# Free Volume Microstructure and Its Relationship to the Chain Dynamics in *cis*-1,4-Poly(butadiene) As Seen by Positron Annihilation Lifetime Spectroscopy

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*Received October 11, 1996; Revised Manuscript Received May 27, 1997*⊗

ABSTRACT: The annihilation characteristics of the orthopositronium (o-Ps) in the structurally simplest elastomer *cis*-1,4-poly(butadiene) has been measured in the temperature range from 15 to 313 K and interpreted in the framework of the free volume concept. The temperature dependence of the mean lifetime of the o-Ps, $\tau_3$, and its relative intensity, $I_3$, reflect a fine interplay between the free volume and microscopic chain dynamics. In addition to a pronounced break on the $\tau_3-T$ plot at the glass transition temperature, $T_g$, a further two bends exist. The first, in glassy state, is relatively slight. The other one, in an elastic state, can be correlated with the melting temperature $T_m$ of the crystalline phase. The order agreement between the temperature coefficients of free volume hole expansion $\alpha_h$ and the mean square displacement of chain atoms $\alpha_{\langle u^2\rangle}$ from a recent neutron scattering study indicates a microscopic cause for the hole size growth with temperature. The decrease of $I_3$ with temperature $T$ above 120 K correlates with the onset temperature of the so-called fast motion from neutron scattering measurements as well as with the so-called Vogel temperature $T_o$ for the primary segmental dynamics. The N-like shape course above $T_g$ correlates with the cold crystallization from DSC measurements. In the melt region above 265 K, the slightly dependent $\tau_3$ and $I_3$ quantities correspond to a formation of the bubble states of the o-Ps in the soft matrix. Finally, the temperature dependence of free volume hole distributions exhibits the essential changes from relative narrow distributions in the glassy state to wide distributions above $T_g$ and ones that do not change much in the melt region of the polymer matrix.

## Introduction

The structure of polymers of a given chemical composition of the monomers with their mutual binding and arrangement determines the set of their physical as well as physico-chemical properties. In the case of amorphous polymers, the structural characterization is more complicated due to the disorder of their chains. For this reason the use of classical diffraction techniques is limited.[1,2] To understand the relationship between structure and properties, information on the local variation of the basic unit arrangement is necessary. According to the free volume concept of mobility in disordered media,[1,3−8] a given motional mode may be only realized in certain local regions of the matrix with lowered local density. It is evident that the detailed knowledge of the local structure opens up the way to a better understanding not only of motional mechanisms but also of mechanical and transport properties.[9,10]

From the experimental point of view, two methods of study of the local structural variation are usually used. Small angle X-ray or neutron scattering (SAXS, SANS) provides information on the density fluctuation on the scale of a few tens of ångstroms. On the other hand, positron annihilation lifetime spectroscopy (PALS) is able to give direct information on the free volume situation in amorphous systems. It is based on the fact that the lifetimes of positron and its bound forms—positronium (Ps)—are sensitive to the existence of structural inhomogenities.[11−13] In condensed media, in addition to $e^+$ annihilation a formation and an annihilation of two forms of the ($e^+e^-$) bound systems occur in dependence on the mutual spin orientation of the positron and the electron. The singlet state of para-positronium (p-Ps) with antiparalell spin orientation has a lifetime $\tau_1 = 0.125$ ns in vacuo. The triplet state of orthopositronium (o-Ps) lives in vacuo for $\tau_3 = 142$ ns. In liquid and solid substances $\tau_3$ is shortened due to an interaction with electrons of surrounding on a few nanoseconds. It is accepted that o-Ps is formed by $e^+$ after very rapid thermalization, following capture in the regions with reduced electron density such as holes, vacancies, and cavities. Recent methodological and interpretation progress revealed possibilities to determine not only the mean (spherical) hole sizes using a quantum-mechanical model[14] but also the free volume hole fractions using various calibration schemes[15−17] as well as hole size distributions.[18] This development has caused a renaissance in applications of the PALS method in solving many actual problems of polymer physics such as the influence of chemical modification,[19,20] the effect of physical aging,[21,22] the effect of mechanical deformation,[23] and the influence of mass,[24] charge,[25] and free valence[26] transport. Most of the studies so far were carried out on plastics with a glass transition temperature, $T_g$, above room temperature for reasons of easier experimentation; essentially less attention was focused on elastomers.[27−30] As for the PALS data, a puzzling aspect is the fact that the temperature coefficients of hole expansion are about 1 order of magnitude higher than the temperature coefficients of macroscopic volume expansion.[13,16,20] In addition, some

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⊗ Abstract published in *Advance ACS Abstracts,* September 15, 1997.

S0024-9297(96)01512-4 CCC: $14.00

polymers with a rather complicated chemical structure exhibit complicated courses in $I_3$-$T$ dependences, ascribed to the side group mobilities[27,31,32] or to the coalescence of small holes.[21,29] Finally, in a few cases practically a saturation in the lifetime $\tau_3$ and/or of the relative intensity $I_3$ was observed at temperatures well above $T_g$ not only for low molecular weight substances[33,34] but also for some epoxy polymers.[35]

The above-mentioned problems imply the need to obtain some more fundamental answers on relationships between the free volume microstructure and the internal dynamics as well as on a mutual interaction between the o-Ps probe and the medium. According to our opinion this requires combined investigations on suitable simple polymer systems in a wide temperature range, including very low temperatures.

