

Applying Positron Annihilation Lifetime Spectroscopy in Measuring the Free Volume in Cycloester and Silicon Polymers

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Abstract:

Positron annihilation lifetime spectroscopy (PALS) was used to measure the free volume in two homopolymers namely Poly-Silicon (amorphous polymer) and Poly-Cyclo-ester (1,4-butanediol cyclohexane carboxyl) (semicrystalline polymer). The free volumes of both homopolymers were determined by analyzing the lifetime (LT) spectra

using a three-components fit. In the case of the Poly-Silicon the LT spectra were analyzed using a three-components fit while in the Poly-Cyclo-ester, the LT spectra of the Poly-Cyclo-ester were analyzed twice. Firstly a three component fit analyzes is done then a four-components fit analyzes is used. In this paper, however the discussion is also focused on relating the variation in the free volume to the morphological futures of the polymers. The morphological futures were investigated using atomic force microscopy (AFM). Results indicate that positron annihilation characteristics (the longest lifetime components (τ_3) and their intensities (I_3)) are very useful for studying the effect of the morphological parameters (namely crystallinity futures) on the free volume.

Keywords: Free volumes, Positron annihilation lifetime spectroscopy, Poly-Silicon, Poly-Cyclo-ester.

1 Introduction:

Positron annihilation techniques have been used extensively to study various semicrystalline and amorphous polymers.¹⁻⁹ However the use of PALS in free volume characterization is unique. PALS is a non-destructive technique and is sensitive to a free volume on a molecular level. The free

volume can be understood as the volume within the polymeric structure that is not occupied by molecules. It has a great influence on the physical properties and durability of polymers.¹⁰⁻¹³ Consequently, since the characterization of the free volume is related to the mechanical and thermal history of the polymer, its investigation is of great interest.^{14,15}

PALS is based on measuring the lifetimes of positrons "injected" into a material.^{16,17} Positrons emitted from a radioactive source enter the polymer matrix, thermalize, and may either annihilate with electrons or form positronium (Ps). The typical lifetime of the Ps depends on the spin state. The singlet state or para-positronium (p-Ps) annihilates in 0.1–0.2 ns. It is referred as τ_1 . This value is lower than the typical lifetime of the positron itself, referred to as τ_2 , which is in the range 0.3–0.5 ns. The triplet state or ortho-positronium (o-Ps) has a lifetime of 142 ns in vacuum; however, it decreases typically in a matter of a few nanoseconds: 1.5–4 ns. This is due to collisions of Ps with molecules (pick-off annihilation).^{18,19} The lifetime of the o-Ps is considered to have the longest lifetime component (τ_3 or τ_4) depends on the number of component fit.

In investigations of the free volume in polymer material, it is widely accepted that the longest lifetime component (τ_3 or τ_4) connected with the

o-Ps is expected to give information on characteristics of the holes that appear due to the structural disorder in the amorphous regions in the polymer.^{20,21} It has been found in amorphous polymers that τ_3 increases with an increase in the holes volume,²² i.e. the o-Ps lifetime increases with the free volume. Further, it is assumed that in glassy polymers the fraction of the positron forming o-Ps (I_3) is correlated to the density of holes in the material, but the exact nature of this correlation is unknown.²³

However, in semicrystalline polymers the picture is even more clouded, since one has to account for the many possible types of holes arising from the complex morphology that is commonly present in this class of materials, i.e. disordered regions between lamellae in the spherulites structure as well as the amorphous regions between the spherulites. In addition, the crystalline regions are not defined with sharp and clear boundaries or crystalline faces separating them from the surrounding amorphous regions. The crystallites themselves also contain many defects and dislocations arising from the extensive chain entanglements of molecules in the bulk state. The noncrystalline phase must be subdivided into the noncrystalline-amorphous and the crystalline-amorphous interfacial portions. The interfacial region is amorphous but has

a constrained molecular mobility, due to the presence of crystallinity, and is usually described as the rigid-amorphous fraction.^{24,25}

