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Positron Annihilation Lifetime Study of High and Low Free Volume Glassy Polymers: Effects of Free Volume Sizes on the Permeability and Permselectivity

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ABSTRACT: Free volume in a big group of glassy polymers distinguished by a wide range of gas permeability (P in the range $1-10^4$ Barrer) was studied using the positron annihilation lifetime (PAL) method. To take into account an additional channel of decay of positronium (Ps), caused by the reaction with sorbed O_2, measurements were performed both under ambient conditions and under a nitrogen atmosphere. The finite-term and continuous lifetime analyses (PATFIT and CONTIN programs) were used for the treatment of the positron annihilation decay curves. It was shown that better statistical fitting parameters can be obtained for four component PAL spectra of a vast majority of the glassy polymers studied. The presence of two Ps lifetimes ($\tau_3 = 1.7-3.3$ ns and $\tau_4 = 2.7-10.9$ ns) indicates that size distribution of free volume elements (FVE) in glassy polymers is typically bimodal. The presence of smaller and larger FVE ($R_3 = 2.5-3.5$ Å, $R_4 = 3.5-7.0$ Å) was proved by PATFIT analysis of the data. Continuous analysis clearly indicated two broad peaks, especially for more permeable polymers. As permeability and free volume of the polymers decrease, the two peaks start to approach and overlap each other, ending with one broader or asymmetric peak for the less permeable polymers. In the presence of oxygen both lifetimes τ_3 and τ_4 are shifted to shorter values; this shift is more pronounced for the polymers with larger radii R_4 of FVE. A novel correlation of diffusion selectivity of glassy polymers with the size of FVE is demonstrated.

Introduction

Positron annihilation lifetime (PAL) spectroscopy can be considered as the most direct probe method to estimate free volume in polymers.[1−3] Traditionally, PAL spectra of amorphous (one phase) polymers have been analyzed in terms of three exponential components. The longest lifetime component τ_3 (in the range 2−3 ns), characteristic for the annihilation in the bound state e^+-e^- (a hydrogen-like orthopositronium atom, o-Ps), is indicative of free volume in a material.[1,4] A square-box approximation for the Ps atom in free volume elements (FVE) or microcavities in polymers has been proposed to relate τ_3 and the radius R_3 of FVE.[5−9] Qualitatively, the higher τ_3 values, the larger are the radii of FVE. Typical radii of FVE in amorphous polymers should be in the range 2.5−4 Å.

However, it was shown[10] that, at least for one amorphous glassy polymer, poly(trimethylsilyl propyne) (PTMSP), which is known for having the largest gas permeability, diffusion, and solubility coefficients among all polymeric materials,[11] a four-component spectrum gave a far better description of the data. Later, the unusual behavior of this polymer was confirmed by other authors.[12,13] In this case, the difference between the two positronium components was more than 8 ns, and the splitting could not be explained, e.g., by the suggestion[14] of a nonexponential character of the PAL spectra. These results imply two features of free volume in PTMSP: (1) its FVE have much larger sizes (the radii of FVE are in the range 6−8 Å) than those in conventional polymers; (2) the size distribution of free volume in PTMSP is bimodal, in contrast to conventional polymers, where it is supposed to be unimodal. Interestingly, similar four-component PAL spectra have been observed for another high permeability group of glassy materials—amorphous copolymers of perfluorodioxole and tetrafluoroethylene (amorphous Teflons AF of DuPont Co.) with an entirely different chemical structure.[15−18] It should be also remembered that four-component PAL spectra have been reported as well for highly porous inorganic sorbents[19,20] and porous polymeric ultrafiltration membranes.[21] This suggested some structural similarities between porous sorbents and high free volume materials such as PTMSP and amorphous AF Teflons. Indeed, some observations on mixed gas permeation at least in PTMSP revealed similar regularities of gas transport in this polymer and in activated carbons:[22] selectivity of mixed gas permeation was found to be larger than ideal separation factors, a behavior rather unusual for conventional polymers.

It should be noted that four-component PAL spectra can be anticipated for semicrystalline polymers such as polyolefins that are usually two-phase materials. In these materials, two positronium components of PAL spectra might characterize free volumes in crystallites and more loosely packed amorphous phases. Though in numerous PAL investigations of polyethylene and other semicrystalline polymers three component PAL spectra have been reported (see, e.g., refs 23−25), a recent detailed investigation of semicrystalline polyethylene and poly(tetrafluoroethylene) (PTFE) showed that two long-lived components (τ_3 and τ_4) can be identified and attributed to o-Ps annihilation in crystalline regions

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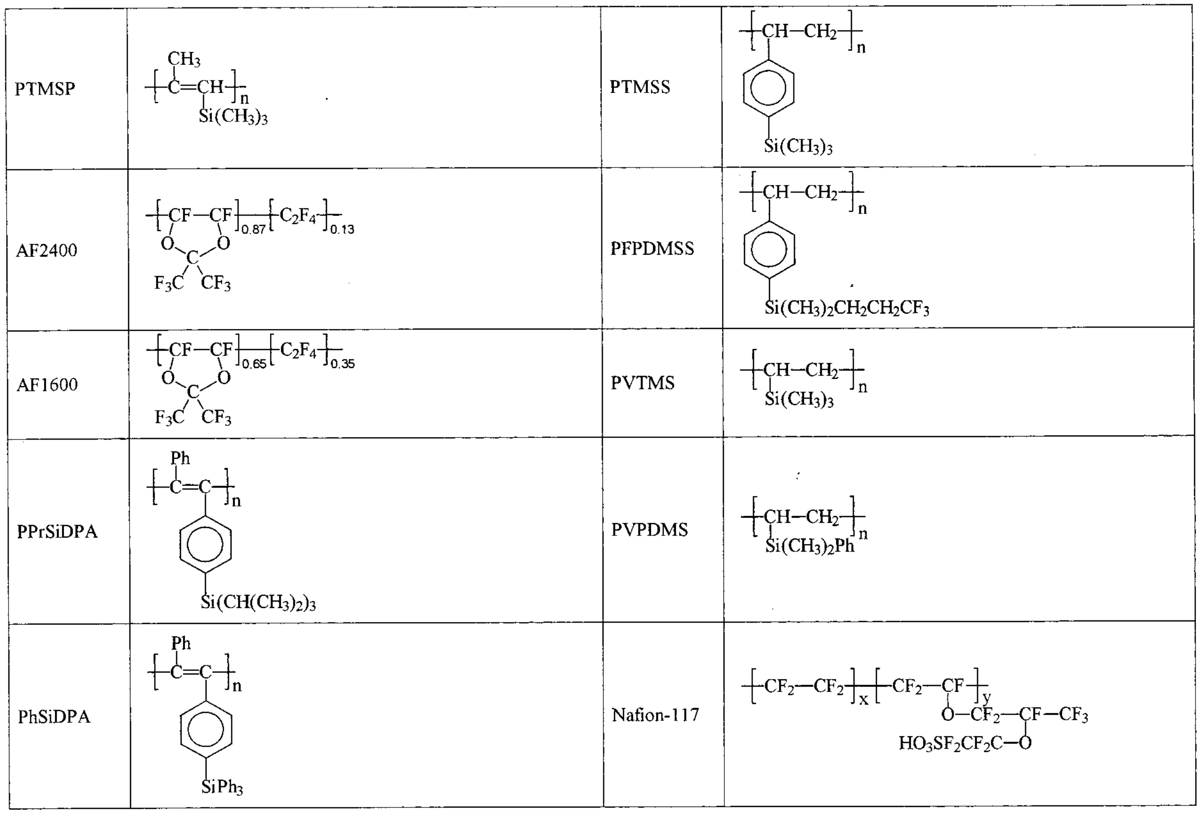

Figure 1. Chemical structures of the studied polymers.

(interstitial cavities) and in holes in the amorphous phase, respectively.[26] Whatever may be the real microstructure of free volume in semicrystalline polymers, this question is beyond the scope of the present paper, which deals with PAL probing of amorphous glassy polymers.

Investigation of free volume in highly porous inorganic sorbents using the PAL method can be complicated because of an additional channel for the disappearance of o-Ps due to its reaction with molecular oxygen sorbed on pore walls.[27] Consolati et al.[13] demonstrated the same quenching effect for highly permeable PTMSP, where the longest lifetime is much larger if measured in the absence of oxygen (in a nitrogen atmosphere or in a vacuum). No similar observation of this phenomenon has been reported so far for other polymers.

In most positron annihilation studies of polymers, the primary experimental data, the decay curves, were decomposed into several components (three or four) using PATFIT or similar computer programs. In this approach, the annihilation lifetime distribution is represented in a discrete manner, i.e., in terms of several exponents, each one being characterized by its decay rate $\lambda_i = 1/\tau_i$ (in ns^{-1}) and intensity I_i (%). Inverse Laplace transformation of PAL spectra (CONTIN)[28-30] and maximum entropy lifetime analysis (MELT)[31] have been proposed for obtaining a continuous distribution of positronium lifetimes. In this way, a continuous lifetime and free volume size distributions can be achieved. However, CONTIN analysis of PAL distributions was applied mainly to polymers whose PAL spectrum consists of three components; the longest lifetime τ_3 is in the range 2−3 ns, with corresponding radii of FVE being about 2−4 Å. Later, the continuous lifetime distribution was reported by us for PTMSP in contact with air.[21]

Thus, several questions can be posed regarding the investigation of free volume in polymers using positron annihilation lifetime spectroscopy.

1. How general is the four-component description of PAL distributions in polymers and the resulting bimodal size distribution of FVE? Is it a feature of free volume structure of such unusual material as PTMSP, or can it be observed in other polymers with high or, perhaps, not so high gas permeability?

2. Is there any difference in the resolving power of the PATFIT and CONTIN (or MELT) analysis of bimodal distributions of Ps lifetimes?

3. To what extent does the effect of sorbed O_2 during PAL measurements influence the sizes and size distributions of FVE found in different polymers? If these effects are strong, the sizes of free volume elements in polymers should be determined under conditions where undesirable decay processes induced by oxygen are absent.

