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Relation between free-volume quantities from *PVT*–EOS analysis and PALS

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Abstract

Unique information about the properties of free-volume sites in polymers is gained from positron annihilation lifetime spectroscopy (PALS). After calibration with the free-volume hole-fraction h_{PVT} from pressure–volume–temperature and equation-of-state (*PVT*–EOS) analysis using the Simha–Somcynsky theory, PALS data (*ortho*-positronium (*o*-Ps) lifetime τ_3 and *o*-Ps intensity I_3) may be used to calculate free-volume fractions h_{PALS} from $h_{\mathrm{PALS}} = C \times V(\tau_3) \times I_3$, where $V(\tau_3)$ is the subnanometer cavity hole-volume. The widespread use of this equation, in particular the correlation constant *C*, is given some attention, clarification and further improvement. From *PVT* data and PALS data, measured on chemically and physically identical amorphous poly(methyl methacrylate) samples, both below and above the glass transition temperature, we find improved relations: $h_{\mathrm{B}} = B \times V(\tau_3)$ and $h_{\mathrm{PVT}} = k_1 + k_2 \times V(\tau_3)$, where *B*, k_1, and k_2 are correlation constants. We propose and show that the freezing fraction of polymer glasses can be calculated from the temperature coefficients of $V(\tau_3)$, which further supports its close relation to h_{PVT}. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Simha–Somcynsky equation-of-state theory; Free volume; Positron annihilation

1. Introduction

The free volume of polymers in the glassy state can be studied *indirectly* as a free-volume fraction $h(V,T) = 1 - y(V,T)$ determined from pressure–volume–temperature (*PVT*) data and the Simha–Somcynsky equation-of-state (EOS) theory [1–4]. A *direct* measure of free volume is the mean free-volume cavity size $V(\tau_3)$ that is uniquely determined from positron annihilation lifetime spectroscopy (PALS) [5–10]. There still remains uncertainty about the quantitative relation between the two free-volume quantities in the equilibrium melt as well as in the glassy state of both amorphous homopolymers and copolymers, despite their known qualitative relation.

In brief, the Simha–Somcynsky EOS theory [1] expresses the configurational or Helmholtz free energy *F* in terms of the volume *V*, temperature *T* and the occupied lattice-site fraction $y = y(V,T)$:

$$F = F(V,T,y) \tag{1}$$

The unoccupied lattice-site fraction is the free-volume fraction $h(V,T) = 1 - y$ and is obtained from Eq. (1) through the pressure equation $P = -(\partial F/\partial V)_{\mathrm{T}}$ and the minimization condition $(\partial F/\partial y)_{\mathrm{V,T}} = 0$ applied to the equilibrium melt. The latter two constitute the EOS that is generally written in terms of reduced *PVT* variables ($\tilde{P} = P/P^*$, $\tilde{V} = V/V^*$, $\tilde{T} = T/T^*$) using the characteristic scaling parameters P^*, V^* and T^* in MPa, cm^3/g and K, respectively. They are determined from the *PVT* equilibrium melt data and contain the molecular characteristics of the system. In the melt, *h* can be calculated from the pressure equation and the minimization condition on *F* together with the scaling parameters P^*, V^* and T^*. In the glassy state, the Simha–Somcynsky EOS cannot, strictly speaking, be applied unconditionally due to violation of the equilibrium assumption. However, assuming P^*, V^* and T^* to be constant below the pressure-dependent glass transition temperature $T_{\mathrm{g}}(P)$, the theory can also be applied to the glassy state to calculate *h* [2,3,11–17]. The latter can be determined using the adjustable parameter (AP) method [3,12] that treats the occupied volume fraction *y* as an adjustable rather than equilibrium parameter in combination with the pressure equation and experimental *PVT* data.

