RESEARCH ARTICLE | AUGUST 22 2023

Mapping positron annihilation lifetime spectroscopy data of a polymer to classical molecular dynamics simulations without shifting the glass transition temperature *I*

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Check for updates J. Chem. Phys. 159, 084903 (2023) https://doi.org/10.1063/5.0160034

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Cite as: J. Chem. Phys. 159, 084903 (2023); doi: 10.1063/5.0160034
Submitted: 29 May 2023 • Accepted: 31 July 2023 •
Published Online: 22 August 2023

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ABSTRACT

Positron annihilation lifetime spectroscopy (PALS) enables the nondestructive measurement of nanoscale cavities in materials. In this study, a strategy was proposed for mapping PALS measurement data of isotactic polypropylene to classical molecular dynamics (CMD) simulations. The discrepancy between simulated and experimental glass transition temperatures was resolved by shortening the polymer chains, rather than adjusting for the temperature, using the Williams–Landel–Ferry (WLF) equation. The effective probe radii of ortho-positronium (o-Ps), determined by comparing PALS data with CMD simulations, were ~0.8 nm, which was consistent with the o-Ps size given by the solution of the Schrödinger equation. The free-volume fraction corresponding to the effective probe radius was 12.3% at the glass transition temperature, close to the value estimated using Simha–Boyer theory. The cavity number density was proportional to the effective probe radius and the -1/3 power of the monomer number density, and increased with increasing temperature. These findings suggest that combining PALS measurements with CMD simulations may provide insight into cavities in polymeric materials without relying on the WLF equation.

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I. INTRODUCTION

The free-volume theory, one of the most successful concepts in polymer physics, was discovered in the process of investigating the temperature dependence of viscosity¹⁻³ and was first applied by Doolittle to describe the viscosity of polymer melts.⁴ Since then, the free volume has been considered an important property because it relates many physical properties to a single parameter, though its definition is somewhat abstract. The free volume has been studied not only in relation to macroscopic properties, as described by the Vogel–Fulcher–Tammann (VFT) equation^{1–3} and the Williams–Landel–Ferry (WLF) equation,⁵ but also in relation to microscopic properties such as molecular permeability.⁶ Although nanoscale cavities are difficult to quantify precisely, the free volume can be controlled to some extent by changing the temperature and pressure, and is generally associated with nanoscale cavities in materials. Therefore, the molecular permeability of polymeric membranes for water purification,^{7–9} bioprocessing,^{10,11} and fuel cells^{12,13} has been experimentally evaluated based on the free volume of the membranes, even though permeability essentially depends on the relationship between guest molecule size and membrane cavity size.¹⁴

Positron annihilation lifetime spectroscopy (PALS) has been used for more than 40 years as an experimental technique to measure the "local" free volume.^{15–19} PALS reveals the cavity size in a material because it correlates with the time from positron irradiation to positron annihilation. Some of the positrons irradiated into amorphous materials, such as plastics and silica glasses, form positron-



ium (Ps) particles in a bound state with electrons in the material. The spin-antiparallel (singlet) positronium particles are called parapositronium (p-Ps), and the spin-parallel (triplet) positronium particles are called ortho-positronium (o-Ps). The annihilation process of Ps differs between p-Ps and o-Ps. While p-Ps quickly self-annihilates through the reaction between electrons and positrons, o-Ps diffuses and localizes in regions of low electron density, which can be exploited as a probe of the cavities. Therefore, it is possible to evaluate the local free volume in polymeric materials from the lifetime of the o-Ps that is trapped and annihilated in the cavities. PALS experiments have been used to evaluate the cavity size and guest molecule permeability of amorphous polymers,^{20–27} polymer blends,^{28,29} polymer membranes,^{30–35} and polymer films,³⁶ silica gel.³⁷

