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Positron annihilation spectroscopy as a probe of microscopic structure and physical aging in polymer

Yu, Minzi, Ph.D.

Case Western Reserve University, 1992
POSITRON ANNIHILATION SPECTROSCOPY
AS A PROBE OF MICROSCOPIC STRUCTURE
AND PHYSICAL AGING IN POLYMER

by

MINZI YU

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

Thesis Advisor: John D. McGervey

Department of Physics
CASE WESTERN RESERVE UNIVERSITY
MAY, 1992
CASE WESTERN RESERVE UNIVERSITY
GRADUATE STUDIES

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candidate for the Ph.D. degree.*

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(chairman)

Date 4/9/92

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POSITRON ANNIHILATION SPECTROSCOPY AS A PROBE OF
MICROSCOPIC STRUCTURE AND PHYSICAL AGING

IN POLYMER

Abstract

by

MINZI YU

Positron annihilation is studied as a characterization method for the properties of polymers. Previous studies indicate that the ortho-positronium lifetime $\tau_1$ and intensity $I_1$ is correlated to the free volume "hole" size and number density of holes in a polymer. Positron annihilation lifetime (PAL) studies in polymers measure the change in free volume, and they are sensitive to different physical environments. PAL studies of the temperature dependence of a bisphenol-A polycarbonate shows that the free volume increases with increasing temperature, and it also obtains the transition temperatures $T_g$ and $T_g'$ from the $\tau_1$ curve and the $I_1$ curve, respectively. The isothermal aging in polycarbonate shows that: $I_1$ decreases while $\tau_1$ remains
constant during a long-time annealing at a temperature far below $T_g$; and $I_1$ remains constant while $\tau_1$ goes through a "over shooting" in the first few hours after quenching and annealing at a temperature just below $T_g$. The free volume in polycarbonate increases (as a result of an increase in $\tau_1$) with applied tensile strain up to 4%, then levels off. Similarly, the free volume in polymethyl methacrylate (PMMA) decreases (as the result of $\tau_1$) with applied compressional strain also up to ~4% then levels off. A negative change in both $\tau_1$ and $I_1$ has been observed when polycarbonate is under 3% tensile strain and after release of strain.

A more advance technique of positron annihilation, PAL-momentum correlation which can give more detailed information about free volume structure in polymers, has also been studied and improved. Two 5-cm-diameter, 5-cm-long CsF scintillation detectors for lifetime measurement, and a 30-cm-diameter Anger camera whose y-analog pulse gives one-dimensional ACAR information, comprise a new experimental arrangement of PAL-momentum correlation system. Its triple-coincidence counting rate is about 2.5 per minute per microcurie of positron source and system time resolution is 260 ps and angular resolution is 3.5 mrad.
To:

Mommy and Dady
Acknowledgements

The author wishes to express her deepest appreciations to Professor John D. McGervey for his patient, supports and guidance throughout this work.

Special thanks give to Professor A. M. Jamieson, who gave me much instructive advice and help. I am also in debt to Professor R. Simha for his stimulating suggestions.

I am grateful to my lab mates: Mr. Zheng, Dr. Meyer, Dr. Kobayashi, Mr. Yu and Ms. Shang for their friendly environment, helpful discussion and assistance.

Finally, I would like to thank my family: my parents for their constant encouragement; Weizhi, Huizi and Shenzhi for their support and understanding; especially my husband Jason for his loving care and great sacrifices for supporting me to complete this work.
TABLE OF CONTENTS

Abstract ...................................................... ii
Dedication ....................................................... iv
Acknowledgements .............................................. v
Table of Contents ........................................... vi
List of Figures ................................................ viii
List of Tables ................................................ xii

INTRODUCTION ................................................. 1

CHAPTER 1 THEORIES AND MODEL ......................... 8
  1.1 Free Volume Theory ................................. 8
  1.2 Positron And Positronium ......................... 11
  1.3 Positron Annihilation ............................. 15
  1.4 PAL And Momentum Correlation ................... 20

CHAPTER 2 PAL EXPERIMENTAL APPARATUS AND DATA ANALYSIS ........................................ 25
  2.1 PAL Spectrometer .................................. 25
  2.2 Software And Data Analysis ....................... 32
  2.3 System Calibration ................................ 36

CHAPTER 3 PAL STUDIES OF FREE VOLUME TEMPERATURE DEPENDENCE ............................ 44
  3.1 Apparatus ......................................... 44
  3.2 Experimental ..................................... 46
  3.3 Results And Discussion ........................... 48
  3.4 Conclusions ...................................... 54

CHAPTER 4 PAL STUDIES OF ISOTHERMAL PHYSICAL AGING ........................................ 55
  4.1 Experimental ..................................... 55
  4.2 Results And Discussion ............................ 57
  4.2A Long time period of isothermal aging .......... 57
  4.2B Isothermal aging over short time periods ..... 63
  4.3 Conclusions ...................................... 68

CHAPTER 5 PAL STUDIES UNDER MECHANICAL DEFORMATION .................................... 71
  5.1 Apparatus And Experimental ..................... 71
  5.1A Free Volume Tensile Strain Dependence .......... 71
  5.1B Free Volume Compression Dependence .......... 76
  5.2 Results And Discussion ............................ 78
  5.2A Tensile Strain Dependence on Polycarbonate 78
CHAPTER 6  PAL STUDIES OF PHYSICAL AGING UNDER APPLIED STRAIN AND AFTER RELEASE OF STRAIN ................................. 101
  6.1 Experimental 101
  6.2 Results And Discussion 102
  6.3 Conclusions 110

CHAPTER 7  PAL-MOMENTUM CORRELATION .................. 111
  7.1 Apparatus 111
  7.2 Improvement Of Data Acquisition Rate 118
  7.3 Supporting Software 120
  7.3A Control And Acquisition 120
  7.3B Data Analysis 122
  7.4 System Calibration 123
  7.5 Experiments And Results 129

SUMMARY AND FUTURE WORK ................................. 133

REFERENCE .................................................... 135
LIST OF FIGURES

Fig. 1-1. Schematic DSC diagram of endotherm heat flow in annealed and unannealed glassy polymers at \( T_g \) .......................... 4

Fig. 1-2. Molecular scheme of polycarbonate and polymethyl methacrylate (PMMA) .......... 9

Fig. 2-1. The nuclear decay scheme of a positron source \(^{22}\text{Na}\) ...................... 26

Fig. 2-2. A block diagram of PAL spectrometer ...... 28

Fig. 2-3. Energy spectrum of \(^{22}\text{Na}\) from BaF\(_2\) Scintillator ......................... 30

Fig. 2-4. The typical PAL spectrum of polycarbonate ...................... 33

Fig. 2-5. A flow chart of supporting software for PAL spectrometer ..................... 37

Fig. 2-6 The nuclear decay scheme of \(^{207}\text{Bi}\) ........... 40

Fig. 2-7 Result sheet of RESOLUTION program ....... 43

Fig. 3-1. The diagram of the sample chamber for PAL studies at different temperatures .... 45

Fig. 3-2. Temperature dependence of o-Ps intensity, \( I_1 \), in polycarbonate ............... 49

Fig. 3-3. Temperature dependence of o-Ps lifetime, \( r_1 \), in polycarbonate .................. 50

Fig. 3-4. Temperature dependence of apparent free volume fraction, \( h \), in polycarbonate ..... 52

Fig. 4-1. The o-Ps intensity, \( I_3 \), in polycarbonate during isothermal physical aging in long time period at temperatures far below \( T_g \) 58

Fig. 4-2. The o-Ps lifetime, \( r_3 \), in polycarbonate during isothermal physical aging in long time period at temperatures far below \( T_g \) 59

Fig. 4-3. The apparent fractional free volume, \( h/C \),
in polycarbonate during isothermal physical aging in long time period at temperatures far below $T_g$ ............. 60

Fig. 4-4. The o-Ps intensity, $I$, of polycarbonate is as a function of aging time during short aging period at temperatures just below $T_g$ ..................................... 64

Fig. 4-5. The o-Ps lifetime, $\tau$, of polycarbonate is as a function of aging time during short aging period at temperatures just below $T_g$ ..................................... 65

Fig. 4-6. The free volume fraction, $h/C$, of polycarbonate is as a function of aging time during short aging period at temperatures just below $T_g$ ..................................... 66

Fig. 4-7. The $\tau$ temperature dependence curve of polycarbonate is modified by short time aging experiment data ........................................... 69

Fig. 5-1. Sample load frame for tensile strain measurements and a dog-bone shaped sample of Instron ......................... 72

Fig. 5-2. Two test programs of tensile strain dependence of polycarbonate by using PAL spectrometers A and B respectively ...... 75

Fig. 5-3. Sample load cell for linear compression test ......................... 77

Fig. 5-4. The o-Ps intensity, $I$, of polycarbonate as function of sequential incremental tensile strain under program I(A) ....................... 79

Fig. 5-5. The o-Ps lifetime, $\tau$, of polycarbonate as function of sequential incremental tensile strain under program I(A) ............... 80

Fig. 5-6. The free volume fraction, $h/C=I<\nu>$, of polycarbonate as function of sequential incremental tensile strain under program I(A) ....................... 81

Fig. 5-7. The o-Ps intensity, $I$, of polycarbonate as
function of sequential incremental tensile strain under program I(B) .................. 82

Fig. 5-8. The o-Ps lifetime, $\tau$, of polycarbonate as function of sequential incremental tensile strain under program I(B) .................. 83

Fig. 5-9. The free volume fraction, $h/c$, of polycarbonate as function of sequential incremental tensile strain under program I(B) ............................. 84

Fig. 5-10. Tensile stress-strain curve of polycarbonate sample from Instron ........ 86

Fig. 5-11. The relative variations of o-Ps intensity, $I_r-I_r(0)$, under tensile strain from strain free for experimental programs I(A) and II ......... 88

Fig. 5-12. The relative variations of o-Ps lifetime, $\tau_r-\tau_r(0)$, under tensile strain from strain free for experimental programs I(A) and II .... 89

Fig. 5-13. The relative variations of free volume fraction under tensile strain from strain free for experimental programs I(A) and II ................................. 90

Fig. 5-14. The increase in $\Delta V_r/V_o$ and $\Delta V/V_o$ of polycarbonate versus applied strain ...... 92

Fig. 5-15. The o-Ps intensity, $I_r$, of PMMA as a function of static applied compression ... 94

Fig. 5-16. The o-Ps lifetime, $\tau_r$, of PMMA as a function of static applied compression ... 95

Fig. 5-17. The free volume fraction in PMMA as a function of static applied compression ... 96

Fig. 5-18. The percent decrease in $\Delta h/h_o$, and $\Delta V/V_o$ in PMMA versus of applied compression ... 98

Fig. 6-1. Time-evolution of o-Ps intensity, $I_r$, of polycarbonate during 3% applied tensile
strain and after the release of strain ... 103

Fig. 6-2. Time-evolution of o-Ps lifetime, $\tau_i$, of polycarbonate during 3% applied tensile strain and after the release of strain ... 104

Fig. 6-3. Time-evolution of free volume fraction $h/C$ of polycarbonate during 3% applied tensile strain and after the release of strain ... 105

Fig. 6-4. The percent decrease in $\Delta V_r/V_o$, and $\Delta V/V_o$ in polycarbonate during physical aging under 3% static strain and after release of strain 109

Fig. 7-1. PAL-ACAR correlation system .............. 113

Fig. 7-2. Block diagram of PAL-ACAR correlation system ............................................. 115

Fig. 7-3. Geometry of double slits for two-peak momentum distribution on whole Anger camera range ......................... 121

Fig. 7-4. STREAMER.EXE program ...................... 124

Fig. 7-5. Flow chart for control of data acquisition ...................................................... 125

Fig. 7-6. Flow chart for 2d-data analysis .......... 127

Fig. 7-7. A PAL-momentum correlation 2D-Spectrum of PMMA sample ......................... 128
LIST OF TABLES

Table 1-1. List of similarities and differences between positron and electron .......... 13

Table 1-2. List of similarities and differences between positronium and Hydrogen atoms... 16

Table 2-1. The optimization of PAL systems for thermal mechanical studies ................. 31

Table 7-1 Condition of PAL-ACAR correlation system. 131

Table 7-2 Data results for 2D-spectra of PMMA ..... 132
Introduction

Polymer free volume is defined as the difference between the total volume of the material and the volume occupied by the molecules.\textsuperscript{1,2,3} It is a characteristic of amorphous polymers since it is created by chain entanglement and/or folding. Investigation of free volume in polymers has both practical importance and theoretical interest. Not only does free volume have a controlling effect on the molecular mobility and the kinetic and dynamic behavior in the polymeric matrix, but it is also closely related to mechanical, physical, and performance characteristics of the polymers.\textsuperscript{2,4} For instance, the chain molecular mobility, $M$, increases with the free volume, $h$, around the chain as defined in the following general form:

$$\ln(M) = A - B(T)/h^r + \phi(T)$$  \hspace{1cm} (1)

The impact strength, fracture toughness, and loss modulus all increase as the free volume increases because free volume facilitates the deformation of materials.

To this end, several methods have been developed to measure the free volume. Photochromic,\textsuperscript{5} Florescence,\textsuperscript{6,7,8,9,10} Electron Spin Resonance (ESR),\textsuperscript{11,12,19} and Small Angle
Diffraction (SAD)$^{12}$ are probably the most commonly used ones. None of them, however, is able to determine the number of the "holes" constituting the free volume or the sizes of individual holes. These methods cannot quantitatively detect the small changes in the free volume associated with temperature variation or physical aging (vide infra) because of probe size variations,$^{5-10,12}$ poor sensitivity,$^{9,12}$ or possible uncertainties in other temperature-dependent parameters.$^{5-13}$ The positron annihilation technique offers the possibility of avoiding all these difficulties and eventually to determine both the number and size of the free volume elements.$^{14,15,16,17,18,19}$ In addition, it can give information related to shape of the free volume and inhomogeneity of the free volume distributed in the polymeric matrix.$^{16-19}$

As early as the 1960's, there were many studies on positron and positronium in metal defects, surface physics, liquids, and wide variety of areas.$^{16-19}$ In polymers, most of this work was limited to measuring the mean values of the free volume hole size and the hole density, assume to be related to the lifetime and intensity of orthopositronium (o-Ps).$^{17}$ These studies generally used the well-established positron annihilation lifetime (PAL) technique. Only a few of them were
employed to investigated the macroscopically mechanical properties or physical aging.