In condensed matter, positrons annihilate in at least three

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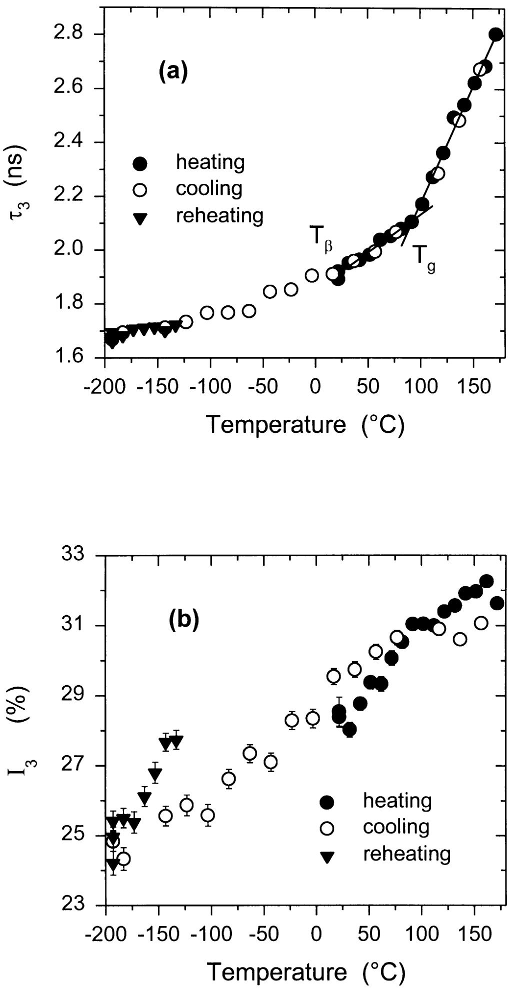

Fig. 1. (a) *o*-Ps lifetime τ_3 and (b) *o*-Ps intensity I_3 for PMMA as a function of temperature and thermal cycling: (●) heating 20–170°C; (○) cooling 170 to −193°C; and (▼) reheating −193 to −130°C. In (a) T_β and T_g are the secondary transition and glass transition temperatures of PMMA, respectively. Lines are linear regressions (Eqs. (4a) and (4b)).

different ways [5,6], and these annihilation events give rise to characteristic lifetimes. The third lifetime belongs to the *ortho*-positronium (*o*-Ps) species that probes free-volume sites in polymers. The positron of the *o*-Ps annihilates with a surrounding electron of opposite spin (pick-off annihilation) within an *o*-Ps lifetime τ_3 of 1–5 ns. Since τ_3 is inversely proportional to the square of the overlap of the positron component of the Ps wave function with the lattice or cavity wall electron wave function, it is related to the size of the low-electron density free-volume sites [18]. Assuming spherical free-volume sites of radius R, obtained by using a spherical potential of radius R_0 with an electron layer of thickness $\Delta R = R_0 - R$, the semi-empirical Tao–Eldrup equation between τ_3 in ns, R and R_0 in Å was established [7,8] and optimized with $\Delta R = 1.656$ Å [19] for molecular solids:

$$\tau_3 = \frac{1}{2}\left[1 - \frac{R}{R_0} + \frac{1}{2\pi}\sin\left(\frac{2\pi R}{R_0}\right)\right]^{-1} \tag{2a}$$

$$V(\tau_3) = (4\pi/3) \times R^3 \tag{2b}$$

In the literature, Eqs. (2a) and (2b) have been widely used for polymers to convert mean τ_3-values to hypothetical radii and volumes of free-volume holes.

The *o*-Ps formation probability is called *o*-Ps intensity I_3 and has been claimed to be directly related to the number of free-volume hole sites in polymers. I_3 has found its application in a widespread semi-empirical equation for the calculation of free-volume fractions from PALS data [20]:

$$h_{\mathrm{PALS}} = h_{\mathrm{C}} = C \times V(\tau_3) \times I_3 \tag{3}$$

where $V(\tau_3)$ is from Eq. (2b). Strictly speaking, the constant C can only be obtained from a comparison of temperature-dependent PALS data and *PVT* data analyzed in the framework of the Simha–Somcynsky EOS theory [20]. In short, the temperature-dependent free-volume fractions h_{PVT} and h_{C} are equated at a common reference temperature T_{ref} that is assigned a value above the glass transition temperature T_g, as measured by both PALS and *PVT* analysis. That is, $h_{\mathrm{PVT}}(T_{\mathrm{ref}}) = h_{\mathrm{C}}(T_{\mathrm{ref}})$, where commonly $T_{\mathrm{ref}} = T_{g,\mathrm{PALS}} + 25$°C. Note that the choice of T_{ref} will affect the value of C. Some examples of C-values are: 3.08×10^{-3} Å^{-3} for PVAc [20], 2.00×10^{-3} Å^{-3} for PC [21], 1.67×10^{-3} Å^{-3} for polystyrene [22] and 1.52–1.67×10^{-3} Å^{-3} as a function of molecular weight for PS [22]. Further drawbacks inherent in Eq. (3) are that the *o*-Ps intensity I_3 is very sensitive to: inhibition reactions taking place in the positron spur [6,23]; source exposure time [24–27]; exposure to visible light [28]; exposure to electric fields [6,29,30]; and magnetic fields [31]. This implies that changes in the *o*-Ps intensity I_3 cannot be accounted for solely on the basis of free volume.

We have recently studied the *PVT* and free-volume properties of isotropic pressure-densified *atactic* poly(methyl methacrylate) (*a*-PMMA) glasses using the Simha–Somcynsky EOS theory and PALS [17]. In the present work, we use one of these glasses, formed at atmospheric pressure and at a cooling rate of 0.5°C/min (referred to as 0-MPa glass in this work) and measure its temperature dependent free-volume properties with PALS.

The aim of this study is to investigate the relation between free-volume quantities determined from a *PVT*–EOS analysis and those from PALS, measured on chemically and thermodynamically identical PMMA samples in both the equilibrium melt and the glassy state. Moreover, the recent and rather liberal use [32–36] of the correlation constant C in Eq. (3) to calculate free-volume fractions from PALS data deserves some attention, clarification and further improvement.

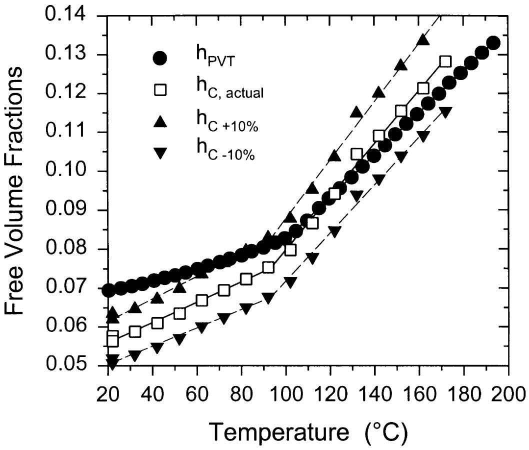

Fig. 2. Free-volume fractions of PMMA determined from (a) the Simha–Somcynsky EOS and experimental *PVT*-data, h_{PVT} (●) and (b) PALS-data and Eq. (3), h_C with the actual *C*-value of 2.28×10^{-3} Å^{-3} (□) and two *C*-values that are out by +10% (▲) and −10% (▼), respectively.

2. Experimental

We have previously measured the *PVT* properties of the 0-MPa PMMA glass [17] with a commercial high-pressure bellows-type dilatometer (Gnomix Inc. PVT apparatus) [37–39] using the standard isothermal mode of operation with 5°C temperature and 10 MPa pressure steps. We have also previously discussed the accuracies of the *PVT* measurements and the derived quantities [16]. The Gnomix PVT apparatus is designed to ensure hydrostatic pressure throughout the sample in the melt-, semicrystalline and glassy state compared with high-pressure, piston-type dilatometers [39,40]. The cooling rate was 0.5°C/min during glass formation. In the context of this paper, a pressure of 0 MPa is equivalent to atmospheric pressure (0.1 MPa), and all other pressures quoted are in excess of atmospheric pressure.