The observations of different authors about the relationship between the o-Ps lifetime and molecular structure of semicrystalline polymers²¹ can be summarized as follows. For several semicrystalline polymers the changes in the crystalline regions do not show any effect on the lifetime of the o-Ps annihilation. The lifetime spectra of the polymers are found to be best resolved in three-components, similar to in the case of the amorphous polymers. This has led to the conclusion that there is only one long-lived component ($\tau_3 \cong 1.5\text{--}4$ ns), regardless of the presence or the absence of the crystalline phase. Some examples of semicrystalline polymers in this group are polyetheretherkethone,²⁶ polyethyleneterephthalate (PET)²³ and polypropylene.¹⁴ On the other hand, four lifetime (τ_4) components have been found for polyethylene (PE),⁶ polyamides,⁷ polytetrafluoroanethylene¹⁴ and 1,4-polybutadiene.²⁷ In this group of semicrystalline polymers, two long-lived o-Ps components were obtained, where the first ($\tau_3 \cong 1$ ns) is attributed to o-Ps annihilation in the chain folded regions, and the second ($\tau_4 \cong 2.4\text{--}4$ ns) is attributed to pick-off annihilation of o-Ps entrapped in the free volume in the pure amorphous phase of the polymer.²⁸

A decrease in I_3 (the longest-lived component intensity) with increasing crystallinity has been reported for semicrystalline PET polyester.²³ However, the extrapolation gave $I_3 \cong 6\%$ at 100% crystallinity. It was concluded that the semicrystalline phase in PET contributed to the o-Ps formation. The similarity of the structures of the Cyclo-ester polymer molecules and the PET molecules lead the authors of this article to presume that similar results might be obtained for the Cyclo-ester homopolymer. However, in other semicrystalline polymers, such as PE, there are also evidences to suggest that the annihilation characteristics may be related to the average distance between crystallites, thickness of the crystallites, and the concentration of chain defects.²⁹ Furthermore, the Ps that is formed in crystalline and amorphous phases has also been assumed to tunnel through the interface between both phases, which complicates the situation.²¹

In the light of this somewhat ambiguous situation (the reliable number of fit for LT spectra and how to relate the PALS results to the polymers structure) the aim of this investigation was to determine the free volume for Poly-Silicon (amorphous polymer) and Poly-Cyclo-ester (semicrystalline polymer). It was hoped that this would shed further light on the relationship between the mechanism of positron annihilation and the

microstructure of the Poly-Silicon and Poly-Cyclo-ester. Poly-Silicon and Poly-Cyclo-ester with well-known chemical and morphological structure were reported in our previous work.³⁰

2 Experimental:

2.1 Samples Characteristics:

The samples under investigation were synthesized via condensation polymerization and characterized using proton-NMR and chromatography techniques, as described elsewhere.³⁰ The morphologies of these polymers were investigated using atomic force microscopy (AFM). AFM images were obtained on a multimode AFM, using a low resonance frequency silicon cantilever with a resonance frequency of 60 kHz, and a spring constant of $K = 50$ N/m. All experiments were carried out at ambient conditions. The scan rate was set in the range of 0.4 to 0.6 Hz. Topography and phase images were captured simultaneously for tapping mode. Noise was removed with the Veeco imaging software.³⁰

2.2 Sample preparation:

Two identical samples, approximately $2.5 \times 10 \times 10$ mm³, were sandwiched around a positron source, made by evaporating carrier-free (²²NaCl) solution onto aluminium foil (Figure 1). Positron lifetime measurements were performed using a fast-fast coincidence system with a

time resolution of 240.34 ps full width of half maximum (FWHM) and a total of 1024 channel.

The radioactive source (^{22}Na) was placed between two sample pieces, for each sample measurements, and wrapped very carefully in aluminium foil to ensure that the positrons interacted effectively with the material. The duration of each measurement was 80 min maximum, during which time 1×10^6 counts were collected.

