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ORIGINAL CONTRIBUTION

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Free volume microstructure of amorphous polymers at glass transition temperatures from positron annihilation spectroscopy data

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Abstract The analysis of annihilation characteristics of ortho-positronium at conventional calorimetric glass transition temperatures for a series of amorphous polymers reveals empirical correlations of average lifetime of o-Ps $\bar{\tau}_{3g}$, and of its product with a relative intensity I_{3g} with appropriate T_g^{DSC} values. These trends in terms of free volume mean that both the average size of free volume hole entity $\bar{v}_{hg}$ and the fractional free volume grow with increasing T_g^{DSC}. The results are discussed considering the chemical microstructure as well as possible mechanisms acting in glass transition. A relation is indicated between geometric and flexibility characteristics of chains and the $\bar{v}_{hg}$ and f_g parameters of free volume microstructure on the one side and potential motional processes responsible for solidification of the amorphous system on the other side.

Key words Free volume – glass transition – amorphous polymers – positron annihilation

Introduction

The structure of amorphous state and the origin of the glass transition process appear to be one of the key problems of the physics of disordered systems, especially polymers [1, 2]. The phenomenon is in fact the solidification of a liquid into a glassy state without crystallization, characterized by a sharp change of first derivations of macroscopic thermodynamic parameters such as volume and enthalpy measured by dilatometry [3] and calorimetry [4], respectively. For practical reasons the phenomenon is characterized by one value so-called glass transition temperature T_g in spite of the fact that it always occurs in certain temperature range [5]. Structural studies in the glass transition region did not reveal any difference between liquid and glassy state; both are characterized by an existence of short-range order [1, 2, 6]. On the other hand, the mentioned states differ significantly from each other in the values of structural relaxation times as measured by, for example, viscosity [1, 2]. Extensive phenomenological research revealed a kinetic origin of the process manifesting itself by a dependence of T_g on the time scale of the experimental equipment used [3–5]. T_g is defined operationally as a temperature at which the time scale of the experiments is related to the viscosity 10^{13} P. A large number of models and theories has been suggested for the description and explanation of experimental data as documented, for example, by reviews [5, 7–9]. Computer simulations based on more or less realistic multichain systems have been involved in the investigation recently as well [10, 11].

One of the pseudomolecular approaches to the structure of amorphous state and glass transition is based on a conceptionally simple and intuitively acceptable idea regarding the relation between so-called free volume and molecular mobility [12–23]. At present, the free volume characteristics of condensed phase can be directly measured using positron annihilation lifetime spectroscopy (PALS) [24, 25].

This paper is aimed to an analysis of data obtained by conventional PALS measurements on mean lifetime $\bar{\tau}_3$ and relative intensities of o-Ps I_3 for a series of amorphous polymers at T_g^{DSC}. An effort was devoted to reveal the relations between chemical and physical free volume microstructures. It is assumed that this approach can contribute to a better look at microstructural-dynamical relations at T_g; thus, molecular aspects responsible for the phenomenon may be better understood.

Background

Comparative success of the free-volume idea is connected with its versatility given by an existence of various operational definitions of free volume. These can be generalized in a relation:

$$V_f(T) = V(T) - V_0 , \tag{1}$$

where $V(T)$ is macroscopic volume of the system at the temperature T and V_0 is so-called occupied volume postulated as either 1) van der Waals volume – empty free volume $V_f^e(T)$, 2) occupied volume at 0 K – expansion free volume $V_f^{exp}(T)$ or 3) fluctuation free volume swept out by the center of gravity of the molecule as a result of thermal motion [15, 20]. In early stages a further parameter was introduced, the so-called fractional free volume:

$$f(T) = \frac{V_f(T)}{V(T)} , \tag{2}$$

and an isofree-volume concept of the glass transition was formulated using isobaric coefficients of the volume expansion in glassy α_g and elastic state α_l [12, 16]. A limited validity of this concept was revealed by later analysis resulting in a conclusion that $f_g \equiv f(T_g)$ is linearly growing in dependence on increasing T_g [18, 19].

