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Determination of Free-Volume Properties in Polymers Without Orthopositronium Components in Positron Annihilation Lifetime Spectroscopy

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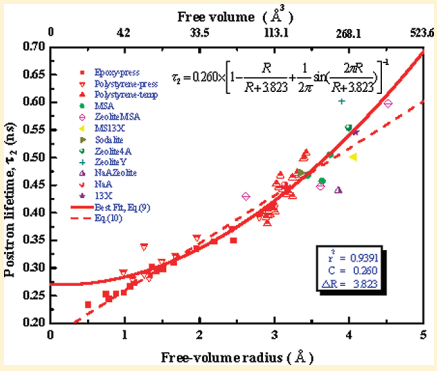
ABSTRACT: Existing positron annihilation lifetime spectroscopy (PALS) uses the orthopositronium components, lifetimes, and intensities observed in molecular substrates, such as in polymers, to determine free-volume properties based on an infinitive potential spherical model originally proposed by Tao in 1972. However, in many molecular systems, positronium is either quenched or inhibited by interacting with chemical functional groups and leads to no or nearly no orthopositronium component in PALS. In this Article, a newly modified equation is developed by following the Tao's quantum model using the positron component (not orthopositronium) of PALS. This modified equation is examined by fitting free-volume results obtained from *o*-Ps lifetimes with the positron lifetimes in pressure- and temperature-dependent data in polymers and calibrated with known or calculated cavity sizes in zeolite materials. A newly modified positron lifetime-free volume correlation equation is established for the determination of free volumes up to the mean radius of 5 Å in polymeric systems, where no orthopositronium component is observed in PALS.



1. INTRODUCTION

During the last three decades, a novel method, positron annihilation spectroscopy (PAS), has been used to investigate atomic and molecular defects and interfacial properties.[1,3] One of PAS techniques, positron annihilation lifetime spectroscopy (PALS), is capable of determining the free-volume and hole properties directly at the atomic level and nanoscales.[1−3] This special capability arises from the theory and experimental evidence[4,5] that positronium (the bound state of positron and electron, Ps) is preferentially localized in the regions of low electron density sites, such as free volumes, holes, interfaces, and pores. The primary mechanism of annihilation of triplet positronium (*o*-Ps) in molecular substrates is by pick-off with electrons of the materials under study. Therefore, the intrinsic *o*-Ps lifetime (142 ns) is typically shortened to a few nanoseconds (1−10 ns) via two-γ annihilation processes in molecular substrates. According to the Ps-free volume theory,[4] the lifetime of *o*-Ps is determined by the reciprocal of integral between the positron and the electron densities in the free volumes of molecular systems. Therefore, *o*-Ps lifetime is expected to correlate directly with the dimensions where Ps is localized. A large hole, which contains a low mean electron density, results in a long *o*-Ps lifetime. A simple quantum mechanical model, where *o*-Ps resides in a spherical well having an infinite potential barrier of radius R_o with a homogeneous electron layer ΔR in the region between the hole radius R and R_o ($R_o = R + \Delta R$) was proposed to derive a relationship between R and *o*-Ps lifetime by Tao in 1972.[6] Such a model provides a simple relation among the *o*-Ps lifetime, usually denoted as τ_3, the third mean lifetime as analyzed from experimental PALS spectra, and the mean free-volume radius (R). A semiempirical equation by fitting the measured *o*-Ps lifetime (τ_3) in a spherical infinitive potential model with known cavity sizes has been established as[6−8]

$$\tau_3 = 0.5 \times \left[1 - \frac{R}{R + \Delta R} + \frac{1}{2\pi}\sin\left(\frac{2\pi R}{R + \Delta R}\right)\right]^{-1} \quad (1)$$

where τ_3 and R are expressed in the units of nanoseconds and angstroms, respectively, and ΔR was calibrated to be 1.656 Å.[8]

Equation 1 is popularly used in the positron and polymeric communities because of its simplicity and with a reasonable precision to estimate a mean value of free-volume size at the atomic molecular level for most polymers. However, positronium (Ps) is the lightest atom, which can chemically react with molecules and different functional groups by two processes, chemical quenching, which decreases *o*-Ps lifetime (τ_3), and chemical inhibition, which decreases the probability of *o*-Ps formation (I_3). Typical chemical function groups, which exhibit strong quenching are nitroaromatics, quinones, maleic anhydride, and ions with

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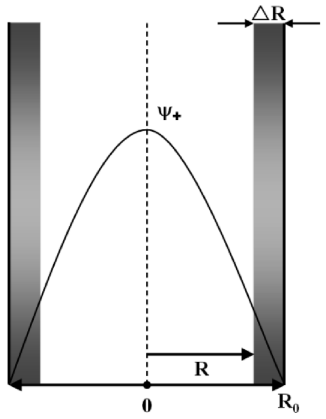

Figure 1. Schematic diagram of positronium or positron wave function ψ_+ in an infinite spherical potential well confined in a radius R_o and an electron density layer. The R is the hole radius of media and ΔR is the electron layer thickness.[6]

redox potential < −0.9 eV.[1] Some important and common materials that show no *o*-Ps or very small fraction of *o*-Ps intensity (<2%) are polyimides[9−16] and materials containing only carbon.[17−20] This chemical process hampers the use of eq 1 to obtain the correct free-volume data from PALS. In this Article, instead of using *o*-Ps component (τ_3), we develop a newly modified correlation equation by using the second-component positron lifetime (τ_2) of PALS spectra, which is useful in the determination of the free-volume size in polymeric materials, where no *o*-Ps component is observed.

