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On Estimation of Concentration of Free Volume Elements in Polymers

Yuri Yampolskii*

A.V. Topchiev Institute of Petrochemical Synthesis,
Russian Academy of Sciences, 119991, 29, Leninsky Pr.,
Moscow, Russia

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Today free volume in polymers is the subject of experimental determination and computer modeling. Now there exist several so-called probe methods for evaluation of free volume. Beside the methods of photochromic probes, ^{129}Xe NMR, and inverse gas chromatography, positron annihilation lifetime spectroscopy (PALS) is considered as the most informative, detailed, and widely accepted technique in this field.[1] Advantages of PALS are: it allows estimation of not only average size but also size distribution of free volume elements (holes) in polymers, possibility to measure free volume in bulk and in thin films, easy measurements of free volume at different temperature and pressure, and, in addition, PALS, in contrast to other probe methods, is capable to determine the concentration of these elements (hole number density).

The methodology of PALS study of polymers implies obtaining lifetime spectrum of positrons. In typical cases it consists of three components τ_i ($i = 1-3$) with corresponding intensities I_i. The third component of the spectrum characterized by the longest lifetimes belongs to lifetime of orthopositronium (o-Ps), hydrogen-like bound state, the combination of electron and positron (e^-e^+) having parallel spins. The paradigm of the method is that o-Ps atoms get into holes in the polymer matrix, and their lifetime is sensitive to the size of free volume element (FVE) in which they annihilate: the larger FVE, the longer are lifetimes. It is commonly assumed that FVEs have spherical geometry. A semiempirical equation was proposed to relate the o-Ps lifetime τ_3 to the average radius R_i of spherical FVE:[2]

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

where $R_0 = R_i + \Delta R$ (the adjustable parameter $\Delta R = 1.66$ Å). The graphical representation of this transcendental equation shows that R_i increases nearly linearly when τ_3 increases. For spherical holes the average volume $v_f = 4\pi/3R_i^3$ is in the range 50−1000 Å.

The rate of mass transfer in polymers depends not only on v_f but also on the hole number density N (cm^{-3}) or average distance between neighboring holes.[3] With known v_f and N it is possible to estimate the dimensionless quantity, the fractional free volume (FFV):

$$\mathrm{FFV} = v_f N \qquad (2)$$

Several approaches have been proposed to find the N values.[4] However, the most reliable method for the determination of hole number density N involves joint consideration of (i) the temperature dependences of τ_3 below and above the glass transition temperatures T_g and (ii) PVT data, i.e., temperature dependence of the specific volume of the polymer below and above T_g. These methods, especially the last one, were extensively used by several groups of researchers for polymers having T_g values in the range ca. 200−500 K and produced the main body of information on variation of N values in polymers with different chemical structure.[1b,5]

Nonetheless, applications of these methods meet with difficulties. Thus, some of the glassy polymers with rigid chains having high permeability and large free volume do not exhibit glass transitions; that is, their T_g values are above the onset of thermal decomposition. Such highly permeable polymers as poly(trimethylsilylpropyne),[6] poly(trimethylsilylnorbornene),[7] and polymer of intrinsic microporosity PIM-1[8] are examples of such behavior. Their lifetimes do not depend on temperature or show a maximum in glassy region, so it is difficult to compare $\tau_i(T)$ with coefficients of thermal expansion of the materials. Besides, the determination of temperature dependence of specific volume requires sophisticated equipment.

The aim of this Communication is to consider a simple though approximate way for estimation of the hole number density N using minimum information.

Fractional free volume (FFV) at room temperature is among the basic physicochemical parameters usually reported for glassy polymers together with T_g, density, and, sometimes, mechanical parameters. For its calculation, minimal information is needed: polymer density ρ and van der Waals volume of repeat unit V_w that can be computed using group contributions tabulated by Van Krevelen.[9] According to Bondi,[10] FFV can be defined as

$$\mathrm{FFV} = (V_{sp} - V_{oc})/V_{sp} \qquad (3)$$

where $V_{sp} = 1/\rho$ and occupied volume V_{oc} can be estimated as $1.3V_w$. In spite of the approximate character of this equation, good correlations of the permeability and diffusion coefficients with FFV can be often found in the literature, especially for series of polymers of the same class (see e.g. ref 11). For most polymers, the FFV values are in the range 0.1−0.3. It means that in 1 cm^3 of polymers total free volume amounts (1−3) × 10^{23} Å^3. On the other hand, for the vast majority of polymers PALS studies have been performed only at room temperature; hence, the value v_f found via R_i is also known at room temperature. Therefore, the hole number density N can be found as the ratio $10^{24}\mathrm{FFV}/v_f$, where v_f is expressed in Å^3.

