Positron annihilation response and viscosity of a glass-forming system within the two-order

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J Bartoš

Polymer Institute of SAS, Dúbravská cesta 9, 842 36 Bratislava, Slovak Republic

E-mail: upolbrts@savba.sk

Abstract
This paper presents a combined description of the ortho-positronium (o-Ps) response from positron annihilation lifetime spectroscopy (PALS) and viscosity data on *bis[m-(m-phenoxy) phenoxyphenyl] ether* within the free volume version of the two-order parameter (TOP) model of disordered phase. The quasi-sigmoidal form of the temperature dependence of the o-Ps lifetime, τ_3, over a wide temperature interval, can be described by an expression with the distribution function for liquid-like domains $1 - F(T)$ which follows from a phenomenological analysis of the viscosity using the modified Vogel–Fulcher–Tamman–Hesse (MVFTH) equation. This simultaneous description indicates a close connection between the PALS response and the viscosity behavior for the matrix and gives support for the liquid-like and solid-like domain physical picture of all the physical states of the disordered phase.

1. Introduction

The long-standing challenge of chemistry, physics, and materials science as related to condensed systems is to acquire a detailed understanding of the mutual relationships between chemical and physical structures and their physical properties. The structural aspect of disordered materials is often treated by means of the free volume hypothesis due to its conceptual simplicity and physical plausibility in the interpretation of thermodynamic, dynamic, and transport physical behavior [1, 2]. A sophisticated utilization of this concept requires a firm establishment of some standard method for free volume characterization. In this context, positron annihilation lifetime spectroscopy (PALS) based on the annihilation of a bound system of positron and electron with mutually parallel spins, the so-called ortho-positronium (o-Ps), is relevant. The o-Ps probe is a very sensitive indicator of the presence of local regions of reduced electron density, such as vacancies in real crystals or free volume holes in amorphous phases [3–5]. The basic o-Ps annihilation parameter, i.e. o-Ps lifetime, τ_3, is interpreted within the free volume concept as a measure of the size of these local free volume hole regions. Then, semi-empirical models are used to characterize the PALS data in terms of free volume hole characteristics such as the mean free volume hole size [6]

and free volume fraction [7–9]. Subsequently, these free volume quantities are used in correlating various dynamics and transport phenomena such as viscosity, primary α relaxation and ionic conductivity [10–16].

In general, when measured over a sufficiently wide temperature range, the PALS response of amorphous glass-forming systems, i.e. o-Ps lifetime, τ_3, as a function of temperature T, exhibits a typical quasi-sigmoidal course without or with a plateau level at relatively high temperatures [17–27]. Phenomenological model-free analysis of these τ_3–T dependences in a series of small molecular and polymeric glass-formers revealed the existence of several characteristic PALS temperatures marked according to a unified notation [13] as T_g^{PALS}, T_{b1}^{L}, and $T_{b2}^{L} = T_r$ [18] $= T_e$ [19] $= T_k$ [20], and located at $T_{b1}^{L} \sim 1.2$–$1.4 T_g^{\mathrm{PALS}}$ [12, 13, 21, 27] and $T_{b2}^{L} \sim 1.4$–$1.7 T_g^{\mathrm{PALS}}$ [12, 13, 18–20].

Evidently, the full utilization of the PALS method for the characterization of any disordered system requires a description of the τ_3–T plot as well as revealing the origin of the PALS temperatures, as completely as possible.

By phenomenological comparison with the dynamic methods such as viscosity [28] or broad-band dielectric spectroscopy [29], some progress has been achieved. Thus, it was found [18] that an onset of the higher temperature region

in PALS response at $T_{b2}^L = T_r$ lies quite close to the so-called Arrhenius temperature, T_A, above which the viscosity exhibits Arrhenius behavior [28]. Moreover, at T_{b2}^L, τ_3 is often close to the mean relaxation time of the primary α process, $\tau_\alpha(T_{b2}^L)$, from a standard peak analysis [12, 27]. A slighter change in the slope at T_{b1}^L closer to the glass transition temperature T_g is often observed [12, 13, 18, 21–23, 26] and sometimes quantified by the best linear fitting [12, 13, 21, 27]. Similarly, it is found that T_{b1}^L can be related to the temperature $T_\alpha(-6)$, at which the mean α relaxation time from DS $\tau_\alpha(T_{b1}^L)$ reaches $10^{-6\pm1}$ s [13, 27] which corresponds to the viscosity value of about $\log \eta(T_{b1}^L) \sim 4$.