The aim of the present study was to answer these and some other related questions. To pursue this goal, PAL spectra were measured in several silicon- and fluorine-containing polymers. The selected set of polymers was distinguished by a wide range of variation of gas permeability and, supposedly, free volume. Their permeability coefficients vary in the range from 10^4 to 1 Barrer (1 Barrer = 10^{-10} cm^3(STP)·cm/cm^2·s·cmHg). The fractional free volume (FFV) evaluated using the increments in the van der Waals volume[32] was in the range of about 10−30%.

Experimental Section

Polymers. A set of the glassy polymers with widely varying structures (Figure 1) was selected for the study. First, several

Table 1. Physical Properties of the Polymers

polymer	ρ, g/cm^3	FFV, %	T_g, °C	$P(O_2)$, Barrer	$[O_2] \times 10^{-18}$, cm^{-3}
PTMSP	0.75	0.34	>280	7700	7−10
AF2400	1.74	0.32	240	1140	5.0
AF1600	1.8	0.28	160	170	4.1
PPrSiDPA	1.04	0.12	>270	227	14
PPhSiDPA	1.21	0.15	>430	12	4.2
PTMSS	0.965	0.191	135	56	1.6
PFPDMSS	1.127	0.186	62	38	0.84
PVTMS	0.86	0.195	150	44	2.4
PVPDMS	1.043	0.134	120	2.5	0.43
Nafion-117	2.02		120	1.1	1.0

high free volume polymers, namely PTMSP and amorphous Teflons AF2400 and AF1600, were reinvestigated. To make a comparison with the two latter materials, another perfluorinated polymer, namely Nafion-117, was also studied. It is known as a low gas permeable polymer.[33] Two novel polyacetylenes were also studied: poly(1-phenyl-2-[*p*-triisopropylsilylphenyl]acetylene) (PPrSiDPA) and poly(1-phenyl-2-[*p*-triphenylsilylphenyl]acetylene) (PPhSiDPA) were kindly provided by Prof. T. Masuda. In addition, several vinylic Si-containing glassy polymers were studied as well.

PTMSP was prepared by polymerization in the presence of the catalytic system $TaCl_5$/triisobutylaluminum. Freshly cast PTMSP films were used. Commercial samples of amorphous Teflons AF2400 and AF1600 with the content of perfluorodioxole component of 87 and 65 mol %, respectively, were purchased from DuPont Co. Their other properties had been described in detail elsewhere.[17] Commercial films of Nafion-117 studied were in H-form. Para-substituted derivatives of polystyrene, poly(trimethylsilyl styrene) (PTMSS) and poly(trifluoropropyldimethylsilyl styrene) (PFPDMSS), were prepared by radical polymerization in the presence of azobis(isobutyronitrile). Finally, poly(vinyltrimethylsilane) (PVTMS) and poly(vinylphenyldimethylsilane) (PVPDMS) were synthesized using anionic polymerization. These polymers as well as the derivatives of polystyrene were kindly provided by Dr. V. Khotimskii. Some physical properties of the polymers investigated are given in Table 1.

Measurements. The PAL spectra were measured at room temperature with a conventional Ortec "fast-fast" lifetime spectrometer. The time resolution was 230 ps (fwhm). We used a nickel-foil-supported [^{22}Na] sodium chloride radioactive source of positrons. The contribution from the annihilation in the source material, a background, and instrumental resolution were taken into account in the PATFIT[34] and CONTIN[28−30] computing programs. Each final PAL spectrum was obtained by summing up the results of several cycles of measurements (10^6 counts in each cycle). The integral statistics for each spectrum was equal to (1.5−2.0) × 10^7 coincidences, and namely this spectrum was used for CONTIN analysis. The CONTIN program determined the "chosen solution", corresponding to regularization parameter $\alpha \sim 10^{-4}$. This is a solution having a Fisher F-probability closest to 0.5. Application of the PATFIT program to the results of one cycle gave satisfactory variance of the fit ($\varphi \approx 1.05$) provided the number of the lifetime components (three or four) was chosen correctly. Thus, in most cases the results of one cycle of measurement could be used to discriminate between the three or four components of the PAL spectrum: underestimation of the number of lifetime components (three instead of four) made the fitting parameter much worse ($\varphi \gg 1$); on the other hand, overestimation of these numbers resulted in increased uncertainties of the lifetime components. The latter case will be illustrated using Nafion-117 as an example. To perform measurements in an inert (nitrogen) atmosphere, the samples were kept in a stream of dry nitrogen in a polyethylene hose.

Results

Mono- or Bimodal Size Distribution of Free Volume. Table 2 presents positronium components of the PAL spectra (lifetimes τ_3 and τ_4 and intensities I_3 and I_4) of the polymers studied. The data presented in this table were obtained in measurements performed in air and after treatment of the data using PATFIT program. The lifetimes and intensities of two short living components that are not shown in this table had common values for polymers: the lifetimes τ_1 and τ_2 were close to 0.2 and 0.4 ns, respectively.

Table 2. Lifetime Distribution of Positron Annihilation: Lifetimes τ_i, ns, and Intensities I_i,%, Obtained in Measurements under Ambient Conditions

polymer	τ_3	τ_4	I_3	I_4
PTMSP	1.87 ± 0.29	5.88 ± 0.06	5.40 ± 0.46	33.06 ± 0.67
AF2400	1.26 ± 0.11	5.75 ± 0.03	3.61 ± 0.46	13.74 ± 0.09
AF1600	1.033 (f)[a]	4.92 ± 0.03	4.14 ± 0.53	13.41 ± 0.11
PPrSiDPA	2.65 ± 0.05	7.21 ± 0.06	16.68 ± 0.30	25.76 ± 0.39
PPhSiDPA	2.01 ± 0.08	3.22 ± 0.10	23.13 ± 2.20	15.60 ± 2.47
PTMSS	1.80 ± 0.11	3.14 ± 0.03	10.16 ± 1.14	28.57 ± 1.34
PFPDMSS	1.73 ± 0.11	3.11 ± 0.03	8.44 ± 0.83	26.26 ± 1.03
PVTMS	2.25 ± 0.10	4.06 ± 0.05	14.14 ± 1.15	25.46 ± 1.32
PVPDMS	1.78 ± 0.08	2.72 ± 0.05	16.66 ± 2.17	20.76 ± 2.37
Nafion-117	3.23 ± 0.03		7.07 ± 0.08	

[a] Fixed value.

There is no doubt that for highly gas permeable polymers (PTMSP, AF2400, AF1600), a much better description can be obtained using four-component PAL distribution, in agreement with previous observations.[10,12,13,17] In most permeable polymers (PTMSP and AF2400), the following inequality is obeyed: $I_4 \gg I_3$. As intensities I_3 and I_4 are often considered as a rough measure of the concentration of FVE, it can be interpreted as an indication that the concentration of smaller "holes" in the microstructure of these polymers is essentially reduced in comparison with larger ones. Hence, existence of the fourth component is of principal importance for gas permeation. We will discuss later, however, a more refined way to evaluate the concentrations of FVE having different sizes.

Quite interesting results were obtained for two polyacetylenes: PPrSiDPA and PPhSiDPA. Despite similar chemical structure, their PAL spectra were fairly different. For PPrSiDPA, the PAL spectrum is similar to that of PTMSP: $\tau_4 = 7.21 \pm 0.06$ ns is even larger while $I_4 = 25.76 \pm 0.39$ is comparable with the corresponding parameters of the PTMSP spectrum. Note also that the intensity of the third component obtained for PPrSiDPA is significantly larger than that of PTMSP. On the other hand, PPhSiDPA, which differs from the latter polymer by only replacement of isopropyl by phenyl groups, reveals the spectra with much shorter values of the longest lifetimes independent of the selection of three or four components in the spectrum. This subject will be discussed later in more length (see Table 3). It should aslo be noted that PPhSiDPA represents relatively low-permeable material in the set of polymers considered: its permeability coefficient $P(O_2) = 12$ Barrer, whereas this parameter is equal to 227 Barrer for PPrSiDPA (Table 1). A quite unusual feature of PPrSiDPA is that one deals here for the first time with the situation where free volumes estimated via positron annihilation technique and using densities and the increments of van der Waals volume[32] are in dramatic contradiction. It is seen from Table 1 that the fractional free volume of PPrSiDPA is the smallest whereas its lifetime τ_4 is the longest; therefore, the free volume that can be calculated on the basis of it should be very large. In addition, the FFV found is in contrast to the fairly large permeability of this polymer. So far, PAL parameters and the values

Table 3. Comparison of PAL Spectra (τ_i, ns, and I_i, %) of Nafion-117 with Different Components N_i (Measurements under Ambient Atmosphere)

N	τ_1	I_1	τ_2	I_2	τ_3	I_3	τ_4	I_4
4	0.166 ± 0.025	13.16 ± 3.28	0.399 ± 0.012	79.0 ± 2.40	2.44 ± 0.52	4.80 ± 2.37	4.20 ± 0.89	2.95 ± 2.60
3	0.221 ± 0.015	24.61 ± 3.69	0.432 ± 0.008	65.10 ± 3.63	3.23 ± 0.03	7.07 ± 0.08		

Table 4. Lifetime Distribution of Positron Annihilation: Lifetimes τ_i, ns, and Intensities I_i,% Obtained in Measurements under Nitrogen Atmosphere

polymer	τ_3	τ_4	I_3	I_4
PTMSP	2.68 ± 0.45	10.9 ± 0.22	4.37 ± 0.48	33.8 ± 0.63
AF2400	1.82 ± 0.33	8.04 ± 0.13	2.60 ± 0.30	13.74 ± 0.25
AF1600	1.06 (f)[a]	5.29 ± 0.05	2.44 ± 0.89	14.59 ± 0.16
PPrSiDPA	3.30 ± 0.07	9.38 ± 0.10	16.45 ± 0.40	28.16 ± 0.46
PPhSiDPA	2.07 ± 0.07	3.27 ± 0.09	24.07 ± 2.06	14.94 ± 2.29
PTMSS	1.85 ± 0.20	3.16 ± 0.04	8.11 ± 1.73	31.31 ± 2.01
PFPDMSS	1.73 ± 0.11	3.11 ± 0.03	8.44 ± 0.83	26.26 ± 1.03
PVTMS	2.41 ± 0.13	4.20 ± 0.07	15.44 ± 1.77	27.69 ± 1.96
PVPDMS	1.78 ± 0.16	2.69 ± 0.08	14.83 ± 3.79	21.50 ± 4.10
Nafion-117	3.15 ± 0.04		7.08 ± 0.13	

[a] Fixed value.

of FFV for other high permeability polymers showed a reasonable correlation (see Table 1).

