

# Measurement of Free Volume in Silicon-Cycloester Segmented Copolymer Using Positron Annihilation Lifetime Spectroscopy

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## **Abstract:**

*Positron annihilation lifetime spectroscopy (PALS) was used to measure the free volume in a series of Silicon-Cycloester segmented copolymer by analyzing the lifetime (LT) spectra using a three-components fit and a four-components fit. In this paper, however the discussion is focused on determining the free volumes of the Silicon-Cycloester copolymer series using four-components fit. The characteristics of the longest-lived component(s) in the PALS ascribed to ortho-positronium (o-Ps) atoms decays in free-volume holes, are used to*

get information on the concentration of free-volume holes, the mean size of the holes, and the fractional free volume. The effects of the chemical composition (silicon content), on the *o*-Ps annihilation parameters and thus on the free volume of the Silicon-Cycloester copolymers, were investigated. Results also indicated that positron annihilation characteristics (the longest lifetime components ( $\tau_3$  and  $\tau_4$ ) and their intensities ( $I_3$  and  $I_4$ )) are very useful for studying the effect of the morphological parameters (microphase separation and crystallinity) on the free volume in the copolymer series. Changes in the  $T_g$  values of the silicon segment and the cycloester segment in the copolymers were related to the *o*-Ps lifetime, which is indicative of a change in free volume in the copolymers.

**Keywords:** *Free volume, Positron annihilation lifetime spectroscopy, ortho-positronium, Silicon-Cycloester copolymers and four-components fit.*

## **1.Introduction.**

Polymers contain cavities or holes of atomic and molecular dimension which arise because of irregular molecular packing in the amorphous phase. These holes and cavities is called *free volume*. Free volume appears due to the structural, static and dynamic disorder. It has important influence on molecular properties, such as viscosity [1-4], molecular transport [5, 6], structural relaxation and physical aging. Fox and Flory [7, 8] attributed the glass transition to the falling of the free volume below some critical value. Although the quantitative total specific volume can be connected with molecular properties, it is in fact the microscopic hole volume which has a fundamental effect to the physics.

Hole size and shape play an influential role in the solvation [9, 10] and mixing processes [11], small molecular permeation through hole volume is important in membrane research [12], and most important, accurately characterizing hole size distribution and its concentration is essential to understand the microscopic structure of molecular materials.

Over the past fifteen years, the free-volume hole properties in polymeric materials have been investigated by researchers using positron annihilation lifetime (PAL) spectroscopy [13-20]. PALS is based on measuring the lifetimes of positrons "injected" into a material [21, 23]. 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 to as  $\tau_1$ . This value is lower than the typical lifetime of the positron itself, referred to as  $\tau_2$ , 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) [23, 22].

The relationship between the positron lifetime annihilation and the molecular characteristics of semicrystalline polymers has been the subject of vast number of academic research studies [26]. The observations of different authors about the relationship between the o-Ps lifetime and molecular structure of semicrystalline polymers can be summarized as follows. For several semicrystalline polymers the changes in the crystalline regions did 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 absence of the crystalline phase. Some examples of semicrystalline polymers in this group are polyetheretherketone [28], polyethyleneterephthalate (PET) [29] and polypropylene [21]. On the other hand, four lifetime components have been found for polyethylene (PE) [19], polyamides [17], polytetrafluoroanethylene [21] and 1,4-polybutadiene [30]. 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. 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 [26].

Carrying out such studies of semicrystalline copolymers, one must be sure about the role of crystalline domains in positron annihilation mechanism. However, the question of influence of the presence of crystalline regions on ortho-positronium annihilation characteristics, although having been studied and announced since years, has not been solved yet. However, not always any correlation of the characteristics with crystallinity and morphology of samples was observed. Therefore, the aim of this investigation was to determine whether any correlation exists between the mechanism of positron annihilation and the microstructure of the Silicon-Cycloester copolymer and the respective homopolymers. It was hoped that this would shed further light on the relationship between the free volume of the copolymers and the morphological parameters (microphase separation and crystallinity) in the copolymers. Copolymers with well-known structural and morphological

parameters were reported in our previous work [31]. Furthermore, silicon and cycloester homopolymers free volumes have also been determined in our previous work [32] and in this work a series of Silicon-Cycloester copolymer were chosen in order to investigate the effect of the chemical composition on the free volume of these copolymers.