In addition, theoretical [16, 30–36] as well as atomistic modeling [27, 37, 38] approaches are also relevant. In previous works [16, 30, 32, 35], attempts were made to describe the PALS data or the free volume information extracted from them via a simplified spherical quantum-mechanical model [6], as well as the primary α relaxation and the ion transport properties by means of various free volume models. However, all of these models that are based on the heterophase fluctuation model of liquids by Fischer and Bakai [30, 31], the defect diffusion model by Bendler *et al* [32, 33], the hole lattice model by Simha [16, 34], and finally the extended free volume model by Cohen–Grest [27, 35, 36] are able to describe only *certain* temperature regions of the whole PALS response that exists in a temperature range from glassy state through supercooled liquid state up to the high-temperature region T_{b2}^L. Until now, the high-temperature region has not been treated by any of the mentioned theoretical formalisms.

Recently, the two-order parameter (TOP) model has been formulated by Tanaka in an attempt to describe the numerous dynamic phenomena within a unified theoretical framework [39–42]. This model deals with disordered material over a very wide temperature range as being composed of the stable normal liquid-like regions containing locally favored structures (LFS) and their clusters, and the frustrated metastable solid-like domains. The former type of region is supposed to be dominant in low viscosity liquid and at high temperatures that are above the thermodynamic transition temperature from the ordinary liquid to the frustrated solid-like state of a supercooled liquid T_m^*. This temperature is expected to be close to the melting temperature T_m of the crystalline phase of crystallizing non-frustrated materials, which is often found to be close to the so-called Arrhenius temperature, T_A. At this temperature, going from above the crossover from the Arrhenius type to the non-Arrhenius type, the dynamical regime occurs. For example, in the case of strong glycerol, $T_A = 288$ K and $T_m = 293$ K; for fragile propylene carbonate $T_A = 218$ K and $T_m = 218$ K [42–44]. Thus, the dynamics of ordinary liquids is connected with the Arrhenius regime of the single main relaxation process [42]. Then, in the case of non-crystallizing compounds such as our 6PO system T_A instead of T_m^* might be used. The TOP model considers the liquid–glass transition to be a consequence of the competition of ordering and of the frustration effects on ordering in solid-like domains. The proportion of the frustrated solid-like domains or islands in glass-formers grows with decreasing temperature through the supercooled liquid toward the glassy state. Thus, the dynamics

exhibits a gradually heterogeneous and cooperative character that leads to the non-Arrhenius character of the viscosity or the structural relaxation. Finally, at very low temperatures below T_g, the solid-like domains are not able to reorganize and they should form the rigid glassy state. The phenomenological basis of the TOP model is given by the modified Vogel–Fulcher–Tamman–Hesse (MVFTH) equation for the viscosity which is expected to be valid over a very wide temperature range, which includes both the above-mentioned liquid-like and solid-like states [39]:

$$\eta(T) = \eta_\infty \exp[E_\eta^*/RT] \exp[BF(T)/(T - T_0)] \quad (1)$$

where $\eta(T)$ is the viscosity, η_∞ is the pre-exponent factor, E_η^* is the activation energy above $T_m^* \sim T_A$, T_0 is the divergence temperature, B is the coefficient, and $F(T)$ is a crossover function between *solid*-like and *liquid*-like domains defined as

$$F(T) = 1/\{\exp[\kappa(T - T_m^c)] + 1\} \quad (2)$$

where κ describes the sharpness of the crossover function and T_m^c is the characteristic TOP temperature, i.e. the critical temperature where the free energy of a crystallizing liquid is equal to that of crystal $\Delta G_{lq} = \Delta G_{cr}$ or, in the general case of a non-crystallizing glass-former, to that of solid $\Delta G_{lq} = \Delta G_{sol}$, where ΔG_{sol} is the free energy of the solid.

