

# On the Thermal Expansion of Nanohole Free Volume in Perfluoropolyethers

G. Consolati\*

Dipartimento di Fisica, Istituto Nazionale per la Fisica della Materia, Politecnico di Milano, Piazza Leonardo da Vinci, 32-20133 Milano, Italy

Received: February 2, 2005; In Final Form: March 18, 2005

To determine the free volume in polymers, positron annihilation lifetime spectroscopy data are transformed into nanohole volumes by modeling the cavities as spheres or, more generally, using geometries assuming an isotropic thermal expansion. However, this guess could be unrealistic owing to the irregular shape of nanoholes and constrained movements of the macromolecules. In this work, it is shown that a comparison of hole–lattice theory with positron and dilatometric data for a homologous series of perfluoropolyethers supplies information on the anisotropic expansion of nanoholes; the relation between volume and typical unconstrained size of the cavities can be expressed by a power law with noninteger exponents.

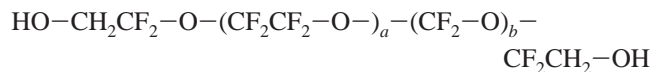
## Introduction

Among the experimental tools able to give information on the free volume (e.g., photoisomerization,<sup>1</sup> small-angle X-ray diffraction,<sup>2</sup> and photochromic labels<sup>3</sup>), positron annihilation lifetime spectroscopy (PALS) gained popularity, since it is a relatively simple technique probing the properties of the free volume holes in a nondestructive way.<sup>4,5</sup> It is based on the fact that some of the positrons injected into the material under investigation are trapped into regions with reduced electron density where they may form positronium (Ps), the positron–electron-bound system. Ortho-Ps (*o*-Ps), the ground state sublevel with parallel spins, interacts with the electrons belonging to the cavity where Ps is trapped; its lifetime is mainly determined by the annihilations of the positron with one of such “external” electrons in a relative singlet state.<sup>6</sup> This involves a correlation between *o*-Ps lifetime and the sizes of the cavity, which can be cast in a quantitative form by suitably modeling the trapping site.<sup>7–9</sup>

Nanoholes are assumed to have a spherical shape in most of the discussions concerning PALS data. Although such a guess is simple and produces results consistent with the expectations, it should be cautiously used. For instance, it implies an isotropic increase of the nanocavities forming the free volume as a consequence of increasing temperature, a strong contention in view of the irregular shape of real holes. This paper discusses this last point. PALS data for a homologous series of oligomeric perfluoropolyethers studied as a function of temperature were compared with the predictions of the lattice–hole theory,<sup>10</sup> with the aim to gain information on the relation between the increase of the typical size of nanoholes with temperature and the corresponding volume expansion.

## Experimental Section

Five oligomeric perfluoropolyethers (FOMBLIN-ZDOL from AUSIMONT S.p.A.) with the following structure:



\* Phone: 0039 2 23996158. Fax: 0039 2 23996126. E-mail: giovanni.consolati@polimi.it.

were used. Molecular weights and glass transition temperature,  $T_g$ , as detected by differential scanning calorimetry (DSC) are reported in Table 1.

The positron source consisted of a droplet of <sup>22</sup>Na from a carrier-free neutral solution (activity 0.3 MBq), dried between two Kapton foils (DuPont, thickness 1.08 mg·cm<sup>−2</sup>), which were afterward glued together. The source was placed in the center of a small copper cup, containing the sample to be analyzed and in direct contact with the heat exchanger of a liquid nitrogen cryostat (DN 1714 Oxford Instruments). Stability of the temperature was ensured within 1 K. All the measurements were carried out in a vacuum; before starting the measurements, each sample was evacuated for 12 h. Positron annihilation lifetime spectra were collected through a conventional fast–fast coincidence setup having a resolution of about 300 ps. Each spectrum contained at least  $2 \times 10^6$  counts; deconvolutions were carried out through the computer code *LT*,<sup>11</sup> with a suitable correction for the positrons annihilated in the Kapton.