The aim of this paper is to present the results of such a study on *cis*-1,4-poly(butadiene). The reasons for the choice of this model polymer were the following: (i) it is the simplest chemical structure that does not contain the complicating effect of the side groups; (ii) the sample has an amorphous character due to the cis geometrical isomeric form observed for a suitable method of preparation, and finally, (iii) it exhibits a relative simple dynamics with the lowest glass transition temperature, $T_g$, among carbon backbone polymers without secondary relaxations as detected by conventional techniques of relaxation spectrometry.[36−38]

## Experimental Section

**1. Sample and Treatment.** *cis*-1,4-Poly(butadiene), *cis*-1,4-PBD [$-CH_2CH{=}CHCH_2-]_n$, from Japan Synthetic Rubber Co., Ltd, with the following molecular characteristics, $M_w = 8.1 \times 10^5$ and $M_n = 2.7 \times 10^5$, was used. The microstructure of chains from infrared measurements was 95.7% of the cis form, 2.0% of trans form, and 2.3% of the vinyl form.

The samples for PALS measurements were in a form of small disks with diameters of 10 mm and thicknesses of 3 mm. After their installation into the measuring apparatus, a pair of the samples was cooled to the starting temperature of 15 K.

The samples for differential scanning calorimetry (DSC) measurements were undergone to the analogical cooling regime from the room temperature to the starting temperature of 140 K.

**2. Positron Annihilation Lifetime Measurements.** PAL measurements have been performed in the temperature range from 15 to 313 K with a mean temperature step of 15 K. Measurements lasted for 3 h at each temperature.

The positron annihilation lifetime spectra were obtained by the conventional fast−fast coincidence method using plastic scintillators coupled to Phillips X 2020 photomultipliers. Ortec 583 constant fraction discriminators were used for selecting the energy and providing timing signals to a time-to-amplitude converter. The time resolution (fwhm) of prompt spectra was 320 ps. A model-independent instrumental resolution function was obtained from the decay curve of the $^{207}$Bi isotope with a single lifetime of 186 ps. In conventional three component analysis the PATFIT-88 software package[39] of Kirkegaard et al. was used. In addition, PALS spectra were analyzed in a form of continuous lifetime distribution using the modified CONTIN program.[40,41]

The annihilation of the orthopositronium (o-Ps) in a spherical hole can be described by a simple quantum-mechanical model of the spherical potential well with an electron layer of thickness $\Delta R$. The semiempirical relation between the radius of the free volume hole $R$ and the ortho- positronium lifetime $\tau_3$ is[14]

$$\tau_3 = \frac{1}{2}\left(1 - \frac{R}{R_o} + \frac{1}{2}\sin\frac{2\pi R}{R_o}\right)^{-1} \qquad (1)$$

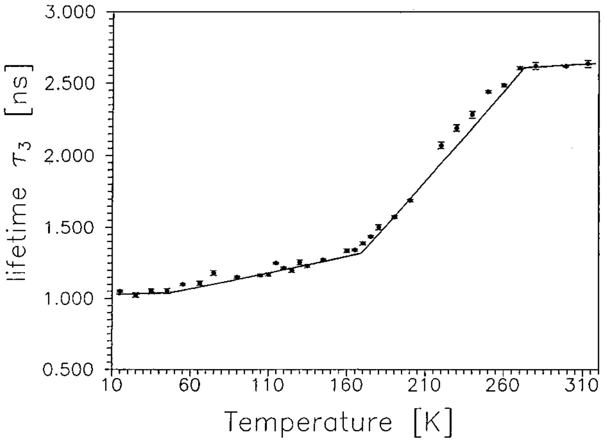

**Figure 1.** Mean o-Ps lifetime $\tau_3$ as a function of temperature in *cis*-1,4-PBD.

where $R_o = R + \Delta R$. The parameter $\Delta R = 1.66$ has been determined from fitting the experimental values of $\tau_3$ obtained for materials with known hole sizes, e.g., molecular crystals and zeolites.

The hole radius probability distribution function is given by[40]:

$$f(R) = 2\Delta R\left(\cos\frac{2\pi R}{R + \Delta R} - 1\right)\frac{\alpha\left(\frac{1}{\tau}\right)}{(R + \Delta R)^2} \qquad (2)$$

Then, the hole volume probability distribution function is given by

$$g(V) = \frac{f(R)}{4\pi R^2} \qquad (3)$$

where $\alpha(1/\tau)$ is the positronium annihilation rate probability distribution function.

**3. Differential Scanning Calorimetry Measurements.** The thermodynamic behavior of the PBD sample has been determined by the DSC method using a Perking-Elmer 7 Series thermal analysis system. DSC thermograms were registered at a heating rate of 10 K min$^{-1}$. The temperature and enthalpy characteristics of the step effect due to glass transition and of the peak effects due to the so-called cold crystallization and melting, respectively, were evaluated using the software Thermal Analysis Data Station.

## Results and Discussion

**1. Finite Term Analysis Data and Mean Free Volume Analysis. (a) Mean Lifetime and Relative Intensity vs Temperature Dependences.** Experimental results from finite term lifetime analysis of *cis*-1,4-PBD in the temperature range from 15 to 313 K are presented in Figures 1 and 2 and Tables 1−3. Typical values of the three-component analysis at several representative temperatures with fixed $\tau_1$ component are given in Table 1. The temperature dependences of annihilation characteristics of o-Ps are shown in Figures 1 and 2. Both graphs have rather complicated courses exhibiting several regions of different behavior of $\tau_3$ and $I_3$. These regions were approximated by the linear regression fits with $A$ and $B$ parameters summarized in Table 2.

