



Research paper

On the mutual relationships between spin probe mobility, free volume and relaxation dynamics in organic glass-formers: Glycerol



J. Bartoš*, H. Švajdlenková

Polymer Institute of SAS, Dúbravská cesta 9, SK-845 41 Bratislava, Slovak Republic

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ABSTRACT

The rotation dynamics of the spin probe *TEMPO* in *glycerol* from ESR is compared with the *ortho-positronium* (*o-Ps*) annihilation from PALS and interpreted using the relaxation dynamics from BDS. Rotation time scale within the slow motion regime exhibits two Arrhenius regions with the characteristic ESR temperature, T_{X1}^E , close to the characteristic PALS temperature, T_{b1}^P , which is related to the secondary β process above T_g . Next, a slow to fast motion regime transition at the characteristic ESR temperature, T_c^E , close to the characteristic PALS temperature, T_{b2}^P , followed by non-Arrhenius fast motion regime region is fully coupled with the primary α process.

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1. Introduction

In addition to classical diffraction [1], scattering [2] and relaxation techniques, such as broadband dielectric spectroscopy (BDS) [3], the structure and dynamics of glass-forming substances can be investigated by means of various small particles using the so-called *external* probe techniques [4–6]. The molecular-sized stable free radicals named the *spin probes* detected using electron spin resonance (ESR) [4] together with the fluorescence probes using fluorescence spectroscopy [5] and the atomic-sized *ortho-positronium* (*o-Ps*) using positron annihilation lifetime spectroscopy (PALS) [6] belong among the most used external probes.

The characteristic triplet spectrum of the spin probes of nitroxyl type and its change from a broad signal at lower temperatures to a narrowed one with increase the temperature reflects change in the rotation dynamics on going from the slow to fast motional regime [4]. The spin probe reorientation is commonly characterized by two dynamic quantities, i.e., spectral parameter of mobility, $2A_{zz'}$ [7] and correlation time, τ_c , as determined by spectral line shape analysis [4,8,9] or spectral simulations [4]. The most pronounced effect in the ESR spectrum consisting is a dramatic decrease of extrema separation and narrowing of the triplet lines manifesting the transition from the slow to fast motional regime is characterized by the operationally defined spectral temperature, $T_{50G}^{2A_{zz'}}$, i.e., the temperature, at which the extreme separation of the outer lines

of the triplet spectrum reaches just 50 Gauss [7] or by the intersection point of the slow and fast correlation times T_c^E [10], respectively [4]. In addition, in some cases further fine crossovers within the individual motion regimes at the characteristic ESR temperatures T_{X1}^{low} , T_{X1}^{ast} were detected [11,12] whose origin remains still to be revealed.

In general, the molecular probe dynamics in a given organic medium depends on the local micro-structure of the medium around the probe and its fluctuation due to internal mobility of the less and/or more surrounding constituents of the medium. Then, it is of importance to reveal the mutual connections between the spin probe mobility and the free volume as well as the inner dynamics by relating the spin probe reorientation to the *directly* measurable free volume or to the *directly* detected molecular mobility of the matrix, respectively.

The microstructural, aspect of the complex problem of the spin probe dynamics in various condensed substances can be addressed via the annihilation behavior of the smallest atomistic probe: *ortho-positronium* (*o-Ps*), i.e., a bound system of one positron e^+ and one electron e^- with antiparallel spins. The annihilation process of this quantum-mechanical particle resembling the simplest atom of hydrogen in condensed media being detectable by PALS technique is closely related to the static or/and dynamic local open space which provides the unique information about the free volume in a given medium [6]. Standard quantum-mechanical (SQM) model relating the observed *o-Ps* lifetime, τ_3 , to the spherical free volume hole size, R_h , has been formulated [13]. Although the free volume

* Corresponding author.

holes in disordered molecular organics are not strictly spherical and may be approximated by rather ellipsoidal or cylinder-like forms [14], the SQM model is utilized in sense of the equivalent sphere radius or equivalent volume.

One of us has performed systematic ESR investigations of the rotation dynamics of one of the smallest spin probe of nitroxyl type: 2,2,6,6-tetramethyl-1-piperidinyl-1-oxy (*TEMPO*) in a series of nine amorphous polymers including *diene*, *vinylidene* and *vinyl elastomers*, *non-polar* and *polar vinyl thermo-plastics* and finally, *engineering thermoplastics* with the glass transition temperatures from DSC, T_g^{DSC} , ranging from ~ 170 K up to ~ 490 K [15]. It was discovered that the slow to fast transition of the *TEMPO* probe is connected with the *ortho-positronium* (*o-Ps*) lifetime, τ_3 ($T_{50G}^{2AZZ'}$), lying in a remarkable narrow range 2.14 ± 0.08 ns almost independently of the detailed chemical structure of amorphous polymers investigated. Recently [16], this empirical finding was confirmed to be valid also for a large set of small *vdW*- and *H*-bonded molecular glass-formers allowing us to make a conclusion about the rather general validity of the empirical rule: $\tau_3(T_{50G}^{2AZZ'}) \cong \text{const.}$, i.e., nearly independence of the *o-Ps* lifetime on the chemical structure of the molecule and related type of intermolecular interactions and the topology of the constituents of the investigated organic medium.