The spectra of both substituted polystyrenes are rather similar: the τ_3 values nearly coincide, and the longer lifetime τ_4 is somewhat larger for more permeable PTMSS. But, nevertheless, the τ_4 values are in the range of longer lifetimes reported for conventional glassy polymers.[4] Therefore, one can assume that bimodal size distribution of free volume elements is characteristic for a much wider range of glassy polymers than has been accepted on the basis of earlier measurements on conventional polymers such as PMMA, PC, etc.

An appropriate selection of the number of the components in the PAL spectra is of crucial importance for this work. In the Experimental Section, it has been explained that a satisfactory variance of the fit $\varphi = 1-1.05$ was considered as a criterion for the correct choice at the statistics of about 10^6 counts in a cycle. Table 3 further illustrates such a selection. In the case of Nafion-117, a transition from three to four components is accompanied by a significant increase in the errors of lifetimes and especially intensities. Thus, the I_4 value is estimated in this case with nearly 100% error. Hence, for Nafion-117, a three component lifetime distribution corresponds to a better description of the data.

A similar conclusion was reached recently by other researchers[35,36] who worked with Nafion in H^+ and salt forms. Different τ_3 values were obtained for H^+ form of Nafion-117 depending on a pretreatment: 2.79 ns for the sample swollen in water and 3.06 ns for the one swollen in ethanol. The latter value coincides with the one obtained in the present work, where the samples were used in the dry state, i.e., in equilibrium with atmospheric moisture, which is always less than 100%. The difference between the τ_3 values in these and the present work can be ascribed to a lower water content of the samples studied by us: Sodaye et al.[36] showed that τ_3 increased when the water content decreased.

The situation is less obvious for another polymer considered in Table 2, for PPhSiDPA. However, a strong increase in the uncertainties of I_3 and I_4 is also observed in the case of the four-component analysis. The reason for giving preference to four-component PATFIT analysis for PPhSiDPA and vinylic type polymers is the satisfactory fit (on the level of 1.02−1.05) in these cases. A comparison with the three-component model indicates that fitting becomes at least 20% worse, and the solution is unacceptable.

In conclusion, it appears to be remarkable that for the whole collection of polymers with permeability varying within nearly 4 orders of magnitude, one can observe a continuous sequence of the longest lifetime and a transition from clearly bimodal to obviously unimodal Ps lifetime distributions (Tables 1 and 2). This result is consistent with a view that in glassy polymers a continuous transition takes place from materials such as PTMSP, in which extra large FVE coexist with FVE having “normal” sizes (bimodal size distribution of FVE), to materials having larger and smaller free volume elements that are comparable and cannot be distinguished by PAL spectroscopy. For the latter case, monomodal size distribution can be observed, e.g., in Nafion-117 and conventional glassy polymers such as poly(methyl methacrylate). Some further confirmation of this viewpoint will be presented later when considering the results of CONTIN analysis.

Effects of Oxygen. It is known[27,37,38,13] that in porous inorganic media and polymers, oxygen is able to quench o-Ps, thus reducing the lifetimes. Several reactions can occur:

$$\text{o-Ps} + O_2 \rightarrow [\text{Ps-}O_2]^* \tag{1}$$

$$[\text{Ps-}O_2]^* \rightarrow [\text{Ps-}O_2] \rightarrow O_2 + 2\gamma \tag{2}$$

$$[\text{Ps-}O_2]^* \rightarrow \text{p-Ps} + O_2 \tag{3}$$

They can be catalyzed on the walls of pores and microcavities thus reducing lifetimes τ_4. Thus, a replacement, during measurements, of sorbed air by an inert gas, for example nitrogen, allows one to eliminate this effect and obtain more realistic lifetimes related to the size of FVE.

Table 4 gives PAL spectra obtained in the atmosphere of nitrogen. It is seen that for high gas permeable polymers, the values of τ_4 measured in the absence of oxygen are noticeably larger than those measured in air (Table 2). The values obtained for PTMSP in an inert atmosphere are consistent with the results reported by Consolati et al.[13,39] For polymers with lower permebility, such as Nafion-117, the appearance of sorbed oxygen does not influence the lifetimes. Therefore, one can assume that conditions for reactions 1−3 are not favorable in smaller FVE existing in these polymers or, more probably, diffusion limitations for positronium and/or oxygen make these reactions less important channel for o-Ps decay.

A feature of the present work is that this effect was demonstrated for a wide set of polymers with various structures and properties. It is also worth noting that the larger τ_4 measured in air is, the more significant is an increase in this lifetime and in τ_3 too, in the presence of an inert atmosphere. Thus, in PTMSP, a shift from 5.88 to 10.9 ns is observed whereas for AF1600 and PVTMS only modest changes could be noted: τ_4 life-

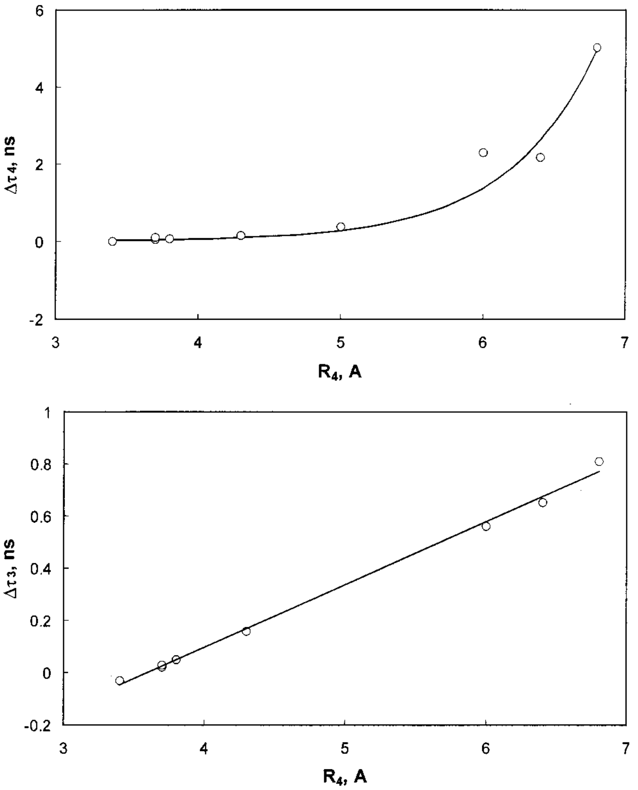

Figure 2. Effects of the radius of larger FVE on the lifetimes shifts due to oxygen quenching.

times are changed from 4.92 to 5.29 ns and from 4.06 to 4.20 ns, respectively. As Figure 2 shows, the shifts in lifetimes $\Delta\tau_4 = \tau_4(N_2) - \tau_4(\text{air})$ and $\Delta\tau_3 = \tau_3(N_2) - \tau_3(\text{air})$ correlate with the radii R_4 (Å) of larger FVE (the details of their calculation will be considered later). It should be emphasized that a replacement of air by nitrogen did not result in strong or systematic changes in the intensities I_3 and I_4.

A practical implication of all these observations is that measurements of PAL spectra of high permeability glassy polymers have to be performed in inert atmosphere in order to obtain the correct values of τ_4 lifetimes and the sizes of FVE deduced therefrom. On the other hand, despite this underestimation of free volume radii, their concentrations, if considered to be related to I_4,[40] are approximately correct, when based on the results of measurements in air atmosphere. A more accurate treatment[4] indicates that common PAL measurements in ambient atmosphere should result in some overestimation of the concentration of FVE, since the trapping rate is dependent on their radii. On the other hand, for conventional glassy polymers, whose PAL spectra contain the longest lifetime in the range 2−3.5 ns, a replacement of air by an inert atmosphere during the measurements does not produce noticeable changes in the PAL spectra.

A comparison of Tables 2 and 4 shows that a replacement of air by nitrogen during measurements results in an increase in τ_3 values too. This effect of variations of positronium lifetime τ_3 should have the same nature (Ps chemical reaction with sorbed oxygen) as that for τ_4. It has been discussed in more detail elsewhere.[18] Similar effects for τ_3 in PTMSP have been reported by Consolati et al.[13] However, the interpretation of this effect is complicated because the presence of sorbed O_2 shortens the lifetimes τ_3 being in the range 2−3 ns of the more permeable polymers with larger total free volume, whereas similar τ_3 values measured for lower permeable polymers are not sensitive to the presence of sorbed O_2 (see Tables 2 and 4).

