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# Determination of Free-Volume and Hole Number Density in Polycarbonates by Positron Lifetime Spectroscopy

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ABSTRACT: Positron lifetime measurements at room temperature have been carried out to determine the average interchain volume in a series of polycarbonates. Applying different hydrostatic pressures of Ar and $CO_2$ and dissolving the corresponding molecules in the polymer allows one to determine the change of the nonoccupied holes of the free-volume by positronium (Ps). A semiempirical relation between the average Ps lifetime and the average free-volume size is used to determine quantitatively the fraction of free volume. Assuming a distribution of hole volumes and a preferential occupancy of large holes by the dissolved molecules gives rise to a decrease of the Ps lifetime in agreement with experiments at low pressures. At higher concentrations, swelling of the polymer occurs and the microstructure changes irreversibly leading to a larger free-volume and therefore to an increase of the Ps lifetime. Three different approaches are used in order to calculate the number density of holes. The results favor an uniform occupancy of all holes by Ps instead of a preferential occupancy of large holes. Depending on the chosen distribution the hole density varies between $2.3 \times 10^{21}$ and $6.6 \times 10^{21}$ cm$^{-3}$.

## 1. Introduction

The structural characterization of polymers is important for understanding and improving their properties. Generally, polymers solidify in an amorphous state where one important point of interest is the free volume and its distribution on an atomic scale. Positron lifetime studies were used frequently to obtain information about this free volume[1−4] because these particles are thought to be annihilated in holes of the amorphous structure. On the other hand, computer simulations[5] have shown that small atoms or molecules incorporated into the interchain free volume occupy energy minima which are surrounded by potential wells. Thus it makes sense to call these positions holes and to attribute a hole volume to them. In particular, the solubility of gas molecules and the macroscopic dilatation due to a misfit between molecules and holes provide information about hole distribution parameters.[6−8] At high concentrations of sorbed molecules, the altered arrangement of the macromolecules will lead to swelling.

For several years positrons have been applied as probes to examine the free-volume of polymers. The interesting point is the formation of positronium (Ps) whose lifetime distribution can be used as a measure of the free volume in organic materials and especially the hole size distribution in polymers.[3,4,9−11]

The present paper deals with changes in the hole size distribution during sorption of gas molecules. It will be shown that from the Ps lifetime distribution the number density of holes in the polymer can be evaluated. Furthermore, information is obtained about which holes are occupied preferentially by Ps.

## 2. Theoretical Background

**2.1. Gaussian Distribution of Hole Volumes.** Generally, glassy polymers can be characterized by a statistical arrangement of the macromolecular chains. This leads to the appearance of intermolecular free-volume “holes” on an atomic scale. The total volume of these holes is called the free volume, *f*, of the polymer. It is of fundamental importance for determining the macroscopic behavior of the polymer, especially mechanical properties and diffusion.[12,13] Following the considerations of Bueche[14] a Gaussian distribution $n(V)$ of hole volumes $V$ is assumed:[6,7]

$$n(V) = C \exp\left[-\frac{(V-V_0)^2}{{\sigma_v}^2}\right] \tag{1}$$

Here $V_0$ is the mean volume of the holes, respectively, and $\sigma_v$ is the width of the distribution. $C$ is a normalizing factor of the distribution. Then the number density $N_0$ of holes can be described by

$$N_0 = \int_0^\infty n(V)\,dV = C\frac{\sqrt{\pi}\sigma_v}{2}\left[1 + \operatorname{erf}\left(\frac{V_0}{\sigma_v}\right)\right] \tag{2}$$

It is defined here as the number of holes per unit polymer volume. Thus, $C$ is found to be

$$C = \frac{2N_0}{\sigma_v\sqrt{\pi}\left(1 + \operatorname{erf}\left(\frac{V_0}{\sigma_v}\right)\right)} \tag{3}$$

The complicated prefactor stems from a truncation of the Gaussian distribution which does not extend to $-\infty$ but terminates at $V = 0$. Thus the average hole volume is

$$\langle V\rangle_1 = \frac{C}{N_0}\int_0^\infty V \exp\left[-\frac{(V-V_0)^2}{{\sigma_v}^2}\right] dV = V_0 + \sigma_v\frac{\exp\left(-\left(\frac{V_0}{\sigma_v}\right)^2\right)}{\sqrt{\pi}\left(1 + \operatorname{erf}\left(\frac{V_0}{\sigma_v}\right)\right)} \tag{4}$$

Measurements of $V_0$ and $\sigma_v$ by positron lifetime spec-

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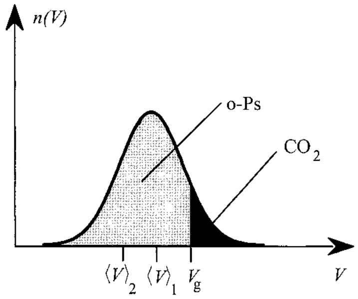


**Figure 1.** Distribution of hole volumes $V$ in a glassy polymer and occupation of the holes by gas molecules and Ps. The gas molecules are supposed to occupy only holes larger than $V_g$ (black part of the distribution): Ps occupies all remaining holes with the same probability (shaded part). $\langle V\rangle_1$ is the average volume detected by Ps before dissolution of gas molecules; $\langle V\rangle_2$ is the average volume after the dissolution.

troscopy[15] show that $V_0 > \sigma_v$, and therefore, the second term on the right-hand side of eq 4 is small compared to the first one. Thus we obtain the expected result $\langle V\rangle_1 \approx V_0$.

