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# The Spin Probe Dynamics and the Free Volume in a Series of Amorphous Polymer Glass-Formers

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**Summary:** We report the results of a combined study of the local structure and the reorientation dynamics in a series of five amorphous polymers of different fragility: *cis-trans*-1,4-poly(butadiene) (*c-t*-1,4-PBD), *cis*-1,4-poly(isoprene) (*cis*-1,4-PIP), poly(isobutylene) (PIB), poly(vinyl methylether)(PVME) and poly(propylene glycol) (PPG) by using two different probe methods. The reorientation dynamics of the molecular spin probe 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) from electron spin resonance (ESR) is related to the annihilation behaviour of the atomic ortho-positronium (o-Ps) one as obtained by positron annihilation lifetime spectroscopy (PALS). It was found that a slow to fast transition in the spin probe rotation mobility at the operationally defined spectral temperature parameter,  $T_{50G}$ , is connected with the mean o-Ps lifetime,  $\tau_3$  ( $T_{50G}$ ) =  $(2.04 \pm 0.26)$  ns. Consequently, using the free-volume concept of the o-Ps annihilation in terms of a quantum-mechanical model of o-Ps lifetime this transition can be connected with the occurrence of the mean free volume hole,  $V_h$  ( $T_{50G}$ ) =  $(102 \pm 17)$  Å<sup>3</sup>, nearly independent of the chemical composition and the basic structural relaxation parameters of the amorphous polymers investigated. Finally, the free volume hole distribution aspect of the slow to fast transition indicates the presence of a sufficient free volume fluctuation at  $T_{50G}$  for both typical fragile PVME and strong PIB polymer and emphasizes the essential role of free volume in the spin probe dynamics.

**Keywords:** amorphous polymers; ESR; free volume; PALS; spin probe reorientation

## Introduction

The structure and dynamics of glass-formers can be investigated via the so-called “reporter” molecular probe techniques such as stable free radicals using electron spin resonance (ESR).

The spectral evolution of the triplet signal from the spin probe of nitroxide type in a given condensed matrix reflects its rotational dynamics which is influenced by the internal factors such as the matrix properties, i.e., chemical composition, physical microstruc-

ture and its static and dynamic fluctuations, the spin probe parameters such as its size and shape as well as by the external ones such as temperature etc. [1–3]

The physical structure and dynamics of disordered systems is often discussed using the free volume concept. [4,5] In the past this idea was utilized to interpret the spin probe dynamics by formulating the various versions of free volume models of spin-probe rotation in polymers without their direct experimental verification. [6–8] Recent progress in positron annihilation lifetime spectroscopy (PALS) methodology allows to obtain the free volume information from the annihilation behavior of the atomically sized probe, the ortho-positronium (o-Ps) in condensed materials. [9,10]

In this contribution we present a combined ESR and PALS study on a series of

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five amorphous polymers aimed to clarify the role of the measured free volume factor in the spin probe rotation dynamics.

## Experimental Part

### Materials

Five amorphous polymeric glass formers were selected for experiments. They included the structurally simple homopolymers of diene type without side group *cis-trans-1,4-poly(butadiene)* (*c-t-1,4-PBD*) and with side group *cis-1,4-poly(isoprene)* (*c-1,4-PIP*), of vinyl type *poly(vinyl methyl ether)* (*PVME*) and of vinylidene type *poly(isobutylene)* (*PIB*) as well as one typical heteropolymer *poly(propylene glycol)* (*PPG*) (Figure 1). The values of molecular weight and basic thermodynamic (glass transition temperature) and dynamic, i.e., structural relaxation and related fragility <sup>[11]</sup> parameters are listed in Table 1.

As the spin probe the stable nitroxyl-type radical 2,2,6,6-tetramethyl-1-*piperidin*-*nyloxy* (*TEMPO*) from Aldrich, Inc. was used. The molecular structure of quasi-spherical molecule of *TEMPO* is also given in Figure 1. Basic molecular parameters of spin probe *TEMPO*, i.e., van der Waals

volume  $V_{\text{TEMPO}}^{\text{W}} = 170.1 \text{ \AA}^3$  corresponding to the equivalent radius of  $R_{\text{eq}}^{\text{W}} = 3.45 \text{ \AA}$  was obtained using the simulation software Cerius<sup>2</sup>, Accelrys, Inc., San Diego.

