

Positron Annihilation Study of Polymer Membrane Materials

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Free volume effects are important for positronium formation, *pick-off* annihilation and chemical reactions. In order to turn positron annihilation lifetime (PAL) measurements into effective tool for quantitative investigations of molecular solids, polymers for example, the relation between the intensity of the long-lived positronium component of lifetime distribution of positron annihilation and concentration of defects (elementary free volumes EFV) has to be derived. This enables not only calculations of the effective size of elementary free volumes but also estimations of the specific free volume. Meanwhile, the studies of EFV in polymer systems are of great interest, because effective sizes and concentrations of EFV determine many transport, mechanical and other properties of polymers. We demonstrate here an approach to the studies of these problems on example of big group of glassy polymers distinguished by a wide range of gas permeability P ($1-10^4$ Barrer) and selectivity. They are used therefore as good gas-separating membrane materials.

1. Introduction

Positron annihilation lifetime (PAL) spectroscopy provides an effective approach for studying elementary free volumes (EFV) in the solid structure. With respect to polymers, this method is based, in particular, on the so-called "free volume model", suggested by Brandt.¹ This model assumes that positronium atom (Ps) tends to localize in the free volume elements of polymer structure due to its repulsion (exchange interaction) from surrounding molecules. The correlation between Ps annihilation characteristics and properties of the materials was studied in many laboratories and a lot of interesting results were obtained. For example, Tao² and Eldrup³ derived a simple semi-empirical equation for the dependence of o-Ps lifetime on the FVE effective size. In addition to well known program PATFIT, describing PAL distribution in terms of several components, Gregory⁴ and Jean⁵ applied the CONTIN computing program to obtain continuous lifetime and size-distribution of EFV in polymers. We are not going to discuss here the whole spectrum of the studies and refer the interested reader to the book⁶ and to some other recent publications of more or less general character.^{7,8} We shall touch here one problem: how Ps atom finds itself in the EFV and, correspondingly, what kinetic equations are to be solved in order to find a dependence between the intensity of the long-lived (positronium) component and EFV concentration. On the basis of our approach, we discuss our PAL results on positron annihilation in glassy polymer membrane materials.

2. The Problem of Ps Trapping

The simplest way to tackle a problem of trapping is to consider corresponding kinetic equations. For the simplest case of the traps of one kind

$$\begin{aligned} dP_f/dt &= -(\lambda_f^{o-Ps} + v_3)P_f, & P_f(0) &= 3Q/4, \\ dP_t/dt &= v_3P_f - \gamma_3P_t, & P_t(0) &= 0, \end{aligned} \quad (1)$$

where P_f is the probability to find a free or trapped (long-lived) o-Ps, λ_f^{o-Ps} stands for free (non-trapped) ortho-positronium

annihilation rate, and v_3 and γ_3 are the trapping and annihilation rates of o-Ps in elementary free volume.

The lifetime distribution of annihilation radiation is given then by the following equation

$$Y(t) = F(t) + I_3\gamma_3 \exp(-\gamma_3 t), \quad (2)$$

where $F(t)$ involves short-lived components. Long-lived component I_3 is related to ortho-positronium in EFV.

$$I_3 = (3Q/4)v_3(\lambda_f^{o-Ps} + v_3 - \gamma_3). \quad (3)$$

Eq 2 shows a typical S-like dependence of I_3 on the Ps trapping rate v_3 into elementary free volumes. Q is fraction of positrons which form Ps in a substance. Subscript "3" comes from the number of the components in the lifetime distribution of positron annihilation. The longest one has a number "3". Obviously, γ_3 is dependent on the mobility of free (just formed in the bulk) positronium atom and on the concentration of elementary free volumes N_3 :

$$v_3 = 4\pi D_f^{o-Ps} N_3 R_3. \quad (4)$$

D_f^{o-Ps} is a diffusion coefficient of free (non-localized) positronium, and R_3 is an effective radius of the elementary free volume. Radius R_3 can be determined from o-Ps lifetime $\tau_3 = 1/\gamma_3$ using a well-known equation

$$\tau_3(ns) = (1/2)[1 - (R_3/R_0) + (1/2\pi)(\text{Sin}(2\pi R_3/R_0))]^{-1}, \quad (5)$$

suggested by Tao and Eldrup. Parameter $R_0 = R_3 + \Delta R$, where R_3 is already mentioned effective EFV radius and $\Delta R = 1.66 \text{ \AA}$.

The two limiting situations can be considered for the eq 3:

1- if one assumes that $v_t < \lambda_f^{o-Ps} - \gamma_3$, then $I_3 = (3/4)QD_f^{o-Ps}R_3N_3$, and fractional free volume V_{f3} is roughly proportional to the product of I_3 and the volume of micro-cavity v_{f3} :

$$V_{f3} = CI_3v_{f3}. \quad (6)$$

A similar empirical equation had been suggested by Jean et al.⁹ They called parameter C an empirical constant.