## 2. Experiment:

### 2.1. Silicon-Cycloester copolymer samples:

The specimens under investigation were synthesized via condensation polymerization and characterized using proton-NMR, SEC and DMA and the morphologies of these copolymers were also investigated, as described elsewhere [31]. Summary of the chemical and morphological characteristics of the studied samples are tabulated in Table 1 [31].

**Table 1: Characteristics of the investigated Silicon-Cycloester copolymers series.**

Sample	Silicon in the copolymer <sup>a</sup> (wt %)	Crystallinity $\omega_m^b$ (%)	Glass temperature of the Silicon segment Tg <sup>c</sup> (°C)	Glass temperature of the Cycloester segment Tg <sup>c</sup> (°C)	Morphology type <sup>d</sup>
SC-1	4.74	23.40	-94	12	spherulitic crystal and silicon spherical domains
SC-2	9.20	16.40	-115	5	silicon spherical domains
SC-3	22.70	14.10	-118	-5	silicon spherical domains and bicontinuous
SC-4	35.76	9.61	-123	-3	bicontinuous
SC-5	52.10	6.10	-121	-7	cycloester spherical domains

<sup>a</sup> determined by <sup>1</sup>H-NMR

<sup>b</sup> determined by WAXD

<sup>c</sup> determined by DMA

<sup>d</sup> determined by AFM

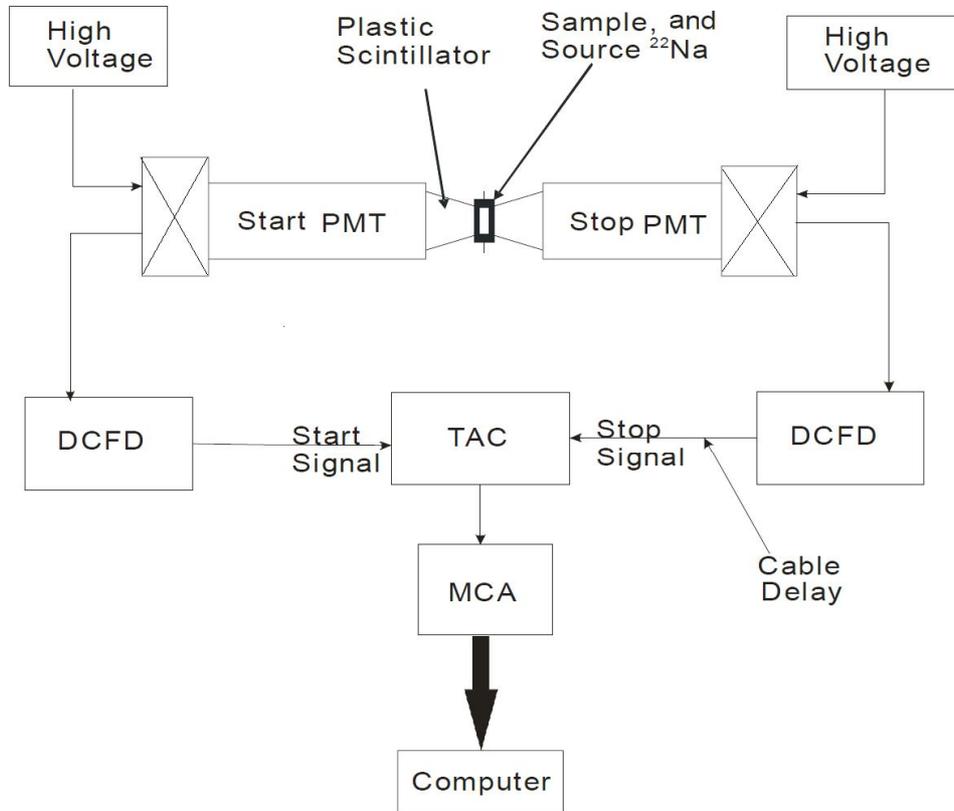
## **2.2. Sample preparation**

Two identical samples, approximately  $2.5 \times 10 \times 10 \text{ mm}^3$ , were sandwiched around a positron source, made by evaporating carrier-free <sup>22</sup>NaCl solution onto aluminium foil. 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 (<sup>22</sup>Na) was placed between two pieces of sample, for each sample, 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  $1 \times 10^6$  counts were collected. Figure 1 shows the instrument system of the positron lifetime experiment that was used in this work.

