Macromol. Symp. ***158**, 111–123 (2000)*

Experimental Free Volume Aspects of the Polymer Rheology as Obtained by Positron Annihilation Lifetime Spectroscopy

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SUMMARY: The ortho-positronium (o-Ps) annihilation parameters, i.e. the mean o-Ps lifetime ,τ_3, and the o-Ps relative intensity, I_3, in cis-1,4-polybutadiene (cis-1,4-PBD) and polyisobutylene (PIB) over a wide temperature range including the glass-liquid transition have been measured by means of positron annihilation lifetime spectroscopy (PALS). From them the free volume microstructural characteristics, i.e. the mean free volume hole size ,V_h, and the free volume hole fraction, f_h, have been determined via a semiempirical quantum-mechanical model of o-Ps in a spherical hole or a phenomenological model of volumetric and free volume hole properties, respectively. Consequently, the literature rheological data for both the above-mentioned polymers have been related to the free volume hole fractions via the WLF-Doolittle type equation. It has been found that i) in the case of PIB this equation holds over 130K above the glass transition temperature T_g and ii) in the case of cis-PBD the WLF-Doolitle equation is valid in the temperature range over 60K above $1.3T_g$,but below $1.3T_g$ down to T_g the modified WLF-Doolittle-Macedo-Litovitz equation with the additional activation-energy term describes the shift factor data better.

Introduction

According to the general point of view, the chemical and physical characteristics of condensed systems, i.e. their composition and morphology, and a wide spectrum of the dynamic properties are closely related [1-4)]. The physical aspect of amorphous polymers is often discussed within the free volume idea as a measure of the structural disorder and subsequently, the various dynamic and transport properties are explained in terms of a simple and physically plausible free volume concept[2,3)]. However, the relative success of this idea is connected with its ambiguity given by the existence of a number of operational definitions of the free volume depending on the nature of system or/and of property investigated [5,6)]. This versatility does not allow to explain the various properties of different systems within a unified framework and consequently, to utilize fully a potential of this physical concept.

CCC 1022-1360/00/$ 17.50+.50/0

This rather unsatisfactory situation was until recently connected with the absence of a direct way of the free volume measurements in condensed matter. At present, however, the physical structure of disordered systems in terms of free volume is still effectively studied by means of positron annihilation lifetime spectroscopy (PALS) 7). This method is based on measurement of the annihilation characteristics of both the positron and its bound form with the electron - the ortho - positronium (o-Ps), which are sensitive to the defectiveness of the structural arrangement of matrix constituents. Continued methodological progress in this technique as well as in an evaluation of the annihilation data of the ortho - positronium (o-Ps), i.e. the mean o-Ps lifetime,τ_3, and the o-Ps relative intensity, I_3,enables to characterize the free volume microstructure of a polymer. According to a semiempirical quantum-mechanical model of o-Ps in a spherical hole, the first quantity is related to the mean free volume hole radius R_h 7-9):

$$\tau_3 = \tfrac{1}{2}[\ 1 - R_h/R_0 + (1/2\pi)\sin\,(2\pi R_h/R_0)\ ]^{-1} \qquad (1)$$

where $R_h = R_0 - \Delta R$, ΔR is the thickness of surface electron layer around free volume hole, being 1.656 Å from fitting the observed o-Ps lifetimes in a series of molecular solids with the known hole sizes9,10).The second aspect of the free volume state of disordered matrix, i.e. the free volume hole fraction, f_h, is expressed by the phenomenological equation linking the mean (spherical) free volume hole size $V_h = (4\pi/3)R_h^3$ and the relative intensity I_3 which is, in the absence of atoms or atomic groups of high electron affinity such as halogens, carbonyls, a measure of the free volume hole density11,12):