### Sample Preparation

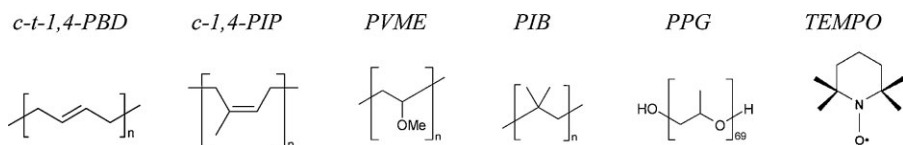
The soft solid matrices were prepared by diffusion of the vapor of the *TEMPO* at elevated temperature. The liquid matrices were prepared by dissolution of the *TEMPO* in a given matrix at concentration of about  $10^{-3} \text{ spin} \cdot \text{mol}^{-1}$ .

### Electron Spin Resonance

ESR measurements were carried out on the X-band Bruker-ER 200 SRL with a Bruker BVT100 temperature variation controller unit. The ESR spectra were recorded over a wide temperature range from 100 K up to 370 K. The ESR spectra of all the amorphous *polymer/TEMPO* systems have been evaluated in terms of the spectral parameter of mobility,  $2A_{\text{zz}}$ , (see Figure 2) as a function of the temperature.

### Positron Annihilation Spectroscopy

PALS investigations on *c-t-1,4-PBD*, *PPG* and *PVME* were carried out by the Bratislava's group, Slovakia and on *c-1,4-PIP* and *PIB* by the Halle's team, Germany. The



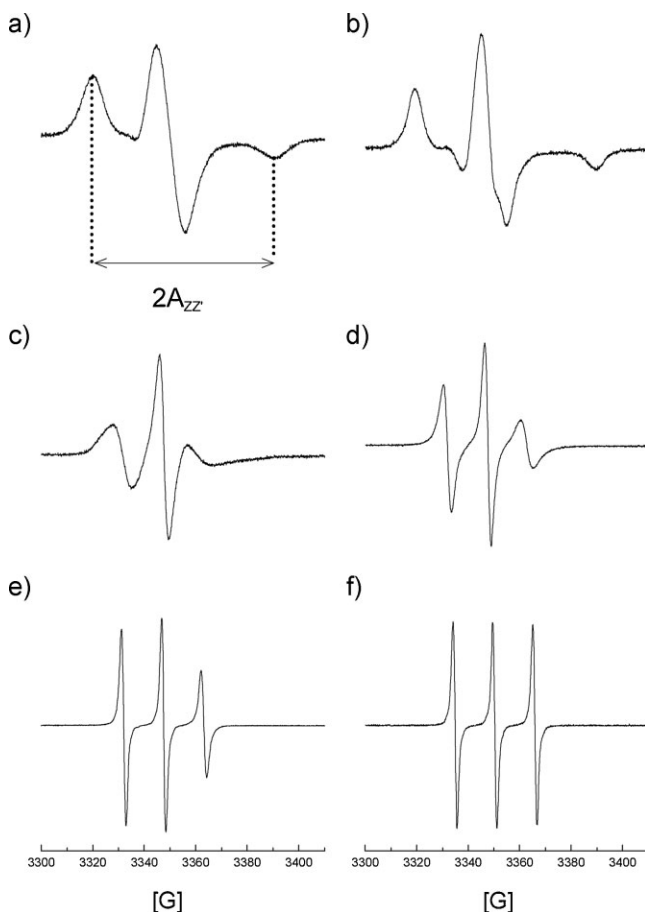
**Figure 1.**

Chemical structures of polymer matrices: *cis-trans-1,4-poly(butadiene)* (*c-t-1,4-PBD*), *cis-1,4-poly(isoprene)* (*c-1,4-PIP*), *poly(vinyl methyl ether)* (*PVME*), *poly(isobutylene)* (*PIB*) and *poly(propylene glycol)* (*PPG*) as well as of spin probe *TEMPO*.

**Table 1.**

The *polymer* and *polymer/TEMPO* parameters: molecular weight,  $M_n$ , glass-liquid transition temperature from DSC,  $T_g$ , fragility,  $m_g$ , <sup>[11]</sup> characteristic ESR temperature,  $T_{50G}$  and mean o-Ps lifetime,  $\tau_3(T_{50G})$ . <sup>[12–16]</sup>

Polymer	$M_n$ Da	$T_g$ K	$m_g$ -	$T_{50G}$ K	$T_{50G}/T_g$ -	$\tau_3(T_{50G})$ ns	Ref.
<i>c-t-1,4-PBD</i>	$2.2 \times 10^3$	174	84	224	1.29	2.06	12
<i>PPG</i>	$4 \times 10^3$	198	83	242	1.21	2.17	13
<i>c-1,4-PIP</i>	$8 \times 10^5$	200	65	255	1.28	2.26	14
<i>PIB</i>	$1 \times 10^6$	205	46	263	1.29	1.78	15
<i>PVME</i>	$3.7 \times 10^4$	250	75	276	1.11	1.98	16



**Figure 2.**

Spectral evolution as a function of the temperature for the *PPG/TEMPO* system at a) 100 K, b) 200 K, c) 250 K, d) 275 K, e) 300 K and finally, f) 350 K.

details of both experimental set up and evaluation procedures of the PALS spectra can be found in Refs. <sup>[17,18]</sup>.