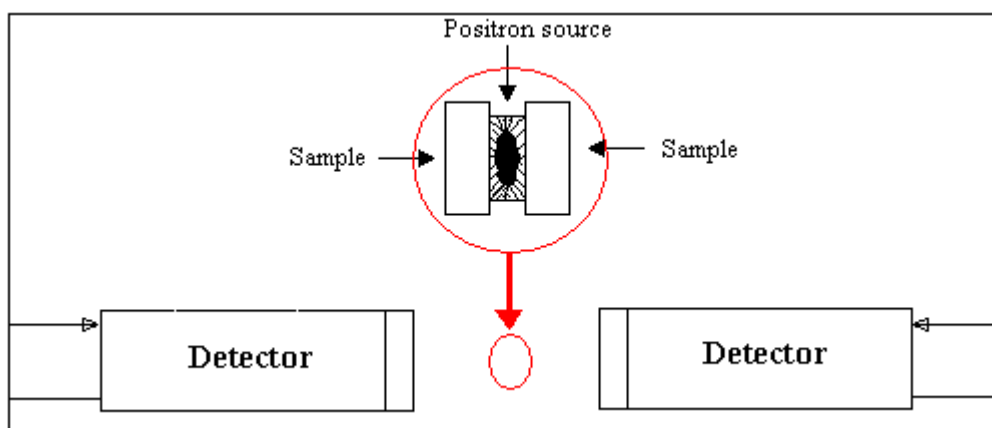


Figure 1: The radioactive source placed between the two copolymer samples.

2.3 Data analysis:

Each positron annihilation spectrum, with a summit height of approximately 1×10^6 counts, was obtained at room temperature.

Mathematically, using the PATFIT computer program, the spectra were analyzed as the sum of exponentials. The following procedure was used to analyze the LT spectra. The lifetime spectra for each sample were first analyzed in terms of three lifetime components. The magnitudes of the three lifetimes τ_1 , τ_2 and τ_3 suggest that they originate mainly from the annihilation of p-Ps, free positron and o-Ps, respectively.¹⁶ The last lifetimes (τ_3) with the respective intensity (I_3) are the most important lifetime components. This is because the τ_3 and I_3 analysis determine the free volume of the media in which the positron annihilation occurs.²¹ The following equation shows the relationship between o-Ps lifetime (τ_3) and free volume radius.²¹

$$\tau = (1/2) \{ 1 - (R/R_0) + [\sin(2\pi R/R_0)] / 2\pi \}^{-1} \quad [\text{Eq 1}]$$

where R is the hole radius and R_0 is the infinite spherical potential radius, and $R_0 = R + \Delta R$, where ΔR is an empirical parameter. The average free volume size (fv) is calculated assuming spherical cavity shape using the following equation:²¹

$$fv = 4\pi R^3/3 \quad [\text{Eq 2}]$$

The free volume fraction (ffv), which is related to the polymer mechanical properties, is calculated as the average of the hole size and the

hole concentration, as shown in the following equation.²¹

$$ffv = CI_3 [fv(\tau_3)] \quad [\text{Eq 3}]$$

where ffv is the free volume fraction, C is an empirical scaling constant, I_3 is the total fraction of o-Ps formed in the polymer, $fv(\tau_3)$ is the mean hole volume in \AA^3 .

Analysis of the measured spectra of Poly-Cyclo-ester by four lifetime components was also attempted. The analysis was first applied without any constraints where the shortest of the four lifetimes was scattered in the range between 0.1 and 0.3 ns with very large variances fit. This lifetime is consistent with that of the p-Ps lifetime. In order to reduce the scatter of the points the final four lifetime analyses were carried out by fixing the intrinsic p-Ps lifetime at 0.125 ns. Furthermore, the four-components fit was also applied by fixing τ_2 at 0.5 ns and τ_1 at 0.125 ns, however, negative values of the τ_3 or τ_4 were obtained for these samples, with no significant improvement in the fit. This indicates that the four-components fit when only τ_1 was fixed at 0.125 ns gave the best results, which are reported here for these samples.

3 Results and discussion:

Figure 2 shows the AFM images of two films of Poly-Cyclo-ester and Poly-Silicon the results obtained using AFM tapping mode at ambient temperature. Poly-Cyclo-ester image on Figure 2(a) shows spherulitic crystal structure while Poly-Silicon image on Figure 2(b) shows relatively flat surface (amorphous structure).