**2.2. Limiting Case of $T = 0$.** Applying several approximations from elastic theory[16] also leads to a Gaussian distribution of hole energies for the dissolution of small molecules in a polymer.[6] The thermal occupancy of the holes is described by Fermi–Dirac statistics assuming that only one molecule can occupy a free hole. Elastic energy has to be provided if a molecule is incorporated in a smaller hole. This energy is greater the smaller the hole, and therefore, dissolved molecules will occupy the larger holes preferentially. For simplicity this is described by the limiting case of an occupation of all holes larger than a limiting volume $V_g$ visualized in Figure 1 by the black region. This case is equivalent to the Fermi–Dirac function degenerating to a step function at $T = 0$. Holes that are occupied by a gas molecule no longer belong to the average free-volume of the hole size distribution. The average hole volume that remains after an occupation of all holes larger than $V_g$ is given by

$$\langle V\rangle_2 = \frac{C}{N_0 - N_g}\int_0^{V_g} V \exp\left[-\left(\frac{V - V_0}{\sigma_v}\right)^2\right] \mathrm{d}V \tag{5}$$

where $N_g$ is the number density of dissolved gas molecules or of occupied holes, respectively:

$$N_g = C\int_{V_g}^{\infty} \exp\left[-\left(\frac{V - V_0}{\sigma_v}\right)^2\right] \mathrm{d}V = \frac{C\sqrt{\pi}\sigma_v}{2}\left[1 - \mathrm{erf}\left(\frac{V_g - V_0}{\sigma_v}\right)\right] \tag{6}$$

Integration of eq 5 and substitution of $N_g$ from eq 6 leads to

$$\langle V\rangle_2 = V_0 + \frac{\sigma_v}{\sqrt{\pi}}\,\frac{\exp\left(-\left(\frac{V_0}{\sigma_v}\right)^2\right) - \exp\left(-\left(\frac{V_g - V_0}{\sigma_v}\right)^2\right)}{\mathrm{erf}\left(\frac{V_0}{\sigma_v}\right) + \mathrm{erf}\left(\frac{V_g - V_0}{\sigma_v}\right)} \tag{7}$$

There are two characteristic volumes of interest: the average hole volume $\langle V\rangle_2$ as a function of occupied holes in the polymer and the limiting volume $V_g$. The number density of holes that are occupied can be calculated from the concentration $c$ of dissolved gas molecules:

$$N_g = \frac{N_A}{V_{m0}}c = N_0\frac{1 - \mathrm{erf}\left(\frac{V_g - V_0}{\sigma_v}\right)}{1 + \mathrm{erf}\left(\frac{V_0}{\sigma_v}\right)} \tag{8}$$

Here $c$ is defined in this context as the cm$^3$ of gas at STP (standard conditions) per cm$^3$ polymer and, therefore, $V_{m0}$ is 22413.8 cm$^3$/mol, and $N_A$ is Avogadro's number. Therefore, the dependence of $\langle V\rangle_2$ on the concentration in eq 7 is described via $V_g$ in eq 8.

**2.3. General Case and Its Relation to the Partial Molar Volume of Gas Molecules.** In the previous model, the thermal occupancy is described in the limiting case that only the largest free holes will be occupied. For the more general case that holes of free energy $G$ are filled according to a given thermal occupancy function $o(G)$, and allowing also for $G$ to depend on $V$, the average volume of empty holes is given by

$$\langle V\rangle_2 = \frac{\int_0^{\infty} V n(V)[1 - o(V)]\,\mathrm{d}V}{\int_0^{\infty} n(V)[1 - o(V)]\mathrm{d}V} = \frac{N_0\langle V\rangle_1 - \int_0^{\infty} V n(V) o(V)\,\mathrm{d}V}{N_0 - N_g} \tag{9}$$

In the following, we show that the integral on the right-hand side of eq 9 can be obtained from measurements of the volume change $\Delta V$ caused by the sorption of $N_g$ small molecules per unit volume of polymer. If a molecule has a volume $V_{gas}$ and if this is larger than the volume $V$ of the occupied hole, the corresponding volume change $\Delta v$ shall be proportional to the misfit $V_{gas} - V$, i.e.

$$\Delta v = \gamma(V_{gas} - V) \tag{10}$$

where $\gamma$ is a constant elastic quantity. It can be calculated for the analogous macroscopic case of pressing a sphere of volume $V_{gas}$ in a spherical hole of volume $V$ being part of an elastic continuum. For a stiff volume $V_{gas}$ and a Poisson ratio $\nu = 1/3$ (common for glassy polymers) $\gamma = 1.5$,[6,7] whereas for the case of identical elastic behavior of sphere and continuum $\gamma = 1$. As discussed in refs 5 and 6 the latter case appears to be more appropriate for gases in glassy polymers. Integrating over all holes yields the total macroscopic volume change

$$\Delta V = \int_0^{\infty}(V_{gas} - V)n(V)o(V)\,\mathrm{d}V = V_{gas}N_g - \int_0^{\infty} V n(V) o(V)\,\mathrm{d}V \tag{11}$$

A partial molar volume $V_p$ is then defined by the following relation:

$$V_p = \frac{\Delta V}{N_g} \tag{12}$$

Eliminating $\Delta V$ in eqs 11 and 12 and eliminating the integral from the right-hand sides of eqs 9 and 11, too, gives

$$\langle V\rangle_2 = \frac{N_0\langle V\rangle_1 - N_g V_{gas} + N_g V_p}{N_0 - N_g} \qquad (13)$$

This result is independent of the functions $n(V)$ and $o(G)$, and therefore, a rather general relation between the average hole volume and the concentration of dissolved gas molecules is obtained. Rearrangement of eq 13 leads to

$$\frac{\langle V\rangle_2 - \langle V\rangle_1}{\langle V\rangle_1} = \left[\frac{N_g}{N_0 - N_g}\right]\left(1 - \frac{V_{gas}}{\langle V\rangle_1} + \frac{V_p}{\langle V\rangle_1}\right) \qquad (14)$$

Equation 14 can be used to calculate the number density of holes $N_0$ because the remaining quantities can be determined experimentally. The number density $N_g$ of dissolved gas molecules can be measured by sorption experiments. Furthermore, measurements of the dilatation of the polymer during sorption[6-8] yield $V_p$ and $\langle V\rangle_1$. $V_{gas}$ is obtained either from the density of the corresponding liquefied gas or from volume changes that occur during sorption of this gas in organic liquids.[8] The relative volume change on the left-hand side of eq 14 is evaluated from positronium lifetime data as described in the following section.