In this paper, a novel account of both the PALS and viscosity data on *bis[m-(m-phenoxy)phenoxyphenyl] ether* (6PO) is presented. We develop a free volume version of the recent two-order parameter (TOP) treatment of the disordered state [39–42] in order to describe simultaneously the viscosity data as well as the PALS response consistently within a unified theoretical framework. It will be shown that such a theoretical approach leads to a description of the whole PALS response of glass-former and gives an explanation of the above-mentioned characteristic PALS temperatures T_g^{PALS}, T_{b1}^L, T_{b2}^L, and finally contributes to a deeper understanding of the relationship between the free volume microstructure and the viscosity of the glass-forming liquid.

2. Empirical databases

2.1. Material and experimental methods

Bis[m-(m-phenoxy) phenoxyphenyl]ether (6PO) has been used as a model of a relatively small molecular glass-forming system. The reason for this choice is that this material has been already studied by both PALS and viscosity methods in [18], as well as by further relevant methods. All the datasets were obtained by digitalization of the original figures from [18].

3. Results and discussion

3.1. PALS data and their phenomenological analysis

Figure 1 displays the o-Ps lifetime, τ_3, as a function of the temperature over a wide temperature range from 208 K up to 378 K [18]. As usually observed for many small molecular and polymer glass-formers [12–27], the τ_3–T plot exhibits a quasi-sigmoidal dependence. The two most pronounced bend effects
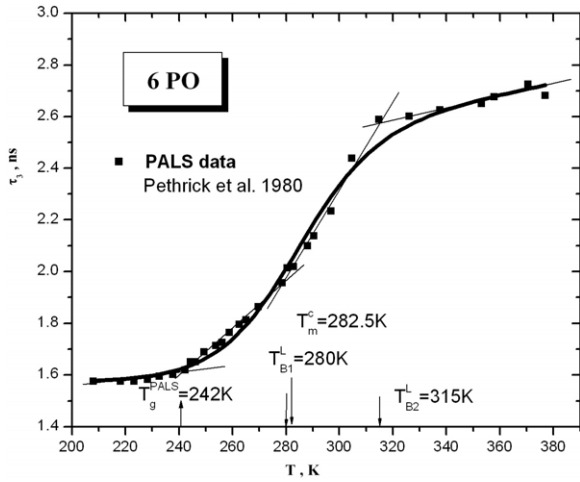
Figure 1. Ortho-positronium lifetime, τ_3, as a function of temperature for 6PO with phenomenological model-free analysis equations (3a)–(3d) using the best linear fitting providing the characteristic PALS temperatures: $T_g^{\mathrm{PALS}} = 240$ K, $T_{b1}^L = 280$ K, and $T_{b2}^L = 315$ K and fit of the FV-TOP model, equation (4), on the PALS data.

Figure 2. Application of the MVFTH expression, equation (1), on the viscosity data for the 6PO sample. The fitting parameters are given in the text.

are situated at around ∼240 and ∼315 K. Phenomenological model-free analysis of the τ_3–T dependence using the best linear regression fitting [12, 13, 21, 27] reveals the presence of four temperature regions of apparently different thermal behavior. These can be satisfactorily approximated by the following linear expressions:

for region I from 208 K up to 238 K:

$$\tau_3 = (1.01 \pm 0.16) \times 10^{-3} T + (1.355 \pm 0.037) \qquad r = 0.952 \tag{3a}$$

for region II from 242.5 K up to 278.5 K:

$$\tau_3 = (8.95 \pm 0.28) \times 10^{-3} T - (0.551 \pm 0.074) \qquad r = 0.995 \tag{3b}$$

for region III from 283 K up to 314 K:

$$\tau_3 = (1.85 \pm 0.09) \times 10^{-2} T - (3.235 \pm 0.264) \qquad r = 0.995 \tag{3c}$$

and finally, for region IV from 326 K up to 378 K:

$$\tau_3 = (2.07 \pm 0.49) \times 10^{-3} T + (1.928 \pm 0.175) \qquad r = 0.902. \tag{3d}$$

