



## Positron annihilation response and broadband dielectric spectroscopy: Poly(propylene glycol)

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### ABSTRACT

The results of phenomenological analysis of the ortho-positronium (o-Ps) lifetime,  $\tau_3$ , from positron annihilation lifetime spectroscopy (PALS) and of the dielectric relaxation spectra from broadband dielectric spectroscopy (BDS) on poly(propylene glycol) (PPG) are presented. A number of coincidences between the characteristic PALS temperatures  $T_g^{PALS}$ ,  $T_{b1}^L$  and  $T_{b2}^L$  obtained from a phenomenological analysis of a quasi-sigmoidal PALS response and the various characteristic BDS temperatures for the spectral and relaxation parameters have been revealed. Thus, an onset of the quasi-plateau level at the PALS temperature  $T_{b2}^L = 1.44 T_g^{PALS}$  is characterized by the equality of the o-Ps lifetime, and the primary relaxation time:  $\tau_3 \cong \tau_\alpha$ . Moreover, a deviation toward the quasi-plateau level at  $T_{b2}^L$  is related to a saturation in both spectral width and relaxation strength parameters of the  $\alpha$ -process and a merging of the relaxation times of the primary ( $\alpha$ ) and secondary ( $\beta$ )-processes. In addition,  $T_{b2}^L$  lies in the vicinity of a high-temperature crossover of the main relaxation process from the non-Arrhenius to the Arrhenius behavior. The another characteristic PALS temperature,  $T_{b1}^L = 1.18 T_g^{PALS}$ , is also connected with the change in temperature behavior of time and strength parameters of the secondary effective  $\beta$ -relaxation. All these findings indicate a close connection between the PALS response and the dielectric relaxation in PPG.

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### 1. Introduction

The structure and property relationships belong to long-standing topics of physics, chemistry and materials sciences of condensed matter. The structure-dynamic state of disordered glass-forming systems is often treated using the free volume concept which became very useful for its simplicity and physical plausibility in interpretation of the thermodynamic and dynamic as well as transport behavior [1,2]. Positron annihilation lifetime spectroscopy (PALS) based on the annihilation of the ortho-positronium (o-Ps), i.e. a bound atom which consists of an electron and the positron, serves as an effective tool for the free volume characterization [3,4]. In PALS, the o-Ps probe acts as a very sensitive indicator of the presence of static (permanent) and dynamic (transient) local regions of reduced electron density, such as vacancies in real crystals or free volume holes in amorphous phases [5].

In glass-forming systems, the o-Ps lifetime,  $\tau_3$ , as a function of temperature,  $T$ , exhibits a typical quasi-sigmoidal course with

(quasi)-plateau level at high temperatures [6–9]. Phenomenological analysis revealed the existence of several characteristic PALS temperatures in the liquid state marked according to a unified notation [9] as  $T_g^{PALS}$ ,  $T_{b1}^L$  and  $T_{b2}^L = T_r$  [7] =  $T_e$  [8], the two latter being located at  $T_{b1}^L \sim 1.2\text{--}1.4 T_g^{PALS}$  [9–11] or  $T_{b2}^L \sim 1.4\text{--}1.7 T_g^{PALS}$  [7–9], respectively.

Evidently, the full utilization of PALS method for the structural-dynamic characterization of any disordered system requires understanding of the physical significance of these PALS temperatures. Some progress has been reached by relating the PALS response to the dynamic ones such as viscosity [7,9,12–14] or broadband dielectric (BDS) spectroscopy [15–17]. Thus, it was revealed [7] that an onset of the higher temperature quasi-plateau region in PALS response at  $T_{b2}^L = T_r$  lies quite close to the so-called Arrhenius temperature,  $T_A$ , [12,15,17] above which the dynamics occurs approximately in the Arrhenius regime. Moreover, at both  $T_{b2}^L$  and  $T_{b1}^L$ , some relationships between the PALS response and various changes in the dynamic parameters of the primary [9,18,19] or the secondary relaxations [18–20] from BDS have been revealed. Thus, both the bend effects at  $T_{b2}^L$  and  $T_{b1}^L$  on  $\tau_3 - T$  plots are found to be related to the corresponding relaxation times of the primary  $\alpha$ -process,  $\tau_\alpha(T_{b2}^L) \sim 10^{-9}$  s or  $\tau_\alpha(T_{b1}^L) \sim 10^{-6\pm 1}$  s [9,18–20].