Equation 13 can also be derived in a different but very simple way. Assuming the validity of eq 10 (with $\gamma = 1$) means that one molecule blocks the volume $V = V_{gas} - \Delta v$ for occupancy by Ps. Summation over all $N_g$ molecules per unit volume of polymer leads to $N_g V_{gas} - N_g V_p$ as that part of the total free volume $N_0\langle V\rangle_1$ which is no longer available for Ps. Then the remaining $N_0 - N_g$ holes have a free volume of $N_0\langle V\rangle_1 - N_g V_{gas} + N_g V_p$. in agreement with eq 13.

**2.4. Occupancy of Holes by Ps.** The spectra measured by positron lifetime spectroscopy (PLS) for polymers very often contain the long life component of orthopositronium (o-Ps). This component responds very sensitively to the size and the distribution of the hole volumes due to the fact that Ps atoms are preferentially trapped in holes of atomic dimensions.

Calculating the wave function of Ps in a spherical box and assuming annihilation of Ps by electrons from the polymer matrix extending a distance $\Delta R$ into the box yields a relation between the o-Ps lifetime $\tau_{o-Ps}$ and the size of spherical holes[1-4]

$$\tau_{o-Ps} = \frac{1}{\Lambda[1 - R/(R + \Delta R) + 1/2\pi \sin(2\pi R/(R + \Delta R))]} \qquad (15)$$

where $R$ is the radius of the holes. $\Lambda$ is an average decay rate of Ps which was estimated to be 2 $ns^{-1}$. $\Delta R$ was determined to be 1.66 Å by fitting data of molecular solids and zeolites with known hole size to eq 15. Recently it was discussed whether PLS will be able to provide information about the hole size distribution of the polymer or not.[17-19] Additional evidence in this context can be received by filling part of the holes in a polymer with small molecules[20] as discussed later.

The models mentioned above assume that Ps will occupy one hole during its lifetime only but will detect all holes with the same probability (Figure 1). Then the average Ps-lifetime is related to the average hole volume $\langle V\rangle_1$ or $\langle V\rangle_2$ and corresponding models will be called "average volume" models (AV) in the following.

In addition we will also consider cases where Ps will visit several holes during its lifetime but stays preferentially longer in the larger holes as shown in Figure 2. Corresponding models will be called "large-volume"-models (LV). We further assume that the gas molecules occupy the larger holes first and Ps cannot coexist in the same hole with a gas molecule. Then the large holes are successively blocked with increasing concentrations of gas molecules and the Ps lifetime should decrease very rapidly. The theoretical description of this scenario requires the introduction of a cutoff volume $V_{co}$; otherwise the Ps in a gas free polymer would occupy holes of infinite volume.

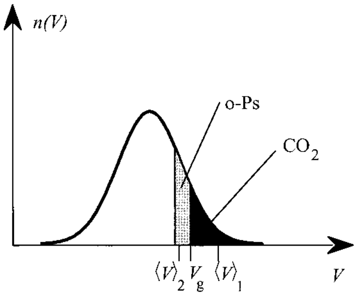


**Figure 2.** Same as Figure 1 but Ps occupies larger holes preferentially. However, if present the sorbed molecules block the largest holes.

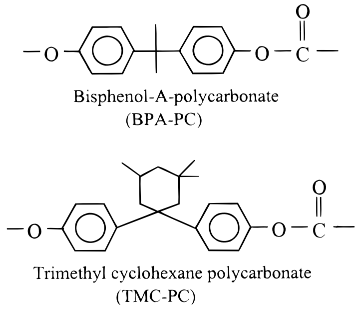


**Figure 3.** Structural units of the polymers used.

## 3. Experimental Section

Bisphenol A−polycarbonate (BPA−PC) and trimethyl cyclohexane polycarbonate (TMC−PC) with structural units as shown in Figure 3 were studied at various gas pressure (0−2 MPa) of $CO_2$ and Ar, respectively. The polymers were received from Bayer AG (Leverkusen, Germany), dried from a solution of dichloromethane and aged at 393 K for 4 h. All measurements were carried out with fast lifetime spectrometer at room-temperature. Using a $^{60}$Co source the spectrometer had a time resolution of 230 ps fwhm (full width at half-maximum). For the measurements a film source of about 1.5 MBq of $^{22}$Na was prepared using Kapton (PMDA−ODA) with a thickness of 7.5 $\mu$m. This source was sandwiched between the samples. Spectra were evaluated with the aid of a program called PATFIT[21]. Then $\langle V\rangle$ is obtained from the PLS data by using eq 15 and the o-Ps lifetime component. By application of the program CONTINPALS,[22-24] based on CONTIN,[25] a distribution of the Ps lifetime is extracted from the PLS data, yielding a volume distribution via eq 15 with an average value $\langle V\rangle$ and a width $\sigma_v$. To obtain the concentration of the dissolved gas at various gas pressures, sorption isotherms of $CO_2$ and Ar were measured in BPA−PC and TMC−PC. Details can be found elsewhere.[6]

