



In memory of Prof. Yu.P. Yampolskii

Positron Annihilation and Permeation of Amorphous Polymers

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Highlights

- Yu. P. Yampolskii's role in membrane science
- Positron annihilation lifetime spectroscopy (PALS) for amorphous polymeric materials
- Free volume distribution and effective size
- Low temperature gas sorption
- Thermostimulated luminescence

Abstract

This paper is not a usual review and is written to illustrate the scientific activity of the outstanding researcher Yuri Pavlovich Yampolskii in one of the fields of interest: the creation and investigation of the new amorphous polymeric materials with chosen characteristics of gas separation and permeation. In this review, the specific property of the free volume number densities and the effective size of polymers determined using positron annihilation will be described. The exciting results will be highlighted, touching on several points of the research, such as the relations between permeation properties and elementary free volume characteristics, the multimodality of the distribution of ortho-positronium lifetimes, the dependence of the size of elementary free volumes on the conformation rigidity of the polymer chain, the relation between local rigidity and multimodality and the experiments with thermostimulated luminescence, and the low-temperature gas sorption connected to the free volume elements. These studies' importance for solving chemistry and ecology problems is obvious.

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1. Introduction

In the contemporary scientific literature, plenty of publications discuss the effect of positron annihilation and the application of this effect to the studies of solid-state structure. In this paper, the interconnection between ortho-positronium (the bound state of positron and electron with a parallel orientation of electron and positron spins, PsT) pick-off annihilation intensity and rate (the inverse value of ortho-positronium lifetime τ), as well as concentration and effective size of elementary free volumes (EFV) in polymer structures are considered. The bases of the positron annihilation method, particularly positron annihilation lifetime spectroscopy (PALS) are described in many reviews and books [1-7]. For this reason, details about this side of the problem are not necessary. The term "pick-off annihilation" identifies a mechanism of shortening of ortho-positronium lifetime (compared to the intrinsic

lifetime $\tau_0 = 140$ ns) due to the annihilation of the constituent positron at collision with one of the alien electrons with opposite spin orientation. This is a two-photon event. The most important is that, according to previous investigations, the intensity and rate of pick-off annihilation of ortho-positronium are governed by the number density of electrons in the positron spur (Ps formation) and the number and size of elementary free volumes (Ps trapping). It came out, particularly from the works of Yu.P. Yampolskii and coworkers, that these characteristics are responsible for important properties of polymers such as permeability to gases, selectivity, aging, mechanical strength, etc. However, the ways of calculating the free volume number densities and effective size are sometimes not obvious. This review tries to estimate the obtained results touching on the following research points:

Graphical abstract



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- (1) Foreseeing and demonstrating the interconnection between the permeation properties and elementary free volume characteristics obtained by positron annihilation lifetime spectroscopy (PALS).
- (2) Multimodality of the distribution of *ortho*-positronium lifetimes.
- (3) The idea of "local rigidity" (LR), when (at close energies of inter-chain interaction) the size of elementary free volumes EFV is essentially dependent on the conformation rigidity of the polymer chain. LR and multimodality.
- (4) LR and the experiments with thermostimulated luminescence (TSL).
- (5) Low-temperature gas sorption (LTGS): when PALS does not see some free volume elements.
- (6) LTGS and multimodality of some of the EFV size distributions.

The approach, developed by Yu.P. Yampolskii, is standing on the bases of the previous positron annihilation studies, summarized particularly in the reviews and original papers of other authors (see, for example, [1-11]) and in his adjacent investigations, presented, according to "WoS data collection", in more than four hundred publications. In the discussions of positron annihilation data, he permanently referenced a comprehensive database of the gas permeation parameters [12], collected and registered in the A.V. Topchiev Institute of Petrochemical Synthesis Russian Academy of Sciences, the permanent place of his work.

2. Permeation and free volume characteristics obtained in PALS experiments

The first paper on the topic [13], entitled "Study of the microstructure of polymers and its relation with diffusional properties by positron annihilation method", was written by Yu.P. Yampolskii and V.V. Volkov together with the scientists from the Institute of Chemical Physics Russian Academy of Sciences (Moscow). In this institute, in the department of academician V.I. Goldanskii, one of the first-lifetime annihilation spectrometers was built up.

Applications of positron annihilation in chemistry have been developing here since 1968 [1]. In paper [13], the wide range of amorphous polymers in the rubber-like and glassy state were studied by this method.

The parameters of the spectrum of positron and positronium annihilation lifetimes were compared with coefficients of diffusion of gases (H₂, CH₄) in polymers and with their T_g. The correlation between T_g and free volume in non-ordered regions of the polymers was also shown. The diffusion coefficients of gases in rubbers depended on the free volume in non-ordered regions.

Further studies were concerned with elucidating the data processing in PALS experiments in polymers. Usually, there are at least three components in the lifetime distribution of positron annihilation in amorphous polymers. The first component is associated with the annihilation of the short-lived singlet positronium (Ps^S) – lifetimes τ₁, intensity I₁. The longer component (τ₂, I₂) is related to the free positron annihilation (without positronium formation), and the third component (τ₃, I₃, sometimes also τ₄, I₄) describes the pick-off annihilation of the long-lived triplet positronium (PsT), trapped in the free volume holes (free volume elements, FVE). The first program of analysis of the PALS spectrum in terms of several discrete components PATFIT was originally published in [14]. Later on, the spectrum was described by a continuous distribution of the lifetimes (probability density of the decay with a given lifetime) - CONTIN (see, [15], for example) and MELT [16] programs.

Table 1 and Fig.1 [18] demonstrate the results of their application to the PALS data for some membrane materials, glassy polymers of different classes (silicon substituted polystyrenes and several polyfluorocarbons), studied in nitrogen temperature and also in air: Poly(4-[methyl- trimethylsilyl]styrene) PFPDMSS; poly(4-trimethylsilyl styrene) PTMSS; poly(4-[methyl-trimethylsilyl]styrene) PTMSMS; poly(vinylphenyldimethyl styrene) PVPDMS; poly(viyltrimethyl silate) PVTMS; copolymers of 2,2-bisfluoromethyl-4,5-ifluoro-1,3-dioxole (I) and tetrafluoroethylene (II): AF 2400 (content of (I)- 90%) and AF 1600 (content of (I)- 65%); poly(trimethylsilyl propine) PTMSP; poly(1-phenyl-2-[4-(triisopropylsilyl) phenyl] acetylene) PIPSIDPA; poly(1-phenyl-2-[4-(triphenylsilyl) phenyl] acetylene) PPSIDPA; Nafion 117 (fom Du Pont) with molecular formula poly(tetrafluoroethylene-co-polytrifluoro-oxy-hexafluoro-propylene-2-oxy-difluoroethylene sulfoacid).

According to contemporary views, Ps atoms spring up in a positron spur [19] in a combination of a positron with one of the spur electrons. Later, the newly born electron-positron pair stabilizes and localizes in one of the elementary free volumes due to the repulsive interaction (Van-der-Waals forces) with valent electrons of neighboring molecules. The motion and

trapping of the pair into the hole are described conventionally by the diffusion coefficient of the free (non-localized) positronium [17,18]:

$$D'_{Ps} = L^2/6\tau_f \quad (1)$$

where τ_f stands for the lifetime of free (non-localized) positronium, and L is the average distance between the centers of EFV. The coefficient was found in the limits $0.5 \times 10^{-4} < D'_{Ps} < 1.5 \times 10^{-4}$ cm²/s. This order of magnitude is important since at lower mobility non-localized Ps would not be able to find appropriate free volume during its lifetime τ_f, which is about 0.3-0.4 ns. The concentration of the elementary free volumes (EFV) of about 10¹⁹ cm⁻³ was estimated by solving kinetic equations of Ps trapping and using annihilation characteristics [17, 18, 20]. Another method (by G. Dlubek), based on the study of the temperature dependence of the trapped positronium lifetimes and so-called pressure-volume-temperature (PVT) experiments [21, 22], gave approximately the same result.

