

# Molecular probe dynamics and free volume in glass-formers: 1,2- and 1,4-poly(butadiene)s



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## ABSTRACT

We report on the mutual relationships between reorientation and free volume in two *poly(butadiene)s* as seen by *TEMPO* and *ortho-positronium* (*o-Ps*) using ESR or PALS, respectively. The slow to fast transition of *TEMPO* in *cis-trans-1,4-PBD* and *1,2-PBD* occurs at the similar characteristic ESR temperature  $T_{50G}$  with  $T_{50G}/T_g^{DSC} = 1.22$  for the former in contrast to  $T_{50G}/T_g = 0.85$  for the latter. In spite of the  $T_{50G} < T_g$  relation an empirical rule  $\tau_3(T_{50G}) = 2.17 \pm 0.15$  ns is confirmed suggesting that the main transition of *TEMPO* in *1,2-PBD* occurs at the same free volume fluctuation independently of the physical state of the host matrix.

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## 1. Introduction

Recently, we reported on the guest molecule dynamics represented by rotation of the spin probe 2,2,6,6-tetramethyl-1-piperidinyloxy (*TEMPO*) in a series of small molecular and polymer glass-formers by electron spin resonance (ESR) and on its connection with the *ortho-positronium* (*o-Ps*) annihilation and the related free volume properties from positron annihilation lifetime spectroscopy (PALS) [1]. All of these spin systems exhibited similar inverse quasi-sigmoidal dependencies of the spectral parameter of mobility of the *TEMPO* probe  $2A_{zz}$  vs.  $T$  with the most pronounced effect marked by the temperature parameter,  $T_{50G}$ , and some additional fine effects above and below  $T_{50G}$ . Here, the main characteristic ESR temperature  $T_{50G}$  of the spin probed matrix is operationally defined as the temperature at which the extreme line separation of the triplet spectra reaches just 50 G and it serves to parametrise a slow to fast motional regime transition of the spin probe *TEMPO* [2]. In a series of fourteen small molecular and polymer glass-formers the respective  $T_{50G}$  values are situated above the corresponding glass-liquid temperatures,  $T_g^{DSC}$ , with  $T_{50G}/T_g = 1.1$ – $1.5$ . In particular, it was found that the  $T_{50G}/T_g$  ratio depends relatively strongly on the type of glass-forming compound being lower for the van der Waals-bonded substances and higher for the H-bonded ones. In addition, the further characteristic ESR temperature,  $T_{X1}^{fast}$ , usually depicting a crossover between two sub-regimes within the fast motional one was indicated [3–5]. The  $T_{X1}^{fast}$  values were determined for a rather limited but representative set of strong and fragile glass-formers and the  $T_{X1}^{fast}/T_g^{DSC}$  ratios were observed to lie in a wide range (1.18–1.67)  $T_g^{DSC}$  [3–5]. In the specific case of

*poly(vinylmethylether)* (*PVME*), three regions of distinct mobility were found [4].

Next, from PALS measurements of the *o-Ps* lifetime,  $\tau_3$ , as a function of temperature in the same series of amorphous glass-formers it follows that at the first characteristic ESR temperature,  $\tau_3(T_{50G})$ , their values lie in a relatively narrow range  $2.17 \pm 0.15$  ns being almost independent of the constituent's topology, i.e., small vs. chain molecules and of the type and extent of the intermolecular interaction, i.e., vdW- or H-bonded substances. Subsequently, by applying a standard quantum-mechanical model of *o-Ps* annihilation in a spherical free volume hole approximation [6–8] it was concluded that this main transition is associated with the free volume fluctuation of  $V_h(T_{50G}) = 114 \pm 15 \text{ \AA}^3$  [1]. Moreover, the similar *o-Ps* lifetimes values at the next characteristic ESR temperature,  $\tau_3(T_{X1}^{fast}) = 2.85 \pm 0.18$  ns, where  $i = 1$  or  $2$ , indicate that a crossover between the various sub-regimes of the rapidly moving spin probes *TEMPO* is connected with the mean hole volume fluctuation comparable with the van der Waals volume of the *TEMPO*:  $V_h(T_{X1}^{fast}) \cong V_{TEMPO}^W$ ,  $V_h(T_{X1}^{fast}) = 185 \pm 18 \text{ \AA}^3 \cong V_{TEMPO}^W = 170 \text{ \AA}^3$  at  $T_{X1}^{fast}$  for *poly(isoprene)* (*PIP*), *poly(isobutylene)* (*PIB*) and *poly(propylene glycol)* (*PPG*) [3,5] with the two distinct fast sub-regimes and at  $T_{X2}^{fast}$  for *PVME* with the three distinct ones [4].