## **2.3. Data analysis**

Each positron annihilation spectrum, with a summit height of approximately  $1 \times 10^6$  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  $\tau_1$ ,  $\tau_2$  and  $\tau_3$  suggest that they originate mainly from the annihilation of p-Ps, free positron and o-Ps, respectively [22]. The last

parameter with the respective intensity ( $\tau_3$  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 [26].



where Multichannel Analyzer is (MCA), Time-to-Amplitude converter is (TAC), photomultiplier tubes is (PMT), and differential constant fraction discriminator is (DCFD)

**Figure 1: Scheme of positron annihilation lifetime spectroscopy (PALS) instrument system.**

Analysis of the measured spectra of Silicon-Cycloester copolymer 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 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. Further, the four-components fit was also applied by fixing  $\tau_2$  at 0.5 ns and  $\tau_1$  at 0.125 ns. However, negative values of the  $\tau_3$  or  $\tau_4$  were obtained for several samples, with no significant improvement in the fit (high variances fit). Therefore, the results of the four-components fit reported here were obtained when only  $\tau_1$  was fixed at 0.125 ns.

The following set of equations is used to determine the free volume:

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

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

$$R_o = R + \Delta R \quad [\text{Eq 3}]$$

$$ffv = CI_3 [fv(\tau_3)] \quad [\text{Eq 4}]$$

where R is the hole radius,  $R_o$  is the infinite spherical potential radius,  $\Delta R$  is an empirical parameter, fv is the average free volume size in  $\text{\AA}^3$  (calculated assuming spherical cavity shape), ffv is the free volume fraction (calculated as the average of the hole size and the hole concentration), C is an empirical scaling constant, and  $I_3$  is the total fraction of o-Ps formed in the polymer.

### 3. Results and discussion

Figure 2 shows the longest o-Ps lifetimes ( $\tau_3$  and  $\tau_4$ ) and intensities of the corresponding o-Ps ( $I_3$  and  $I_4$ ), as obtained after using the four-components fits. In contrast to the homopolymers [32], the four-components fit in the copolymer series is necessary in order to understand the complex structure and morphology of such phase separated

copolymer series and to have physical meaning of the lifetimes obtained. The three-components fits has the advantage that the fitting procedure is easier to apply than the four-components fits and gives a fitting usually very stable with small statistical scatter parameters ( $\tau_i$  and  $I_i$ ) in most of the cases compared with unconstrained four-components fits. However, constrained four-components fits in several samples of the Silicon-Cycloester copolymer (namely SC-1, and SC-2) did show lower variance fit and less statistical scatter parameters than the three-components fits.

In the complex semicrystalline copolymers with microphase separated morphology the three-components fits has no relevant physical meaning and gives only a more or less sufficient fit to the experimental data. Because of the structures of these semicrystalline Silicon-Cycloester copolymers, positronium can form in both the crystalline (cycloester region) and amorphous (cycloester and silicon regions) phases. The possible regions with free volume holes probed by o-Ps in these copolymers are in: (1) open amorphous texture and interfaces in spherulites, (2) interlamellar phase and lamellar defects, (3) interstitial cavity in the crystalline unit cell [33], and the intermediate phase that forms between the silicon domains and (4) the cycloester dominant phase.

Figure 2 shows the effect of the silicon content on the lifetime (Figure 2(a)) and intensity (Figure 2(b)) of the o-Ps annihilation in the copolymer series, when four-component fits was used to analysis the LT spectra. The values of the lifetime and the intensity depend largely on the silicon content in the copolymers. In the case of the Silicon-Cycloester copolymers, when using a four-components fits there is an increase in long-lived component  $\tau_4$  and its intensity ( $I_4$ ) as the silicon content increases. This can be considered to be an indication of an increase in the free volume in the silicon region. The increase in the  $\tau_4$  represents an

increase in the size of the free volume holes in the silicon phase. The increase in the intensity in the silicon phase represents an increase in the number of the free volume holes and indicates the higher fraction of o-Ps annihilating in the silicon phase as the silicon content increases. The free volume increases as the silicon phase becomes the dominant phase and the morphology changes from small spherical domains of silicon to larger domains, to bicontinuous phase, and then to small spherical domains of cycloester in a matrix of silicon (see Table 1).

The shortest long-lived component  $\tau_3$  and its intensity ( $I_3$ ) show an unstable increasing trend. This long-lived component ( $\tau_3$ ) can be attributed to the change in the free volume in cycloester phase. Here an interesting question arises: are the o-P characteristics in the PALS influenced by the presence of crystalline regions in the cycloester phase of the samples or not. The answer is clearly yes, since dislocation can form very easily in the crystalline region of the Silicon-Cycloester copolymer and it is now particularly easier in Silicon-Cycloester copolymer than in cycloester homopolymer.