Removing atmospheric oxygen in paper [17] was applied due to the effect of oxygen on *o*-Ps lifetimes in some polymers [23]. Table 1 demonstrates the shortening of Ps lifetimes τ₃ and τ₄ (relative to those in the nitrogen atmosphere) because of the positronium interaction (conversion or chemical reaction) with adsorbed atmospheric oxygen. The intensities of these components (I₃, I₄) did not practically change. Since the oxygen concentrations in the glassy polymers under study are far below the concentration of EFV (about 10¹⁹-10²⁰ cm⁻³), many elementary free volumes are free from oxygen. Therefore, the Ps atom has to change several EFV by the moment of its interaction with oxygen. This behavior causes positronium quenching (shortening of *o*-Ps lifetime). Vice versa, if a positronium atom remains in a single EFV after the first trapping, the interaction will look like inhibiting the Ps formation for those Ps atoms in contact with oxygen. The described results can be used for a rough estimation of the diffusion coefficient D_{Ps}^{loc} of localized (trapped) Ps, which is different from D'_{Ps} (diffusion coefficient of non-localized, free Ps), used in calculations of the trapping rates. According to the equations of positronium chemistry

$$\Lambda^{ox}_{3,4} = \lambda_{3,4} + k[O_2]_s; \quad k = 4\pi D_{Ps}^{loc}(R_{Ps} + R_{Ox}), \quad (2)$$

where R_{Ox} = 1.2 Å, R_{Ps} = 0.53 Å and [O₂]_s concentrations given in Table 2. Providing R_{Ps} = 0.53 Å, R_{Ox} = 1.2 Å, one can estimate average values $D_{Ps}^{loc} = 0.38 \times 10^{-4}$ cm²/s from the variations of τ₄ and $D_{Ps}^{loc} = 1.17 \times 10^{-4}$ cm²/s from the variations of τ₃. A large difference in the estimations is not unexpected. Different properties of micro-heterogeneities can explain it: by different conditions of detrapping and by deviation of oxygen content from the average value [O₂]_s (Table 1) in micro-heterogeneities with large and small EFV. In most glassy polymers, excluding probably PTMSP, the oxygen mobility may be neglected compared to the Ps-atom. According to authors [17], measurements for PIPSIDPA, exhibiting strong Ps quenching by atmospheric oxygen, indicated D_{O2} = 7 · 10⁻⁷ cm²/s. The values of D D_{Ps}^{loc} are at least one order of magnitude higher than those obtained earlier for PC: 0.58 · 10⁻⁵ cm²/s [24]. In agreement with the estimations of Ps tunneling [25], in some glassy polymers, once-trapped Ps, an atom can still be very mobile.

Thus, the interconnection of positronium annihilation characteristics with the permeation of typical membrane materials was clearly demonstrated.

3. Multimodality of the lifetime distribution of ortho-positronium annihilation

In some materials studied in [17], the CONTIN program reveals undoubtedly two components of positronium lifetimes (Fig. 1(a, b)), whose maxima positions depend on the concentration of sorbed oxygen (Table 1). If Ps migration proceeds through the homogeneously distributed EFV of different sizes, it would give rise to a smooth unimodal distribution of the long-lived ortho-positronium lifetimes. The opposite experimental results for several glassy polymers confirm a nonhomogeneous distribution of EFV. There are micro-regions of larger and smaller holes (micro-regions of lower and higher density). The characteristic size L of the micro-regions can be estimated from the diffusion coefficient of the localized positronium D_{Ps}^{loc} and the lifetime τ of the once-trapped positronium [$L \geq (6 \times D_{Ps}^{loc} \tau)^{1/2}$], assuming that the Ps atom is not able to get out of the micro-region during its lifetime. The estimation gives $L \geq 150$ Å. Here, there are no transitions between the holes of different sizes (between micro-regions of different densities).

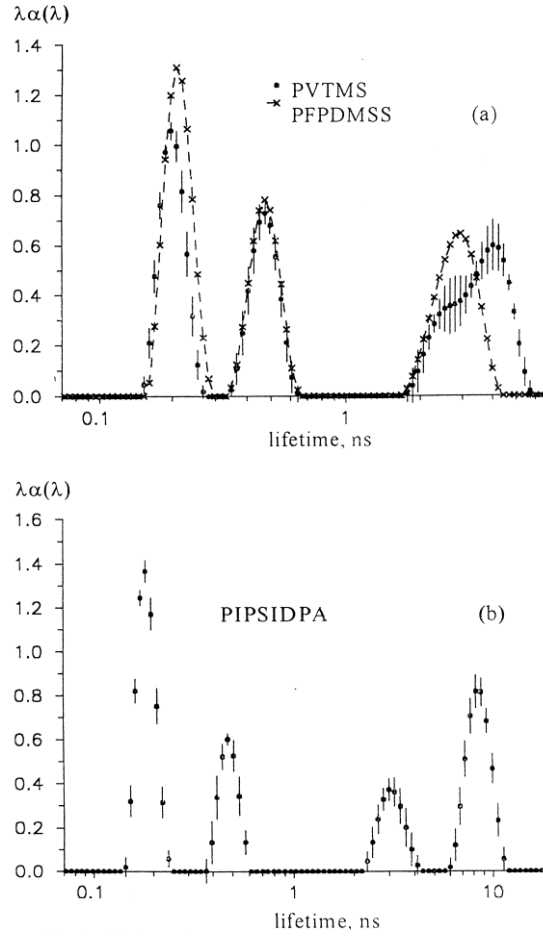


Fig. 1. Probability density function $\lambda\alpha(\lambda)$ of positronium annihilation lifetime $\tau=\lambda^{-1}$ (ns) obtained with CONTIN program: (a) PFPDMSS and PVTMS; (b) PIPSIDPA [18].

Table 1
Positronium annihilation characteristics of glassy polymeric films, concentration of sorbed oxygen [O₂], and permeability coefficient P of oxygen [18].

Substance	[O ₂] _s × 10 ⁻¹⁸ , cm ⁻³	P, Barrer	Air		Nitrogen	
			τ_3 , ns I ₃ , %	τ_4 , ns I ₄ , %	τ_3 , ns I ₃ , %	τ_4 , ns I ₄ , %
PTMSP	7.1-10.5	5000	1.87±0.29	5.88±0.06	2.68±0.45	10.90±0.22
			5.40±0.46	33.06±0.67	4.37±0.48	33.8±0.63
PIPSIDPA	14	200	2.65±0.05	7.21±0.06	3.30±0.07	9.38±0.10
			16.68±0.30	25.76±0.39	16.45±0.40	28.16±0.46
AF-2400	5.0	1200	1.26±0.11	5.75±0.03	1.82±0.33	8.04±0.13
			3.61±0.46	13.74±0.09	2.60±0.30	13.74±0.25
AF-1600	4.1	600	1.03 fixed	4.92±0.03	1.06 fixed	5.29±0.05
			4.14±0.53	13.41±0.11	2.44±0.89	14.59±0.16
PVTMS	2.4	44	2.25±0.10	4.06±0.05	2.41±0.13	4.20±0.07
			14.14±1.15	25.46±1.32	15.44±1.77	27.69±1.96
PPSIDPA	4.2	12	2.01±0.08	3.22±0.10	2.07±0.07	3.27±0.09
			23.13±2.20	15.60±2.47	24.07±2.06	14.94±2.29
PTMSS	1.56	56	1.80±0.11	3.14±0.03	1.85±0.20	3.16±0.04
			10.16±1.14±	28.57±1.34	8.11±1.73	31.31±2.01
PFPDMSS	0.84	38	1.73±0.11	3.11±0.03	-	-
			8.44±0.83	26.26±1.03	-	-
PVPDMSS	0.43	2.5	1.78±0.08	2.72±0.05	1.78±0.16	2.69±0.08
			16.66±2.17	20.76±2.37	14.83±3.79	21.50±4.10
PTMSMS	-	14	1.57±0.12	2.61±0.03	-	-
			10.00±1.47	27.55±1.78	-	-
Nafion	-	-	3.06±0.03	-	3.15±0.04	-
			7.72±0.10	-	7.08±0.13	-

Elastic and glassy polymers are typically considered homogeneous, disordered materials with unimodal (symmetric, Gaussian, for example) distribution of elementary free volumes. More complex (asymmetric, bi-central) distributions obtained from mathematical analyses of experimental *ortho*-positronium annihilation lifetime spectra were sometimes explained as “artifacts”, which is a result of incorrect mathematical treatment (deconvolution) of the lifetime spectra [26, 27]. The conclusion is based mainly on the generation and analysis of so-called “virtual” lifetime distributions with a wide scattering of lifetimes. Accepting this conclusion as a reasonable formal explanation in some cases, attention is paid to the new additional examples of asymmetry or complex character of the pore size distributions found later [28 - 31].