$$f_h\,(T) = K_{Vh}.V_h(T).I_3(T) \qquad (2)$$

where K_{Vh} is the proportionality coefficient which can be determined by various calibration procedures based on relating the free volume hole fraction to the macroscopic volume expansion coefficients 11,12). We have recently formulated a phenomenological model linking the macroscopic volumetric behavior found from dilatometry to the microscopic free volume hole properties from PALS allowing to quantify the free volume hole fraction via physically reasonable picture13). The starting expression is a linear dependence of the macroscopic volume V on temperature T for a liquid phase above the glass transition temperature T_g:

$$V\,(T) = V_i + \beta_V^{\,l}\,(\,T - T_i\,) \qquad (3)$$

where $\beta_V^{\,l}$ is the liquid state expansivity, and V_i and T_i are the initial volume or initial temperature, respectively, at which the free volume defined as the excess volume $V(T) - V_i$ begins to appear. These free parameters of our model can be determined from PALS data and consequently, their physical meaning have to be established. Continuing with the usual definitions for the free volume fraction $f(T) = V_f(T)/V(T)$ and for its thermal expansion coefficient $\alpha_{f,g} = [1/f(T_g)].[\Delta f(T)/\Delta T]$, we can arrive to a quadratic equation in T_i:

$$T_i^2 + bT_i + c = 0 \tag{4}$$

where the coëfficients contain only experimentally accessible quantities:

$$b = -[1 + \alpha_{V,g}^1(T+T_g)]/\alpha_{V,g}^1 \tag{4a}$$

$$\begin{aligned} c = {} & [(1 + \alpha_{V,g}^1 T_g)T]/\alpha_{V,g}^1 + [(1 + \alpha_{V,g}^1 T)T_g]/[\alpha_{f,g}^1(T - T_g)\alpha_{V,g}^1] \\ & - [(1 + \alpha_{V,g}^1 T_g)T]/[\alpha_{f,g}(T - T_g)\alpha_{V,g}^1] \end{aligned} \tag{4b}$$

where $\alpha_{V,g}^1$ is the thermal expansion coefficient of the macroscopic volume, and $\alpha_{f,g}^1$ is the free volume fraction expansion coefficient. In the context of the PALS method, the free volume fraction f(T) may be identified with the free volume *hole* fraction $f_h(T)$ through the o-Ps annihilation data - eq.(2). Then, K_{Vh} can be determined from eqs.(4) and (3) using the V - T liquid state data .

In the field of rheology, the rheological properties such as viscosity η , relaxation time τ and etc. of a polymer liquid as a function of temperature are usually represented by the Vogel-Fulcher-Tamman-Hesse (VFTH) equation[14)]:

$$M(T) = A_{T,M}.\exp[B_{T,M} / (T - T_0)] \tag{5}$$

where M(T) is the generalized mobility $M \equiv \eta$ or τ ,$A_{T,M}$, $B_{T,M}$ are the corresponding empirical coefficients and T_0 is the divergence temperature. Equivalently in polymer physics, the Williams-Landel-Ferry (WLF) equation[3,15)] for the shift factor $a_T = M(T) / M(T_g)$ is used:

$$\log a_T = -C_{1g}(T - T_g) / [C_{2g} + (T - T_g)] \tag{6}$$

where C_{1g}, C_{2g} are the empirical coefficients depending on the reference temperature $T_{ref} = T_g$, the glass transition temperature. In Ref. 15, eq. (6) was interpreted within the operationally defined free volume fraction by using the modified Doolittle equation[16)] linking the mobility M to the free volume fraction f(T):

$$M(T) = A_{f,M}.\exp[B_{f,M} / f(T)] \tag{7}$$

giving the WLF - Doolittle equation:

$$\log a_T = (B_{f,M}/2.303)[1/f(T) - 1/f(T_g)] \tag{8}$$

The original free volume interpretation of the WLF scaling[15] relies on the following two additional, so far unverified assumptions: i) a linearity between the free volume fraction and temperature, i.e., $f(T) = f_g + \beta_f^1(T - T_g)$, where $f_g \equiv f(T_g)$ is the free volume fraction at T_g ; β_f^1 is the slope of the f - T dependence and ii) the postulate that $B_{f,M} = 1$. Consequently,

$$C_{1g} = B_{f.M}/2.303f_g \quad \text{and} \quad C_{2g} = f_g/\beta_f. \tag{9}$$