When determining the cavity size based on the pair annihilation of o-Ps with electrons in the material, the Tao–Eldrup equation,^{38,39} a semiempirical quantum model that assumes that the cavity is a sphere is used:

$$\tau = \frac{1}{2} \left[1 - \frac{R}{R + \Delta R} + \frac{1}{2\pi} \sin\left(\frac{2\pi R}{R + \Delta R}\right) \right]^{-1},\tag{1}$$

where τ is the o-Ps mean lifetime obtained from the long-lived component of the positron annihilation lifetime spectrum, R is the cavity radius, and $\Delta R = 0.166$ nm. Notably, since the τ is the average lifetime value, R also corresponds to the mean cavity volume. Therefore, the cavity size that can be measured by PALS is only the average value, assuming that the cavity shape is spherical. To solve this problem, a model has previously been devised to generate a fitting curve using the shape of the o-Ps decay curve and the o-Ps average lifetime value, using the deviation from the curve, to calculate the cavity size distribution.^{40,41} However, the accuracy of this method is limited because the o-Ps lifetime has a greater dependence on the size than on the number of cavities,³¹ and the amount of data on the long-time side of the o-Ps decay curve is naturally small. The high sensitivity of the o-Ps decay curve to radicals/electrons trapped in cavities and to electric fields accumulated in the material from repeated annihilation also affects the accuracy.^{16,21} It is generally difficult to determine the total fractional cavity volume as a percentage of total volume, as well as the cavity size/shape distribution, by PALS alone.⁴² In particular, it is difficult to extract information on cavity shape, and the introduction of simplified geometries for the potential wells (spheres, cubes, cylinders, etc.) biases the relationship between the o-Ps lifetimes and cavity volumes.43 Therefore, most approaches are based on PALS measurements performed under varying conditions, observing changes in cavity size (distribution) to predict changes in the nanostructure, followed by additional experiments based on completely different principles and theories to justify the predictions.4

Conversely, molecular simulations can be applied directly and accurately to estimate cavities, as long as a sufficiently reliable molecular model is available.⁴⁵ Attempts have been made to characterize the cavity shape (distribution) by combining PALS measurements and molecular simulations,^{43,46} and it has been reported that deviations from the spherical approximation of cavity shape can be systematically corrected.^{46,47} Based on a similar concept, a combined approach of PALS experiment and theory has been used to estimate the cavity shape.^{48,49} It may also be possible to

obtain more detailed information about the shape of the cavities by characterizing the degree of order in molecular clusters.^{50,51} Thus, molecular simulations may elucidate the nanoscale details that cannot be obtained by PALS, and the combination of PALS measurements and molecular simulations has often been considered.⁴² Molecular simulations have mostly been used to augment insights based on PALS measurements,^{52–60} but several studies have been attempted to directly map PALS measurements and molecular simulations. However, mapping studies conducted on polymeric materials often face challenges associated with high cooling rates in computer simulations,^{61–63} and the cavity shapes are far from idealized spherical shapes.^{43,46} Thus, a sufficient correspondence between PALS measurements and molecular simulations has not been demonstrated.

In this study, PALS measurement data were mapped to classical molecular dynamics (CMD) simulations using isotactic polypropylene (iPP) as an example. Because the cooling rate in the simulation is several orders of magnitude larger than that in the experiment, their glass transition temperatures do not agree, which has often been shifted by employing the WLF equation⁶⁴⁻⁶⁶ or VFT equation.^{67,68} Note that the VFT equation is equivalent to the WLF equation.⁶⁹ However, since these equations are based on the macroscopic motion of isoviscous materials, it is questionable whether this correction can be widely applied to crystalline polymers, polymer blends, composites, and membranes. Here, instead of correcting the temperature using the WLF equation, the glass transition temperature was matched to the experiment by shortening the polymer chains. This strategy was developed considering that the temperature dependence of the o-Ps mean lifetime in short linear polymers is the same regardless of chain length, and a master curve for the temperature-lifetime can be obtained by shifting the glass transition temperature by a certain value.^{70,71} The o-Ps effective probe radius was obtained by comparing the mean cavity sizes determined by PALS and CMD. The relationships between the o-Ps effective probe radius and the free volume, number of cavities, and monomer number density were primarily investigated.