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Moreover, several further relations of the bend effect at  $T_{b1}^L$  with the various parameters of the secondary  $\beta$  relaxation for *glycerol* (GL) [20] and *diethyl phthalate* (DEP) [18] have been recently found.

In this contribution we present the phenomenological analysis of PALS and dielectric relaxation responses on a typical amorphous polymer – *poly(propylene glycol)* (PPG). Such a phenomenological approach leads to establishing numerous connections of the o-Ps annihilation parameters and relaxation characteristics of BDS response indicating close relationships between both responses.

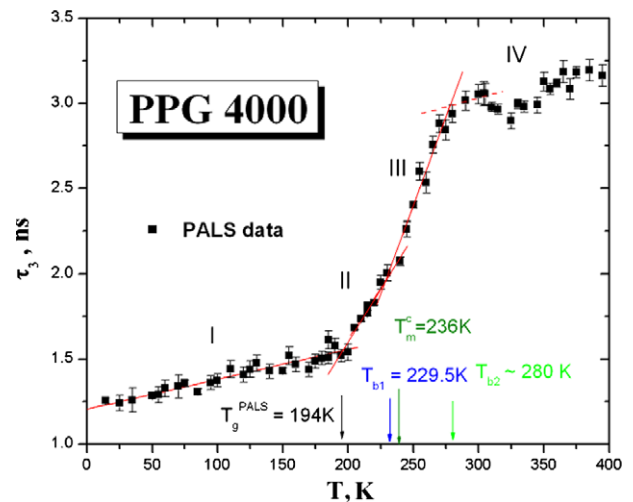
## 2. Experimental

### 2.1. PALS method

The positron annihilation lifetime spectra of PPG 4000 from Aldrich Inc. were obtained by the conventional fast–fast coincidence method using plastic scintillators coupled to Phillips XP2020 photo-multipliers. The time resolution of prompt spectra was about 320 ps. The radioactive positron  $^{22}\text{Na}$  source plus samples assembly was kept under vacuum in a rotary pump. During the low temperature measurements from 15 K up to 300 K, samples in a holder under vacuum were fixed at the end of a cold finger of a closed-cycle helium gas refrigerator Leybold with automatic temperature regulation. The high temperature study was performed in a chamber without vacuum. The temperature stability was about 1 K [21]. The positron lifetime spectra were analyzed using the well-known PATFIT-88 software package [22] 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,  $\tau_3$ . The PPG sample pre-treated with the drying procedure from [27] was measured during heating cycle. The acquisition time per each temperature point was at least 2 h.

### 2.2. BDS techniques

The dielectric measurements were performed on a high resolution Novocontrol dielectric analyzer covering the broad frequency range ( $10^{-2}$ – $10^7$  Hz), and an Agilent RF impedance material analyzer 4291B in the frequency range  $10^6$ – $10^9$  Hz. Isothermal (within  $\pm 0.02$  K) frequency scans of the complex dielectric function,  $\varepsilon^*(f) = \varepsilon'(f) + i\varepsilon''(f)$ , were performed every third degree over the temperature range 120–350 K. These measurements and the corresponding experimental details were already reported in previous works [23–25]. However, in this work the treatment of the dielectric data is different and has been done assuming the picture originally developed by William and Watts [26]. In this picture, one considers that the total dielectric relaxation in the liquid state is driven by two separated mechanisms. The faster one, usually the  $\beta$  relaxation, is attributed to the restricted motions in an otherwise rigid environment, being this mechanism the dominant one below the glass transition temperature. Only above  $T_g$  where primary ( $\alpha$ ) relaxation takes the dominant position, the total relaxation of the dipolar unit is achieved. Through this analysis we can obtain the relaxation time, dielectric strength and shape parameters for both  $\alpha$  and  $\beta$ -processes. A complete description of this evaluation method can be found in Ref. [18]. Besides to the  $\alpha$  and  $\beta$ -processes we have analyzed here an additional low temperature relaxation, the so-called  $\gamma$ -process. The relaxation time for this  $\gamma$ -process follows an Arrhenius-like behavior (see Eq. (5) in Ref. [18]) where the distribution of the relaxation times can be interpreted in terms of a Gaussian distribution of activation energies with  $\log \tau_0 = -11.8 \pm 0.2$ , a mean activation energy of  $12.5 \pm 0.9$  kJ/mol and a variance of  $7.0 \pm 3.0$  kJ/mol. The  $\gamma$ -process was not included