2. THEORETICAL ASPECTS

Positronium (Ps) was first considered by Ferrell in 1957[21] as a self-trapped state, the so-called positronium-bubble, to account for the long lifetime of *o*-Ps in liquids. The equilibrium bubble size of Ps in liquids is balanced by the zero-point energy of localized Ps and the surface tension of liquids.[1,21] The model of Ps in a bubble was later developed by Tao[6] in 1972, where Ps was considered to be the particle in an infinite spherical potential confined in a radius R_o. The Ps wave function inside R_o for the particle in an infinite spherical potential of Schrödinger equation is expressed by $\Psi_{Ps}(r) = (2\pi R_o)^{-1/2} \sin(\pi r/R_o)/r$. Tao further proposed a simple model with a uniform electron density layer of thickness ΔR instead of solving electron wave functions and obtained the probability (p) of Ps inside the electron layer [$\Delta R = R_o - R$] as[2,6]

$$p = \left[1 - \frac{R}{R + \Delta R} + \frac{1}{2\pi}\sin\left(\frac{2\pi R}{R + \Delta R}\right)\right] \quad (2)$$

He finally derived an equation that describes the relationship between the *o*-Ps pick-off annihilation lifetime (reciprocal of p) and the bubble radius (R) in liquids as eq 1. Equation 1 has a parameter ΔR, the electron layer thickness, which has been semiempirically calibrated to be 1.656 Å by fitting known spherical cavities in molecular and zeolite systems.[7,8] During the last two decades, this equation has been introduced to polymeric systems to determine the mean free-volume size and distributions.[2,22,23] Figure 1 schematically shows the concept of the infinitive potential spherical model for eq 1.

Whereas this infinitive potential spherical model has been widely used in the polymeric community, it is not directly applicable for molecular substrates without observable *o*-Ps intensity, I_3. This phenomenon is caused by the "quenching" or "inhibition" effect.[1,3] The specific chemical environment will accelerate the annihilation rate and shows a reduced *o*-Ps lifetime, that is, τ_3 in PALS results. The inhibition effect is caused by interaction of radiation species induced due to the positron with media in competing with the combination of the positron and electrons in forming Ps. The inhibition shows reduced or no *o*-Ps intensity, I_3 in PALS. The quenching effect also can cause inhibition by intercepting electrons in combining with positrons to form Ps.[1] The objective of this work is to use the positron lifetime τ_2 to determine the free-volume size. This idea is supported by the observation of similar localization of the positron in the free volume as that of Ps in molecular substrates. (See the Experimental Section and ref 24.)

To apply eq 1 based on the infinite potential spherical model from *o*-Ps (τ_3) to the positron (τ_2), we rewrote eq 1 in a general form as

$$\tau_2 = C\left[1 - \frac{R}{R + \Delta R} + \frac{1}{2\pi}\sin\left(\frac{2\pi R}{R + \Delta R}\right)\right]^{-1} \quad (3)$$

Two parameters to be determined as transforming from *o*-Ps to the positron lifetime are C and ΔR, the intrinsic positron lifetime and the electron layer thickness for the positron penetration to the wall region of R_o.

To parametrize C, we should consider observable positron lifetimes (τ_2) in molecular substrates from PALS. When a positron (typically a few hundred kiloelectronvolts from ^{22}Na positron source) enters a molecular system, it loses kinetic energy within the time on the order of picoseconds; then, the positron may pick up an electron to form positronium. Normally, the triplet state, orthopositronium (*o*-Ps), has 3/4 formation probability, and the singlet state, *para*-positronium (*p*-Ps), has 1/4 formation probability. The free *o*-Ps and *p*-Ps have the intrinsic lifetime of 142 and 0.125 ns, respectively.[1] In molecular substrates, the *o*-Ps lifetime could be reduced to a few nanoseconds by picking off the electrons and annihilating into 2-γ. Therefore, the mean intrinsic lifetime of Ps from *o*-Ps and *p*-Ps should be very close to 0.5 ns ($= (3/4\ \tau_3^{-1} + 1/4\tau_1^{-1})^{-1}$). That is, the 0.5 ns in the original eq 1 for Ps.[2,6] In molecular substrates, C value for the positron (not forming Ps) should be close to the dense bulk lifetime for the positron (τ_2), such as at a state that the substrate has nearly no defects. In molecular substrates, besides Ps formation, there is usually a large fraction of positrons that are trapped in free volume and will not pick up electrons to form Ps but directly annihilate into 2-γ, that is, I_2. In the data analysis, a PALS spectrum from real molecular systems is often resolved into three finite lifetimes: $\tau_1 \approx 0.125$ ns due to *p*-Ps annihilation with intensity as I_1, typical $\tau_2 \approx 0.2$ to 0.5 ns due to the positron (localized or delocalized) annihilation with intensity I_2, and $\tau_3 \approx$ 1−5 ns due to *o*-Ps annihilation with intensity I_3. In a substrate with large pores (R > 5 Å), there will be additional long *o*-Ps lifetime τ_4 > 5 ns. For the value of C, the known lowest positron lifetimes in molecular substrates without *o*-Ps formation are close to 0.2 ns, such as in the single crystal of graphite τ = 0.195 ns[17] and τ_2 = 0.22 ns in a highly compressed epoxy polymer.[24] The C value may depend on the chemical and crystallographic structures of molecular systems. This will be discussed in the latter section that C can vary between 0.14 and 0.28 ns and may be materials-dependent.

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For ΔR, both the quantum effect of positron localization and fitting the τ_2 data with known hole/cavity sizes in molecular systems such that τ_3 for *o*-Ps should be considered. For the particle in an infinite potential well with a radius R_o, the ground-state energy is given by[1]

$$E = \frac{h^2}{8mR_o^2} \tag{4}$$

where m is the mass of the particle and h is the Planck's constant. In the infinite potential spherical model, $R_o = R + \Delta R$, the minimal ΔR required for Ps (at $R = 0$) equals the ground-state energy of the localized particle. Therefore, eq 4 could be expressed in general as[25]

$$\Delta R = \frac{h}{\sqrt{8mE}} \tag{5}$$

where E is the binding energy and m is the mass of the localized particle. For Ps, the ground-state binding energy and the mass are 6.8 eV and 1.82×10^{-30} kg, respectively. Therefore $\Delta R = 1.656$ Å, which is precisely the same as the semiempirically fitted value.[8] For the positron, the mass is half of Ps, that is, 9.1×10^{-31} kg. However, the positron binding energy will depend on the substrate. In molecular systems, the positron binding energy is very little known. In graphite, it was reported to be 3.0 ± 0.2 eV from the lifetime temperature data.[17] Then, the electron layer thickness ΔR for positron localized in an infinite spherical potential for graphite could be estimated to be 3.526 Å according to eq 5. For the positron localized in a spherical hole, the value of electron layer thickness could be estimated if the positron binding energy, B.E., with the substrate is known. The ΔR of eq 5 could be expressed (using E = *B.E.* of the positron, h = Planck's constant, and m = mass of the positron) by the following equation

$$\Delta R = \frac{6.107}{\sqrt{B.E.}} \tag{6}$$

where *B.E.* is the positron binding energy with the molecular substrate and ΔR is expressed in electronvolts and angstroms, respectively. The best C and ΔR parameters for positron lifetime τ_2 equation could be obtained by a semiempirical method in fitting with known hole/cavity size data.

