

Positron annihilation and relaxation dynamics from dielectric spectroscopy and nuclear magnetic resonance: *Cis-trans*-1,4-poly(butadiene)

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We report a joint analysis of positron annihilation lifetime spectroscopy (PALS), dielectric spectroscopy (BDS), and nuclear magnetic resonance (NMR) on *cis-trans*-1,4-poly(butadiene) (*c-t*-1,4-PBD). Phenomenological analysis of the orthopositronium lifetime $\tau_3 - T$ dependence by linear fitting reveals four characteristic PALS temperatures: $T_{b1}^G = 0.63T_g^{\text{PALS}}$, T_g^{PALS} , $T_{b1}^L = 1.22T_g^{\text{PALS}}$, and $T_{b2}^L = 1.52T_g^{\text{PALS}}$. Slight bend effects in the glassy and supercooled liquid states are related to the fast or slow secondary β process, from neutron scattering, respectively, the latter being connected with the *trans*-isomers. In addition, the first bend effect in the supercooled liquid coincides with a deviation of the slow effective secondary β_{eff} relaxation related to the *cis*-isomers from low- T Arrhenius behavior to non-Arrhenius one and correlates with the onset of the primary α process from BDS. The second plateau effect in the liquid state occurs when τ_3 becomes commensurable with the structural relaxation time $\tau_\alpha(T_{b2})$. It is also approximately related to its crossover from non-Arrhenius to Arrhenius regime in the combined BDS and NMR data. Finally, the combined BDS and NMR structural relaxation data, when analyzed in terms of the two-order parameter (TOP) model, suggest the influence of solidlike domains on both the annihilation behavior and the local and segmental chain mobility in the supercooled liquid. All these findings indicate the influence of the dynamic heterogeneity in both the primary and secondary relaxations due to the *cis-trans* isomerism in *c-t*-1,4-PBD and their impact into the PALS response. © 2011 American Institute of Physics. [doi:10.1063/1.3578446]

I. INTRODUCTION

The structure-dynamic state of condensed matter and especially of soft glass-forming materials determines a series of mechanical as well as physical properties such as small- and large scale deformation behavior or diffusion of small molecules and macromolecules, respectively. Therefore, a detailed understanding of the mutual relationships between the structure and dynamics in amorphous glass-formers over an extraordinary wide temperature range is of a great importance. This concerns especially the basic and long-term topic in soft matter physics and chemistry started up by thermodynamic techniques such as dilatometry and calorimetry, i.e., the physical nature of the liquid to glass transition at the glass transition temperature, T_g .¹⁻⁵

Structural aspects of condensed materials are usually studied by x-ray or neutron diffraction techniques. From a classical viewpoint, liquid and glassy phases are practically indistinguishable disordered states characterized by short-range order, lacking the long-range which exists in the crystalline materials only.⁶ On the other hand, direct dynamic techniques such as broadband dielectric spectroscopy (BDS), magnetic resonances (NMR), neutron, and light scattering

(NS, LS) point strongly to the existence of close connections of the glass transition phenomenon to the evolution of structural relaxation dynamics of glass-formers on going from the low viscosity (rapidly relaxing) normal liquid through the supercooled one toward the very high viscosity (very slowly relaxing) solid glass.⁷ One of the typical features of all the structural glass formers is the dynamic heterogeneity with respect to temperature,⁸ space and time.⁹ As for the former aspect, several dynamic regimes over a wide temperature interval ranging from the normal liquid through the supercooled one toward the glass are marked by various characteristic dynamic temperatures, e.g., the Arrhenius T_A ,^{10,11} Stickel T_B^{ST} ,¹² Alegría-Colmenero $T_B^{\beta_{\text{KWW}}}$ ¹³ and Schönhals T_B^{SCH} temperature.¹⁴ Evidently, explanation of the physical origin of these dynamically distinct regions in a wide T interval and the closely related crossover temperatures can significantly contribute to our understanding of the glassification in various types of glass-formers.⁸ In contrast to older diffraction works,⁶ recent joint experimental and modeling search for the possible structural origin of the vitrification problem revealed new connections between the clusterlike heterogeneities or the local order and the dramatic dynamic slowing down as well as the characteristic dynamic temperatures in a few small molecule and polymer glass-formers.¹⁵ Next, these diffraction data for some of the former type compounds¹⁵ could be interpreted in the framework of the hetero-phase

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fluctuation (HPF) model¹⁶ or the two-order parameter (TOP) model¹⁷ in terms of the solidlike and liquidlike domain picture of glass-forming liquids,¹⁷ respectively. Despite certain progress in understanding of the connection between structure and dynamics, the number of papers dealing with this fundamental problem of glass-forming systems is still limited.

Alternatively, the structural-dynamic state of glass-formers is often treated in terms of a simple and physically plausible free volume concept serving as a measure of the structural disorder or/and the mobility of the constituents of condensed material which became very useful in the interpretation of the thermodynamic, dynamic, and transport properties of polymers.^{18,19} In this context, positron annihilation lifetime spectroscopy (PALS) as a unique structure-dynamic sensitive method is of high relevance. It is based on the annihilation behavior of the atomic orthopositronium (o-Ps) probe, i.e., a bound system of a positron and an electron which is formed and localized in local static (permanent) and dynamic (transient) regions of reduced electron density, i.e., vacancies or free volume holes.^{20–22} The o-Ps probe decays by pick-off interaction with an electron of opposite spin in the surrounding medium. o-Ps lifetime, τ_3 , is a measure of the size of these free volume regions.²³

In the contrast to crystalline compounds,²⁴ the PALS response of amorphous small-molecule and polymeric glass-formers is more complicated showing a basically sigmoidal or quasi-sigmoidal dependence of $\tau_3(T)$ extended over a more or less wide temperature range depending on fragility of glass-former and finished by a pronounced plateau or quasi-plateau effect at higher temperatures with respect to T_g .^{25,26} Phenomenological analyses of these $\tau_3(T)$ plots revealed several regions of a linear behavior marked by the characteristic PALS temperatures which, according to a unified notation in Ref. 26, are depicted as T_{b1}^G , T_g^{PALS} , T_{b1}^L , and $T_{b2}^L = T_r = T_k$.^{26,27} The first temperature lies at $T_{b1}^G \cong (0.6 - 0.8)T_g^{\text{PALS}}$ (Ref. 26) and the two latter ones are situated at $T_{b1}^L \cong (1.2 - 1.4)T_g^{\text{PALS}}$ (Refs. 26 and 28) and $T_{b2}^L \cong (1.4 - 1.7)T_g^{\text{PALS}}$,^{26–28} respectively.