More reliable correlations and quantifications of the relations between the free volume and glass transition temperature require direct measurements of free-volume characteristics of the polymers. At present, this can be reached using PALS, which, due to small dimensions of ortho-positronium o-Ps, is sensitive to small holes in Å range for times of molecular motions $> 10^{-9}$ [24, 25]. The annihilation of o-Ps in a spherical hole may be described by a quantum-mechanical model of spherical potential well with an electron layer ΔR [26]. This model leads to a semiempirical dependence of the lifetime of o-Ps τ_3 on the radius of the hole R:

$$\tau_3 = \frac{1}{2}\left[1 - \frac{R}{R_0} + \frac{1}{2\pi}\sin\frac{2\pi R}{R_0}\right]^{-1} \tag{3}$$

where $R_0 = R + \Delta R$. The parameter $\Delta R = 1.66$ Å was obtained by curve-fitting of experimental values τ_3 of materials with known size of holes, e.g., molecular crystals and zeolites. A relative intensity of o-Ps I_3 is another quantity measurable by PALS method. A relation between this parameter and a fractional free volume detectable by o-Ps is given by the equation:

$$f_h(T) = C \cdot \bar{\tau}_3(T) \cdot I_3(T) , \tag{4}$$

C being a coefficient dependent on the mode of calibration using experimental or theoretical quantities [27–30], such as expansion coefficient difference $\Delta\alpha$ at T_g [27], $\Delta\alpha$ at low temperature transitions [28] and hole fraction at T_g from fitting of hole model [29] on pVT behavior of polymers [30]. The methods [27] and [30] are model-dependent; f_h is calibrated to the free volume change related to glass transition while the method described in [28] is assumed to be based on the overall free volume accessible to o-Ps unlike the former methods considering only the dynamical contribution related to glass transition.

Analysis and discussion

Empirical correlations

Annihilation data of o-Ps have been analyzed for 13 amorphous polymers covering sufficiently broad range of glass transition temperatures T_g^{DSC}. The set of polymers is formed by typical diene elastomers with very low T_g values, vinyl elastomers and vinyl thermoplastics with intermediate T_g's as well as aromatic polymers with phenyl moieties in main chains or side groups with high T_g values. The range of T_g^{DSC} is from 170 to 470 K. The $\bar{\tau}_{3g}$ and I_{3g} data at given glass transition temperatures have been found from the temperature dependencies of both annihilation parameters [31–39]. The results are summarized in Figs. 1 and 2 and in Table 1.

As seen in Fig. 1, the mean lifetime of o-Ps at glass transition temperature is rising with increasing T_g^{DSC}. This trend can be described by a linear empirical relation:

$$\bar{\tau}_{3g} = A_\tau \cdot T_g^{DSC} + B_\tau , \tag{5}$$

where $A_\tau = 4.13 \times 10^{-3}\ \mathrm{K ns^{-1}}$ and $B_\tau = 0.736$ ns. The value of correlation coefficient $k = 0.948$ is reasonable enough regarding the fact that the data are taken from various sources. The linearity of the dependence means that the mean dimension $\bar{R}_{hg}$ of the free-volume entity at T_g of the polymer is rising from 2.2 A for low-T_g cis-1,4-PB to 3.4 Å for high-T_g TMPC. Thus, the increase of T_g of the polymer by 300 K results in a three-fold increase of the mean hole volume $\bar{v}_{hg}$ as seen from the third column in Table 1. $\bar{v}_{hg}$ divided by van der Waals volume of basic