Table 5. Sizes of Free Volume Elements and Computed Fractional Free Volume

polymer	R_3, Å	R_4, Å	v_{f3}, Å^3	v_{f4}, Å^3	$C(v_{f3}I_3 + v_{f4}I_4)$
PTMSP	3.41 ± 0.35	6.81 ± 0.06	166 ± 50	1323 ± 35	0.80
AF2400	2.68 ± 0.35	5.95 ± 0.04	81 ± 32	882 ± 18	0.22
AF1600		4.89 ± 0.03		490 ± 9	0.13
PPrSiDPA	3.83 ± 0.05	6.38 ± 0.03	235 ± 10	1088 ± 15	0.62
PPhSiDPA	2.87 ± 0.07	3.78 ± 0.06	99 ± 7	226 ± 10	0.105
PTMSS	2.71 ± 0.20	3.74 ± 0.02	83 ± 21	219 ± 4	0.135
PFPDMSS	2.59 ± 0.11	3.71 ± 0.02	73 ± 9	214 ± 3	0.11
PVTMS	3.21 ± 0.10	4.35 ± 0.04	138 ± 13	345 ± 10	0.21
PVPDMS	2.64 ± 0.18	3.42 ± 0.06	77 ± 16	168 ± 9	0.085
Nafion-117	3.74 ± 0.03	-	219 ± 5	-	0.028

One can assume that it can be related to diffusional limitations of the reactions 1−3. Since the concentrations of sorbed oxygen in the glassy polymers under study (Table 1) are much lower than the concentrations of FVE (about $10^{19}-10^{20}$ cm^{-3} according to our estimates), many free volume elements are free from oxygen. Therefore, the positronium atom has to sample several FVE until it meets and interacts with an oxygen molecule. This rate of mutual diffusion should depend on the environment in the vicinity of free volume elements and on spatial distribution of FVE. Recently it has been shown[18] that this distribution of FVE in high free volume glassy plymers is not uniform. At least for PTMSP, the scale of this nonuniformity corresponds to 150 Å or somewhat more. This result is consistent with earlier study of this polymers,[41,42] which revealed domainlike structures of a size about 100 Å. The existence of such a nonuniform microstructure can explain the fast physical aging of PTMSP at ambient temperature, much lower than its glass transition temperature. This aging is manifested in a strong reduction of gas permeability and increases in density.[11] So at present, we can only suppose that this nonuniformity and, perhaps, interphase boundaries make easier, as compared to low free volume polymers, the penetration of oxygen into smaller FVE.

Since measurements of the PAL distribution in a nitrogen atmosphere gave corrected lifetimes τ_3 and τ_4, it is possible now to calculate the radii R_i of smaller and larger FVE (in Å) and corresponding volumes $V_{fi} = ({}^4/_3)\pi R_i^3$ (in Å^3). The mean radii of FVE can be found by the following semiempirical equation[5−7]

$$\tau_i = {}^1/_2[1 - (R_i/R_o) + ({}^1/_2\pi)\sin(2\pi R_i/R_o)]^{-1} \quad (4)$$

where $\tau_i = \tau_3$ or τ_4 are o-Ps lifetimes and $R_i = R_3$ or R_4 are the radii of FVE elements, expressed in ns and Å, respectively; $R_o = R_i + \Delta R$, where $\Delta R = 1.66$ Å is the fitted empirical electron layer thickness. The values of R_3, R_4, v_{f3}, and v_{f4} in the glassy polymers studied are presented in Table 5.

Continuous Lifetime and Size Distributions of FVE. Contrary to the PATFIT treatment of positron annihilation decay curves, where the number of components in a PAL spectrum is established arbitrarily (and then the variance of the fit is used as a criterion of the appropriate selection of the number of components), the CONTIN program selects the number of components automatically; therefore, the results of its application might be more conclusive.

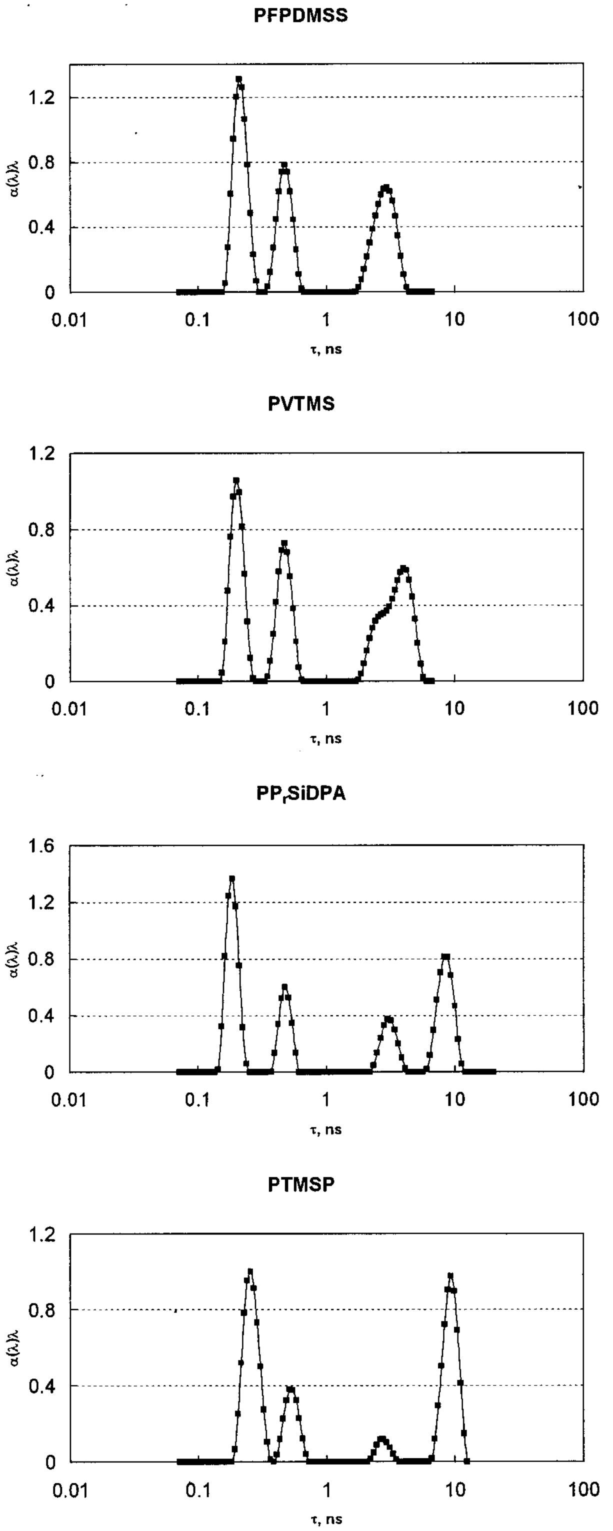

Figure 3. CONTIN PAL spectra (lifetimes τ in ns) of the glassy polymers with increasing free volume.

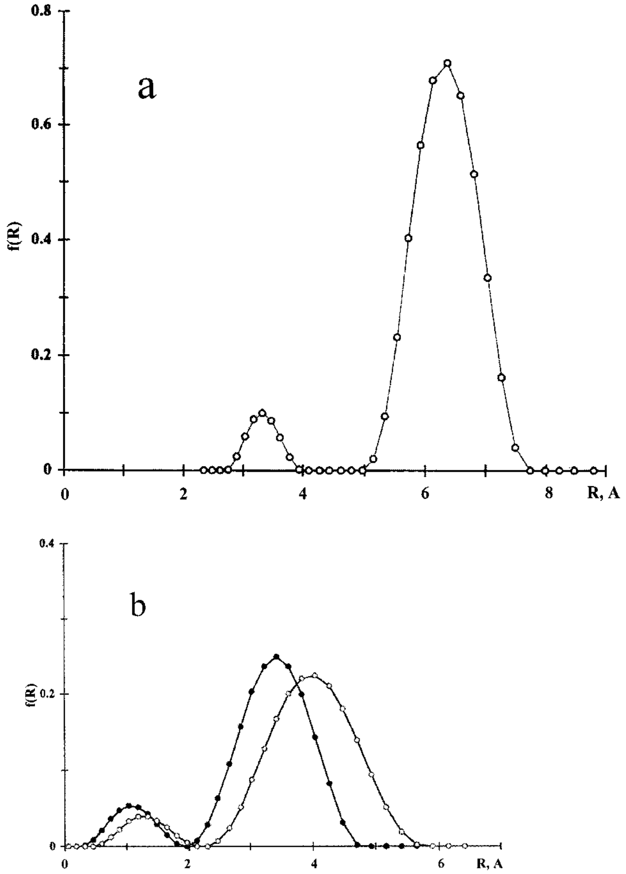

Figure 4. Size distributions of free volume elements in PTMSP (a) and AF2400 (b): open points in nitrogen; filled points in air.

In this study, four-component PAL spectra of high permeability polymers were also confirmed by CONTIN analysis. This result was achieved by treatment of the data obtained both in ambient atmosphere and in nitrogen. Figure 3 gives an example of evolution of continuous PAL spectra obtained for polymers with increasing gas permeability and free volume (measurements in nitrogen atmosphere). For the most permeable ones among the group of polymers considered, PTMSP and PPrSiDPA, two distinct o-Ps peaks of lifetimes τ_3 and τ_4 are observed. Similar spectra were observed for AF copolymers. Then, as permeability and free volume get smaller, the peaks approach each other: it is seen that for PVTMS, which can be considred as a boundary between high free volume and conventional glassy polymers, these two peaks have nearly coincided and the smaller one is shown as a shoulder. With a further decrease in free volume, one broad peak is displayed in a continuous lifetime distribution, as in the case of PFPDMSS. Note that this broad peak is asymmetric: its slope at smaller times is less steep than the other slope. This non-Gaussian lifetime distribution might indicate that a complex size distribution exists in such polymers. Note that a symmetrical (Gaussian) peak has been obtained using CONTIN analysis of the PAL data for such a low free volume, conventional glassy polymer as poly(methyl methacrylate).[42]

It can also be noted that the maxima of the peaks in the CONTIN lifetime distributions agree well with the results of the PATFIT analysis.

Using eq 4, the PAL spectra were converted into size distributions of FVE in the studied glassy polymers. Figure 4a presents such a distribution for PTMSP obtained due to measurements performed in nitrogen atmosphere. It is obvious from this figure that holes with radii of 6−7 Å prevail. A comparison with previous CONTIN study[15] of this polymer,where the measurements were performed in air atmosphere, shows that the real dimensions of FVE in PTMSP are significantly larger than could be assumed. The same effect is further illustrated in Figure 4b for amorphous Teflon AF2400, where the FVE size distributions shown are based on measurements in air and in nitrogen. The figure well illustrates the sensitivity of the CONTIN lifetime distribution to the atmosphere during measurement in the case of high free volume materials. It can be seen that the calculation of size distributions based on measurement in the ambient atmosphere for such materials gives underestimated values of free volume sizes.