3. EXPERIMENTAL SECTIONS

3.1. Materials and Sample Preparations. Polystyrene (PS) was purchased from Pressure Chemical Company. The molecular weight and polydispersity index (M_w/M_n) are 300 000 Da and 1.06, respectively. It was in amorphous form without specified tacticity and degree of crystallinity. The molecular sieves A and X types were commercial products from Molecular Factory of Shanghai, China. The zeolite A samples were supplied by Toyo Soda Kogyo (Tokyo, Japan), and sodalite was kindly supplied by Exxon Nuclear Idaho (Tokyo, Japan). All samples were used as received. All samples were pumped under high vacuum (10^{-4} to 10^{-5} Torr) for 4−12 h before the PALS experiments were performed. All PALS experiments were performed for samples under continuous pumping, except the PS-pressure dependence experiment was under an ambient atmosphere.

3.2. Positron Annihilation Lifetime Spectroscopy. A conventional fast−fast coincidence spectrometer with a time resolution of 250 ps was used for PALS measurements.[2,24,26] The positron source (10 μCi) ^{22}Na was deposited in an envelope of Kapton foils (6 μm thick) and then sandwiched in between sufficient thickness of the samples. One million counts were recorded at each PALS spectrum for a typical period of acquisition of 3−5 h. In conventional analysis, the PATFIT-88 program was employed and the PALS spectra were typically analyzed into three components (τ_1, τ_2, and τ_3) with their intensities (I_1, I_2, and I_3) in polymers or into four components in zeolite systems. Source correction terms were made from each spectrum in data analysis.

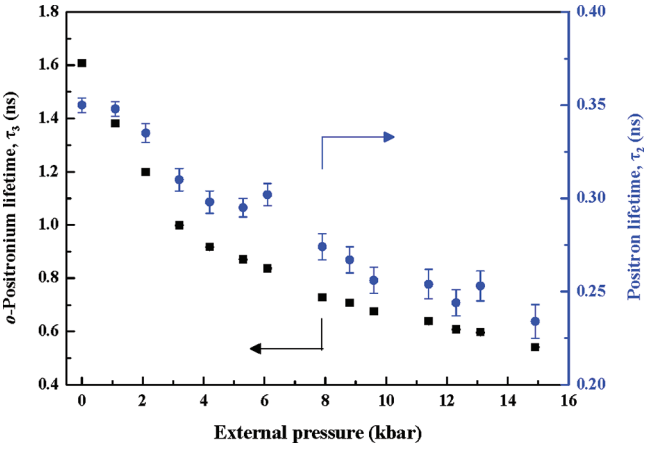


Figure 2. Positron and *o*-positronium lifetime versus pressure in an epoxy. Data were taken from ref 24. Error bars of *o*-Ps lifetimes are less than the size of data points shown.

3.3. Pressure-Dependent PALS Setup. An anvil system and a 25-ton hydraulic press (Carves) were used to generate a quasi-isotropic pressure up to 14.9 kbar. The O.D. of anvil (tungsten alloy) was 25 mm with a working diameter of 14 mm. Two polymeric samples (diameter = 4 mm and thickness = 1.0 mm) were housed in a gasket (9.0 mm O.D. made of pyrophyllite) that was precisely machined to match the sizes of samples. In such a design, a uniform distribution of quasi-isotropic pressure can be achieved for this diameter/thickness ratio. A 15-μCi positron source, ^{22}Na, was directly deposited on one surface of the samples. All positron annihilation took place within a 1 mm radius of the source. The principle of generating quasi-isotropic pressure and its design were described in one of our previous papers.[24] The pressure was cycled twice, and no hysteresis was detected.

3.4. Temperature-Dependent PALS. Two pieces of samples were sandwiched in between a ^{22}NaCl (15-μCi) source, which was sealed in two 6 μm Kapton films. The sample with source was put in a quartz tube with a wrapped heating wire. The PALS spectra were acquired under different temperature range as computer programmed with a temperature control within ±1.5 °C. All measurements were carried out under continuous vacuum pumping system (<10^{-4} Torr). The temperature setup was the same as that described in one of our recent papers.[26]

4. RESULT AND DISCUSSIONS

Three series of PALS experiments along with one series of our previous results were used to develop a new correlation equation between positron lifetime and free-volume size: pressure dependence in epoxy,[24] pressure and temperature dependence in PS, and zeolite materials with different known sizes.

4.1. Pressure Dependence PALS Data in Epoxy Polymer. When a polymer is under a static isotropic pressure, the free volume is significantly decreased, and thus it provides a good calibration for the variations of free-volume size with respect to both *o*-Ps and positron lifetime, τ_3, τ_2. Pressure PALS experiments were reported by us in studying free-volume properties in

an amine-cured epoxy (diglycidyl ether of bisphenol A and *N,N′*-dimethy-1,6-diaminohexane and 1,4-diaminobutane) as a function of quasi-isotropic pressure in the range of 0−15 kbar.[24] This series of PALS data is used here first to obtain *C* and ΔR values of eq 3 for τ_2. The data *o*-Ps and positron lifetimes versus external quasi-isotropic static pressure in an amine cured epoxy polymer are plotted in Figure 2.[24]

As shown in Figure 2, both the *o*-Ps and positron lifetimes (τ_3 and τ_2) were found to decrease significantly and similarly as a function of pressure while the corresponding intensities, I_2, and I_3, slightly increased and decreased, respectively (not shown, see ref 24). The pressure variations provide evidence that both Ps and the positron are localized at free-volume holes in epoxy polymers.