## Results and Discussion

Since positron measurements will be discussed in connection with specific volume data, it is suitable to recall results from dilatometric experiments carried out on the same perfluoropolyethers investigated here. Messa<sup>12</sup> carried out dilatometric measurements in a temperature range containing  $T_g$ ; specific volume,  $V$ , shows a linear relation with temperature in the liquid phase (the only one of interest in the present investigation) as well as in the glassy phase, although with different slopes. Therefore, specific volume is written as

$$V = V_g[1 + \alpha_{sp}(T - T_g)] \quad (1)$$

Values of  $V_g = V(T_g)$  and of the thermal expansion coefficient

$$\alpha_{sp} = \frac{1}{V_g} \frac{dV}{dT}$$

taken from<sup>12</sup> are reported in Table 1.

Dilatometric data are essential in order to evaluate the theoretical free volume fraction,  $h$ , within the framework of the lattice–hole theory<sup>10</sup> as well as to calibrate PALS data, as will be shown below. Concerning the first point, the theory supplies an equation of state which is valid for any polymeric structure;

**TABLE 1: Molecular Weights, Glass Transition Temperatures,  $T_g$ , Reduced Parameters  $V^*$  and  $T^*$ , Specific Volumes,  $V_g$ , at  $T_g$ , and Thermal Expansion Coefficients of the Specific Volume,  $\alpha_{sp}$ , for the Investigated Perfluoropolyethers**

MW (Da)	$T_g^a$ (K)	$V_g^a$ (cm <sup>3</sup> g <sup>-1</sup> )	$10^4\alpha_{sp}^a$ (K <sup>-1</sup> )	$V^*$ (cm <sup>3</sup> g <sup>-1</sup> )	$T^*$ (K)
439	189	0.532	9.39	0.531	6954
947	171	0.501	10.91	0.502	6396
3250	157	0.473	11.84	0.480	6143
4610	153	0.472	12.72	0.478	5892
9410	153	0.466	12.18	0.474	6062

<sup>a</sup> From ref 12.

at atmospheric pressure, it is expressed in terms of reduced thermodynamic coordinates  $\tilde{T} = T/T^*$  and  $\tilde{V} = V/V^*$ , where  $T^*$  and  $V^*$  are scaling parameters which depend on the specific material.  $h$  is derived from the equation of state, and in Figure 1, a mastercurve  $h(T/T^*)$  is shown. The parameters  $T^*$  and  $V^*$  for each perfluoropolyether result from a fitting procedure by means of the following expression<sup>13</sup> which is successfully used for a wide class of polymers,<sup>14</sup> including oligomers:<sup>15</sup>

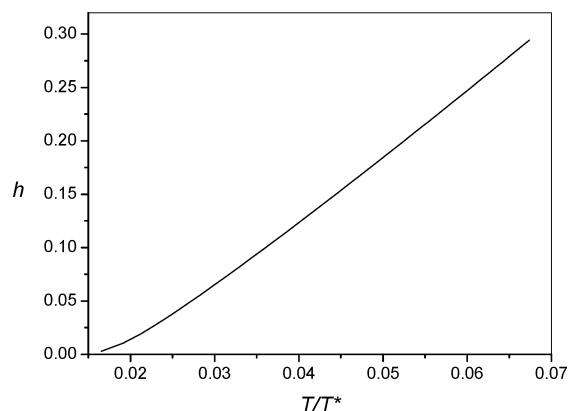
$$\ln \frac{V}{V^*} = A + B \left( \frac{T}{T^*} \right)^{3/2} \quad (2)$$

with  $T$  being the absolute temperature; the values of the coefficients  $A$  and  $B$  are  $-0.1033$  and  $23.835$ , respectively. The parameters  $V^*$  and  $T^*$  are shown in Table 1 for the studied oligomers. In the range of temperatures investigated in this work ( $0.026 < T/T^* < 0.040$ ), the behavior of  $h$  versus  $T$  is perfectly linear:

$$h = h_g[1 + \alpha_{th}(T - T_g)]$$

Values of  $h_g = h(T_g)$  and  $\alpha_{th}$  for each investigated molecular weight are reported in Table 2.

Annihilation time spectra were successfully deconvoluted into three discrete components;  $\chi^2$  tests supplied values in the range 0.98–1.10. An attempt to analyze the spectra in terms of a lifetime distribution for the longest component did not produce meaningful results, with the relative uncertainty of the distribution width being around 100%. The longest component is attributed to *o*-Ps decays, and the discussion will be limited to it. Figure 2 shows the lifetime,  $\tau_3$ , of the longest component versus the temperature ratio,  $T/T_g$ . All the investigated structures show the same behavior, a linear trend below  $T_g$  followed by a dependence on the temperature which is still linear but with a higher slope above  $T_g$ . Finally, at the highest temperatures, the increase of  $\tau_3$  becomes slower.