Thus, on the basis of the PAL study of a big group of glassy polymers in air and in nitrogen and after treatment of positron annihilation decay curves using PATFIT and CONTIN programs, one can distinguish three groups of polymers with characteristic positronium lifetime distributions.

(1) The first is high free volume materials including some polyacetylenes (PTMSP, PPrSiDPA) and amorphous Teflons. The characteristic features are as follows: two positronium lifetime components are distinctly resolved by PATFIT and CONTIN programs; replacement of air by nitrogen is accompanied by marked changes in lifetimes and lifetime distributions.

(2) The second is conventional (low free volume) glassy polymers. In the collection of the polymers considered, only Nafion-117 undoubtedly belongs to this group. Their PAL spectrum consists of a single o-Ps lifetime component. CONTIN lifetimes distribution reveals a single peak. No effects can be noted after replacement of air by nitrogen during measurements. Numerous PAL studies of conventional glassy polymers such as poly(methyl methacrylate), polycarbonate, etc. exhibit the same behavior; however, the effects of oxygen have not been documented so far in sufficient detail.

(3) Last is the intermediate group. Among the polymers considered in this work, PPhSiDPA and vinylic polymers belong to this group. They also reveal a four-component PAL spectrum (in PATFIT analysis); however, the difference between monomodal and bimodal PAL distributions are only marginal. The presence of oxygen hardly affects the PAL spectra: the changes of lifetimes in some cases are close to the experimental errors.

All these changes in positron annihilation behavior occur steadily and are accompanied by variations in gas permeability, diffusivity, solubility, and, in most cases, changes of FFV calculated via specific volume.

Free Volume in Glassy Polymers. Assuming that FVE have the geometry of spheres with the radii R_3 and R_4, their volumes $v_{f3} = 4\pi(R_3)^3/3$ and $v_{f4} = 4\pi(R_4)^3/3$ can be found based on the observed τ_3 and τ_4 values. These volumes are presented in Table 5. It is seen that high gas permeability materials such as PTMSP and other polymers presented in the upper part of the table are distinguished by the volumes of microcavities larger by an order of magnitude than those of conventional glassy polymers having distinct three component PAL spectrum and τ_3 close to 2−3 ns. It is also obvious that high gas permeability, diffusivity, and solubility characteristic of the former are caused by larger sizes of FVE of these polymers. It is more difficult to find a quantitative relationship between the fractional free volume calculated on the basis of PAL data and the transport parameters of the polymers.

In principle, FFV or V_{fP} can be defined as the sum

$$\mathrm{FFV} = \sum v_{fi} N_i \tag{5}$$

so if v_{fi} values are known, the problem is how to find N_i, the concentration of the holes of the ith sort. It has been assumed that intensities I_3 and I_4 can be used as the measures of the concentrations of free volume of different size. Indeed, an empirical equation with adjustable (scaling) parameter C (Å^{-3}) has been proposed and widely used[43−51] for calculating the fractional free volume in rubbery and conventional glassy polymers that have three component PAL spectrum

$$V_{fP} = C v_{f3} I_3 \tag{6}$$

where v_{f3} (Å^3) is the volume of spherical FFV calculated using the radius of eq 4 found from τ_3, I_3 is the intensity of the single Ps component of the PAL spectrum, and C is the empirically determined constant found by comparison of the PAL data with independent free volume values estimated via bulk volume−temperature data.[44,45,52]

Good correlations of FFV values found in such a way with sorption, permeation, and mechanical properties of polymers have been reported.[47,49,50] Although the adjustable coefficient C may range from 0.001 to 0.002 for conventional glassy polymers, usually the value $C = 0.0018$ has been accepted.[48,50] It is not clear, however, if this constant is temperature independent and keeps this narrow range of variation for polymers with larger free volume and, hence, a four-component PAL spectrum.

Bearing in mind these circumstances, we attempted to use a similar equation with the same scaling constant C for calculating FFV in the polymers with four component PAL spectrum:

$$V_{fP} = C(v_{f3} I_3 + v_{f4} I_4) \tag{7}$$

The found values of the fractional free volume are also given in Table 5.

For many polymers studied in this work the values found via PALS are in the range 3−20%. As has been observed for other materials,[49] these values of FFV are smaller than those calculated by Bondi method (Table 1): FFV(Bondi)/FFV(PALS) = 1.5 ± 0.3. This result does not seem to be unexpected: the Bondi method takes into account all accessible free volume beacuse it is defined as the difference between the specific volume and corrected the van der Waals (or occupied) volume, whereas the PALS method should be sensitive to only a part of the whole size distribution of free volume.

However, for some high free volume polymers (PTMSP, PPrSiDPA) eq 7 gives unrealistic values, as high as 80% for example in the case of PTMSP. It means that an assumption of a constant and universal value of C for all the glassy polymers may not be correct. It has been shown that in some polymers the intensities I_3 and I_4 vary with temperature in such a way that cannot be explained by changes of the concentrtaions of FVE.[26] The problem would be simplified if the concentrations N_i of FVE were directly proportional to the trapping rates ν_i. However, one can assume that the ν_i values are related in a complicated manner to the intensities I_i (i = 3, 4) as well as nontrapped o-Ps annihilation rate λ_f, and γ_i (i = 3, 4), the annihilation rates of o-Ps in the FVE having different sizes. Therefore, other approaches are needed to calculate the fractional free volume based on PAL spectra.

A model for diffusion-controlled kinetics of Ps annihilation in polymers has been proposed.[53] It was based on the assumptions that, first, nonlocalized (free) o-Ps are formed with subsequent diffusion (D^{f}_{Ps}) and capture into free volume elements. This model is not an alternative to the recently suggested relations between the free volume fraction V_f and annihilation characteristics.[49,54] We consider it as a generalization of the contemporary views. According to ref 53, in the case of trapping centers of one type N_3 (unimodal distribution of o-Ps lifetimes), the long-lived positronium component I_3 can be found as a function of the positronium trapping rate ν_t, free positron (and positronium) annihilation rate λ_f, and pick-off annihilation rate in the traps $\gamma_3 = 1/\tau_3$

$$I_3 = 3Q\nu_t/4(\lambda_f + \nu_t - \gamma_3) \qquad (8)$$

where $\nu_t = 4\pi D^{f}_{Ps} R_3 N_3$. The two limiting situations should be considered. If one assumes that $\nu_t < \lambda_f - \gamma_3$, then $I_3 = (^3/_4)QD^{f}_{Ps}R_3N_3$ and fractional free volume V_{fP} is roughly proportional to the product of I_3 and the volume of microcavity v_{f3} ($V_{fP} = \eta I_3 v_{f3}$). A similar empirical equation has been suggested by Jean et al.[49] and discussed earlier for the case of two o-Ps lifetimes (eq 7). The difference in these approaches is that in the present work the parameter η represents the diffusion-controlled rate constant of o-Ps trapping, i.e., $V_{fP} = N_3 v_{f3}$.

The second alternative appears when $\nu_t \gg \lambda_f - \gamma_3$. In this case, I_3 is independent of the concentration of FVE, i.e., $I_3 \sim Q$. This idea was discussed recently[54−56] and may be checked by age−momentum correlation (AMOC) experiments.

It is likely that the relations in eqs 7 and 8 are more realistic, while the assumption that o-Ps atom is immediately and irreversibly trapped after its origin would be an oversimplification. Indeed, there are several observations which, in our opinion, demonstrate a dependence of I_3 on the concentration of FVEs.

1. A number of polymers are known that exhibit very small values of I_3, sometimes approaching zero (e.g., polyimide Kapton, cross-linked oligoetheracrylates[57]). They are low gas permeable materials; on the other hand, it would be strange to assume that it is caused by the vanishing value of Q.

2. The existence of 2 o-Ps component PAL spectra in some polymers and only the single o-Ps component in PAL spectra of others makes the assumption of the saturation of o-Ps localization rate in the defects far-fetched.

3. Similar conclusions were reached in the PAL study of deformation effects in several polymers. Thus, it was shown that uniaxial compression of the Vectra copolyester[58] and polycarbonate[59] produced substantial variation of I_3 (that is the concentration of FVEs) while keeping τ_3 values unchanged. It seems much easier to explain these observations by assuming a variation of FVE concentration and not the fraction of e^+, which forms o-Ps.

4. It is well-known that the fractional free volume evaluated using Bondi's approach (V_{fB}) is always larger than V_{fP} estimated by the PALS method (see, e.g., ref 49). This means that o-Ps "sees" only a part of the unoccupied (or accessible) free volume, which determines V_{fB}.

5. Numerous evidences have been reported[4,47,49,60,61] that diffusion and permeability coefficients correlate with the intensity of the o-Ps component I_3 or the product $v_{f3}I_3$. They must convince one that in most polymers these quantities should characterize the fractional free volume. Hence, in the limiting case, $\nu_t < \lambda_f - \gamma_3$ is a more realistic approximation.

Later this model was generalized for the case where two sorts of FVE with different sizes exist within the polymer matrix, and a four component PAL spectrum is observed.[62] It will be used here for interpreting the results obtained for the big group of polymers considered.