Early application of eqs.(6)-(9) on a series of polymers with f_g as *a fitting parameter* provided plausible estimations: $f_g \cong 0.025$ and $\beta_f^1 \cong \Delta\alpha_{V,g} = \alpha_{V,g}{}^l - \alpha_{V,g}{}^g = 4.8 \times 10^{-4}\ K^{-1}$ where $\Delta\alpha_{V,g}$ is the difference between the corresponding expansion coefficients of macroscopic volume in the liquid and glassy state[15)]. Although it was argued that the WLF equation works over a wide temperature range from T_g up to about T_g+100K, the further studies revealed that the "universal "coefficients (C_{1g}=17.4, C_{2g}=51.6K) must at best be considered as the first approximation, both being dependent on the chemistry of polymers investigated [2,3,6)]. More precise measurements of polymer dynamics revealed that often two VFTH or WLF equations with different parameters are able to account for the data over such a wide temperature range [17-19)]. In many cases it was found the breakdown of the thermo-rheological simplicity of the response spanning from the main chain segmental motion at short times to the terminal or normal process at long times[17-22)]. The temperature dependence of the relaxation time of the segmental motion is stronger than that of the terminal (or normal) mobility implying the different VFTH parameters : $A_s > A_t$, $B_s >$ or $< B_t$ and $T_{0,s} \geq T_{0,t}$[19-24)].

From the theoretical point of view, several approaches to explain this complex behavior have been present. According to the free volume concept, these facts are believed to reflect the different free volume parameters governing the respective processes [17,25)]. In addition, further models and concepts such as the coupling model [25,26)] and the fluctuation approach [23,27)] for both the segmental and terminal (normal) processes or the reptation (or tube) model [28)] for terminal motion try to explain the origin of such a complicate behavior.

From the above-mentioned overview it follows that the free volume idea is often used to rationalize the complex relaxation and viscosity behavior. Until recently, however, *direct* verifications of the relevant assumptions of the free volume analysis, and consequently, *direct* interpretations of the rheological properties in terms of *independently* determined free volume characteristics were missing. At the present stage, the significant progress in the PALS methodology opens up the opportunity to test potential links between two the branches of material science, i.e., the structure and the dynamics.. We expect to obtain more information about role of the free volume factor in the mobility as well as deeper insight into the nature of the underlying motional processes.

Experimental

Materials: Cis-1,4-polybutadiene, (cis-1,4-PBD) -[CH_2-CH=CH-CH_2]- from Japan Synthetic Rubber Co., Ltd with $M_w = 8.1x10^5$ and microstructure: 95.7% of cis-form, 2 % of trans-form and 2.3% of vinyl form and polyisobutylene (PIB) -[CH_2-C(CH_3)$_2$]- from Aldrich with $M_w = 4.2x10^5$ were used.

Method: The standard lifetime set up with the time resolution of 300 ps was used. In the finite terms analysis of annihilation data the PATFIT - 88 software package was applied to fit up three component in the lifetime spectra. For details see Ref.29.

Results And Discussion

cis - 1,4 - Polybutadiene

Fig.1 gives the temperature dependences of both the o-Ps annihilation parameters over a wide temperature interval including the glass - liquid transition zone with the corresponding glassy and liquid state regions at low or high temperatures, respectively29). The pronounced effect in the mean o-Ps lifetime τ_3 at around 170K is consistent with the glass transition temperature from DSC method T_g = 168 +/-1 K, indicating that this quantity is closely related to the basic state change of the amorphous phase. On the other hand, the o-Ps relative intensity I_3 exhibits rather small change at low temperatures up to about 220K, where the slight increase of I_3 begins to appear. Fig.2 shows the temperature dependences of the corresponding free volume hole characteristics. The mean free volume hole size V_h was calculated by using of a semi-empirical quantum-mechanical model - eq.(1), whereas the effective free volume hole fraction f_h was calculated from our phenomenological model - eqs.(3) and (4) applying the definition equation (2). The input data were as follows: $\alpha_{V,g}^{1} = 7.5x10^{-4}K^{-1}$ 30), $\alpha_{fh,g}^{1} = 5.8x10^{-2} K^{-1}$ from the slope of the product $V_h.I_3$ vs. T dependence (not shown, but proportional to the f_h-T plot in Fig.2) divided by the product value at T_g. Then, a solution of eq.(4), being T_i = 151K is used for determination of the second output parameter V_i from eq.(3) and the state data30). The packing coefficient at $T_i = V^w_{mon} / V_i = 0.705$, where V^w_{mon} is van der Waals volume of monomer unit, falls between those for the closest regular packing (0.7405) and the closest