## 4. Results

The PLS data are best described by three free lifetime components. The lowest of about 220 ps is much longer than the one expected for para-positronium (p-Ps) which is about 125 ps. One possible explanation of this lowest component could be a contribution from short-lived

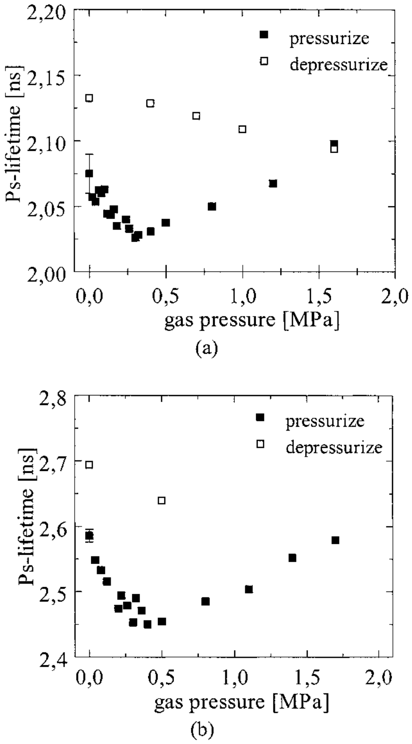


**Figure 4.** O-Ps-lifetime component vs $CO_2$ pressure in (a) BPA–PC and (b) TMC–PC.

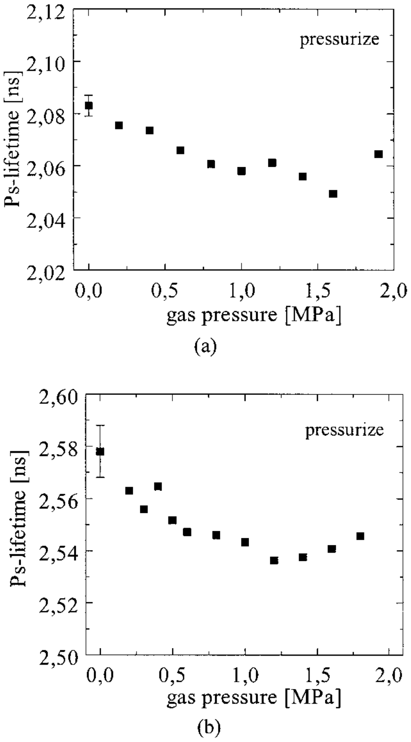


**Figure 5.** O-Ps-lifetime component vs Ar pressure in (a) BPA–PC and (b) TMC–PC.

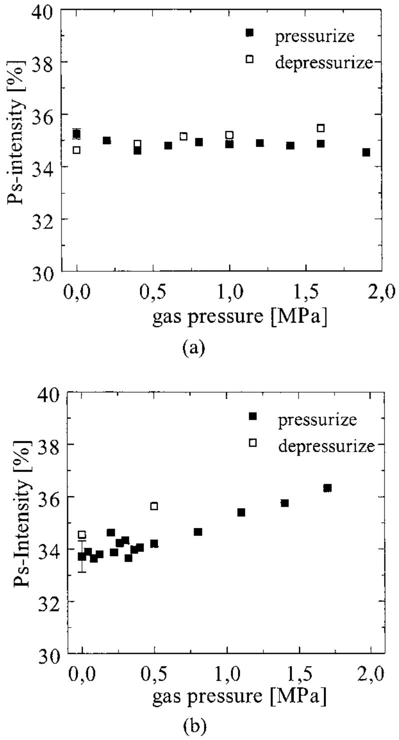


**Figure 6.** O-Ps-lifetime intensity vs $CO_2$ pressure in (a) BPA–PC and (b) TMC–PC.

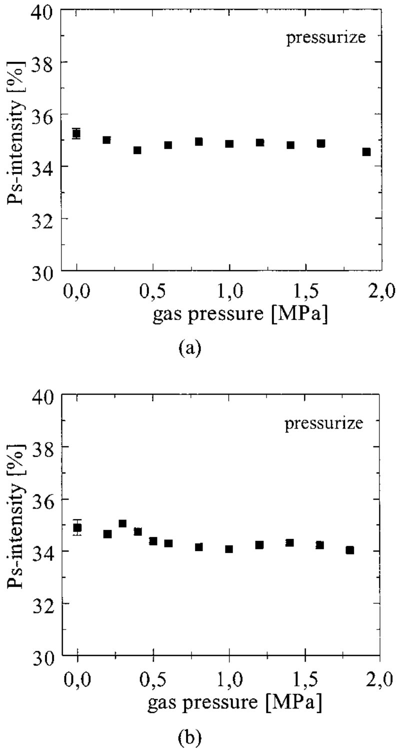
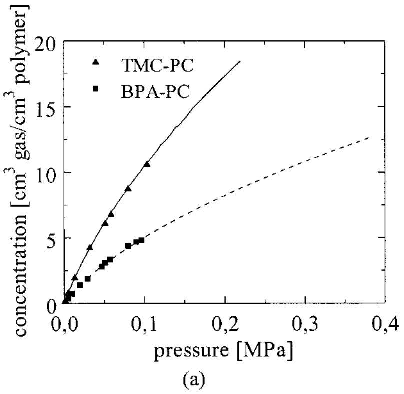


**Figure 7.** O-Ps-lifetime intensity vs Ar pressure in (a) BPA–PC and (b) TMC–PC.

o-Ps[26] in agreement with McGervey et al.[27] assuming a second o-Ps lifetime. This additional component leads to a better description of the intensity ratio being 3:1 for the two Ps components. A second component in our spectra appears at about 550 ps, which is assumed to be a polymer component. Both lifetimes do not show significant changes during gas sorption. The third component is the long-lived component of o-Ps, which is determined to be about 2.1 ns in BPA–PC and 2.6 ns in TMC–PC under vacuum. This component changes during sorption of $CO_2$ and Ar. Two characteristic pressure regions were found (Figures 4 and 5). In the low-pressure region up to about 0.4 MPa for $CO_2$ and 1.2–1.5 MPa for Ar, the Ps lifetime decreases whereas in the high-pressure region the lifetime increases with increasing pressure.