If the rates of capture in the smaller and larger FVE are ν_3 and ν_4, respectively, and corresponding rates of pick-off annihilation $\gamma_3 = 1/\tau_3$ and $\gamma_4 = 1/\tau_3$, the concentrations N_3 and N_4 of two kinds of FVE can be estimated using the following relationships:

$$\nu_3 = 4\pi D^{f}_{Ps} N_3 \qquad (9)$$

$$\nu_4 = 4\pi D^{f}_{Ps} N_4 \qquad (10)$$

Accordingly, the following equations were obtained for N_3 and N_4

$$N_3 = (^1/_4\pi D_{Psf})(I_3/A)\{(\lambda_f - 1/\tau_3)[(3Q/4) - I_4] + (\lambda_f - 1/\tau_4)I_4\} \qquad (11)$$

$$N_4 = (^1/_4\pi D_{Psf})(I_4/A)\{(\lambda_f - 1/\tau_4)[(3Q/4) - I_3] + (\lambda_f - 1/\tau_3)I_3\} \qquad (12)$$

where

$$\lambda_f \approx (\mathrm{I}_1/\tau_1) + (\mathrm{I}_2/\tau_2) + (I_3/\tau_3) + (I_4/\tau_4) \qquad (13)$$

$$A = [(3Q/4) - I_3][(3Q/4) - I_4] - I_3 I_4 \qquad (14)$$

and the relationships for Q, the probability of formation of initially nonlocalized Ps, for different limiting cases have been considered in ref 62.

Equations 11 and 12 were obtained for the system with FVE elements that are distributed in a spatially uniform manner within a polymer matrix. If a polymer has a microheterogeneous structure, i.e., where larger and smaller FVE prevail in different regions that are separated by a certain minimum length L, such that o-Ps cannot, during its lifetimes, leave one domain for another, or, in other words, see either smaller or larger FVE, then the kinetics of the process should be described by equations that characterize separately its decay in the regions with smaller or larger FVE. The conclusion on heterogenity of polymer matrices emerges from a combination of the following results: (1) positronium quenching by atmospheric oxygen and, hence, essential positronium mobility between the free volume elements; (2) distinct resolution of the two o-Ps components (τ_3, I_3; τ_4, I_4) despite this mobility. In this case the following equations hold[63]

$$N_3 = [(^1/_4\pi D_{Psf})(4I_3/3)(\lambda_f - 1/\tau_3)]/[Q/\xi_3 - (4I_3/3)] \qquad (15)$$

$$N_4 = [(^1/_4\pi D_{Psf})(4I_4/3)(\lambda_f - 1/\tau_4)]/[Q/\xi_4 - (4I_4/3)] \qquad (16)$$

where

$$\xi_i = I_i/(I_3 + I_4) \qquad (17)$$

It is supposed that Q and λ_f have identical values for both microphases. It can be also noted that in both cases

Table 6. Concentrations (cm^{-3}) of Smaller (N_3) and Larger (N_4) FVE in Glassy Polymers

	homogeneous model			heterogeneous model		
polymer	$N_3 \times 10^{-19}$	$N_4 \times 10^{-19}$	$N_3/(N_3 + N_4)$	$N_3 \times 10^{-19}$	$N_4 \times 10^{-19}$	$N_3/(N_3 + N_4)$
PTMSP	1.4	6.1	0.19	11.5	6.9	0.63
AF2400	1.5	4.0	0.28	8.8	4.8	0.65
AF1600	1.6	3.9	0.29	9.4	4.7	0.67
PPrSiDPA	4.7	4.9	0.49	12.3	8.0	0.61
PPhSiDPA	7.8	3.5	0.69	12.0	10.0	0.55
PTMSS	4.2	11.6	0.26	18.0	14.7	0.55
PFPDMSS	4.3	9.4	0.32	16.6	12.6	0.57
PVTMS	6.7	8.7	0.43	17.7	14.0	0.56
PVPDMS	6.3	7.3	0.46	15.0	12.7	0.54

Table 7. Fractional Free Volume of Smaller (V_{f3}) and Larger (V_{f4}) Microcavities in Glassy Polymers

	homogeneous model				heterogeneous model			
polymer	10^3V_{f3}	10^3V_{f4}	$10^3(V_{f3} + V_{f4})$	$V_{f3}/(V_{f3} + V_{f4})$	10^3V_{f3}	10^3V_{f4}	$10^3(V_{f3} + V_{f4})$	$V_{f3}/(V_{f3} + V_{f4})$
PTMSP	2.5	80.6	83.1	0.030	22.5	91.0	113.5	0.198
AF2400	1.3	34.2	35.5	0.037	7.3	43.3	50.6	0.144
AF1600	0.3	19.3	19.6	0.015	0.74	24.4	25.1	0.029
PPrSiDPA	10.5	54.0	64.8	0.162	28.4	88.1	116.2	0.244
PPhSiDPA	7.7	8.0	15.7	0.490	11.9	22.4	34.3	0.347
PTMSS	3.4	25.6	29.0	0.117	14.9	32.2	47.1	0.316
PFPDMSS	2.8	17.8	20.6	0.136	10.9	26.7	37.6	0.290
PVTMS	8.4	25.6	34.0	0.247	22.2	48.3	70.5	0.315
PVPDMS	4.9	12.3	17.2	0.285	11.6	21.3	32.9	0.352

the concentrations N_3 and N_4 should be evaluated using PAL spectra obtained in the absence of oxygen.

The N_3 and N_4 values for the two models, with homogeneous and heterogeneous spatial distribution, are presented in Table 6. It is seen that N_i values differ for the two models, with the greater difference the smaller the intensities I_i are: thus, for PTMSP, the concentrations N_4 are close for both models whereas N_3 differ by nearly an order of magnitude. On the other hand, the difference between N_3 values for PPhSiDPA is the smallest. It is caused by the difference of large numbers $Q\xi_i - 4I_i/3$ in the denominator of formulas 15 and 16.

The total concentration of FVE $N = N_3 + N_4$, depending on the polymer structure and the choice of model, ranges from 0.5×10^{20} to 3.3×10^{20} cm^{-3}. This value is in a reasonable agreement with the estimations of the concentrations of FVE in amorphous parts of semicrystalline polyethylene (7.3×10^{20} cm^{-3}) and poly(tetrafluoroethylene) (3.6×10^{20} cm^{-3}) made using an entirely different approach.[26] It should be noted that the fraction of smaller FVE, $N_3/(N_3 + N_4)$ (Table 6), is rather sensitive to a choice of the model of microstructure: for a homogeneous one, it is varied in a wide range, whereas for the heterogeneous model it remains, interestingly, constant having virtually the same value for all the polymers studied: 0.59 ± 0.04. Further scrutiny is required before this observation can be correctly interpreted, i.e., whether it is a manifestation of a general regularity of free volume microstructure in glassy polymers or simply a feature of the considered group of materials. It is worthwhile also to remark that the N_3 and N_4 values found for both models hardly correlate with permeability or diffusivity of the polymers.

Now using the obtained values N_3 and N_4, the fractional free volume components V_{f3} and V_{f4} as well as the total FFV = $V_{f3} + V_{f4}$ can be computed. The results of this estimation are given in Table 7. Since τ_4 and R_4 vary in the series of the polymers more strongly than N_i values, an increase in free volume in high permeability polymers is related mainly to the sizes of the microcavities and not to the concentrations of them.

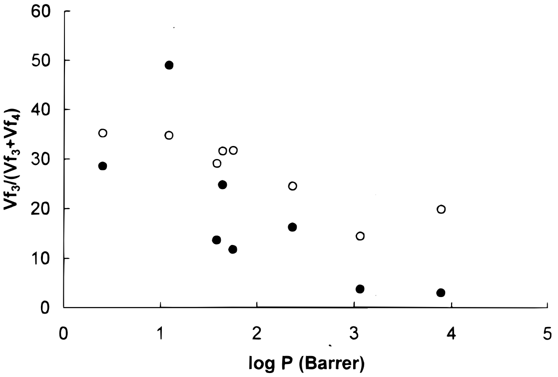

Figure 5. Variation of the fraction of free volume elements related by smaller microcavities $V_{f3}/(V_{f3} + V_{f4})$ in polymers with different permeability $P(O_2)$: open points, heterogeneous model; closed points, homogeneous model.

The following inequality holds especially for high free volume materials: $V_{f4} \gg V_{f3}$. The absolute values of FFV of less permeable polymers are in the range 2−3%, and only for PTMSP and PPrSiDPA are they 6−12%. Again a comparison with the fractional free volume calculated using the Bondi method can be made. FFV values found by the PALS method as it is described above are several times smaller than those found via density. This discrepancy has been discussed earlier.

The fraction of free volume related to smaller cavities $V_{f3}/(V_{f3} + V_{f4})$ correlates qualitatively with permeability of polymers independent of a choice of the model of polymer microstructure (Figure 5). This means that extrapolation to smaller permeabilities such as those of poly(methyl methacrylate) for which $P(O_2)$ is about 0.1 Barrer[64] implies the prevalence of smaller FVE in these polymers, a result consistent with the PAL finding.[42]

It is interesting to check an ability of free volume found via PAL data to describe transport properties of polymers. Figure 6 shows the correlations of the permeability coefficients of the glassy polymers with respect to oxygen versus the fractional free volume V_{f4} and $V_{f3} + V_{f4}$. Both assumptions regarding polymer microstruc-