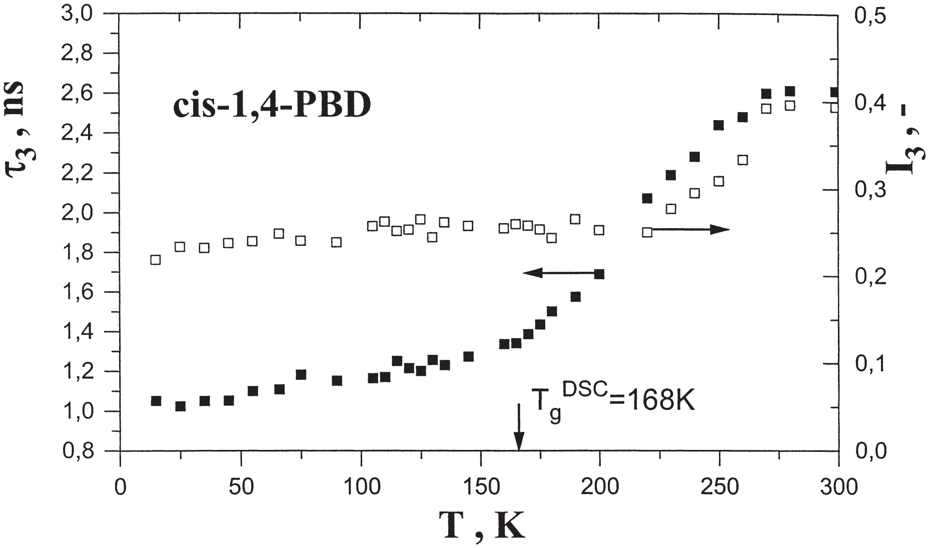

Fig.1 o-Ps lifetime and o-Ps relative intensity as a function of temperature in cis-1,4-PBD

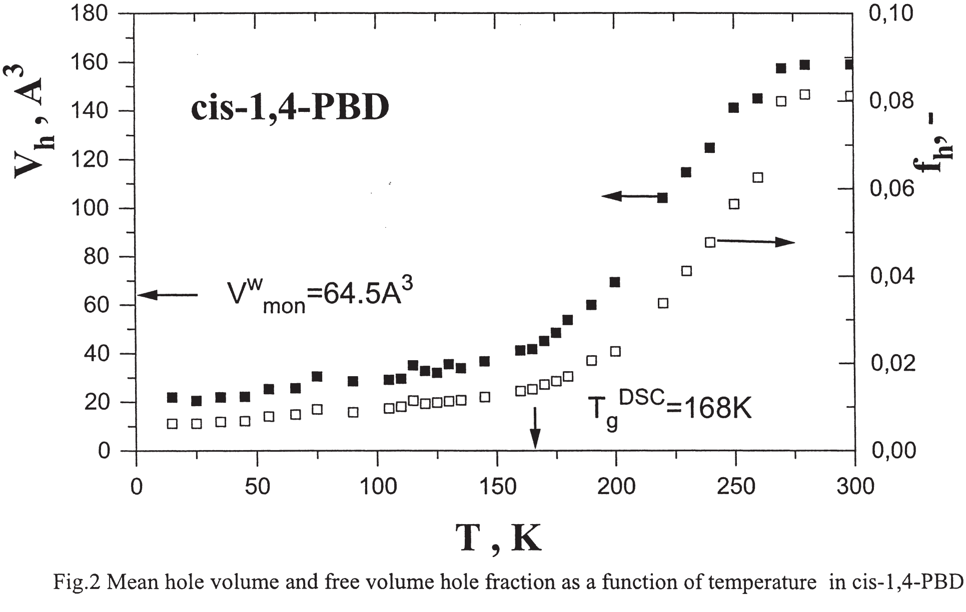

Fig.2 Mean hole volume and free volume hole fraction as a function of temperature in cis-1,4-PBD