Evidently, the complete structure-dynamic characterization of any disordered substance by PALS over a wide temperature range requires understanding of the origin of these different regions and the closely related characteristic PALS temperatures. To achieve this goal, distinct features of the PALS response may be compared with the various characteristic temperatures as detected by traditional techniques indicating thermodynamic and/or especially, dynamic changes. At present, certain relations between various features of the PALS response and those in viscosity¹⁰ or dielectric spectra^{11–14,29–31} seem to suggest a dynamic character of the PALS response in the liquid state of glass-formers, at least. Thus, in 1980 it was revealed²⁷ that an onset of the quasi-plateau feature in the PALS response at $T_{b2} = T_r$ lies close to the Arrhenius temperature, T_A , above which the structural, i.e., viscosity¹⁰ or primary α relaxation,^{11,30,31} dynamics exhibits approximately the thermally activated character. Recent instrumental and spectral analytical advances in BDS^{29–31} enable to reveal further connections between the various features of the PALS response and the glassy dynamics.^{26,32–40}

Two empirical T_{b2} and T_{b1}^L rules establish the specific relationships between the o-Ps lifetime, τ_3 , and the primary α relaxation time, τ_α , namely, $\tau_\alpha(T_{b2}) \sim 10^{-9}$ s or $\tau_\alpha(T_{b1}) \sim 10^{-6 \pm 1}$ s, respectively.^{26,32} In the former case, for many glass-formers at the onset of the plateau or quasi-plateau effect in the PALS response the relation $\tau_3 \cong \tau_\alpha$ has been often found. Moreover, in some cases, such as strong glass-formers: glycerol (GL) (Refs. 33 and 34) and propylene glycol (PG) (Ref. 32) or fragile ones: propylene carbonate (Pc) (Ref. 37) and poly(propylene glycol) (PPG) (Ref. 36 and 38) as well as a series of propylene glycols of different fragility,³⁹ T_{b2}^L lies in the vicinity of the characteristic Stickel, T_B^{ST} , or Schön-hals, T_B^{SCH} , temperatures, where the structural relaxation significantly changes its character.^{33–39} However, in other cases, T_{b2}^L lies above T_B^{ST} and rather T_{b1}^L is situated close to the characteristic BDS temperature, T_B^{ST} .⁴⁰ The latter rule seems to suggest some role of the primary process in the PALS response, but some indications about a possible role of the slow secondary relaxations in a few small molecular and polymer glass-formers were also suggested.^{32,34–36,38} In summary, the current empirical situation is still incomplete and further systematic combined investigations are needed.

In the polymer dynamics community, 1,4-poly(butadiene)s (1,4-PBD) belong to the most frequently studied and the best characterized and consequently, perhaps, to the best understood class of polymer glass-formers from both the structural and dynamic viewpoints. In general, PBD has the simplest chemical structure among diene-type polymers, so that its 100% *cis*- or 100% *trans*-isomer forms exhibit strong crystallization tendency due to the regular geometric microstructure along the polymer chains. On the other hand, the fully amorphous PBD polymer can be obtained under special synthesis conditions of anionic polymerization with the appropriate combinations of the major *cis*- and *trans*-isomer and minor vinyl-isomer microstructures giving *cis-trans*-1,4-poly(butadiene)s (*c-t*-1,4-PBD).⁴¹ A number of structural⁴² and especially, dynamic methods such as rheology,⁴³ dynamic neutron scattering (NS),⁴⁴ BDS,⁴⁵ and dynamic light scattering (LS) (Ref. 46) have been used in investigations of these PBD's. In addition, extensive molecular dynamics simulations of the structural and various dynamic aspects of *c-t*-1,4-PBD have been also performed.^{47,48}

In this contribution, we present a detailed joint phenomenological analysis of the PALS response of a prototypical structurally simple amorphous polymer, *c-t*-1,4-PBD, from recent PALS study of some of us²⁶ extended toward lower and higher temperatures using the relevant new dielectric and magnetic resonance spectroscopic data and also utilizing the reported neutron scattering and molecular dynamics simulation results. This combined approach reveals further new connections between the o-Ps annihilation and the spectral and relaxation characteristics of three phenomena, i.e., dipolar relaxation, nuclear spin reorientation, and density fluctuation, especially in the glassy state as well as in the supercooled liquid one. This underlines the existence of a close relationship between both the PALS and various dynamic responses and points rather to the dynamic character of the PALS response.

II. EXPERIMENTAL

A. Material

Structurally simple and microstructurally heterogeneous amorphous polymer, *cis-trans*-1,4-poly (butadiene), $[\text{CH}_2 - \text{CH} = \text{CH} - \text{CH}_2]_n$, almost without side groups with the isomer composition, 52% *cis*-, 41% *trans*- and 7% vinyl-forms, from Polymer Source was used. Molecular weights were $M_w = 1.87 \times 10^4$ and $M_n = 1.8 \times 10^4$ giving polydispersity $M_w/M_n = 1.04$.

B. PALS method

Positron annihilation lifetime spectra of the *c-t*-1,4-PBD sample were performed at the Institute of Physics of SAS, Bratislava by the conventional fast-fast coincidence method using plastic scintillators coupled to Phillips XP2020 photomultipliers. The time resolution of prompt spectra was about 320 ps. The radioactive positron ^{22}Na source and the sample assembly were kept under vacuum in a cryogenerator. During the low temperature measurements from 14 K up to room temperature, the samples were mounted in a holder at the end of a cold finger of a closed-cycle refrigerator from Leybold with an automatic temperature regulation. Measurements at higher temperatures above room temperature up to 350 K were performed in a chamber without vacuum. The stability of the temperature was about 1 K.⁴⁹ The positron lifetime spectra were analyzed using the well-known PATFIT-88 software package⁵⁰ in terms of a short-term component from the annihilation of parapositronium *p*-Ps, τ_1 , an intermediate one attributed to “free” positron annihilation, τ_2 , and a long-term one related to free volume due to the pick-off annihilation of orthopositronium *o*-Ps, τ_3 . The acquisition time was at least 2 h for each temperature.