**Fig. 1.** o-Ps lifetime,  $\tau_3$ , as a function of temperature for PPG with phenomenological analysis Eqs. (1a), (1b), (1c) using the best linear fitting providing the characteristic PALS temperatures  $T_g^{\text{PALS}} = 194$  K and  $T_{b1}^L = 229.5$  K and  $T_{b2}^L \sim 280$  K.

in the WW-ansatz analysis due to its low relaxation strength and the lack of overlap with the  $\alpha$  and  $\beta$ -processes in the temperature range here analyzed.

## 3. Results

### 3.1. PALS data

Fig. 1 shows the o-Ps lifetime,  $\tau_3$ , as a function of temperature for PPG obtained over a wide temperature range from 15 K up to 400 K. As usually observed for many small molecular and polymer glass-formers [6–9], the  $\tau_3 - T$  plot of PPG exhibits a quasi-sigmoidal course. The two most pronounced bend effects are seen at around  $\sim 200$  K and  $\sim 280$  K. Phenomenological analysis of the  $\tau_3 - T$  dependence for PPG using the best linear regression fitting [9–11] reveals the presence of four temperature regions of distinct thermal behavior.

The first three regions can be satisfactorily approximated by the following linear expressions:

for region I from 15 K up to 195 K :

$$\tau_3 = (1.76 \pm 0.13) \times 10^{-3} T + (1.201 \pm 0.16) \quad r = 0.945 \quad (1a)$$

for region II from 205 K up to 220 K :

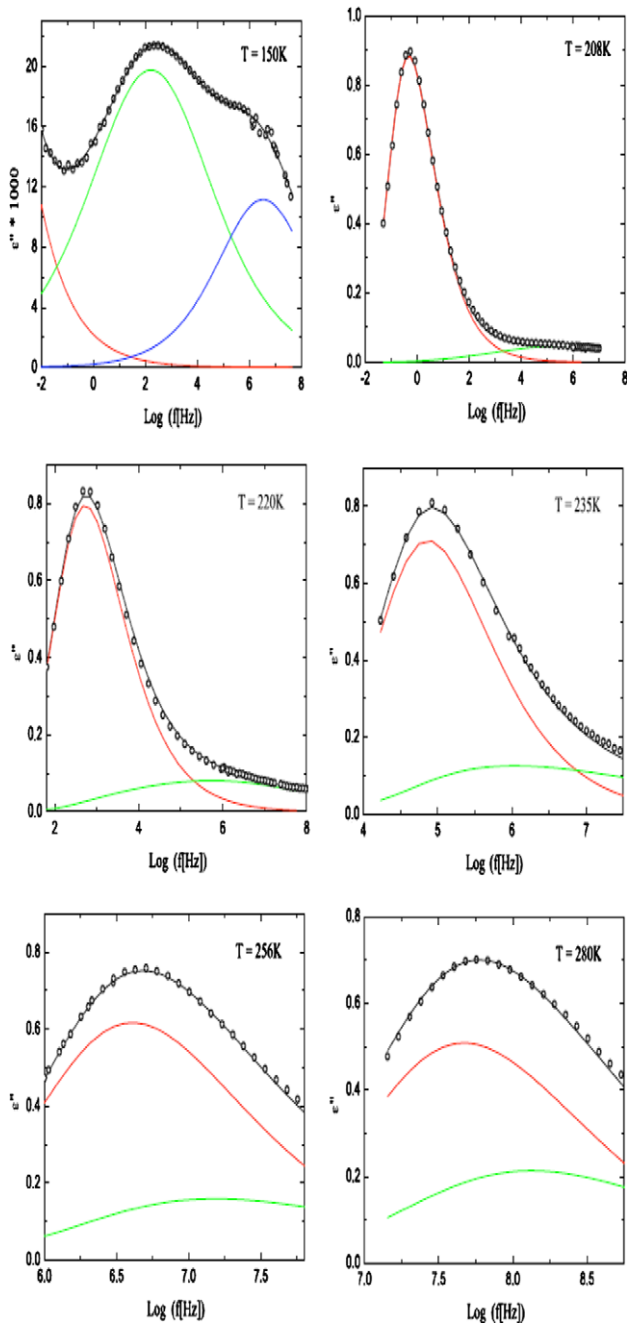
$$\tau_3 = (1.19 \pm 0.09) \times 10^{-2} T - (0.76 \pm 0.19) \quad r = 0.985 \quad (1b)$$