Fig. 2 [29] demonstrates the probability density functions (pdf) for the sizes of elementary free volumes of polymers AF2400 and AF1600 (see repeat unit in Fig. 3), calculated by molecular modeling in the *Rmax* approximation. The *Rmax* identifies the method of determining the effective size of the pore of complex configuration (*Vconnect*) (Fig. 4).

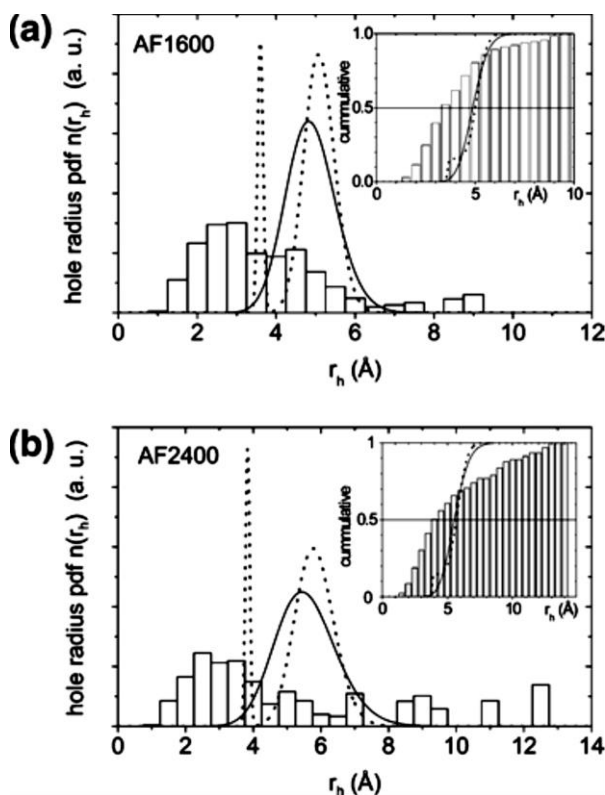


Fig. 2. Pore radius probability density function for AF 1600 and AF 2400 polymers (Fig. 3) [29]. The solid and dashed lines show the curves for one *ortho*-Ps component and two *ortho*-Ps components analysis of the lifetime spectrum. The burs show the volume-weighted distributions from molecular modeling (*Rmax* approximation) accessible free volume distribution for a probe molecule with the radius $r_p=1.1 \text{ \AA}$.

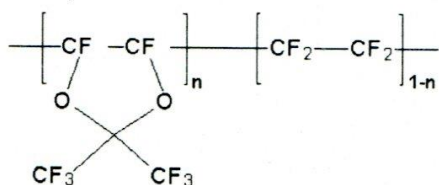


Fig. 3. Repeat unit of the Teflon AF copolymer.

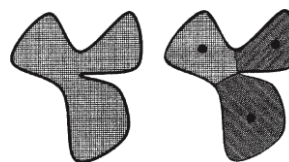


Fig. 4. *Vconnect* (left) and *Rmax* (right) view on a large hole of complex topology [30].

Continuing this line, the paper [33] called “Relation of the gas transport parameters of amorphous glassy polymers to their free volume: positron annihilation study” was produced. It was accepted there that in highly permeable polymers lifetime spectrum looks like consisting of the two *o*-Ps components (τ_3, τ_4), and namely $\tau_4 \gg \tau_3$ determines free volume [34]. Therefore, in polymers characterized by bimodal size distribution, the free volume was calculated using τ_4 [8,9]. Positron annihilation data were taken from [35-37]. Correlation of the transport parameters (diffusion coefficient *D* of the penetrant and permeations *P* of gases) and thermodynamic parameters (solubility coefficients *S* and parameters C_H' of sorption isotherms) with the sizes of free volume elements, v_h , as estimated via positron annihilation lifetime spectroscopy, were analyzed based on the data array obtained for glassy polymers. The observed linear correlation of $\log D$ and $\log P$ with $1/v_h$ (Fig. 6) corresponded to the free volume model in the condition of small changes in the number of the free volume elements in various polymers. Some deviations from linear correlation with $1/v_h$ for polymers with high free volume were interpreted as evidence that connectivity (openness) of pores increased with the size of free volume elements. Remarkably, for the description of the lifetime distribution with one *o*-Ps component (let us call it τ_3'), $\tau_4 > \tau_3' > \tau_3$, the deviations would be still higher. This is also in favor of description in terms of two *o*-Ps components. For solubility coefficients and Langmuir parameters of sorption C_H' , a good linear correlation with the value of the hole radius r_h was also demonstrated.

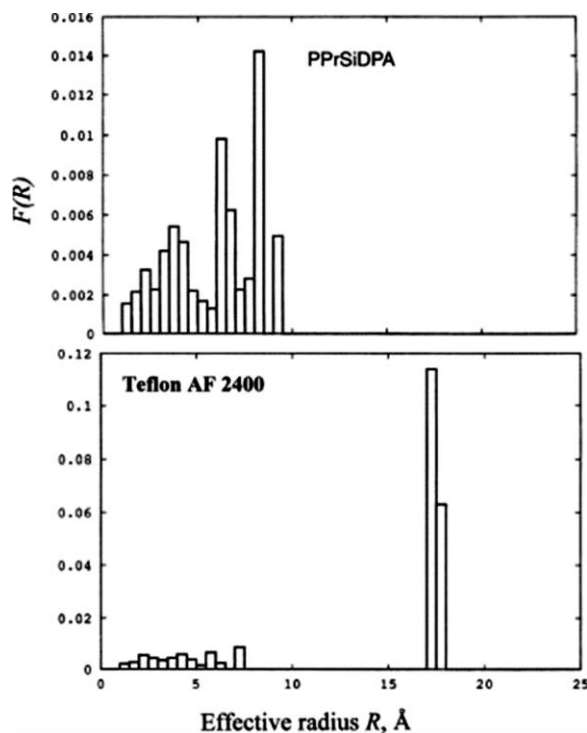


Fig. 5. *Vconnect* accessible free volume distribution *FFV* in membrane materials PPrSiDPA and AF2400 for the positronium probe atom ($R_p = 1.1 \text{ \AA}$) (compare with the distributions for the same materials in *Rmax* approximation Fig. 2) [29].

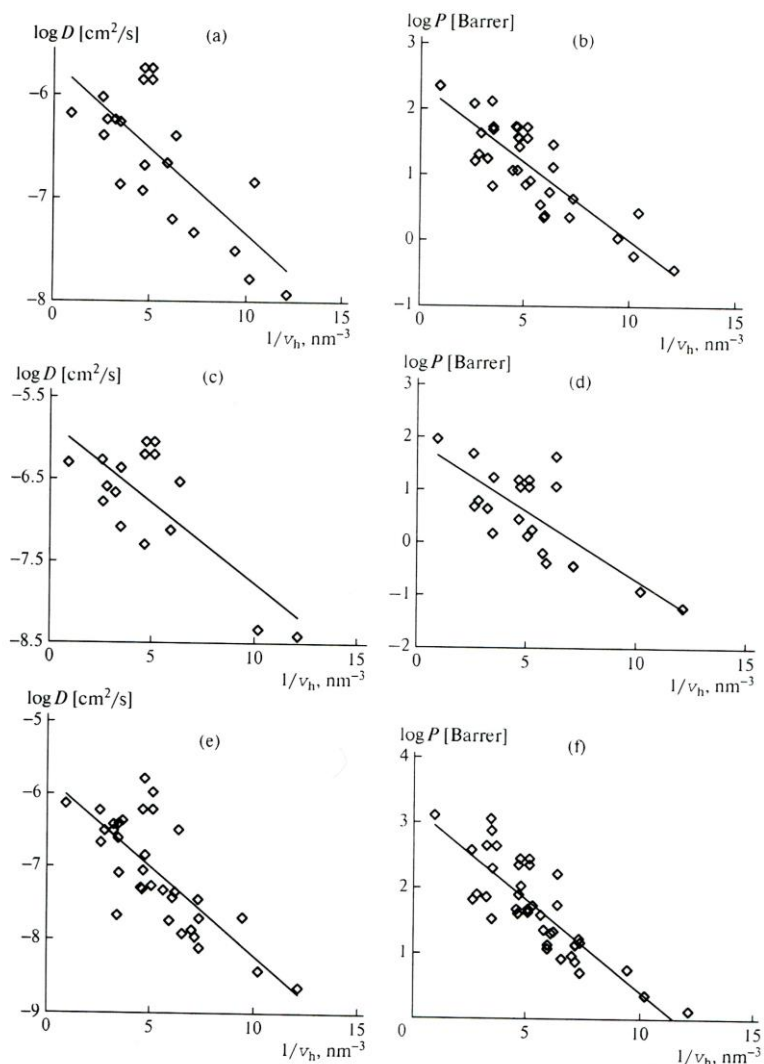


Fig. 6. Dependences of the diffusion coefficient D (a, b, c) and permeation coefficient P (d, e, f) on the size of the free volume element in polymers, (a, b) O₂, (c, d) N₂, (e, f) CO₂ [33].