C. BDS method

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 ± 0.02 K) frequency scans of the complex dielectric function, $\varepsilon^*(f) = \varepsilon'(f) - i\varepsilon''(f)$, were performed over the temperature range 133–273 K. The dielectric spectra were treated by a phenomenological analysis based on the empirical Havriliak–Negami (HN) equation:^{31,51}

$$\varepsilon^*(\omega) - \varepsilon_\infty = \frac{\Delta\varepsilon}{[1 + (i\omega\tau_{HN})^\alpha]^\beta} \quad (2.B.1)$$

where, $\Delta\varepsilon$ is the relaxation strength, τ_{HN} is a relaxation time and α and β are shape parameters. In particular, the dielectric data analysis has been done assuming the picture originally developed by William and Watts⁵² and following the procedure described elsewhere.^{53–55} 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 β^{DS} 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 (α) 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 α and β^{DS} processes. A complete description of this evaluation method can be found in Ref. 53.

D. NMR method

Our BDS study on *c-t*-1,4-PBD was limited up to 273 K because around this temperature the relaxation peak moves out of our experimental frequency window. Therefore, in order to obtain the dynamic data over a wider temperature range we decided to extend the measured T range by using NMR. We performed ^{13}C nuclear magnetic measurements (NMR) on *c-t*-1,4-PBD at a series of temperatures between 235 and 288 K on a Varian VXR300 spectrometer. The ^{13}C spin-lattice relaxation times T_1 were measured corresponding to the various carbon atoms in the monomeric unit of *c-t*-1,4-PBD at a Larmor frequency of 75.4 MHz using the proton noise decoupling technique. The value of the spin-lattice relaxation time at each temperature was determined from exponential regression of the magnetization as a function of recovery time.⁵⁶

III. RESULTS

A. PALS results

Figure 1 presents the *o*-Ps lifetime, τ_3 , as a function of the temperature, T , for *c-t*-1,4-PBD over an extraordinary temperature range from 15 K up to 350 K. The τ_3 vs T plot is the result of superposition of the following three measuring runs: (i) 1st heating run from 15 K up to 300 K with larger T step after cooling from RT, (ii) 2nd heating run from 40 K up to RT with smaller T step, and finally, (iii) 3rd heating run from 280 K up to 350 K. All the three runs exhibit very good mutual overlap demonstrating that the PALS response of the *c-t*-1,

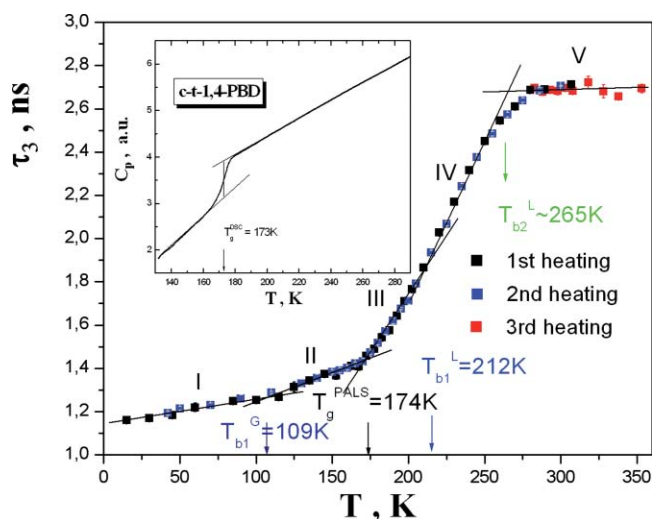


FIG. 1. *o*-Ps lifetime as a function of temperature for *c-t*-1,4-PBD. The inset shows DSC trace measured in heating regime with 10K/min. For the details see the text.

TABLE I. Fitting parameters of the linear expressions of a form $\tau_3 = aT + b$ for regions I–V in *c-t-1,4-PBD*.

Region	I	II	III	IV	V
ΔT , K	15 – 100	125 – 165	185 – 210	220 – 245	280 – 356
$a \times 10^3$ ns/K	1.230 ± 0.119	2.570 ± 0.244	12.53 ± 0.34	14.87 ± 0.46	0.306 ± 0.106
b , ns	1.141 ± 0.007	0.995 ± 0.039	-0.769 ± 0.066	-1.26 ± 0.111	2.608 ± 0.046
R	0.970	0.985	0.997	0.996	0.95

4-PBD sample is independent of the way of thermal treatment.

Several features and trends can be seen. At first sight, the $\tau_3 - T$ plot exhibits a typical quasi-sigmoidal course as usually observed for many small molecule and polymer glass-formers.^{20–22,25–28,32–40} Closer inspection of the PALS response reveals basically five regions of distinct thermal behavior marked as I–V. Relatively low-T region from 15 K up to ~ 170 K shows two similar regions, the same is observed for the followed sharply increasing intermediate region between ~ 180 K and ~ 265 K region finished by development toward a plateau effect in relatively high-T region. A phenomenological analysis of the PALS response by a linear fitting procedure^{26,28} provides the following linear expressions in a form: $\tau_3 = aT + b$ for five regions of the distinct thermal behavior of the o-Ps lifetime with the parameters listed in Table I which provide the four characteristic PALS temperatures: $T_{b1}^G = 109\text{K} = 0.63T_g^{\text{PALS}}$, $T_g^{\text{PALS}} = 174\text{K}$, $T_{b1}^L = 212\text{K} = 1.22T_g^{\text{PALS}}$, and $T_{b2}^L \approx 265\text{K} = 1.52T_g^{\text{PALS}}$.

B. BDS results

Figure 2 summarizes the dielectric loss of *c-t-1,4-PBD* as a function of frequency for a series of temperatures from 133 K up to 273 K. The dielectric spectra of *c-t-1,4-PBD* over the measuring frequency window ranging from $10^{-1.5}$ Hz up to 10^9 Hz show a typical evolution from a small relatively broad peak at low temperatures toward a large relatively narrow peak at high temperatures through some su-