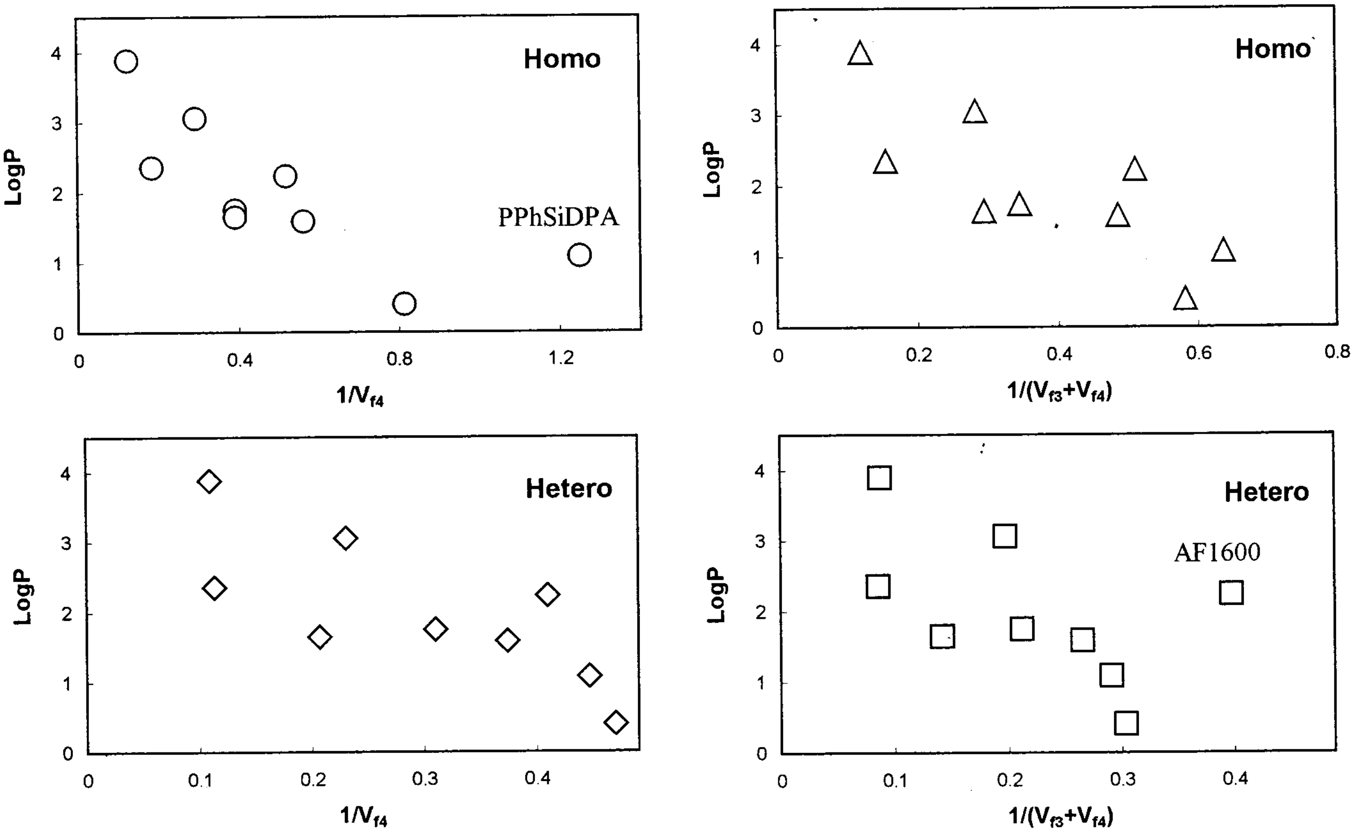

Figure 6. Correlations of permeability coefficients $P(O_2)$ with fractional free volume defined as V_{f4} or $V_{f4} + V_{f3}$: both homogeneous and heterogeneous models are considered; V_{f4} and $(V_{f4} + V_{f3})$ are in %.

ture are considered. It can be seen that in all the cases reasonabely good correlations are observed. Different reasons might cause a noticeable scatter of the points on these correlations. Strictly speaking, there are no grounds to assume that a certain model of microstructure is valid for all of the polymers, whose properties are varied in such a wide range. For example, this can be a reason for a large deviation of the data point for PPhSiDPA on the plot, where the correlation of the permeability coefficients with V_{f4} is checked for the case of the homogeneous model of microstructure.

Free Volume Size and Diffusion Selectivity of Glassy Polymers. Thus, the results of the present work show that there exists a strong correlation between (1) PAL distribution and free volume in glassy polymers having extra large and "normal" free volume and (2) their gas permeability and diffusivity. However, another property is of even more importance for membrane materials, their permselectivity or ideal separation factor

$$\alpha_{ij} = P_i/P_j \tag{18}$$

where P_i and P_j are low-pressure limits of permeability coefficients of gases M_i and M_j. As the permeability coefficient is the product of diffusion and solubility coefficients

$$P = DS \tag{19}$$

solubility $\alpha_{ij}{}^{S} = S_i/S_j$ and diffusivity $\alpha_{ij}{}^{D} = D_i/D_j$ contributions can be distinguished in the separation factors α_{ij}, that is

$$\alpha_{ij} = \alpha_{ij}{}^{S}\, \alpha_{ij}{}^{D} \tag{20}$$

It is known that permselectivity for light gases in conventional glassy polymers is determined mainly by their diffusion selectivity.

Figure 7 illustrates the dependence of diffusion coefficients in various polymers on the square of the kinetic diameter d^2 of the diffusing molecules. The latter quantity was taken according to ref 65. It can be seen that the larger the diffusion coefficient in a polymer for a certain gas, the smaller is the slope of the dependency of D on d^2. The slope of these lines determines diffusion selectivity of a polymer. Thus, diffusion selectivity of large free volume polymers, like PTMSP and AF2400, is markedly lower than that of conventional glassy polymers such as polycarbonate.

It is interesting to examine this regularity in a more quantitative manner. This is shown in Figure 8 for the polymers of the present work as well as conventional glassy polymers (polystyrene, polycarbonate, polysulfone). The lifetimes of the latter have been reported,[4] and the diffusion coefficients were taken from a database created by the authors.[66] The parameter a, which is used as a measure of diffusion selectivity, was found by the least-squares treatment of the equations log $D_i = a(d_i)^2 + b$ that describe the dependences shown in Figure 7. It is seen that when the size (in Å^3) of FVE of glassy polymers increases, diffusion selectivity monotonically decreases. This dependence is characteristic only for glassy polymers, since rubbers, which exhibit relatively small τ_3 values and hence smaller sizes of FVE, are characterized by much lower diffusion selectivity as the data point of poly(dimethylsiloxane), which is also shown as an example in Figure 8, indicates. Doubtless, this is related to different mechanisms of gas permeation in glassy and rubbery polymers. On the

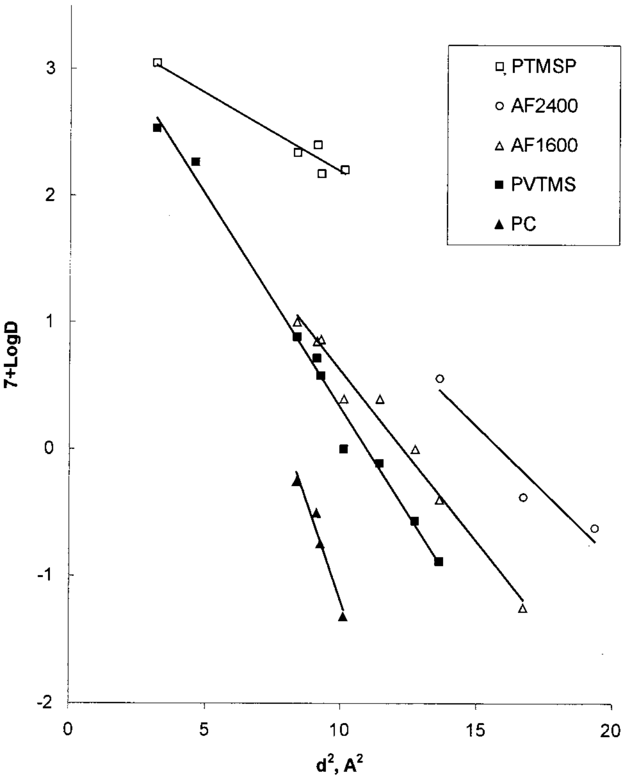

Figure 7. Diffusion coefficients D (cm^2/s) in polymers versus kinetic cross sections of the gas molecules: PTMSP, poly(trimethylsilyl propyne);AF1600, copolymer of perfluorodioxole (65%) and tetrafluoroethylene (35%); AF2400, copolymer of perfluorodioxole (90%) and tetrafluoroethylene (10%); PVTMS, polyvinyltrimethylsilane; PC, polycarbonate; PTFE, poly(tetrafluoroethylene).

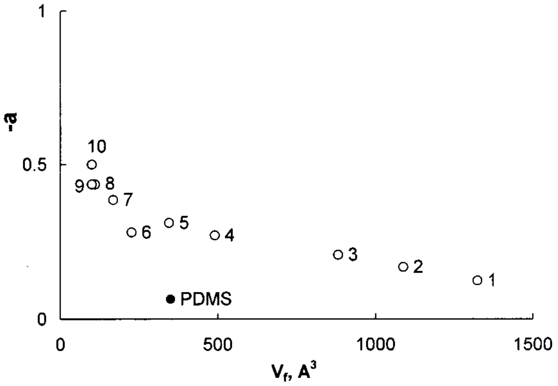

Figure 8. Diffusion selectivity as a function of the volume of microcavity v_f (Å^3): 1, PTMSP; 2, PPrSiDPA; 3, AF2400; 4, AF1600; 5, PVTMS; 6, PPhSiDPA; 7, PVPDMSS; 8, polystyrene; 9, polycarbonate; 10, polysulfone. PDMS is a rubbery material, poly(dimethylsiloxane).

other hand, this result enables an application of PAL spectroscopy for fast assessment of selectivity of prospected glassy membrane materials, because obtaining of the dependencies shown in Figure 7 is often a time- and effort-consuming procedure.

Discussion

As this work presents the results of the PALS investigation of free volume in a big number of glassy polymers with widely varying structure and properties (gas permeability in a range of nearly 4 orders of magnitude and qualitative and quantitative differences in free volumes) a question can be asked regarding possible advantages and deeper insight that are given by this rather sophisticated approach for probing free volume in polymers in comparison with semiquantative but much more easier-to-determine methods such as Bondi's method for evaluating fractional free volume in polymers[32] or assessment of "unrelaxed free volume" using the Langmuir adsorption capacity parameter C_H', which can be accomplished from the analysis of sorption isotherms in glassy polymers.[67] In answering this question, one should bear in mind that free volume in polymers is a complicated object that can be described either by macroscopic or phenomenological characteristics (V_f, cm^3/g, or FFV, %) or at microscopic or atomistic level (size, size distribution, or even architecture and topology of clusters of free volume).[68] In contrast to rubbers, where free volume has a fluctuational nature and moves along the matrix thus facilitating diffusion of sorbed molecules, in glassy polymers it consists of microcavities frozen-in in a more dense matrix.[69] Therefore, the diffusion rate must depend not only on the properties of free volume but also on the parameters of the processes that take place in the environment of FVE, that is when a diffusing molecule jumps from one microcavity into another.