The temperature-dependent PALS measurements were performed at the Materials Department at Risø National Laboratory in Denmark with a fast–fast spectrometer. The spectrometer has a FWHM of 252 ps and a channel width of 26.8 ps. A 1.5 MBq ^{22}Na source was sandwiched between two pieces of Kapton foil and gave an effective count rate of 30 cps. The sample cell was under vacuum. Some control measurements were made without vacuum at RT, and results similar to those under vacuum were obtained. At each temperature, one spectrum containing up to 2.5 Mcts was measured within about 16 h and evaluated with POSITRONFIT [41] using a 0.385 ns and 5% source correction and no fixed lifetimes or intensities. The sample was first measured from RT to 170°C with 10°C temperatue steps, followed by cooling from 170 to −193°C with 20°C temperature steps, except for the T_g-region where an effective cooling rate of about 0.5°C/min was maintained. The sample was then measured three times isothermally at −193°C prior to reheating to −130°C with 10°C temperature steps.

3. Results and discussion

Fig. 1(a) shows the *o*-Ps lifetime τ_3 as a function of temperature. Evidently, the thermal cycling does not affect τ_3. On the other hand, the *o*-Ps intensity I_3 in Fig. 1(b) shows a measurable dependence on thermal cycling, even between RT and T_g. This result immediately raises the question of the role of I_3 in free volume. In fact, Wang et al. [26] have found similar results for another grade of PMMA as well as for poly(vinyl acetate), and they give a detailed account of the observed variations in I_3 on the basis of the spur reaction model. In Fig. 1(a) the glass transition temperature T_g is seen to occur at 93.2°C at an effective heating rate of 0.01°C/min. This T_g ($T_{g,PALS}$) compares with 100.5°C, as measured volumetrically at an effective heating and cooling rate of 0.5°C/min. 5.5°C of the 7°C temperature difference can be explained in terms of the differences in effective heating rates, since PMMAs T_g decreases (increases) by 3.3°C as the cooling (heating) rate is changed by a factor of 10 [42].The remaining 1.5°C may be due to other effects. We note furthermore that the secondary transition temperature T_β occurs at 11°C. For the purpose of the present work we need a linear regression of τ_3 in the glassy state and in the equilibrium melt. From the data in Fig. 1(a) we find that:

$$\tau_3(T) = 1.848 + 2.834 \times 10^{-3} T, \text{ for } T : 20 \le T \le 93.2°\mathrm{C} \tag{4a}$$

$$\tau_3(T) = 1.299 + 8.724 \times 10^{-3} T, \text{ for } T : 93.2 \le T \le 170°\mathrm{C} \tag{4b}$$

Fig. 2 shows the free-volume fractions of chemically and physically identical PMMA samples determined from the Simha–Somcynsky EOS and *PVT*-data (h_{PVT}) [17] in addition to the free-volume fractions calculated by the method of Kobayashi et al. [43] (Eq. (3)) and Eqs. (2a) and (2b). We used $T_{ref} = T_{g,PALS} + 25°\mathrm{C} = 118.2°\mathrm{C}$ and thus obtained $C = 2.28 \times 10^{-3}$ Å^{-3}. The agreement between h_C and h_{PVT} progressively worsens below T_{ref} such that deviations from h_{PVT} up to 30% occur in the glassy state. Also, in the melt the two free-volume fractions deviated from each other. This implies that even a rigorously calculated h_C cannot really replace the theoretical h_{PVT}. If the constant *C* in Eq. (3) is not rigorously determined from *PVT* and PALS data on identical polymer samples with the same thermomechanical history, or if it is given a generalized value [32–35], then it can be out by at least ±10%. The consequences of using a wrong *C*-value (±10% of C_{actual}) are clearly illustrated in Fig. 2. We also note that the approach of Yu et al. [22] of calculating the correlation constant *C* in Eq. (3) requires two data points, selected at different temperatures either in the melt or in the glass [44] or both [21]. The choice of the two reference temperatures will affect the magnitude