At the lowest temperatures up to 50 K, we observe a practically constant course with $\tau_3 = 1.05$ ns. This value is very low in comparison with rare data on polymers at cryogenic temperatures, e.g., polycarbonate (BPA-PC) where $\tau_3$ (50 K) = 1.78 ns.[16] The corresponding limiting mean free volume hole size is $R_h = 1.75$ Å, i.e., $V_h = 22$

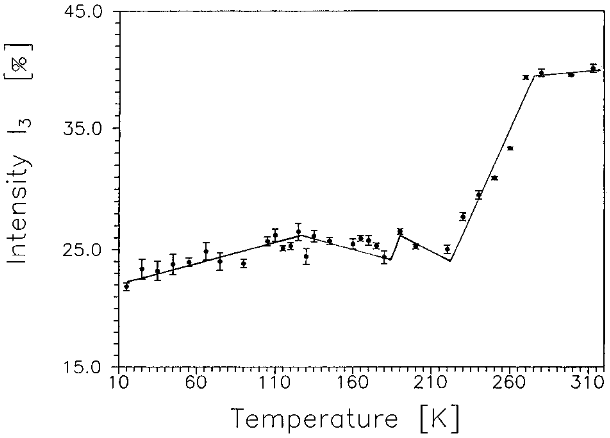

**Figure 2.** Relative intensity $I_3$ of o-Ps as a function of temperature in *cis*-1,4-PBD.

**Table 1. Typical Values of the Three-Component Fit of Positron Annihilation Spectra in *cis*-1,4-PBD at Several Temperatures**

| $T$/K | $\tau_2$/ns | $\tau_3$/ns | $I_2$/% | $I_3$/% |
|---|---|---|---|---|
| 45 | 0.314 ± 0.009 | 1.052 ± 0.018 | 67.95 ± 2.73 | 23.77 ± 0.87 |
| 75 | 0.333 ± 0.009 | 1.182 ± 0.018 | 63.95 ± 2.23 | 24.01 ± 0.74 |
| 200 | 0.364 ± 0.004 | 1.690 ± 0.009 | 57.20 ± 0.77 | 25.26 ± 0.19 |
| 300 | 0.391 ± 0.002 | 2.614 ± 0.005 | 42.98 ± 0.30 | 39.45 ± 0.07 |

[a] The first component $\tau_1$ is fixed to the value of 125 ps.

**Table 2. Parameters of the Linear Fits $Y = AX + B$ for the Mean Lifetime $\tau_3$ and Relative Intensity $I_3$ in *cis*-1,4-PBD**

| quantity | region | $T$/K | $A$ | $B$ |
|---|---|---|---|---|
| $\tau_3$[a] | I | 15–50 | 0 | 1.05 ± 0.01 |
| | II | 55–170 | (2.275 ± 0.211) × $10^{-3}$ | 0.958 ± 0.026 |
| | III | 175–265 | (1.319 ± 0.048) × $10^{-2}$ | 0.903 ± 0.100 |
| | IV | 265–313 | (4.43 ± 1.78) × $10^{-4}$ | 2.482 ± 0.052 |
| $I_3$[b] | I | 15–125 | (3.138 ± 0.422) × $10^{-2}$ | 21.790 ± 0.399 |
| | II | 130–180 | (−1.342 ± 0.944) × $10^{-3}$ | 25.945 ± 1.666 |
| | III | 220–265 | (2.760 ± 0.05) × $10^{-1}$ | 37.45 ± 1.286 |
| | IV | 270–313 | (8.03 ± 2.35) × $10^{-3}$ | 37.08 ± 7.01 |

[a] $A$ in ns $K^{-1}$ and $B$ in ns. [b] $A$ in %$K^{-1}$ and $B$ in %.

**Table 3. Temperature Coefficients of Annihilation of o-Ps ($\tau_3$, $I_3$), of free volume holes ($V_h$), and of Dynamic Parameter ($\langle u^2 \rangle$)**

| | temp interval/K | $\beta_x$[a] | $\alpha_x$/$K^{-1}$ | $\beta_{\langle u^2 \rangle}$/Å$^2$ $K^{-1}$ | $\alpha_{\langle u^2 \rangle}$/$K^{-1}$ |
|---|---|---|---|---|---|
| $\tau_3$ | 55–170 | 2.3 × $10^{-3}$ | 1.7 × $10^{-3}$ | | |
| | 175–265 | 1.3 × $10^{-2}$ | 9.8 × $10^{-3}$ | | |
| | 270–313 | 4.4 × $10^{-4}$ | 3.3 × $10^{-4}$ | | |
| $V_h$ | 55–170 | 1.6 × $10^{-1}$ | 3.7 × $10^{-3}$ | 2.1 × $10^{-4}$ | 5.5 × $10^{-3}$ |
| | 175–265 | 1.2 | 2.7 × $10^{-2}$ | 1.95 × $10^{-3}$ | 5.1 × $10^{-2}$ |
| | 270–313 | 7.0 × $10^{-2}$ | 1.7 × $10^{-3}$ | | |
| $I_3$ | 15–120 | 3.1 × $10^{-2}$ | 1.2 × $10^{-3}$ | | |
| | 125–180 | −1.3 × $10^{-3}$ | −5.2 × $10^{-5}$ | | |
| | 220–265 | 2.8 × $10^{-1}$ | 1.1 × $10^{-2}$ | | |
| | 270–313 | 8.0 × $10^{-3}$ | 3.1 × $10^{-4}$ | | |

[a] $\tau_3$ in ns $K^{-1}$ and $V_h$ in Å$^3$ $K^{-1}$.

Å$^3$. It is about one-third of the van der Waals volume of the monomer unit, $V^w_{mon} = 62$ Å$^3$. The small size of free volume holes indicates a very effective packing of the chains deeply in the glassy state of PBD. It is a consequence of the chemical structure as characterized by a relatively high internal flexibility which may be quantified by the characteristic ratio $C_\infty = 5.1$.[42] This high flexibility results in small holes in comparison with the long rigid aromatic bonds in BPA-PC. The second temperature region is characterized by a linear increase of the o-Ps lifetime, and its upper boundary agrees with the glass transition temperature $T_g = 168$ K (see Figure 5). The mean hole radius at $T_g$ is $R_{hg} = 2.15$ Å ($V_{hg} = 42$ Å$^3$); it represents about two/thirds of the van der Waals volume of the basic structural unit. In the elastic state from 170 to 265 K, one observes the pronounced increase of $\tau_3$ with temperature. It corresponds to an enhancement of the mean hole size from $R_{hg} = 2.15$ Å to $R_h = 3.4$ Å or $V_h = 150$ Å$^3$, i.e. $2.4V^w_{mon}$. Finally, the fourth high temperature region is characterized by slight temperature change.