4. The idea of “local rigidity” (LR), when (at close energies of inter-chain interaction) the size of the elementary free volume (EFV) is essentially dependent on the conformation rigidity of the polymer chain

A system characterized by local rigidity is not homogeneous, and, correspondingly, the size distribution of EFV found from PALS must have a complex character, providing Ps annihilates mostly in the limits of one locality. That was the reason for investigating the connection between the transport behavior of polymers and the conformation rigidity of their chains [34,35]. Paper [34] was devoted to polyimides. Considering the isomeric polyheteroarylenes with different substitutions of para- and meta-phenylene rings in the backbone, the meta-isomers demonstrated lower permeability and free volume values along with higher polymer density ρ and gas perm-selectivity. This phenomenon is usually attributed to the rotational mobility of para-phenylene rings around the symmetry axis. In asymmetric meta-phenylene substituents, this degree of freedom is absent. It is known that meta-substituted polyheteroarylenes exhibit much lower conformational rigidity of chains than para-isomers. Since para- and meta-isomers are characterized by the same energy of cohesion, these series are suitable for studying the effect of chain rigidity on the transport parameters of polymers.

A measure of conformational rigidity is the statistical Kuhn segment

$$A = \lim_{n \rightarrow \infty} [\langle R^2 \rangle / nl_0] \quad (3)$$

where $\langle R^2 \rangle / nl_0$ is the ratio of the mean square end-to-end distance, averaged over all possible conformations to its contour length, n is the number

of units, and l_0 is the contour length of the repeating unit (macromolecular conformation-independent sum of segments connecting centers of virtual bonds of the unit). The values of Kuhn segment lengths were calculated under the assumption of free rotation around virtual bonds A_{fr} through the Monte Carlo procedure, as described in [36].

Among the other glassy membrane materials are AF 1600 and AF 2400, copolymers of tetrafluoroethylene, containing different links of the components in a copolymer chain: (PFD)_N(TFE)_{1-N}; $N=0.65$ and 0.83 , correspondingly. They were also considered [35] from the point of view of glass rigidity. The authors discussed different models of polymer chains consisting of 10 elementary links and established the existence of the two spatial isomers with a difference between the two energy minima of 10 kJ/mol. The kinetic rigidity was determined using constants of the force field in the natural vibrational coordinates for the chain fragments PFP-PFP, FP-TFE-PFD. The ratios between the fragments were different for AF 2400 (“1”) and AF 1600 (“2”). The constant of the force field was found as the second derivative of potential energies $U_{1,2}$ of the model fragments over the angle φ between the planes of the fragments:

$$U_1'' = \partial^2 U_1 / \partial^2 \varphi > U_2'' = \partial^2 U_2 / \partial^2 \varphi \quad (4)$$

Thus, a local rigidity was found as an intermolecular characteristic of a polymer, derived from sophisticated calculations. Notably, according to [35], the rigidity of AF 2400 is higher than that of AF 1600 and the expected free volume. This is actually seen in the PAL experiments.

5. Local rigidity and experiments on thermostimulated luminescence (TSL)

The idea of local rigidity comes from theoretical considerations and comparison with permeation. The data on thermostimulated luminescence (TSL) directly depend on the polymer matrix rigidity, and it can be compared with PAL and permeation data [37, 38]. TSL is the energy (light) emission by a substance on heating after preliminary gamma-irradiation at low temperature. PAL and TSL methods are genetically interconnected by the same radiation-chemical nature of the process (spur process). At low temperatures, the integral intensity of TSL and the intensity of positronium formation depend on the storage of the spur electrons (weakly bound electrons). The obtained results prove the spur mechanism of positronium formation [7].

Paper [38] checked the benefits of combining the room temperature PALS data and low-temperature TSL data to investigate new membrane materials and hetero-polymers (as cross-linked polystyrenes). The logic of interpretation was as follows. Polymer membrane permeation for some gases depends on local

free volume. This elementary free volume determines *o*-Ps lifetime too. On the other hand, there is a theoretical suggestion that the free volume (and, correspondingly, the long-lived *o*-positronium component) depends on the polymer's local rigidity (see the previous section). In its turn, the rigidity determines the shape of the curve of the integral intensity of the TSL. The shape is suggested to characterize [37, 38] by the relative intensity of the high temperature (above 200-250K) component (so-called parameter " α "). The procedure of the parameter $\alpha = S_{HT}/S_{LT}$ calculation is shown in Fig. 7.

The higher the local rigidity and the higher the local free volume, the higher the meaning of parameter α . Fig. 8 illustrates that such a correlation exists.

The lower part of Fig.8 includes data for the cross-linked polystyrenes. Thus, TSL data were used to confirm that the largest free volume holes are usually situated in the sites of higher local rigidity detected by intensive high-temperature parts of the TSL curves.

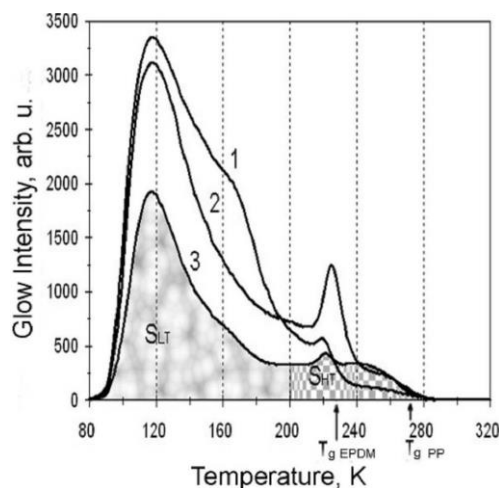


Fig. 7. Fluorescence intensity versus temperature for a number of polymer blends (1- 3) from [38]. The procedure of the parameter $\alpha = S_{HT}/S_{LT}$ calculation is shown as an example of the sample (3).

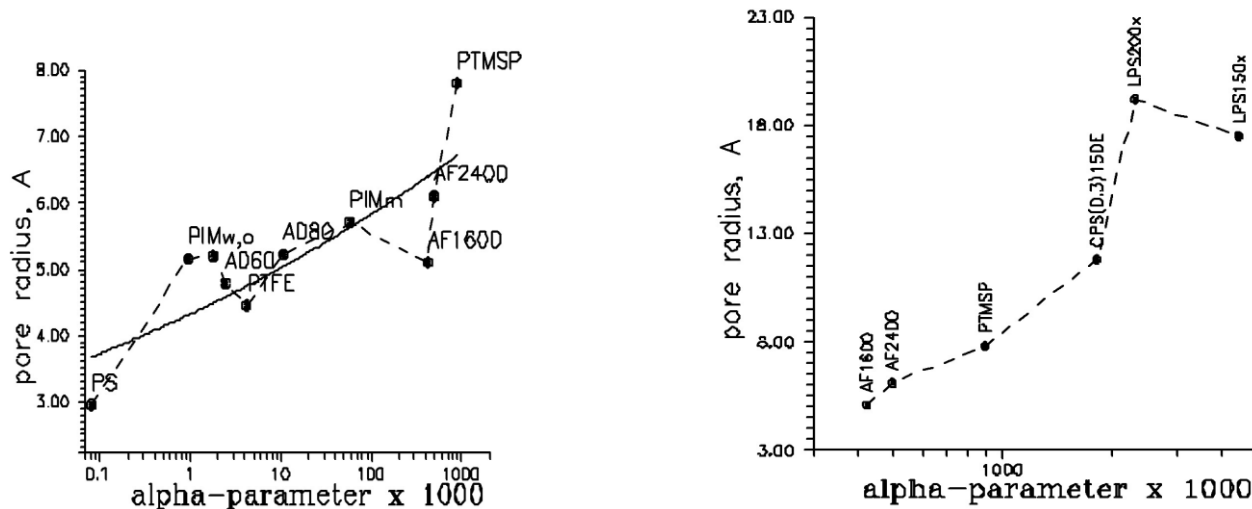


Fig. 8. Correlation of the pore effective radius (PAL experiments) and α parameter from TSL experiments (see the text) [38] for a number of membrane materials (left) and including some cross-linked polystyrenes (right) [31].