**Figure 1.** Theoretical free volume fraction,  $h$ , versus the reduced temperature,  $T/T^*$ .**TABLE 2: Free Volume Fractions at  $T_g$ ,  $h_g$ , Free Volume Thermal Expansion Coefficients,  $\alpha_{th}$ , Calculated from the Lattice–Hole Theory, Thermal Expansion Coefficients of Free Volume,  $\alpha_f$ , as Determined from the Experiment in Spherical Approximation, Exponents  $p$ , Nanohole Densities,  $N$ , and Experimental,  $V_{occ}$ , and Theoretical,  $v_{o,th}$ , Occupied Volumes for the Investigated Perfluoropolyethers**

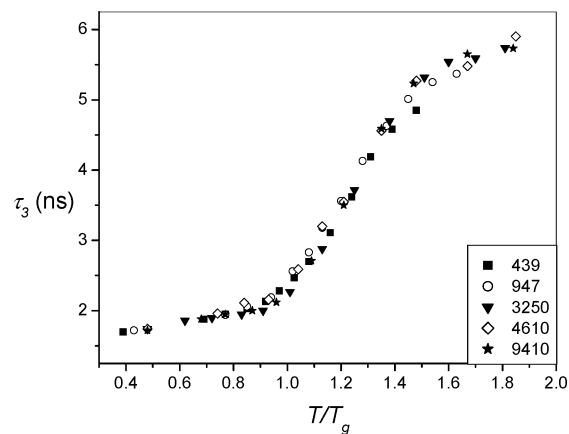
MW (Da)	$h_g$	$10^3\alpha_{th}$ (K <sup>-1</sup> )	$10^3\alpha_f$ (K <sup>-1</sup> )	$p$	$10^{-21}N$ (g <sup>-1</sup> )	$V_{occ}$ (cm <sup>3</sup> g <sup>-1</sup> )	$v_{o,th}$ (cm <sup>3</sup> g <sup>-1</sup> )
439	0.049	17	38	2.13	2.6	0.508	0.506
947	0.046	19	37	2.15	2.2	0.479	0.479
3250	0.039	24	51	2.25	1.9	0.456	0.457
4610	0.041	24	44	2.40	1.4	0.451	0.456
9410	0.038	25	50	2.40	1.4	0.448	0.452

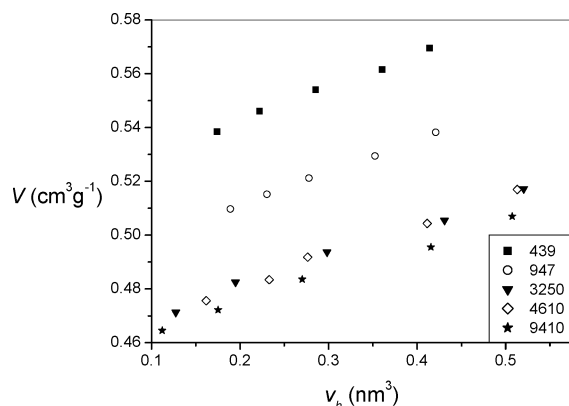
Such a behavior partly mirrors that of the free volume: indeed, below  $T_g$ , interchain motions are strongly hindered and the free volume shows only small variations with temperature; above  $T_g$ , chain segments become mobile and the free volume increases with the temperature at a higher rate; accordingly, the expansion coefficient is higher than that in the glassy state. The range of the highest temperatures where  $d\tau_3/dT$  is again moderate will be no longer considered, since there is a general agreement about the contention that *o*-Ps in this region does not give correct information on the free volume. Various explanations were invoked: the formation of a Ps bubble in the liquid phase,<sup>16</sup> digging of holes by Ps itself,<sup>17</sup> or relaxation time of the molecular chains comparable to  $\tau_3$ <sup>18</sup> (in this case, Ps would not be able to correctly probe the sizes of the nanovoids trapping it).