The temperature variations of o-Ps relative intensity $I_3$ is more complicated. Nevertheless, five regions of distinguished behavior can be found. In the first region, a slight increase of 3.5% is observed. Then, we can see the first decreasing zone with a slightly decreasing trend up to 180 K. The upper boundary of this region overcomes $T_g$. Further, the second anomalous region characterized by an N-like shape dependence is present. In the fourth region, above 220 K, the pronounced increase of $I_3$ is evident. In the last, high temperature region above 265 K, $I_3$ behaves similar to $\tau_3$. The origin of these slight temperature dependences of $\tau_3$ and $I_3$ will be discussed in the last part of the paper.

**(b) Relations between Temperature Coefficients of Free Volume Hole Size and Geometric Parameters of Chain Microdynamics.** The temperature coefficients of o-Ps annihilation quantities, including free volume characteristics calculated from eq 1, are defined as

$$\beta_x = \frac{\Delta X}{\Delta T} \tag{4}$$

$$\alpha_x = \frac{1}{X_g}\left(\frac{\Delta X_g}{\Delta T}\right) \tag{5}$$

and are summarized in Table 3. Here, $X = \tau_3$, and $V_h$, $I_3$, and $X_g$ are particular quantities at $T_g$. The temperature expansion coefficients of free volume $\alpha_h$ are compared with the macroscopic volume expansion coefficient $\alpha_V$. Thus, a comparison of $\alpha_h$ from Table 3 with $\alpha_V = 1.93 \times 10^{-4}$ $K^{-1}$ for glassy state from ref 43 confirms a finding on the other polymers; i.e., the hole expansion in the glassy state is 1 order of magnitude higher than the expansion of macroscopic volume.[44] Similarly, in the elastic state up to about $T_g + 100$ K, the $\alpha_h$ value is almost 2 orders of magnitude higher than the $\alpha_V = 7.5 \times 10^{-4}$ $K^{-1}$ from ref 43. But $\alpha_V$ is a global property of the whole system consisting of free and occupied volume, while $\alpha_h$ is a local quantity which characterizes the hole expansion only. Therefore, we propose to relate the temperature hole expansion to some quantity characterizing the microscopic dynamics. One possibility is to use the dynamical parameter of chain motion—the mean square displacement $\langle u^2 \rangle$ accessible from the elastic neutron scattering experiment. The temperature coefficients $\beta_{\langle u^2 \rangle}$ and $\alpha_{\langle u^2 \rangle}$ of chain scatterer in the same kind of polymer were calculated from the $\langle u^2 \rangle - T$ dependence for the energy resolution $\delta\epsilon = 0.02$ meV[45] using eqs 4 and 5 (see Table 3). The order agreement between $\alpha_h$ and $\alpha_{\langle u^2 \rangle}$ in both the glassy and elastic states as well as the closeness of its ratios below and above $T_g$ (1.3 for $\alpha_h$ vs 1.1 for $\alpha_{\langle u^2 \rangle}$) suggest that the free volume hole expansion has an origin similar to that of microscopic small-scale and high-frequency chain dynamics observed by neutron scattering.

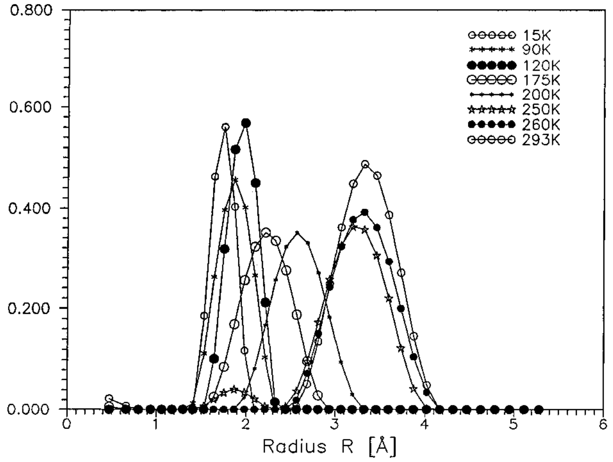

**Figure 3.** Free volume hole radius distributions *f*(*R*) of *cis*-1,4-PBD at given temperatures of 15, 90, 120,175, 200, 250, 260, and 293 K.