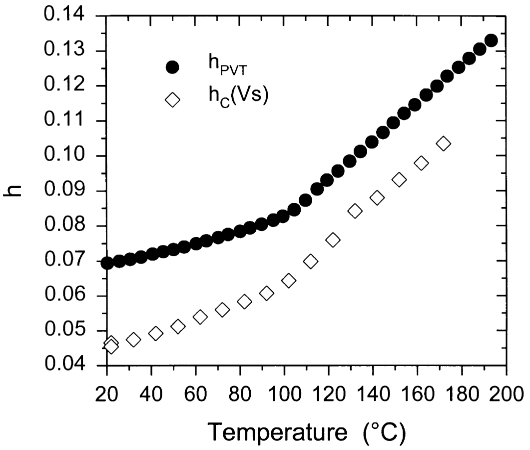

Fig. 3. Free-volume fractions of PMMA determined from (a) the Simha–Somcynsky EOS and experimental *PVT*-data, h_{PVT} (●); (b) PALS-data with a $C(V_s)$-value (see text) of 1.83×10^{-3} Å^{-3}, $h_C(V_s)$ (◇).

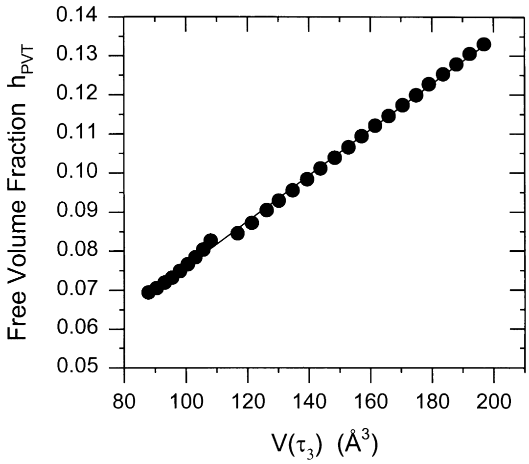

Fig. 5. Free-volume fractions of PMMA determined from the Simha–Somcynsky EOS and experimental *PVT*-data, h_{PVT} (●) as a function of free-volume cavity size $V(\tau_3)$ from PALS data.

of C [21]. Furthermore, expressing h_C in terms of an excluded or occupied volume V_{occ} allows the occupied volume to be calculated. We have used a second reference temperature 25°C below $T_{g,PALS}$ which gave a $V_{occ} = 0.8088$ cm^3/g and $C = 1.83 \times 10^{-3}$ Å^{-3}. However, this C-value is a function of V_{occ}, which implies that C is a function of the polymer structure and can therefore not be generalized. A drawback of this approach is that $h_C(V_s)$ is shifted vertically to lower free-volume fractions compared with h_{PVT}. This is illustrated in Fig. 3.

In the introduction we have shown that changes in the *o*-Ps intensity I_3 cannot be accounted for on the basis of free volume. Therefore, ignoring I_3 by absorbing it and C into a new constant B results in a simpler equation:

$$h_B = B \times V(\tau_3). \tag{5}$$

As for the determination of C, h_B is set equal to h_{PVT} at $T_{match} = 118.2$°C, and $B = 7.136 \times 10^{-4}$ Å^{-3} is obtained. Thus, a much-improved agreement between h_{PVT} and h_B, the new free-volume fraction from PALS, is achieved not only in the glassy state, but also in the equilibrium melt. This is illustrated in Fig. 4. These results are in accordance with some earlier observations and conclusions from positron annihilation lifetime measurements as well as sorption and gas diffusion measurements in different polymer systems [45–47]. The authors found a better correlation between free-volume hole size and diffusion characteristics than for the free-volume hole size multiplied by I_3 and the same quantities. Furthermore they concluded from their measurements that C is dependent on the polymer structure and that I_3, therefore, does not represent a good measure of the number of free volume cavities in polymers.