6. Low-temperature gas sorption (LTGS). When PALS does not see some of the free volume elements in polymer

Positron annihilation lifetime spectroscopy is a recognized method for studying nanoporosity in solids. However, until recently [38-40], no attempts were made to estimate the concentration limits of sensibility of this method to elementary free volumes. The reason was that no alternative methods applied to the same problem were discussed.

One of the most popular methods is low-temperature gas sorption (LTGS). The results of several investigations by Yampolskii et al. [41,42] of polymer membrane materials and sorbents were considered. PALS and LTGS methods were applied to the same objects in those papers. Some practical recommendations for the studies of this type were discussed.

All nanoporous polymers were ranked in Table 2 [41,42] according to the pore size (micropore and mesopore) and condition of the material (ready-made membrane or powder). The last specificity (condition) springs up because the process of membrane casting can change the accessible free surface to slow down an adsorption rate. Therefore, four kinds of objects were distinguished (cells 1-4 in Table 2) [41, 42].

Table 2
Applicability of PALS and LTGS methods to studying nanoporous polymer materials.

Dispersion	Pore width	
	Micropores (<2 nm)	Mesopores (2-50 nm)
Powder	(1) LTGS (HK, SF), sorbate CO ₂ PALS	(3) LTGS (BJH), sorbate N ₂
	(2) PALS	(4) LTGS (BJH), sorbate N ₂ ; Swelling with Sc-CO
Membrane (film)		

The table indicates the proper method for the different materials. The Horvath-Kawazoe (HK) and Saito-Foley (SF) methods were applied to CO₂ sorption - desorption isotherms for calculating the micropore size distribution PSD (1, 2). The mesopore distributions (cells 3, 4) were found using the BJH (Barrett- Joyner- Halenda) method and N₂ sorption. The inscription "swelling with Sc-CO₂" for membrane mesopores (cell 4) means LTGS experiment on mesopores in polymers swelled by CO₂ in a super-critical state (7.38 MPa, 31.1°C) [40]. Different conditions determine the possibility of applying each of the two methods for EFV studies. For PALS, the critical point is the concentration of the positronium trapping centers (10¹⁸ - 10²⁰ g⁻¹), which has to be enough to localize the *o*-Ps atom before annihilation. For LTGS measurements, the crucial point is the rate of polymer saturation with gas. In groups 1 and 2 (Table 2), CO₂ gas is used as a sorbate for the study instead of N₂. The reason is briefly explained. Traditionally, N₂ adsorption at 77.4 K is applied. However, it is known that at such a low temperature, nitrogen diffusion into micropores is extremely slow. In this case, the diffusion limitations can affect adsorption in ultramicropores (width *w* is less than 0.7 nm). For porous carbons, for example, containing a wide range of micropores, a correct PSD study may require very long measurements. It has been established that studying CO₂ adsorption at 273.15K (0°C) can overcome such difficulties. The CO₂ vapor pressure at zero temperature (*p*₀) is very high (26141 torr). Therefore, the low relative pressure (*p*/*p*₀) necessary for the analysis of micropores is achievable at moderate absolute pressures (1-760 torr). In this case, CO₂ molecules more quickly than N₂ at 77.4 K, reach micropores, although the sizes of adsorbate molecules are almost the same. Thus, measurements can be performed without requiring vacuum equipment and for a shorter time than in the case of N₂.

For nitrogen on porous carbon, adsorption occurs already at *p*/*p*₀=10⁻⁶ and makes about 20% of the total, whereas the adsorption of CO₂ begins at *p*/*p*₀=10⁻⁴.

Let's consider the example of mesoporous powder (cell 3 in Table 2), where the LTGS (N₂) method is recommended. The polymeric sorbents are the heterogeneous copolymers of mesoporous divinylbenzene (MD) with low-molecular-weight rubbers, such as polyisoprene (MD/PI) or polybutadiene (MD/PB). An example of mesopore widths distribution of MD/PB (7%) is given in Fig. 9 [39].

Fig. 9 is a histogram, each point of which contributes to the total volume of pores with a diameter in the interval of 1 nm (see, for example, the shaded interval in Fig. 9). This result is understandable. The ordinate dimension is [cm³g⁻¹nm⁻¹]. The most characteristic mesopores for the chosen material are beyond the limit of detection of the positron annihilation method (shaded interval in Fig. 9). The value of effective pore width *D*₄^{PAL} [nm] found for the

longest-lived positronium component τ_4 is significantly less than the D_{av}^{BJH} values determined by LTGS technique. This result is understandable. In Fig. 9, the contributions of free volumes from pores with *D*=3 and *D*=20 nm are approximately the same, but the concentration of the latter pores is reduced (by approximately 300 times!) since it is inversely proportional to the cubic radius. Accordingly, the probability of Ps trapping in them before annihilation is low. The values of the maximum diameter *D*₄ of the positronium detectable pores and the information on the volume *V*₄ were used again to determine the diffusion coefficient of nonlocalized positronium *D*^{Ps} (see Eq (1)) in the polymer. It has been used the relation $D^{Ps} = L^2/6\tau$, where $L = N_4^{(1/3)}$ is equal to the diffusion length of an untrapped positronium atom. For the MD/PB this gives 3×10⁻⁴ cm²/s, which does not contradict previous estimations.

Similar conclusions were made in the studies of the effect of supercritical carbon dioxide on the nanoporosity of polyhexafluoropropylene (PHFP) [40], related to box 4 in Table 2. Again, the positron annihilation technique was used in combination with LTGS (N₂) method. A comparison of measurement results has shown that the change in permeability of the swelled material is mainly due to mesopores. There are PALS detectable changes in micropores, but they are most likely secondary in character and are not responsible for changes in permeability.

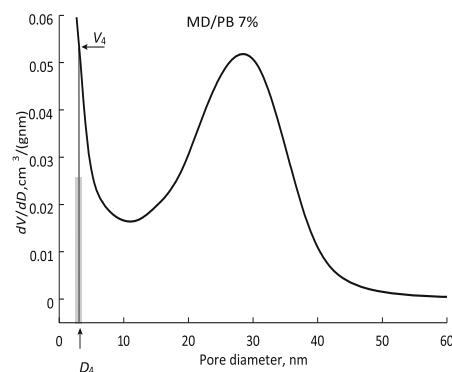


Fig. 9. Comparison of positron annihilation (shaded interval) and sorption data on pore size distribution in the MD/7% PB copolymer [39].

7. LTGS and PALS data and multimodality of the micropore size distribution

Two recent papers [43,44] on this topic were completed by coworkers of Yu.P. Yampolskii, unfortunately without his participation, but influenced by the same ideology. The nature and character of the size distribution of micropores in several membrane materials, particularly polynorbomenes containing in the side chain with several substituent groups, were studied using CO₂ sorption and PALS data. Here we are in box 1 of Table 2. Let's remember that the local stiffness of highly permeable glassy polymers suggests they are microheterogeneous. In this case, bimodal distributions seem quite possible, although unimodal asymmetric cases cannot be excluded. The positron annihilation sorption data agree in most cases. However, sometimes there are discrepancies. These are explained by the limited mobility of the positronium atom or by the inaccuracy of the description of the sorption curve according to density fluctuation theory (NLDFT) and Monte Carlo Method. Let's consider the results in some detail. Substituted polynorbomenes are promising for fabricating gas separation membrane materials [45]. Their general chemical structure is given in Fig. 10 [43].

