would take about \( 10^{-15} \) seconds to make a round trip across the hole and back, and hence will strike the barrier \( 10^6 \) times during its lifetime of one nanosecond. This would make the mean time for escaping the hole of order \( 10^{-2} \text{ ns} \), and its chance of remaining in the hole virtually zero.

Obviously this one-dimensional calculation cannot tell the whole story, but it does show that tunneling of o-Ps from one hole to another can happen and it cannot be overlooked.

The above result encourages us to make a further investigation in a three dimensional model on the escaping probability of Ps atom from one...

\(^{21}\)This computation follows the method used by Gamow and by Condon and Gurney in successfully deriving the half lives for alpha-particle decay of heavy elements. See, for example, Ref. 20, page 567.
hole to another. We use the same free volume model used in last section, which is a finite spherical potential well, illustrated in Figure (6-1), with potential barrier $V_o$, and well radius $R$. The positronium wave function was presented in Equation (6-6). Consider a cubic lattice, shown in Figure (6-5), consisting of free volumes with the same radius $R = 4 \text{ Å}$ and free volume fraction being 5%, then the distance from the center of one hole to the center of nearest hole (referred to as $d$ in the figure) is 17.5 Å. The probability of escape can be presented as:

$$P = \int_0^d |\psi_{Ps}|^2 dR$$  \hspace{1cm} (6-28)

where $v$ is the volume excluding the cube of edge $d$ shown in Figure (6-5). Since the wave function is spherically symmetric, the integral with a spherical border is much easier to deal with than one with a cubic border. We define $R'$ in the following equation:

$$\frac{4}{3} \pi R'^3 = d^3$$  \hspace{1cm} (6-29)

and

$$P' = \int_{R'}^{\infty} |\psi_{Ps}|^2 dR = \frac{2 \pi \alpha^2}{\lambda} e^{-2\alpha R'}$$  \hspace{1cm} (6-30)

Therefore, we have
Figure 6-5. Cubic lattice with hole on the lattice sites, $d$ is the distance between the center of one hole to the center of the nearest hole. $R'$ satisfies $4\pi R'^{3}/3 = d^{3}$. 
We set the free volume hole radius to a typical number, $R \approx 4$ Å, and the binding energy of Ps atom in the hole, $(V_o - E)$, to 0.5 $eV'$. From Equation (6-9), we obtain: $E = 0.63$ $eV'$, and then $V_o = 1.13$ $eV'$. Combining Equations (6-11) and (6-30), we have $P' = 1.6 \times 10^{-4}$. Therefore the escaping probability is bigger than $1.6 \times 10^{-4}$ which is even bigger than the transmission probability ($T = 1.2 \times 10^{-4}$) obtained from one dimensional barrier tunneling of Ps atoms.

With the same method used before, we obtain the mean time for escaping the hole of order $10^{-2}$ ns, and that means it is almost impossible for a Ps atom to stay in a specific hole for its entire lifetime. This result does not mean that all o-Ps atoms sample holes of all possible sizes; there still may be a distribution of mean lifetime in the o-Ps component due to variation in the Ps trapping probability as a function of hole size and some other factors. But there seems to be no justification for a one-to-one correlation of lifetime components with specific hole sizes.

### 6.4 CONCLUSION

Under the free volume model, we have used a finite spherical potential well to work out the relation between o-Ps annihilation mean lifetime and free volume hole size. Positronium as a probe has a threshold to sense free volume holes, i.e., it can probe the holes larger than certain values. The calculation of a one dimensional transmission probability and a three dimensional escaping probability show that the chance for a Ps
atom to remain in one particular hole for its entire lifetime is of the order 1%, i.e., each positronium can sample a number of holes of different sizes before annihilating with electron. The lifetime of o-Ps reflects an average effect of distribution of free volume hole size in polymer materials. Even if a reliable measurement of the o-Ps lifetime distribution has been obtained, there is no reason to believe that this distribution directly gives the hole-size distribution.
Chapter 7

Summary and Future Work

7.1 Summary

Positron annihilation lifetime spectroscopy is a very useful tool to probe the structure in terms of free volume in macromolecular materials. The mean lifetime of ortho-positronium reflects the size of free volume hole, and it is very sensitive to the changes of free volume caused by changes of the molecular structure, chain length, temperature, and the physical aging process.

From the time dependent measurements, we found the physical aging only reduces the intensity of positronium, the o-Ps lifetime remains essentially unchanged. However, the conclusion can not be made without considering the possible effect of the irradiation of positron source, which can reduce the intensity of positronium as the physical aging does, though no effect on o-Ps meant lifetime has been found.

The temperature dependence of o-Ps mean lifetime gives a clear look at the change of free volume hole size and glass transition, but
apparently, the so measured transition temperature is about 5-10° lower than that measured by Differential Scanning Calorimetry.

The free volume fraction measured by positron lifetime method agrees well with the one calculated from the Simha-Somcynsky theory in the melting state, but a systematic deviation between the experimental and theory is observed in the glassy state. Possible reasons for this have been discussed. A free volume quantity, computed from the bulk volume, which is in good numerical agreement with the Simha-Somcynsky free volume fraction in the melt, gives improved agreement with positron measurement result in both melting and glassy states.

The computer simulation studies showed the system time resolution plays a very important role in obtaining the accurate results, especially when there exists a distribution of o-Ps mean lifetimes. The measured intensity of positronium can be severely distorted when FWHM is bigger than 280 $\mu$s. This conclusion has been confirmed experimentally by a set of lifetime spectrometers with the different FWHM on the same specimen.

The localization of positronium in free volume holes was reviewed theoretically by means of the calculation of the barrier transmission probability and the escaping probability of positronium from one hole to the others, the results showed that it is unlikely for Ps atom to remain in one hole for its entire lifetime, therefore the one-to-one correlation of o-Ps lifetime components with specific hole sizes is untenable.
7.2 Future Work

- Improving system time resolution function and counting efficiency. The system time resolution function plays a very important role in getting the reliable results. Until the discovery of a new and better scintillator, using smaller BaF$_2$ single crystals can reduce FWHM, and by using multi-detectors, the loss of the counting efficiency can be retrieved.

- Four component fitting. The theoretical ratio of one to three between the intensity of p-Ps and o-Ps is seldom found experimentally in positron lifetime measurements; both a poor system time resolution function and too many decay components are blamed for this problem. With our current system (the FWHM can reach less than 180 ps with careful adjustment), it is possible to resolve this long standing problem by putting the radiation source on the sample directly to minimize the source correction term in the spectrum analysis, and fitting the spectrum to four decay components. A temperature dependent measurement is necessary for interpreting the fourth component.

- The correlation of o-Ps mean lifetime with the absolute free volume hole size. The current theory of the free volume and o-Ps lifetime in macromolecular materials is still far from complete. The proposed model, which gives a scaled relation between o-Ps mean lifetime and hole size, has to be implemented by comparing positron lifetime results with the results from other measurements and theories.
Chapter 1


2. C. D. Anderson, *Phys. Rev.* 43, 491 (1933); *Science* 76, 238 (1932)


**Chapter 2**


Chapter 3


Chapter 4


Chapter 5


Chapter 6


18. It can be found in most Quantum Mechanics text book, as an example, see J. D. McGervey's *"Introduction to Modern Physics"*, Academic Press, (1983)


20. For example, J. D. McGervey, *"Introduction to Modern Physics"*, 2nd ed., 167 (1983)
21. This computation follows the method used by Gamow and by Condon and Gurney in successfully deriving the half lives for alpha-particle decay of heavy elements. See, for example, Ref. 20, page 567.