To test this possibility, several works were chosen, where extensive data on positron annihilation lifetimes and FFV were reported for different polymers. For this purpose the works by Tanaka et al.[12] provided the data for various polyimides of FDA and BPDA type. Polycondensation materials such as polysulfone, polycarbonate, and its functional derivatives were extensively studied by the PALS technique, and the data are available from various sources. Interestingly, the reported τ_i and calculated v_f values found by different authors are in good agreement and limited in rather narrow ranges. Thus, for bisphenol A polycarbonate different works reported v_f in the range 98−113 Å^3, so an average v_f value can be taken. FFV parameters for this group of polymers were taken from the review by Pixton and Paul.[11] The polymers selected for consideration had T_g in the range 100−400 °C and v_f from 80 to 900 Å^3.

Figure 1 shows the variation of the found N values for polymers having different sizes of FVE. It is seen that the polymers with entirely different structure form unified correlation of N with the volume of holes. Although the hole number density, as has been

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*Corresponding author.

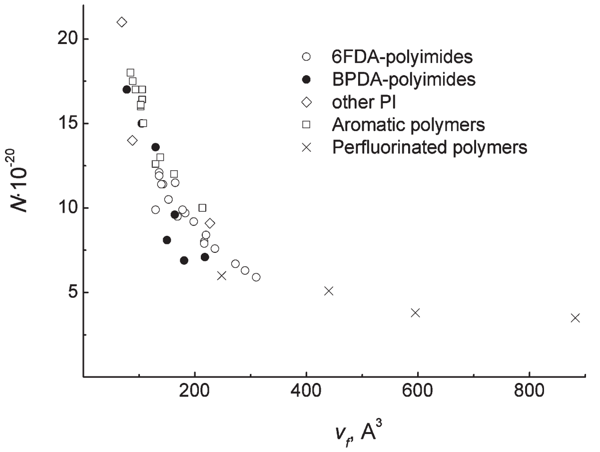

Figure 1. Dependence of hole number density N (cm^{-3}) on the size of FVE v_f (Å^3): 6FDA polyimides;[12b,c] BPDA and other polyimides;[12a] aromatic polymers (various sources); perfluorinated polymers.[13]

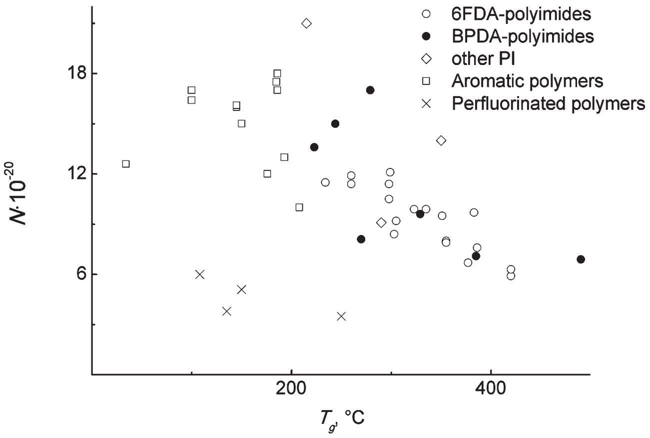

Figure 2. Correlation of hole number density N (cm^{-3}) with T_g: 6FDA polyimides;[12b,c] BPDA and other polyimides;[12a] aromatic polymers (various sources); perfluorinated polymers.[13]

noted earlier,[1a] in different polymers are within one order, when the size of FVE increases, the N values decrease.

This result does not seem unexpected because there should be a limitation of possible values of N. Indeed, if the N value were constant and, say, 10^{21} cm^{-3}, that is, in the middle of found range of variation of N, the expected FFV for polymers with $v_f = 10^3$ Å^3 must be 100%. Meanwhile, the N values decrease slower than the increases in the hole volume v_f. Consequently, FFV in polymers increases for polymers with large v_f as well as the permeability and diffusion coefficients that depend on it.

Such decreases in N are consistent with the simple model proposed in ref 3b. According to this model, the nanostructure of glassy polymers can be described as a combination of randomly distributed spherical holes with constant diameter. It was possible to show that the mean thickness of the walls that surround these holes is close to the diffusion jump length and so is consistent with the observed activation energy of diffusion according to the Meares equation.[3a]

Since for all the glassy polymers considered the glass transition temperatures are known, it was of interest to consider possible correlation between N and T_g. It is made in Figure 2. It can be seen that, statistically, the growth of T_g is accompanied by reduction of N values. Here, however, the scatter of the points is larger than that in Figure 1.