and finally, for region III from 240 K up to 272 K :

$$\tau_3 = (2.11 \pm 0.23) \times 10^{-2} T - (2.87 \pm 0.61) \quad r = 0.965 \quad (1c)$$

The intersection points define the characteristic PALS temperatures:  $T_g^{\text{PALS}} = 194 \pm 4$  K,  $T_{b1}^L = 229.5 \pm 4$  K = 1.18  $T_g^{\text{PALS}}$  and  $T_{b2}^L \sim 280$  K = 1.44  $T_g^{\text{PALS}}$ .

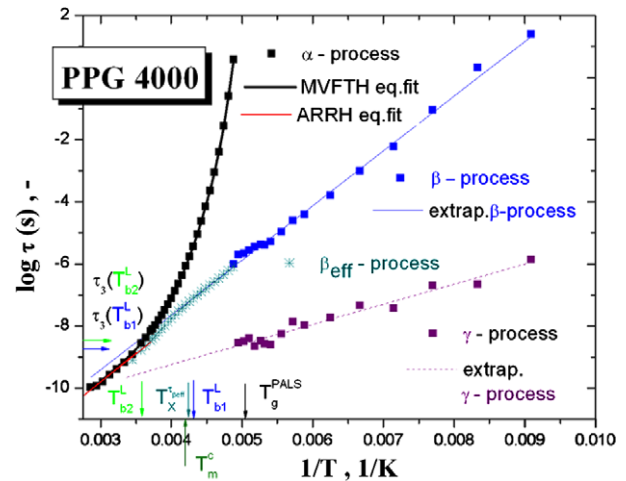
Evidently, the first characteristic PALS temperature is close to the glass transition temperature from calorimetry  $T_g^{\text{DSC}} = 200$  K [27], so that it defines the glass transition temperature as obtained by the PALS method. Below  $T_g^{\text{PALS}}$ ,  $\tau_3 \sim 1.3$ – $1.5$  ns and falls into the typical range for many amorphous systems studied so far. On the other hand, at the highest  $T$ s  $\tau_3$  exhibits a quasi-plateau with a fine structure of a shallow minimum. At this moment, we have no explanation for the dip effect at  $\sim 325$  K after region IV. Analogously, the plateau value  $\tau_3 \sim 3.1$  ns falls into the typical value range for most amorphous polymer glass-formers.



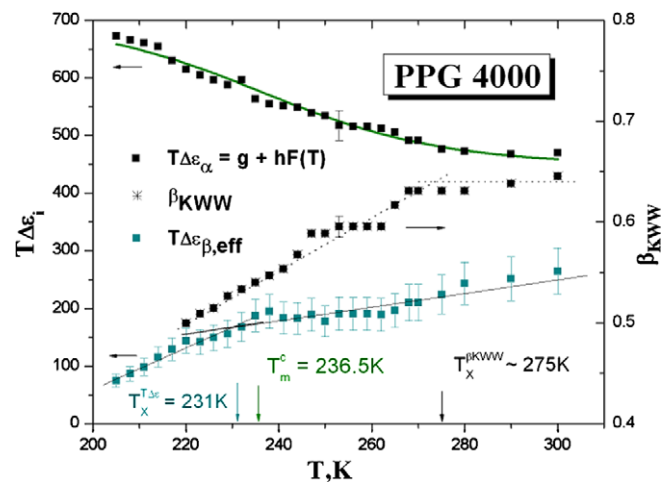
**Fig. 2.** Frequency dependence of the dielectric loss in PPG at selected temperatures in the glassy state at 150 K decomposed into the  $\alpha$ -component (red), the  $\beta$ -component (green) and the  $\gamma$ -component (blue) using the additive scheme and in the liquid state at 208, 220, 235, 256 and 280 K decomposed using the WW-ansatz into the  $\alpha$ -component (red) and  $\beta_{\text{eff}}$ -component (green). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

