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Molecular dynamics and free volume in organic glass-formers: A series of oligomer and polymer *1,4-poly(isoprene)s*

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A B S T R A C T

We present a combined study of the rotational dynamics and free volume in a series of *1,4-poly(isoprene)s* using ESR and PALS, respectively. The spectral parameter of mobility, $2A_{zz'}$, of the spin probe *TEMPO* is related to the annihilation of the *ortho-positronium* (*o-Ps*) probe. The *o-Ps* lifetime $\tau_3(T_{50G}) \cong$ const.1 and $\tau_3(T_{x1}{}^{fast}) \cong$ const.2 rules are valid independent of chain length and moreover, the T_{50G}'s coincides with the bend effect at $T_{b1}{}^{L}$'s. Finally, the new finding is that the first acceleration at $T_{x1}{}^{slow}$ agrees with a change in the *o-Ps* lifetime width parameter, σ_3, below the glass transition temperature.

1. Introduction

Recently [1–5], we reported on the mutual relationships between both the rotational dynamics of stable molecular free radicals, the so-called *spin probes* and the annihilation behaviour of an atomic-sized probe, i.e., *ortho-positronium* (*o-Ps*) and the related free volume properties in a series of amorphous [1–4] and crystalline [5] organic compounds, as measured by electron spin resonance (ESR) or positron annihilation lifetime spectroscopy (PALS), respectively. In the case of the smallest spin probe of nitroxide type *2,2,6,6-tetramethyl-1-piperidinyl-1-oxy* (*TEMPO*) dissolved at very low concentrations in these organics, a number of regularities in its dynamics and its relations to free volume were found. In particular, the spectral parameter of mobility, $2A_{zz'}$, of the triplet signal from the *TEMPO*, being a measure of its rotation dynamics, exhibits the most pronounced effect connected with slow to fast motional transition at the characteristic ESR temperatures, T_{50G} [6,7]. The main finding was that for the vast majority of amorphous glass-formers of different chemical structure the T_{50G} values lie *above* the corresponding glass–liquid temperatures, $T_g{}^{DSC}$, in the liquid state of small molecular compounds or in the elastic state of polymers, respectively [1,2]. One exception found so far concerns *poly(butadiene) (PBD)* isomers, where for *1,2-PBD* a T_{50G}/T_g ratio smaller than 1 was observed. This contrasts with *cis–trans-1,4-PBD*, which displays 'usual' $T_{50G}/T_g > 1$ relation, indicating that the main transition of the spin probe *TEMPO* occurs deep in the glassy host matrix [3]. In addition to the main T_{50G} transition, a few further characteristic ESR temperatures reflecting the subtle changes in rotational dynamics of the *TEMPO* were revealed both in the slow motion regime at $T_{x1}{}^{slow}$ below T_{50G}, as well as in the fast regime at $T_{x1}{}^{fast}$ and $T_{x2}{}^{fast}$ above T_{50G} [1–4].

Despite these diametrically distinct T_{50G} vs. T_g relations, a comparison of the ESR data for the spin probe *TEMPO* with the PALS results revealed that the *o-Ps* lifetime τ_3 at T_{50G}, lies in the remarkable narrow range of $\tau_3(T_{50G}) = 2.17 \pm 0.15$ ns [1–3]. This $\tau_3(T_{50G})$ value is almost independent of the chemical structure, topology, type (vdW- vs. H-bonded) of intermolecular interaction between the constituents [1,2], as well as of the physical (glassy vs. liquid) state [3] of the host matrix. Similarly, for several polymers, it was revealed the almost constant value of the *o-Ps* lifetime $\tau_3(T_{x1}{}^{fast}) = 2.85 \pm 0.18$ ns [2,4]. In the following, these two empirical findings are marked as the $\tau_3(T_{50G}) \cong$ const.1 and $\tau_3(T_{xi}{}^{fast}) \cong$ const.2 rules. As the *o-Ps* lifetime τ_3 is a measure of the local free volume within the matrix, an application of the standard quantum–mechanical model of *o-Ps* annihilation [8–10] resulted in the discovery that the local free volume, connected with the main T_{50G} transition, reaches $V_h(T_{50G}) = 114 \pm 15$ Å^3, while that at $T_{x1}{}^{fast}$ or $T_{x2}{}^{fast}$ being $V_h(T_{x1}{}^{fast})$ or $V_h(T_{x2}{}^{fast}) = 185 \pm 18$ Å^3, is comparable with the van der Waals volume of the spin probe *TEMPO*: $V^{W}{}_{TEMPO} = 170$ Å^3.

Strictly, our previous statement about the effect of the constituent's topology (small vs. long molecules) and closely related molecular weight on $\tau_3(T_{50G})$ values was based on a rather approximate comparison between small molecular and polymer glass-formers with enormously different chemical structures and related interparticle forces. In fact, we should verify the $\tau_3(T_{50G}) \cong$ const.1 and $\tau_3(T_{x1}{}^{fast}$ or $T_{x2}{}^{fast}) \cong$ const.2 rules by investigating the effect of various chain lengths of the matrix molecules with *the same* chemical constitution, implying *the same* interparticle interactions. In

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this contribution, we address this aspect through a combined ESR and PALS study on a series of *cis-1,4-poly(isoprene)s*, (*c-1,4-PIP*). We will find the validity of both the $\tau_3(T_{50G}) \cong$ const.1 and $\tau_3(T_{xi}{}^{fast}) \cong$ const.2 rules, independently of the molecular mass of the matrix's constituents, varying over the three orders of magnitude. Moreover, in addition to the aforementioned $2A_{zz'}$-T vs. τ_3-T relationships, we will present new empirical relationships between a crossover in the spin probe mobility within the slow motional regime and another *o-Ps* annihilation parameter, i.e., the *o-Ps* lifetime width σ_3. This underlines further the existence of the very close connections between molecular reorientation and local free volume within the host matrix.