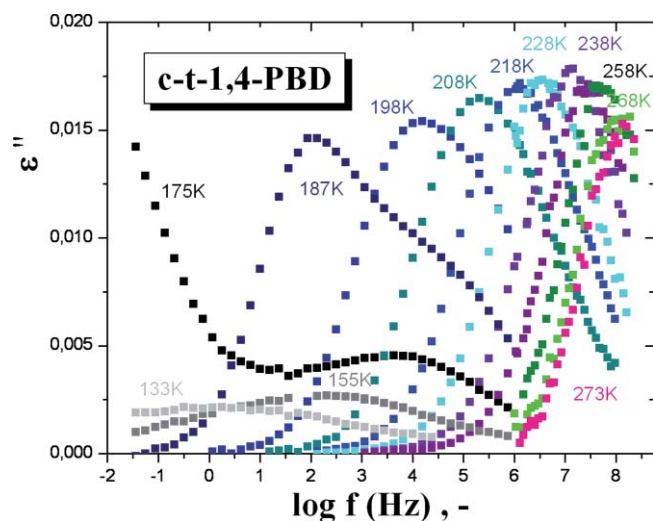


FIG. 2. Dielectric loss of *c-t-1,4-PBD* as a function of frequency at a series of temperatures between 133 K and 273 K.

perposed region at intermediate temperatures where both the peak features appear to coexist. The small peak is ascribed to a slow secondary β^{DS} process, while the larger peak to a primary α relaxation. The phenomenological analysis used to obtain the relaxation parameters of both the primary and secondary relaxation processes was based on the Williams–Watts (WW) approach⁵¹ using (i) a Havriliak–Negami (HN) for the α process⁵² and (ii) a Cole–Cole function for the β^{DS} process.³¹

Figure 3 shows the analysis of the BDS spectra of *c-t-1,4-PBD* by using WW ansatz at several important temperatures with respect to the PALS response. Satisfactory fits can be achieved over a wide temperature range which allows us to determine simultaneously the time scales of all the α and β^{DS} as well as unified main processes above T_g .

Figure 4 summarizes the characteristic time scales of both the structural α relaxation and the effective slow secondary β_{eff} process. In contrast to the simple extrapolation of the low temperature slow β process, relaxation curve resulting from the convolution of the extrapolation of the slow β process with the α relaxation can be quantified over the whole supercooled liquid range resulting in a unified main process in the high-T range. Slightly above T_g it follows low-T extrapolation from the glassy state, but above $T_X^{\beta_{\text{eff}}} \sim 210$ K a clear deviation from the lower-T Arrhenius regime can be found.

C. NMR results

Figure 5 shows the measured ^{13}C NMR T_1 spin-lattice relaxation times for *c-t-1,4-PBD* as a function of the temperature. It can be observed from this figure that the here analyzed C atoms show a similar behavior and exhibit a minimum close to 260 K. We further analyzed the experimental spin-lattice relaxation times shown in Fig. 5 as follows: starting with the assumption of a purely ^{13}C – ^1H dipolar relaxation mechanism, the observed spin-lattice relaxation times T_1 using ^{13}C NMR experiments can be expressed as⁵²

$$\frac{1}{T_1} = \frac{h^2 \gamma_C^2 \gamma_H^2}{40\pi^2 r_{CH}^6} [3J(\omega_C) + 6J(\omega_H + \omega_C) + J(\omega_H - \omega_C)], \quad (3.C.1)$$

where ω_C and ω_H are the Larmour frequencies for carbon and proton, respectively, γ_C and γ_H are the gyromagnetic ratios, and r_{CH} is the carbon–proton inter-nuclear distance. $J(\omega)$ is the spectral density function which is defined as the one-side Fourier transform of the self-orientation function of the carbon–proton bond. Thus, the spectral density $J(\omega)$ can be