The knowledge of physical aging behavior of a material is extremely valuable for predicting its long-term behavior from short-time studies.\(^1\) Physical aging differs from chemical aging (e.g. photo-oxidation); it is a gradual change of the physical properties such as toughness and crack due to a slow process of stress relaxation. At temperatures below \(T_g\), polymer molecular chains retain some mobility, even though much less than above \(T_g\), and they will slowly relax and pack as closely as possible in order to minimize the conformation energy. Consequently, the free volume decreases during aging. This is often observed from Differential Scanning Calorimetry (DSC) curves, especially for those whose \(T_g\) are about 10 °C above room temperatures. The overshooting of the glass transition above \(T_g\) as shown in Fig. 1-1 is attributed to physical aging. The overshooting peak corresponds to the amount of energy required to create the extra free volume which was reduced by physical aging. Overshooting can be removed or significantly suppressed by heating the sample above \(T_g\) for several minutes and quickly quenching to lower temperatures, then run temperature scan immediately
Fig. 1-1. Schematic DSC diagram of endotherm heat flow changes in annealed and unannealed glassy polymers at $T_g$. 
before molecules have enough time to relax and close pack again, i.e. physical aging.

The goal of this work is focused on applications of positron annihilation in monitoring the free volume and its change in polymeric materials. The studies are as follows:

1. PAL studies on the bisphenol-A polycarbonate under different thermal conditions, performed on a complete PAL spectroscopy system which is equipped with a vacuum chamber with precisely controlled of temperature. The positron $\alpha$-Ps parameters in polycarbonate are determined as functions of temperature and aging time. Two groups of isothermal aging tests at temperatures of far below $T_g$ for long-time annealing and at temperatures just below $T_g$ for short-time annealing were designed to test the aging behaviors in these two temperature ranges. The positron data shows that $r$, is sensitive in $T_g$ and $I$, is sensitive in $T_g'$ in the temperature dependent studies; and it also shows an "over shooting" behavior during very first few hours annealing at a temperature just below $T_g$.

2. Investigation of effects of mechanical deformation on free volume. A sample load frame of tensile strain and a compressional sample cell were constructed for the PAL spectroscopy system to investigate free volume changes associated with well-specified mechanical deformations.
The changes (as reported) in the o-Ps parameter $\tau$, on polycarbonate at incremental tensile strain and on polymethyl methacrylate (PMMA) at compressional strain both ranging to 8%. Also changes in o-Ps parameters in polycarbonate during isothermal annealing under a large static tensile strain and after release the strain were continually monitored.

3. Use of a lifetime-momentum correlation method to attempt to magnify the o-Ps component in a PAL spectrum. The momentum of the annihilating positron-electron pair is indicated by the angle between the resulting gamma rays.

It is extremely difficult to measure the angular correlation of annihilation radiation (ACAR) while simultaneously achieving good time resolution. An ACAR time-momentum system with long slits has a very low counting rate owing to the necessity of placing two detectors far away to achieve the required angular resolution.\textsuperscript{15,20} Use of the Doppler shift of the gamma rays for momentum correlation yields a high counting rate but has low momentum resolution due to the limited energy resolution of the detector.\textsuperscript{21} Currently at Queen's University, a ACAR system based on thick microchannel plates correlates two components of momentum with lifetime and has excellent momentum resolution function
but very poor in time resolution because of the timing limitations of the plate. Our new experimental arrangement of lifetime-momentum correlation measurement is designed and completed. A preliminary run on PMMA sample made on this system shows both lifetime spectra correlated with momentum and momentum spectra correlated with specific positron lifetimes.
Chapter 1  Theories and Models

1.1 Free volume Theory

Polymeric material is much more complex than metals, monomers and other systems. The "backbone" of a polymer consists of many monomer repeat units which are normally attached to side chains. Fig. 1-2 shows the structure of polycarbonate and PMMA. Long chains are folded, twisted and not regularly arrayed. Disorder causes some low electron density region "holes" in polymer. Though a simulation of molecular states and movement is almost impossible at the present time, a study of the hole and its changes, (and even the electron momentum distribution) gives a possible way to understand the macro-mechanical properties in polymer and picture the molecular group movement.²³⁴

The free volume, \( V_f \) is defined as the total volume of low electron-density sites:²³⁴

\[
V_f = V_o - V_c \tag{1-1}
\]

where \( V_o \) is the bulk volume and \( V_c \) is the volume occupied by the molecules which is temperature dependent with thermal expansion coefficient, \( \alpha \). The free volume fraction, \( h \), is an important parameter in this theory:
bisphenol-A polycarbonate

polymethyl methacrylate

Fig. 1-2. Molecular schemes of bisphenol-A polycarbonate and polymethyl methacrylate (PMMA)
\[ h = \frac{V_f}{V_0} \]  \hspace{1cm} (1-2)

\( V_f \) is at present only a concept used to qualitatively explain macroscopic properties through the relationship with the molecular mobility and segment movement, because it is the difficult to exactly measure free volume in polymeric material. Nevertheless, it is still a useful theoretically to establish the relationships between free volume and macroscopic properties. The segment mobility \( M \) in matrix increases as the free volume increases as presented in Eq. (1). There are some models to simulate the constant \( A \) and \( \gamma \), and temperature dependent functions of \( B(T), \phi(T) \), but only qualitatively or partially explain the experiment data. The mechanical properties and physical aging are strongly affected by free volume via the mobility. The shift rate, \( \mu \), of physical aging is given by:

\[ \mu = - \frac{d(\log a)}{d(\log t)} = - \frac{d(\log M)}{d(\log t)} \]  \hspace{1cm} (1-3)

The volume sensitivity \( S \) can be expressed as:

\[ S = \left[ \frac{\partial h}{\partial (\log t)} \right]_t \]  \hspace{1cm} (1-4)
The free volume increases as temperature increases and three main regions normally can be defined in amorphous polymer: truly glassy zone below $T_g$; aging range between $T_g$ and $T_s$; and rubbery state above $T_s$. In the truly glassy zone, free volume is very small and almost independent of temperature, and segment movement is practically nil. In the aging range, free volume slowly increases with temperature and decreases with aging time, and molecules may experience side chain and/or crank-shaft rotation of the backbone. Above $T_s$, free volume increases rapidly with temperature and the backbone segment starts into Brownian motion, the length of the segment corresponding to the chain entanglement distance.

1.2 Positron and Positronium

The positron is not like some other well known elemental particles such as electron, proton, neutron and etc., and does not exist naturally in our world except for a very small amount and for a very short time. So the discovery of the positron was far later than the discovery of other natural particles.

Positron is easily known as a positive particle by its name, it labeled as $e'$. It is anti-particle of electron, $e'$. Positron and electron have identical intrinsic physical properties in mass, magnitude of
charge, magnetic moment and gyromagnetic ratio.\textsuperscript{23,19} Table 1-1 list similarities as well as differences between positrons and electrons.

Positron and electron belong to the lepton group of elementary particles which are Fermi particles and participate in weak, electromagnetic, and gravitational interactions. Governed by quantum electrodynamics, the lifetime of a positron depends upon the density of electrons in its environment. Positron and electron are then annihilated, emitting energetic $\gamma$-rays in a process that conserves energy and momentum.

$$e^+ + e^- \rightarrow n\gamma$$ \hspace{1cm} (1-5)

Where $n$ is the number of $\gamma$-rays from a $e^+ e^-$ annihilation event.

Positronium, Ps, is a dynamically stable state of $e^+ e^-$ bound by the Coulomb interaction, just as the proton and electron are bound in hydrogen. The Schrödinger equation of positronium system in the center-of-mass has the same form as hydrogen except that the reduced mass is about half of that in hydrogen system:

$$[-\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r})] \Psi_{Ps} = E \Psi_{Ps}$$ \hspace{1cm} (1-6)
<table>
<thead>
<tr>
<th></th>
<th>$e^-$</th>
<th>$e^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>charge</strong></td>
<td>$+e$</td>
<td>$-e$</td>
</tr>
<tr>
<td><strong>mass</strong></td>
<td>$m_e$</td>
<td>$m_e$</td>
</tr>
<tr>
<td><strong>magnetic moment</strong></td>
<td>$\mu_B$</td>
<td>$\mu_B$</td>
</tr>
<tr>
<td><strong>spin</strong></td>
<td>$1/2$</td>
<td>$1/2$</td>
</tr>
<tr>
<td><strong>orientation of orbital and</strong></td>
<td>parallel</td>
<td>anti-parallel</td>
</tr>
<tr>
<td><strong>spin magnetic moments</strong></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 1-1. List of the similarities and differences between electron and positron.
The interaction potential $V(r)$ in Ps system is exactly the same as in hydrogen atom. The size, energy levels and wave functions of Ps can be obtained by the same calculation as for hydrogen system. The sizes of Ps atom and hydrogen, are also the same,

$$a_{ps} = 2a_o = \frac{\hbar^2}{2\pi^2 m_e e^2}$$  \hspace{1cm} (1-7)

where $a_{ps}$ is the diameter of Ps atom, and $a_o$ is the Bohr radius. The quantum mechanical solution of the Schrodinger equation gives the wave functions $\Psi_{ps}$ and eigenvalues of Ps system. The energy level is similar as hydrogen, but is only half that of the corresponding level in hydrogen:

$$E_n = -m_e c^2 n^2 / 4a^2$$  \hspace{1cm} (1-8)

and the wave functions of Ps system at different levels $\Psi_{ps}$ can be obtained by simply modifying the radius of hydrogen to the $a_{ps}$ in the formula of the hydrogen wave functions. Of special interest in positron annihilation, the ground state of Ps has correspond form of $\Psi_{ps0}(r)$, in radial part:

$$\Psi_{ps}(r) = e^{-r/a_{ps}} / \sqrt{\pi a_{ps}}$$  \hspace{1cm} (1-9)
where $r$ is the distance between of electron and positron in Ps atom.

For the spins equal 1/2, with two spin directions up and down, the hydrogen and positronium atom have four equally possible spin states. When the spins of electron and positron in the positronium states are anti-parallel the total spin is 0 which is singlet state, called para-positronium (p-Ps); when they are parallel the total spin equals 1 and the three states are called triplet, or ortho-positronium (o-Ps). Table 1-2 shows the similarities and differences between these two atoms.

1.3 Positron Annihilation

Positron will annihilate with electron in media governed by electrodynamics. Until now there are three annihilation process discovered: one-photon, two-photon and three-photon annihilations. The most favorable case for one-photon annihilation is a free positron with a 1s electron. This annihilation cross section in the low and high positron energy limits are:

$$\sigma_1 \rightarrow \frac{4\pi r^2 Z^5 \alpha^4 v}{c} \quad \text{when } v \rightarrow 0$$

$$\rightarrow 4\pi r^2 Z^5 \alpha^4 / \gamma \quad \text{when } v \rightarrow c \quad (1-10)$$
<table>
<thead>
<tr>
<th></th>
<th>H</th>
<th>Ps</th>
</tr>
</thead>
<tbody>
<tr>
<td>reduced mass</td>
<td>( m_s )</td>
<td>( m_s /2 )</td>
</tr>
<tr>
<td>radius</td>
<td>( a_s )</td>
<td>( a_o )</td>
</tr>
<tr>
<td>( E_n )</td>
<td>(-m_sC^2\alpha^2/2n)</td>
<td>(-m_sC^2\alpha^2/4n)</td>
</tr>
<tr>
<td>( \psi_n(r) )</td>
<td>( \exp(-r/a_s)/(\pi a_s^3)^{1/2} )</td>
<td>( \exp(-r/2a_o)/(8\pi a_o^3)^{1/2} )</td>
</tr>
</tbody>
</table>

Table 1-2. List of the similarities and differences between positronium and hydrogen atoms.
Where \( r_e \) is the electron radius; \( \alpha \) is fine structure constant; \( c \) is light speed; \( v \) is positron velocity; \( Z \) is atomic number; and \( \gamma = 1/\sqrt{1-(v^2/c^2)} \).

The two-photon annihilation from free positron and free electron is most favorable case. Its two energy limits in cross section are given by following:

\[
\sigma_2 \to \pi r_e^2 c/v: \quad \text{when } v \to 0
\]

\[
\to \pi r_e^2 \left(\ln\gamma\right)/\gamma: \quad \text{when } v \to c
\]  

(1-11)

Three-photon annihilation of a free positron with an electron has a much smaller cross section \( \sigma_3 \) than the cross section \( \sigma_2 \) for two-photon annihilation,

\[
\sigma_3 = \varepsilon \sigma_2 = \sigma_2/378.16
\]  

(1-12)

One-photon annihilation is also possible, but it requires a three-body interaction in the initial state.

The positron annihilation rate \( \lambda_i \) of i-photon annihilation is proportional to the electron density at \( r \), the annihilation cross section of emitting number \( i \) of photons \( \sigma_i \) and positron velocity in media \( v \):

\[
\lambda_i = n \sigma_i v = p_e(x) \sigma_i v
\]  

(1-13)
The electron density $n$ is instead by the probability density $P_e(x)$ of finding the electron between $x$ and $x+dx$ which equals the absolute square of electron wave function:

$$P_e(x) = |\psi|^2$$  \hspace{1cm} (1-14)

Furthermore, the lifetime of positron $\tau_1$ is the reciprocal of annihilation rate $\lambda_1$. For positronium at its ground state the square is:

$$|\Psi_{Ps}(0)|^2 = 1/\pi a_{Ps}^2$$  \hspace{1cm} (1-15)

Therefore,

$$\lambda_2 = r^2 c/a_{Ps}^2 = 2.008 \times 10^5 s^{-1}$$

$$\lambda_3 = \varepsilon\lambda_2 = \lambda_2/378.16 = 5.408 \times 10^6 s^{-1}$$  \hspace{1cm} (1-16)

Positronium self-annihilation is restricted by mass-energy transition selection rules and annihilation cross section. The total angular momentum (includes Ps orbital momentum $l$, and spin momentum $s$) of Ps and the number of photons $i$ which are emitted from annihilation obeys the selection relationship:

$$(-1)^{l+s} = (-1)^i$$  \hspace{1cm} (1-17)
The spin of photon is 1. So for zero spin of (singlet state) p-Ps in its ground state with orbital momentum equal to zero, there is only two-photon annihilation; three-photon annihilation is forbidden. The triple state, o-Ps, has only three-photon annihilation, no two-photon annihilation.