II. METHODOLOGY

A. Molecular dynamics simulations

Hagihara et al. performed PALS measurements on iPP, in the temperature range corresponding to the glass transition and melting point (160-360 K) to clarify the temperature dependence of the mean cavity size.⁷² In this study, an attempt was made to map these experimental PALS data as a target in CMD simulations. First, an all-atom molecular model of iPP was designed using the general AMBER force field.⁷³ Harmonic potentials were used to describe bond stretching and bond angle bending, and standard dihedral angle potentials were used to describe torsional motion. The non-bond interactions were represented by Coulomb and Lennard-Jones 12-6 potentials. Restrained electrostatic potential (RESP) charges⁷⁴ were employed for the atomic charge parameters and were determined using Gaussian 09.75 Several degrees of polymerization (15, 30, and 60) were considered for iPP, and the polymer was hydrogen terminated. To maintain a constant number of carbon atoms in the molecular system regardless of the degree of polymerization, the number of iPP molecules was set to 256, 128, and 64, respectively, in decreasing order of the degree of polymerization. CMD simulations were performed using the molecular dynamics package GROMACS.⁷⁶ The Coulomb interaction was calculated with a smooth particle mesh Ewald sum,⁷⁷ and the Lennard-Jones interaction was terminated above 1.2 nm. Time evolution was performed at 0.5 fs intervals, and the Verlet leapfrog integrator⁷⁸ was used. The cooling simulations for the determination of the glass transition temperature were performed using the following procedure: (i) First, the initial molecular structure created by the random placement of polymer chains under three-dimensional periodic boundary conditions was relaxed for 500 ns using an isothermal-isobaric ensemble⁷⁹ at temperature T = 500 K and pressure P = 100 kPA. The pressure was fixed using the Parrinello-Rahman method.⁸⁰ (ii) The post-relaxation structure at T = 500 K was cooled to 355 K and relaxed for 500 ns using the isothermal-isobaric ensemble. (iii) The post-relaxation structure at T = 355 K was cooled to 175 K at a cooling rate of 1 K/ns under the isothermal-isobaric ensemble. Specifically, stepwise cooling with a 20 K quench every 20 ns was employed. This was determined based on the report that stepwise cooling relaxes the structure more effectively than continuous cooling.⁸¹ Note that the cooling rate of 1 K/ns is considerably (250 000 times) faster than the experimental cooling rate of 4000 K/s.82 (iv) The last 5 ns simulation trajectory at each temperature was defined as the representative post-relaxation structures, and the average specific volume was calculated from these post-relaxation structures.

B. Cavity analysis

The post-relaxation structures obtained at each temperature condition from CMD simulations were considered to contain cavities. Therefore, 100 post-relaxation structures at each temperature condition were sampled, and cavity analysis (CA) was performed using the following procedure. (i) Post-relaxation structures were scanned using a general grid-scanning method. A cubic grid with a grid spacing of 0.05 nm was defined, and the distance d between the nodes of the grid and the iPP atoms in the vicinity of the nodes was calculated. If the d of the atom closest to the node was greater than the radius of that atom r_a , $d - r_a$ was recorded, along with the coordinates of the node. Note that the radii of the hydrogen and carbon atoms were assumed to be van der Waals radii (0.12 and 0.17 nm, respectively). This assumption is equivalent to considering the temperature-independent "hard-core" volume⁶⁹ in the CA. (ii) Post-relaxation structures were probed. A spherical probe was assumed, and the probe radius r_p was determined. The coordinates of the node and the value of $d - r_a$ were referenced, and if $r_p \leq d - r_a$, the node was determined to be a probe-insertable node. (iii) Cavities were detected. Cavities in the post-relaxation structure were determined by examining the contact between inserted probes. If the distance between two probe-insertable nodes was less than or equal to $2r_p$, these nodes were defined as belonging to the same cavity. A fine cubic grid with a grid spacing of 0.01 nm was defined to precisely estimate the cavity volume. The cavity volume was calculated based on the number of fine grids cut into spheres of radius r_p , centered at the coordinates of nodes belonging to the same cavity. Because each fine grid was considered to be a cube of 0.01 nm on a side in the volume calculation, the volume element was 1.0×10^{-6} nm³. The grids inside the cavity did not cause an error in the volume calculation, but the fact that the grids on the cavity surface are cubic can cause