### 3.2. BDS data

Fig. 2 shows the dielectric loss spectra of PPG at several selected temperatures from a temperature range from 120 K up to 350 K. The three basic spectral features in the BDS spectra relevant to the PALS data are: a main peak from the primary  $\alpha$ -process and two smaller peaks on the high-frequency tail of the main peak which are attributed to the secondary  $\beta$  and  $\gamma$ -processes. As the intensity of the  $\gamma$ -peak is very low, the BDS spectra in the liquid state can consequently be deconvoluted within a multiplicative



**Fig. 3.** Temperature dependences of the dielectric relaxation times for the  $\alpha$ - and  $\beta_{\text{eff}}$ -process in the liquid state and the  $\beta$ - and  $\gamma$ -processes in the glassy state together with their extrapolations into the liquid one for the PPG sample. Fit of the MVFTH Eq. (1b) to the relaxation time with the fitting parameters given in the text is included.



**Fig. 4.** Spectral ( $\beta_{\text{KWW}}$ ) and relaxation ( $T\Delta\epsilon$ ) parameters of the  $\alpha$ - and  $\beta_{\text{eff}}$ -processes from the WW-ansatz for PPG. Typical error bars for  $\beta_{\text{KWW}}$  and  $T\Delta\epsilon_\alpha$  are shown in the plot.

scheme using the Williams–Watts (WW)-ansatz for both the  $\alpha$  and the  $\beta_{\text{eff}}$ -processes [26] – see Fig. 2 for temperatures ranging from 208 K up to 280 K.

Fig. 3 displays the dielectric relaxation times of the primary  $\alpha$  and secondary  $\beta$  and  $\gamma$ -processes for PPG as a function of the inverse of temperature over a temperature range from 120 K up to 350 K. In the case of the main relaxation process, two temperature regions of distinct thermal behavior of the relaxation time,  $\tau_\alpha$ , can be distinguished. In the high- $T$  region above  $T_A \sim 290$  K, the main process exhibits a linear trend in accord with many previous observations [15,17] indicating the approximate validity of the Arrhenius equation which suggests the thermal activation control of this process in the high- $T$  normal liquid state. On decreasing the temperature, the relaxation time of the main process begins to behave in the non-Arrhenius fashion. The whole course of dielectric main relaxation time of PPG can be analyzed within some suitable model framework such as, e.g., the two-order parameter (TOP) model [28] as it will be discussed later. On the other hand, the secondary  $\beta_{\text{eff}}$ -process in the liquid state exhibits a change in the character of

the relaxation time from Arrhenius to non-Arrhenius regime at  $T_X^{\tau_{\text{eff}}} \sim 235$  K. On further increasing the temperature, the relaxation times of both the effective  $\beta$  relaxation and the  $\alpha$ -process approach to each other indicating the mutual tendency to their merging towards the main structural relaxation at high temperatures. Finally, the weak  $\gamma$ -process in the glassy state exhibits the Arrhenius behavior as usually observed for very localized motions.

Fig. 4 displays the temperature dependences of the relaxation strength of the  $\alpha$ -process,  $\Delta\epsilon_\alpha$ , and the  $\beta_{\text{eff}}$ -one,  $\Delta\epsilon_{\beta,\text{eff}}$  in  $T\Delta\epsilon$  vs.  $T$  representation and the spectral width of the  $\alpha$ -process,  $\beta_{\text{KWW}}$ , over the whole temperature range analyzed using the WW-ansatz. Crossover in the spectral parameter of the former process is estimated to lie around  $T_X^{\beta_{\text{KWW}}} \sim 275$  K. On the other hand, the  $\beta_{\text{eff}}$ -process exhibits a crossover effect from one linear to another linear course at  $T_X^{T\Delta\epsilon_{\beta,\text{eff}}} = 231 \pm 5$  K. Overall, the crossover effects suggest rather strong qualitative changes in the character of both the  $\alpha$  and  $\beta_{\text{eff}}$ -relaxations around this temperature range.