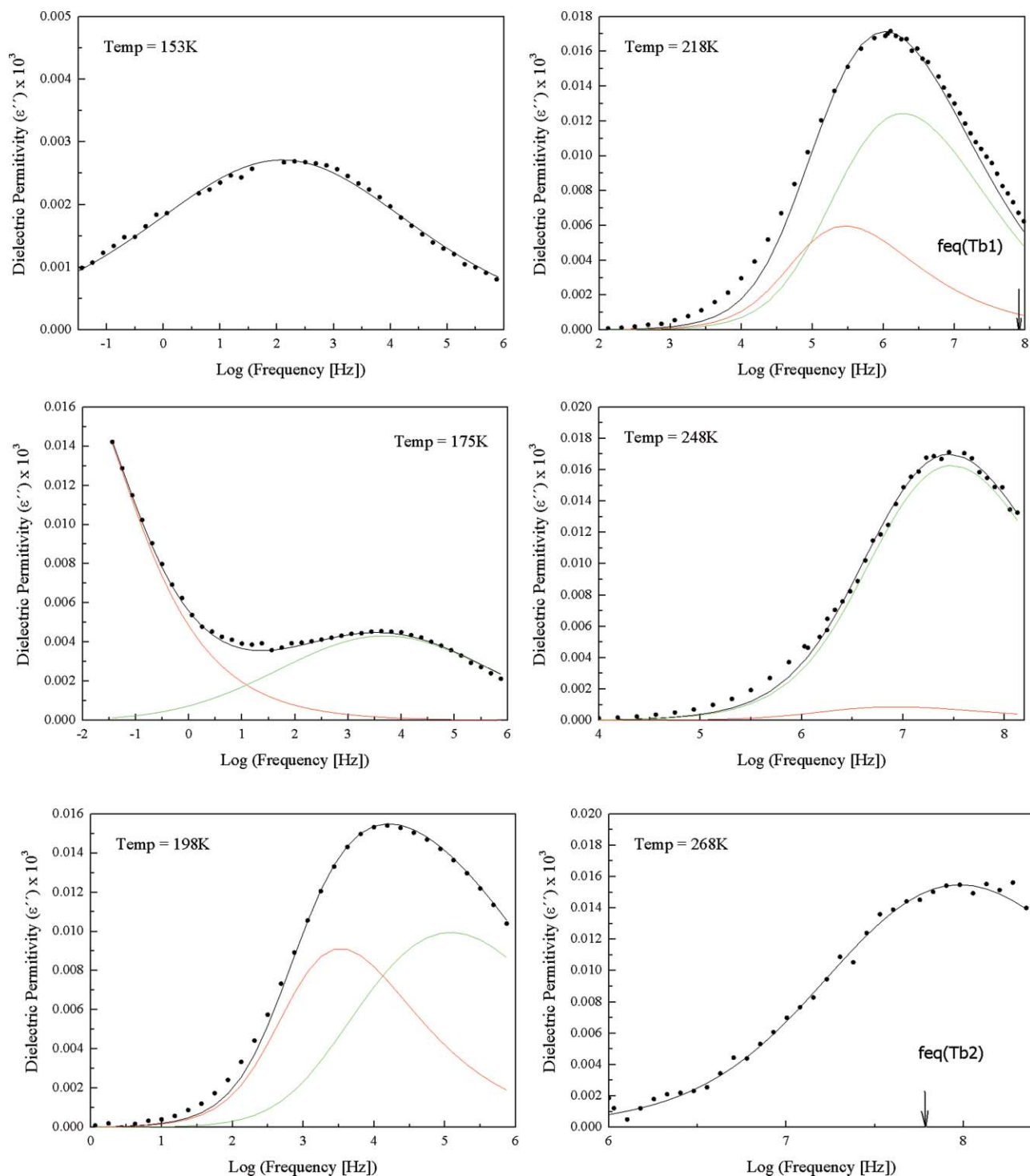


FIG. 3. Frequency dependence of the dielectric loss in *c-t*-1,4-PDB at selected temperatures in the glassy state at 153 K the β process (blue) and in the liquid state at 175, 198, 218, 248, and 268 K decomposed using the WW-ansatz into the α (red), β_{eff} (green), and main $\alpha\beta$ (black) process. The two arrows display the equivalent frequencies of the o-Ps lifetime $f_{eq}(T_{b1}^L)$ and $f_{eq}(T_{b2}^L)$ at the characteristic PALS temperatures T_{b1}^L or T_{b2}^L being close to the high-f tail of the primary peak or the peak of the main process, respectively.

expressed as

$$J(\omega) = \text{Im} \left[\left(\frac{-1}{\omega} \right) \Phi_A^*(\omega, \tau_1) \right], \quad (3.C.2)$$

where we assumed that $\Phi_A^*(\omega, \tau_1)$ would be given as

$$\Phi_A^*(\omega, \tau_1) = A_N \Phi_{HN}^*(\omega, \tau_1), \quad (3.C.3)$$

where the prefactor A_N accounts for any motions present in the sample that is faster than the relaxation process considered here, $\Phi_{HN}^*(\omega, \tau_1)$ being a Havriliak–Negami relaxation function with the shape parameters fixed to those obtained from the dielectric relaxation fits at high temperatures. In the fitting procedure, the prefactor A_N was varied to match the minimum T_1 value for each carbon and found to be lesser

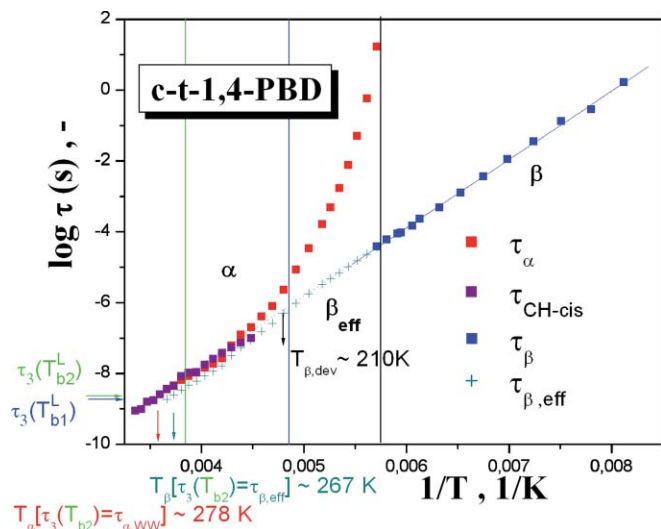


FIG. 4. Relaxation map of the *c-t*-1,4-PBD sample as obtained from spectral analysis of dielectric loss by using the WW ansatz together with the relaxation times of CH_{cis} carbons from ¹³C-NMR study after their small shift to overlap the main (α/β) relaxation times stemming from the *cis*-isomers sequences of the chains in BDS.

than unity in all cases, therefore indicating the presence of contributions from faster motions. Once these A_N values were fixed, the direct correspondence between calculated T_1 and measured data provides the corresponding relaxation time 0.

From all the C atoms, those from the CH-*cis* groups have shown to have the highest value of A_N (0.77) indicating a closer dynamics to that measured by BDS. Although the relaxation times obtained by NMR are systematically faster than the corresponding to DS (we are sensing molecular dipoles in one case and individual atoms in the other), the temperature dependence of the relaxation times is expected to be the same in both cases. As shown in Fig. 6, we observed at these high temperatures an Arrhenius dependence of the relaxation time. Starting from this Arrhenius law the corresponding ¹³C T_1 values can be evaluated and compared with experimental data as shown in Fig. 5.

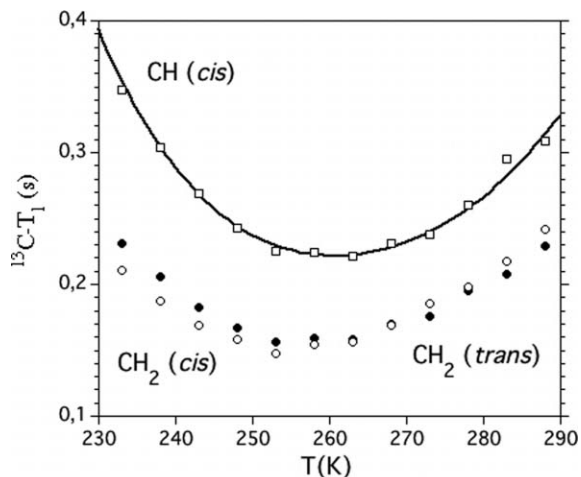


FIG. 5. ¹³C T_1 spin-lattice relaxation times for *c-t*-1,4-PBD as a function of the temperature.

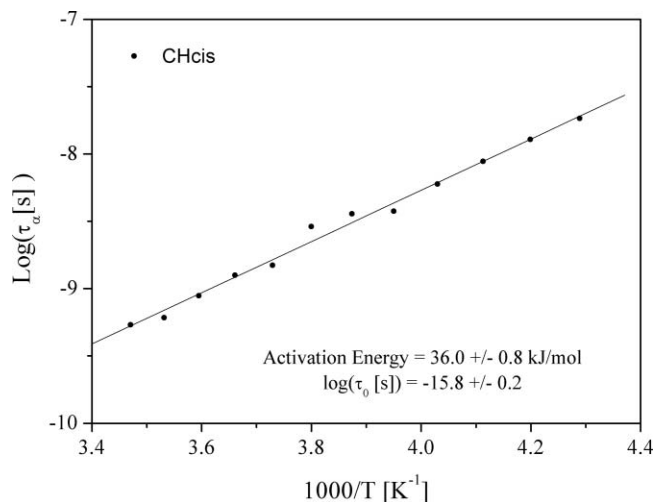


FIG. 6. Arrhenius plot of ¹³C T_1 spin lattice relaxation times as a function of temperature for the CH-*cis* atoms in *c-t*-1,4-PBD.