an error proportional to the cavity surface area. Notably, a method was developed to mitigate the influence from the cubic shape of the volume elements.⁸³ (iv) The mean cavity volume V_c was calculated from the following equation:

$$V_{\rm c} = \frac{\sum_i^{N_{\rm c}} V_i^2}{V_{\rm f}},\tag{2}$$

$$V_{\rm f} = \sum_{i}^{N_{\rm c}} V_i, \qquad (3)$$

where N_c is the number of cavities, V_i is the volume of cavity *i*, and V_f is the free volume. In this study, a weighted average rather than a simple average was employed to estimate the mean cavity volume. This treatment is based on the fact that larger cavities contribute more to the mean lifetime value in PALS measurements.

III. RESULTS AND DISCUSSION

A. Cavity analysis

Before performing the CA, the glass transition temperature T_g was determined to validate the molecular model and CMD simulations in this study. Figure 1 shows the temperature dependence of the monomer-occupied volume v, the reciprocal of the monomer number density, for iPP with the degree of polymerization of 15. The results show that the glass transition temperature was ~275 K, similar to the experimental value.⁸⁴ The transition temperature was also consistent with the inflection point in the temperature dependence of the o-Ps mean lifetime.⁷² Note that the degree of polymerization of iPP in the PALS measurement was ~15000, which was ~1000 times larger than that in the CMD simulation. Despite the extremely large cooling rate used in the CMD, the glass transition temperatures in the PALS measurement and CMD simulation agreed well with each other. This is the result of the strategy described in the Introduction shortening the polymer chains instead of correcting the glass transition temperature using the WLF equation. Recall that the strategy is based on the fact that the temperature dependence of the o-Ps mean lifetime in short linear polymers is the same regardless of chain length and that the master curve can be obtained by shifting the temperature by a certain value.^{70,71} The density at the



FIG. 1. Temperature dependence of the monomer-occupied volume for iPP with the degree of polymerization of 15.

glass transition point according to Fig. 1, 0.814 g/m³, is approximately equal to that previously reported for iPP, 0.824 g/m³, which had a nearly 7-fold larger degree of polymerization and a different force field.⁶⁶ It should be noted, however, that both values were ~9% smaller than the value of 0.897 g/m³ reported in Ref. 85. Considering that the glass transition temperatures of iPPs with degrees of polymerization of 30 and 60 were around 315 and 325 K, respectively; only the results for the degree of polymerization of 15 are presented hereafter.

Figure 2 shows the probe radius dependence of the mean cavity volume, obtained by CA on a semilog scale. For constant $r_{\rm p}$, the $V_{\rm c}$ increased exponentially with increasing temperature for $r_{\rm p} < 0.1$ nm. For constant temperature, the $V_{\rm c}$ increased exponentially with decreasing $r_{\rm p}$.

From the distribution of cavity size and number obtained from CA, it is possible not only to calculate the free volume and mean cavity volume, but also to determine whether the percolation of cavities has started. In this study, the maximum r_p at which percolation begins was determined by observing a histogram of the number of cavities relative to the cavity size at each $r_{\rm p}$. The determined $r_{\rm p}$ was referred to as the critical probe radius r_c . At the onset of percolation, a cavity was observed in the histogram that was significantly larger than the other cavities, as shown in Fig. S1 in the supplementary material. The critical probe radii determined at each temperature by this observation are listed in Table I. The maximum cavity volume $(V_{c,max})$ and free volume (V_f) detected at the critical probe radius, as well as the maximum cavity volume per free volume $(V_{c,max}/V_f)$, are also shown. The maximum cavity volume was generally 1/4-1/3 of the free volume at 175 $\leq T \leq$ 355 K, and the onset of percolation was distinct. It is important to emphasize that the percolation discussed here is the cavity percolation and does not fully correspond to the "free volume percolation" discussed in free-volume theory.^{69,86-89} Cavity percolation has the advantage that it does not require the complex and abstract assumptions of free-volume theory and can be determined simply by observing cavity histograms, as demonstrated in this study.