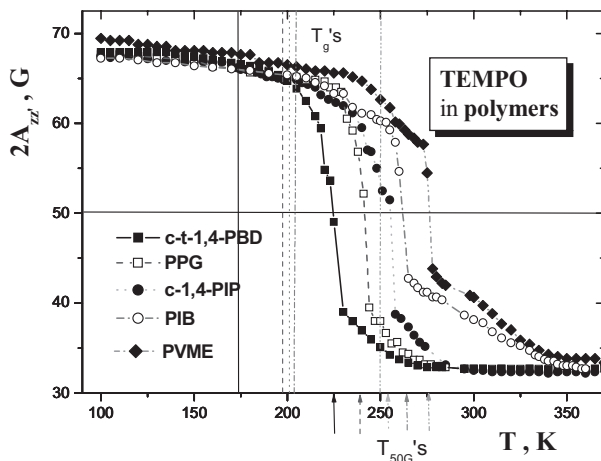
## Results and Discussion

### ESR Data

The typical ESR spectral evolution of the spin probe *TEMPO* with temperature is similar for all the investigated *polymer/TEMPO* systems as it is illustrated by the *PPG/TEMPO* case in Figure 2. The triplet spectrum changes from a broad signal at lower temperatures to a narrow one in higher temperature region. This corresponds to a dynamic change of the *TEMPO*

from the slow motional regime with the higher values of the spectral parameter of mobility  $2A_{zz} \sim 70\text{--}65$  G to the fast motional regime with the lower ones  $2A_{zz} \sim 35\text{--}30$  G.

The spectral parameter of *TEMPO* mobility,  $2A_{zz}$ , as a function of temperature in our series of five amorphous polymers is presented in Figure 3. Typical sigmoidal dependence with a characteristic transition from the slow to fast motional regime is operationally quantified by the spectral temperature parameter  $T_{50G}$  <sup>[19]</sup> (Table 1). For all the investigated *polymer/TEMPO* systems the  $T_{50G}$  values lie about 10–30% above the basic thermodynamic parameter of polymer glass-formers, i.e. the



**Figure 3.**

Spectral parameter of mobility,  $2A_{zz}$ , as a function of the temperature of *TEMPO* in a series of amorphous polymers. The glass-liquid temperatures,  $T_g$ , are depicted by the vertical lines and the characteristic ESR temperature,  $T_{50G}$ , are marked by the arrows; both the quantities are summarized in Table 1.

corresponding glass - liquid transition temperatures,  $T_g$ .

By inspection of the further basic dynamic parameter of glass-forming systems, i.e. fragility,  $m_g$ ,<sup>[11]</sup> characterizing the temperature dependence of the structural relaxation of glass-formers, we find that the strongest polymer *PIB* with  $m_g = 46$  exhibits the relative transition temperature  $T_{50G}/T_g \sim 1.29$  being nearly the same as that for the most fragile polymer *c-t-1,4-PBD* among the used matrices with the essentially higher values of fragility:  $m_g = 84$ . This implies that no direct relationship between the slow to fast transition of the spin probe *TEMPO* and the structural relaxation process is observed. Then, another physical factor has to control the slow to fast transition of the spin probe *TEMPO*.

#### PALS Data

Positron annihilation lifetime spectroscopy (PALS) is a unique method to *direct* observation of free space in condensed matrices.<sup>[9,10,18]</sup> The principle of PALS consists in detecting the annihilation of the atomic-sized ortho-positronium (o-Ps) probe, i.e., a bound system of one positron,  $e^+$ , and one electron,  $e^-$ , with the mutually parallel spins which is trapped in the regions of low electron density, the so-

called free volume. The positron lifetime spectrum of condensed materials is usually a sum of three exponentially decaying channels with its characteristic lifetime values from 1) para - positronium (p-Ps,  $\tau_1 \sim 125$  ps), 2) “free” positron ( $e^+$ ,  $\tau_2 \sim 300$ – $500$  ps) and finally, 3) ortho - positronium (o-Ps,  $\tau_3 \sim 1$ – $5$  ns). In practice, the PALS spectra are evaluated by the PATFIT program<sup>[20]</sup> providing the mean o-Ps lifetime values and also using the MELT or LT 9.0 routines<sup>[21,22]</sup> to obtain the o-Ps lifetime distribution and the related free volume distribution functions.