In the above-mentioned 14 glass-formers, for which a combined ESR and PALS study has been carried out so far, all of the  $T_{50G}$ s were situated above the corresponding  $T_g^{DSC}$ s in the liquid state of small molecular and polymeric glass-formers. In a few scarce cases, however, the  $T_{50G}$  value was found to be localised in the glassy state of some very high- $T_g$  aromatic polymers such as *poly(styrene)* and *poly carbonate* [9]. Then, the natural question arises about the validity of both the  $\tau_3(T_{50G})$  and  $\tau_3(T_{X1}^{fast})$  findings for such glass-formers for which  $T_{50G} < T_g$ . To resolve this problem, we present the results of a combined ESR and PALS study on two suitable amorphous polymers with the same chemical structure but of

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different isomeric forms, namely, *cis-trans-1,4-poly (butadiene)* (*c-t-1,4-PBD*) and *1,2-poly(butadiene)* (*1,2-PBD*). We demonstrate clearly that despite the  $T_{50G} < T_g$  relation for the latter the almost constant *o*-Ps lifetime values appear to be valid irrespective of the physical state, i.e., liquid or glass, of the host glass-forming matrix.

## 2. Experimental

### 2.1. Materials

Amorphous *cis-trans-1,4-poly(butadiene)* (*c-t-1,4-PBD*) and *1,2-poly(butadiene)* (*1,2-PBD*) with the same summary formula  $\sim C_4H_6$ , but with different structural formulae  $\sim [CH_2-CH=CH-CH_2]_n$  and  $\sim [CH_2-CH(CH=CH_2)]_m$  were used. Both the *PBD* samples with very similar molecular weights of  $2.1 \times 10^4$  or  $2.0 \times 10^4$ , respectively, and polydispersity of 1.05 were synthesised by L. Willner and provided kindly by R. Zorn of the Institut für Festkörperforschung, Jülich, Germany [10]. The glass-liquid temperatures were determined by DSC method:  $T_g^{DSC} = 174$  K and  $T_g^{DSC} = 272$  K [10]. As the spin probe the smallest stable radical of nitroxyl type used in our previous ESR studies [1–4] 2,2,6,6-tetramethyl-1-piperidiny-1-oxy (*TEMPO*) from Sigma–Aldrich, Inc. was applied by its dissolving and homogenisation in the viscous liquid samples at concentration of about  $5 \times 10^{-4}$  spin/mol.

### 2.2. ESR

ESR measurements of the spin probed *PBD* samples were performed on the X-band Bruker – ER 200 SRL operating at 9.4 GHz with a Bruker BVT 100 temperature variation controller unit. ESR spectra of the slowly cooled doped *PBD/TEMPO* systems were recorded on heating over a wide temperature range from 120 K up to 350 K with step of 5 K. The sample was kept at the given temperature until thermal equilibrium was achieved before the start of three spectra accumulations. The temperature stability was  $\pm 0.3$  K. The evaluation of ESR spectra was performed in terms of the spectral parameter of mobility,  $2A_{zz}$ , as a function of temperature with subsequent extraction of the spectral parameter of mobility  $T_{50G}$  [2] and further characteristic ESR temperatures in both slow and fast motional regimes.

### 2.3. PALS

The PALS measurements were done using a fast-fast coincidence system [11] with a time resolution of 272 ps [full width at half-maximum (FWHM),  $^{22}Na$  source] and an analyser channel width of 12.8 ps. Two identical samples were sandwiched around a 1 MBq positron source:  $^{22}NaCl$ , deposited between two 2- $\mu m$ -thick aluminum foils. To prevent sticking of the source to the samples, each sample was held in a container of 2 mm width and 88 mm<sup>2</sup> area with a window made of foils of 8- $\mu m$  thick Kapton and 7- $\mu m$  thick aluminum. The temperature of the sample, placed in a vacuum chamber with a pressure of  $10^{-5}$  Pa, was varied between 140 and 420 K in steps of 5 or 10 K, with an uncertainty of  $\pm 1$  K. Before lowering the temperature, the samples were degassed and dried in vacuum for 18 h. Each measurement lasted 7 h leading to a lifetime spectrum of  $5 \times 10^6$  coincidence. Source corrections, 7.5% of 386 ps (Kapton and NaCl) and 10.8% of 165 ps (Al foils), and time resolution were determined by measuring a defect-free *p*-type silicon reference ( $\tau = 219$  ps). The final resolution function used in the spectrum analysis was determined as a sum of two GAUSSIANS. The positron lifetime spectra were analysed using the well-known PATFIT-88 software package [12] in terms of a short-term component from para-positronium *p*-Ps,  $\tau_1$ , an intermediate

one attributed to 'free' positron,  $\tau_2$ , and a long-term one, related to free volume: ortho-positronium *o*-Ps,  $\tau_3$ .