FIG. 2. Probe radius dependence of the mean cavity volume, obtained by CA on a semilog scale.

TABLE I. Critical probe radius r_c at each temperature, and corresponding $V_{c,max}$, V_f , and $V_{c,max}/V_f$.

T (K)	<i>r</i> _c (nm)	$V_{\rm c,max} (\rm nm^3)$	$V_{\rm f}({\rm nm}^3)$	$V_{\rm c,max}/V_{\rm f}$
175	0.055	11.3	44.5	0.25
195	0.056	12.4	45.1	0.27
215	0.057	12.3	45.4	0.27
235	0.058	14.4	45.8	0.31
255	0.061	12.9	46.5	0.28
275	0.064	11.6	46.7	0.25
295	0.064	14.4	47.9	0.30
315	0.069	16.0	48.2	0.33
335	0.073	13.0	49.5	0.26
355	0.078	11.6	51.0	0.23

B. Mapping PALS data to CA results

Next, the mean cavity volume of iPP obtained from the PALS data was compared with that of iPP determined from the CA. PALS data were obtained from Ref. 72. As shown in Fig. 2, the mean cavity volume determined by CA depends on the probe radius. Therefore, the o-Ps effective probe radius is extremely important in considering how accurately PALS measurements can obtain cavity information. Nevertheless, the o-Ps effective probe radius cannot be determined by PALS alone. Therefore, the CA results were fit to the PALS data



FIG. 3. (a) Fitting via PALS and CA, the mean cavity volume, and (b) the o-Ps effective probe radius determined by the fitting.

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by assuming that the o-Ps effective probe radius is the probe radius at which the CA results agree well with the PALS data. Figure 3(a) shows the fitting via PALS and CA, the mean cavity volume, and Fig. 3(b) shows the o-Ps effective probe radius determined by the fitting. As shown in Fig. 2, the effective probe radius can be determined precisely because the mean cavity volume increases or decreases exponentially with the probe radius. The obtained effective probe radius was ~0.8 nm, which was consistent with the o-Ps size given by the solution of the Schrödinger equation.

Investigating the free volume and number of cavities with respect to the o-Ps effective probe radius (r_e) is useful for evaluating the validity of the mapping strategy proposed in this study. Figure 4 shows the temperature dependence of the free-volume fraction V_f/V , which was in the range of 12%–14% for 175 $\leq T \leq$ 355 K and 12.3% at the glass transition temperature $T_g = 275$ K. This result agrees well with the "universal" free-volume fraction of 11.3% predicted by Simha and Boyer.88 However, such a universal freevolume fraction has recently been refuted by the locally correlated lattice (LCL) model proposed by White and Lipson.⁶⁹ Notably, the parameters necessary to calculate LCL predictions for iPP are currently missing. By reducing the degree of polymerization to bring the glass transition temperature of the simulation into agreement with the experiment, the calculated free volume was sufficiently close to that predicted by classical theory and should be considered relevant.

Figure 5(a) shows the temperature dependence of the number density of cavities. The number of cavities decreased with increasing temperature, but the gradient changed around the glass transition temperature and became steeper in the high-temperature range. The results were very similar to those reported by Capponi *et al.* in their molecular simulations of poly(vinyl methyl ether) (PVME) using optimal probe radii (0.08–0.09 nm).⁶⁸ and the results suggest that the simulated short-chain iPP molecular system has a relatively large free volume, similar to that reported for PVME, which is consistent with the free-volume fraction of ~12%–14% (see Fig. 4). Figure 5(b) shows the number density of cavities vs o-Ps effective probe radius. The result appears to be linear, and fitting of the linear function yielded

$$N_{\rm c}/V = -309.27r_{\rm e} + 38.348.$$
 (4)



FIG. 4. Temperature dependence of the free-volume fraction.