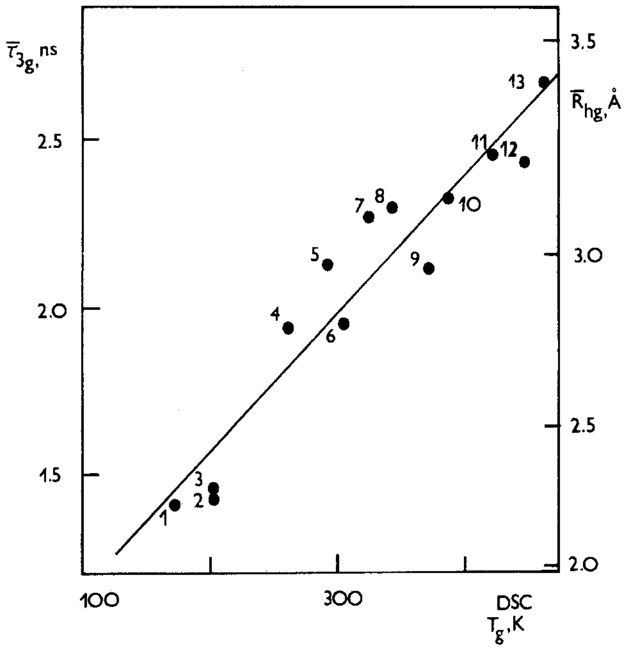

Fig. 1 The dependence of mean lifetime of o-Ps at T_g^{DSC} vs appropriate T_g^{DSC}s values of amorphous polymers described in Table 1

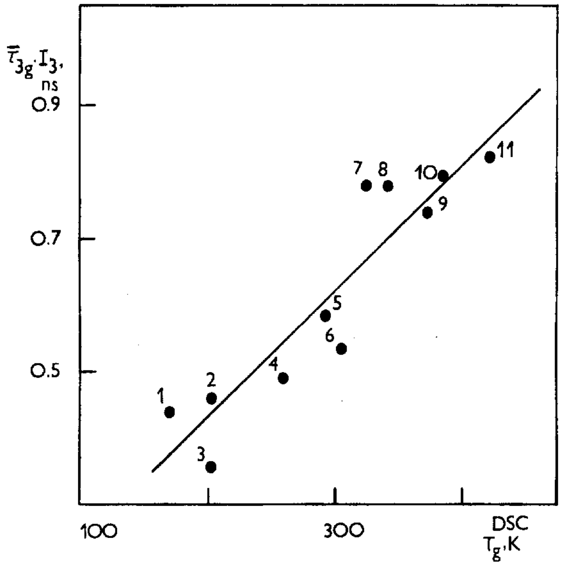

Fig. 2 The product of the mean lifetime of o-Ps and its relative intensity in dependence on the appropriate T_g^{DSC} values of amorphous polymers described in Table 1

structural unit of the polymer v_{mon}^{W} can serve as an indication of mean size of free-volume entity at corresponding T_g^{DSC}/s. v_{mon}^{W} was calculated according to a additive group method using the contributions from ref. [40]. The polymers can be divided roughly to three groups: the ratio is around one-half, or three-fourths, or between one and two times the size of monomeric unit for polycarbonates, diene elastomers or typical vinyl polymers, respectively.

An interesting finding from Fig. 1 and Eq. (5) is an observation that the intercept of the linear dependence $\bar{\tau}_{3g}$ ($T_g = 0$ K) is equal to the hole radius $\bar{R}_{h,o} = 1.14$ Å. This value corresponds well with the Bohr's radius of o-Ps being 1.06 Å.