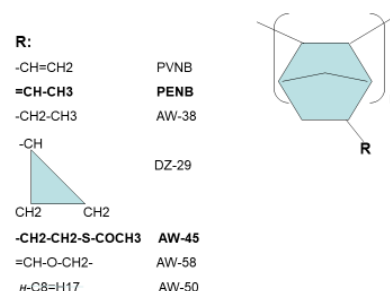


Fig.10. The investigated polynorbomenes with various substituents R. Given in bold are two materials that were studied using both (PALS and LTGS (CO₂) methods [43].

Fig. 11 (a, b) [43] shows the obtained micropore size distribution (PSD) and cumulative free volume of micropores for polyvinylnorbornene (S-PVNB) using data processing by density fluctuation theory (NLDFT) (a) and Monte Carlo (GCMC) theory (b).

As is seen in Table 3 [42], and expected from the previous considerations, the most permeable materials PVNB, PENB, and H-PVNB have two *ortho*-positronium components τ_3 , I_3 , and τ_4 , I_4 , indicating a bimodal size distribution

of micropores widths of $d_3 = 0.6$ nm and $d_4 = 0.9 - 1.0$ nm. According to the sorption data, the same values correspond to the width of micropores. The problem, however, is that for the rest (low-permeability) norbornenes in Table 3, PALS distributions are *unimodal* (one *ortho*-positronium component τ_3 , I_3), but sorption measurements lead to *bimodal* distributions, just as for polyvinylnorbornene (see, for example, PENB in Table 4 [43]).

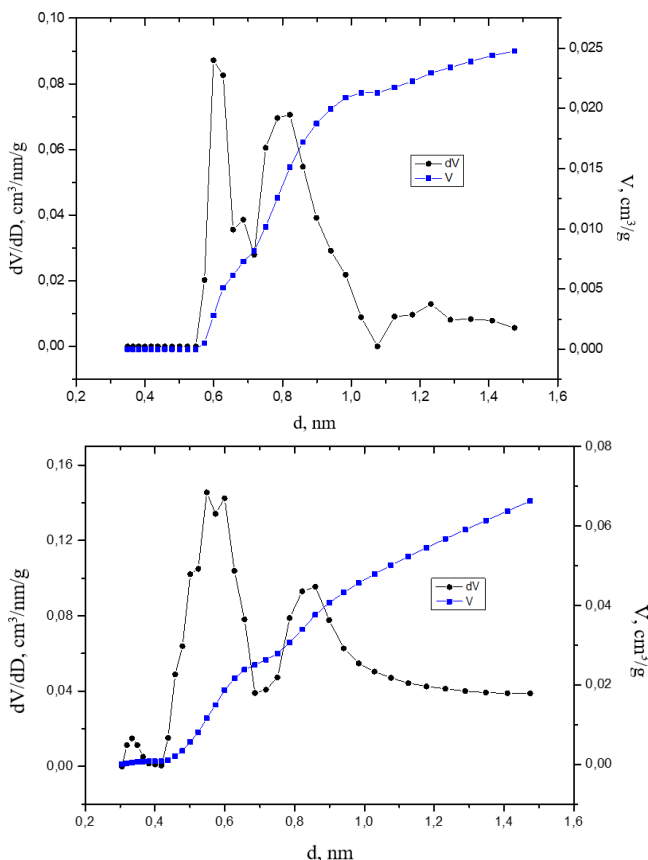


Fig. 11. Pore size distribution dV and cumulative free volume V of micropores found using CO_2 sorption and data processing by density fluctuation theory (NLDFT) - (above), and Monte Carlo (GCMC) theory - (below) for a polyvinylnorbornene sample (S-PVNB, or AW-45, see Fig. 11) [43].

Table 3

Oxygen permeation $P(\text{O}_2)$, annihilation characteristics, and calculated effective pore radii (R_3, R_4) of polynorbornenes shown in Fig. 11 [43].

Polymer	$P(\text{O}_2)$, Barrer	τ_3 , ns	I_3 , %	R_3 , Å	τ_4 , ns	I_4 , %	R_4 , Å
PVNB	48.3	2.27 ± 0.18	15.48 ± 2.96	3.10	4.33 ± 0.14	24.92 ± 2.75	4.5
PENB	80	2.68 ± 0.11	23.77 ± 2.04	3.45	5.28 ± 0.25	14.51 ± 2.18	5.0
AW-38 (H-PVNB)	72	2.06 ± 0.15	11.88 ± 1.27	3.00	4.49 ± 0.12	18.64 ± 1.47	4.57
DZ-29 (Cp-PVNB)	70	2.08 ± 0.14	14.82 ± 1.61	3.00	4.32 ± 0.12	21.31 ± 1.82	4.5
AW-45 (S-PVNB)	1.3	2.23 ± 0.01	24.99 ± 0.15	3.10	-	-	-
AW-58 (O-PVNB)	7.6	2.38 ± 0.02	10.06 ± 0.09	3.20	-	-	-
AW-50 Octyl NB	16.8	2.64 ± 0.01	30.63 ± 0.14	3.45	-	-	-

Table 4

Characterization of micropores AW-45 and PENB samples according to sorption data; V_f is the total volume of adsorbed gas at $p/p_0 = 0.02889$ (753 mm Hg); V_{mic} , d , and S are the micropore volume, diameter, and surface area respectively, calculated by the NLDFT and Monte Carlo methods, and p_0 is the saturated vapor pressure of CO_2 at 273 K [43].

Sample	V_f , cm^3/g	Micropores					
		NLDFT			MC		
		d , nm	V_{mic} , cm^3/g	S , m^2/g	d , nm	V_{mic} , cm^3/g	S , m^2/g
AW-45	5.9	0.55	0.018	52	0.60	0.025	62
		0.82			0.82		
PENB	14.9	0.55	0.066	173	0.60	0.071	174
		0.86			0.82		

This contradiction has two explanations. The first one assumes that the description of the sorption curve in terms of the GCMC and MLDFIT theories by a set standard isotherm [46] for low-permeability polymers is not correct enough, which is subject to further verification.

Similarly, comparable LTGS results for some other polymer membrane materials were recently published by Weber and Elmehalmey [47,48]. The second explanation is that a nonlocalized positronium atom does not have enough time to find larger (more distant from each other) pores before annihilation. Therefore, PALS does not detect the component of larger pores in these cases. For a specific description, let's again use the formula (1) for the mobility of nonlocalized positronium (D_{Ps}^f ; $\tau_f = 0.3 \times 10^{-9}$ s).

The values of the total free volumes corresponding to the individual components of the bimodal distributions (Fig. 11) can be determined from the curves of the cumulative free volume V_{mic} (Table 4, Fig. 11) by the inflection of the curve. These components can be indexed by analogy with positronium components ($V_{mic} = V_3 + V_4$). For example, in AW-45, $V_3 = 0.010$ cm³/g and $V_4 = 0.008$ cm³/g. The single pore volumes (v_3 , v_4) can be found from the corresponding radii R_3 and R_4 (Table 3). The condition for observing the single *ortho*-positronium component in the presence of the two sorption peaks (*bimodal* distribution) depends on the diffusion length LPs of nonlocalized positronium

$$[v_3/(\rho V_3)]^{1/3} < L_{Ps} < [v_4/(\rho V_4)]^{1/3} \quad (5)$$

That is, nonlocalized positronium diffusion length LPs should be greater than the distance between pores of the first group and less than the distance between pores of the second group. Assuming that the density of the material ρ is 1 gcm⁻³ for AW-45, the length of LPs is between 2 nm and 3 nm. Therefore, according to Eq.1, DP in this substance are in the interval $(0.3 - 0.6) \times 10^{-4}$ cm²/s, which does not contradict the earlier estimates [20, 42].

Thus, the second explanation seems also valid, and it is still impossible to draw a conclusion about the reason for the revealed discrepancies between the data of the two methods on the character of the size distribution of micropores. Investigations must be continued.

Conclusions

This short and unusual review highlights the work performed by Yuri Pavlovich Yampolskii on the free volume determined using positron annihilation and its remarkable achievements. However, some points are still to be explored, but, unfortunately, without the contribution of Yuri Pavlovich Yampolskii, the enthusiastic leader who was the creator and engine of this scientific direction for years.