Total Ps i-photon annihilation rate $\lambda_1$ is the sum of weighted p-Ps and o-Ps annihilation rates which are weighted by their number of states:

$$\lambda_1 = \frac{3}{4}\lambda_1(o-Ps) + \frac{1}{4}\lambda_1(p-Ps)$$  \hspace{1cm} (1-18)

Therefore, the lifetimes of p-Ps, $\tau(p-Ps)$, and of o-Ps, $\tau(o-Ps)$ are calculated from Eqs. (1-16), and (1-18) and with radiative corrections:\textsuperscript{24,25}

$$\tau(p-Ps) = 1/\lambda_1(p-Ps) = 1/(4\lambda_1) \approx 0.125\text{ns}$$

$$\tau(o-Ps) = 1/\lambda_1(p-Ps) = 1/(4\lambda_3) \approx 142.1\text{ns}$$  \hspace{1cm} (1-19)

In a polymer material, a positron has more chance to form Ps because of the their higher percentage of localized regions with low electron density than in a metal. Two major theoretical models support different experimental data, but the mechanics of positronium
formation in polymer is still not quite clear, but it is known that positrons from radiation sources slow down and thermalize in $10^{-12}$ sec, and they have a very small chance to annihilate or to form Ps in bulk in this period. Then some of the positrons form Ps with a "free" electron in the free volume hole. The Ps wave function penetrates in the electron layer which surrounds the hole, and overlaps with wave function of another electron in the polymer. The higher degree of overlap, the greater chance for an electron from the layer with opposite spin direction than one in Ps atom to "pick off" the positron from Ps to form new Ps or has free positron annihilation. Since o-Ps has much longer lifetime, the chance of "pick off" is greater. In this case, the o-Ps atom becomes p-Ps which has very short lifetime. The annihilation rate of o-Ps in polymer is mainly determined by "pick off" rate.

1.4 PAL spectrum and momentum correlation

The positron annihilation technique is capable of probing the free volume "hole"s in polymer material based on the fact that positron annihilation lifetime and momentum correlation of annihilation photon pair are very sensitive to the surrounding electron density and distribution in localized sites.
The lifetime of o-Ps in a polymer measures the mean value of free volume "hole" size, since it is mainly determined by the "pick off" rate which depends upon the penetration of o-Ps into the electron layer, which in turn depends on the size of the holes.

A simple model of interaction potential about an o-Ps atom in free volume "hole" is a spherical rigid well with radius $R_o$ and infinite potential barrier. The Schrodinger equation of Ps under this potential in radial part and center-of-mass of Ps is:

$$\left\{-\left(\frac{\hbar^2}{2m}\right)\frac{d^2}{dr^2} - \frac{1}{r}\left(1 + \frac{1}{r^2}\right) + V(r)\right\}\varphi_n(r) = E_n\varphi_n(r) \quad (1-20)$$

and the wave function of Ps, $\varphi(r)$, at its ground state, is none zero only in the well:

$$\varphi_0(r) = (2\pi R_o)^{-1/2}\sin(\pi r/R_o)/r \quad 0 \leq r \leq R_o \quad (1-21)$$

A homogeneous electron layer with a thickness $\Delta R$ is assumed to surround the "hole"$^{26,27,28}$:

$$\Delta R = R_o - R = 1.656A \quad (1-22)$$

Where $R$ is the radius of "hole", and the value 1.656 A comes from a best fit to available data. Therefore, the probability of Ps in ground state penetrating inside of
electron layer is the integral of the square of Ps wave function in the layer:

\[ p = \int_{0}^{r} |\varphi_0(r)|^2 dr = 4\pi \int_{0}^{R_o} |\varphi_0(r)|^2 r^2 dr \]

\[ = 1 - R/R_o + (1/2\pi) \sin(2\pi R/R_o) \]  

(1-23)

A further assumption is made based on previous studies that the average of total Ps annihilation rate in the electron layer is 2 ns\(^{-1}\).\(^{29,30}\) Finally, the o-Ps lifetime is the reciprocal of its annihilation rate which is the product of total rate and the probability of "pick off":

\[ \tau(o-Ps) = \left[2(1 - R/R_o + \frac{1}{2\pi} \sin(2\pi R/R_o))\right]^{-1} (ns) \]  

(1-24)

From this relationship R can be determined when \( \tau \) is known, and the hole volume is:

\[ v_f = \frac{4}{3} \pi R^3(\tau) \]  

(1-25)

Deconvolution of PAL spectrum gives the life time of p-Ps, o-Ps and free positron, and corresponding intensities. We assume the intensity of o-Ps annihilation to be proportional to the number density of free volume holes. The parallel formula of the free volume fraction
of polymer $h_{rs}$ obtained from o-Ps parameters $\tau(o-Ps)$ and $I(o-Ps)$ follows the definition of $h$ in Eq. (1-2):$^{31}$

$$h_{ps} = CI(o-Ps) \times \nu_\tau[\tau(o-Ps)]$$  \hspace{1cm} (1-26)

The constant C can determined by comparing $h_{ps}$ with $h$ which obtained from other method, and may vary with different polymers.

The same quantum mechanics potential model is applied to the momentum correlation spectrum.$^{19}$ The spectrum is the integral of momentum density in momentum space:

$$N(\theta) = \frac{1}{\tau} \int_0^\infty \int \rho(p') dp'$$  \hspace{1cm} (1-27)

From this model the narrowest component of Gaussian distribution in the spectrum $N(\theta)$ is mainly contribution by p-Ps with lowest momentum. The p-Ps momentum density in momentum space is:

$$\varphi(p) = (h)^{-\frac{3}{2}} \int_0^{R_c} \varphi_o(r)e^{-irp/b}dr = \left[ \frac{R_c}{b} \right]^{\frac{3}{2}} \frac{1}{\pi} \sin \left[ \frac{PR_c}{b} \right] \left[ \pi^2 - \left( \frac{PR_c}{b} \right)^2 \right]$$

and
\[ N(\theta) = \left( 4\pi R_c / h \right) \int_0^{\infty} \left( \frac{\sin X}{X} \right)^2 dX \]  

where \( \alpha = (mcR_c / h)\theta \).

The \( \theta_{1/2} \), the FWHM of p-Ps momentum correlation spectrum is defined as:

\[ N(0)/N\left( \theta_{1/2}/2 \right) = 2 \]  

and the solution of this integral is that \( \alpha \) equals 2.148.

It gives the relationship between \( \theta_{1/2} \) in mrad, with the radius of free volume "hole" at \( \mathbb{F} \) direction, \( R \), by considering \( \Delta R \):

\[ R = 16.6 / \theta_{1/2} - 1.656(\text{A}) \]  

So from the momentum spectrum, it may be possible to find the p-Ps annihilation intensity in "hole". The p-Ps annihilation momentum correlation parameters also give the free volume fraction, but with specific orientation. Therefore, the shape of "hole" may be determined by simply rotating the sample.
Chapter 2  PAL Experimental Apparatus and Data Analysis

2.1 Experimental Apparatus

Positron annihilation lifetime (PAL) measurements, the angular correlation of annihilation radiation (ACAR) and Doppler Broadening are the three common positron annihilation techniques. Among them, PAL spectroscopy is probably the most widely used and simple technique. Nowadays the most commonly used positron annihilation method for polymer characterization is PAL.

The principle of the PAL spectrometer is to detect the two different photons which represent the time of birth and annihilation of the positron. The energy of photons emitted when the positron is created depends upon the radioactive type that is used. Currently, sodium $^{22}\text{Na}$ is most commonly used.19 $^{22}\text{Na}$ decays to neon $^{22}\text{Ne}$ with half lifetime of 2.6 years as shown in Fig. 2-1.21 Of these decays, 90 percent are positive $\beta$ decays. The decayed nuclei instantaneously (only 3 pico-second) drop from the high energy state of $^{22}\text{Ne}$ to the ground state with emission of a 1.27 Mev photon. A positron will annihilate with a electron in the material being studied, emitting two photons, each with energy about 0.511 Mev.
Fig. 2-1. The nuclear decay scheme of a positron source $^{22}\text{Na}$. A proton in $^{22}\text{Na}$ nucleus decays to a neutron and a positron ($\text{P} \rightarrow n + e^+$). The $\gamma$-decay of the intermediate state of $^{22}\text{Ne}$ is employed as a "birth" signal of positron. Electron capture is a minor channel in this decay.
Therefore, the 1.27-Mev photon serves as the birth signal and one of the 0.511-Mev photons is the annihilation signal. Fig. 2-2 shows the PAL system. Two detectors both detect a wide range of photon energies; the discriminators only let photons near energy 0.511 or 1.27 Mev pass. Two predefined photons are detected by two photon detectors and respectively pass the energy windows of constant fraction differential discriminators (CFDD). These give the start and stop signal inputs to a time-amplitude convertor (TAC) which give the time difference of two signals' arriving times, which is the lifetime of the positron. The multi-channel analyzer (MCA) and computer record the annihilation events and generate the PAL spectrum.

System time resolution and data acquisition efficiency are the two main concerns when designing a PAL spectrometer for specific application. In the PAL system, the photon detectors and fast timing discriminator's energy window settings are dominant factors for these two system specifications. Each photon detector consists of a scintillator and a photo-multiplier tube. A conical barium fluoride BaF₂ crystal (ϕ0.8" x ϕ1" x 1") was chosen as scintillator; it is coupled to a Hamamatsu H2431Q photomultiplier tube by glycerol. Such a detector has a high time resolution, but the BaF₂ crystal is
CFDD: Constant Fraction Differential Discriminator
TAC: Time to Amplitude Converter
MCA: Multi-Channel Analyzer

Fig. 2-2. A block diagram of PAL spectrometer.
limited in efficiency. A more efficient choice is a cylindrical cesium fluoride CsF crystal (φ1.5" x 1.5") coupled to a Hamamatsu H2431 photo-multiplier. For most amorphous polymer PAL studies a system of using both BaF$_2$ and CsF detectors have been chosen for thermal measurement. The 0.511 Mev peak from BaF$_2$ scintillator is much higher and sharper than 1.27 Mev peak as shown in Fig. 2-3. We use a BaF$_2$ high resolution detector for the 0.511 Mev gamma photons and a CsF high efficiency detector for the 1.27 Mev photons. For the mechanical deformation measurement system, since the count rate is not the main concern, two BaF$_2$ detectors are used for both 0.511 Mev and 1.27 Mev photons to obtain the best system resolution less than 180 ps. Table 2-1 shows the optimization of the PAL system for different applications. The window setting of fast timing discriminators also affect the time resolution and efficiency. It has to be a compromise between these two requirements. The width of energy window for 0.511 Mev photons ΔE/E is set around 50 %; and that for 1.27 Mev photons is set for the lower limit only, to reject 0.511 Mev photons. The time resolution function of the system is obtained from cobalt $^{60}$Co, which emits two γ-rays
Fig. 2-3. Energy spectrum of $^{22}$Na from BaF$_2$ Scintillator.
<table>
<thead>
<tr>
<th></th>
<th>PAL Thermal System</th>
<th>PAL Mechanical System</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{22}$Na source</td>
<td>20$\mu$ci</td>
<td>5$\mu$ci</td>
</tr>
<tr>
<td>detector A &quot;birth&quot;</td>
<td>CsF, H2431, Hamamatsu</td>
<td>BaF$_2$, H2431Q,Hamamatsu</td>
</tr>
<tr>
<td>detector B &quot;death&quot;</td>
<td>BaF$_2$, H2431Q,Hamamatsu</td>
<td>BaF$_2$, H2431Q,Hamamatsu</td>
</tr>
<tr>
<td>window $\Delta E/E$ (A)</td>
<td>100%</td>
<td>100%</td>
</tr>
<tr>
<td>window $\Delta E/E$ (B)</td>
<td>&gt; 50%</td>
<td>&gt; 60%</td>
</tr>
<tr>
<td>count rate</td>
<td>300 $\sim$ 400 cps</td>
<td>&lt; 500 cps</td>
</tr>
<tr>
<td>FWHM in $^{60}$Co</td>
<td>&lt; 230 ps</td>
<td>&lt; 180 ps</td>
</tr>
</tbody>
</table>

Table 2-1. The optimization of PAL systems for thermal and mechanical studies.
within a pico-second. In this measurement, the energy windows are set for $^{22}$Na.

For this simple electrical construction, when the source strength is less than 50 $\mu$Ci, the count rate is about 1000 cps or less, the pulse output rate from detectors is on the order of $10^4$ cps and the TAC resetting time is 50 ns. Under these condition the background is lower than $10^{-4}$ of the total count, which means that the possibility that two positron decay events occur in the TAC resetting time is about $10^{-4}$. For the best shape of positron annihilation lifetime spectra, experiments are run at count rate around 500 cps, which are good for the polymer PAL measurements.

Except a good proper set constant fraction differential discriminator (CFDD EG&G Ortec 583) and time and amplitude convertor (TAC EG&G Ortec 566), 4096 channels of multi-channel analyzer (Nuclear PAC) keeps the accuracy, and the channel time is 10.3 ps/channel.

2.2 Data Analysis and Software

Each annihilation event is measured by and stored in a computer based multi-channel analyzer (MCA). Fig. 2-4 shows a typical PAL spectrum from PAL spectroscopy meters, which can be load on the computer screen under PCA model. The spectrum gives the lifetime of each
*One channel equals to 10.3 ps.