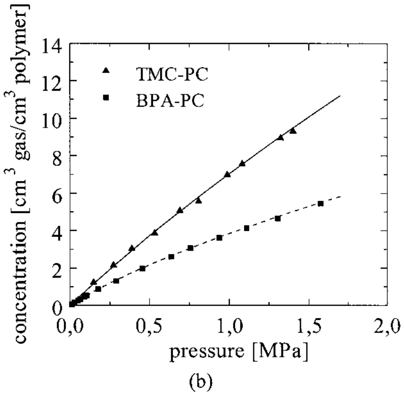


**Figure 8.** Sorption isotherms for (a) $CO_2$ and (b) Ar in BPA−PC and TMC−PC using for gas concentration units of $cm^3$ of gas at STP per $cm^3$ polymer.

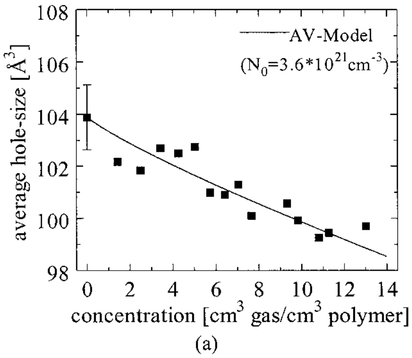
For low concentration of dissolved gas the volume expansion and Ps lifetime during gas sorption are reversible[7,8] and the Ps lifetime decreases as the concentration of dissolved gas molecules increases. However, the intensity of the Ps lifetime is constant vs gas concentration in this pressure region (Figures 6 and 7). This is in contradiction to the concept that the fractional free-volume $f$ of the polymer shall be proportional to the intensity of the o-Ps lifetime[30,31] according to the following relation:

$$f = F \cdot I_{o-Ps} \cdot V_o \qquad (16)$$

where $F$ is a constant determined to be 2 $nm^{-3}$.[32] Using our data, the last equation yields $f$ = 6.6% in BPA−PC and 9.5% in TMC−PC. However, a detectable change of the Ps intensity should occur during sorption of gas molecules because the average hole volume and the number density of free holes are lowered due to the filling of larger holes by gas molecules.

In the high-pressure region, the concentration of dissolved gas molecules becomes so high that structural changes of the polymer (swelling) occur[28] and the volume expansion during gas sorption is not completely reversible.[29] In addition, small but irreversible changes in the Ps intensity are found. After the pressure is released, both the remanent volume expansion and the increased Ps lifetime indicate an increase of the free volume of the polymer. Thus swelling occurred during exposure to large pressures of $CO_2$ and Ar.

To present the results as a function of gas concentration, published sorption isotherms[8] for $CO_2$ and Ar at 20 °C as shown in Figure 8 were used.



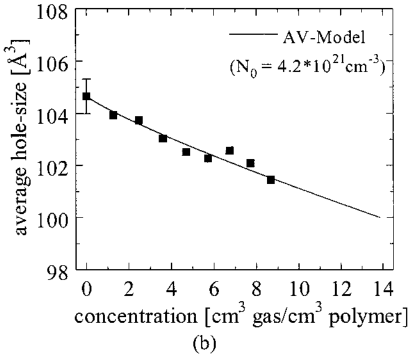
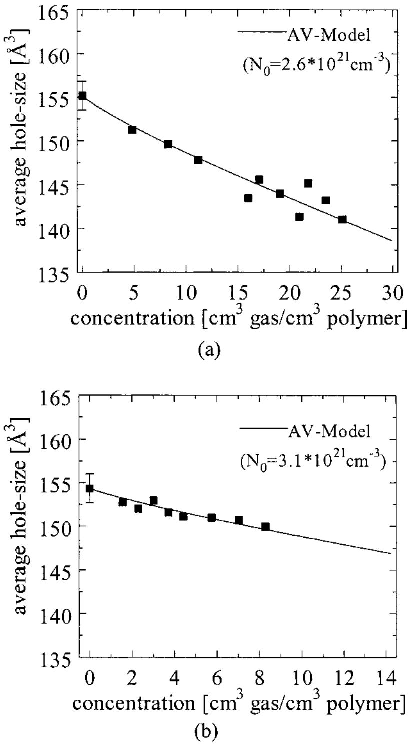


**Figure 9.** Average hole volume calculated from eq 15 plotted vs concentration of dissolved gas. Comparison of experimental results at low pressures with the predictions of eqs 7 and 8 (solid line) using $N_0$ as a fitting parameter: (a) $CO_2$ and (b) Ar in BPA−PC.