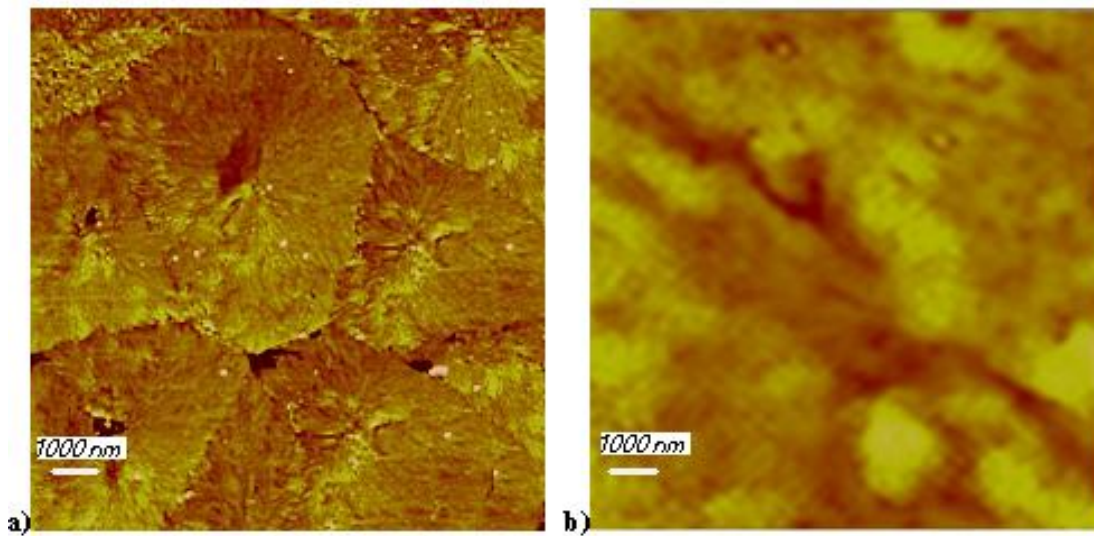


Figure 2: AFM images for a) Poly-Cyclo-ester and b) Poly-Silicon.

The dark and the bright regions in Figure 2(b) is due to the surface roughness, where the bright area is higher than the dark areas. Summary of the morphological characteristics of the samples are tabulated in Table 1.

Table 1: Characteristics of the investigated samples of silicon and Cyclo-ester homopolymers.

Sample	Molecular weight M_n (g/mol)	Crystallinity degree at room temperature ω_m^a (%)	Type of Morphology ^b
Poly-Silicon	200,000	0	Amorphous
Poly-Cyclo-ester	50,000	31.40	Spherulitic crystal

^a determined by WAXD³⁰

^b determined by AFM

The lifetime spectra for Poly-Silicon sample were analyzed in terms of three lifetime components, using the PATFIT computer program, the spectra were analyzed as the sum of exponentials as illustrated in Figure 3.

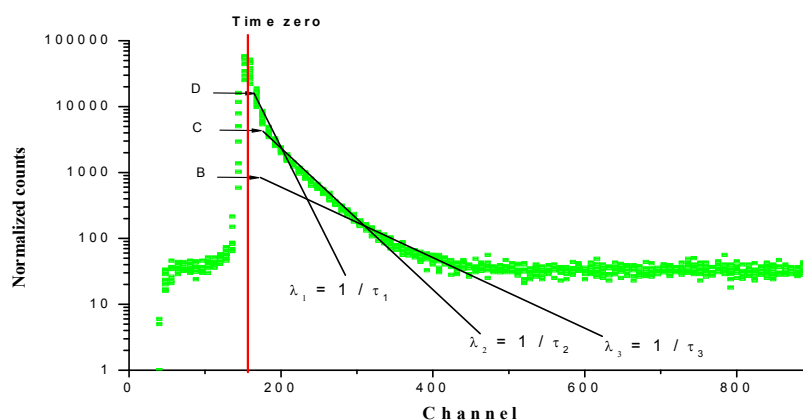


Figure 3: The three-components fit to the LT spectrum of Poly-Silicon.