Fig. 2-4. A typical PAL spectrum of polycarbonate.
positron annihilating in the polymer, in the positron radioactive source material and foil. The observed lifetime is affected by other factors, such as the system resolution function, and positron scattering at each interface. For the application of PAL studies in polymer, modern data analysis and computer technique make it possible to separate the PAL information in polymer from other factors.\(^{35,36}\) Considering all the effects, a PAL spectrum can be represented as:

\[
f(t) = \int_{-\infty}^{+\infty} \sum_{j=1}^{\infty} a_j(\nu) R(t - \nu) dv + B \quad (2-1)
\]

\(R(t-\nu)\) is the system resolution function and \(a_j(\nu)\) is the number of positron in population \(j\) with lifetime \(t=\nu\). where \(B\) is the background. It has been assumed in these PAL experiments in polymer that three population (\(k=3\)) of positrons exist in these polymers. Two other annihilating groups consist of those in aluminum foil with the NaCl source and backscattering between the interface (\(k_s=2\)). The resolution function is approximately simulated by the weighted sum of three Gaussians (\(k_s=3\)).

\[
f(t) = \int_{-\infty}^{+\infty} \sum_{j=1}^{\infty} \sum_{j=1}^{3} \omega_j A_j \ e^{-\frac{(v - \nu)^2}{2\sigma_p^2}} \ e^{-\frac{(v - \nu - \Delta \nu)^2}{2\sigma_p^2}} dv + B \quad (2-2)
\]
where $\tau_j$ is the positron lifetime and $T_0 - \Delta t_p$ is the center of $p$-th Gaussian, where $k_0 = k + k_e$, and

$$\sum_{j=1}^{j_0} A_j = 1$$  \hspace{1cm} (2-3)

Weights of Gaussians are satisfied:

$$\sum_{p=1}^{j_0} \omega_p = 1$$  \hspace{1cm} (2-4)

Also the intensities of positron annihilations in polymer are defined as:

$$I_j = A_j \tau_j / \sum_{i} A_i \tau_i$$  \hspace{1cm} (2-5)

A commercial positron data analysis program PATFIT-88 is used to deconvolute the PAL spectra. The principle of this program is the least-squares criterion and iterative fitting technique to fit a parametric model function $f(t)$ to a experiment data spectrum $Y_j$. It minimizes the difference between them:

$$\Phi = \sum_{i=1}^{n} \omega_i \left( y_i - f(b_1, \ldots, b_k) \right)^2$$  \hspace{1cm} (2-6)
where \( b_1, \ldots, b_k \) are the parameters in prediction model function, \( n \) is the number of total data channel, and \( \omega_i \) is a fixed statistical weighting which is:

\[
\omega_i = \frac{1}{\sigma_i^2} \quad (2-7)
\]

where \( \sigma_i \) is the estimated variance of \( y_i \).

In addition to the deconvolution program, other software supports the data acquisition and data process. Fig. 2-5 is the PAL spectrometer software flow chart.

2.3 System Calibration and Resolution Function

Instrumental system calibration and resolution function determination are also very important to the reliability of PAL results. There are several methods can be used to determine the channel time and the resolution function and compare the results with each other.

A long standard coaxial cable 58A/U extends the delay of annihilation signal and the cable delay time \( \Delta t \) can be found from table and below equation, which is known as 50 ps/cm.

\[
\Delta t = \sqrt{L \cdot C_o} \quad (ps/cm) \quad (2-8)
\]
Fig. 2-5. A flow chart of supporting software for FAL spectrometer.
where $L_o$ is inductance and $C_o$ is capacitance per centimeter of cable. Two $^{60}$Co spectra obtained before and after adding the delay cable ($L$ cm) give two peak position on computer screen. The channel distance between two peaks, $\Delta c$, corresponds total delay time while pulse travels through long cable. The MCA channel time ($\text{chant}$) can be simply calculated from the measurements:

$$\text{chant} = \frac{50L}{\Delta c} \text{(ps/channel)} \quad (2-9)$$

Using different length cables can limit the measuring variance. This method is often used when the PAL spectrometers have any working condition changes because it is a reliable and simple procedure.

Same principle of above method which is delay one pulse and cause the peak position of spectra move to another channel. Because the gamma photon travels in air at the speed of light, we move one detector away from the $^{60}$Co source by certain distance ($d$ cm), and the time interval between detection of the two changes by the corresponding amount.

$$t_d = \frac{d}{c} = (0.03)^{-1} d \text{(ps)} \quad (2-10)$$

and
\[ chant = t_4 / dc(ps/channel) \] (2-11)

Several measurements at different distances and using strong radioactive source will increase the accuracy. But the results are only for the comparing with others.

Random coincidence rate R measurement is a good method to this system calibration when using weak radiation source. Separately measuring the count rate in both detectors \( S_i = N \varepsilon_i \) (count/(channel*sec.)) The random coincidence rate \( R \) (per channel*sec.) can be determined by the region out of the peak and tail in PAL spectrum. The channel time can be obtained as following.

\[ chant = R / (S_1 \times S_2) \] (2-12)

To further test the calibration, the same PAL spectrometer is used, with the energy windows at 1.06 Mev for start signal and 0.57 Mev for stop signal, to measure the mean lifetime spectrum of the excited state of \(^{207}\text{Pb}\) resulting from \(^{207}\text{Bi}\) decay.\(^{19}\) Fig. 2-6 shows the nuclear scheme of \(^{207}\text{Bi}\) decay.\(^{32}\) The spectrum has only one lifetime component decay so it is much less complicated than PAL spectra and a good fit is readily obtained after running PATFIT-88, RESOLUTION program. A value of 182 ± 5ps for this lifetime is obtained, which agrees with the
Fig. 2-6. The nuclear decay scheme of $^{207}$Bi. The $\gamma$-ray emitted from the level of 1.63 Mev is employed as "start" signal and the $\gamma$-ray from the level of 0.576 Mev is as "stop" signal in the calibration of PAL spectrometer.
published result 186 ps.\textsuperscript{33}

The most reliable method is that at same PAL spectrometer working condition for polymer characterization, measuring the PAL spectrum of a well-annealed pure aluminum metal which has only one positron lifetime with a value of 166 ± 3 ps. The NaCl positron source is directly deposited on a small piece of aluminum and another piece covers the source. By using RESOLUTION program, resolution function and two positron lifetimes are obtained, one from positrons annihilating in aluminum, the other from positrons annihilating in NaCl source and backscattering. The lifetime in aluminum is 166 ± 4 ps from these PAL spectrometers. Hence these two methods verify the system calibration.

The following shows how to find a model function as close as possible to real system resolution function. The \textsuperscript{60}Co spectrum obtained from the PAL spectrometer (CFDD's energy windows are set for \textsuperscript{22}Na positron source) is a roughly estimation of system resolution function and can be simulated by a combination of three Gaussians. When running PAL measurements on polymer material, NaCl positron source is foiled by thin aluminum sheet. The positron lifetime in aluminum is known from the calibration procedure, so putting this foiled source between two piece of aluminum plat and measuring the PAL
spectrum, then run the RESOLUTION program to get two lifetime and three Gaussians. This resolution function combined by these three Gaussians and two positron annihilation lifetimes in source correction are close to the real system resolution function and source correction except backscattering is different than in polymer. Fig. 2-7 shows the result sheet of RESOLUTION program for PAL spectrum of polymer. Because total effect to lifetime from backscattering is less than 1%, the difference between aluminum to aluminum and aluminum to polymer is negligible. The intensity of the two lifetime components can be determined by measuring the thickness of aluminum foil and calculating the percentage of energetic positron stopping in this amount thickness of aluminum. For 1.7 g/cm² thick aluminum, about seven percent of positron will annihilate in it. From Fig. 2-7 I₁ and I₂ can be determined.
RESOLUTION ... VERSION MAR 89 ... JOB TIME 17:20:26 19-JUL-91
************************************************************************************************
10191 PPMA-COMPRES-OR
************************************************************************************************
TIME SCALE NS/CHANNEL: 0.0311
AREA RANGE STARTS IN CH. 3 AND ENDS IN CH. 511
FIT RANGE STARTS IN CH. 12 AND ENDS IN CH. 500

INITIAL
FWHM (NS) : 0.2010G 0.1560G 1.2370G
RESOLUTION INTENSITIES (I) : 40.5000 58.9000 0.6000
FUNCTION
SHIFTS (NS) : 0.0000F -0.0100F 1.2200F

OTHER INIT. TIME-ZERO (CH,NS): 17.80000
PARAMETERS
LIFETIMES (NS) : 0.1883F 0.5651F 0.1300G 0.3600G
INTENSITIES (I) : 7.5000F 1.5000F

BACKGROUND FIXED TO MEAN FROM CH. 500 TO CH. 511. = 10.2500

****************************************************************************************** FINAL RESULTS ******************************************************************************************
CONVERGENCE OBTAINED AFTER 9 ITERATIONS
VARIANCE OF THE FIT = 0.066 WITH STANDARD DEVIATION 0.065
CHI-SQUARE = 13.27 WITH 477 DEGREES OF FREEDOM
SIGNIFICANCE OF IMPERFECT MODEL = 1.61 X

RESOLUTION FUNCTION:
G M S
3 0 1


FWHM (NS) : 0.1963 0.1517 1.4665
STD DEVIATIONS : 0.0060 0.0022 0.1914

INTENSITIES (I) : 40.5000 58.9000 0.6000

SHIFTS (NS) : 0.0000 -0.0072 1.6702
STD DEVIATIONS : FIXED 0.0070 0.1291

LIFETIME COMPONENTS:
L T I
5 2 2


LIFETIMES (NS) : 0.1883 0.5651 0.1540 0.3900
STD DEVIATIONS : FIXED FIXED 0.0094 0.0121


INTENSITIES (I) : 7.5000 1.5000 26.932B 43.7649
STD DEVIATIONS : FIXED FIXED 2.2458 2.0462


TIME-ZERO CHANNEL NUMBER: 18.1379
STD DEVIATIONS: 0.1700

TOTAL AREA FROM FIT: 1.10272E+06 FROM TABLE: 1.10330E+06

SHAPE PARAMETERS FOR RESOLUTION CURVE (NS/SEC):
N 2 5 10 30 100 300 1000
FW AT 1/N 0.1653 0.2352 0.3087 0.3622 0.4336 0.5130 0.5736
MIDP AT 1/N 0.0005 0.0012 0.0019 0.0030 0.0040 0.0048 0.0057

PEAK POSITION IS IN CHANNEL #: 17.9618
****************************************************************************************** RESOLUTION ******************************************************************************************
TIME FOR THIS JOB: 73.43 SECONDS.

Fig. 2-7. Result sheet of RESOLUTION program
Chapter 3.  PAL Studies at Different Temperature

3.1 Apparatus

The PAL spectroscopy system for polymer free volume studies at various temperatures consists of a vacuum chamber and PAL spectrometer which was introduced in section 2.1. The vacuum sample chamber as shown in Fig. 3-1 is equipped with vacuum pump and meter, metal cooling Dewar, two heating coils, sample frame, and two thermal diode sensors (DT-470-sd, Lake Shore Cryogenics) and a temperature controller (model 805, Lake Shore Cryogenics). The good thermal contact of the sample with its copper metal frame allows the sample to cooled by dry ice and alcohol, or liquid nitrogen, and to get heat from the heating coils which current is controlled by temperature controller. Uniform and stable sample temperature is maintained by using two sensors to monitor different regions of sample (center and surface of sample). In this system the sample temperature can be kept constant between -40 °C to 200 °C, within ±0.04 °C, and the rate of change of the sample temperature also can be well controlled as desired. High vacuum system (50 mV/110 mA) also contributes to sample temperature stability. But at high temperature, two heating guns blow air to outside surface of chamber to cool down the temperature and keep
Fig. 3-1. The diagram of the sample chamber for PAL studies at different temperatures.
the detectors away from the thermal radiation damage.

The counting efficiency is important for this system, because two detectors can not be very close to the radiation source. As explained in 2.1, the optimum result is obtained from combining CsF and BaF₂ crystal detectors. For a 15 μCi ⁴²Na positron source, the coincidence count rate is about 300 cps. After system time calibration and testing by all the methods introduced in 2.3, the channel width of the multi-channel analyzer is 10.3 ps. ⁶⁰Co spectrum which is measured in same PAL measuring condition (CFDD energy windows setting are for ⁴²Na) and deconvolution of the PAL spectrum for Aluminum with same ⁴²Na source of experiments, show system resolution function is less than 230 ps. Source correction also can be determined from above procedure. One source correction (τₛ, Iₛ) was applied during the fitting procedure.

A 15 μCi ⁴²Na positron source was folded into a 7 mm square shape and sandwiched between two rectangular pieces (1 cm x 1.3 cm x 4 mm) of the polycarbonate sample and kept in the sample frame in the vacuum chamber during all of the measurements.

3.2 Experimental
The bisphenol-A polycarbonate specimens used in the investigations of free volume temperature dependence and physical aging in glass state of amorphous was from Bayer AG Company, Leverkusen, Germany. The glass transition temperature $T_g$ was determined to be 150 °C by Differential Scanning Calorimeter (DSC) at a heating rate of 20 °C per minute. This polycarbonate sample changes color, presumably due to chemical degradation when the sample temperature is taken higher than 155 °C.

Since the physical aging in glassy state of polycarbonate affects the free volume, for the PAL studies of free volume temperature dependence, starting temperature is higher than $T_g$ and for long enough time to get its equilibrium state. It took 1 hour to increase the sample temperature to 151 °C, and 2 hours to erase the history and collect the data for PAL spectrum at this temperature. Then the sample was cooled to the predefined temperature in the glass state at an average rate of 1 °C/min.. After 10 minutes for thermal equilibration, spectral data were acquired for another hour. Subsequently, at the same cooling rate the sample was cooled to the next measuring temperature, and continued this process was repeated to -5 °C. To check experiment result and obtain sufficient data points, this experiment was repeated two additional cycles, in each case
annealing at 151 °C, then cooling at the specified rate to an intermediate temperature values. These three measuring cycles totally took less than 10 hours after starting cooling down. Finally after a further annealing at 151 °C sample temperature was increased to obtain PAL spectra at temperature above $T_s$ until 165 °C.