Theoretically, a highly compressed polymer has nearly zero-free volume; therefore, the smallest τ_2 value provides a good estimate for *C* value in eq 3, which was found to be 0.22 ns.[24] Next, we consider the value of ΔR, the electron layer thickness for the positron for eq 3. Because the positron B.E. in epoxy polymers is unknown, we could not estimate ΔR directly from eq 6. The *o*-Ps lifetime data of Figure 2 can provide the free-volume radius (R) correctly from *o*-Ps lifetimes using the established and calibrated τ_3-R relationship (eq 1). We first calculated the free-volume radius (R) according to the data of *o*-Ps lifetime (Figure 2) and eq 1 and plot the corresponding τ_2 versus calculated R (from τ_3) at different pressures in Figure 3. As expected, τ_2 increases as a function of free-volume radius (R), as shown in Figure 3. Next, τ_2 values, as shown in Figure 2, are fitted with respect to the R (from τ_3) according to eq 3. The best fitted C and ΔR results (correlation coefficient, r^2 = 0.9142) from τ_2 versus R in the epoxy PALS-pressure data according to eq 3 are found to be 0.245 ns and 3.419 Å, respectively, and are plotted as the line shown in Figure 3.

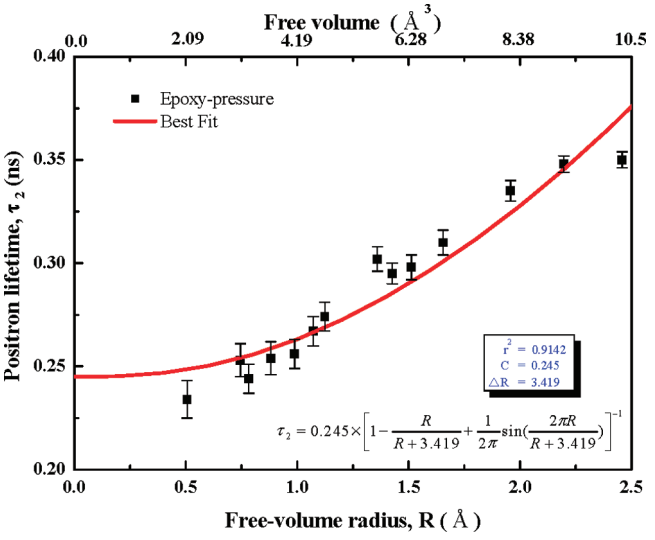


Figure 3. Positron lifetime versus free-volume radius obtained from *o*-Ps data from epoxy pressure-dependent data and eq 1. The line is a newly fitted eq 3 between positron lifetime and free-volume radius (R).

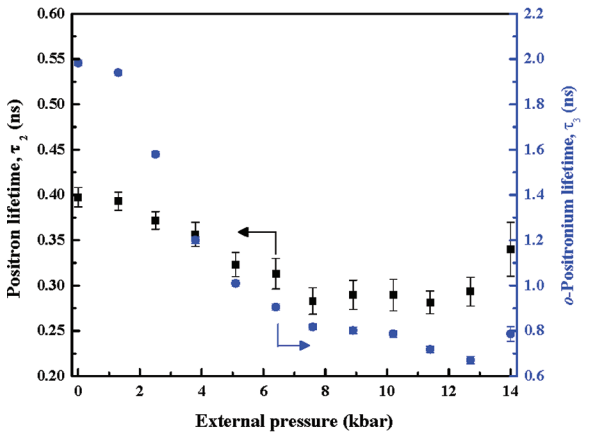
As shown in Figure 3, we have the following results: (1) the fit of eq 3 is reasonably good with correlation coefficient r^2 = 0.9142; (2) the C = 0.245 ns value for epoxy is slightly higher than the extrapolated value at high pressure τ_2 = 0.22 ns[24] but is higher than the positron lifetime in graphite = 0.195 ns;[17] and (3) the best fit, ΔR = 3.419 Å, is close to that theoretically estimated for a B.E. (3.0 eV) of graphite[17] (ΔR = 3.526 Å according to eq 6). Therefore, based on this set of epoxy-pressure data, we obtain a newly modified equation between the positron lifetime (τ_2) and free-volume radius (R) for epoxy polymer as

$$\tau_2 = 0.245 \times \left[1 - \frac{R}{R + 3.419} + \frac{1}{2\pi}\sin\left(\frac{2\pi R}{R + 3.419}\right)\right]^{-1} \quad (7)$$

where τ_2 and R are expressed in the units of nanoseconds and angstroms, respectively

4.2. Test of τ_2-R Equation for PALS Data in Polystyrene-Pressure Results. The newly modified τ_2-R eq 7 above should be tested for its usefulness and evaluated for the determination of the free-volume results from PALS data in different polymers, for example, in a common and most studied thermoplastic polymer, PS, as a function of pressure. We have performed PALS−pressure experiments in PS, and the results of *o*-Ps lifetime (τ_3) and positron lifetime (τ_2) and corresponding intensities are shown in Figure 4 below.

As expected, the variations of τ_3 and τ_2 versus external pressure in PS are similar to that in an epoxy polymer (Figure 2). We plot the positron lifetime versus the free-volume radius (R) calculated from *o*-Ps lifetime (τ_3) according to eq 1 in Figure 5.



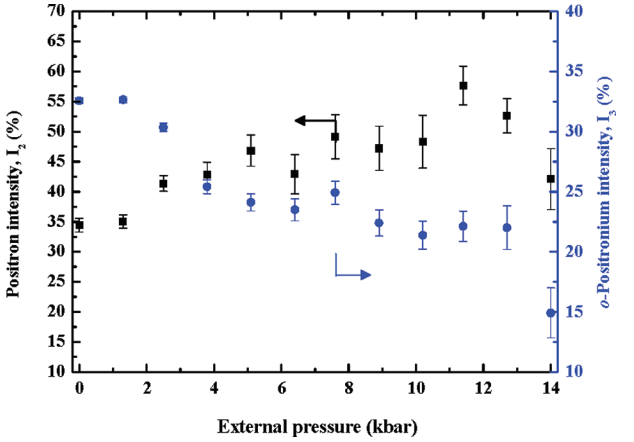


Figure 4. Positron and *o*-positronium lifetimes (left) and intensities (right) versus pressure in polystyrene. Error bars of *o*-Ps lifetimes are less than the size of data points shown.

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Similar to the epoxy, I_2 increases with the pressure. One should not take I_2 in relating to free-volume information as that of I_3 (o-Ps intensity)[2] because in PAFTIT analysis of PALS data the total intensity is always normalized to 100% and I_1 and I_3 are highly correlated because they correspond to p-Ps and o-Ps probability, respectively. When o-Ps intensity decreases, so is I_1, and thus I_2 is expected to increase because total intensity equals 100%. Furthermore, in the data analysis of PALS spectra, τ_1 and τ_2 components are also correlated to each other and could not be completely separated as p-Ps and positron components in the current PALS analysis. The best way to obtain consistent and stable τ_2 values from the current PALS data fit is to fix $\tau_1 = 0.125$ ns, which is the theoretical p-Ps lifetime.