random packing of hard spheres (0.64)[13)]. Consequently, K_{Vh} coefficient has been evaluated by adjusting the free volume fraction at T_g, $f_g = 0.015$ on the corresponding PALS data by eqs.(2,3) with T_i from eq.(3) giving $K_{Vh} = 1.294 \times 10^{-3} Å^{-3}$. Note that the T_i value is insensitive to a choice of the input temperature T indicating the robustness of our model. From Fig. 2 it follows that the temperature dependence of the effective free volume hole fraction has similar course as that of the free volume hole size, since the latter is dominating term in eq.(2). In the liquid state, the f_h values ranges from 1.5% at T_g up to 8% at around 280K. This knowledge of the effective free volume hole fraction vs. temperature data opens up the possibility to test the purely free volume interpretation of the WLF equation. Fig.3 gives the result of such a test on the literature shift data a_T on cis-1,4-PBD[3)] in terms of the WLF-Doolittle eq.(8) with f_h's as the input data. We can see a good fit in the temperature range from 220 K up to 280K, i.e., the shift factor is related to the effective free volume hole fraction as obtained from the dilatometric and o-Ps annihilation data . This means that the free volume holes as detectable by PALS method are the controlling factor for the mobility over this temperature range of 60K, at least. In the context with the original assumption of Ref.15 we note that the fitting coefficient $B' = (B/2.303) = 0.127 \pm 0.002$ in eq.(8) is lower than the *postulated* value $B = 1$ used for *estimation* of the free volume fraction at T_g in the original free volume interpretation of the WLF equation[3,15)].

On the other hand, at relatively lower temperatures from the T_g - $1.3T_g$ range the predicted shift factors with the above-mentioned B coefficient from the high temperature data fit departure from the experimental values . This means that the actual shift factor is lower than the extrapolated one, which is governed by the free volume hole factor only. In other words, although purely free volume hole interpretation describes the main part of the shift factor decrease with increasing temperature in the T_g -$1.3T_g$ region, it is not able to explain completely the observed shift factor behavior due to some additional contribution. For this reason we have modified the original free volume WLF-Doolittle approach by introducing the activation - energy term in the spirit of the Macedo-Litovitz- (ML) treatment [31)]. According to this model of mobility, a moving act can occur when two events take place simultaneously: 1) an empty site (hole) is available due to the density fluctuation into which the molecule or segment of chain can move and 2) the moving unit attains sufficient energy to overcome attractive forces holding it to its neighbors:

$$M(T) = A_{f,M} . \exp [B_{f,M}/f(T)] . \exp [E_{act}/RT] \qquad (10)$$

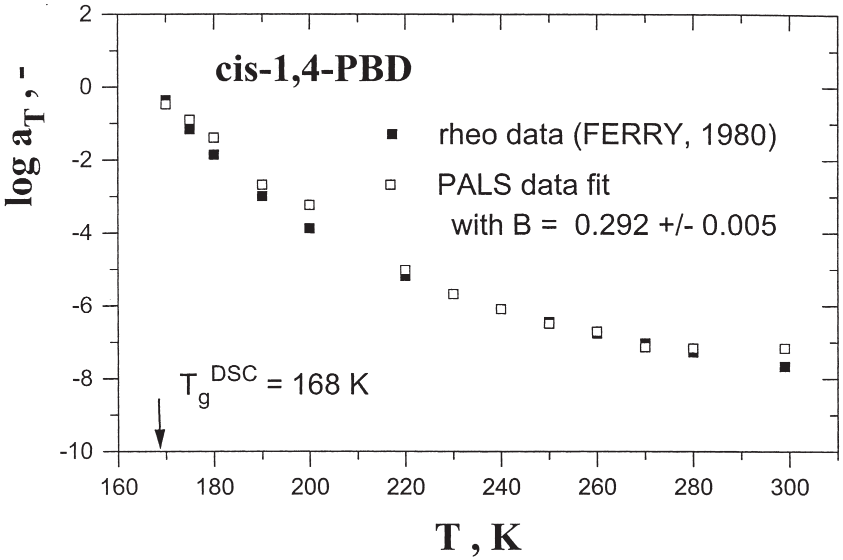

Fig.3 Correlation between the shift factor a_T and the free volume hole fraction f_h in cis-PBD

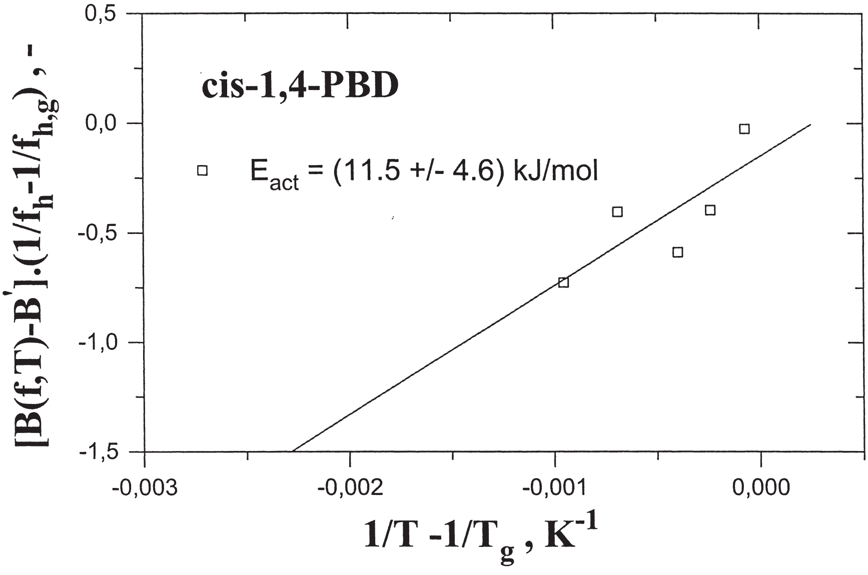

Fig.4 Test of theWLF - Doolittle - Macedo - Litoviz equation in cis-1,4-PBD

so that the combined WLF-Doolittle-Macedo-Litovitz equation reads:

$$\log a_T = (B_{f,M}/2.303).[\,1/f(T) - 1/f(T_g)\,] + (E_{act}/2.303R).(\,1/T - 1/T_g\,) \qquad (11)$$

After simple rearrangements one can arrive to the following expression suitable for application:

$$[B_M(f,T)-B_M/2.303].[1/f(T)-1/f(T_g)] = (E_{act}/2.303R)(\,1/T - 1/T_g\,) \qquad (12)$$

where $B_M(f,T)$ is the coefficient dependent on both the free volume and activation-energy factor, B_M is the coefficient from the high temperature fit which is independent on both the factors. Fig.4 shows the result of a test eq.(12) on the combined shift factor and PALS data on cis-1,4-PBD. Although the relative large scatter exists, the expected linearity is approximately fulfilled allowing an estimation of the activation energy term E_{act} = 11.5 +/-4.6 kJ/mol. It is interesting to note that this value is consistent with the activation energy for the so-called slow ("elementary") motion in the liquid state of cis-1,4-PBD (10.9kJ/mol) as obtained recently by quasi-elastic neutron scattering study on the same material which has been attributed to the change of conformational states of the bonds in polymer chains 32). Moreover it agrees with the results of molecular dynamics simulations on cis-1,4-polybutadiene 33).Thus, the modulation in the mechanism controlling the viscosity over a wide temperature range seems to occur at around $1.3T_g$. At higher temperatures from 220 K up to 280 K, the viscosity is governed only by the density fluctuations connected with the free volume redistribution in the soft matrix, whereas at lower temperatures from 220K down to T_g, the activated dynamics is superimposed on the free volume fluctuations in the relatively more rigid material. This conclusion is consistent with the previously proposed picture 34) as well as with the recent finding of distinct dynamic regimes in the energy landscape of a fragile glass-forming liquid 35,36).