Their intersection points define the three characteristic PALS temperatures: $T_g^{\mathrm{PALS}} = 242$ K, $T_{b1}^L = 280$ K $= 1.15 T_g^{\mathrm{PALS}}$, and $T_{b2}^L = T_r$ [18] $= 315$ K $= 1.32 T_g^{\mathrm{PALS}}$. The first most pronounced characteristic PALS temperature approximately agrees with the glass temperature from classical thermodynamic methods such as dilatometry $T_g^{\mathrm{DIL}} = 248$ K [45], so that it defines the glass transition temperature as obtained by the PALS method. At low temperatures below T_g^{PALS}, the o-Ps lifetime, τ_3, reaches the relatively high value of ∼1.6 ns. This value falls into the typical range for amorphous systems with phenyl groups in molecules [46]. On the other hand, the second most pronounced characteristic PALS temperature, $T_{b2}^L = T_r$ may be related to the qualitative change in viscosity dynamics as demonstrated in [18]. At the
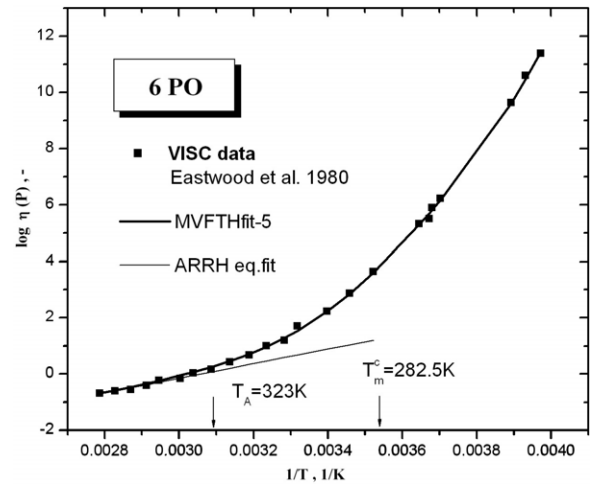
higher temperature region above T_{b2}^L, the value of $\tau_3 \sim 2.6$–2.7 ns falls into the typical range for most amorphous glass-formers [20–27]. Finally, the intermediate characteristic PALS temperature, T_{b1}^L, will be interpreted within the framework of the TOP model below.

3.2. Viscosity data and their analysis in terms of the TOP model

Figure 2 shows the viscosity as a function of the temperature for 6PO over a temperature range from 253 K up to 358 K in the Arrhenius representation adapted from [18]. The two temperature regions of distinct thermal behavior of the viscosity can be distinguished. In the high-temperature region above $T_A = 323$ K the viscosity exhibits a linear trend in the $\log \eta$ versus $1/T$ plot, indicating the approximate validity of the Arrhenius equation, which suggests thermal activation control of the viscosity at high temperatures [28]. On decreasing the temperature, the viscosity begins to deviate from the previous Arrhenius regime and starts to behave in the non-Arrhenius, fashion. The whole course of the temperature dependence of viscosity can be described using the MVFTH expression, equation (1), with the following parameters: $\log \eta_\infty = -7.96$ P, $E_\eta^* = 25.1$ kJ mol^{-1}, $B/2.3 = 322.8$ K, $\kappa = 0.0678$ K^{-1}, $T_m^c = 282.5$ K, and $T_0 = 220$ K.

3.3. Free volume version of the two-order parameter (FV-TOP) model

As mentioned in section 1, the current free volume models offered so far to describe the PALS response are not able to include all the regions of the glass-forming system, i.e. the glassy and supercooled liquid as well as the normal liquid states. Here, we propose our alternative to them represented by a free volume version of the TOP model of all the disordered states.

The TOP model is one of the special cases of the so-called two-state models [42]. In our free volume version of

the TOP model, it is assumed that the free volume detectable by the PALS method is distributed between both the physical objects forming the disordered glass-forming system over a wide temperature range: the normal liquid-like domains and the metastable solid-like regions. A fraction of the latter is given by a crossover function $F(T)$ from the MVFTH equation, so that the difference $1 - F(T)$ represents the fraction of the normal liquid-like domains. Subsequently, the o-Ps lifetime, $\tau_3(T)$, being a measure of free volume detectable by PALS, can be described generally as a weighted summation of the two components:

$$\tau_3(T) = \tau_{0,3} + (a + bT)F(T) + (c + dT)[1 - F(T)]. \quad (4)$$

Here, the first term comes from the minimal detection condition for the o-Ps probe in a free volume hole ($\tau_{0,3} = 0.5$ ns) [6], the second term, representing the contribution from the free volume holes localized in the frustrated metastable solid-like domains, is assumed to expand linearly with temperature as suggested in the raw data in figure 1, and finally the last term describes the free volume contribution from the liquid-like domains with a linear thermal expansion. Thus, equation (4), which we propose to account for the PALS response, is a four-parameter expression with four free fitting constants.