## 5. Discussion

**5.1. Average-Volume Models.** In the lower pressure region the measured lifetime at various gas pressures is used to calculate the average hole volume $\langle V \rangle_2$ at various gas concentration by eq 15. The results are plotted in Figures 9 and 10. Fitting eq 7 to the experimental results yields $N_0 = 3.5 \times 10^{21}$ $cm^{-3}$ for $CO_2$ or $4.1 \times 10^{21}$ $cm^{-3}$ for Ar in BPA−PC and $N_0 = 3.0 \times 10^{21}$ $cm^{-3}$ for $CO_2$ or $3.6 \times 10^{21}$ $cm^{-3}$ for Ar in TMC−PC. These $N_0$ values correspond to the curves presented in Figures 9 and 10. For the evaluation the other quantities in eq 7 have to be known and they were obtained as follows. The width $\sigma_v$ = 36.3 Å$^3$ for BPA−PC and 51.1 Å$^3$ for TMC−PC is calculated from Ps lifetime distributions as obtained from vacuum spectra by using the program CONTINPALS.[22−24] Similar results in polycarbonates were published by Jean et al.[15] Then $V_0$ can be calculated from $\langle V \rangle_1$ and eq 4 (the second term on the right-hand side of eq 4 is very small compared to the first one and therefore $\langle V \rangle_1 \approx V_0$). $N_g$ values from sorption isotherms (cf. Figure 8) are inserted in eq 8 in order to calculate $V_g$ which allows us to calculate $\langle V \rangle_2$ via eq 7. The only unknown quantity remaining is $N_0$, which was used as a fitting parameter as mentioned before.

The good agreement between experimental findings and the simple theoretical model was achieved by the following assumptions: (i) a Gaussian distribution of hole volumes is present, (ii) *relative* volumes can be calculated via eq 15 (note that a proportional relation between true $V$ and $\sigma$ values and those calculated via eq 15 will not affect eq 7 because the proportionality constant will be eliminated), and (iii) large holes are filled sequentially by gas molecules and o-Ps occupies the remaining empty holes with equal probability.



(a)

(b)

**Figure 10.** Same as Figure 9 but for TMC−PC.

**Table 1. Average Value $V_0$ and Width $\sigma_v$ of a Gaussian Distribution of Hole Volumes as Determined by Positron Lifetime Spectroscopy (PLS) and by Sorption and Dilatation Measurements (SD)**

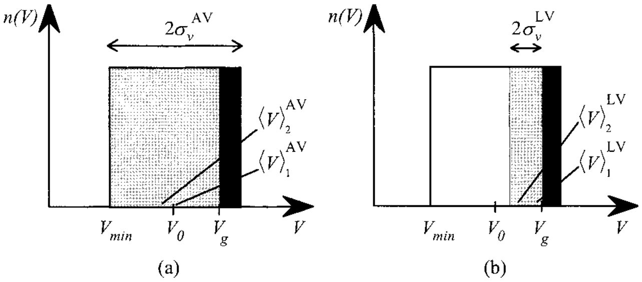
| polymer | $V_0$ (PLS) (Å$^3$) | $\sigma_v$ (PLS) (Å$^3$) | $V_0$ (SD) (Å$^3$) | $\sigma_v$ (SD) (Å$^3$) | $V_0$(PLS)/ $V_0$(SD) | $\sigma_v$(PLS)/ $\sigma_v$(SD) |
|---|---|---|---|---|---|---|
| BPA−PC | 104.0 | 36.3 | 30.7 | 11.0 | 3.4 | 3.3 |
| TMC−PC | 155.1 | 51.1 | 36.9 | 13.1 | 4.2 | 3.9 |

The number density $N_0$ of holes given before is in agreement with estimated values derived elsewhere.[6] One method of estimation is based on the packing density of several gases in the liquid or solid-state being about $2 \times 10^{22}$ cm$^{-3}$. If molecules are dissolved only in the free-volume part of the polymer, the number density of holes will be reduced. If we assume that the free-volume is present with a fraction of 0.1, the hole density would be about $2 \times 10^{21}$ cm$^{-3}$.

Results of sorption experiments and dilatation experiments (SD) offer another method to determine $V_0$ and $\sigma_v$ via eqs 10 and 11 as described in ref 5. Corresponding data[8,20] are summarized in Table 1 and compared with PLS data.

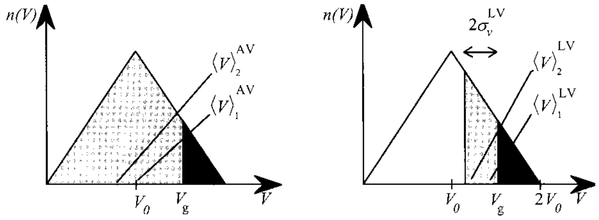
It is interesting to note that the values determined by o-Ps lifetimes are larger by a scaling factor of 3−4. We will not argue at present which method allows a better determination of $V_0$ and $\sigma_v$ since the scaling factor vanishes by using ratios of $V$ and $\sigma_v$. Therefore it is reasonable to insert positron data on the left-hand side of eq 14 and the dilatation data on the right-hand side to derive another value for $N_0$. This procedure is described in the following section.

The partial molar volume of $V_p = 17.3$ Å$^3$ for CO$_2$ and 13.8 Å$^3$ for Ar in BPA−PC and 7.6 Å$^3$ for CO$_2$ in TMC−PC are rather independent of the gas pressure within the range covered by the present study.[8] Therefore, a linear decrease of the relative volume change $(\langle V\rangle_2 - \langle V\rangle_1)/\langle V\rangle_1$ is predicted as a function of concentration by eq 14 in agreement with the experiment (cf. Figures 9 and 10). From the slopes of a linear fit through the data points in Figures 9 and 10 the following values are calculated: $N_0 = 6.7 \times 10^{21}$ cm$^{-3}$ for CO$_2$ and $4.0 \times 10^{21}$ cm$^{-3}$ for Ar in BPA−PC and $6.4 \times 10^{21}$ cm$^{-3}$ for CO$_2$ in TMC−PC (no $V_p$ values were available for Ar in TMC−PC). These values differ from those obtained via eq 7 by less than a factor of 2. This is considered to be satisfactory agreement taking into account how different the approaches are. This becomes more obvious by repeating the assumptions for the validity of eq 14: (i) sorbed molecules cause a volume change described by eq 10, (ii) remaining empty holes are occupied by o-Ps with equal probability, and (iii) the average hole volumes $\langle V\rangle_1$ can be determined as described in ref 4 assuming a Gaussian distribution of hole volumes.