We first plot the τ_2-R eq 7 obtained from epoxy data in Figure 5. It is seen in Figure 5, whereas the free-volume results in polystyrene follow τ_2-R eq 7 derived from epoxy-pressure data but with a worse goodness of fit ($r^2 = 0.599$) than in epoxy. We therefore proceeded to fit eq 3 for the polystyrene—pressure data and obtained the best values of $C = 0.280$ ns and $\Delta R = 4.288$ Å, respectively, with a much better correlation coefficient ($r^2 = 0.8581$) for polystyrene. Both values are larger than epoxy and are probably due to larger free volumes in polystyrene than in the epoxy polymer. Equation 7 obtained from epoxy data requires some modification for its usefulness in the determination of free volumes in a different polymer, that is, polystyrene.

4.3. Test of τ_2-R New Equation in Polystyrene—Temperature PALS Results. Whereas the test of τ_2-R equation for PALS data is consistent between epoxy-pressure and polystyrene—pressure experimental data, one should test it in common PALS data, which have been often reported in the temperature-dependence studies. We have performed PALS experiments in well-annealed polystyrene as a function of temperature, cycled twice, and found no hysteresis. The results of o-Ps and positron lifetimes, τ_3 and τ_2, and corresponding intensities versus temperature are shown in Figure 6. Both τ_3 and τ_2 increase as a function of temperature, and o-Ps lifetime τ_3 undergoes a large increase near 100 °C, which indicates the glass-transition temperature as in many reported data.[27−35] It is also seen that the precision of τ_2

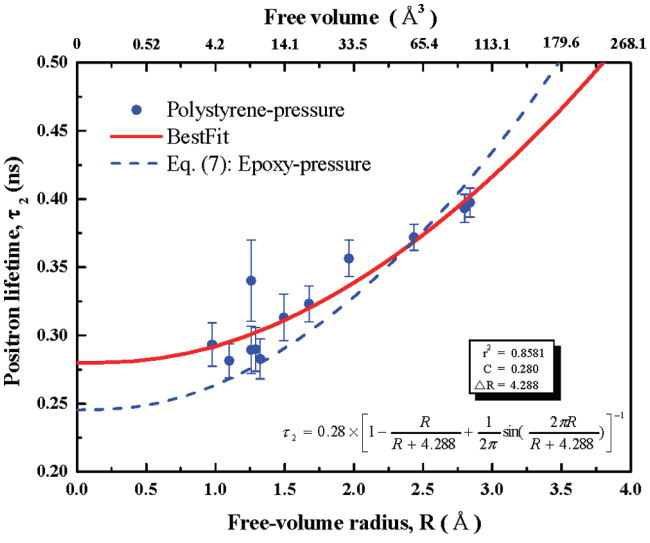


Figure 5. Positron lifetime (τ_2) versus free volume radius (R) calculated from o-Ps data (τ_3) according to eq 1 in polystyrene (pressure dependence). The solid line is the result of best fit eq 3, and the dashed line is the modified eq 7 from epoxy data.

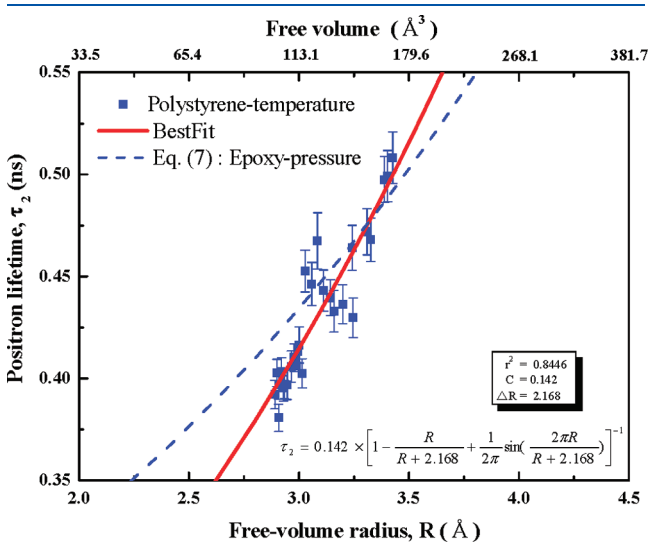
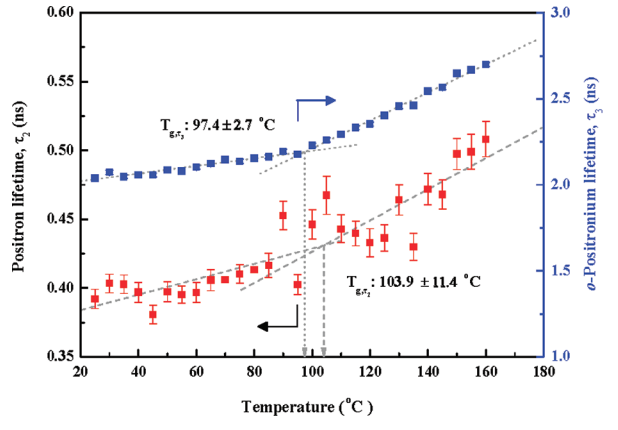


Figure 7. Positron lifetime versus free volume radius (R) calculated from o-Ps (τ_3) according to eq 1 in polystyrene (temperature dependence). The line is the best fit result to the data and the dashed line is the eq 7 obtained from epoxy-pressure data.



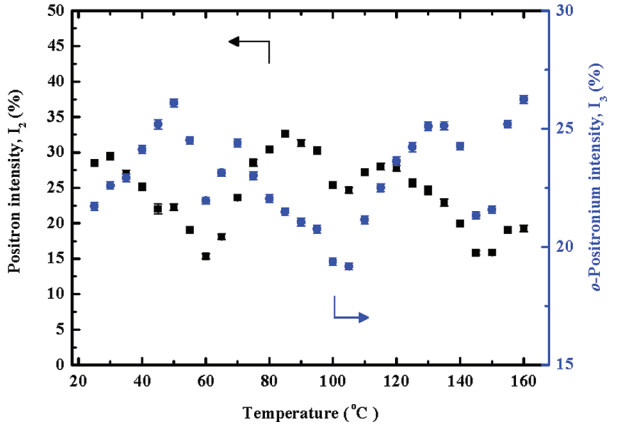


Figure 6. Positron and o-positronium lifetimes (left) and intensities (right) versus temperature in polystyrene. Error bars of o-Ps lifetimes are less than the size of data points shown.