Polyisobutylene

The same procedure as for cis-1,4-PBD was applied on PIB. Fig.5 shows τ_3 and I_3 vs.T plots37). Similarly as in the previous case, an abrupt change in the slope of τ_3 at around 200K agrees with the glass to liquid transition as detected by DSC method at T_g^{DSC} = 205K. In addition, the slighter change of the slope in the o-Ps lifetime in the liquid state together with the change of I_3-T course occur at around 270K correlate with the liquid-liquid transition from other methods38). Fig.6 gives the corresponding free volume hole characteristics in dependence on the temperature. Subsequent application of our model with $\alpha_{V,g}^{\,l} = 5.7\times10^{-4}K^{-1}$

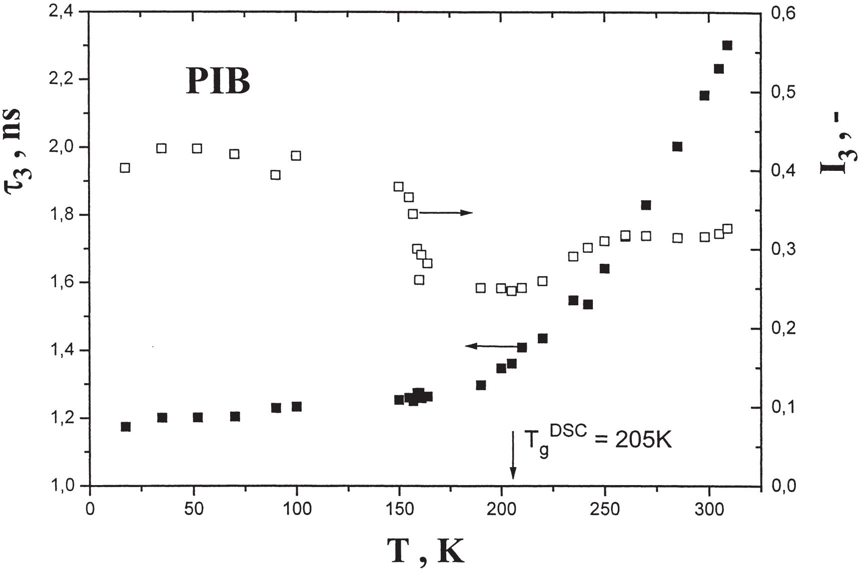

Fig.5 o-Ps lifetime τ_3 and o-Ps relative intensity I_3 as a function of temperature in PIB