2. Experimental

2.1. Materials

A series of three samples of *1,4-poly(isoprene)s*, (*1,4-PIP*), $\sim$[CH$_2$—CH=C(CH$_3$)—CH$_2$]$_n$$\sim$, with different number average molar masses: $M_n = 8 \times 10^2$, 4.27×10^3 g/mol from Polymer Source, Canada and 8×10^5 g/mol from Sigma-Aldrich, Inc., Germany was used. In the following text they will be identified as *1,4-PIP 0.8k*, *1,4-PIP 4.3k* and *1,4-PIP 800k*. The glass-liquid temperatures measured by low-*T* DSC with a cooling rate of −10 K/min were: 188, 201.5 and 205 K. One of the smallest stable radicals of nitroxyl type, as used in our previous ESR studies [1–5] *TEMPO* from Sigma-Aldrich, Inc., Germany, was used as the spin probe by its dissolving and homogenisation by mixing in the low viscous liquid samples of *1,4-PIP 0.8k*, *1,4-PIP 4.3k* at a concentration of about 5×10^{-4} spin/mol. In the case of the rubbery *1,4-PIP 800k* material the spin probe *TEMPO* was introduced via vapour diffusion at elevated temperature until the resolved characteristic triplet spectrum stable during time of homogenisation with approximately the same spin probe concentration, was achieved.

2.2. ESR

ESR measurements of the spin-probed *1,4-PIP* 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 *1,4-PIP/TEMPO* systems were recorded while heating over a wide temperature range from 120 up to 350 K with a 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 ±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 a subsequent extraction of the spectral parameter of mobility T_{50G} [6,7] and further characteristic ESR temperatures in both the slow and fast motional regimes.

2.3. PALS

The PALS measurements were performed 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-µm thick aluminium foils. To prevent the source sticking to the samples, each sample was held in a 2-mm-wide container with an area of 88 mm^2 with a window fabricated from foils of 8-µm-thick Kapton and 7-µm-thick aluminium. The temperature of the sample, placed in a vacuum chamber with a pressure of 10^{-5} Pa, was varied between 140 and 360 K in steps of 5 or 10 K with an uncertainty of ±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 5×10^6 coincidence. Source corrections of 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 Lifetime routine LT version 9.0, in terms of a short-term component from *para*-positronium *p*-Ps, τ_1, an intermediate one attributed to 'free' positron, τ_2, and a long-term one related to free volume: *ortho*-positronium (*o-Ps*), τ_3 and their corresponding normal distribution widths σ_i of their log normal distributions [12,13].

3. Results and discussion

3.1. ESR data

Figure 1 displays the temperature dependence of the spectral parameter of mobility of the spin probe *TEMPO* $2A_{zz'}$ in three *1,4-PIP* matrices over a wide temperature range from 120 K up to 300–360 K. Despite these matrices having *the same* chemical structure, the ESR responses are similar in some aspects but different in others. All of the $2A_{zz'}$ vs. T plots exhibit similar inverse quasi-sigmoidal courses with several regions 1–5 of different thermal behaviour. The most pronounced feature of the ESR response is the existence of two main regions of distinct mobility, as characterised by the significantly different values of the $2A_{zz'}$ parameter. In the lower T region, the relatively high $2A_{zz'}$ values steems from the slowly moving spin probes and the relatively smaller $2A_{zz'}$ ones arise from the quickly reorienting *TEMPO* molecules at relatively higher temperatures. The slow to fast transition of the spin probe *TEMPO* is operationally quantified by the characteristic ESR temperature T_{50G}, which increases in the oligomeric region from 227 K for *1,4-PIP 0.8k* through 233 K for *1,4-PIP 4.3k,* up to 254 K for the polymer *1,4-PIP 800k* sample.

In addition to the main dynamic transition, several further regions of slightly or strongly distinct spin probe *TEMPO* mobility

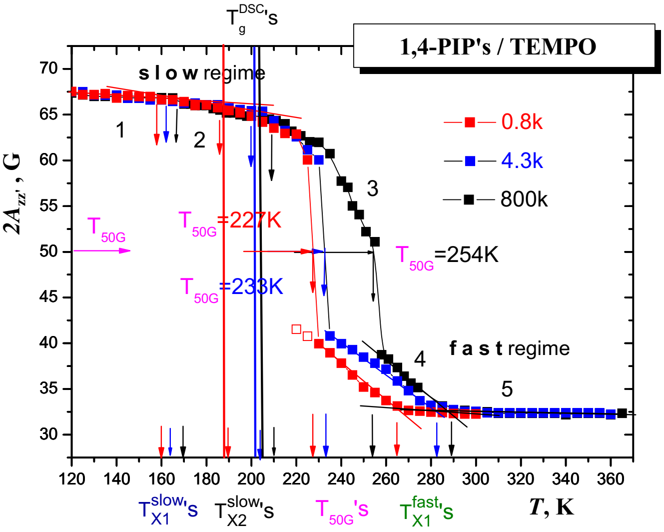

Figure 1. Spectral parameter of mobility of the spin probe *TEMPO*, $2A_{zz'}$, as a function of temperature for *1,4-PIP 0.8k* (red) , *1,4-PIP 4.3k* (blue) and *1,4-PIP 800k* (black). The respective characteristic ESR temperatures T_{X1}^{slow}, T_{X2}^{slow}, T_{50G} and T_{X1}^{fast} (marked by arrows) given by the intersection points of the linearised regions together with the corresponding glass transition temperatures, T_g^{DSC}, (marked with vertical lines) are listed in Table 1. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)