## 4. Discussion

### 4.1. Phenomenological relationships between PALS and BDS responses

We begin our discussion with comparisons of the phenomenological PALS and BDS responses, i.e., the crossover effects in the  $\tau_3$  vs.  $T$  dependence and in the various spectral parameters of both the main and secondary processes on PPG. The PALS response of PPG exhibits the basic features similar to those found for many other glass-formers studied so far [6–11,18,19]: (i) its form is quasi-sigmoidal and (ii) basically four different regions of distinct thermal behavior with the three characteristic PALS temperatures:  $T_g^{\text{PALS}}$ ,  $T_{b1}^L = 1.18 T_g^{\text{PALS}}$  and  $T_{b2}^L = 1.44 T_g^{\text{PALS}}$ . These are rather close to the lower limit of the typical ranges for glass-forming liquids mentioned above as expected for the fragile systems. Further, by comparison of PALS and BDS data in Figs. 1 and 3, several correlations can be found. In Fig. 3, the arrows on left-axis mark the o-Ps lifetime at the first characteristic PALS temperature  $\tau_3(T_{b1}^L)$  and the onset of plateau one  $\tau_3(T_{b2}^L)$ . The later reaches the main relaxation time,  $\tau_a$ , at around the plateau temperature  $\sim 280$  K in agreement with our previous findings [9,18,19]. Moreover, this finding appears to be consistent with a qualitative change in the spectral width of the  $\alpha$ -process, at  $T_X^{\beta_{\text{KWW}}} = 275$  K – see Fig. 4. The slighter bend effect in the PALS response of PPG at  $T_{b1}^L$  lies close in the vicinity of the crossover temperature of the  $\beta_{\text{eff}}$  relaxation time,  $T_X^{\tau_{\text{eff}}} = 235$  K, at which its character changes from the Arrhenius to non-Arrhenius regime. The last finding appears to be also consistent with the crossover from one linear to another linear dependence in other relaxation parameter of the  $\beta_{\text{eff}}$ -process: its relaxation strength at  $T_X^{T\Delta\epsilon_{\beta,\text{eff}}} \sim 231$  K – Fig. 4. Thus, the changes in the PALS response and relaxation parameters of the  $\beta_{\text{eff}}$ -process at  $T_{b1}^L$  likely have a common origin. As the  $\tau_3(T_{b1}^L)$  is about 1.5 order of magnitude more rapid than the relaxation time of the  $\beta_{\text{eff}}$ -process and lies rather in the vicinity of the extrapolated  $\gamma$ -relaxation time into the liquid state, this localized process seems to be one of the possible origins of the crossover phenomena in the PALS and BDS responses. Another possible reason will be presented later in the context of application of the TOP model on the relaxation data of PPG.

### 4.2. BDS data on PPG within the TOP model

The whole course of the temperature dependence of the structural relaxation time can be accounted for by the modified Vogel–Fulcher–Tamman–Hesse (MVFTH) equation, Eq. (1b) proposed in the two-order parameter (TOP) model [28], which is expected to be valid over a very wide temperature range:

$$\tau_\alpha(T) = \tau_\infty \exp[E_\alpha^*/RT] \exp[BF(T)/(T - T_0)] \quad (2)$$

where  $\tau_\alpha(T)$  is the primary  $\alpha$  relaxation time,  $\tau_\infty$  is the pre-exponent factor,  $E_\alpha^*$  is the activation energy above  $T_m^c \sim T_A$ ,  $T_0$  is the divergence temperature,  $B$  is the coefficient and  $F(T)$  is a crossover function between solid-like and liquid-like domains defined as

$$F(T) = 1 / \{ \exp[\kappa(T - T_m^c)] + 1 \} \quad (3)$$

where  $\kappa$  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 liquid phase should be equal to that of solid one  $\Delta G_{\text{liq}} = \Delta G_{\text{sol}}$ . Fig. 3 contains the structural relaxation time fitted over a very wide  $T$  range from 205 K up to 350 K with the following parameters:  $\log \tau_\infty$  (s) =  $-15.36$ ,  $E_\alpha^* = 16.4$  kJ/mol,  $B/2.3 = 164.4$  K,  $\kappa = 0.0512$  1/K,  $T_m^c = 236.5$  K and  $T_0 = 185.2$  K.