The Figure shows the lifetime interval spectrum of Poly-Silicon, representing the N coincidence time distribution that comes from the positron and the positronium annihilation processes. Mathematically, the spectra could be analyzed as the sum of exponentials. The applied equation for the fit is ²¹

$$N = D \exp(-\lambda_1 t) + C \exp(-\lambda_2 t) + B \exp(-\lambda_3 t) \quad [\text{Eq 4}]$$

where N is the number of accumulated coincidences, the slopes λ are the rates of annihilation, D , C and B are the slope intercepts of each component at the zero time axis. The magnitudes of the three lifetimes τ_1 , τ_2 and τ_3 suggest that they originate mainly from the annihilation of p-Ps, free positron and o-Ps, respectively.¹⁶ The last parameter with the respective intensity (τ_3 and I_3) are the most important ones, because their analysis will determine the free volume and the physical–chemical characteristics of the media where the positron annihilation occurs.²¹

Figure 4 and Figure 5 show the lifetime interval spectrum of Poly-Cyclo-ester, representing the N coincidence time distribution that comes from the positron and the positronium annihilation processes.

Mathematically, the spectra could be analyzed as the sum of exponentials. Also in this case [Eq 4] is applied for the fit as illustrated in Figure 3.

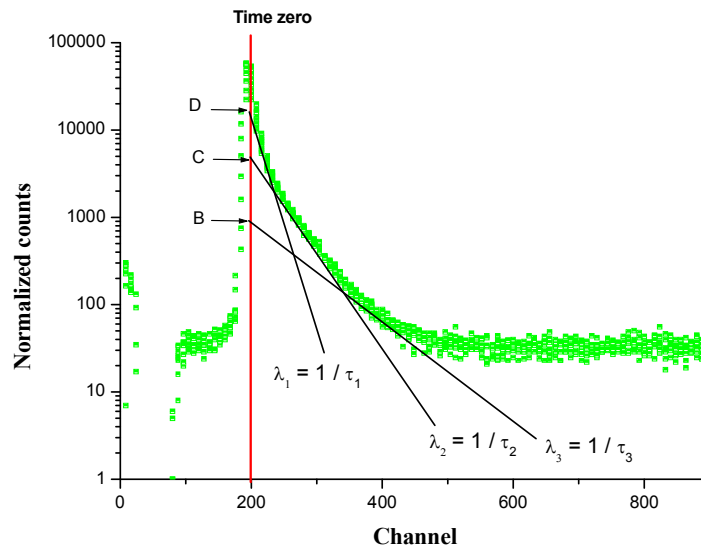


Figure 4: The three-components fit to the LT spectrum of Poly-Cyclo-Ester.

Analysis of the measured spectra of Poly-Cyclo-ester by four lifetime components was also attempted, as shown in Figure 5. The applied equation in the fit in the Figure 5 is now: ²¹

$$N = D \exp(-\lambda_1 t) + C \exp(-\lambda_2 t) + B \exp(-\lambda_3 t) + A \exp(-\lambda_4 t) \quad [\text{Eq 5}]$$

where N is the number of accumulated coincidences; and D , C , B and A are the slope intercepts of each component at the zero time axis.

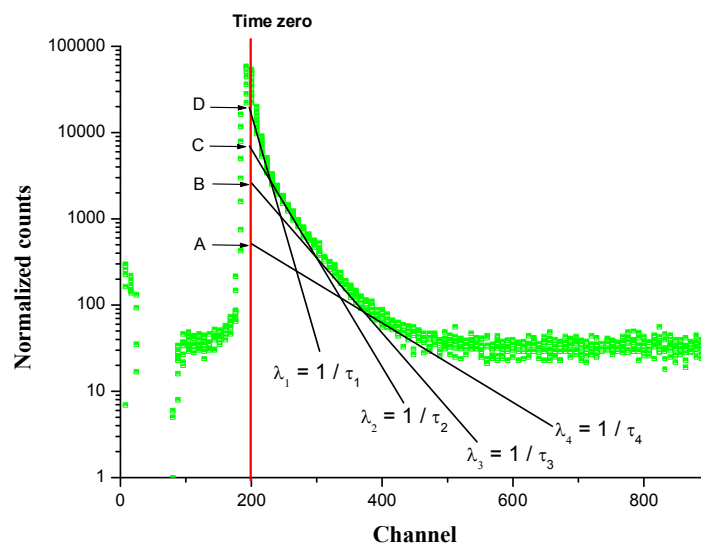


Figure 5: The four-components fit to the LT spectrum of Poly-Cyclo-Ester.