The PAL spectra were deconvoluted from system resolution function with fixed source correction ($\tau_s$, $I_s$) and give the values of three lifetime decay $\tau_1$, $\tau_2$, $\tau_3$ and $I_1$, $I_2$, $I_3$. Over the whole temperature range $\tau_1$, $\tau_2$ varied randomly near their mean values 0.12 ns and 0.5 ns, respectively.

3.3 Results and Discussion

From the PAL investigation of polycarbonate, the o-Ps's parameters vary with temperature as shown in Figs. 3-2 and 3-3. The $\tau_s$ increases with temperature in the entire temperature range, and shows the large change of curve slope at 150 °C. This discontinuity agrees with the results from DSC showing that is the glass transition. $I_s$ also shows its feature of discontinuity at 80 °C known as temperature of sub $T_g$ secondary transition, $\beta'$ (or $\alpha^{39}$) transition, but different than $\beta$ transition, of
Fig. 3-2. Temperature dependence of $o$-Ps intensity, $I$, in polycarbonate. The location of the $\beta'$ transition is shown at $80 \, ^{\circ}C$. 
Fig. 3-3. Temperature dependence of o-Ps lifetime, \( \tau_3 \), in polycarbonate. The location of the glass transition is shown at 150 °C as well as the \( \beta' \) transition at 80 °C.
polycarbonate by previous studies. The $\beta$ and $\beta'$ transitions are probably attributed to the rotations of the carbonyl group and the two methyl groups, respectively. Since the two methyl groups are larger than the carbonyl group in size, they start to rotate at higher temperatures than the carbonyl group due to the steric hindrance.\textsuperscript{40} From the relation of the o-Ps parameter and free volume holes of polymer explained in section 1.3, it can be informed from this PAL studies that free volume hole size decreases as temperature decrease and shows the glass transition in very narrow temperature region. The number density of holes almost remains in constant until temperature below $\beta'$ transition, then it has a quite slope decrease.

From above data and using Eq. (1-26), a parameter proportional to the free volume fraction $h/C$ can be calculated. From theoretical PVT data of polycarbonate, $C$ can be obtained as 0.0272 nm$^{-3}$ by choosing a data point of free volume fraction $h_{th}$ above $T_g$ as a reference point at which PAL result $h$ is assuming equal to $h_{th}$.\textsuperscript{131} Fig. 3-4 shows both free volume fraction $h$ results of PVT theoretical and PAL measurements. The free volume decreases rapidly as temperature decreases above $T_g$, and decreases very slowly between $T_g$ and $T_{\beta'}$, then has a
Fig. 3-4. Temperature dependence of apparent free volume fraction, $h$ which is computed from Eq. (1-26) and $C=0.0272 \text{ nm}^{2}$. The solid lines are theoretical calculation of the Simha-Somcynsky free volume function.
large slope to decrease below $T_b'$. Since the free volume will relax rapidly at temperatures between $T_g$ and $T_b'$, and because it took one hour to collect a spectrum, detected free volume is smaller than it should be. The amount of decrease is proportional to the difference between the measured temperature and $\beta'$ transition. Hence, the slope of the h curve between $T_g$ and $T_b'$ is much flatter than below $T_b'$.

Fig. 3-4 shows that the free volume temperature dependence of polycarbonate does not match the theoretical prediction. The slopes above and immediately below $T_g$ of the positron data appear quite similar to the theoretical results. However, the behavior of $\tau$, near discontinuity at $T_g$, is not consistent with free volume theory. Similar effects have been observed at order-disorder transitions in materials and could reflect some change in the interchain interactions. However, the effect may alternatively be related to an apparent chemical effect (discoloration of the sample) observed in this polycarbonate sample $T=160^\circ$C, and further studies will be necessary to clarify this. Also, the change in temperature coefficient at $T_b'=80^\circ$C, observed in this measurement as well as those of other studies, is again inconsistent with free volume theory and, indeed,
with physical intuition. One possible interpretation is that this phenomenon involves a change in the coefficient C, perhaps due to the activation of some high localized molecular motion which increases the effective electron density of the matrix surrounding the holes.

3.4 Conclusions

It has demonstrated that PAL studies in polymer not only give the information about free volume variation with temperature but also separate the contributions by "hole" size and "hole" number density to free volume. PAL technique can detect \( \beta' \) transition of polycarbonate which is not able to be detected by conventional thermal analyzers, such as DSC. Furthermore, the temperature dependence of free volume of polycarbonate shows that glass transition is result of the change in slope of the "hole" size while the \( \beta' \) transition corresponds the slope change of the "hole" number density.
Chapter 4  PAL Studies of Isothermal Physical Aging

4.1 Experimental

The same PAL spectrometer system and vacuum chamber described last chapter, in section 3.2, were used for the PAL studies of isothermal physical aging of polycarbonate.

The same polycarbonate sample from Bayer AG Company as for temperature dependence studies was also used to investigate isothermal physical aging below the glass transition for long time periods. Since the goal of this investigation is to characterize the change of free volume in polycarbonate glass during physical aging, the thermal and mechanical history must be precisely controlled. Thus, for each aging experiment below $T_g$, at 42 °C, 24 °C, -10 °C, and -23 °C, the annealing temperature was held slightly higher than $T_g$, at about 154 °C. It required one hour to steadily increase the sample temperature from room temperature to the annealing temperature, where it was held for two hours at equilibrium to erase the prior thermal history. After quenching to the aging measuring temperatures in time ranging from 15 minutes (to 43 °C) to 30 minutes (to -23
°C) and a further thermal equilibrium period of 20
minutes, temperature of the entire sample was uniform and
stable. Each spectrum includes all coincident events in 4
hours. Total aging annealing times elapsed from 60 hours
(43 °C) to 150 hours (-23 °C).

The polycarbonate sample used to investigate the
short time period aging process at temperature between $T_s$
and $T_p'$ is from DSM Research BV, Geleen, with $T_s$ at 150 °C
determined by DSC. This sample also was annealed at 154
°C in vacuum chamber for 2 hours by using the same
experimental procedure. The sample was then quenched down
to the annealing temperatures (146 °C, 140 °C, 120 °C,)
with cooling at the rate of 3 °C/min. Only 3 minutes was
required to reach a uniform and stable temperature,
because of higher mobility in the sample at these high
temperatures (lower temperatures experiment time required
20-minutes). Measurements then began immediately, for
18-hours of isothermal aging. The data accumulation time
for each measuring point was only 15 minutes for first
two hours and then 2 hours for later elapsed annealing
time. To obtain a good statistical result and to test its
reliability, these PAL aging experiments at these
temperatures were repeated. Since data analysis results
from duplicates at same temperature are very much the
same, spectra of the two runs in same aging time were
summed together. Those summed spectra give the final PAL result after convolution of the data.

4.2 Results and Discussion

4.2A Long time period of isothermal aging process

Fig. 4-1, 4-2 and 4-3 show, respectively, the changes of o-Ps intensity, lifetime and free volume parameter h/C during isothermal physical aging in long time period at 42 °C, 24 °C, -10 °C, and -23 °C following a quench from 154 °C. The lifetime $\tau$, remains almost constant with aging time $t_a$, but the intensity $I$, shows a large decrease with increasing $t_a$ during isothermal annealing at temperatures far below $T_s$. Since the o-Ps intensity decreases during annealing, it appears that the number density of free volume cavities, $N$, decreases. Likewise, since the o-Ps lifetime remains constant the mean cavity size $<v_c>$ does not change. It seems that the change in the free volume $h$ during physical aging in polycarbonate involves primarily loss of holes. Again, this behavior is consistent with the previous positron study of polycarbonate\textsuperscript{31} and, in fact is consistent with observations of positron spectra in some other polymers during physical aging.\textsuperscript{45,46}
Fig. 4-1. Orthopositronium annihilation in polycarbonate during isothermal physical aging in long time period at four temperatures in the glass: 42 °C, 24 °C, -10 °C and -23 °C following a quench from the temperature 154 °C above $T_g$: o-Ps intensity, $I_\gamma$, versus aging time.
Fig. 4-2. Orthopositronium annihilation in polycarbonate during isothermal physical aging in long time period at four temperatures in the glass: 42 °C, 24 °C, -10 °C and -23 °C following a quench from the temperature 154 °C above $T_g$: o-Ps lifetime, $\tau_3$, versus aging time.
Fig. 4-3. Orthopositronium annihilation in polycarbonate during isothermal physical aging in long time period at four temperatures in the glass 42 °C, 24 °C, -10 °C and -23 °C following a quench from the temperature 154 °C above T_g: apparent fractional free volume, h/C, versus aging time.
Decreases in $I$, during aging were also observed for polystyrene$^{6}$ and polyvinylacetate.$^{31}$ For polycarbonate, the change in the mean size $<v_r>$ of free-volume "holes" is not measurable, but in previous PAL studies of PVAc the mean size $<v_r>$ also decreased as well as $N$, so $<v_r>$ changes during aging of same polymers. However, PAL studies of physical aging in polymers suggests that in general the fractional free volume decrease is primarily or partially due to a decrease in number density of holes. The mechanism by which holes are "lost" is not quite clear. It could be understood as following. The o-Ps lifetime $\tau$, only measures the mean value of $<v_r>$, not the distribution of hole sizes in a glassy polymer. The shape of the "hole" size distribution can change during annealing while $\tau$, keeps the same mean value, and this change can cause a decrease in $I$, if the smaller holes cannot trap o-Ps. In general, $I$, is proportional to both the probability of o-Ps formation and number density of free volume holes in the sample. The change in $I$, may be influenced by both factors.

From PAL studies, glassy polycarbonate has a bigger negative change during isothermal aging process than PVAc and PMMA. This observation is consistent with the mechanical results which predict that polycarbonate has a
wide aging range and higher shift rate \( \mu \) (Eq. 1-3) which increases the speed of the aging process.\(^2\)\(^3\) Also, when a specimen of polycarbonate is quenched from an equilibrium state above \( T_s \), its fractional free volume changes more rapidly than one quenched from temperature below \( T_s \). These facts can be explained by free volume theory, which says that free volume reaches its maximum value at a given temperature after a direct quench from a state above \( T_s \). At this environment, the mobility of segment movement is larger, and as well as free volume changing rate due to this large free volume in sample. From Doolittle equation to get shift rate \( \mu \), which is a parameter to describe aging rate in glassy state, with aging time \( t_s \):\(^\text{1}\)

\[
\mu(t_s) = \frac{\frac{1}{t_s} \log a(t_s)}{\frac{1}{t_s} \log a} = A \frac{\frac{1}{t_s} \log a(t_s) - \frac{1}{t_s} \log h(0)}{\frac{1}{t_s} \log a(0)}
\]  

(4-1)

where \( a(t_s) \) is a shift at \( t_s \) and \( A \) is a constant dependent on the polymer. \( h(0) \) and \( h(t_s) \) are the free volume fraction at reference time and \( t_s \). Positron results show the nonlinearity in \( \mu \), as observed in PVAc,\(^31\) which does not agree with the mechanical results which indicates that \( \mu \) is almost unity during all aging time for all
glassy polymers in their aging range those temperature is
between $T_g$ and $T_g'$.  

4.2B Isothermal aging over short time periods  

Free-volume behavior in glassy Polycarbonate is
quite different when isothermal annealing temperature
above or below $T_g'$. Fig. 4-4, 4-5 and 4-6 exhibit the
positron results of polycarbonate annealing at
temperatures 146 °C, 140 °C, and 120 °C, not far below $T_g$
and above $T_g'$ for relatively short aging period. The o-Ps
intensity, $I_1$, shows almost no change at temperatures so
close to $T_g$ and for so short period as have been observed
in long period aging and of other polymers: $I_1$ has big
negative change only when annealing at a temperature far
below $T_g$ and for long period. The o-Ps lifetime $\tau_1$ usually
does not change in those aging process as in previous PAL
studies. In Fig. 4-5, $\tau_1$ does not remain constant during
first few hours of annealing time, acting like "over
shooting" process after suddenly quench from a
equilibrium state at temperature above $T_g$: $\tau_1$ decreases in
the beginning at annealing temperature and reaches its
minimum value, then increases and keeps at certain value
between the initial value and the minimum. The magnitude
Fig. 4-4. The o-Ps intensity $I_3$ is as a function of aging time during short aging periods at 146 °C, 140 °C and 120 °C following a quench from the temperature 154 °C. The points on the $I_3$-axis are the values of $I_3$ at 154 °C.
Fig. 4-5. The o-Ps lifetime $\tau_3$ is as a function of aging time during short aging periods at 146 °C, 140 °C and 120 °C following a quench from the temperature 154 °C. Lines drawn for orientation purposes only.
Fig. 4-6. The o-Ps free volume fraction $h/C$ of polycarbonate is as a function of aging time during short aging periods at 146 °C, 140 °C and 120 °C following a quench from the temperature 154 °C. Lines drawn for orientation purposes only.
of decrease, the rate of decrease, and the rate of recovery in $\tau$, when annealing at higher temperature is significantly higher than one annealing at lower temperature. It may be explained by the relationship between the free volume and the mobility of segment motion in polymers. At high temperature, the sample has relatively large free volume, high mobility and fast changing rate of free volume, therefore, the degree of "over shooting" is large and it also recovers fast. This effect may can be seen from very detail results of previous PAL studies PVAc. Currently, Sichina reported a similar and opposite aging phenomena in polycarbonate by using Dynamic Mechanical Analysis (DMA)." The mechanical elastic modulus $E'$ increases during one-hour isothermal annealing at 130 °C after fast increasing the sample temperature from room temperature with 2 °C/min. Parallel, the free volume reaches its maximum value and then quickly relaxes to its equilibrium state. From results of that the aging process at 130 °C effect on $\beta$ transition peak in DMA, it is been know that this aging fact changes the rotational motions of the phenylene-carbonate and carbonate molecular groups. The mechanism of this behavior is still under investigation.
This short time period aging experiment was designed to study the observation of a change in slope just below \( T_g \) in free volume \(<v_r>\) temperature curve. Since every data point was obtained by first hour after only 10 minutes from the quenching, those points especially just below \( T_g \) were lower value than their equilibrium value at those temperatures. Fig. 4-7 shows the modification of temperature dependence curve of \( \tau \) from short time period aging result.