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Table 1. Results of Glass-Transition Temperature (T_g), Free-Volume Expansion Coefficient (α_{fv}), and Free-Volume Compressibility (β_{fv}) Compared with the Bulk Values

T_g (°C) τ_3 data	T_g (°C) τ_2 data	T_g (°C) DSC[36]	α_{fv} (K^{-1}) < T_g	α_{fv} (K^{-1}) > T_g	α_{bulk} (K^{-1}) < T_g[36]	α_{bulk} (K^{-1}) > T_g[36]	β_{fv} ($kbar^{-1}$)	β_{bulk} ($kbar^{-1}$)[37]
97.4 ± 2.7	103.9 ± 11.4	101.2	$2.0 \pm 0.1 \times 10^{-3}$	$6.2 \pm 0.1 \times 10^{-3}$	2.1×10^{-4}	5.5×10^{-4}	4.0(<2 kbar) 0.3(14 kbar)	0.3 (1 bar) 0.2 (2 kbar)

Table 2. Cavity Radii Results of PALS in Selected Molecular Sieves and Zeolites Used for Calibration τ_2-R Equation 3

sample	τ_2 (ns)	τ_3 (ns)	τ_4 (ns)	I_2 (%)	I_3 (%)	I_4 (%)	radius $\overline{R}_{o\text{-Ps}}$ (Å)	theoretical radius (Å)
13X[45]	0.547	2.485 ± 0.103	6.174 ± 0.438	60.990	14.370 ± 1.060	10.130 ± 1.060	4.25	6.5
molecular sieves 3A	0.457 ± 0.002	1.558 ± 0.035	4.581 ± 0.052	60.923 ± 0.167	8.517 ± 0.160	11.478 ± 0.245	3.83	3.3,5.7
molecular sieves 4A	0.468 ± 0.002	1.648 ± 0.054	4.582 ± 0.041	57.985 ± 0.170	10.225 ± 0.142	8.809 ± 0.159	3.64	3.3,5.7
molecular sieves 5A	0.505 ± 0.002	2.003 ± 0.036	5.475 ± 0.061	61.041 ± 0.138	11.998 ± 0.134	8.831 ± 0.200	3.94	3.3,57
zeolite MS-3A	0.430 ± 0.002	1.420 ± 0.082	2.496 ± 0.125	57.917 ± 0.277	12.728 ± 0.082	7.265 ± 0.526	2.67	3.3,5.7
zeolite MS-4A	0.448 ± 0.002	1.591 ± 0.056	4.211 ± 0.041	59.425 ± 0.190	9.368 ± 0.195	15.053 ± 0.309	3.78	3.3,5.7
zeolite MS-5A	0.598 ± 0.002	3.206 ± 0.125	6.496 ± 0.246	52.782 ± 0.101	12.696 ± 0.006	11.292 ± 1.070	4.63	3.3,5.7
molecular sieves 13X	0.501 ± 0.002	2.261 ± 0.097	4.957 ± 0.095	54.805 ± 0.122	8.686 ± 0.508	12.924 ± 0.603	4.17	6.5
sodalite	0.473 ± 0.001	1.782 ± 0.016	7.681 ± 0.110	54.323 ± 0.109	11.685 ± 0.086	3.300 ± 0.052	3.69	-
zeolite Y[47]	0.602 ± 0.008	2.500 ± 0.030	6.000 ± 0.060	32.800 ± 0.800	12.000 ± 0.080	5.850 ± 0.080	4.05	3,6.5
NaAZeolite[42]	0.440 ± 0.008	1.340 ± 0.086	4.870 ± 0.043	48.29 ± 0.660	8.980 ± 0.320	18.610 ± 0.320	4.09	5.7
NaA[46]	0.450 ± 0.020	1.550 ± 0.040	9.860 ± 0.090	38.800	3.200	0.700	3.66	5.7
zeolite 4A[44]	0.554 ± 0.013	2.431 ± 0.376	4.918 ± 0.340	12.900 ± 0.200	2.500 ± 0.300	2.700 ± 0.600	4.09	5.7

is less than τ_3 because the τ_2 values are closer to the PALS' lifetime resolution (0.25 ns). In temperature-dependence experiments, τ_2 data scatter more than that of pressure-dependence data (Figure 4) because τ_2 varies with temperature less than pressure.

In Figure 7, we plot τ_2 versus free-volume radius (R) obtained by *o*-Ps lifetime (τ_3) according to eq 1. We also plotted the τ_2-R eq 7, as obtained from epoxy-pressure data to compare with the free-volume radius in polystyrene−temperature data in Figure 7 (dashed line).

Whereas the τ_2 increases with temperature but data scatter, it is also seen that the free-volume data obtained from τ_2-R follow eq 7 but less goodness of fit (r^2 = 0.821). We again fit polystyrene−temperature data to eq 3 and obtain the best C = 0.142 ns, and ΔR = 2.168 Å with an improved goodness of fit (r^2 = 0.8446). The best fit polystyrene−pressure data and a new equation for eq 3 are shown in Figure 7. Both C and ΔR values for temperature dependence are different from and less than that of pressure dependence. It is worthwhile to point out that the precision in the determination of the free volumes using τ_2-R eq 3 is intrinsically less than that from τ_3-eq 1, particularly for the PALS−temperature studies, because the τ_2 temperature variations are less than that in pressure dependence.