IV. DISCUSSION

A. Phenomenological relationships between the PALS response and the thermodynamic and dynamic databases

In the following sections, we present a detailed comparison of the PALS response with the thermodynamic data and the spectral evolutions of the electric dipole relaxation and the nuclear spin relaxation as well as of the density fluctuation to identify the processes responsible for the effects characterized by the characteristic PALS temperatures.

1. Glass-liquid transition region

The most pronounced bend effect at relatively lower T 's in $\tau_3 - T$ plot in Fig. 1 characterized by the intersection point defines the glass-liquid transition temperature, $T_g^{\text{PALS}} = 174\text{K}$ as seen by PALS method. This assignment is based on comparison with classical thermodynamic method such as dilatometric (DIL) and calorimetric (DSC) one, i.e., with the temperature dependence of the macroscopic volume⁵⁷ or specific heat,⁵⁸ respectively. The latter case is shown in the inset of Fig. 1, where the pronounced step in C_p vs T plot defines the thermodynamic glass-liquid DSC temperature $T_g^{\text{DSC}} = 173\text{K}$ as obtained in heating run with heating rate 10 K/min . Similar finding is reported for the temperature dependence of the density.⁵⁷

2. Glassy state region

Close inspection of the PALS response of *c-t*-1,4-PBD in low- T region below glass-liquid transition temperature in Fig. 1 reveals an additional slight bend effect at $T_{b1}^G = 109\text{K} = 0.63T_g^{\text{PALS}}$.

In analogy with the classical dilatometry work on a series of amorphous thermoplastics over extraordinary wide T ranges on both the sides of T_g (Ref. 57), where the slight bend effects in the macroscopic volume V vs. T dependence, even

in the glassy state were correlated with the secondary mobility from mechanical and dielectric relaxation studies, the similar slight bend effect in the τ_3 vs T , where τ_3 is a measure of free volume, V_h , can be discussed in terms of two dynamic hypotheses: (i) slow secondary β^{DS} process from DS data⁴⁹ or (ii) fast secondary β^{NS} process from NS data. The first possibility has already been discussed in Ref. 26 in connection with dielectric work on the similar *c-t-1,4-PBD* sample,⁴⁵ where on the basis of the dielectric β^{DS} relaxation time distribution $G[\log \tau_\beta(T)]$ slightly *extrapolated* toward lower T 's some of us tentatively proposed that this slight bend effect could be associated with a high- f tail of the slow secondary β^{DS} process. As for the second hypothesis, the scattering intensity coming from the harmonic motion of the H atoms in low- T region and any nonelastic contribution from various types of the H-mobility at higher temperatures can be measured by elastic and quasi-elastic neutron scattering (NS) experiments.⁵⁹ Fig. 4 of Ref. 59 shows the geometric characterization of the H atom mobility where the linear dependence of the mean square displacement, $\langle u^2 \rangle$ on temperature in low- T region up to ca $T_f \sim 110$ K reflects the harmonic character of the H scatters motion, whereas the nonlinear behavior above T_f comes from the so-called fast β_f secondary motion. Thus, on the basis of acceptable agreement between both the characteristic PALS and NS temperatures we may conclude that a slight bend effect in the glassy state of *c-t-1,4-PBD* at $T_{b1}^G \sim 109$ K might be associated with the onset of the anharmonicity in the hydrogen mobility. Similar effect has been found by us also for other amorphous polymer: poly (vinyl methylether) (PVME).⁶⁰

3. Supercooled and normal liquid state regions

a. Comparison of PALS with BDS and NMR data.

Figure 1 shows that the detailed PALS response at immediate and high temperatures above $T_g^{\text{PALS}} = 174$ K exhibits an additional slight bend effect at $T_{b1}^L = 212$ K = $1.22T_g^{\text{PALS}}$ and the second pronounced effect at around $T_{b2}^L \approx 265$ K = $1.52T_g^{\text{PALS}}$.

First, we discuss both the liquid effects in the context with the DSC response in the inset of Fig. 1. Simple comparison of the macroscopic DSC technique and the microscopic PALS one demonstrates clearly the essentially increased sensitivity of the latter to various structural or/and dynamic processes in the bulk material.

Next, to identify the physical processes being responsible for the T_{b1} and T_{b2} effects in the PALS response in the liquid range, various internal dynamic probes such as electric dipoles via BDS and nuclear spins using NMR as well as density fluctuation by means of NS can be used in comparison of the PALS and DYN databases at level of (i) the characteristic PALS and DYN (BDS, NMR, ...) temperatures and (ii) the correspondence between time scales of the o-Ps lifetime at these characteristic PALS temperatures with the characteristic times of the dynamic processes as obtained from various techniques.

Thus, the dielectric loss spectra in Fig. 2 have been evaluated within the WW ansatz in terms of the HN function

for the structural relaxation and the CC function for the slow secondary β^{DS} one. BDS reveals the relative closeness between the former, $\tau_{\alpha, \text{HN,ave}}$ and the characteristic times for the *cis*-carbons from the higher- T 's ¹³C-NMR study. This finding can be explained by considering that the BDS experiment indeed detects mainly the mobility of the dielectrically active *cis*-isomers in the *c-t-1,4-PBD* chains. On the other hand, the slow secondary β^{DS} process can be evaluated reliably by a simple peak-type analysis via the CC function in the glassy state only (below T_g) and can be parameterized by the Arrhenius equation: $\tau_\beta(T) = \tau_{\beta\infty} \cdot \exp(E_\beta/RT) = 1.35 \times 10^{-15} \exp(35.1 \text{kJ/mol}/RT)$.

From a simple additive analysis of the main and small peak by using the HN or CC function, respectively, it follows that the value of the primary α relaxation time at the first liquid characteristic PALS temperature $T_{b1}^L = 212$ K is $\tau_\alpha(T_{b1}^L) = 1.2 \times 10^{-6}$ s in accord with the T_{b1}^L rule.^{26,32} In addition, T_{b1}^L lies close to the *hypothetical* $\alpha\beta$ merging temperature $T_{\alpha\beta} \sim 210$ K from crossing $\tau_\alpha(T)$ and the extrapolated $\tau_\beta(T)$ (not shown). This seems to suggest that a change of the slope in τ_3 vs T could be related to the dominance of the primary α process. However, the situation is not so simple because of the hypothetical character of a long range extrapolation of $\tau_\beta(T)$ from the glassy state toward the liquid one.