Previous PAL studies of temperature dependence in polycarbonate indicates discontinuities at 80 °C in both \( \tau \), and \( I \), curves. This discontinuity is labeled as \( \beta' \) transition which can't not been seen from simple DSC results. Since there are big aging process during isothermal annealing at temperature below 80 °C, so this transition is another sub \( T_g \) transition besides of \( \beta \) transition. Below \( T_g \) segmental motion ceases therefore no aging process is observed. Even though the behavior of this transition needs further studies, that the aging processes are different above and below this transition can be understood from free volume concepts.

4.3 Conclusions
Fig. 4-7. The o-ps lifetime, $\tau_3$, temperature dependence in polycarbonate is modified in temperature range between 120 °C and 150 °C by short period aging experiment results (open circles).
The decrease in the number density \( N \) of holes in polycarbonate during a isothermal annealing at far below \( T_g \) for long aging period, while no change in the size of free volume "hole" \(<v_f>\), is observed from previous PAL studies in polycarbonate by Hill et al.\(^45\) The change rate of free volume during annealing after quench directly from above \( T_g \) is larger than from a equilibrium state below \( T_g \). The shift rate \( \mu \) of aging process is non-unity during annealing. A series of PAL measurements of free volume in short aging period at temperature range between \( T_g' \) and \( T_g \) is performed to explain in detail the step below \( T_g \) in temperature dependence of o-Ps spectrum of polycarbonate. It shows an "over shooting" effect in \(<v_f>\) parallel to fractional free volume which could be due quick relaxation of molecules because of the relative high mobility in the specimen in this temperature region.
Chapter 5  PAL Studies under Mechanical Deformation

5.1 Apparatus and Experimental

5.1A Free Volume Tensile Strain Dependence

The PAL spectroscopy system used in studies of free volume changes in room temperature under tensile strain consists of a load frame to enable in situ PAL measurements of polymer samples under well-specified strains. This device, shown in Fig. 5-1, utilizes a strain transducer consisting of a resistance wire connected to a linear variable differential transformer by means of which the voltage measured across the wire is made proportional to the incremental strain. To minimize the experimental error of tensile strain measurement, both sides of the crimp distances were measured and their average was taken as sample length. The sample cramps were adjusted so that the two distances are as close to each other as possible to ensure parallel cramping. For directly results comparison of mechanical and positron measurements, a typical Instron specimen, in dog-bone shape as shown in Fig. 5-1, was directly used in positron measurements. Area of PAL measurement is 6 mm x 3 mm. Therefore the $^{22}$Na positron source was small in size, NaCl
Fig. 5-1. Sample load frame for tensile strain measurements and a dog-bone shaped sample of Instron.
being deposited on a point less than 1.5 mm in diameter. The Aluminum foil covering the source was 6 mm x 6 mm.

Two different PAL spectrometers were used in this investigation for two experiments on tensile strain dependence of free volume. Spectrometer A used the same basic devices as the one for temperature studies (see 3-1), but was a completely individual spectrometer with a different shape of system time resolution function. The FWHM of $^{60}$Co spectrum for this spectrometer was 230 ps and its high detection efficiency made it possible to using very weak positron sources, whose strength was less 5 $\mu$Ci, to minimize the effect of radiation damage on the studies of free volume. Spectrometer B, used two BaF$_2$ conical crystal detectors, each with diameters of 1.5 and 2.5 cm and length of 2.5 cm, instead one of BaF$_2$ and one of CsF crystals in spectrometer A. This system had very good time resolution function, the FWHM being less than 180 ps. A source strength of 4 $\mu$Ci of $^{22}$Na was used for positron measurements in spectrometer B. In data analysis of PAL spectra from spectrometer A by using PATFIT-88 program, one component of source correction was fixed as $\tau_s$ equal to 0.2 ns. Two components of source correction 0.188 ns and 0.565 ns in $\tau_s$ were fixed for spectra from spectrometer B.
Commercially produced polycarbonate sheets from Mobay Company were used in these tensile strain studies. The glass transition temperature was determined to be 150 °C by DSC at heating rate 20 °C/min. The two measurements, using two different spectrometers followed different mechanical deformation program I and II, as shown in Fig. 5-2, using PAL spectrometers A and B, respectively. In program I, measurements was done by spectrometer A and called experiment I(A). A well-aged sample was directly used in PAL measurements. A pair of dog-bone shaped specimens was sited on sample load frame, and tensile strain was gradually increased from 0 to 7% in steps of less than 1%. At each strain step, a one-hour PAL spectrum was obtained. The necking point was observed to be higher than 7%. Experiment I(B) used a new sample pair, in this run the o-Ps parameters in the sample necking region were measured after release of strain. In the experiment following program II using spectrometer B, the thermal and mechanical history of the sample was well controlled. The sample was annealed at 120 °C for 24 hours in a vacuum oven and then slowly cooled down to room temperature and kept in vacuum for four weeks. For every data point up to 7%, a new pair of specimens without any previous strain history was measured at zero strain for an original reference point, then measured
Fig. 5-2. Shown are two test programs of tensile strain dependence of polycarbonate by using PAL spectrometers A and B respectively. In program I, one pair of samples was used for whole test up to 7%. A new sample pair was used for every strain level test in program II.
under strain. Monitoring o-Ps parameters of specimens when strain free established the reliability of the system and eliminated effect of any previous aging process. Since spectrometer B has lower count rate than A, the accumulation time for every data point is 1.5 hour for the equally good statistical results when almost the same strength of source as in experiment I(A) was used. Every continually dark step line shown in Fig. 5-2, program II, represents the mechanical treatment on a single pair of specimens.

5.1B Free Volume Compressional Strain Dependence

In investigating the behavior of free volume with compressional strain, spectrometer B was used with the very high system time resolution function, described in 5.1A. A simple compression cell shown in Fig. 5-3 was able to keep the sample under a fixed mount of linear compressional strain. The sample was polymethyl methacrylate (PMMA), a commercial product of Lucite sheet with 11 mm thickness from DuPont Company. The glass-transition temperature of this PMMA sample is 125 °C determined by DSC with heating rate 20 °C/min. Two pieces of rectangular PMMA sample 7 mm x 7 mm x 11 mm, sandwiched around a foil covered 15 μCi $^{22}$Na source, were loaded on the compression sample cell. The PAL spectrum
Fig. 5-3. Sample load cell for linear compression test.
for the compression free sample found as a reference point. The compression on the sample was gradually increased from zero to 7%, i.e. the strain decreased to -7 %. Further compression caused a twist deformation in sample. For each compressional strain, an half hour was required to obtain a PAL spectrum. The PAL measurement procedure was repeated by using a new pair of PMMA samples and weaker $^{23}$Na radiation source with strength only 4 μCi. In this case, one and an half hours was needed to record a PAL spectrum at each data point.

5.2 Results and Discussion
5.2A Tensile Strain Dependence on Polycarbonate

From tensile strain experiment I, PAL spectra were determined on a well-aged polycarbonate specimen at T=25 °C subjected to increasing tensile strain up to 7 %. The results from experiments of program I(A) and I(B) are shown in Figs. 5-4 to 5-6, and Figs. 5-7 to 5-9, respectively. As evidence in Figs. 5-4 and 5-5, and Figs. 5-7 and 5-8, application of strains up to a level of around 4 % produces in increase in $\tau_1$, and hence in $<v_1>$, but little change in I, i.e. in number N of holes. Above 4% strain, no further variation in $<v_2>$ or in N is
Fig. 5-4. The o-Ps intensity, $I_0$, of polycarbonate as a function of sequential incremental tensile strain under program I(A).
Fig. 5-5. The o-Ps lifetime, $\tau_3$, of polycarbonate as a function of sequential incremental tensile strain under program I(A). Lines drawn for orientation purposes only.
Fig. 5-6. The free volume, $h/C = I_1 \langle v_r \rangle$, of polycarbonate as a function of sequential incremental tensile strain under program I(A). Lines drawn for orientation purposes only.
Fig. 5-7. The o-Ps intensity, $I_3$, of polycarbonate as a function of sequential incremental tensile strain under program I(B). Open circles present the values of o-Ps inside the necking region.
Fig. 5-8. The o-Ps lifetime, $\tau_3$, of polycarbonate as a function of sequential incremental tensile strain under program I(B). Open circles present the values of o-Ps inside the necking region. Lines drawn for orientation purposes only.
Fig. 5-9. The free volume fraction h/C of polycarbonate as a function of sequential incremental tensile strain under program I(B). Open circles present the values of o-Ps inside the necking region. Lines drawn for orientation purposes only.
apparent. The corresponding free volume fraction h, computed from the positron annihilation data, which parallels the behavior of \(<v,>_z\), is exhibited in Fig. 5-6 and Fig. 5-9. At 8\% strain, two values of \(\tau, I\), and \(h/C\) are shown in Fig. 5-7 to 5-9. These represent data taken, respectively, outside the necking area of the specimen under 8 \% strain and inside the necking area after releasing the strain. There appears to be a distinct decrease in the \(o-Ps\) free volume in the necking region. However, it is interesting to remark that the free volume in the necking region remains larger than that of the initial, undeformed well-aged polycarbonate. It is pertinent to remark that the stress-strain curve, in Fig. 5-10, for this polycarbonate specimen shows typical macroscopic yield behavior at 6\% strain and the linear region is up to a value around 4 \%, at which point a broken line indicates on this curve the point in the pre-yielding region at which leveling off occurs in the strain-dependence of the free volume determined from the positron annihilation spectra.

Since large strains were involved, and this increases the segmental mobility,\(^\text{40}\) experiment II was designed to avoid the physical aging occurring under previous strains, that could affect the PAL strain dependence results. For every PAL test, a new well-
Fig. 5-10. Tensile stress-strain curve of polycarbonate sample from Instron used in these positron studies under applied strain. The broken line indicates the approximate location of the point at 4% strain where the apparent leveling-off occurs in the strain-dependence of free volume.
annealed polycarbonate specimen without any previous strain or other mechanical history was used. Figs. 5-11, 5-12 and 5-13 show the results which are similar to experiment I(A). The values of \( r_i \), i.e. \( <v_r> \), and h increase up to 4% strain and then level off; the corresponding I, almost remains constant during the whole strain investigation range. It should be pointed out that the increase of h in measurements with tensile strain of zero to 4% is not significantly higher than that in experiment I(A). Since a complete strain dependence experiment A only takes about 15 hours and free volume aging process under tensile strain is very slow (which will be shown next chapter), it is safe to ignore any physical aging effect in strain dependence studies in a short period.

Several studies of the properties of polycarbonate show distinctive modification in the pre-yielding regime. First, measurements of the bulk volume are reported to show an increase with tensile strain, \( \varepsilon \), up to 4.0%, at which point the volume begins to level off and decrease with further strain.\(^{17}\) The initial volume increase is numerically consistent with that anticipated since the Poisson's ratio, \( \nu \), of polycarbonate, is smaller than 0.5.\(^{2,40}\)
Fig. 5-11. The relative variations of o-Ps intensity, $I_3 - I_3(0)$, in polycarbonate under tensile strain for experimental programs I(A) and II. $I_3(0)$ is the initial value of $I_3$ prior to the application of strain.
Fig. 5-12. The relative variations of o-Ps intensity, $\tau_3 - \tau_3(0)$, in polycarbonate under tensile strain for experimental programs I(A) and II. $\tau_3(0)$ is the initial value of $\tau_3$ prior to the application of strain.
Fig. 5-13. The relative variations of o-Ps intensity, $(h/C)-(h/C)(0)$, in polycarbonate under tensile strain for experimental programs I(A) and II. $(h/C)(0)$ is the initial value of $h/C$ prior to the application of strain.
\[
\frac{\Delta V}{V_0} = (1 - 2\nu)\varepsilon
\]  

(5-1)

For bisphenol-A polycarbonate, \(\nu=0.385\). Even though the relative increase in fractional free volume with strain, measured by the o-Ps annihilation spectrum, i.e. \(\Delta h/h_0\), is substantially larger than the fractional increase in bulk volume, \(\Delta V/V_0\), the absolute increase in the free volume \(\Delta V_f/V_0\) is slightly less than that in bulk volume as shown in Fig. 5-14. This indicates that the increase of the bulk volume subject to the tensile strain is primarily due to the increase of the free volume.

Second, a study\(^4\) of the so-called strain-induced "rejuvenation" or reversal of the physical aging process in the mechanical properties of polycarbonate found characteristic changes when the applied strain reaches 4%. Specifically, the storage and loss tensile moduli, \(E'\) and \(E''\), were measured at 10 Hz on well-aged polycarbonate during stress relaxation at static tensile strains from 1.2 to 6.5 % at 50 °C. It was observed that \(E'\) and \(1/E''\) decrease when the static strain is applied and then increase monotonically with time. This behavior was attributed to an initial increase in segmental mobility with applied strain, followed by physical aging. The magnitude of these changes increases uniformly with the
Fig. 5-14. The absolute increase in free volume in polycarbonate, \( \Delta V_f/V_o \), as functions of applied strain is compared to the fractional increase in bulk volume, \( \Delta V/V_o \), from ref. 47.
applied strain until it becomes 4 %, and then levels off. Clearly, such an observation suggests that the free volume increases with strain up to 4 % and then becomes constant, and hence is quite consistent with these positron results.

Finally, a comment can be derived on the positron data in the necking region. Here, there is a decrease in the measured free volume fraction, h/C, compared to the plateau value reached in the pre-yield region. This is consistent with the known development of extensive interchain orientation and macroscopic densification which accompanies the necking phenomenon. However it is noteworthy that h/C remains above the value measured for well-aged amorphous polycarbonate. This supports the idea that cold-drawing may decrease the macroscopic densities because of enhanced interchain orientation and packing, and yet increase the free volume. The latter concept has been advanced on the basis of the observation that the rate of volume relaxation is enhanced by cold drawing.