In the framework of free volume interpretation of the o-Ps annihilation in condensed matter and the standard quantum-mechanical model of o-Ps annihilation in spherical free volume hole, the o-Ps lifetime,  $\tau_3$ , is related to the free volume hole size,  $R_h$ , as follows:<sup>[23]</sup>

$$\tau_3 = \tau_{3,0} \{ 1 - R_h / (R_h + \Delta R) + (1/2\pi) \sin[2\pi R_h / (R_h + \Delta R)] \}^{-1} \quad (1)$$

where  $\tau_{3,0}$  is the spin averaged lifetime of p-Ps and o-Ps equals to 0.5 ns and  $\Delta R = R_0 - R_h = 1.66$  Å is the thickness of electron layer about free volume hole obtained as a parameter from fitting the observed o-Ps lifetimes to known vacancy or free volume

hole sizes in molecular crystals and zeolites.<sup>[23]</sup> In reality, the shape of free volume entities is not spherical, so that the standard model (Eq. 1) is used in the sense of the mean o-Ps lifetime and subsequently, to estimate the *equivalent* mean hole radius. Then, the corresponding mean hole volume is given  $V_h = (4/3) \pi R_h^3$ . Moreover, in any real disordered material a distribution of free volume holes is present giving the corresponding distribution of o-Ps lifetimes. Then, if one-to-one correspondence between the o-Ps lifetime and the free-volume hole radius is valid, the o-Ps lifetime distribution from MELT or LT programs can be transformed into the free-volume hole radius distribution, Eq. 2:

$$f(R_h) = -2\Delta R \left\{ \cos \left[ 2\pi \left( \frac{R_h}{R_0} \right) \right] - 1 \right\} \frac{\alpha(\lambda_3)}{R_0^2} \quad (2)$$

and finally,  $f(R_h)$  can be converted into a free-volume distribution function, eq 3:

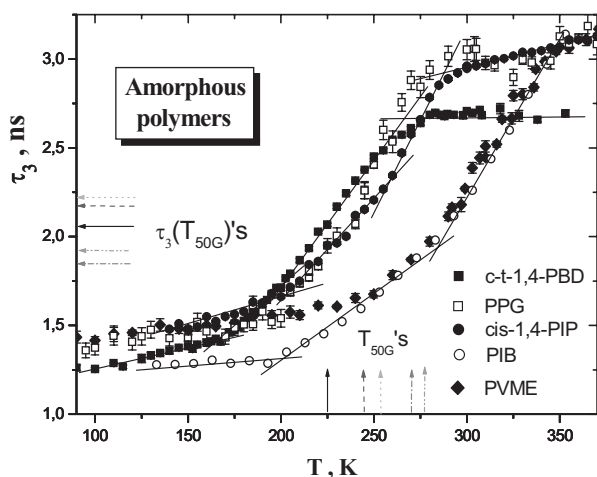
$$g(V_h) = \frac{f(R_h)}{4\pi R_h^2} \quad (3)$$

Next, a role of the local free volume in the rotational dynamics of the spin probe *TEMPO* in our series of amorphous poly-

mers from ESR investigations will be evaluated from both the phenomenological and geometrical points of view.

### Phenomenological Relationship between the ESR and PALS Databases

The mean o-Ps lifetimes,  $\tau_3$ , as a function of temperature,  $T$ , for the same five amorphous polymers used in ESR study are plotted together in Figure 4. In all the investigated polymer glass-formers a typical sigmoidal form of  $\tau_3$  vs.  $T$  dependence is observed. The detailed  $\tau_3$  vs.  $T$  plot is displayed for the case of *poly(vinyl methyl-ether)* in Figure <sup>[16]</sup>. The existence of several regions of distinct thermal behavior of  $\tau_3$  can be found by a linear fitting procedure <sup>[12,15]</sup>. Basically, three significantly distinct regions with the two characteristic PALS temperatures can be revealed: the first most pronounced effect at lower  $T$ 's is connected with the glass to supercooled liquid transition at  $T_g^{\text{PALS}}$  and the other one in higher  $T$  region marked by a plateau or quasi-plateau level tendency is connected with supercooled to normal liquid transition at  $T_{b2}^L \sim (1.4 - 1.75) \times T_g^{\text{PALS}}$  <sup>[12,13,15]</sup>. In addition, more or less slighter bend effect depending on the matrix fragility at  $T_{b1}^G \sim (0.5-0.7) \times T_g^{\text{PALS}}$