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2 - the second alternative appears when $v_3 \gg \lambda_f^{o-Ps} - \gamma_3$. In this case, I_3 independent on concentration of EFV, i.e. $I_3 \sim Q$ and can not be used for calculations of concentration of elementary free volumes N_3 .

The choice between the two alternatives can be done on experiment by creating or removing elementary free volumes N_3 artificially and by measuring corresponding intensities I_3 . We have done such experiments for the cross-linked oligoetheracrylates¹⁰: I_3 decreased with increasing of the number of links. We refer here also to the experiments of Suzuki and Goworek,¹¹ where compression or cooling of the sample, which are also supposed to decrease the number of EFV, gave strong inhibition of Ps formation (I_3 intensity). Thus we get some arguments in favor of the first alternative (I_3 is a function of the trapping rate v_3 and of the concentration of elementary free volumes N_3), and the most correctly would be to use eqs 3, 4 describing intermediate situation. Additional argument has been obtained, on our opinion, by Dauwe et al.¹² who used age-momentum-correlation technique AMOC for the studies of poly(methylmetacrylate) PMMA. This technique enables one to estimate o-Ps lifetime till the moment of final localization (trapping). This lifetime came out to be very long (0.54 ± 0.04 ns). It would be difficult to suppose that Ps atom is formed inside of the EFV and it takes such a long time for stabilization inside of this cavity. We suggest that the observed lifetime is a time of positronium diffusion from deeper to the deepest trap till the moment of final localization, and we describe this motion by some effective diffusion coefficient D_f^{o-Ps} (see eq 4).

Now, what can we say about the value of this coefficient? This value can be found in the experiments, when the number of EFV is known because, for example, you are creating them (experiment with porous poly(phenylene oxide) PPO,¹³ or changing the size of some of them, using a known amount of cross-linking agent. You calculate the trapping rate from annihilation characteristics using the equation

$$v_3 = [(\lambda_f^{o-Ps} - \gamma_3) (4I_3/3)] / (Q - 4I_3/3), \quad (7)$$

and, further on, determine D_f^{o-Ps} .

Such experiments gave $D_f^{o-Ps} \sim 10^{-5}$ cm²/s, which is much lower than diffusion coefficient of free e⁺ ($D_f^+ \sim 10^{-1}$ cm²/s). Therefore, we conclude that trapped particle is not positron, which could form positronium after trapping, but non-localized positronium.

All these facts support, to our mind, the described above approach to calculations of the number of EFV and, correspondingly, of the specific free volume on the basis of measurements of PAL spectra.

3. Positron Annihilation in Glassy Polymer Membrane Materials

A group of polymers, selected for this study, attract attention as candidate materials for gas-separation membranes. Many of them are characterized (using PATFIT program) by a long o-Ps lifetime (>10ns), which is probably due to bulky silyl groups, typical for their structure. It came out that, inspite of generally-accepted homogeneity of the glass structure, some of these compounds have bimodal size-distribution of elementary free volume or FVE of two types. We were first to report such characteristic for poly(trimethylsilylpropyne) PTMSP. Now we are going to discuss similar results for three groups of such polymers, prepared in the form of thin (~1 μm) sheets.

- (1)- silicon bearing polystyrenes;
- (2)- polyacetylenes;
- (3)- perfluorinated polymers.

These polymers include poly(4-trifluoropropyl-dimethylsilylstyrene) PFPDMSS, poly(4-trimethylsilyl-

styrene) PTMSS, poly(4-methyltrimethylsilylstyrene) PTMSSMS, poly(vinyltrimethylphenylsilane) PVPDMS, poly(vinyltrimethylsilyl) PVTMS, copolymers of 2,2-bifluoromethyl-4,5-difluoro-1,3-dioxole and tetrafluoroethylene with different ratio of the components (AF1600 and AF2400), poly(trimethylsilylpropyne) PTMSP, poly(1-phenyl-2-*p*-triisopropylsilylphenylacetylene) PIPSDPA, poly(1-phenyl-2-*p*-triphenylsilylphenylacetylene) PPSDPA, and Nafion-117.

After using CONTIN program to the spectra, obtained by PAL measurements, these systems show a smooth transition from substances with unimodal distribution of o-Ps lifetimes (unimodal distribution of elementary free volumes) to those with bimodal distribution (Figure 1). This result shows that complex (non-statistical) distribution of elementary free volumes is a general feature of many polymer compounds.