5.2B Compression Dependence of PMMA

The extensive PAL studies on free volume of polymer under mechanical deformation was next focused on testing the free volume compressional strain dependence property of PMMA. Figs. 5-15, 5-16 and 5-17 show the results of
Fig. 5-15. The $o$-Ps intensity $I$, in PMMA as a function of static applied compressional strain $-\varepsilon$. Shown are two runs.
Fig. 5-16. The o-Ps lifetime $\tau_3$ in PMMA as a function of static applied compressional strain $-\varepsilon$. Shown are two runs.
Fig. 5-17. The free volume fraction $h/C$ in PMMA as a function of static applied compressional strain $-\varepsilon$. Shown are two runs.
two PAL measurements on a well-aged PMMA sample subjected uniaxial compress up to 7%. Closed circles show the first run and open circles the second one which used a weaker positron source. Results of the two runs agree with each other, with a very small standard deviation, less 1%. Values of $r_1$ and hence of $<v_r>$ decrease under compression up to a level between 3% to 4% and do not change vary much above 4% compression. $I_3$, i.e. $N$ does not change much in the whole compressional range. It appears that the free volume fraction $h$ parallels the behavior of the calculated $<v_r>$. Two individual compressional dependence experiments, one finished in 5-hour period and another in 15 hours, have very similar results. Again, even under this large mechanical compression, physical aging caused by previous compressional loading still does not much influence PAL results on mechanical deformation dependence. As later explained, physical aging in free volume recovery is mainly affected by $N$ and not $<v_r>$. However, among the properties of mechanical deformation dependence, tensile strain, $\varepsilon$, and compressional strain, $-\varepsilon$, only $<v_r>$ is instantaneously sensitive with applied mechanical deformation.

Compressional deformation is an anti-tensile strain
Fig. 5-18. The percent decrease in fractional free volume in PMMA with applied compression, $\Delta h/h_o$, measured from $\alpha$-Ps annihilation, is compared with the percent decrease in bulk volume, $\Delta V/V_o$, computed from Poisson's ratio via Eq. (5-1).
mechanical deformation. The application of Eq. 5-1 to compression test is suitable with a Poisson's ratio, $\nu$, of PMMA, smaller than 0.5. For PMMA, $\nu = 0.33^\circ$. Fig. 5-18 exhibits the comparison of the relative decrease in free volume fraction $h$ with absolute value of compressional strain and the decrease in bulk volume $V$ which from theoretical calculation. Again, the relative decrease in $\Delta h/h_0$ from PAL data is much large than that of $\Delta v/V_0$, but the absolute decrease in the free volume is less than that in the bulk volume.

5.3 Conclusions

PAL measurements on polymer under isothermal condition indicate that the free volume changes with a small applied strain, in agreement with mechanical results. The free volume "hole" size $\langle v_\rangle$ and its fraction $h$ in polycarbonate increase with applied tensile strain up to 4%, after which they level off. This is consistent with observed enhancement of the aging rate of the mechanical properties with observed enhancement of the aging rate. In the necking region, the free volume decrease but remains higher than the value for well-aged amorphous polycarbonate. The free volume levels of PMMA in $\langle v_\rangle$ and $h$ decrease on application of static
compressional strain up to a absolute value of 4%, then level off. Both tensile and compressional strain dependence experiments show that the number density of holes is not sensitive to suddenly applied strain. The changes in free volume under mechanical strain are the main contribution to the change in bulk volume.
Chapter 6  PAL Studies of Physical Aging Process under Applied Tensile Strain and After Release of Strain

6.1 Experimental

PAL studies of the free volume changes in well-annealed polycarbonate subjected to static tensile strain at 25 °C were carried out with the same PAL spectroscopic system A described in 5.1A and used for tensile strain dependence studies of polycarbonate. The sample specimen is also in dog-bone shape and is the same polycarbonate sample as used in tensile strain dependence studies from Mobay Company. A weak $^{22}$Na positron source is used to reduce the damage that could result from long time period exposure to radiation. For every data point, the accumulation time is four hours and every spectrum has 4.5 million counts for good statistics.

Since it was a study of physical aging under static applied strain, the previous free volume condition of the sample should be known in advance. The sample used in the PAL aging experiment was first tested to determine the aging process in this "old" sample, to see if radiation damage was apparent after radiation exposure for 3 days under isothermal and strain free conditions.
A well-aged sample was sited on load frame without any strain and was tested by PAL measurements to get original initial value of free volume as reference point. Recording of PAL spectra was started immediately after application of static tensile strain of 3%, one spectra were recorded for 200 hours of stress relaxation and physical aging. Then the applied strain was released and physical aging was continually monitored for 140 more hours.

6.2 Results and Discussions

The sample used was a well-annealed polycarbonate sample previously used in PAL studies of tensile strain dependence. This sample had reached a state close to equilibrium, the results of PAL pre-testing show no significant change in o-Ps parameters during three days. The whole physical aging and stress relaxation process under static tensile strain and release of the strain was monitored by PAL measurements. Figs. 6-1, 6-2 and 6-3 show the variation of \( I_3 \), \( \tau_3 \), and the fractional free volume \( \text{h} \) during aging process under 3% tensile strain and after releasing the strain. The horizontal line indicates the initial values for the unstrained specimen. Application of strain causes an initial increase of \( \tau_3 \), and hence \( \langle v_3 \rangle \), while \( I_3 \), and hence \( N \), remain constant.
Fig. 6-1. Time-evolution of o-Ps intensity, $I_3$, of polycarbonate during isothermal physical aging at 24 °C, and 3% applied tensile strain and after release the strain. Closed circles represent data taken under applied strain; open circles are values after the release of strain; the horizontal broken line indicates the initial values of $I_3$ prior to the application of strain.
Fig. 6-2. Time-evolution of o-Ps lifetime, $\tau$, of polycarbonate during isothermal physical aging at 24 °C, and 3% applied tensile strain and after release the strain. closed circles represent data taken under applied strain; open circles are values after the release of strain; the horizontal broken line indicates the initial values of $\tau$, prior to the application of strain.
Fig. 6-3. Time-evolution of free volume fraction h/C of polycarbonate during isothermal physical aging at 24 °C, and 3% applied tensile strain and after release the strain. Closed circles represent data taken under applied strain; open circles are values after the release of strain; the horizontal broken line indicates the initial values of h/C prior to the application of strain.
within experimental error. During the physical aging process accompanying stress relaxation of polycarbonate under applied tensile strain, both $\tau$, and $I$, decrease. In this 200-hour physical aging period, $\tau$, decreases by about 0.6% (hence $<\nu>$ decreases 1.1%) and $I$, decreases 2.0%. As a result of these decreases in both $<\nu>$ and $N$, the fractional free volume $h$ decreases about 1.7%. Release of the tensile strain causes an instantaneous decrease in $\tau$, with no sudden change in $I$, $\tau$, returns back to its unstrained initial value and $h$ drops to even lower than its initial value. Subsequently both $\tau$, and $I$, decrease about 0.7% and 1.3%, respectively, during the next 140-hour period after releasing the strain. As a consequence, $h$ decrease 1.6%. There is a continual decrease of $h$ in both aging periods (under applied static tensile strain and after release strain) until after 340 hours, $h$ is smaller than it was initially.

The discontinuity in both $\nu$-Ps lifetime $\tau$, and fractional free volume $h$ when tensile strain is applied and when it is released agrees with the result of PAL studies of free volume tensile strain dependence of polycarbonate, which is described in chapter 5.

Clearly, the application of strain to a
well-annealed polycarbonate specimen has reactivated the aging process. The fractional free volume increases by subject a static tensile strain due to the increase in volume of free volume "holes". The experiment shows that h decreases and the physical aging resumes in this sample after applied strain as predicted by free volume theory: increasing free volume increases the mobility of segment movement in polymer and further increases the free volume changing rate β. Further aging process after releasing the strain has been observed even when h is below the unstrained initial value. The decrease in h throughout the duration of this experiment, under strain and after release of strain, involves not only τ, and also a large change in I,. This observation implies that h decreases mainly because of physical aging process, not only a just stress relaxation in free volume holes. The phenomenon of involving change of I,, (i.e. N) during physical aging process also has been observed from isothermal aging experiments in polycarbonate and positron measurements in other polymers. However, its mechanism needs further research.

The mechanism by which the fractional free volume decreases to levels below those of a well-annealed polycarbonate is unclear. It is interesting to note,
however, that Legrand et al.\textsuperscript{50} have reported a decrease in the bulk volume of a polycarbonate specimen subjected to a very similar aging history at 3 % strain and subsequent strain recovery. The implication of these observations is that prolonged tensile strain permits a loss of free volume through a progressive reorientation and more efficient packing of chains. In this regard, it is relevant to remark that in cold-drawn polycarbonate, both the density and the density fluctuations increase. Also, despite the densification, the free volume shows an enhanced rate of relaxation. It was inferred that cold drawing results in an increase in the free volume fraction.\textsuperscript{51,52} It has also been suggested that the densification reported at strain above 3.5%, but below the yield point in polycarbonate, may be due to local chain orientation.

It is interesting to note that the absolute decrease in magnitude of free volume $\Delta V/V_o$ in polycarbonate during application of strain and after release of the strain is less than that of bulk volume $\Delta V/V_o$ as shown in Fig. 6-4.

Finally, it is useful to note from this aging experiment that neither o-Ps parameters and nor free volume fraction have any measurable progressive change during the first 15 hours of aging and stress relaxation. This is very significant for the PAL measurements of free
Fig. 6-4. The percent decrease in free volume of polycarbonate during physical aging under static strain $\Delta V_f/V_o$, measured from PAL spectra, is compared with the percent decrease in bulk volume, $\Delta V/V_o$, studied by Legrand et al.\textsuperscript{6-1}
volume strain dependence reported in the previous chapter, in which an effort had been made to avoid the influence of physical aging and stress relaxation on the PAL strain dependence results. Even for a longer experiment period than 15 hours, since the aging process is mainly caused by the change in $N$, not $\tau_s$, the sensitivity of $\tau_s$ to applied strain is still valid.

6.3 Conclusions

The o-Ps spectrum of polycarbonate subjected to long-term aging at 3% strain, followed by further aging during strain recovery indicates that the application of strain reactivates the physical aging in a well-annealed polycarbonate specimen, and that there is a negative change of free volume (densification). This is consistent with literature observations of a negative increment of bulk volume of specimens subjected to a similar mechanical history. It has been further observed that the average size of a free volume hole $\langle v_f \rangle$ is sensitive to applied strain regardless of previous strain loading history.
Chapter 7  PAL-Momentum Correlation

7.1 Apparatus

PAL-momentum correlation is the combination of a PAL spectrometer and an ACAR spectrometer to simultaneously measure the lifetime of position and the angle between the directions of the two gamma rays resulting from the annihilation of the positron with an electron in sample. Fig. 7-1 shows the experimental arrangement of PAL-momentum correlation measurement system. This combined system consists of a 30-cm-diameter NaI scintillate Anger camera, A, a Pho/Gamma HP Scintillation Camera System from Nuclear-Chicago Company, and two 5-cm-diameter and 5-cm-long cylindrical CsF detectors, B and C. The PAL spectrometer includes two detectors B and C, and works in a way similar to one described in the section 2.1. $^{22}$Na was used as the positron radiation source, and detector C, located close to the source, detects the $\gamma$-rays with energy of 1.27 Mev to provide the signal of the positron's "birth" time, while detector B detects one of a pair annihilation $\gamma$-rays with energy of 0.511 Mev to provide the signal of the positron's annihilation time. In this arrangement, PAL and ACAR spectrometers share the same detector B to correlate the
lifetime and momentum correlation measurements. Detector B detects one of annihilated γ-rays to provide the positron "death"-time signal for the lifetime measurement as well as the coincident signal (with the Anger camera) as the reference direction for the angular measurement. While detector B detects one γ-ray, camera A produces a γ-analog pulse as well as a pulse E proportional to the energy it receives from the other annihilation γ-ray. The direction of the first γ-ray is restricted by a horizontal slit in front of detector B. The angle between this γ-ray and the other one is determined by the magnitude of γ-analog pulse, which is proportional to vertical coordinate of the point of interaction in the camera. Three signals—the lifetime signal from detectors B and C, the ACAR signal from detector B and camera A, and a gate signal produced when each detector records the proper energy—are sent as a time-ordered series of pulses to the multi-channel analyzer (MCA). The first two are digitized and stored as a 2 dimensional array in the computer's memory. The whole operation is controlled by a computer.

Fig. 7-2 shows the device arrangement in a block diagram. The Anger camera produces four negative pulses,
Fig. 7-1. PAL-ACAR correlation system
X, X, Y, and Y, whose amplitudes depend on the x and y coordinates of the γ-ray interaction in the camera. The sum of all these outputs is independent of positron; it gives the energy, E, received by the camera. The pulse amplitude's difference (Y - Y = Y, or X - X = X) determines the γ-ray received position along the Y or X axis; the axis origin is the center of the camera. In this system we measure only in one dimension, momentum along Y. Dual sum and invert amplifiers (DS&IA) determine Y - Y, to generate the Y-analog pulse stated before. These also are used to add the pulses Y, Y, X, and X, to produce the energy pulse needed for the gate signal. Since there is 1 us internal delay in TSCA for the gate signal E, an adjustable Delay circuit makes the Y-analog pulse reach the Linear Gate and Stretcher (LG&S) almost at the same time as the E gate pulse does. Since LG&S requires a positive input, the Y-analog pulses follow two paths. One path goes directly through LG&S gated by the E, logic pulse to input 1 of the Multiplexer; the other path goes through a DS&IA unit and another LG&S to input 2. This provides a way to distinguish between the negative Y-analog pulses from the lower half of camera and the positive Y-analog pulses from the upper half. A positive Y pulse produces a positive pulse at input 1, and a
B,C: CsF Detector  
TAC: Time to Amplitude Converter  
M: Multiplexer  
DS&IA: Dual Sum and Invert Amplifier  
LA: Linear Amplifier  
LD: Logic Delay  
G&DG: Gate & Delay Generator  
CFD: Constant Fraction  
LG&S: linear Gate and Stretcher Discriminator  
MCB: Multi-Channel Buffer

Fig. 7-2. Block diagram of PAL-ACAR correlation system
negative pulse (because of the invert) at input 2; a negative Y pulse does the opposite. The multiplexer causes the information to be stored in one 512-by-512-channel block in 2D-memory or the other block, depending on which input receives a positive pulse. Thus one block stores lifetimes correlated with the lower half of the camera, and the other block stores lifetime correlated with the upper half of the camera. Since these two LG&S modules are gated by the E, pulse, the Y-analog pulses are accepted by Multiplexer only if they originate from γ-ray with energy of about 0.511 Mev. Therefore, this function completes the discrimination of camera output pulses. Two Linear Amplifiers (LA) in both paths adjust the analog pulse's amplitude below 5 volts when finally reach the 2D MCA and to balance the Y unit scales on both upper and lower half camera.