(a) (b)

**Figure 11.** Rectangular distribution of hole volumes and occupation of the holes by gas molecules (black area) and Ps (shaded area). $\langle V\rangle_1$ is the average volume detected by Ps before dissolution of gas molecules; $\langle V\rangle_2$ is that after the dissolution. The gas molecules are supposed to occupy only holes larger than $V_g$ (black): (a) Ps occupies all remaining holes with same probability; (b) Ps occupies remaining larger holes preferentially.



(a) (b)

**Figure 12.** Same as Figure 11 but for a triangular distribution.

**5.2. Large-Volume Models.** If we drop the assumption that Ps occupies all empty holes with equal probability, we encounter the problem that Ps-lifetime data for $V_0$ and $\sigma_v$ are not representing the hole volume distribution. The additional assumption that Ps occupies the largest available holes requires the definition of a cutoff volume for distributions which extend, like the Gaussian one, to infinity. To avoid these problems of a LV model, we consider two simple distribution functions, a rectangular and a triangular one (cf. Figures 11 and 12).

The rectangular distribution function is defined by

$$n(V) = \begin{cases} \dfrac{N_0}{2\sigma_v}: & V_0 - \sigma_v \le V \le V_0 + \sigma_v \\ 0: & \text{elsewhere} \end{cases} \qquad (17)$$

The AV model yields the average hole volume before sorption

$$\langle V\rangle_1^{AV} = \frac{1}{N_0}\int_0^\infty V n(V)\,dV = V_0 \qquad (18a)$$

**Table 2. Number Density $N_0$ of Holes, Average Hole Volume $V_0$, and Total Fraction of Free Volume $f = N_0V_0$ for the Different Models of This Study (Each as an Average for the Two Gases Ar and CO$_2$)**

| polymer | model function | limiting case | $V_0$ (Å$^3$) | $N_0$ ($10^{21}$cm$^{-3}$) | $f$ (%) |
|---|---|---|---|---|---|
| BPA−PC | Gaussian | AV | 104.0 | 3.8 | 39.5 |
| TMC−PC | Gaussian | AV | 155.1 | 3.3 | 51.2 |
| BPA−PC | rectangular | AV | 104.0 | 2.6 | 27.0 |
| TMC−PC | rectangular | AV | 155.1 | 2.4 | 37.2 |
| BPA−PC | rectangular | LV | 70.2 | 10.0 | 70.2 |
| TMC−PC | rectangular | LV | 103.1 | 10.0 | 103.1 |
| BPA−PC | triangular | AV | 104.0 | 6.3 | 65.5 |
| TMC−PC | triangular | AV | 155.1 | 5.9 | 91.5 |
| BPA−PC | triangular | LV | 76.2 | 150 | 1143 |
| TMC−PC | triangular | LV | 111.1 | 114 | 1267 |

and after sorption

$$\langle V\rangle_2^{\mathrm{AV}} = \frac{1}{N_0 - N_g}\int_{V_0-\sigma_v}^{V_g} V n(V)\,\mathrm{d}V = V_0 - \frac{N_g}{N_0}\sigma_v \tag{18b}$$

of $N_g$ molecules of gas per polymer volume unit. The result on the right-hand side of eq 18a and 18b are obtained by integration or by simple geometrical considerations using Figure 11. For the LV model $\langle V\rangle_1 \neq V_0$, and the width $\sigma_v^{\mathrm{LV}}$ determined from Ps lifetimes is different from the width of the distribution. Here the relations between the volume change during gas sorption and the number of dissolved gas molecules are calculated to be

$$\langle V\rangle_1^{\mathrm{LV}} = 2V_0 - \sigma_v^{\mathrm{LV}} - V_{\min} \tag{19a}$$

$$\langle V\rangle_2^{\mathrm{LV}} = \langle V\rangle_1^{\mathrm{LV}} - (\langle V\rangle_1^{\mathrm{LV}} + \sigma_v^{\mathrm{LV}} - V_{\min})\frac{N_g}{N_0} \tag{19b}$$

Again the number density $N_0$ of free-volume holes can be determined from measured data as described above. Since no information about $V_{\min}$ is available it is assumed to be zero. Both AV and LV models yield a linear dependence of $\langle V\rangle_2$ on concentration, and linear fits to the data points in Figures 9 and 10 give values for $N_0$ as compiled in Table 2. The triangular distribution function like the one shown in Figure 12 is defined by

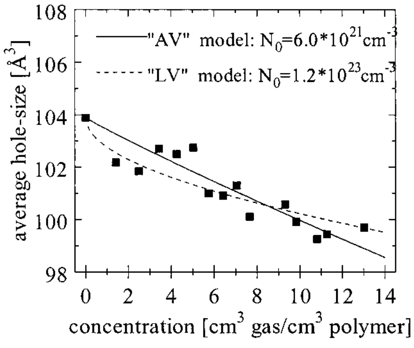
$$n(V) = \begin{cases} \dfrac{N_0}{V_0^2}\cdot V: & 0 < V \leq V_0 \\ \dfrac{N_0}{V_0}\left(2 - \dfrac{V}{V_0}\right): & V_0 < V \leq 2V_0 \\ 0: & \text{elsewhere} \end{cases} \tag{20}$$