Next, the structural α relaxation time from the WW ansatz form Fig. 4 at T_{b1}^L reaches $\tau_\alpha(T_{b1}^L) = 4x10^{-6}$ s in accord with the T_{b1}^L rule^{26,32} again. Further, the o-Ps annihilation time scale can be directly compared with the time scale of this effective β^{DS} process *above* T_g . Although the first liquid characteristic PALS temperature at $T_{b1}^L = 212$ K coincides with a deviation of the effective β^{DS} relaxation time from the low- T Arrhenius dependence toward the non-Arrhenius regime above 210K the time scales of both the PALS and BDS effects differ by more than two orders of magnitude. On the other hand, as it follows from Fig. 3 the equivalent frequency $f(T_{b1}^L)$ ³⁴ corresponding to the o-Ps lifetime at T_{b1}^L is close to the high - frequency tail of the primary α peak indicating that the onset of the primary α process may contribute to a change in the slope in the PALS response at T_{b1}^L .

Finally, the second liquid characteristic PALS temperature $T_{b2}^L \sim 265$ K is rather smaller compared to the α identity temperature: $T_\alpha[\tau_3(T_{b2}^L) = \tau_{\alpha, \text{WW}}] = 280$ K. However, as shown in Fig. 1 a crossover from region IV on the plateau level in the PALS response occurs through a certain region ca 15 K, i.e., the tendency toward the plateau effect starts at around 250 K and the true plateau effect is reached at around 280 K. Then, the T_{b2}^L rule^{26,32} is valid for this later temperature.

b. Comparison between PALS and NS data. Although T_{b1}^L coincides with the deviation of the β_{eff} process from the Arrhenius regime at ~ 210 K, the significant difference between the corresponding mean time scales does exist $\tau_3 \ll \tau_{\beta_{\text{eff}}}^{\text{DS}}$ reaching more than 2.5 orders of magnitude. As mentioned, one possible origin for the T_{b1}^L effect based on the BDS data can be the onset of the primary α process – see Fig. 3. Another one can be identified by considering a compilation of the characteristic times of all the dynamic processes in *c-t-1,4-PBD* as detected by various techniques in Fig. 1 of Ref. 48. In addition to the slow secondary β^{DS} relaxation from DS,

several further faster secondary processes in the liquid *c-t-1,4-PBD* have been found by neutron⁴⁴ and light scattering.⁴⁶ Comparison of the o-Ps lifetime at T_{b1}^L with the first faster process from NS study⁴⁸ leads to the identity β^{NS} temperature $T_{\beta}^{NS}[\tau_3(T_{b1}) = \tau_{\beta}^{NS}] \sim 218$ K which is quite close to $T_{b1}^L \sim 212$ K. This finding suggests that this faster secondary process detectable by NS technique ascribed on the basis of MD simulations⁴⁸ to the mobility of the dielectrically inactive *trans*-isomers units along the chains may also contribute to the first bend effect in the PALS response of the supercooled liquid state of the *c-t-1,4-PBD* sample.

B. Structural relaxation in terms of the TOP model and its connections with the secondary dynamics and PALS response

It is well known that the temperature dependence of the structural relaxation time over a wide temperature range in small molecule and polymer glass-formers can be rather seldom described by one phenomenological expression.^{4,7} Usually, the structural relaxation time over more or less limited temperature range is parameterized by some phenomenological expression such as the Vogel–Fulcher–Tamman–Hesse (VFTH) equation or by the Arrhenius equation and consequently, over a wider T range by their combinations giving to arise the various dynamic regimes marked by the crossovers in the various dynamic parameters and the corresponding characteristic DYN temperatures mentioned in the Introduction.^{10–14} Alternatively, in the case of the accessibility of the structural relaxation times over a sufficiently wide temperature range, they can be consistently described by the recently formulated two-order parameter (TOP) model of disordered glass-forming systems.¹⁷ This model deals with disordered materials over an extraordinary temperature range assuming them to be composed of stable normal liquidlike regions, containing locally favored structures and their clusters, and frustrated metastable solidlike domains. The former type of region is supposed to play a dominant role in low viscosity (fast relaxing) liquids and at high temperatures that are above the thermodynamic transition temperature, T_m^* . This temperature is expected to be close to the melting temperature, T_m , of the crystalline phase of crystallizing nonfrustrated materials, which is often found to be close to the so-called Arrhenius temperature, T_A .¹⁷ On going from above, at this temperature, the crossover from the Arrhenius to non-Arrhenius-type dynamical regime occurs. Thus, the structural dynamics of normal liquids is connected with the Arrhenius regime of the single main relaxation process.¹⁷ Then, in the case of noncrystallizing compounds such as our *c-t-1,4-PBD* system, T_A instead of T_m^* might be used. The TOP model considers the liquid-glass transition to be a consequence of the competition of ordering and the frustration effects on ordering in solidlike domains. The proportion of the frustrated solidlike domains or islands in glass-formers grows with decreasing temperature through the supercooled liquid toward the glassy state. Thus, the dynamics exhibits the gradually cooperative and heterogeneous character that leads to the non-Arrhenius dependence of the viscosity or the structural relaxation. Finally, at very low temperatures below

T_g , the solidlike domains are not able to reorganize and they should form the rigid glassy state. The phenomenological basis of the TOP model is given by the modified VFTH (M-VFTH) equation for the viscosity or relaxation time which is expected to be valid over a very wide temperature range including both the normal and supercooled liquid states:¹⁷

$$\tau_{\alpha}(T) = \tau_{\alpha\infty} \exp[E_{\tau}^*/RT] \exp[BF(T)/(T - T_0)] \quad (4.B.1)$$

where $\tau(T)$ is the structural relaxation time, τ_{∞} is the pre-exponent factor, E_{τ}^* is the activation energy above $T_m^* \sim T_A$, T_0 is the divergence temperature, B is the coefficient and $F(T)$ is a probability function for solidlike domains. The latter is defined as

$$F(T) = 1/\{\exp[\kappa(T - T_m^c)] + 1\} \quad (4.B.2)$$

where κ describes the sharpness of the probability function and T_m^c is the characteristic TOP temperature, i.e., the critical temperature where the free energy of a crystallizing liquid is equal to that of the crystal $\Delta G_{lq} = \Delta G_{cr}$ or, in the general case of noncrystallizing materials, the free energy of a noncrystallizing liquid is equal to that of a solid: $\Delta G_{lq} = \Delta G_{sol}$.