### 4.3. Common discussion of the phenomenological and model analyses of PALS and BDS data

The PALS and dielectric relaxation responses on PPG can further be discussed within a framework of the original TOP model for the latter as follow. From comparison of the PALS response in Fig. 1 with the spectral parameters of the main process in Figs. 3 and 4 it is evident that the existence of the high temperature quasi-plateau region in the PALS response of PPG above  $T_{b2}^L$  corresponds approximately to a qualitative change in the character of the main process as indicated by the transition to Arrhenius-like dynamical regime above  $T_A$  and the crossovers in the relaxation strength,  $T\Delta\epsilon_\alpha$ , and spectral width,  $\beta_{\text{KWW}}$ . According to the TOP model, the higher  $T$  region in the dynamic response as well as the quasi-plateau region of the PALS response should be connected with the dominance of the liquid-like domains [28]. On decreasing the temperature, the proportion of these liquid-like domains begins to reduce significantly and the solid-like regions appear. This results in the significant change in the dynamic response, i.e. the slowing-down of the primary  $\alpha$ -process as well as in the change of the character of the PALS response for the slightly supercooled liquid below  $T_{b2}^L$ . Thus, the  $\alpha$  relaxation time begins to increase in the non-Arrhenius fashion together with the corresponding increase in the relaxation strength,  $T\Delta\epsilon_\alpha$ , and decrease in the spectral width,  $\beta_{\text{KWW}}$ . As seen in Fig. 4, the product  $T\Delta\epsilon_\alpha$  can be satisfactorily fitted using the function  $F(T)$  suggesting that the reorganization, i.e. disappearance and formation of solid-like domains, is responsible for the primary  $\alpha$ -process in accord with the postulate of the TOP model. At the same time, on crossing  $T_{b2}^L$  the o-Ps lifetime starts to decrease in more rapid way. On further cooling, the PPG sample crosses an inflection point at  $T_m^c = 236$  K, from the fitting of the structural relaxation data, which is quite close to  $T_{b1}^L = 229.5$  K from the best linear fits of the PALS data. This is accompanied by further dramatic changes in both the dynamics and PALS responses. The  $\alpha$ -relaxation time increases more steeply in the non-Arrhenius fashion towards the glass transition temperature on crossing  $10^{-6}$  s – Fig. 3. This appears to be consistent with our recent empirical finding of the correlation between  $T_{b1}^L$  and  $T_\alpha(\tau_\alpha = 10^{-6}\text{s})$  for many glass-forming systems [19] given in the introduction. In addition, the  $\beta_{\text{eff}}$  relaxation time exhibits a crossover from the Arrhenius regime to non-Arrhenius one together with the change in its relaxation strength parameter – Figs. 3 and 4. At the same time, the o-Ps lifetime starts to slow down as suggested by the simplified phenomenological analysis. All these effects seem to be consistent with the increasing dominance of the solid-like domains in the deeply supercooled liquid. Finally, on further decreasing the temperature, the solid-like domains begin to percolate resulting into the glassy state of disordered system with the small expansivity of free volume in the solid-like domains forming the glassy state of PPG.

## 5. Conclusion

We present phenomenological and theoretical analyses of both the structural relaxation data from BDS and the o-Ps lifetime data from PALS for *poly(propylene glycol)*. BDS data were analyzed within the original TOP model for disordered system. Phenomenological consistent correlations between both the PALS and BDS responses and the theoretical description of BDS data within the TOP model for a typical polymer glass-forming system over a wide temperature range has been achieved. Overall, the empirical relationships and performed TOP description of the BDS responses indicate a close connection between the PALS response and the dielectric relaxation for PPG. It seems to support the physical picture of liquid-like and solid-like domains determining the properties of the disordered phase, indicating close links between the decrease in free volume, the evolution of solid-like domains and the slowing-down of the dielectric  $\alpha$ -process.

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