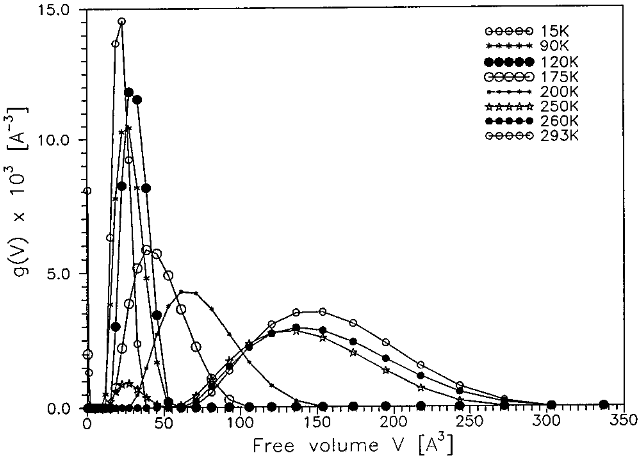

**Figure 4.** Free volume distributions *g*(*V*) of *cis*-1,4-PBD at the same temperatures as in Figure 3.

**2. Continuous Term Analysis Data and Free Volume Distributions.** The PAL spectra measured in the temperature interval from 15 to 313 K with high statistics have been evaluated by using the CONTIN programm to give continuous lifetime distributions. These were converted into the hole radius and the hole volume distributions according to eqs 2 and 3, respectively. Although this procedure has been questioned,[46] a very recent analysis[47,48] of this problem showed that only the special case had been treated in ref 46. Figures 3 and 4 show the hole size distributions at several temperatures from various regions of Figures 1 and 2. Qualitatively, the maxima of both distributions shift to higher values with a rise in temperature. Simultaneously, widening of both distributions occurs, which is especially pronounced in the elastic state. Above 265 K, small changes can be observed with increasing temperature. Similar trends exhibit free volume distributions in a typical plastic—poly(styrene) (PS).[49] From a quantitative point of view, the free volume hole distributions in PBD are very narrow below $T_g$. For instance, at 15 K it ranges from 15 to 40 Å$^3$, i.e., 25–65% of $V^w{}_{mon}$. At 90 K, i.e., 80 K below $T_g$, it is 20–50 Å$^3$ corresponding to 0.3–0.8, $V^w{}_{mon}$. These data can be compared to analogical values in PS[49] ($T_g = 368$ K) for identical temperature differences ($T - T_g$). In this polymer the width of the hole volume distribution ranges from 40 to 190 Å$^3$. For a typical elastomer in the glassy state, the hole volume distributions for identical $T - T_g$ are narrower than that in the above-mentioned plastics. Thus, not only the mean hole size but also the width parameter of hole size distribution indicate a very effective arrangement of chains in the glassy state. On the other hand, in elastic state, pronounced widening in the distribution boundaries occurs, especially at a high value tail. For example, at 200 K ($T_g + 30$ K) the width ranges from 30 to 150 Å$^3$. The analogous value for PS at 398 K is from 50 to 250 Å$^3$. Thus, despite the narrower distributions at $T < T_g$, a stronger relative growth of the hole size fluctuation takes place in the elastic state of PBD. We can say that it is related to higher flexibility and to more intensive chain dynamics in PBD in comparison with PS ($C_\infty = 10.8$).[42]

**3. Relationships between Free Volume Microstructure and Segmental Dynamics. (a) Glassy State Region.** As mentioned above, one of the reasons for the choice of *cis*-1,4-poly(butadiene) was its very simple relaxation behavior. The temperature dependence of the mechanical loss exhibits a relatively wide primary relaxation peak without any evident secondary relaxations.[36−38] This finding seems to be consistent with the results of previous parts of this paper indicating a high degree of packing efficiency. The small holes do not form appropriate conditions for a local secondary mobility. However, it does not mean an absence of any other motional possibilities in the glassy state suggested by Figure 2. Above 120 K up to 180 K a slight decrease in $I_3$ occurs. Such a phenomenon has been observed in several amorphous and semicrystalline polymers[21,31,32] and interpreted by two different methods, both based on the idea about the proportionality between the $I_3$ and the hole concentration. The coalescence hypothesis argues that the hole size increases with temperature, which takes place at the cost of hole coalescence.[21,29] On the other hand, a blocking concept assumes that part of the holes may be excluded for o-Ps localization due to some local motion.[27,31,32] While the first idea is hardly verifiable by independent means, the second one can be tested by a comparison of the o-Ps lifetimes and the hole sizes with time as well as the geometric characteristics of potential motions. A recent quasielastic scattering (QENS) study of segmental dynamics on the same polymer revealed an existence of the so-called fast motion. This motion of a relaxational nature on a picosecond time scale starts to appear at the onset temperature $T_f = 120 \pm 7$ K.[45,50,51] Good agreement between an appearance of the intensity decrease and the onset temperature of fast motion as well as a fullfilling of the condition[31] of a mutual relation between the characteristic time of motion and the lifetime of o-Ps indicates their link. From QENS measurements it follows that the fast motion has a localized, cage character and it is ascribed to the relaxational motion in the C−C torsion potential.[45,51] Assuming that this motion may be described by a a two-site model, an additional analysis of the scattering data by using eq 6 from ref 51 leads to an amplitude of hydrogen motion of about 1.3−1.4 Å between 120 K and $T_g$. This is a sufficiently large displacement which can block part of the free volume holes of mean radius 2 Å, considering that the o-Ps diameter $d_{o-Ps} = 2.12$ Å.[13] Thus, on the basis of the combined PALS and QENS analysis, we conclude that the intensity decrease above 120 K can be caused by a blocking effect of the fast motion in the glassy matrix.

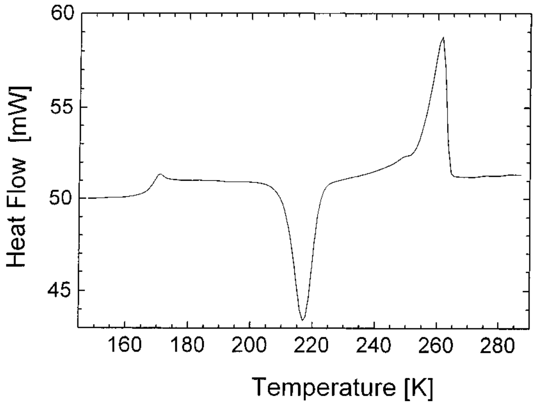

**Figure 5.** DSC thermogram of *cis*-1,4-PBD.

We note that the onset of intensity decrease correlates not only with the onset of fast motion but also with the temperature parameter $T_o$ from an empirical Vogel equation for the segmental dynamics

$$\tau_\alpha = \tau_{\infty\alpha} e^{B/(T - T_0)} \qquad (6)$$

where $\tau_{\infty\alpha}$ and $B$ are the empirical coefficients and $T$ is the absolute temperature. On the basis of agreement between $T_f$ and $T_o = 118$ K is believed that the fast motion is a precursor for α segmental mobility.[45,51] This seems to be consistent with the existence of a broad shoulder on the low temperature side of the relaxation peak from dynamic-mechanical measurements,[37,38] indicating the course of α mobility in the glassy state. Thus, the intensity decrease is an independent evidence not only for the fast motion but also for the local segmental mobility at $T < T_g$. However, the nature of the coupling between fast and segmental mobility is still unclear. One possibility is that the fast motion works as a free volume reorganizer which shifts very small free volume entities through a matrix. An occasional accumulation of these entities allows the course of segmental motion, presumably of conformational character.