The TOP model has been successfully used by the original author to describe simultaneously the structural features such as a sub-peak of the static structure factor, $S(q)$, being an indicator of medium-range solidlike ordering, in propylene carbonate (Pc) and phenyl salicylate (salol)¹⁵ with the corresponding structural relaxation.¹⁷ Recently, the structure of *c-t-1,4-PBD* has been studied by neutron diffraction and molecular dynamics,⁴⁷ but unfortunately, the small q region has not been addressed, so that a check on the medium range order in the spirit of TOP model as for Pc and salol could not be performed. On the other hand, some of us have discussed the M-VFTH parameters of the viscosity or structural relaxation in relation to various effects in the PALS response in small molecule (glycerol, Pc, and three propylene glycols)^{37,39,61} as well as one polymer (poly(propylene glycol)) glass-formers.³⁸ These findings describing simultaneously both the o-Ps annihilation reflecting the free volume microstructure and the structural relaxation from the different dynamic techniques prompt us to test the potential of the TOP model for *c-t-1,4-PBD*.

Figure 7 displays a fit of the structural relaxation times of the *c-t-1,4-PBD* sample over the whole temperature range by using Eq. (4.B.1). Satisfactory description of the combined BDS and NMR structural relaxation times over 120 K is achieved. Consequently, the dynamic behavior from BDS and NMR as well as the PALS response can be discussed by using the TOP parameters for the structural relaxation as follows: the Arrhenius temperature, $T_A \sim 253$ K lies quite close to the onset of the plateau region starting above 250 K which indicates the relationship between the dramatic change in the PALS response and the crossover between non-Arrhenius and Arrhenius character of the structural relaxation Fig. 1 and 4. Further, the characteristic TOP temperature $T_m^c \sim 205$ K is quite close to the deviation temperature of the slow

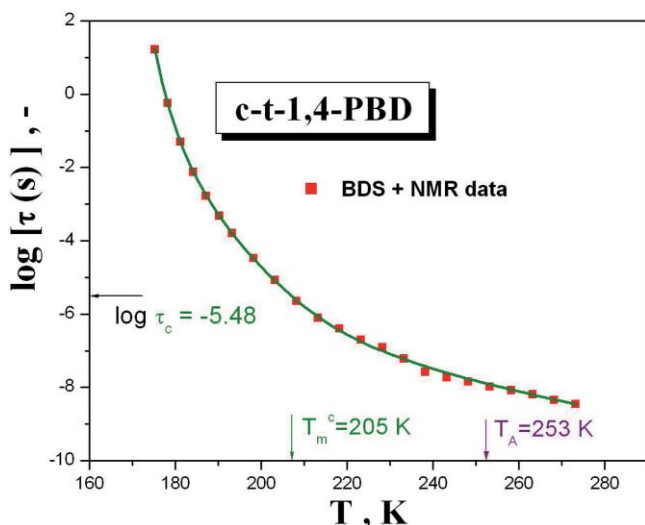


FIG. 7. Combined characteristic times from BDS and NMR as a function of temperature for *c-t*-1,4-PBD with the characteristic TOP temperatures, i.e., the Arrhenius temperature: $T_A = 253$ K and the TOP temperature: $T_m^c = 205$ K. The line represents the corresponding fit using the M-VFTH expression with the following parameters: $\log \tau_{\infty} = -15.8$, $B = 139.4$ K, $\kappa = 0.111$ 1/K, and $T_0 = 164.5$ K.

effective secondary β^{DS} process from the lower-T Arrhenius regime to the high-T non-Arrhenius one at ~ 210 K in Fig. 4. This relation between the structural and secondary relaxation from BDS data can be explained with help of Eq. (4.B.2) for $F(T)$, i.e., the change in the dynamic regime of the effective slow β^{DS} process stemming from the *cis*-isomers in the chains ~ 210 K appears to be related to a change in the dominance of the solidlike domains in the deeply supercooled liquid state below the characteristic TOP temperature T_m^c in favor of the liquidlike ones in the weakly supercooled liquid state. Finally, a closeness between $T_{b1}^L \sim T_m^c$ is consistent with the onset of the high-f tail of the primary α process which suggests that the fastest components of the primary relaxation time distribution contribute to a change in the slope of the o-Ps lifetime above the first liquid characteristic PALS temperature. This finding together with a correlation of the o-Ps lifetime with the relaxation times of the faster slow β^{NS} process suggest on a complex interplay between the *cis*- isomer and *trans*-isomer mobility and the PALS response of the *cis-trans*-1,4-PBD sample.

V. SUMMARY AND CONCLUSIONS

In summary, we presented a joint analysis of the annihilation behavior of the o-Ps probe from PALS and the dynamic behavior from newly measured BDS and NMR data as well as from the relevant literature NS and MD simulation results over wide temperature and frequency ranges on an archetypal amorphous polymer: *c-t*-1,4-PBD.

A number of the mutual relations between the o-Ps annihilation and the dynamic parameters have been found. Thus, phenomenological analysis of the o-Ps lifetime $\tau_3 - T$ dependence by linear fittings reveals four characteristic PALS temperatures: $T_{b1}^G = 0.63T_g^{\text{PALS}}$, T_g^{PALS} , $T_{b1}^L = 1.22T_g^{\text{PALS}}$ and $T_{b2}^L = 1.52T_g^{\text{PALS}}$, which were found to be related to the

fast β^{NS} process, to glass – liquid transition, to the onset of the α process together with the slow β^{NS} and finally, to the main relaxation from BDS and NMR. Phenomenological description of the structural relaxation in terms of the TOP model indicates that the crossover in the dielectric slow β^{DS} process from Arrhenius regime at low temperatures to non-Arrhenius one may be related to the change in the dominance between the solidlike and the liquidlike ones in the amorphous polymer.

All these observed empirical relationships as well as a successful description of the structural relaxation in terms of the TOP model indicate very close connections between the PALS response and the dynamic behavior from various techniques for *c-t*-1,4-PBD. Especially, the selective influence of the chain microstructure due to the *cis-trans* isomerism on the secondary dynamics in the *c-t*-1,4-PBD chains and their subsequent impact into the PALS response has been found.

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