**Figure 4.**

The mean o-Ps lifetime,  $\tau_3$ , as a function of the temperature for a series of pure amorphous polymers. The arrows depict the values of o-Ps lifetimes  $\tau_3(T_{50G})$  corresponding to the spectral temperatures  $T_{50G}$  for *TEMPO* from Figure 3.

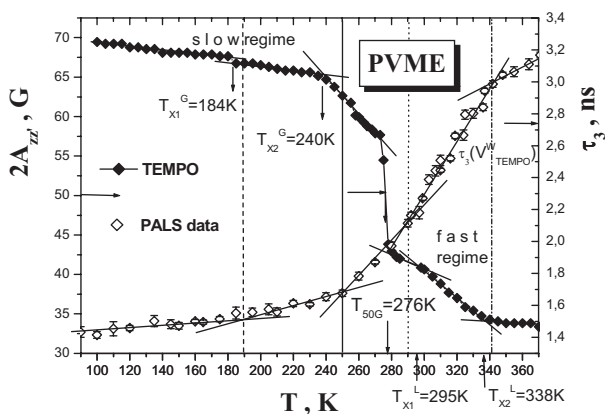
and  $T_{b1}^L \sim (1.2 - 1.4) \times T_g^{\text{PALS}}$  which mark the presence of two various glass or supercooled liquid regions can be distinguished.<sup>[12,15]</sup> The  $\tau_3$  values and their changes with  $T$  over more or less extended  $T$  range reflect differences in the free volume microstructure depending on the chemical and physical, i.e. free volume, structure and the dynamics of various polymers.<sup>[9,10,12,18]</sup>

In the context with our ESR results in Figure 3, the most remarkable empirical finding is that the o-Ps lifetime,  $\tau_3(T_{50G})$ , corresponding to the most pronounced effect in  $2A_{ZZ}$  vs.  $T$  plot i.e. the slow to fast transition in the spin probe *TEMPO* dynamics, are in a relative narrow range (Table 1) characterized by the average value:  $\tau_{3,\text{ave}}(T_{50G}) = (2.04 \pm 0.25)$  ns. Thus, a change of the spin probe *TEMPO* between the two basic motional regimes is associated with the mean o-Ps lifetime being almost independent of the chemical composition and the fragility of the polymer matrices used. From Eq. 1 this corresponds to the mean free volume  $V_{h,\text{ave}} = (102 \pm 17) \text{ \AA}^3$ . This finding can be interpreted in such a way that the spin probe *TEMPO* transition occurs at the presence of the average free volume reaching about 60% of van der Waals volume of *TEMPO*,  $V^W = 170.1 \text{ \AA}^3$ .

In addition, in connection with our combined ESR and PALS approach we find some further mutual coincidences between various discontinuity effects in the ESR or PALS response as it is demonstrated for *PVME* (Figure 5). They include the following relations between the corresponding characteristic ESR and PALS temperatures:  $T_{X1}^G \cong T_{b1}^G$  and  $T_{X2}^G \approx T_g^{\text{PALS}}$  in the slow regime,  $T_{50G} \approx T_{b1}^L$  and  $T_{X2}^L \cong T_{b2}^L$  in the fast one. These coincidences suggest the similar origin of underlying dynamic processes which cause both the significant changes in the reorientation of molecular spin probe *TEMPO* as well as in the annihilation of the atomic o-Ps probe. Detailed discussion of these effects requires the further relevant dynamic information exceeding the extent of this paper and this aspect will be published elsewhere.