**(b) Glass−Liquid Transition Region.** The most pronounced feature in the $\tau_3 - T$ dependence is the large change of slopes below and above 170 K. This break temperature agrees with the glass transition temperature $T_g = 168$ K from DSC measurements—Figure 5. Such a finding is quite general, and it has recently been analyzed by one of us from phenomenological, chemical, and free volume structural points of view.[42] Our values of $\tau_{3g}$ and the product $\tau_{3g}I_{3g}$ at $T_g^{DSC}$ confirm the empirical correlations between both quantities vs $T_g^{DSC}$ values for a series of 13 amorphous polymers.[42] The change of $\tau_3$ at $T_g$ correlates not only with the change of macroscopic property—enthalpy—but also with the onset of the so-called slow motion at $T_s = 171$ K as detected by the QENS method on the same material.[45] This motional mode is characterized by a time scale of $10^{-10}$ s and an amplitude of about 2.5 Å.[50] On the basis of a comparison of this amplitude with that from the analysis of potential motional modes in the basic structural unit of *cis*-1,4-PBD, it was concluded[45,50] that the slow motion consist of local conformational transitions of α bonds in ${=}CHCH_2{-}$ as well as of $\beta$ bonds in $-CH_2CH_2-$ parts of the chains.

According to the free volume concept of mobility in condensed media, a particular motion is realized when a critical hole in the immediate vicinity of the moving unit exists.[5,6] For vinyl polymers, a conformational transition in the $T_g$ region is connected with a reorientation of the whole monomer unit;[52] it has been evidenced in the case of atactic poly(propylene) by 2D $^{13}C$-NMR measurements[53] and supported by analysis of the PALS data for this as well as for other vinyl polymers.[42] Similar analysis of the annihilation data from Figures 1, 3, and 4 shows that at $T_g$ the mean hole radius is $R_{hg} = 2.15$ Å with a fluctuation from 1.75 to 2.75 Å. It corresponds to the hole volume distribution range from 25 to 90 Å$^3$ with the mean value at about 42 Å$^3$, i.e., $0.4-1.4V^w_{mon}$ with the mean about $0.67V^w_{mon}$. The above-mentioned conclusion from the QENS study as well as the free volume holes findings is also consistent with the results of recent molecular-dynamics (MD) simulations of mobility in bulk *cis*-1,4-PBD.[54,55] According to them, the conformational motions consist of 70% uncorrelated and 30% correlated transitions; the proportion of the latter rises with decreasing temperature. The effective activation energies of both types of transitions, (8.2 and 12 kJ/mol) are on the order of one to two barrier heights[55] in a good agreement with an experimental value for the slow motion from a QENS measurement (about 12 kJ/mol).[50] Since the rates of individual transitions of α and $\beta$ bonds are comparable and the correlated transitions are dominant by ±2 transitions of bonds separated by a $\beta$ bond or double bond, the motion are quite localized at the level of the three-bond kinetic segment[54] with reasonable agreement with the mean hole size from our PALS study.

The intensity decrease starting in the glassy state overcomes the $T_g$ at roughly 10−15 K—Figure 2. It may suggest that with increasing temperature the blocking effect of the fast motion may be replaced by that of larger scale slow mobility. Since the hole size at $T_g$ is commensurate with the size of kinetic segments in both types of transitions, it may result in a continuing blocking effect of the slow dynamics on stabilization of a part of o-Ps at and slightly above $T_g$.

From these findings a good consistency among free volume characteristics from the PALS measurement, the neutron scattering motional modes from QENS investigation, and MD calculations follows.

**(c) Elastic State Region.** The o-Ps lifetime $\tau_3$ increases practically linearly above $T_g$ up to about 270 K. On the other hand, the $I_3 - T$ dependence is more complicated. After the suggestion of increase at 190 K, there is a N-like shape course with a minimum in the vicinity of 210 K followed by a relatively large increase up to about 270 K again. This course can be correlated with two phenomena. The first is the so-called cold crystallization detectable by dilatometry[56] or calorimetry.[57] Our DSC thermogram exhibits an exotermic peak effect characterized by an extrapolated initial temperature $T_{cc,i} = 210$ K with a minimum at $T_{cc,m} = 217$ K. Good temperature correlation indicates that the N-like shape effect is connected with the course of phase change, which reduces the number of holes. The second phenomenon is an observation of the so-called spectral collapse temperature $T_{coll}$ from $^{13}C$-NMR study[58] which agrees quite well with the liquid−liquid transition temperature $T_{ll} = 205$ K.[59] According to Boyer's analysis, the $T_{ll}$ transition marks the transition of elastic phase from rigid to the true liquid state.[60] Coincidence between $T_{cc}$ from DSC measurements, $T_{coll}$, and $T_{ll}$ seems to be quite natural because the orderning process requires sufficient mobile chains. Then, the relative intensity $I_3$ is reduced due to the elimination of part of the holes during local formation of crystallites with the extent being about 19% as determined from the melting peak by using $\Delta H_m = 9.2$ kJ mol$^{-1}$.[61] Above 220 K the intensive conformational–segmental dynamics results in the formation of further holes and leads to an increase of the $I_3$ with rising temperature in the semicrystalline matrix.