For the AV model $\langle V\rangle_1 = V_0$ and

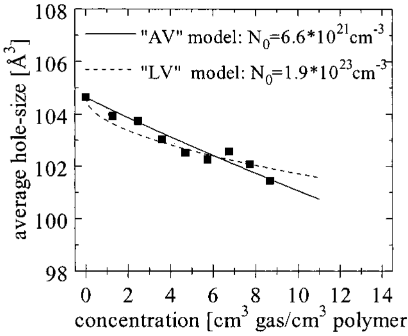
$$\langle V\rangle_2^{\mathrm{AV}} = \frac{V_0\left[2N_g\sqrt{\dfrac{2N_g}{N_0}} + 3(N_0 - 2N_g)\right]}{3(N_0 - N_g)} \tag{21}$$

Using the LV-model a relation between the average volume size and the cutoff-volume $2V_0$ is obtained as

$$\langle V\rangle_1^{\mathrm{LV}} = 2V_0 - \frac{4}{3}\sigma_v^{\mathrm{LV}} \tag{22}$$

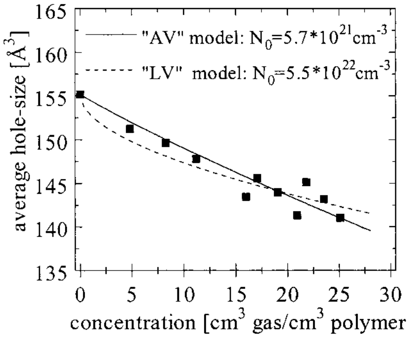


(a) CO$_2$

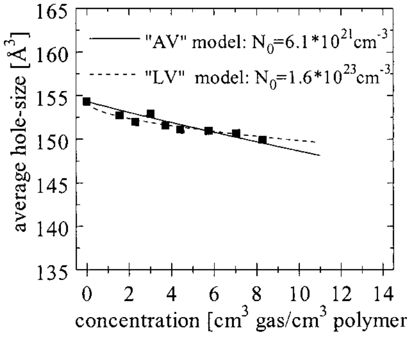


(b) Argon

**Figure 13.** Comparison of experimental data at low gas concentrations with the predictions for the triangular distribution (eqs 21 and 23): (a) CO$_2$ and (b) Ar in BPA−PC. O−Ps is allowed to occupy all remaining holes (AV-model, eq 21) or larger remaining holes preferentially (LV-model, eq 23). Best fits were obtained with $N_0$ values given in the figure.



(a) CO$_2$



(b) Argon

**Figure 14.** Same as Figure 13 but for TMC−PC.

If $\langle V\rangle_1^{\mathrm{LV}}$ and $\sigma_v^{\mathrm{LV}}$ are evaluated from PLS, the quantity $V_0$ can be calculated by eq 22. After sorption of $N_g$ gas molecules per unit of polymer volume, the average volume changes to

$$\langle V\rangle_2^{\mathrm{LV}} = \frac{2V_0(V_0 - \sigma_{\mathrm{v}}^{\mathrm{LV}})\sqrt{\dfrac{2N_{\mathrm{g}}}{N_0}} - 2V_0^{\,2}\dfrac{N_{\mathrm{g}}}{N_0} + \sigma_{\mathrm{v}}^{\mathrm{LV}}\left(2V_0 - \dfrac{4}{3}\sigma_{\mathrm{v}}^{\mathrm{LV}}\right)}{V_0\sqrt{\dfrac{2N_{\mathrm{g}}}{N_0}} + \sigma_{\mathrm{v}}^{\mathrm{LV}}} \qquad (23)$$

with $N_0$ remaining as the only unknown parameter which is used as a fitting parameter to get agreement with experimental data as shown in Figures 13 and 14. Corresponding values of $N_0$ are compiled in Table 2.

Applying the LV model, the average volume $V_0$ differs from the measured volume $\langle V\rangle_1$ and has to be recalculated from the available model parameters. For the rectangular model $V_0$ is given by eq 19a with $V_{\min} = 0$ and for the triangular model by eq 22.

The resulting $N_0$ values for the AV model are found to be rather insensitive to the form of $n(V)$. Applying the LV model to the different distributions leads to considerably larger values for $N_0$. For the triangular distribution the values even exceed the packing density of gas molecules in the liquid state by more than 1 order of magnitude.

The average hole volume $V_0$ and the hole density $N_0$ can be used to calculate the free-volume fraction $f$ via the trivial equation

$$f = N_0 V_0 \qquad (24)$$

For the various cases discussed in this paper $f$ values are compiled in Table 2. The fractional volume is especially large or even above 100% for the LV cases as a consequence of the large $N_0$ values. But even for the AV cases, $f$ is above 10%, a value which is supported by interpreting the change of the thermal expansion coefficient at the glass transition temperature.[26,33,34] The latter discrepancy may be due to $V_0$ values from PLS being too large. If we use data obtained from the partial molar volume of $CO_2$ and other gases[6] being about three times smaller than PLS data (cf. Table 1) reasonable values for $f$ are obtained. It is also difficult to comprehend that penetrant molecules such as $CO_2$, Ar, and $N_2$ with a molecular volume being much smaller than the PLS values for the hole volume $V_0$ cause a considerable volume expansion of polymers.[6] Despite the doubt about the reliability of $V$ values calculated from eq 15, it should be mentioned again that the evaluation in this study is based on ratios of $V$ and $\sigma$ values. Therefore, any systematic error between calculated and true values which can be expressed by a constant factor has no effect on the value of $N_0$. This proportionality is supported by the proportionality between PLS and sorption/dilatation data (cf. Table 1).

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