Supposing that the relative intensity o-Ps is related to the number of holes in the solid material, the product $\bar{\tau}_3 I_3$ is proportional to fractional free volume accessible for o-Ps at given conditions [27, 28]. In Fig. 2, the dependence is shown of this value at T_g^{DSC} vs respective T_g^{DSC}. Similar to the previous case, a more or less linear increase is observed, expressed by an empirical equation:

$$\bar{\tau}_{3g} \cdot I_{3g} = A_{\tau I} \cdot T_g^{DSC} + B_{\tau I} \qquad (6)$$

for 11 polymers for which the I_3 data exist. The appropriate coefficient values are as follows $A_{\tau I} = 1.915 \times 10^{-3}$ nsK^{-1} and $B_{\tau I} = 0.045$ ns. The correlation coefficient 0.917 is quite satisfactory regarding the data from various authors. The intercept of the linear dependence $\bar{\tau}_{3g} I_{3g}$(OK) should be related to a hypothetical structural free volume of disordered phase at OK which is detectable by o-Ps.

Assuming that the proportionality coefficient between the fractional free volume f_h and the product $\bar{\tau}_3 I_3$ in Eq. (4) does not depend on the nature of the polymer, the fractional free volumes of the polymers at T_g^{DSC} can be estimated using the coefficient $C = 0.40$ ns^{-1} determined in our previous paper [28]. The results are shown in the fifth column of Table 1. The functional expression is a simple modification of Eq. (6) with the coefficients $A_f = 7.66 \times 10^{-4\,K^{-1}}$ and $B_f = 0.018$ leading to a conclusion that the fractional free volume f_{hg} is rising with enhanced T_g; within the investigated range of T_g values a 72% increase was observed. On the other hand, in the limiting case $T = 0$ K, the corresponding fractional free volume is 1.8%. Such a low value seems to be consistent with the limiting size of holes at 0 K which corresponds with the size of the o-Ps.

Our empirical correlation is quite consistent with another empirical relation of f_g vs T_g based on the difference of volume expansion coefficients at T_g [19]:

$$f_g = 1 \times 10^{-4} T_g + 0.07 \, .$$

Besides this, by application of the Simha–Somcynsky hole model [41] on the pVT behavior of a set of polymers in the glass transition region an increasing trend was observed of the fraction of vacancies $h_g = (1 - Y_g)$ with rising T_g [29]. However, the regression analysis of $h_g(T_g)$ values results in a nonphysical negative intercept of the linear dependence.

One of the common free-volume parameters frequently used for the characterization of structural situation in

Table 1 Free volume characteristics of a series of amorphous polymers at T_g's

Polymer	T_g^{DSC} a) (K)	Ref.	$\bar{v}_{hg}$ (Å^3)	$\bar{v}_{hg}/v^{w}_{mon}$ (−)	f_{hg} (−)	C_∞ a, b) (−)	f_g^e (−)
1 cis-1, 4-PB	171	31	48	0.75	0.176	5.1	0.298
2 PIB	203	32	48.5	0.70	0.142	6.6	0.304
3 cis-1, 4-PIP	203	33	50	0.61	0.183	5.5	0.309
4 a-PP	259	34	92	1.78	0.195	7.6	0.348
5 PnBMA	298	35	111	0.76	0.234	8.3	0.350
6 PVAc	306	36	93	1.21	0.214	8.8	0.363
7 PiBMA	324	35	123	0.81	0.313	12.0	0.364
8 PEMA	340	35	125	1.12	0.313	10.0	0.347
9 a-PS	373	37	108	0.98	0.296	10.8	0.340
10 a-PMMA	378	35	130	1.38	0.317	10.6	0.351
11 BPA-PC	423	38	143	0.59	0.320	2.4	0.336
12 BPZ-PC	447	39	140	0.50			
13 TMBPA-PC	465	39	166	0.54		3.1	0.368

a) Bandrup, J., Immergut, E.H. Eds. Polymer Handbook 2nd ed. Wiley & Sons, New York 1975

b) Wu S. Polym. Int. 1992, 29, 229

1-cis-1,4-poly(butadiene), 2-poly(isobutylene), 3-cis-1,4-poly(isoprene), 4-atactic poly(propylene), 5-poly(n-butyl methacrylate), 6-poly(vinyl acetate), 7-poly(isobutyl methacrylate), 8-poly(ethyl methacrylate), 9-atactic poly(styrene), 10-atactic poly(methyl methacrylate), 11-bisphenol A polycarbonate, 12-bisphenol Z polycarbonate, 13-tetramethyl bisphenol A polycarbonate