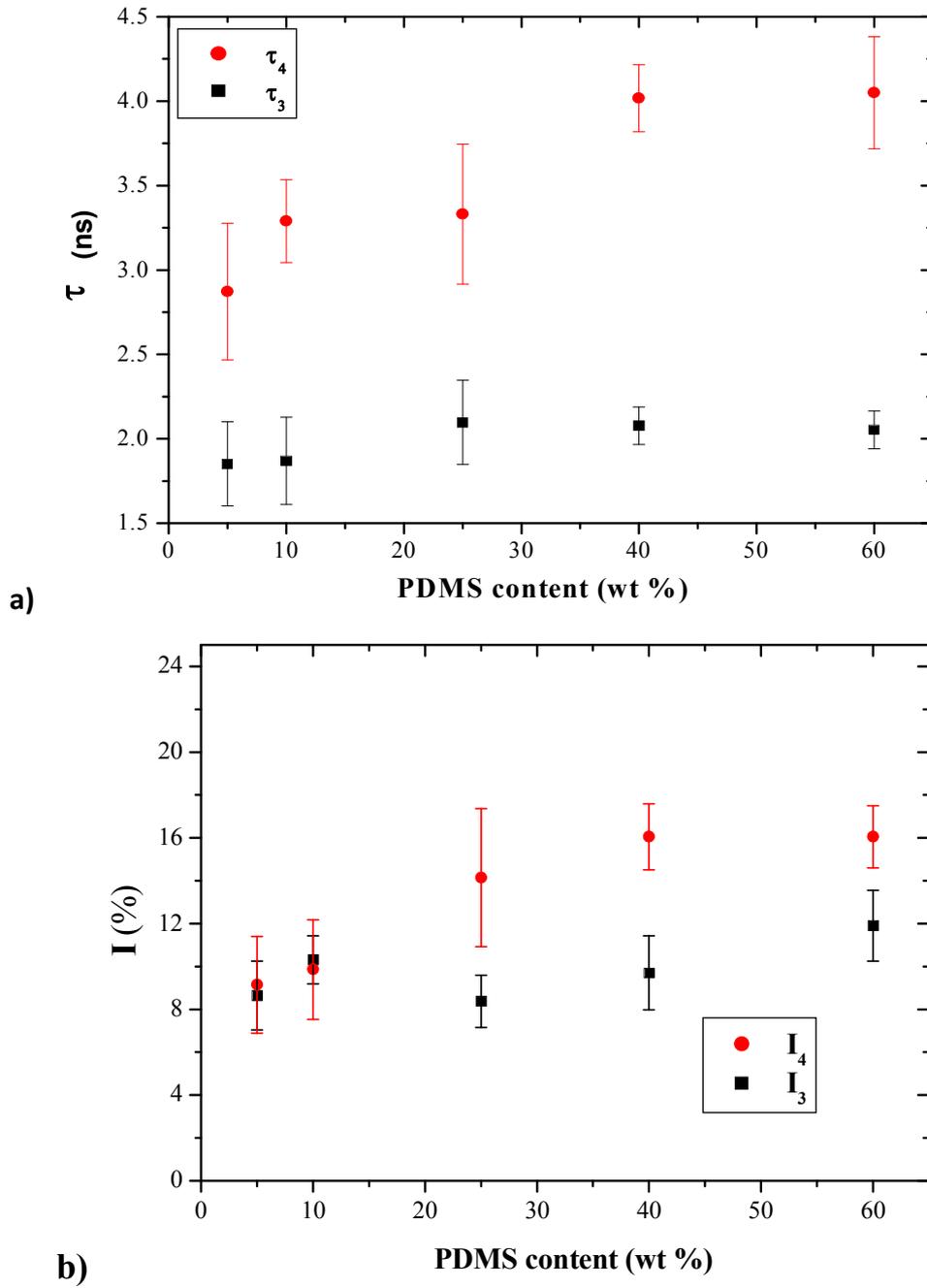


Figure 2: Dependence of (a) o-Ps lifetime ( $\tau$ ) and (b) intensity ( $I$ ) on the silicon content in Silicon-Cycloester copolymer series.