FIG. 5. (a) Temperature dependence of the number density of cavities and (b) number density of cavities vs o-Ps effective probe radius.

The R-squared value in the fitting was 1.0. In PALS measurements, the cavity number is assumed to be related to the intensity of the PALS signal (i.e., the probability of o-Ps formation), but the origin of the intensity behavior has not been adequately explained. Therefore, the cavity number has often been approximated as a constant,^{22,62,90,91} but the distinct linear function obtained in this study implies that the constant approximation is not accurate. This linear function may provide a new model for the o-Ps formation probability.

To examine the o-Ps effective probe radius (r_e) , its temperature dependence was compared with the critical probe radius (r_c) and monomer-occupied volume (ν) . Figure 6(a) shows the temperature dependence of r_e , r_c , and $\nu^{1/3}$. Because their temperature dependences were similar, the correlations among them were investigated in detail. Figure 6(b) shows the $\nu^{1/3}$ dependence of r_e and r_c . Both r_e and r_c were proportional to $\nu^{1/3}$. r_e , and r_c were found to be highly correlated with $\nu^{1/3}$, exhibiting *R*-squared values of 0.97 and 0.99, respectively. Notably, the critical probe radius is a physical property that is uniquely determined once the material and thermodynamic conditions are determined. In contrast, the o-Ps effective probe radius was simply determined by fitting the mean cavity volume obtained from PALS measurements with the CMD results, but its temperature dependence was shown to be similar to that of the critical probe radius. Figure 6(c) shows the correlation between



FIG. 6. (a) Temperature dependence of r_e , r_c , and $v^{1/3}$, (b) $v^{1/3}$ dependence of r_e and r_c , and (c) correlation between r_e and r_c .

 r_e and r_c . r_e was proportional to r_c , with an *R*-squared value of 0.98. For the temperature range used in this study, the o-Ps effective probe radius was always slightly larger than the critical probe radius, while remaining proportional to each other.

To clarify the origin of the proportional relationship between r_e and $v^{1/3}$, histograms of the cavity volume were examined, as shown in Fig. 7. With increasing temperature, the number of cavities with a volume smaller than 0.01 nm³ as did the number of cavities with a volume larger than 0.6 nm³. This result is consistent with the physical interpretation of thermal expansion. Therefore, the origin of the proportional relationship between r_e and $v^{1/3}$ is likely the change in the cavity volume distribution due to thermal expansion.



FIG. 7. Histogram of cavity volume. At lower temperatures, smaller cavities were detected because of the smaller o-Ps effective probe radius. The distribution of the number density of cavities in the cavity volume range of 0.01–0.1 nm³ was almost independent of temperature.

TABLE II. o-Ps effective probe radius r_e at each temperature, and corresponding $V_{c,max}$, V_f , and $V_{c,max}/V_f$.

T (K)	r _e (nm)	$V_{\rm c,max} (\rm nm^3)$	$V_{\rm f} ({\rm nm}^3)$	$V_{\rm c,max}/V_{\rm f}$
175	0.068	1.07	38.6	0.028
195	0.070	1.14	38.9	0.029
215	0.071	1.15	39.4	0.029
235	0.073	1.19	39.8	0.030
255	0.074	1.73	41.1	0.042
275	0.078	1.60	40.6	0.039
295	0.076	2.24	44.0	0.051
315	0.079	2.29	45.0	0.051
335	0.083	3.21	46.6	0.069
355	0.087	3.83	47.1	0.081

For $r_e > r_c$, the cavities detected by o-Ps should not percolate. To clarify this, the maximum cavity volume, free volume, and maximum cavity volume per free volume corresponding to the o-Ps effective probe radius are shown in Table II. The maximum cavity volume was ~3%–8% of the free volume at 275 $\leq T \leq$ 355 K, indicating that cavity percolation did not occur (cf. Table I).