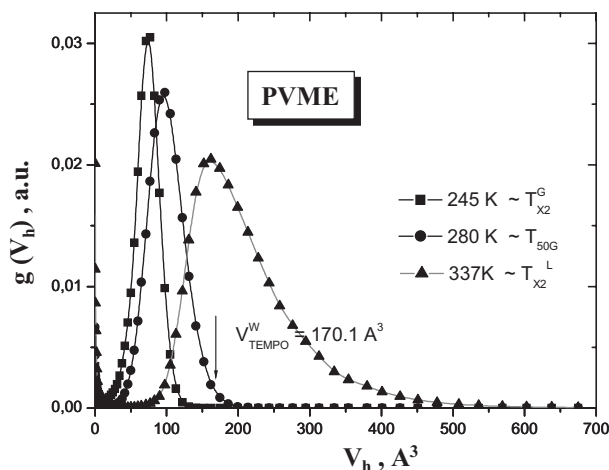
#### Geometrical Relationships between the Spin Probe *TEMPO* and Free Volume Hole Distribution

Another level of the ESR and PALS analysis consists in a direct comparison of the spin probe *TEMPO* size with the detailed free volume hole microstructure as obtained from the continuous analysis of



**Figure 5.**

Comparison of the spectral parameter of *TEMPO* mobility,  $2A_{ZZ}$ , with the mean o-Ps lifetime,  $\tau_3$ , for the *PVME* sample as a function of the temperature. The characteristic ESR temperatures:  $T_{X1}^G = 184$  K,  $T_{X2}^G = 240$  K,  $T_{50G} = 276$  K and  $T_{X1}^L = 295$  K and  $T_{X2}^L = 338$  K are related to the characteristic PALS ones depicted by vertical lines as follows:  $T_{X1}^G \cong T_{b1}^G = 190$  K (dash),  $T_{X2}^G \approx T_g^{\text{PALS}} = 250$  K (solid),  $T_{50G} \approx T_{b1}^L = 290$  K (dot) and  $T_{X2}^L \cong T_{b2}^L = 342$  K (dash-dot).



**Figure 6.**

Relationships between the free volume distributions  $g(V_h)$  at the selected temperatures 245 K, 280 K and 337 K close to the characteristic ESR ones from Figure 5 for PVME. The arrow depicts the van der Waals volume of the spin probe *TEMPO*,  $V_{\text{TEMPO}}^W$ .

the PALS spectra by using the MELT or LT programs.<sup>[15,16]</sup>

Figure 6 shows a relationship between the van der Waals volume of the *TEMPO*,  $V_{\text{TEMPO}}^W$ , and the free volume hole distributions  $g(V_h)$  in the relatively fragile *PVME* sample as obtained from Eq. 3 at several temperatures close to the characteristic ESR ones in Figure 4 using the program MELT. In general, when the temperature increases,  $g(V_h)$  moves to the larger values and at the same time broadens. The van der Waals volume of *TEMPO*,  $V_{\text{TEMPO}}^W$ , is depicted by the arrow also. At low temperature,  $T=245$  K, the  $V_{\text{TEMPO}}^W$  lies outside of the corresponding hole volume distribution. This indicates that in the slow regime the spin probe *TEMPO* forms a certain type of structural perturbation of the *PVME* matrix and moves due to very small fluctuation in its surrounding. On increase the temperature, the free volume hole distributions  $g(V_h)$  approaches the vdW volume of the spin probe *TEMPO* and at  $T_{50G}$  the high-value tail of the  $g(V_h)$  reaches just the  $V_{\text{TEMPO}}^W$  value. Thus, the spin probe *TEMPO* at the  $T_{50G}$  has a sufficient local free space for the pronounced change in its rotation dynamics in the *PVME* matrix. This indicates that a

transition of the spin probe *TEMPO* from the slow to rapid regime appears to be associated with the occurrence of a local free volume fluctuation in the surrounding *PVME* matrix.

Finally, at higher temperatures, the cross-over effect within the fast motional regime of the spin probe *TEMPO* at  $T_{X2}^L$  (Figure 5) appears to be associated with the maximum of  $g(V_h)$  which corresponds to the maximal probability of the occurrence of free volume holes being nearly equal to the  $V_{\text{TEMPO}}^W$ . Recently, similar findings were reported also for a typical strong member from our series of the investigated polymer glass-formers samples - *poly (isobutylene) (PIB)*.<sup>[24]</sup>

Thus, the observed relationships between the changes in spin probe *TEMPO* reorientation and the free volume fluctuation suggest on their close mutual connections independently of the chemical composition, the structural relaxation and the related strong or fragile dynamic character of the polymer glass-former.

## Conclusion

The rotational dynamics of the spin probe *TEMPO* in a series of polymer glass-formers



of different chemical composition, glass transition temperature and fragility has been related to the annihilation behavior of the atomic o-Ps probe and the closely related free volume microstructure information as obtained from the PALS studies. Thus, a joint ESR and PALS approach enables to obtain better understanding of the relative role of various physical factors controlling the reorientation dynamics of small molecules in the various polymer matrices.

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