Figure 1 contains the result of fitting the PALS response with equation (4) using the parameters κ and T_m^c, which were obtained from the fitting of the viscosity data in figure 2. The quality of the fit over such a wide temperature range is satisfactory with very reasonable parameters: $a = 1.05$ ns, $b = 1.00 \times 10^{-3}$ ns K^{-1}, $c = 1.44$ ns, and $d = 2.08 \times 10^{-3}$ ns K^{-1}. The a and b constants, the former found after adding the value of $\tau_{0,3} = 0.5$ ns, are consistent with the parameters obtained from simplified phenomenological model-free analysis of the PALS data in figure 1 and equation (3a): an intercept $\tau_{3,0} = (1.36 \pm 0.04)$ ns and o-Ps lifetime expansivity $\beta_{\tau 3} = (1.01 \pm 0.16) \times 10^{-3}$ ns K^{-1} below T_g^{PALS}.

3.4. Mutual relationships between viscosity and PALS data within the TOP model

The viscosity and o-Ps lifetime findings can be discussed as follows. By comparison of figures 1 and 2, it was revealed by Pethrick [18] that the existence of the high-temperature region with a smaller slope in the PALS response around 10 K above T_{b2}^L corresponds quite well to the occurrence of the Arrhenius-like dynamical regime above T_A. This indicates the approximate closeness $T_{b2}^L \cong T_A$. According to equation (2) above $T_m^* \sim T_A$, only the normal liquid-like regions are present. Thus, the higher T region of the PALS response should be connected with the existence of the normal liquid-like domains together with the LFSs and their clusters and the absence of the solid-like domains. The non-zero value of the d coefficient manifested by the non-zero slope of the o-Ps lifetime above T_{b2}^L means that the free volume is gradually increasing with temperature in the normal liquid domains of 6PO. On decreasing the temperature below T_{b2}^L, the proportion of liquid-like domains begins to reduce significantly and the solid-like regions start to appear. This

results in the essential changes in behavior of both the viscosity and the PALS response on cooling. The former quantity begins to increase in a non-Arrhenius fashion, whereas the latter one starts to decrease significantly. These features are consistent with equation (2), that is, in between $T_m^* \sim T_A$ and T_m^c the stable liquid regions and the metastable solid-like islands coexist, with the former dominating over the latter. On further cooling, the PALS response of the 6PO sample crosses an inflection point at $T_m^c = 282.5$ K, which is evaluated from the fitting of the viscosity data. It is interesting that this characteristic TOP temperature T_m^c is in good agreement with the characteristic PALS temperature $T_{b1}^L = 280$ K as obtained from the phenomenological model-free analysis. This agreement gives us some insight into the physical meaning of the latter temperature being estimated by the model-free procedure. Thus, a change from the larger slope in the weakly supercooled liquid to the smaller one below 280 K appears to be consistent with an onset of the dominancy of the solid-like domains in the deeply supercooled liquid over the liquid-like domains. Below T_m^c, the solid-like domains gradually play a growing role, leading to the pronounced cooperative character of the dynamics. Finally, on further decreasing the temperature, the solid-like domains begin to percolate, resulting in the glassy state of the disordered system with the essentially smaller expansivity of free volume in the solid-like domains that form the glassy state of the matrix.

4. Conclusion

In summary, we carried out a novel type of simultaneous analysis on the viscosity and PALS data within the TOP model for disordered systems. To perform the latter, a free volume version of the TOP model was formulated and subsequently applied successfully on the o-Ps annihilation results for a typical van der Waals type of glass-forming system: *bis[m-(m-phenoxy)phenoxyphenyl]ether*. The satisfactory description of the whole PALS response of this amorphous glass-former over a wide temperature range—including all the physical (normal, supercooled, and glassy) states of the disordered phase— has been achieved for the first time. In the future, further systems of different bonding types, as well as other dynamical (e.g. dielectric relaxation) properties, will be tested using this novel analytical tool of simultaneous, combined analysis of PALS and dynamic data.

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