Indeed, there is confidence that these studies will be successfully continued by his assistants, his students, the researchers of his laboratory of membrane materials, and colleagues in other institutions spread worldwide.

References

- [1] V.I. Goldanskii, Physical chemistry of positron and positronium, *At. Energy Rev.* 6(2) (1968) 3-148. <https://www.iaea.org/publications/1934/atomic-energy-review-vol-6-1968-no-2>
- [2] H.J. Ache, Positronium and Muonium Chemistry, *Adv. in Chem. Series.* 175, American Chemical Society, Washington, D.C., 1979.
- [3] J. Green, J. Lee. Positronium Chemistry, Academic Press Inc., New York, 1964.
- [4] D.M. Schrader, Y.C. Jean, Positron and Positronium Chemistry, Elsevier, Amsterdam, 1988.
- [5] A.T. Stewart, L.O. Roellig, Positron Annihilation, *Proc. Conf. held at Wayne State University on July 27-29, 1965, 1st Ed.*, Academic Press, New York, 1967.
- [6] Y.C. Jean, Positron and Positronium Chemistry, *Proc. 3rd Workshop on Positron and Positronium Chemistry, Milwaukee, USA on July 15-18, 1990*, World Scientific Publishing Company, Singapore, 1990.
- [7] O.E. Mogensen, Positron Annihilation in Chemistry, Springer Series in Chemical Physics, Springer-Verlag, Berlin, Heidelberg, 1995.
- [8] S.J. Tao, Positron Annihilation in Molecular Substances, *J. Chem. Phys.* 56 (1972) 5499. <https://doi.org/10.1063/1.1677067>
- [9] M.M. Eldrup, D. Lightbody, J.N. Sherwood, The Temperature Dependence of Positron Lifetimes in Solid Pivalic Acid, *Chem. Phys.* 63 (1981) 51-58. [https://doi.org/10.1016/0301-0104\(81\)80307-2](https://doi.org/10.1016/0301-0104(81)80307-2)
- [10] V.A. Onischuk, V.S. Pudov, V.P. Shantarovich, L.L. Yasina, Investigation of oxidized polymers using a positron annihilation technique, *Polym. Sci. U.S.S.R.* 24(12) (1982) 2966-2971. [https://doi.org/10.1016/0032-3950\(82\)90251-9](https://doi.org/10.1016/0032-3950(82)90251-9).
- [11] A.V. Goldanskii, V.A. Onischuk, V.P. Shantarovich, Some Principles of the Studies of Positron Annihilation in Polymer Systems, *Phys. Stat. Sol.* A559 102(2) (1987) 559-564. <https://doi.org/10.1002/psa.2211020212>
- [12] Gas Separation Parameters of Glassy Polymers. Inform Register of Russian Federation № 3585, 1998. http://www.ips.ac.ru/index.php?option=com_content&task=view&id=853&Itemid=1&lang=english
- [13] V.V. Volkov, A.V. Goldanskii, S.G. Durgar'yan, V.A. Onischuk, V.P. Shantarovich, Yu. Yampolskii, A positron annihilation method of studying the microstructure of polymers in relation to their diffusional properties, *Polym. Sci. U.S.S.R.* 29(1) (1987) 217-224. [https://doi.org/10.1016/0032-3950\(87\)90104-3](https://doi.org/10.1016/0032-3950(87)90104-3)
- [14] P. Kirkegaard, M. Eldrup, O.E. Mogensen, N.J. Pedersen, Program system for analysing positron lifetime spectra and angular correlation curves, *Comp. Phys. Comm.* 23(3) (1981) 307-335. [http://doi.org/10.1016/0010-4655\(81\)90006-0](http://doi.org/10.1016/0010-4655(81)90006-0)
- [15] R.B. Gregory, Analysis of positron annihilation lifetime data by numerical Laplace inversion: Corrections for source terms and zero-time shift errors, *Nucl. Instrum. Methods Phys. Res. A*, 302(3) (1991) 496-507. [https://doi.org/10.1016/0168-9002\(91\)90367-Y](https://doi.org/10.1016/0168-9002(91)90367-Y)
- [16] A. Shukla, M. Peter, L. Hofmann, Analysis of positron lifetime spectra using quantified maximum entropy and a general linear filter, *Nucl. Instrum. Methods Phys. Res. A*, 335(1-2) (1993) 310-317. [https://doi.org/10.1016/0168-9002\(93\)90286-Q](https://doi.org/10.1016/0168-9002(93)90286-Q)
- [17] V.P. Shantarovich, Yu.A. Novikov, Z.K. Suptel, I.B. Kevdina, T. Masuda, V.S. Khotimskii, Yu. Yampolskii, Influence of deformation and chemical structure on elementary free volumes in glassy polymers, *Radiat. Phys. Chem.* 58(5-6) (2000) 513-520. [http://doi.org/10.1016/S0969-806X\(00\)00209-7](http://doi.org/10.1016/S0969-806X(00)00209-7)
- [18] V.P. Shantarovich, Z.K. Azamatova, Yu.A. Novikov, Y. Yampolskii, Free-volume distribution of high permeability membrane materials probed by positron annihilation, *Macromolecules*, 31(12) (1998) 3963-3966. <http://doi.org/10.1021/ma971128c>
- [19] S.V. Stepanov, V.M. Byakov, Physical, and Radiation Chemistry of the Positron and Positronium, In: Y.C. Jean, P.E. Mallon, D.M. Schrader (Eds.), Principles and Applications of Positron and Positronium Chemistry, World Scientific: New Jersey-London- Singapore-Hong Kong, 2003, pp.117-149. <https://doi.org/10.1142/5086>
- [20] V.P. Shantarovich, Positron annihilation and free volume studies in polymer glasses, *J. Polym. Sci. B Polym. Phys.*, 46(23) (2008) 2485-2503. <http://doi.org/10.1002/polb.21602>
- [21] G. Dlubek, K. Saarinen, H.M. Fretwell, The temperature dependence of the local free volume in polyethylene and polytetrafluoroethylene: A positron lifetime study, *J. Polym. Sci. B Polym. Phys.*, 36(9) (1998) 1513-1528. [http://doi.org/10.1002/\(SICI\)1099-0488\(19980715\)36:9<1513::AID-POLB9>3.0.CO;2-K](http://doi.org/10.1002/(SICI)1099-0488(19980715)36:9<1513::AID-POLB9>3.0.CO;2-K)
- [22] G. Dlubek, V. Bondarenko, J. Piontek, M. Supej, A. Wutzler, R. Krauze-Rehberg, Free volume in two differently plasticized poly(vinyl chloride): A positron lifetime and PVT study, *Polymer* 44(6) (2003) 1921-1926. [https://doi.org/10.1016/S0032-3861\(03\)00056-9](https://doi.org/10.1016/S0032-3861(03)00056-9)
- [23] G. Consolati, I. Genko, M. Pegoraro, L. Zanderighi, Positron annihilation lifetime (PAL) in poly[1-(trimethyl-silyl)propine] (PTMSP): Free volume determination and time dependence of permeability, *J. Polym. Sci. B Polym. Phys.*, 34 (1996) 357-357. [https://doi.org/10.1002/\(SICI\)1099-0488\(19960130\)34:2<357::AID-POLB17>3.0.CO;2-I](https://doi.org/10.1002/(SICI)1099-0488(19960130)34:2<357::AID-POLB17>3.0.CO;2-I)
- [24] K. Hirata, Y. Kobayashi, Y. Ujihira, Diffusion coefficients of positronium in amorphous polymers, *J. Chem. Soc. Faraday Trans.*, 92(6) (1996) 985-988. <https://doi.org/10.1039/FT9969200985>
- [25] J.D. McGervey, Z.B. Yu, A.M. Jamieson, R. Simha, Computer Simulation of Positron Lifetime Distributions, *Mater. Sci. Forum*, 175-178 (1995) 727-730. <https://doi.org/10.4028/www.scientific.net/MSF.175-178.727>
- [26] G. Dlubek, S. Eichler, C. Hubner, C. Nagel, Does the MELT program accurately reveal the lifetime distribution in polymers? III. Effects due to an e+ lifetime distribution, *Phys. Stat. Sol. A*, 174(2) (1999) 313-325. [http://doi.org/10.1002/\(SICI\)1521-396X\(199908\)174:2<313::AID-PSSA313>3.0.CO;2-2](http://doi.org/10.1002/(SICI)1521-396X(199908)174:2<313::AID-PSSA313>3.0.CO;2-2)
- [27] G. Dlubek, S. Eichler, Do MELT or CONTIN programs accurately reveal the o-Ps lifetime distribution in polymers? Analysis of simulated lifetime spectra, *Phys. Stat. Sol. A*, 168(2) (1998) 333-350.