In contrast to the usual arrangement, the PAL spectrometer in this correlation system uses the 1.27 Mev nuclear γ-ray as the stop signal rather than the start signal for input of the Time to Amplitude Converter (TAC). This make it possible to achieve a high counting rate in detector C without saturation of the TAC, whose dead time is in the order of 1 μs. A long delay cable used here switches the time orders of two pulses, and
delays the pulse in time, \( t_o \), to reach TAC, which presents the "birth" time of positron far later than the pulse for annihilation time of positron. The PAL original spectra from this system are contrast spectra in time axis \( t_o-t \), from one of usual PAL spectrometer \( t \). Optional purpose of LA model in this PAL spectrometer is also to keep the amplitude of lifetime pulse \( r \) in input to 2D MCA lower than 5 volts.

The PAL and ACAR spectrometers individually generate two pulses which present two different pieces of information, lifetime \( r \) and momentum \( P \), from a single e-e' annihilation event. The following is a summary of this system, which combines two one-dimensional analog pulses \( r \) and \( p \). These are digitized and stored in a two-dimensional array. Two Logical Delay (LD) circuits equalize the total time which pulses spend to travel through PAL and ACAR spectrometers. Three modules of Gate & Delay Generators (G&DG), separately, provide three coincidence pulses in time delayed by 1 \( \mu s \), 15 \( \mu s \) and 30 \( \mu s \). After a model of DS&IA, the Multi-Channel Buffer (MCB), model 918A from EG&G Ortec, working as a 2D-MCA receives three 1-us-width pulses in sequence as shown in Fig. 7-2: the first pulse is the \( p \) analog pulse from the camera, and the second is the \( r \) analog pulse from TAC,
and third pulse with fixed amplitude 7 volts is a gate pulse generated when the energy pulses from all three detectors are in the required energy ranges. The digitized information about the first two then is used to locate the correct position in two 512-by-512 array (for positive and negative $\gamma$-analog pulses, respectively) in MCB and to increment the number stored at that position, as in any two-dimensional MCA. A personal computer with installed interface card connected with MCB controls MCB to collect the 2D data and continually read a 2k data block from MCB's memory to its own memory.

7.2 Improvement of Data Acquisition Rate

The usual geometrical arrangement in ACAR is to keep camera A and detector B far away from the radiation source to achieve good angular resolution. For a practical instrument, a high strength radiation source is usually used to get high count rate. Therefore, the radiation damage in polymer sample under very strong radiation exposure or for too long exposure period limits the application of this technique in polymer characterization. A combined PAL and ACAR correlation measurement has even lower detecting efficiency than a single ACAR system. Therefore, some compromises in both
time and angular resolution have been made to increase counting efficiency.

To use the full camera, both positive and negative $\gamma$-analog pulses were processed, this can double the count rate. The use of the MCB with Multiplexer solves the difficulty of collecting both positive and negative $\gamma$-analog pulses in a positive-pulse input. Further efficiency is gained by using two large CsF crystals for detectors B and C used to increase the solid angle area and the probability of a $\gamma$-ray interaction in the long length of the crystal.

A double slit of lead brick was placed front of detector B instead of one slit shown in Fig. 7-1, to double the counting rate. For having two reference directions in angular correlation measurement, this results in a two-peak momentum distribution detected by camera. Fig. 7-3 shows the two slits separated by 70 mrad as seen from the source. Thus the $\gamma$-analog pulses from the Anger camera yield two angular distributions, one for each slit; one of these is detected as positive $\gamma$-analog pulses from the upper half of the camera, the other as negative $\gamma$-analog pulses from the lower half.

As stated early in this chapter, a reversal of a time order between positron "birth" and "death" time signals to as start and stop signals of TAC is used in
the PAL spectrometer. It is an effective way to improve the count rate by one or two orders. Model TAC 566 from EG&G Ortec used in this system is selected for 50 ns full scale time conversion range. But its reset time is 1 μs under this work condition after "overrange" (which means stop signal does not occur within 50 ns after a valid-start signal). To maximize the counting rate, detector C for the 1.27 Mev γ-ray runs at about 10^6 cps. But detector B is far away from source and the detector count rate is as low as ten to hundreds per-second. Thus, the overrange is practically avoided by using detector B for start signal.

7.3 Supporting Software

The PAL-ACAR correlation system is controlled by a personal computer. Some commercial software and programs written here for this system are used for controlling and data analysis.

7.3A Control and Acquisition

The computer can give commands to control MCB automatically in collecting and in storing the data. For every operation done by MCB, the computer has single command. But for convenience, a commercial program STREAMER.EXE provided with the MCB model from EG&G Ortec
Fig. 7-3. Geometry of double slits and two-peak momentum distribution on whole Anger camera range
to computer hard disk. All steps as shown in Fig. 7-4 for a usual measurement can be done by running this single program. A complete flow chart for this PAL-ACAR measurement is shown in Fig. 7-5.

Besides using STREAMER.EXE and the usage flow chart, single commands can be used as one desires. These are defined in the manuals of MCB, for MCB.EXE in MCB working mode.

7.3B Data Analysis

After a PAL-ACAR measurement, a completed data file is stored in computer memory. It only records every detected lifetime-momentum correlation event, and always has 2k events pair as data count unit in this file, which means the total count in this file is always a multiple of 2K. Other commercial software HISTO.EXE completes 2D-MCA's job, reading the raw data file and creating a 2D-data array 1024-by-1024. Using this program, one runs HISTO.EXE, then types the raw data file name and the 2D-data array file name.

A group of programs written in FORTRAN, BASIC, and Turbo BASIC languages completes the 2D-data analysis; showing lifetime-momentum (P,r) 2D spectrum, P-dependent PAL spectra, and r dependent momentum spectra,
deconvolution of the p or $\tau$ spectra to get radius of free volume holes,... Fig. 7-6 is a complete flow chart for data analysis. Fig. 7-7 shows a 2D spectrum of PMMA sample from the data process by using group "1" software in Fig. 7-6.

7.4 System Calibration

The PAL system resolution function and calibration have been discussed in sections 2.1 and 2.3. In general all methods used to determine system time resolution function and calibrate the system apply to PAL-ACAR correlation. Since the detector for start signal (0.511 Mev-$\gamma$-rays) is kept far away from the source, the count rate is very low and the method of using long cable is more practical than other calibration methods. For MCB and Multiplexer, final maximum (8 volts) conversion is 512 channels, and $\tau$ pulses are smaller than 5 volts. From previous studies, whole ranges of PAL spectra of glass polymer require no longer than 20 nsec. The PAL software PCA for PAL one dimension measurement always can be used to closely monitor the change of $\tau$-pulse during the adjustment of pulse amplitude. But the final channel time determination only after read HISTO output 2D file,
SYSTEM SETUP

1 - Set a preset real time for acquiring data
2 - Set a present number of data blocks for acquisition
3 - Clear any previously set presets
4 - Name the output file
5 - Begin the data acquisition
6 - Quit the program

Which - 6

Fig. 7-4. STREAMER.EXE program
Reset MCB
Load STREAMER.EXE
Reset system "3"

Input:
- acquisition time* "1" or
- number of data blocks "2" file name "4"

Start data acquisition "5"

* The time should be set longer than one for accumulating 2K data pairs

Fig. 7-5. Flow chart for control of data acquisition
and the difference of $\tau$-peak positions in 2D file for two PAL-ACAR measurements in using two different length delay cables.

The system angular resolution function can be estimated from its geometrical arrangement. The camera has geometrical resolution 5 mm and it is 2 meters away from the source. The width of the slit in front of the CsF detector B is 1 mm, and detector B is 40 cm away from the source. The intrinsic instrumentation resolution function is 2.5 mrad, and the system angular resolution function is 3.5 mrad considering the sample thickness as well. It has been noticed that the effect of positron motion on resolution at room temperature is less 1%. So the system angular resolution is mainly determined by the intrinsic instrumental resolution function:

$$F_{WHM} = \sqrt{R_i^2 + R_?^2}$$ (7-1)

where $R_i$ and $R_?$ are the intrinsic instrumental angular resolution function for camera A and detector B. Measuring the FWHM of pure quartz spectrum also gives the actual system angular resolution function; it is only slightly higher than the one calculated from Eq. (7-1).
Fig. 7-6. Flow chart for 2d-data analysis
Fig. 7-7. A PAL-momentum correlation 2D spectrum of PMMA sample.
A simple way to calibrate the momentum channel is to directly count the p-channel difference between the two peaks in HISTC output 2D file, which corresponds to two slits having 70 mrad separation. Also, it can be done by moving the camera vertically to get 2D-spectra when the camera is in a different position relative to source and detector B, and calculating from the change in peak position.

Table 7-1 shows the condition of present PAL-ACAR system.

7.5 Experiments and Results

A preliminary test was made on polymer sample of PMMA, a 5.5-mm-thick Lucite Sheet from Du Pond Company, and cut in a 1.5-cm square shape. The $^{22}$Na positron source was about 60 $\mu$Ci strength and covered by aluminium foil. The interfaces between the sample and sandwiched source foil are parallel to the x-axis of camera and slit. The measurements were done with less than the final system setting efficiency which is described in Table 7-1. The total number of lifetime-momentum correlation events was of $10^6$, recorded over a time of five weeks in five runs. The 2D spectral file was created by running a summation program ADD-2D.FOR on five spectra, the procedure of which was detailed in 7-3.
The 2D spectrum with $10^6$ counts was separated into three lifetime curves A, B, and C. Each of them contains about 300,000 counts. Curve A was correlated with angles between -2.2 and +2.2 mrad, curve C was with angles of magnitude greater than 13.2 mrad, and the third curve B was with angles in between. Analysis of the overall Table lifetime distribution (the sum of A, B and C) into three components following the Lifetime Analysis Data Process program (in Fig. 7-6), gave values of 120 ps and 450 ps for $\tau_1$ and $\tau_2$, respectively. The results of the individual lifetime spectral deconvolution with fixed $\tau_1$ and $\tau_2$ in these values are shown in Table 7-2 for other o-Ps parameters.

The only clear conclusion is that such measurements can give statistically significant results. $I_1$ decreases about 20.2 % with angle and $I_2$, about 9.2 % and $\tau$, increases about 6.6 %. The decrease in $I_1$ with angle is statistically significant and also surprising, in view of the accepted identification of the long-lived component with o-Ps, and the belief that pickup of o-Ps would be associated with higher observed momentum. The free volume quantity $h$ can be obtained from Eq. (1-26) and decreases with momentum.
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>positron source</td>
<td>60 $\mu$Ci of $^{22}$Na</td>
</tr>
<tr>
<td>&quot;start&quot; signal detector</td>
<td>B / for 0.511 MeV $\gamma$-ray</td>
</tr>
<tr>
<td>&quot;stop&quot; signal detector</td>
<td>C / for 1.27 MeV $\gamma$-ray</td>
</tr>
<tr>
<td>window $\Delta E/E$ (B)</td>
<td>$&gt;100%$</td>
</tr>
<tr>
<td>window $\Delta E/E$ (C)</td>
<td>$&gt;85%$</td>
</tr>
<tr>
<td>$\tau$-channel time</td>
<td>50.1 ps/channel (for total 512 channels)</td>
</tr>
<tr>
<td>$p$-channel angle</td>
<td>0.14 mrad/channel (for total 512 channels)</td>
</tr>
<tr>
<td>FWHM($\tau$)</td>
<td>280 ps</td>
</tr>
<tr>
<td>FWHM(P)</td>
<td>3.5 mrad</td>
</tr>
<tr>
<td>count rate ($\tau$-channel)</td>
<td>22.5 cps</td>
</tr>
<tr>
<td>count rate ($\tau$-P correlation)</td>
<td>2.5 cps</td>
</tr>
</tbody>
</table>

Table 7-1 The condition of this PAL-ACAR correlation system.
<table>
<thead>
<tr>
<th></th>
<th>$\tau_3$</th>
<th>$I_1$</th>
<th>$I_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>curve A</td>
<td>1.98±0.03</td>
<td>13.1±1.7</td>
<td>34.8±0.45</td>
</tr>
<tr>
<td>curve B</td>
<td>2.05±0.03</td>
<td>12.5±1.7</td>
<td>33.3±0.43</td>
</tr>
<tr>
<td>curve C</td>
<td>2.11±0.03</td>
<td>10.9±1.7</td>
<td>31.6±0.39</td>
</tr>
</tbody>
</table>

Table 7-2  Data results for 2D-spectra of PMMA solved by Lifetime Analysis Data Process program in three individual curves A, B and C.
Summary

1. Positron annihilation is a powerful technique for probing free volume in polymer.
2. PAL studies show changes in free volume hole's size and the number density of holes in polycarbonate at $T_s$ and $T_b$, respectively.
3. Relaxation during the physical aging process far below $T_s$ mainly involve a decrease in concentration of free-volume holes in polycarbonate; "over-shooting" phenomena in hole size was observed when polycarbonate annealed at a temperature just below $T_s$.
4. Free volume hole's size in polycarbonate and PMMA are sensitive with the temperature and applied strain, but not change with aging time.
5. PAL-momentum correlation can give more detailed information about momentum distribution and shape of free volume holes. New arrangement of this correlation system has been completed and implemented.

Future Work:

1. Free volume mechanical compression dependence
2. Multi-temperature step history effect on physical aging.
3. High momentum electron effect on polymer properties and determination of the shape of free volume holes.
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