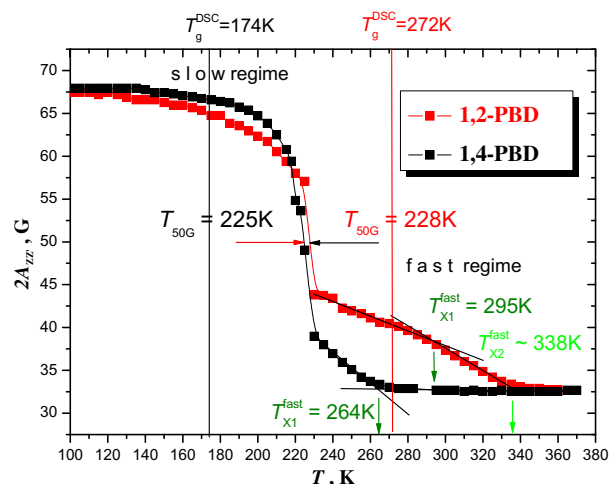
## 3. Results and discussion

### 3.1. ESR data

Figure 1 displays the temperature dependencies of the spectral parameter of mobility of the spin probe *TEMPO*,  $2A_{zz}$ , in the *c-t-1,4-poly(butadiene)* and *1,2-poly(butadiene)* samples. The ESR data for the former polymer have already been reported in our very recent works [1,3]. In spite of the same chemical structure of both *PBD* matrices, the ESR responses were in some aspects similar but diametrically different in others. Thus, at low temperatures in the slow motional regime the  $2A_{zz}$  values are lower for *1,2-PBD* in comparison with *1,4-PBD* which indicate the faster rotational mobility of the spin probe *TEMPO* in the former matrix in comparison to the latter. On the other hand, the most pronounced effect in the spin probe *TEMPO* mobility consisting of the slow to fast motional regime transition occurs at the very similar characteristic ESR temperatures:  $T_{50G}(1,2-PBD) = 228$  K and  $T_{50G}(c-t-1,4-PBD) = 225$  K [1,3]. The most significant difference between the *PBD* samples is that in *1,2-PBD*,  $T_{50G}$  lies below its  $T_g^{DSC}$  value, while for the *c-t-1,4-PBD*, the  $T_{50G} > T_g^{DSC}$  relation is valid as it follows from their relative positions with respect to the vertical lines marking the corresponding glass-liquid transition temperatures.

In addition to the  $T_{50G}$  transition, further crossover phenomena in the spin probe *TEMPO* mobility can be seen at higher temperatures. Here, very significant qualitative and quantitative differences between the respective ESR responses exist. These consist in the presence of two regimes in *c-t-1,4-PBD* and the existence of three ones in *1,2-PBD* within the fast motional regime. The corresponding characteristic ESR temperatures are  $T_{X1}^{fast} = 264$  K =  $1.52T_g^{DSC}$  for *c-t-1,4-PBD* or  $T_{X1}^{fast} = 295$  K =  $1.09T_g^{DSC}$  and  $T_{X2}^{fast} = 338$  K =  $1.25T_g^{DSC}$  for *1,2-PBD*, respectively.

At this moment it is of interest to compare the ESR responses of both *PBD* samples at  $T_{50G}$  as well as in the fast motional regime for *c-t-1,4-PBD* and *1,2-PBD* with those for other polymers [1,3]. Thus, the  $T_{50G}/T_g^{DSC} = 1.22$  for *c-t-1,4-PBD* falls into the  $T_{50G}/T_g^{DSC} \in (1.1 - 1.5)$  range revealed for a relatively large series of small



**Figure 1.** Spectral parameter of mobility of the spin probe *TEMPO*,  $2A_{zz}$ , as a function of temperature for *1,2-PBD* (red) and *c-t-1,4-PBD* (black). The characteristic ESR temperatures are as follows: *1,2-PBD*:  $T_{50G} = 228$  K,  $T_{X1}^{fast} = 295$  K and  $T_{X2}^{fast} = 338$  K; *c-t-1,4-PBD*:  $T_{50G} = 225$  K and  $T_{X1}^{fast} = 264$  K. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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