The dynamic aspect of the reorientation problem of the spin probes in various organic media, especially, polymers, has been already considered by comparison of the rotation correlation times with the various dynamic data [17]. In general, the internal dynamics in the glass-forming media considered to be the most relevant to molecular rotation mobility is investigated in the most effective way via reorientation of the *effective electric dipoles*, i.e. in *ternal probes of the medium*' constituents using BDS over an extremely wide time range (10^6 – 10^{-12} s) [3] covering also the whole time scale of the spin probe ESR method (10^{-6} – 10^{-11} s) [4]. In most cases, the $T_{50G}^{2AZZ'}$ or T_c^r transition of the *TEMPO* probe [4,11,12] and sometimes, further crossover effects in the slow and fast regime at T_{Xi}^{slow} , T_{Xi}^{fast} [11,12,18] are situated *above* the thermodynamic, T_g^{DSC} , or dynamic, e.g. from dielectric spectroscopy T_g^{DS} , glass transition temperature, so that not only the relaxation data of the structural (primary) relaxation used previously for correlating at high temperatures [17] but also, and especially, those of the secondary process(es) in the hardly accessible *T* region *above* T_g are necessary for comparative purposes with the ESR data. At the present time, such relaxation data are relatively scarce but due to a progress in both the experimental instrumentation in BDS and the subsequent spectral analyses [3,19,20] the time scales of the secondary processes above T_g become available.

In our previous joint ESR and PALS papers [16,18] for some small molecular, oligo- and polymer organics relations between the characteristic ESR temperature $T_{50G}^{2AZZ'}$ and the characteristic PALS ones T_{b1} or T_{b2} have been occasionally found but not discussed. This rather scarce ESR vs. PALS coincidence combined with the empirical finding from a series of the joint PALS and BDS studies [21–24], i.e. $\tau_3(T_{b2}) \cong \tau_\alpha(T_{b2})$ revealing the equality of the corresponding time scales of the *o-Ps* annihilation at the (quasi-) plateau region of the PALS response τ_3 vs. *T* with the primary α relaxation seems to suggest that the similar dynamic origin could be behind the $T_{50G}^{2AZZ'} \sim T_{b2}$ coincidence. However, a direct comparison and verification of the potential mutual relationships between the time scales of ESR and PALS as well as those of various relaxation modes from BDS is still sporadic [25].

In this paper, we address the mutual relationships between the ESR, PALS and BDS results at the time scale level to reveal the role of free volume and internal dynamics in the rotation dynamics of the molecular probe in appropriate organic medium. As a spin system we have chosen the spin probe *TEMPO* in a prototypical small molecular H-bonded glass-former – *glycerol* (*GL*). The main aim consists in an identification of the specific

motional modes in this chosen model organic glass-former which are responsible for the crossover and transition phenomena in the spin probe *TEMPO* rotation dynamics being closely related to the bend effects in the PALS response using the detailed dynamic data from BDS as well as establishing of their influence on or control of the individual spin probe motion regimes. Finally, some further microscopic insight into the nature of these motions can be obtained by comparing of the ESR and PALS responses with the reported neutron scattering (NS) data on *glycerol*.

2. Experimental

Glycerol from Aldrich Chemical Comp. was used. Glass transition temperature was determined by DSC method to be $T_g^{DSC} = 190$ K [21].

2.1. ESR data

In spin probe ESR experiment a quasi-spherical spin probe 2,2,6,6-tetramethylpiperidine-1-oxy, known as *TEMPO*, from Aldrich Chemical Comp. was used by its dissolving in the host medium at a concentration of about 5×10^{-4} spin mol $^{-1}$. In our ESR study, an X-band Bruker-ER 200 SRL with a Bruker BVT 100 temperature variator system was used. ESR spectra were measured over a wide temperature range from 100 K up to 340 K with the stability of temperature of ± 0.5 K. The ESR spectra were evaluated by the line shape analysis using the Goldman - Bruno - Polnaczek equation [8] in the slow motion regime and the Freed - Fraenkel expression [9] in the fast motion regime.

2.2. PALS and dynamic BDS and NS data

The reorientation behavior of the spin probe *TEMPO* in this prototypical small H-bonded molecular glass-former as obtained from ESR study is discussed with help of the extended PALS results [21,26] and interpreted by using the internal electric dipole probe reorientation data from BDS [19]. Finally, further deeper insight into the microscopic origin of the molecular motions responsible for the changes in the corresponding dynamic and annihilation parameters and their mutual relationships might be obtained from the reported results of elastic neutron scattering (NS) study on *GL* [27].

3. Results

3.1. ESR data

Figs. 1 and 2 display both measures of the spin probe dynamics, as obtained from the temperature evolution of the triplet spectra of the spin system *TEMPO/glycerol*, i.e. the spectral parameter of mobility, $2A_{zz'}$, and the correlation time, τ_c , as a function of temperature or of inverse of temperature, respectively. The first case of $2A_{zz'}$ vs. *T* dependence has already been mentioned in Ref. [16]. In brief, (i) in the low *T* range of the slow motional regime, the relatively higher value of $2A_{zz'}$ with respect to typical van der Waals glass-formers, decreases very slightly over a quite wide temperature range from 100 K through $T_g^{DSC} = 190$ K up to ~ 240 K–245 K. This indicates the restricted rotation mobility of the spin probe *TEMPO* over the glassy and the deeply supercooled liquid due to the existence of extensive H-bonded network between the *GL* molecules; (ii) on increase the temperature, a decrease in the $2A_{zz'}$ parameter begins to occur above an acceleration temperature $T_{X1}^{slow,2AZZ'} \cong 243$ K causing an onset of motional narrowing of the triplet spectra which subsequently leads to a transition from the slow

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