amorphous materials is a fractional empty free volume f_g^e [15]. This parameter can be calculated from the specific volume V_g at T_g and van der Waals volume V_W by a combination of Eqs. (1) and (2):

$$f^e = \frac{V(T) - V_w}{V(T)} \,. \qquad (7)$$

The results using the volume data given in [18, 19, 42 and 43] are shown in Table 1. In spite of that the values are roughly increasing with the rising T_g^{DSC}, extensive scatter of the data does prevent a formulation of a correlation similar to Eq. (6) (correlation coefficient of such an equation is only 0.70). On the other hand, the relation of $f_{hg}/f_g e$ vs T_g^{DSC} may be useful for further consideration. The result is presented in Fig. 3 and can be roughly described by an equation:

$$\frac{f_{hg}}{f_g^e} = 1.86 \times 10^{-3}\, T_g^{DSC} + 0.168 \qquad (8)$$

with a better correlation coefficient being 0.874.

A hypothetical fractional free volume at $T \to 0$ K can be estimated by extrapolation from Eq. (8). The parameter is equal to $f_g^e(0\ \mathrm{K}) = 16\%$, which is an acceptable value. On the other hand, Eq. (8) brings at least an idea of the degree of detectability of the free volume in polymers at T_g using o–Ps. Since all polymers are in the same dynamic state at T_g's ($\eta = 10^{13}$p corresponding to a structural relaxation time of the order 10^2 s) the ratio is growing with both increasing mean size at T_g and rising number of free-volume entities. Rough estimate leads to the conclusion that complete free volume should be detected by o-Ps at $T_g > 176\,^\circ$C. However, the situation is not so simple since the real effective empty free volume should be somewhat lower than f_g^e. Therefore, both limits should be understood as a rough estimation only.

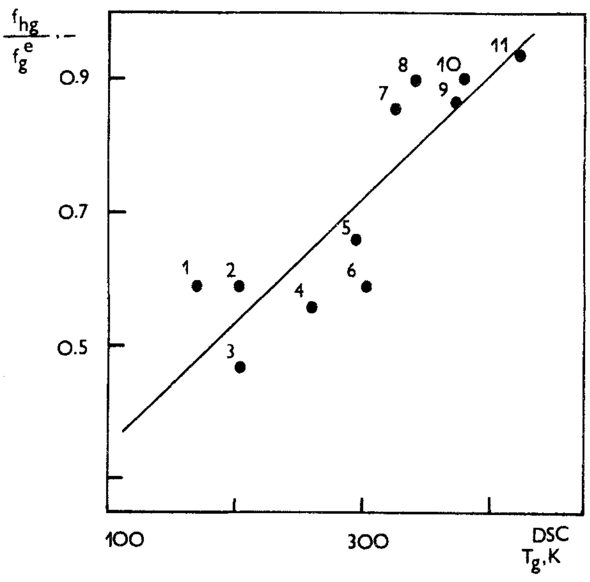

Fig. 3 The ratio of fractional hole free volume from PALS and fractional empty free volume at T_g^{DSC} in dependence on the appropriate T_g^{DSC} values of amorphous polymers described in Table 1

Relations of free volume characteristics to chemical structure and segmental mobility