**(d) High-Temperature Region.** In the high-temperature region above 265 K both the o-Ps lifetime $\tau_3$ and relative intensity $I_3$ exhibit a similar behavior. The courses of both quantities are characterized by slight temperature dependences. Analogous dependences have been found for some low molecular weight substances when investigated in wide temperature ranges,[33,34] and an indication of such a trend is observed for some amino–epoxy polymers at very high temperatures above $T_g$.[35] By analogy to liquids, this slight temperature dependence can be connected with formation of the so-called bubble state. We note that this bubble state of o-Ps is not connected with the concept of free volume. The bubble state of o-Ps is considered to be a result of a competition between the quantal zero-point motion of o-Ps and matrix resistance. Then, the bubble size is determined by the balance between outward pressure due to the zero-point motion of o-Ps and inward pressure due to surface tension, $\gamma$, and internal pressure, $p_{int}$, of the medium[62]

$$\frac{\pi\hbar^2}{4m_e r_b^2} = 4\pi r_b^{\,2}\gamma + \frac{4}{3}\pi r_b^{\,3} p_{int} \qquad (7)$$

where $m_e$ is the mass of the positron and $r_b$ is the bubble radius. To test this hypothesis, we estimated the bubble size at room temperature and compared with the rsults of Figure 3 using $\gamma = 32 \times 10^{-3}$ N m$^{-1}$ [63] and $p_{int} = 5.3 \times 10^8$ Pa from the *pVT* equation of *cis*-1,4-PBD.[64] The calculation gives $r_b(293\ \mathrm{K}) = 3.9$ Å. Comparison with Figure 3 shows that this $r_b$ value falls between the most probable radius $R_h$ (293 K) = 3.4 Å and the maximal radius $R_{h,max}$ (293 K) = 4.2 Å. A further argument in favor of the bubble concept is a correlation between the onset of a slight temperature dependence and the melting temperature $T_{m,e} = 263$ K—Figure 5. Then, the increase of temperature leads to the melting of crystalline phase formed inevitably during the measurement. Consequently, this melting process removes the steric hindrance for equilibrium interaction of o-Ps with the soft matrix and results in the slightly changing bubble state of o-Ps in the *cis*-1,4-PBD melt.

## Conclusions

The annihilation characteristics of orthopositronium in *cis*-1,4-poly(butadiene) in the temperature range from 15 to 313 K are presented. The temperature dependences of the mean lifetime $\tau_3$ and the relative intensity $I_3$ as well as the lifetime distributions were interpreted in the framework of free volume concept as the mean hole size, the number of hole entities, and the hole size distributions. It was found that these temperature dependences reflect a close interplay between free volume microstructure and internal microdynamics at lower temperatures below the melting temperature and an interaction of the o-Ps with the soft matrix in the melt phase.

**Acknowledgment.** The authors express their thanks to the Grant Agency for Science of the Slovak Republic for support of this research (Grants No. 2/4008/1997 and 2/2035/1995).