A further improvement in the correlation between h_{PVT} and free-volume from PALS can be achieved by plotting h_{PVT} versus the free-volume cavity size $V(\tau_3)$. Evidently, in Fig. 5, the data in the glass fits onto the same linear

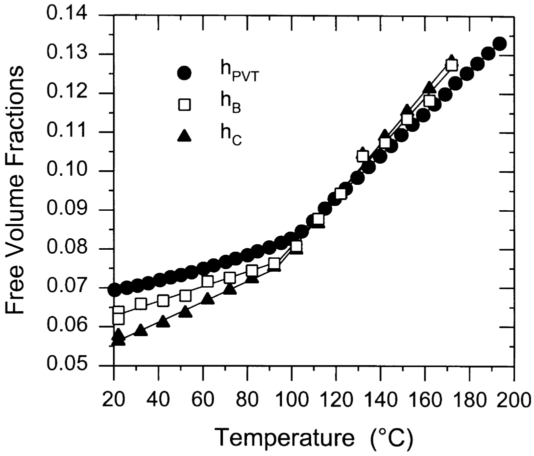

Fig. 4. Free-volume fractions of PMMA determined from (a) the Simha–Somcynsky EOS and experimental *PVT*-data, h_{PVT} (●); (b) PALS-data and Eq. (3) with the actual C-value of 2.28×10^{-3} Å^{-3}, h_C (▲); (c) PALS-data and Eq. (5) with $B = 7.136 \times 10^{-4}$ Å^{-3}, h_B (□).

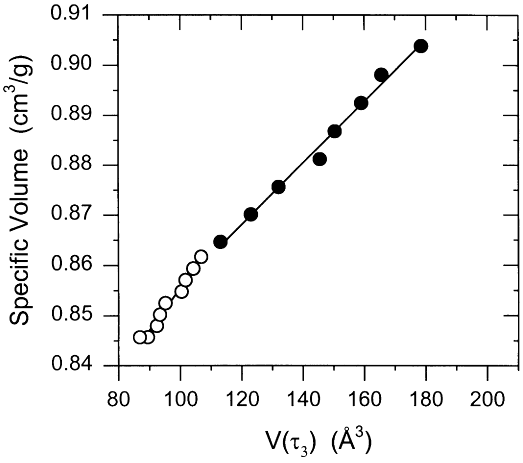

Fig. 6. Specific volume versus $V(\tau_3)$ in the melt (●) and glassy state (○) according to the hole-concentration method (see text).

regression line as that in the equilibrium melt, neglecting data very close to but still below T_g:

$$h_{PVT} = 0.0179 + 5.825 \times 10^{-4} \times V(\tau_3)\ \text{Å}^{-3}\quad (r^2 = 0.999) \tag{6}$$

It is interesting to note that a zero cavity size implies a free-volume hole fraction h of almost zero (1.8%) This is also predicted by an empirical hole-concentration method that was initiated by Dlubek et al. [48] in order to avoid the known limitations of invoking the *o*-Ps intensity I_3 as a measure of the hole concentration. The method is based on the concept of expressing the specific volume v in terms of a hole concentration n, the mean free-volume cavity size $V(\tau_3)$ and an occupied volume V_{occ}:

$$v = n \times V(\tau_3) + V_{occ} \tag{7}$$

Since the specific volume v is known from *PVT* measurements and $V(\tau_3)$ from PALS, both n and V_{occ} in Eq. (7) can be determined experimentally without invoking any fractional free volume a priori. This is shown in Fig. 6 for our PMMA, and we obtain from a linear regression in the melt:

$$v = 0.7941 + 6.160 \times 10^{-4} V(\tau_3) \tag{8}$$

From Eqs. (7) and (8) it follows that $n = 0.6160 \times 10^{21}\ \text{g}^{-1}$ and $V_{occ} = 0.7941\ \text{cm}^3/\text{g}$. Once the hole concentration n is known, then the fractional free volume h_{hole} can be readily calculated. Incidentally, at T_g we find that $h_{hole} = 0.076$, which agrees rather well with $h_{PVT} = 0.081$ (Fig. 2). Moreover it has been shown for a number of polymers that the experimental $V_{occ,exp}$ agrees very well with theoretical $V_{occ,th}$-values determined from [49,50]:

$$V_{occ,th} = K(\tilde{T}) \times V^*. \tag{9}$$

where V^* and $\tilde{T}$ are the characteristic volume and the reduced temperature, respectively, from the Simha–Somcynsky theory and $K(\tilde{T}) \approx 0.9567$ [50]. With our $V^* = 0.8300\ \text{cm}^3/\text{g}$ [17] for PMMA Eq. (9) yields $V_{occ,th} = 0.7941\ \text{cm}^3/\text{g}$, which is in excellent agreement with $V_{occ,exp}$ from the hole-concentration method as well as with the occupied volume from the method of Yu et al. ($0.8088\ \text{cm}^3/\text{g}$). By definition, the hole-concentration method actually assumes that the hole concentration n in Eq. (7) is a constant which would require I_3 to be constant, too, if it were to be a measure of the hole concentration in polymers. This is clearly not the case as shown in Fig. 1(b).

A closing remark concerns the freezing fraction of polymers that is a measure of how much the free volume is frozen-in below T_g relative to the melt. The freezing fraction F_T is expressed in terms of the temperature coefficients of h_{PVT} in the melt and in the glassy state [2,3,51]:

$$F_T = 1 - [(\partial h/\partial T)_g/(\partial h/\partial T)_m] \tag{10}$$

A freezing fraction of one corresponds to a completely frozen glass, i.e. a glass with a constant free-volume fraction, i.e. $(\partial h/\partial T)_g = 0$. A liquid-like glass, on the other hand, would behave like the equilibrium melt and is thus assigned an F_T-value of zero, i.e. $(\partial h/\partial T)_m = (\partial h/\partial T)_g$. High-$T_g$ polymers tend to have freezing fractions near 0.5, whereas low-T_g polymers lie closer to one [2]. Recently, it has been shown that the freezing fraction can be changed by not only varying the chemical structure but also by changing the physical structure as in variable formation-history glasses [52]. With Eqs. (5)–(7) in mind, it should be possible to express Eq. (10) in terms of the temperature coefficients of $V(\tau_3)$:

$$F_{T,PALS} = 1 - [(\partial V(\tau_3)/\partial T)_g/(\partial V(\tau_3)/\partial T)_m] \tag{11}$$

We have tested this hypothesis and find from Eq. (11) and Eqs. (4a) and (4b) a PALS-freezing fraction of 0.68. This is in excellent agreement with a *PVT*-freezing fraction of 0.69 [17]. The possibility to determine freezing fractions from the free-volume cavity size emphasizes its free-volume nature and its close relation to the free-volume fraction from *PVT*–EOS analysis.

4. Conclusions

We have addressed and clarified the use of the correlation constant C and the *o*-Ps intensity, I_3, in the widespread semi-empirical equation for the calculation of free-volume fractions h_{PALS} from PALS data: $h_{PALS} = C \times V(\tau_3) \times I_3$, where $V(\tau_3)$ is the subnanometer cavity hole-volume. From chemically and physically identical PMMA samples, we determined independent free-volume fractions (h_{PVT}) from the Simha–Somcynsky theory and *PVT* measurements as well as free-volume cavity sizes $V(\tau_3)$ from the Tao–Eldrup equation and PALS measurements as a function of temperature. From this unique set of data we found an excellent correlation between the two free-volume quantities: $h_{PVT} = k_1 + k_2 \times V(\tau_3)$, where k_1, and k_2 are correlation constants. This result supports the view that the *o*-Ps intensity I_3 is not related to the free-volume fraction but rather represents, to an appreciable degree, the processes involved in the slowing down of energetic positrons and their positronium formation probability. We conclude, furthermore, that the above correlation constant C is related to the occupied or excluded volume whose value is structure dependent. Hence, different C-values for different polymers. We have also improved the relations between the free-volume quantities from *PVT*–EOS analysis and PALS both in the melt and in the glassy state. Based on these improved relations, we have concluded that the freezing fraction of polymer glasses can also be calculated from $V(\tau_3)$-data.

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