- [http://doi.org/10.1002/\(SICI\)1521-396X\(199808\)168:2<333::AID-PSSA333>3.0.CO;2-V](http://doi.org/10.1002/(SICI)1521-396X(199808)168:2<333::AID-PSSA333>3.0.CO;2-V)
- [28] M. Rudel, J. Krauze, K. Ratzke, F. Faupel, Yu. Yampolskii, V. Shantarovich, G. Dlubek, Temperature Dependence of Positron Annihilation Lifetimes in High Permeability Polymers: Amorphous Teflons AF, *Macromolecules*, 41(3) (2008) 788-795. <https://doi.org/10.1021/ma071563z>
- [29] Y. Ito, H.F.M. Mohamed, V.P. Shantarovich, T. Suzuki, Vacancy Spectroscopy Using Positronium. What are we Looking at by Positronium in Polymers, *Membrane*, 34(4) (2009) 164-278. https://www.jstage.jst.go.jp/article/membrane/34/4/34_164/_pdf
- [30] D. Hofmann, M. Entrialgo-Costano, A. Lerbret, M. Heuchel, Yu. Yampolskii, Molecular Modeling Investigation of Free Volume Distributions in Stiff Chain Polymers with Conventional and Ultrahigh Free Volume: Comparison between Molecular Modeling and Positron Lifetime Studies, *Macromolecules*, 36(22) (2003) 8528-8538. <https://doi.org/10.1021/ma0349711>
- [31] M. Mazo, N. Balabaev, A. Alentiev, Yu. Yampolskii, Molecular Dynamics Simulation of Nanostructure of High Free Volume Polymers with SiMe₃ Side Groups, *Macromolecules*, 51(4) (2018) 1398-1408. <http://doi.org/10.1021/acs.macromol.7b02470>
- [32] V.P. Shantarovich, Suzuki, C. He, V.A. Davankov, A.V. Pastukhov, M.P. Tsurupa, K. Kondo, Y. Ito, Positron Annihilation Study of Hyper-Cross-Linked Polystyrene Networks, *Macromolecules*, 35(26) (2002) 9723-9729. <http://doi.org/10.1021/ma020615b>
- [33] V.E. Ryzhikh, A.Yu. Alentiev, Yu. Yampolskii, Relation of gas-transport parameters of amorphous glassy polymers to their free volume: Positron annihilation study, *Polym. Sci. A*, 55 (2013) 244-252. <https://doi.org/10.1134/S0965545X13040068>
- [34] A.Yu. Alentiev, I.A. Ronova, B.V. Schukin, Yu. Yampolskii, Correlation between the transport behavior of polyimides and the conformational rigidity of their chains, *Polym. Sci. A*, 49 (2007) 217-226. <https://doi.org/10.1134/S0965545X07020162>
- [35] A.V. Tokarev, G.N. Bondarenko, Yu. Yampolskii, Chain structure, and stiffness of Teflon AF glassy amorphous fluoropolymers, *Polym. Sci. A*, 49 (2007) 909-920. <https://doi.org/10.1134/S0965545X0708007X>
- [36] S.A. Pavlova, I.A. Ronova, G.I. Timofeeva, L.V. Dubrovina, On the flexibility of cyclochain polymers, *J. Polym. Sci. B Polym. Phys.*, 31 (1993) 1725-1757. <https://doi.org/10.1002/polb.1993.090311208>
- [37] V. Shantarovich, V. Gustov, A. Polyakova, E. Belousova, M. Filimonov, Yu. Yampolskii, Positron annihilation lifetime data and actual porosity of polymers, *Phys. Stat. Sol. C*, 6 (2009) 2387-2391. <https://doi.org/10.1002/pssc.200982057>
- [38] V.P. Shantarovich, V.W. Gustov, E.V. Belousova, A.V. Polyakova, V.G. Bekeshev, I.B. Kevdina, Yu.P. Yampolskii, A.V. Pastukhov, Local Rigidity as a Criterion of Gas Permeation of Polymer and Composition Materials: PAL and TSL Experiments, *Acta Phys. Pol. A*, 125(3) (2014) 806-811. <http://doi.org/10.12693/APhysPolA.125.806>
- [39] E.V. Belousova, V.G. Bekeshev, V.W. Gustov, V.A. Davankov, O.K. Krasilnikova, I.B. Kevdina, A.V. Pastukhov, M.K. Filimonov, V.P. Shantarovich, Specifics of positron studies of microheterogeneous systems as applied to new polymeric sorbents, *High Energy Chem.*, 49 (2015) 199-206. <https://doi.org/10.1134/S0018143915030042>
- [40] V.P. Shantarovich, V.G. Bekeshev, N.A. Belov, I.A. Ronova, A.Yu. Nikolaev, V.W. Gustov, I.B. Kevdina, M.K. Filimonov, Effect of supercritical carbon dioxide on nanoporous polyhexafluoropropylene, *High Energy Chem.*, 50 (2016) 287-291. <https://doi.org/10.1134/S0018143916040160>
- [41] V.P. Shantarovich, V.G. Bekeshev, I.B. Kevdina, Yu.P. Yampolskii, M.V. Bermeshev, N.A. Belov, *Acta Phys. Pol. A*, 132(5) (2017) 1548-1551. <http://doi.org/10.12693/APhysPolA.132.1548>
- [42] V.P. Shantarovich, V.G. Bekeshev, I.B. Kevdina, Yu.P. Yampolskii, M.V. Bermeshev, N.A. Belov, Nanoporosity of Polymer Membrane Materials and Sorbents According to Positron Annihilation and Low-Temperature Gas Sorption Data, *High Energy Chem.*, 52 (2018) 275-282. <https://doi.org/10.1134/S0018143918040148>
- [43] V.P. Shantarovich, V.G. Bekeshev, I.B. Kevdina, M.V. Bermeshev, A.I. Wozniak, Microporosity of Polynorbornenes by Positron Annihilation and Sorption Data *High Energy Chem.*, 55 (2021) 80-87. <https://doi.org/10.1134/S0018143921010112>
- [44] V.P. Shantarovich, V.G. Bekeshev, M.V. Bermeshev, D.A. Alentiev, V.W. Gustov, E.V. Belousova, I.B. Kedina, Yu.A. Novikov, Study of Microporosity of Polymer Glasses Using Techniques of Positron Annihilation and Low-Temperature Sorption of Carbon Dioxide, *High Energy Chem.*, 53 (2019) 276-281. <https://doi.org/10.1134/S0018143919040118>
- [45] A.I. Wozniak, E.V. Bermesheva, I.L. Borisov, D.I. Petukhov, M.V. Bermeshev, A.V. Volkov, E.S. Finkelshtein, Addition Polyalkylnorbornenes: A Promising New Class of Si-Free Membrane Materials for Hydrocarbons Separation, *Macromol. Rapid Commun.* 40(20) (2019) 1900206. <https://doi.org/10.1002/marc.201900206>
- [46] *NOWAWIN2 Version 2.1: operating Manual*, Boynton Beach, FL: Quantachrome Instruments, 2004.
- [47] J. Weber, Du. Najying, M.D. Guiver, Influence of Intermolecular Interactions on the Observable Porosity in Intrinsically Microporous Polymers, *Macromolecules*, 44(7) (2011) 1763-1767. <https://doi.org/10.1021/ma101447h>
- [48] W.A., Elmehalmey, R.A. Azzam, Y.S. Hassan, M.H. Alkordi, T.M. Madkour, Imide-Based Polymers of Intrinsic Microporosity: Probing the Microstructure in Relation to CO₂ Sorption Characteristics, *ACS Omega*, 3(3) (2018) 2757-2764. <https://doi.org/10.1021/acsomega.7b02080>