## References and Notes

(1) Zallen, R. *The Physics of Amorphous Solids*; Wiley: New York, 1986.
(2) Voigt-Martin, I.; Wendorff, J. H. *Encycl. Polym. Sci.* **1985**, *1*, 789.
(3) Fox, T. G.; Flory, P. *J. Appl. Phys.* **1951**, *21*, 581.
(4) Doolittle, A. K. *J. Appl. Phys.* **1951**, *22*, 1471.
(5) Cohen, M. H.; Turnbull, D. *J. Chem. Phys.* **1959**, *31*, 1164.
(6) Turnbull, D.; Cohen, H. H. *J. Chem. Phys.* **1961**, *34*, 120.
(7) Cohen, M. H.; Grest, G. S. *Phys. Rev. B* **1979**, *20*, 1077.
(8) Grest, G. S.; Cohen, M. H. *Adv. Chem. Phys.* **1981**, *48*, 455.
(9) Ferry, J. D. *Viscoelastic Properties of Polymers*, 3rd ed.; Wiley: New York, 1980.
(10) *Diffusion in Polymers*; Crank, J., Part, G. S., Eds.; Academic Press: New York, 1968.
(11) *Positron Solid State Physics*; Brandt, W., Dupasquier, A., Eds.; North Holland: Amsterdam, 1983.
(12) *Positron and Positronium Chemistry*; Schrader, D. M., Jean, Y. C., Eds.; Elsevier: Amsterdam, 1988.
(13) Jean, Y. C. *Microchem. J.* **1990**, *42*, 72.
(14) Nakanishi, H.; Wang, S. J.; Yean, Y. C. In *Positron Annihilation Studies of Fluids*; Sharma, S. C. Ed.; World Science: Singapore, 1988; p 292.
(15) Wang, Y. Y.; Nakanishi, H.; Yean, Y. C.; Sandreczki, T. C. *J. Polym. Sci., B: Polym. Phys.* **1990**, *28*, 1431.
(16) Krištiak, J.; Bartoš, J.; Krištiaková, K.; Šauša, O.; Bandžuch, P. *Phys. Rev. B* **1994**, *49*, 6601.
(17) Yu, Z.; Yashi, U.; McGervey, J. D.; Jamieson, A. M.; Simha, R. *J. Polym. Sci., B: Polym. Phys.* **1994**, *32*, 2637.
(18) Gregory, R. B. *J. Appl. Phys.* **1991**, *70*, 4665.
(19) Kluin, J. E.; Yu, Z.; Vleeshouwers, S.; McGervey, J. D.; Jamieson, A. M.; Simha, R.; Sommer, K. *Macromolecules* **1993**, *26*, 1853.
(20) Bartoš, J.; Krištiaková, K.; Šauša, O.; Krištiak, J. *Polymer* **1996**, *37*, 3397.
(21) Kobayashi, Y.; Zheng, W.; Meyer, E. F.; McGervey, J. D.; Jamieson, A. M.; Simha, R. *Macromolecules* **1989**, *22*, 2302.
(22) Li, X. S.; Boyce, M. C. *J. Polym. Sci., B* **1993**, *31*, 869.
(23) Hasan, O. A.; Boyce, M. C.; Li, X. S.; Berko, S. *J. Polym. Sci., B* **1993**, *31*, 185.
(24) Kobayashi, Y.; Haraya, K.; Hattori, S.; Sasuga, T. *Polymer* **1994**, *35*, 925.
(25) Peng, Z. L.; Wang, B.; Li, S. Q.; Wang, S. J. *J. Appl. Phys.* **1995**, *77*, 334.
(26) Bartoš, J.; Hloušková, Z. *Polymer* **1993**, *34*, 4570.
(27) Hsu, F. H.; Tseng, P. K.; Chuang, S. Y.; Chang, Y. L. *Positron Annihilation, Proc. 5th Int. Conf.* **1979**, 581.
(28) Arifov, P. U.; Vasserman, S. N.; Dontsov, A. A.; Tishin, A. A. *Dokl. Acad. Sci. SSSR* **1984**, *277*, 889.
(29) Lin, D.; Wang, S. J. *J. Phys. Condens. Matter* **1992**, *4*, 3331.
(30) Wang, C. L.; Wang, S. J. *Phys. Rev. B* **1995**, *51*, 8810.
(31) West, D. H. D.; McBrierty, V. J.; Delaney, C. F. G. *Appl. Phys.* **1975**, *7*, 171.
(32) Millán, S.; Geckle, U.; Levay, B.; Ache, H. J. *Ber. Bunsen-Ges. Phys. Chem.* **1990**, *94*, 781.
(33) Pethrick, R. A.; Jacobsen, F. M.; Mogensen, O. E.; Eldrup, M. *J. Chem. Soc., Faraday Trans. 2* **1980**, *76*, 225.
(34) Malhotra, B. H.; Pethrick, R. A. *J. Chem. Soc., Faraday Trans. 2* **1982**, *78*, 297.
(35) Jean, Y. C; Sandreczki, T. C.; Ames, D. P. *J. Polym. Sci., B* **1986**, *24*, 1247.
(36) Gupta, R. P. *J. Phys. Chem.* **1962**, *66*, 1.
(37) Morgan, R. J.; Nielsen, L. E.; Buchdahl, R. *J. Appl. Phys.* **1971**, *42*, 4653.
(38) Mathew, J.; Shen, M.; Schatzki, T. F. *J. Appl. Polym. Sci.* **1979**, *23*, 299.
(39) Kirkegaard, P.; Eldrup, M.; Morgensen, E.; Pedersen, N. Y. *Comput. Phys. Commun.* **1989**, *23*, 307.
(40) Gregory, R. B. *Nucl. Instrum. Methods* **1990**, *A290*, 172.
(41) Provencher, S. W. *Comput. Phys. Commun.* **1982**, *27*, 229.
(42) Bartoš, *J. Colloid. Polym. Sci.* **1996**, *274*, 14.
(43) Sharma, S. C.; Mandelkern, L.; Stehling, F. C. *J. Polym. Sci. Lett.* **1972**, *10*, 345.
(44) Deng, Q.; Sundar, C. S.; Jean, Y. C. *J. Phys. Chem.* **1992**, *96*, 492.
(45) Kanaya, T.; Kawaguchi, T.; Kaji, K. *Physica B* **1992**, *182*, 403.
(46) Yu, Z.; McGervey, J. D.; Jamieson, A. M.; Simha, R. *Macromolecules* **1995**, *28*, 6268.
(47) Baugher, A. H.; Kossler, W. J.; Petzinger, K. G. *Macromolecules* **1996**, *29*, 7280.
(48) Jean, Y. C. *Macromolecules* **1996**, *29*, 5756.
(49) Liu, J.; Deng, Q.; Jean, Y. C. *Macromolecules* **1993**, *26*, 7149.

(50) Kanaya, T.; Kaji, K.; Inoue, K. *Macromolecules* **1991**, *24*, 1826.
(51) Kanaya, T.; Kawaguchi, T.; Kaji, K. *J. Chem. Phys.* **1993**, *98*, 8262.
(52) Helfand, E. *Science* **1984**, *226*, 647.
(53) Zemke, K.; Chmelka, B. F.; Schmidt-Rohr, K.; Spiess, H. W. *Macromolecules* **1991**, *24*, 6874.
(54) Gee, R. H.; Boyd, R. H. *J. Chem. Phys.* **1994**, *101*, 8028.
(55) Kim, E. G.; Mattice, W. L. *J. Chem. Phys.* **1994**, *101*, 6242.
(56) Dannis, M. L.; *Rubb. Chem. Technol.* **1959**, *32*, 1005.
(57) Daiton, F. S.; Evans, D. M.; Hoare, F. E.; Melia, T. P. *Polymer* **1962**, *3*, 297.
(58) Axelson, D. E.; Mandelkern, L. *J. Polym. Sci., B: Polym. Phys.* **1978**, *16*, 1135.
(59) Boyer, R. F.; Heeschen, J. P.; Gillham, J. K. *J. Polym. Sci.* **1981**, *19*, 31.
(60) Boyer, R. F. *J. Polym. Sci., B: Polym. Phys.* **1988**, *26*, 893.
(61) Natta, G.; Moraglio, G. *Makromol. Chem.* **1963**, *66*, 218.
(62) Mogensen, O. E. *Electrochim. Acta* **1988**, *33*, 1203.
(63) van Krevelen, D. W. *Properties of Polymers*. Elsevier Publ. Co.: Amsterdam, 1972; p 100.
(64) Rodgers, P. A. *J. Appl. Polym. Sci.* **1993**, *48*, 1061.

MA961512U