For the completeness of discussing PALS results in polystyrene as a function of temperature and pressure, we calculate and report the glass-transition temperature (T_g), free-volume thermal expansion coefficients (α_{fv}), and free-volume compressibility (β_{fv}) defined as $\alpha_{fv} = \Delta V_{fv}[\Delta T \cdot \overline{V}_{fv}]^{-1}$ and $\beta_{fv} = \Delta V_{fv}[\Delta P \cdot \overline{V}_{fv}]^{-1}$, respectively, where $\overline{V}_{fv}$ is the mean free volume ($= 4\pi R^3/3$) from average R as calculated according to τ_3 data shown in Figures 4 and 6 and eq 1 between two adjacent temperatures or pressures. The regions of data points in linear fit in Figure 6 were chosen at temperatures above and below the known T_g of polystyrene (T_g = 101.2 °C from DSC). The resulting α_{fv} has two values, one for above T_g and the other for below T_g, respectively. β_{fv} decreases with P because V_{fv} follows an exponential function $V_{fv} = 0.106 \exp(-0.27\ P)$, where V_{fv} and P are in the units of cubic nanometers and kilobars, respectively. This is similar to that reported in epoxy.[24] The results of T_g, α_{fv}, and β_{fv} are listed in Table 1 and compared with the bulk data.

The obtained T_g results are consistent with the DSC[36] and existing PALS data,[27,35] whereas it is noted that T_g obtained from τ_2 is less precise than that from τ_3, as expected. The free-volume expansion coefficients as well as the free-volume compressibility are found to be one order of magnitude larger than that obtained from the bulk.[36,37] This is because the PALS is especially sensitive in probing free volumes.

4.4. Calibration of τ_2-R Equation with Known Cavity Sizes. From the above results, the τ_2-R eq 3 has been tested, and its applicability to polymeric systems having the free-volume radii up to 3.5 Å and τ_2 = 0.50 ns or corresponding τ_3 =2.8 ns has been evaluated. Whereas the fitting parameters vary slightly from system to system for the τ_2-R relationship of eq 3, we proceed to establish the best fitted τ_2-R equation for common polymers and zeolite systems[38] for R > 3.5 Å. The extension of eq 3 for R > 3.5 Å requires a calibration with known cavity sizes similar to that for eq 1, which was established.[8,38,39]

First, we examine the extension of eq 3 for R to 5 Å, where some zeolites with spherical cavities are ideal systems for this calibration. We have performed PALS in selected molecular sieves and zeolites, where the cavities are known to be spherical.[40] Acceptable results from PALS data of PATFIT analysis (VOF < 1.1) in those systems were found only from four-lifetime analysis because of the porous structures existing in those materials. For example, in type-A zeolites, two cavities, the α,β cages, are known to have spherical radius of 6.5 and 3.3 Å, respectively.[40] In the three-lifetime analysis, VOFs were found to be consistently >1.3. The four-lifetime analyzed lifetime and intensity results in those selected zeolites and molecular sieves are listed in Table 2. The

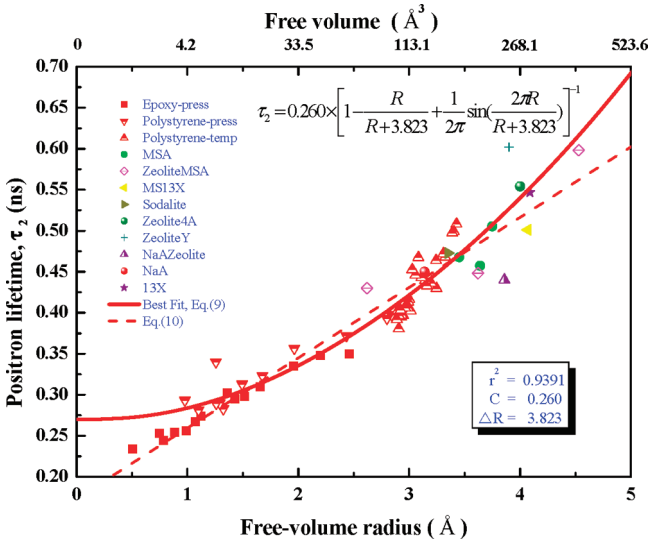

Figure 8. Positron lifetime versus free volume radius (R) in various polymer and zeolite systems. The best-fitted τ_2-R (eq 9) to all data is the solid line (C = 0.26 ns, ΔR = 3.823 Å, r^2= 0.9391). The dashed line is approximated linear fit eq 10. Legends: epoxy-pressure (Figure 3, ref 24); PS-press: polystyrene pressure (Figure 5); PS-temp: polystyrene-temperature (Figure 7); MSA: molecular sieves A-type (this work); zeolite MSA/zeolite type A (this work); MS13X (this work); Sodalite (this work); NaAzeolite;[42] Zeolite4A;[44] Zeolite Y;[47] NaA: Na-zeolite;[46] and 13X: zeolite-13X.[45]

results of Table 2 are comparable to those existing data in zeolite systems.[41−49] It is noted that in the PATFIT analysis of PALS data, we have fixed the shortest lifetime τ_1 = 0.125 ns, which corresponds to the p-Ps lifetime so that the results for the other three lifetimes are more stable and consistent. We also attempted to constrain I_1 = 1/3 of o-Ps intensity in the PATFIT analysis. However, the fit results are not as satisfactory without constraint, that is, VOF > 1.1, and results of lifetime variations are less stable. We therefore report those unconstrained results here.

We observed two o-Ps lifetime (τ_3 and τ_4) in those materials with spherical cavities. Examining the results of free-volume radii R according to o-Ps lifetimes and eq 1, the corresponding free-volume radii from two o-Ps lifetime (τ_3 and τ_4) are not the exactly same as the cavity radii of α,β cages in those materials. They are significantly smaller than the ideal cavities' sizes. This is likely because of the hydrates absorbed inside the cavities and some intergrain defect structures in those materials. Although some people have attempted to apply high temperature and pumping to remove hydrates and impurities from the inner surfaces, the PALS results are known not to be able to mirror the α,β cages' sizes precisely.[41−49] In this study for the purpose of calibration τ_2-R equation, instead of using ideal α,β cage sizes, we use the experimental o-Ps lifetimes (τ_3 and τ_4) according to eq 1 to calculate the mean hole radii. For a real substrate with multi-components of o-Ps lifetime, i, we calculate the mean radius from o-Ps lifetime $\overline{R}$ by the following equation

$$\overline{R} = \sum_i R_i(\tau_{o-Ps}) \cdot I_i / \sum_i I_i \qquad (8)$$

where $R_i(\tau_{o\text{-}Ps})$ and I_i are the corresponding ith o-Ps lifetime according to eq 1 and intensity, respectively. In zeolite systems, we have two o-Ps terms, that is, i = 2. The results of τ_3, τ_4, and $\overline{R}$ are listed in Table 2. The values of $\overline{R}$ are in the range from 3 to 5 Å.