The second effect, which is typical for these substances, is a strong positronium quenching (shortening of o-Ps lifetime) by atmospheric oxygen in situation, when the number of oxygen atoms N_{OX} is smaller, than the number of elementary free volumes. These two facts must be discussed together.¹⁴ Positronium quenching enables determination of the diffusion coefficient of localized Ps D_f^{o-Ps} (this coefficient can be different from diffusion coefficient of nonlocalized, just formed Ps D_f^{o-Ps} , which we considered above) from the equation

$$\lambda_4^{OX} - \lambda_4^{VAC} = 4\pi D_f^{o-Ps} (R_{Ps} + R_{OX}) N_{OX}. \quad (8)$$

Thus, for Ps quenching by nitrobenzene in polycarbonate

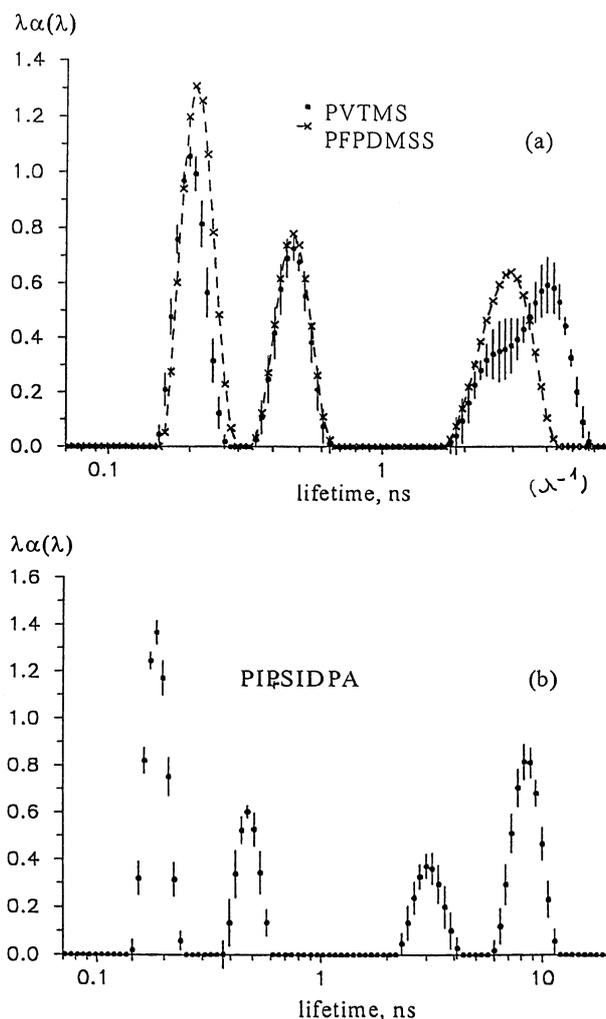


Figure 1. Probability density function $\lambda \alpha(\lambda)$ of positron annihilation lifetimes $\tau = \lambda^{-1}$, obtained by CONTIN program from PAL spectra of some of the membrane materials (for explanation of abbreviations see the text). Long-lived components are related to Ps and, using (5), can be transformed to size-distribution of EFV.

Hirata et al.¹⁵ had found $D_f^{o-Ps} \sim 10^{-6}$ cm²/s. In our case, for PTMSP, it came out one order of magnitude higher, about the same as D_f^{o-Ps} . This is probably due to highly developed system of free volumes in the membrane materials.

As we said, observation of the two long-lived positronium components τ_3 , τ_4 actually means existence of the two types of positronium traps (EFV). For homogeneous distribution of defects it can be described by eq 9:¹⁴

$$\begin{aligned} dP_f/dt &= -(\lambda_f + v_3 + v_4)P_f, & P_f(0) &= 3Q/4, \\ dP_3/dt &= v_3P_f - (\gamma_3 + v_{34})P_3, & P_3(0) &= 0, \\ dP_4/dt &= v_4P_f + v_{34}P_3 - \gamma_4P_4, & P_4(0) &= 0, \end{aligned} \quad (9)$$

which is similar to (1) and includes also a possibility of detrapping and transition from the trap "3" to the trap "4". In the simplest case $v_{34} = 0$

$$\begin{aligned} v_3 &= (I_3/A)[(\lambda_f - \gamma_3)(3Q/4 - I_4) + (\lambda_f - \gamma_4)I_4], \\ v_4 &= (I_4/A)[(\lambda_f - \gamma_4)(3Q/4 - I_3) + (\lambda_f - \gamma_3)I_3]. \end{aligned} \quad (10)$$