If one considers a group of structurally related polymers, e.g., polycarbonate derivatives, the scatter is smaller. It is worth noting that amorphous glassy perfluorinated polymers show a separate correlation with N values; the points are located lower, at corresponding T_g, than other, hydrogen-based polymers. This observation requires further elucidation. At present, the following qualitative explanation can be given. The observed T_g are determined by the intrinsic factor, stiffness of the main chain, and also by interchain interactions. Perfluorinated polymers should be characterized by reduced cohesion energy as compared to other considered polar polymers. In absence of this effect their T_g would be much higher.

Several circumstances should be discussed regarding the accuracy of the proposed procedure.

(1) To begin with, Bondi's method for calculation of v_f and FFV, though widely used, has been much criticized in the literature, especially the introduction of the coefficient 1.3 in calculation of the occupied volume via the van der Waals volume of the repeat unit (see e.g. ref 14). By definition, such an approach provides the upper limit of free volume which includes a big fraction of very small holes that are not accessible for orthopositronium in the PALS method or different gas diffusant molecules. Hoffman et al.[15] showed that FFV values found by molecular dynamics calculations strongly increase as the size of the virtual probe particle used in the simulation decreases. This can be a reason that FFV values calculated according to Bondi's method and used in combination with PALS data can be overestimated.

(2) The second complication can be related to the bimodal size distribution of free volume in highly permeable, high free volume polymers like PTMSP.[1d] However, the correction into the N values that takes into account the presence of smaller holes in such polymers is not big. Thus, calculation of N for PIM-1 using only the size of larger holes gave the value of 2.5×10^{20} cm^{-3}, while taking into account the presence of smaller holes results in the N values in the range $(2.1-3.2) \times 10^{20}$ cm^{-3}.

(3) The third and most important problem is related to the fact (partly discussed above) that the distribution of free volume seen by PALS is within the "window" between upper and lower limits. Small (and abundant) holes are not accessible to o-Ps (its size is 1.06 Å), but they contribute into total free volume in calculations of FFV using Bondi's method. It should be noted that this circumstance may produce complications in other methods for determination of N via PALS data as well.

The possible existence of very large holes in polymers cannot be excluded *a priori*. So they can affect the results of estimation of N. Such holes are met with in polymers very seldom, so the times of diffusion of o-Ps to them are so long so other routes of annihilation would be more probable. However, even in high-permeability polymers like PTMSP and PIM-1 (let alone conventional glassy polymers such as polyimides considered in this work), there are no holes with the radii $> 8-10$ Å according to MD simulations.[15] Such radii should be "sensed" by PALS. Bigger holes are characteristic for some polymeric sorbents like cross-linked polystyrene, where the radii as large as 13−15 Å are observed,[16] but this should be considered rather as an exception. Since holes frozen in glassy polymers originated in rubbery state, the idea of appearance of very large holes in polymer glasses seems to be counterproductive.

In conclusion, it can be assumed that the effects of larger holes can be neglected, while the importance of the errors caused by smaller holes can be assessed by comparison the proposed approach for estimation of N with the results of more rigorous methods.

Therefore, a comparison of the N values found in this work with the results of more sophisticated determination of N is quite desirable. For this purpose, the most suitable are the data for the perfluorinated polymers reported in the work,[5h] where the hole number densities were determined with accurate account of $\tau_3(T)$

Table 1. Different Estimations of Hole Number Density N (10^{-20} cm^{-3})

polymer	this work	Dlubek et al.[5h]
AF2400	3.5−4.1	4.4
AF1600	5.1	4.3

Table 2. Hole Number Densities N (10^{-20} cm^{-3}) Estimated via Different Probe Methods[7,13,18]

	technique		
polymer	PALS	IGC	^{129}Xe NMR
PIM-1	2.4	1.6	
PTMSN	3.6	2.3	
Hyflon AD80	3.9	3.8	2.4
AF2400	3.5	3.0	1.44

lines below and above T_g, PVT data, and the parameters of equations of state. A reasonable agreement is observed as can be seen from Table 1.

Somewhat worse agreement is achieved in comparison of the N values in a poly(ether imide) on the basis of the approximate Simha−Boyer equation[17] and the current approach. Shantarovich[5i] found $N = 4.4 \times 10^{20}$ cm^{-3}, while the proposed procedure gave $N = 6.9 \times 10^{20}$ cm^{-3}. Bearing in mind possible errors of the proposed approach, it can be concluded that independent data are in reasonable agreement. Therefore, the proposed simple procedure results in sufficiently reliable N values.

The same approach is applicable in other probe methods which provide the values R_i or v_f but give no information for N. Table 2 shows as an illustration the N values calculated on the basis of determination of v_f using inverse gas chromatography (IGC) and ^{129}Xe NMR methods.

So this approach can make other probe methods more versatile. No doubt, further estimations of N are possible for much wider set of glassy polymers.

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