From the data in Figs. 1 and 2, a conclusion can be made that larger fractional free volume f_{hg} at higher T_g is realized via larger mean free-volume entities $\bar{v}_{hg}$. Within this trend the connection can be traced of free-volume characteristics with chemical structure which determines a chain flexibility. The last parameter is often quantified by means of characteristic ratio C_∞ [44, 45]. Rather high elasticity given by low C_∞ values is observed for diene elastomers with double bonds in the main chain. This should lead to more effective packing of the structural units in a space resulting in small hole formation and low level of overall free volume; this was actually observed. Vinyl elastomers and thermoplastics are less flexible; less suitable conditions for packing in the space are expected. This leads to both larger mean holes and larger fractional free volume. On the other hand, aromatic polymers are more flexible than the polydienes, but the presence of long rigid bonds, namely phenyl rings in the main chain prevents the structural units from being more effectively packed. Lower degree of space filling is expected and, consequently, larger mean free-volume entities and higher level of fractional free volume is observed. These identifications indicate a close relation between the chemical and physical free-volume microstructure in a process of solidification. In other words, gassification of an amorphous liquid is from a structural point of view connected with a building of certain formations, i.e., free-volume entities via local configurations of structural units. The mean size and concentration of these formations is intimately connected with a particular chemical structure of the polymers. Therefore, higher number of larger holes is formed in the aromatic polymers with bulky phenyl rings in main chains, in spite of a presence of highly flexible carbonate groups; the structure freezes at higher temperature as compared to vinyl or even diene polymers.

A physical picture obtained from PALS results is consistent with some structural models and simulations of the glass transition. Thus, according to geometric cluster glass transition model [7, 46], i.e., modification of the original Tamman description of local congealing of liquid [47], the rigidification proceeds as a process of certain ordering in three stages: 1) aggregation into locally differentiated regions of comparative rigidity in a matrix of supercooled liquid, 2) impingement and freezing of these aggregates, and 3) rigidification of the mass via interlocking the clusters. In the context of the results of our analysis the aggregates can be considered as local arrangements of chain segments possessing certain free volume.

Besides this, our free-volume picture of the glassy structure at T_g is consistent with the results of recently made extensive dynamical Monte–Carlo simulations of the dense multichain systems using a bond-fluctuation model [11, 48, 49]. These calculations are based on an idea of so-called geometric frustration of chain segments due to a competition between energetic and topological constraints. According to this idea, the tendency of the chain bonds to achieve the lowest energetic state is hindered by the presence of neighboring chains. The existence of certain portion of excited bonds results from this competition; when discussing our problem, a presence of these excited bonds is a potential source of the holes between the chain segments.

From a dynamic point of view, the glass transition is considered to consist of a freezing in of certain dynamic degrees of freedom [50]. According to a free-volume concept, if a particular motional mode should proceed, an existence of certain critical free volume is required in close vicinity of the moving unit [14, 22]. The transition should occur at lower temperature if smaller holes and/or lower hole concentration is required for the critical motion mode. A comparison of mean hole volumes at T_g and appropriate van der Waals volumes of the structural units indicates that the critical mode can be the process of moving around one to two structural units (one phenyl group of the monomeric unit should be considered in the case of polycarbonates). This segmental motion is probably connected with a rotational reorientation of one to two units of libration or even conformational type. In the latter case both the localized uncorrelated transitions and some correlated transitions of Helfand's type [51] are suitable candidates of the motion mechanisms at T_g. Recent neutron scattering dynamics measurements on cis-1, 4-PB [52] as well as multidimensional ^{13}C NMR study on a- PP [53] revealed that localized conformational transitions proceed in the temperature region around glass transition. The molecular - dynamical simulation in bulk polyethylene with realistic parameters indicates the localized conformational transitions situated in T_g region [10, 54].

Finally, it should be noted that the above-mentioned empirical correlations based on the mean lifetimes of o–Ps lead to a basic understanding of the relation of free-volume microstructure and dynamics in T_g. An understanding of further phenomenological features, e.g., the range of the temperature interval needs further information on free-volume distributions in the glass transition temperature region. First experiments of this type have been recently made with a typical vinyl thermoplastic a- PS [30]. Our effort in this direction was concentrated on a typical diene elastomer 1, 4-cis-PB and typical vinyl elastomer a- PP; the results will be published in separate papers [55].

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