Parameter A is also a function of I_3 and I_4 . This approach gives N_3 and N_4 on the level 10^{19} – 10^{20} cm⁻³, while concentration of oxygen atoms is below 10^{18} cm⁻³. It means that, in order to get quenching, the same Ps atom must move from hole to hole and stay there, sometimes with oxygen (if oxygen is trapped in the given hole) and sometimes without it. Now, the question comes up: if Ps moves from hole to hole, why can we resolve distinctly bimodal distribution of positronium lifetimes in such polymer glasses as PTMSP, PIPSDPA and some others? The answer can be only one: the distribution of elementary free volumes in such systems is inhomogeneous, and, once formed, positronium atom is not able to go out of the limits of the micro-region of this inhomogeneous structure. To be more accurate, kinetic eq 9 must be changed on the equations, describing separately positronium annihilation in the micro-regions with large pores and in those with smaller pores. Correspondingly, initial conditions (eq 9) should be changed, because there is a competition between two types of the regions for the initial emergence of Ps. Roughly assuming that these probabilities are proportional to intensities I_3 and I_4 , respectively, we get equations similar to eq 1:

$$\begin{aligned} dP_f/dt &= -(\lambda_f^{o-Ps} + v_i)P_f, & P_f(0) &= 3Q\xi_i/4, \\ dP_i/dt &= v_iP_f - \gamma_iP_i, & P_i(0) &= 0, \end{aligned} \quad (11)$$

where $i=3,4$ and $\xi_3 = I_3/(I_3+I_4)$; $\xi_4 = I_4/(I_3+I_4)$.

Correspondingly,

$$v_i = (4I_i/3)(\lambda_f - \gamma_i)/(Q\xi_i - 4I_i/3) = 4\pi D_f^{o-Ps} N_i R_i. \quad (12)$$

It is assumed that Q , λ_f and D_f^{o-Ps} are identical for the both types of micro-phases.

The fractional free volume, calculated in this way, for example, for PTMSP as $(N_3v_3 + N_4v_4)$, attains 20% which is normal for the systems with highly developed free volume.

Thus, we are able to make two conclusions:

(a) In many polymer membrane materials (PTMSP, PIPSDPA, etc.) size-distribution of elementary free volumes is non-statistical and looks complicated (sometimes bimodal). This conclusion correlates well with the recent results of molecular modeling.¹⁶

(b) Distribution of elementary free volumes in glassy polymer matrix is inhomogeneous. Estimations of o-Ps diffusion length L , using the equation $L = (6D_f^{o-Ps})^{1/2}$, gives the effective size of microregions with different EFV about 300 Å. Remarkably that the problem of non-homogeneous character of such polymer glasses was discussed previously by some authors on the basis of different data.^{17,18}

Furthermore, results on the size and amount of elementary free volumes were compared with permeation and selectivity of thin layers of the mentioned polymer glasses. It was found that namely N_4 , v_4 (but not N_3 , v_3) are responsible for permeation (Figure 2).¹⁰ Permeation selectivity a is a coefficient of proportion between diffusion coefficients D of different gases in a given polymer and square of kinetic diameter d of penetrating molecules:

$$\log D = ad^2 + b. \quad (13)$$

A nice correlation was found between the selectivity coefficient a and the size of elementary volume v_4 in the studied materials. This correlation is useful for express determination of membrane selectivity on the basis of PAL measurements, instead of time-consuming and difficult measurements of penetration for different gases.

Finally we conclude that positronium annihilation lifetime measurements can be a useful instrument for investigations of membrane materials, providing the conditions of positronium formation and trapping are estimated correctly.

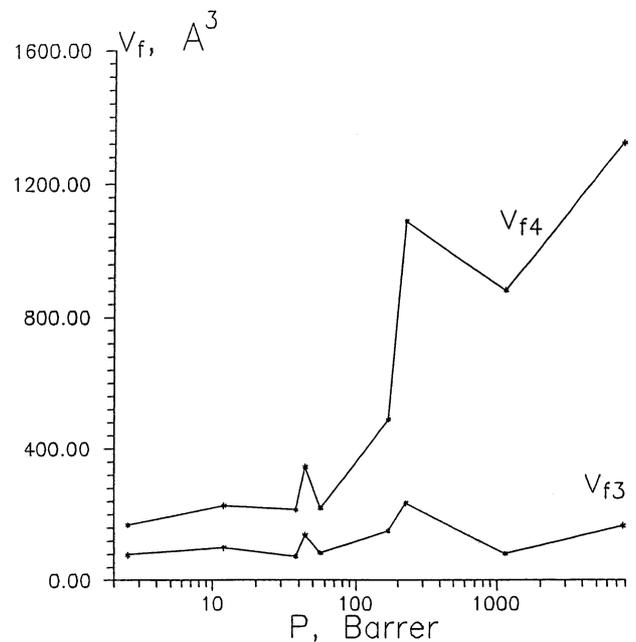


Figure 2. Correlation between the size of elementary free volumes v_{f3} and v_{f4} (\AA^3), calculated as $4\pi R_3^3/3$ and $4\pi R_4^3/3$ from the lifetimes τ_3 and τ_4 in the PAL spectra of the substances, listed in the text (PATFIT data, Eq 5), and their permeation P for oxygen, measured in Barrer.

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