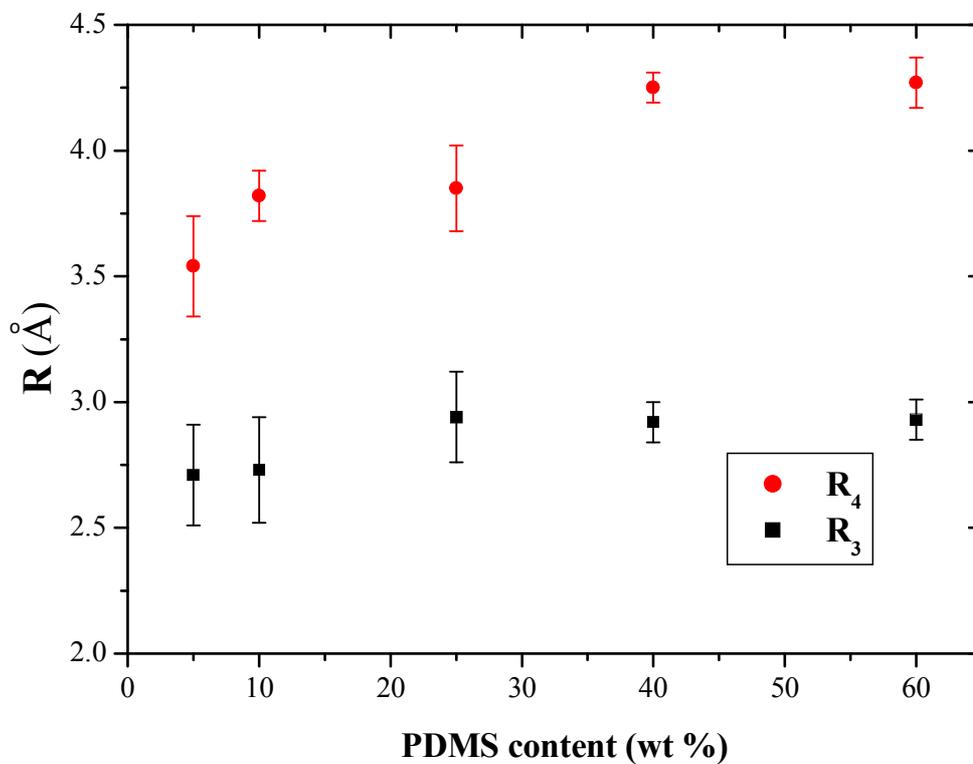
It is also worthwhile considering the possibility that Ps trapping in dislocations or in vacancies that are associated with dislocations in the crystalline region of the cycloester segment could also affect the o-P characteristics in the PALS. Therefore, in order to understand the cycloester phase in more detail consideration of five-components fit of the LT spectra is recommended. Such fits have been used for hypercrosslinked polystyrene, using both the PATFIT and MELT system [14]. The process of resolving five exponential components is extremely difficult and leads to large variances and was not done on the current data. Nevertheless, by using four-components fit the silicon phase can be identified and understood clearly and this study is limited to four-component fit (using five-component fit might be subject of another future study).

Therefore, in addition to, the microphase separation, the change in the crystallinity in Silicon-Cycloester copolymer can have influence on the positron annihilation mechanism and increasing in the free volume in the cycloester region ( $\tau_3$ ) can be an evidence of looser packing of the cycloester macromolecular chains and of the formation of additional free volume at the phase boundaries. This might offer additional evidence of the formation of o-Ps in both the crystalline and amorphous phases, depending on the material under investigation, as was reported in several articles in the literature [28]. In this case the increasing  $I_3$  as well as  $I_4$  with silicon content is most probably a result of the decreasing crystallinity in the cycloester phase. The increases in the  $\tau_3$ ,  $\tau_4$ ,  $I_3$  and  $I_4$  with an increase in the silicon content shows a nonlinear relationship.

In copolymers with a high silicon content (SC-5) (60 wt %) the longest lifetime ( $\tau_4$ ) and intensity ( $I_4$ ) were observed, meaning that these copolymers have a higher free volume of holes and a high density of such

holes. This can be clearly seen from the radius of the free volume hole in Figure 3 and from the free volume values in Table 2.

Figure 3 shows the effect of the silicon content on the radii of the free volume holes. Although in reality the free volume holes may not be completely spherical, the two free volume radii  $R_3$  and  $R_4$  may be used as a rough estimate of the actual hole size. The smaller value ( $R_3$ ) corresponds to the free volume holes in the cycloester phase and the larger one ( $R_4$ ) to the free volume holes in the silicon phase. Both radii of the free volume holes in Figure 3 increase as the silicon content increases, which explains the decrease in the  $T_g$  values of the silicon and the cycloester segments, as shown in Table 2.