The data shown in Figure 2 are generally transformed into average sizes of the free volume holes by using the Tao–Eldrup semiempirical eq 3:<sup>7,8</sup> the cavity hosting Ps is assumed to be a spherical void with effective radius  $R$ . Such a Ps trap has a potential well with finite depth; however, for convenience of calculations, the depth is considered to be infinite, but the radius is increased to  $R + \Delta R$ , with  $\Delta R$  (0.166 nm) being an empirical parameter<sup>8</sup> which describes the penetration of Ps wave function into the bulk. The electron density is supposed to be zero for  $r < R$  and constant for  $r > R$ . The relationship between *o*-Ps lifetime,  $\tau_3$  (ns), and radius,  $R$  (nm), is the following:

$$\tau_3 = 0.5 \left[ \frac{\Delta R}{R + \Delta R} + \frac{1}{2\pi} \sin \left( 2\pi \frac{R}{R + \Delta R} \right) \right]^{-1} \quad (3)$$

Other relationships were deduced between  $\tau_3$  and the typical size,  $s$ , of a nanocavity having a different shape with respect to the spherical one (e.g., cubic, prismatic, or cylindrical).<sup>9</sup> Anyway, the same lifetime produces similar values of  $s$  for the

**Figure 2.** *o*-Ps lifetime,  $\tau_3$ , as a function of the temperature ratio,  $T/T_g$ , in the investigated structures.



**Figure 3.** Specific volume,  $V$ , as a function of the nanohole volumes,  $v_h$  (calculated in spherical approximation) in the investigated structures.

various geometries.<sup>19</sup> Furthermore, it is meaningless to try to deduce an exact value of the cavity size, since real holes are irregularly shaped. The values of  $s$  must be considered as approximate estimates. These remarks lead to the following conclusion: eq 3 or analogous equations are all equivalent in order to get from  $\tau_3$  a typical nanohole dimension,  $s$ ; although they are deduced by assuming for the hole a particular geometry, nevertheless the result (that is, the value of  $s$ ) is in fact largely independent of the adopted model. This allows one to extend the calculation of the volume of holes in the case they are partially constrained and therefore they expand anisotropically, as will be discussed later.

The total free volume can be expressed as the product of the density,  $N$ , of nanoholes times the average volume of nanoholes,  $v_h$ :

$$V_f = Nv_h \quad (4)$$

If  $v_h$  represents the volume of nanocavities of size  $s$  which expand isotropically, then  $v_h \approx s^3$ . The most usual assumption is  $v_h = 4/3\pi s^3$ , with  $s = R$  obtained from eq 3.

Specific volume is then given by<sup>20</sup>

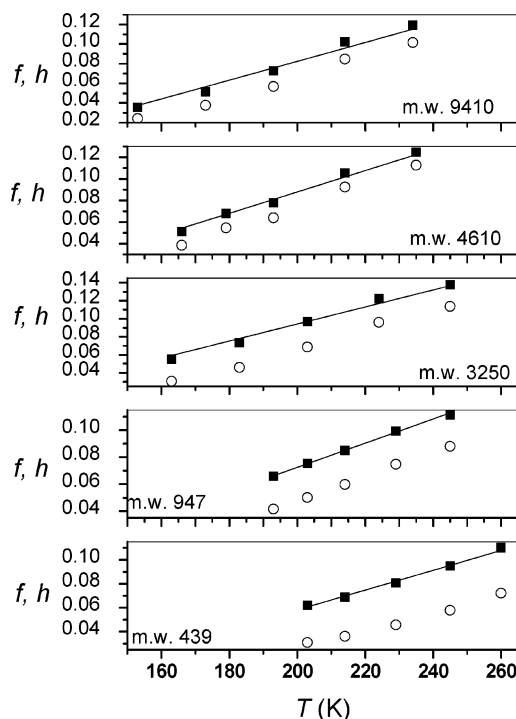
$$V = Nv_h + V_{occ} \quad (5)$$

with  $V_{occ}$  being the occupied volume. A key quantity appearing in eqs 4 and 5 is  $N$ . According to the data discussed here, it can be assumed constant, that is, independent of the temperature, for  $T > T_g$ . Indeed, Figure 3 shows the specific volume,  $V$ , for the investigated structures (evaluated according to eq 1 at the same temperatures of positron data) versus the nanohole volumes,  $v_h$ , calculated in spherical approximation: the data are fitted by straight lines and the correlation coefficients are in all cases higher than 0.99. The parameters  $N$  and  $V_{occ}$  are respectively the slope and intercept of the straight line with the vertical axis. The result does not depend on the adopted approximation: cubic, cylindrical, or prismatic geometries produce the same linear correlation, although with slightly different values for  $N$  and  $V_{occ}$ .