IV. CONCLUSIONS

In this study, the PALS measurement data of iPP were mapped to CMD simulations. The discrepancy between simulated and experimental glass transition temperatures was resolved by shortening the polymer chains, rather than adjusting for the temperature, using the WLF equation. The o-Ps effective probe radius at which the mean cavity volumes of PALS measurements and CMD simulations agree with each other was determined. The effective probe radius was ~0.8 nm, which was consistent with the o-Ps size obtained using the Schrödinger equation. The free-volume fraction corresponding to the effective probe radius was 12.3% at the glass transition tem28 August 2023 00:28:14

perature. The calculated free volume was close to that described in the Simha-Boyer theory, despite the bold strategy of reducing the degree of polymerization to match the glass transition temperature of the simulation with that of the experiment. The cavity number density followed a linear function, with the effective probe radius as a variable. A constant approximation has often been employed because the cavity number is difficult to accurately estimate from PALS measurements alone, but this linear function may provide a new model for the o-Ps formation probability. The o-Ps effective probe radius was proportional to both the critical probe radius and the -1/3 power of the monomer number density, and increased with increasing temperature, which originated from the change in the cavity volume distribution due to thermal expansion. These results suggest that the combination of PALS measurements and CMD simulations provide insight into the cavities of polymeric materials without resorting to the WLF equation.

Overall, the present results demonstrate the potential of combining PALS measurements and CMD simulations to determine the o-Ps effective probe radius and estimate more detailed information about its relationship to the free-volume fraction, cavity number density, and monomer number density. However, the following three points could not be fully investigated in this study and may be addressed in the future research. (i) The effect of short polymer chains was not discussed in detail. In this study, short polymer chains were used to shift the glass transition temperature of the simulation. This strategy is based on observations reported in PALS experiments,^{70,71} but it is also an application of the Flory-Fox equation.⁸⁶ This equation indicates that the glass transition temperature is lower for short polymer chains, which is explained by the higher number density of chain ends in short-chain polymer melts compared to long-chain polymer melts. Therefore, it should be noted that the simulated glass transition temperature in this study was tuned by the combined effects of cooling rate and polymer chain length. Moreover, Flory theory points to an increase in free volume with an increasing number of chain ends. The influence of the above factors on the present results should be investigated in more detail. (ii) The consistency of the present results with freevolume theory was not thoroughly discussed. The topic of this study is the mapping between PALS measurements and CMD simulations, and does not deeply consider the complex and abstract aspects of free-volume theory. For example, the Cohen-Grest model⁸⁹ deals with free-volume percolation at the glass transition, whereas the present study only discusses cavity percolation, which is simpler and more clearly defined. However, findings such as the proportionality between the cavity number density and the o-Ps effective probe radius obtained in this study may provide a new perspective on free volume and its interpretation. (iii) There is a limit to the spatial size that can be investigated by CA because it is computationally intensive. Although polymers, such as iPP, form complex structures consisting of crystalline and amorphous portions, it is difficult to prepare a molecular system that encompasses all the practical structures for CMD and CA. Despite these challenges, the combination of PALS and CMD helps to elucidate the relationship between cavity size/shape distribution and free volume, and improves the reliability of cavity and free-volume measurements with PALS.

SUPPLEMENTARY MATERIAL

Histogram of cavity volume at T = 355 K and $r_p = 0.05$ nm (Fig. S1).

ACKNOWLEDGMENTS

This work was supported by JST, PRESTO Grant No. JPMJPR22O6, Japan.

AUTHOR DECLARATIONS

Conflict of Interest

The author has no conflicts to disclose.

Author Contributions

Kazuaki Z. Takahashi: Conceptualization (equal); Data curation (equal); Formal analysis (equal); Funding acquisition (equal); Investigation (equal); Methodology (equal); Project administration (equal); Resources (equal); Software (equal); Supervision (equal); Validation (equal); Visualization (equal); Writing – original draft (equal); Writing – review & editing (equal).

DATA AVAILABILITY

The data that support the findings of this study are available within the article and its supplementary material.

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