As a result of the homogenous silicon amorphous pure phase the three-components fit was suitable and applicable. The variance of the fits was also small, it was 1.1. However, in the case of the semicrystalline Cyclo-ester homopolymer the LT spectrum was analyzed using both the three-components unconstrained fit and the four-components constrained fit (using 0.125 ns for p-Ps annihilation lifetime (τ_1)). The variances of the fits were 1.13 and 1.6 for the three- and four-component fits, respectively. Regardless of constraints used in the four-components fit there was no significant improvement in the variance of the fit. The errors (standard

deviations) in the lifetime and intensity of the o-Ps annihilation were higher than the respective values when the LT spectra were fitted with three exponential components. Thus, in Cyclo-ester homopolymers there was only one o-Ps component. If however, there were two components (one for the amorphous region and another for the crystallinity region), then they are very close to each other (at about 2.06 ns) and cannot be resolved mathematically. This could be an indication to the similarity in the shape and size of the many possible types of holes arising from the complex morphology of this polymer, i.e. disordered regions between lamellae in the spherulites structure as well as the amorphous regions between the spherulites (Figure 2).

The suitability of the three-components fit for the Cyclo-ester polyester is consistent with that reported in literature for other polyesters, such as PET.²³ Table 2 shows the annihilation lifetime of the o-Ps (τ_3) and the corresponding intensity (I_3), which is indicative of the relative number of o-Ps annihilations. The radius and the volume of the holes, as well as the free volume fraction, obtained using Eq 1, Eq 2 and Eq 3 are also listed in Table 2.

Table 2: The o-Ps characteristics of silicon and Cyclo-ester homopolymers determined using the three- components fit

Sample	τ_3^a (ns)	$\Delta\tau_3^a$ (ns)	I_3^b (%)	ΔI_3^b (%)	$R^c(\text{\AA})$	$\Delta R^c(\text{\AA})$	fv^d (\AA^3)	Δfv^d (\AA^3)	ffv^e (%)	Δffv^e (%)
Cyclo- ester	2.06	0.012	19.42	0.098	2.10	0.007	110.00	0.97	3.21	0.06
Silicon	4.14	0.009	37.48	0.156	4.32	0.003	338.50	8.73	22.9	0.12

^a the average lifetimes of the o-Ps

^b the average intensities of the free volume holes

^c the average radii of the free volume holes

^d the average of the free volume holes

^e the average of the free volume fractions

Table 2 shows that about a quarter ($22.9 \pm 0.12\%$) of the silicon volume is free volume, which explains the very low glass transition temperature of this polymer ($-123\text{ }^\circ\text{C}$). This value of the free volume fraction is larger than the value reported in literature for the silicon pure homopolymer.³¹ This variation might be a result of the difference in the degree of the crosslinking in the silicon molecules. On the other hand, the free volume in the Cyclo-ester homopolymer, which has not been measured

by PALS before, represents only $3.21 \pm 0.06\%$ of the total volume of the polymers, even though the T_g of this polymer is lower than room temperature. The relatively low free volume fraction in the Cyclo-ester homopolymer of the Cyclo-ester can be attributed to the crystallinity degree in this polymer, determined previously using WAXD³⁰ to be about 31.4%, resulting in a lower o-Ps yield. The possible regions with free volume holes probed by o-Ps in these polymers are in: (1) open amorphous texture and interfaces in spherulites, (2) interlamellar phase and lamellar defects, and (3) interstitial cavity in the crystalline unit cell.²⁵ Therefore, the o-P lifetime and its intensity, as extracted from the lifetime spectra, can provide an indication of the polymer's structure, and eventually provide more information on the region where the o-Ps could be annihilating.

4 Conclusions:

The ability to determine the free volume in Poly-Silicon (amorphous polymer) and Poly-Cyclo-ester (semicrystalline polymer) using the PALS technique was investigated. The LT spectra were analyzed using the three-components fit. In the case of the Poly-Cyclo-ester further analysis using the four-component fit was applied. The results showed that the mean

lifetime of o-Ps reflects the size of the free volume holes, and the lifetime of o-Ps found to be very sensitive to changes in the free volume in both polymers. The results also showed that the o-P lifetime and its intensity, can provide an indication of the polymer's structure namely the disordered regions between lamellae in the spherulites structure as well as the amorphous regions between the spherulites in the Poly-Cyclo-ester, and it is appeared that the crystal structure could affect the free volume of the semicrystalline polymer.

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