Fractional free volume,  $f$ , can be calculated according to the definition:<sup>20</sup>

$$f = \frac{V_f}{V} = \frac{Nv_h}{Nv_h + V_{occ}} \quad (6)$$

Its behavior versus the temperature is shown in Figure 4 together with the theoretical free volume fraction,  $h$ : the values of  $f$  (obtained using spherical nanoholes, circles in Figure 4) are systematically lower than  $h$ , for all the structures; furthermore,



**Figure 4.** Free volume fractions,  $f$ , as evaluated from positron data compared with the analogous theoretical quantity,  $h$  (continuous lines): (○) spherical nanoholes; (■) anisotropic nanoholes (see text).

the expansion coefficients of  $f$ ,  $\alpha_f$  (reported in Table 2 using for  $v_h$  the spherical approximation), are higher than  $\alpha_{th}$ .

It is worth pointing out that these results do not depend on the spherical geometry adopted for the calculation of the nanovoid dimensions; indeed, it was checked that almost the same discrepancies are obtained using cubic, prismatic, or cylindrical holes. All these models assume an isotropic expansion of nanoholes, that is,  $v_h \approx s^3$ , as previously noted. In the author's opinion, this is the reason for the deviation from the theory. In this connection, other guesses for the nanohole expansion supply a different dependence of their volume on the sizes,  $s$ , which are allowed to increase. For instance, by framing the nanoholes as cylinders with a fixed height,  $\sigma$ , their volumes would increase according to the square of the radius,  $s$ :  $v_h \approx \sigma s^2$ . As a further, naïve example, if the nanocavities are modeled as voids between two parallel planes (as the interlayer gaps in clays<sup>21</sup>), the increase of their volume should be linearly related to the distance between the planes. In these cases, the thermal expansion coefficient of the free volume should be lower than that in the case of spherical holes. More generally, since the cavities are irregular and the macromolecular movements are partly constrained, it can be supposed that the volume expansion of nanovoids follows a power law with respect to the sizes,  $s$ , which change consistently with the constraints, with the other, constrained dimensions,  $\sigma$ , remaining fixed:  $v_h \approx \sigma^{3-p}s^p$ ; isotropic (i.e., unconstrained) holes would imply  $p = 3$ . For the perfluoropolyethers under study, agreement with the theory is expected for  $p < 3$ . To obtain  $p$ , first of all, it is necessary to transform the  $o$ -Ps lifetime,  $\tau_3$ , into an average, unconstrained dimension of the cavity. To this purpose, any equation supplying a relationship between  $\tau_3$  and  $s$  can be used, as previously observed (see the remarks following eq 3). In this work, the Tao–Eldrup equation was used. Once  $s$  was obtained, the nanohole volume,  $v_h$ , was calculated as  $v_h = \sigma^{3-p}s^p$ , for a fixed  $p$  (constant  $\sigma$  was taken equal to 1). A fitting of the specific volume,  $V$ , versus  $v_h$  by straight lines (analogous to that used for spherical holes, see Figure 3) supplied for each  $p$  the

parameters  $N$  and  $V_{\text{occ}}$ . These quantities entered into eq 6 to calculate the fractional free volume,  $f$ , which was compared with  $h$ . The values of  $p$  giving the best agreement between  $f$  and  $h$  (Figure 4, squares) are shown in Table 2; the exponents range between 2 and 3 and are rather similar to each other, with the average value being  $2.3 \pm 0.1$ . This result supports the interpretation of an anisotropic nanohole expansion with temperature. It is worthwhile to point out that identical values of  $p$  were obtained by using other equations than eq 3, framing the holes as cubes, prisms, and cylinders. In Table 2, the values of  $N$  and  $V_{\text{occ}}$  are also shown; the hole density tends to decrease by increasing the molecular weight, in agreement with the expectations, since the higher the molecular weight, the lower the density of chain ends which contribute to the free volume. Of course, only the order of magnitude for  $N$  should be considered, since the proportionality factor between  $v_h$  and  $s^p$  cannot be obtained with this approach. Occupied volumes,  $V_{\text{occ}}$ , experimentally determined from eq 5 favorably compare with the values  $v_{\text{o,th}}$  calculated from the lattice-hole theory (last column of the table), with the differences being below 1.2%.