For limited sets of polymers (often belonging to the same chemical class) satisfactory correlations of the type

$$\ln D = \ln A_1 - B_1/\mathrm{FFV} \qquad (21)$$

$$\ln D = \ln A_2 - B_2/V_f \qquad (22)$$

where V_f and FFV are estimated using Bondi's method, have been demonstarted (see, e.g., ref 70). A fulfillment of such correlations with phenomenological parameters could mean that microstructure of free volume for the whole set of polymer is similar or varies in parallel with V_f and FFV. It should be noted that some of the scatter in these correlations is definitely larger than the error in measurement and, thus, can reflect issues not well accounted for in the model. The latter observation becomes more obvious when larger sets of polymers are taken into consideration.[71,72] Therefore, macroscopic parameters such as FFV cannot replace the information on free volume obtained on atomistic level that can be directly compared with the results of computer simulations or used in development of detailed model of sorption and diffusion in polymers.

Another macroscopic property, which is freqently used as a characteristics of unrelaxed free volume in glassy polymers is the Langmuir sorption capacity C_H' (cm^3(STP)/cm^3 of polymer), one of the parameters of the dual mode sorption model in glassy polymers.[67] It is known that enhanced solubility coefficients in glassy polymers are determined by this mode of sorption, because the apparent solubility coefficient in unrelaxed volume $S_H = C_H'b$, where b (atm^{-1}) is the affinity constant, comprises up to 90−95% of the whole solubility coefficients S.[73] Although C_H' values correlate sometimes with FFV or sizes of FVE in polymers they can serve as only an approximate measure of free volume. First, for small gas probes such as O_2 and N_2, the C_H' values increase and not decrease with the size of a solute[74] in contrast to what can be expected for hole filling model. Second, the C_H' values experimentally found are sensitive to the gas pressure range under which they have been determined.[75] In addition, at low-pressure, $p \leq 1/b$, they cannot be estimated accurately at all, whereas at higher pressure, $p \gg 1/b$, the onset of plasticization can result in distortion of sorption isotherms and appearance of inflection points due to the transition into the rubbery state.[76,77]

A disadvantage of most phenomenological models of free volume is an absence of an explicit indication of temperature dependence of free volume. This can be related to the coefficient of thermal expansion of hole volume $\alpha_{h,g}$ below T_g, which can be estimated by the PALS method. According to Dlubek et al.,[26] $\alpha_{h,g} \cong 10^{-3}$ K^{-1}. This slope of temperature dependence corresponds at 300 K to an activation energy of diffusion of about 4 kcal/mol. For most polymer–gas systems activation energies of diffusion are several times larger. Hence, one has to account for temperature dependence of the diffusion process in polymer matrix that form “walls” of free volume elements. Transition state theory in combination with free volume model should be utilized for description in such media. Corresponding equations were proposed by Vrentas and Duda[79] and Miyamoto and Shibayama.[80] After some simplification, the diffusion coefficient can be expressed by the following equation

$$D = A_3 e^{-E/RT}\, e^{-B/V_f} \qquad (23)$$

An analysis of the temperature dependences of diffusion coefficients and free volume[81,82] indicated that the first exponential term dominates in eq 23. Therefore, local properties of a dense phase of hole “walls” should strongly affect the diffusion rate. The PALS method gives no direct information on the properties of these areas of glassy polymers, though some attempts are being made to use for this purpose another positron annihilation technique—angular correlation of annihilation radiation (ACAR).[83]

The determination of the concentration of FVE in different polymers made in the present work enables an estimation of average diffusion length needed for a diffusion molecule to get from one hole into another. It was shown that in all the glassy polymers the total concentration of FVE $N = N_3 + N_4 = 10^{20}$ cm^{-3} (Table 6). It is interesting to note that other methods of the estimation of N using alternative approaches for different polymers gave the same order of maginitude of N.[26,82] This concentration of FVE corresponds to average volume of a polymer per one hole of about 10^4 Å^3. In other words, if the holes are distributed uniformely within the polymer matrix, the average distance that separates two adjacent FVE is about 20 Å. Amazingly, this value is close to the FVE size in the most permeable polymers such as PTMSP (Figure 4a). If we assume, as is made in the models used in the treatment of the PALS data, that FVE have spherical shape, than the mean distance between two holes should be about twice as large as the difference between 20 and 12–14 Å (Figure 4a), that is, about 7 Å. As it should be taken into account that elongated geometry of FVE is much more probable in polymers,[69,84] then the distance between some FVE can be even smaller. This estimation is in excellent agreement with the prediction made by Gusev et al.[85] and based on computer simulation of glassy polycarbonate according to which accessible clusters with a diameter of 5–10 Å are connected by bottleneck regions ca. 5–10 Å long. A conclusion that the mean distance between neighboring free volume clusters can be as small as 5 Å was made independently by Theodorou.[68] It means that for highly permeable polymers, the formation of the passages between two adjacent FVE requires only small scale thermal fluctuation depending on the detailed geometry, conformational preference and interaction forces among chains, whereas for the polymers having lower permeability and smaller sizes of FVE the length of diffusion pathways is markedly longer and requires more substantial rearrangement of the chains.

This conclusion correlates with extremely low activation energies of diffusion and gas permeation reported for PTMSP,[86] as well as with mixed permeation behavior of this polymer similar to that of sorbents having systems of open pores such as activated carbon.[22,87] Another fact, which should be taken into account, is the negative correlation between activation energies of diffusion and free volume: glassy polymers having lower free volume reveal larger activation energies of diffusion.[78] It is in line with the assumption of larger length of the diffusion jump in these polymers in agreement with Meares equation.[88]

It should be noted, however, that the observed transport parameters can be sensitive to the factors which are not directly related to the sizes of FVE. As a good illustration of such a possibility one can consider the behavior of the two highly permeable large free volume polymers—PTMSP and amorphous Teflon AF2400, whose size distribution of free volume are shown in parts a and b of Figure 4. It is seen that average sizes of FVE and half-widths of size distribution in these polymers are rather similar. However, their properties are quite different in one aspect. PTMSP exhibits an unusual, for a glassy polymer, solubility-controlled permeation behavior revealed as the sequence of gas permeability for the *n*-alkane series: the permeability coefficients of PTMSP increase with molecular mass of diffusing hydrocarbons, a trend typical for rubbery polymers.[87,89] It was explained by an unusually weak dependence of diffusivity on the diffusant size (Figure 7). Because of it, selectivity of solubility becomes the prevailing factor, which determines permselectivity. This is not true for AF2400, which behaves as a normal mobility-controlled glassy polymer.[90] It can be assumed that the chemical environment of the free volume elements in this polymer is arranged in a different way, resulting in longer diffusion pathways or higher energy barriers. The former assumption seems to be more likely because of known weak interchain interaction energies in perfluorinated materials. PTMSP has probably more rigid chains than AF2400 as can be judged by its higher glass transition temperature,[11] so they should be packed less efficiently allowing easier pathways between the holes.

An important finding of the present work is the demonstration of bimodal size distribution of FVE for a wide range of glassy polymers. This result apparently validates the simulation approaches, because the probability density function for accessible cluster volume was shown[69] to reveal several extrema in glassy atactic polypropylene; that is, clusters of a particular size may be more probable than either slightly larger or smaller ones. Recently, hole size distribution with the gaps at certain hole radii were also demonstrated for several other polymers.[91] It is a subject of future research to elucidate if more sophisticated PALS data analysis will show more complex hole size distribution than bimodal one observed in this paper.

Conclusions

A study of a number of glassy polymers with widely varying free volume and gas permeability showed that a bimodal size distribution of free volume elements previously observed in PTMSP is not an exception but is a typical feature of the microstructure of amorphous glassy polymers. Indications of the existence of complex size distributions of free volume elements was obtained by using both finite-term and continuous procedures of the data treatment. Each of these approaches has its advantages: the CONTIN program automatically selects the number of the components in the PAL spectrum and, hence, the type of size distribution. However, if two components of the size distribution of FVE have radii which differ insignificantly as compared with the width of the peaks, the CONTIN treatment can result in a single broad peak. In this case, the PATFIT treatment with a preselected number of the components in the PAL spectrum can give more decisive arguments. As a whole, profound reasons for postulating bimodal size distribution of FVE in a group of polymers should be based on the use of both approaches, as has been demonstrated in this work.

When one proceeds from more to less permeable polymers, the evolution of the size distribution of FVE takes place continuously. For such polymers as PTMSP or AF2400, the CONTIN analysis indicates two sorts of microcavities with radii in the ranges 2.5−4.0 and 5−7.5 Å, respectively. On the other hand, for PVTMS and less permeable polymers, a superposition of two peaks of larger and smaller FVE is observed.

Oxygen-induced quenching of Ps lifetimes was demonstrated for all polymers having larger free volume. It was shown that a reduction of the lifetimes τ_3 and τ_4 correlate with the radius R_4 of larger free volume elements.

A model of diffusion-controlled capture and annihilation of Ps was used to calculate the concentrations of smaller (N_3) and larger (N_4) free volume elements. These values as well as the total concentration $N_3 + N_4$ do not vary significantly in the glassy polymers and have the order 10^{20} cm^{-3}. Using these concentrations and the volumes of smaller and larger microcavities, the fractional free volume in the polymers studied was found to be in the range 2−11% depending on the microstructure of the polymers.

It was shown that gas diffusion selectivity of glassy polymers correlates with the volumes of microcavities: low selectivity is characteristic for high free volume polymers such as PTMSP and PPrSiDPA whereas conventional glassy polymers such as polycarbonate or polysulfone that have three-component PAL spectra and smaller sizes of FVE are distinguished by larger diffusion selectivity. Such a correlation can be used for a fast assesment of gas permeation properties of novel polymers using positron annihilation data.

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