**Figure 3: Effect of the silicon content on the radius (R) of the free volume holes in the copolymer series.**

The increase in the radius obtained for the cycloester phase in the copolymer when compared with the radius of the free volume holes in the cycloester homopolymer could be a result of the increase in the dislocations and imperfections in the cycloester phase in the copolymers due to the silicon segment disruption of the lamella structure, as has been reported using AFM [31]. The change in the degree of crystallinity can lead to a change in the amorphous regions, and subsequently to a change in the lifetime and intensity of the o-Ps annihilations. No clear relationship can be drawn, however, between the degree of crystallinity and the o-Ps characteristics, because in all the Silicon-Cycloester copolymer series the degree of crystallinity decreases as the silicon content increases, which can also affect the o-Ps characteristics.

One can expect a higher free volume to occur due to both the microphase separation and the change in the degree of the crystallinity in the Silicon-Cycloester copolymer. In other words, a high free volume and density is the result of the influence of the silicon regions on the cycloester amorphous regions, and the cycloester amorphous regions in turn affect the neighbouring crystalline structure of the cycloester region. Changing the crystalline regions as the silicon content changes could result in broadening the amorphous regions as the silicon content increases in between the crystalline regions of the cycloester folding chains in the lamella structure [31]. Obviously, broadening the amorphous regions will lead to an increase in the size of the free volume holes in the intermediate region between the crystalline region and the amorphous region, and also in the crystalline region. In addition to the volume of the holes, Table 2 also shows the free volume fraction for the Silicon-Cycloester copolymer series.

**Table 2: Free volume holes and free volume fractions of the holes in silicon phase ( $fv_3$  and  $ffv_3$ ) and cycloester phase ( $fv_4$  and  $ffv_4$ ) in the Silicon-Cycloester copolymer series based on the four-components fit.**

Sample	$fv_3$ ( $\text{\AA}^3$ )	$\Delta fv_3$ ( $\text{\AA}^3$ )	$ffv_3(\%)$	$\Delta$ $ffv_3(\%)$	$fv_4$ ( $\text{\AA}^3$ )	$\Delta fv_4$ ( $\text{\AA}^3$ )	$ffv_4(\%)$	$\Delta$ $ffv_4$ (%)	Total $ffv$ (%)
SC-1	102.5	8.70	0.72	0.18	187.3	31.6	3.08	1.41	3.80
SC-2	103.8	8.70	0.69	0.19	234.7	18.9	4.16	1.52	4.85
SC-3	104.7	11.60	0.84	0.38	239.5	31.7	6.09	2.19	6.93
SC-4	103.4	12.00	1.58	0.54	322.5	14.7	9.31	1.31	10.89
SC-5	105.7	11.30	1.50	0.60	326.5	24.4	9.43	1.55	10.93

The free volume fraction was determined in both the silicon and cycloester phases, based on the four-components fit parameters ( $\tau_3$ ,  $\tau_4$ ,  $I_3$ , and  $I_4$ ) using Eq 4. The total fraction of the free volume in each copolymer was calculated as the sum of the free volume fractions in both phases. The free volume fraction is directly related to the mechanical properties of the polymers. This parameter can be thought of as the product of the average hole size and the hole concentration [26]. From the table, one can see a significant change in the free volume fractions in all the copolymers series, and copolymer SC-5 has the largest free volume fraction (10.93%) while copolymers SC-1 has the smallest fraction (3.80%). This is clearly due to the fact that copolymer SC-5 has highest silicon content and copolymers SC-1 has lowest silicon content.

## 4. Conclusions

The ability to determine the free volume in Silicon-Cycloester semicrystalline copolymers using the PALS technique was investigated. In this case, where the three-components fit becomes meaningless, the LT spectra of the Silicon-Cycloester copolymer series were analyzed using

the four-component fit. 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 caused by changes in the molecular structure of the copolymers. It also appeared that the crystal structure and the phase separation morphology could affect the free volume of the Silicon-Cycloester copolymers. The free volume in a series of Silicon-Cycloester semicrystalline copolymers with various silicon content was determined using the PALS technique. In the series, it was found that increasing the silicon content lead to an increase in the intensity of Ps and the lifetime of the o-Ps.

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