Table 3. Best Fit Results from Various Systems for Calibration τ_2-R Equation 3

equations/figures	C (ns)	ΔR (Å)	r^2
eq 7	0.245	3.419	0.9142
Figure 5	0.280	4.288	0.8581
Figure 7	0.142	2.618	0.8446
eq 9, Figure 8	0.260	3.823	0.9391
eq 10, linear fit	= 0.174 (1 + 0.494R)		0.9268

Whereas there are many reported PALS data in zeolite systems, only limited and selected data are useful for this calibration purpose. Those existing data included in this calibration are from: (1) those zeolites or molecular sieves have known spherical cavity with radius ∼3−6 Å; (2) both o-Ps (τ_3 and/or τ_4) and the positron lifetimes (τ_2) were reported explicitly in the same systems; and (3) those PALS experiments and data are good quality and comparable precision to the current PALS measurements. Table 2 also lists those existing zeolite-PALS results selected for this calibration purpose. In Figure 8, we plot the results of experimental τ_2 versus the mean radius from o-Ps lifetimes and the best fitted eq 3 to all of those data.

As shown in Figure 8, the best-fit τ_2-R eq 3 results are C = 0.260 ns and ΔR = 3.823 Å with a reasonably good correlation coefficient (r^2 = 0.9391) for all polymers, zeolites, and molecular sieves with spherical cavity between 0.5 and 5 Å of radius. Therefore we established the best calibrated τ_2-R eq 9 for the determination of free volumes in the radius up to R = 5 Å for all materials as

$$\tau_2 = 0.260 \times \left[1 - \frac{R}{R + 3.823} + \frac{1}{2\pi}\sin\left(\frac{2\pi R}{R + 3.823}\right)\right]^{-1} \qquad (9)$$

Equation 9 should be useful with a reasonable precision, particularly in the polymers that have free-volume radius up to 5 Å and without o-Ps components in PALS.

Furthermore, for simplicity, the τ_2-R data shown in Figure 8 could be approximated and empirically fitted by a linear equation with a slightly less goodness of fit (r^2 = 0.9268) for R < 5 Å as

$$\tau_2 = 0.174(1 + 0.494R) \qquad (10)$$

where τ_2 and R are expressed in the unit of nanoseconds and angstroms, respectively. Table 3 summarizes all fit results of eq 3.

Finally, we attempted to extend eq 9 for radius >5 Å similar to the extension of eq 1 for the hole R > 5 Å based on the infinite potential spherical model.[38] Because the positron is different from o-Ps in the annihilation mechanism, the positron can undergo only 2-γ annihilation in condensed matter, whereas o-Ps can annihilate via 2-γ pick-off or 3-γ process, and the observed value of τ_2 in large holes of condensed matter remains in the region of 0.5 to 0.6 ns.[41−49] Therefore, it is also seen in Figure 8 that the deviation from eq 9 from the data in zeolite materials become more noticeable for radius >4 Å. The fitting of eq 9 to converge to $\tau_2 \approx 0.6$ ns is mathematically difficult. Thus, the semiempirical fitting of the quantum mechanical model of infinitive potential spherical for τ_2-R relationship breaks down for the hole radius R > 5 Å. It will be impractical to use τ_2-R relationship to determine free-volume dimension for R > 5 Å. Fortunately, in most of molecular substrates with R > 5 Å, some fractions of o-Ps component remain observable because

quenching and inhibition effects of *o*-Ps are reduced in large holes,[41−49] except for those with strong chemical-reacting functional groups, which are localized on the inner surface of holes.

4.5. Applicability of τ_2-*R* Correlation Equation. From the above calibration, eq 9 should be applicable well to τ_2 values from 0.260 to 0.60 ns or the hole radius up to 5 Å. For the practical use of eq 9 in this range of size based on analyzed PALS results without *o*-Ps component, there are two cases: (1) There exists only single positron lifetime, such as in polyimides. In this case, the single lifetime should be used as τ_2 value for eq 9. For example, Kapton is known to have only single positron lifetime of 0.382 ns.[50] The free-volume radius is found to be 2.62 Å according to eq 9. This is consistent with the free-volume results measured from τ_3 and eq 1 in some polyimides in which a significant fraction of *o*-Ps component (I_3) is retained.[13−16] (2) There exist two positron lifetimes, τ_1 and τ_2, in some molecular substrates without *o*-Ps. In this case, according to the two-state trapping model,[51] τ_2 is due to positron annihilation in defects (holes), and it could be used to calculate *R* in eq 9. For example, materials with only carbon, such as carbon molecular sieves,[52] which have two positron lifetimes without *o*-Ps, typically $\tau_1 < 0.2$ ns and $\tau_2 \approx 0.35$ to 0.40 ns. In that system, τ_2 values correspond to 2.26 Å (0.35 ns) and 2.81 Å (0.40 ns) according to eq 9. Those calculated *R* values are reasonable for cavity sizes in carbon materials and also are in the range of kinetic radii among those separation gases.

As far as for $\tau_2 < 0.26$ ns, eq 9 is not applicable, and in fact the deviation of eq 9 from the experimental free-volume radii for $R < 1.0$ Å (or $\tau_2 = 0.28$ ns) becomes noticeable, as seen in Figure 8. The linear eq 10 works better for small *R*, particularly for $\tau_2 < 0.26$ ns when eq 9 is not applicable. Furthermore, τ_2-*R* correlation may be more useful than τ_3-*R* correlation when the analyzed I_3, *o*-Ps intensity, is <2%. This is not only from the reduced precision in using τ_3-*R* for small I_3. This small I_3 could also be contributed from others, such as the surface, ^{22}Na source components, intergrains, and so on and may not be directly related to the free volumes of the materials studied.

5. CONCLUSIONS

In this study, a modified correlation equation between the positron lifetime (τ_2) and free volume radius using PALS is developed based on the infinite potential spherical model originally proposed by Tao. This newly modified equation is calibrated well for the radius up to 5 Å. Whereas the precision of using positron lifetime (τ_2) data to obtain free volumes is less than that of using *o*-Ps lifetime, this newly developed correlation equation based on the infinite potential spherical model is particularly useful for those molecular substrates for *R* up to 5 Å and when no *o*-Ps or very small fractions of *o*-Ps components are observed in PALS.

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