## Conclusion

PALS in combination with another technique such as dilatometry makes it possible to estimate the behavior of the free volume fraction versus the temperature. Although the result is largely independent of the geometry adopted for the nanoholes, nevertheless it still depends whether the nanohole expansion is "isotropic" or "anisotropic". Comparison with the theory (the results of the Symha-Somcynsky theory were used in the present investigation) supplies information about the nanovoid expansion for the investigated oligomers, even though only for  $T > T_g$ —indeed, since the theory is valid only for structures at equilibrium, the glassy phase must be excluded from the analysis. In particular, the anisotropic expansion of the nanohole volumes is well evidenced by determining the

relation between volume and typical unconstrained size, expressed by a power law with noninteger exponents.

**Acknowledgment.** The author is grateful to Drs. B. Bassetti, P. Jona, and F. Quasso for stimulating discussions.

## References and Notes

- (1) Victor, J. G.; Torkelson, J. M. *Macromolecules* **1987**, *20*, 2241.
- (2) Roe, R. J.; Song, H. H. *Macromolecules* **1985**, *18*, 1603.
- (3) Lamarre, L.; Sung, C. S. P. *Macromolecules* **1983**, *16*, 1729.
- (4) Schmidt, M.; Maurer, F. H. J. *Polymer* **2000**, *41*, 8419.
- (5) Dlubek, G.; Pionteck, J.; Kilburn, D. *Macromol. Chem. Phys.* **2004**, *205*, 500.
- (6) Jean, Y. C. In *Positron Spectroscopy of Solids*; Dupasquier, A., Mills, A. P., Jr., Eds.; IOS Press: Amsterdam, The Netherlands, 1995; pp 563–580.
- (7) Tao, S. J. *J. Chem. Phys.* **1972**, *56*, 5499.
- (8) Eldrup, M.; Lightbody, D.; Sherwood, N. J. *Chem. Phys.* **1981**, *63*, 51.
- (9) Jasinska, B.; Koziol, A. E.; Goworek, T. *Acta Phys. Pol.* **1999**, *95*, 557.
- (10) Simha, R.; Somcynsky, T. *Macromolecules* **1969**, *2*, 342.
- (11) Kansy, J. *Nucl. Instrum. Methods Phys. Res., Sect. A* **1996**, *374*, 235.
- (12) Messa, L. M.A. Thesis, Politechnic of Milan, 1999.
- (13) Simha, R.; Wilson, P. S.; Olabisi, O. *Kolloid Z. Z. Polym.* **1973**, *251*, 402.
- (14) Rodgers, P. A. *J. Appl. Polym. Sci.* **1993**, *48*, 1061.
- (15) (a) Wilson, P. S.; Simha, R. *Macromolecules* **1973**, *6*, 902. (b) Simha, R.; Wilson, P. S. *Macromolecules* **1973**, *6*, 908.
- (16) Mikhin, K.; Stepanov, S. V.; Byakov, V. M. *Radiat. Phys. Chem.* **2003**, *68*, 415.
- (17) Ito, Y.; Mohamed, F. H. M.; Tanaka, K.; Okamoto, K.; Lee, K. J. *Radioanal. Nucl. Chem.* **1996**, *211*, 211.
- (18) Bartos, J.; Sausa, O.; Kristiak, J.; Blochowicz, T.; Rossler, E. *J. Phys: Condens. Matter* **2001**, *13*, 11473.
- (19) Consolati, G. *J. Chem. Phys.* **2002**, *117*, 7279.
- (20) Srithawatpong, R.; Peng, Z. L.; Olson, B. G.; Jamieson, A. M.; Simha, R.; McGerwey, J. D.; Maier, T. R.; Halasa, A. F.; Ishida, H. *J. Polym. Sci., Part B: Polym. Phys.* **1999**, *37*, 2754.
- (21) Consolati, G.; Natali-Sora, I.; Pelosato, R.; Quasso, F. *J. Appl. Phys.* **2002**, *91*, 1928.