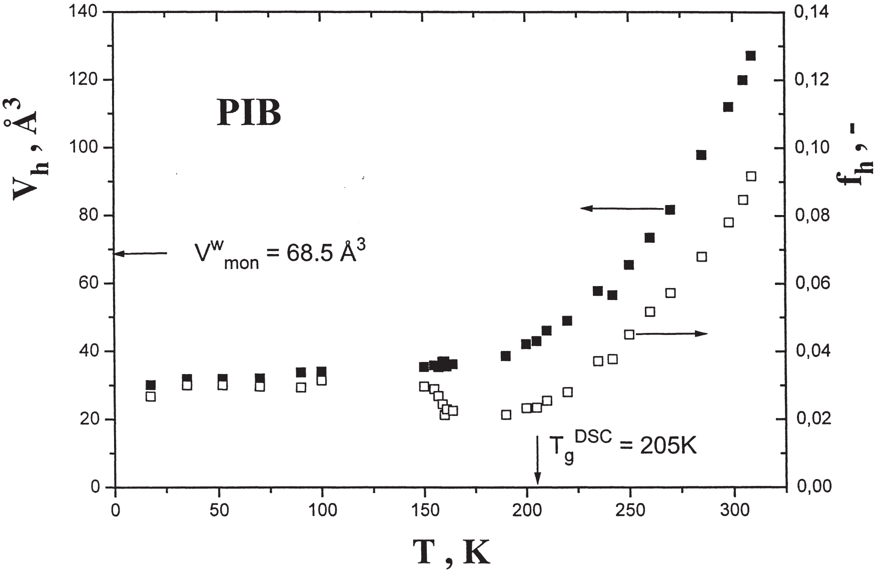

Fig.6 Mean hole volume V_h and free volume hole fraction f_h as a function of temperature in PIB

30) and $\alpha_{fh,g}^{l} = 2.33\text{x}10^{-2}$ K^{-1} leads to the initial temperature $T_i = 164$ K. The packing coefficient at T_i is 0.703 close to the previous case. Then, the free volume fraction at T_g, $f_g = 0.022$ leads to the K_{Vh} value equal to $2.21\text{x}10^{-3}$ Å^{-3}. The right side of Fig.6 shows the temperature dependence of the effective free volume hole fraction ranging from 2.2% at T_g up to 11% at 310K. Fig. 7 presents the mutual relationship between the viscosity and the effective free volume hole fraction from PALS in terms of the WLF-Doolittle equation. Two sets of the shift factor data were tested: the older data from the classic Ferry's book 3) and the newer ones on viscosity by Plazek et el.39). In both the cases the satisfactory fits can be achieved with the slightly different (B/2.303) coefficients: 0.254 ± 0.010 or 0.235 ± 0.006 respectively40,41). These findings indicate that the free volume term as detectable by PALS method governs the rheological behavior of PIB over 130K, where the shift factor decreases on the order of eight order of magnitude.

Acknowledgement

The authors wish to thank the VEGA Agency, Slovak Republic for support this study by grants No.2/4008/97 and 2/5080/98 and Dr.T.Kanaya for kindly supplying the PBD sample.

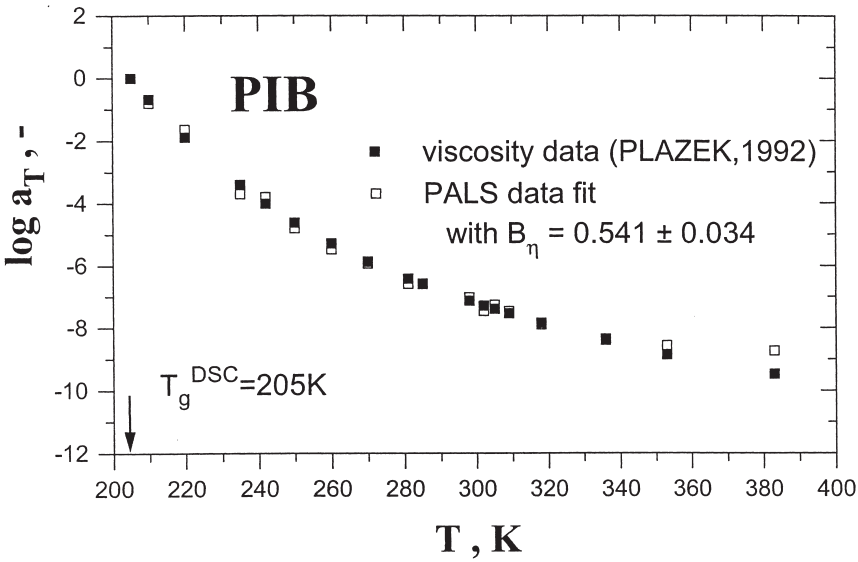

Fig.7 Correlation between the shift factor for viscosity a_T with the free volume hole fraction f_h(
via the WLF-Doolittle type equation

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40.In the previous application[41] of our phenomenological model we have considered in the first approximation the expansion coefficient of the free volume hole size $\alpha_{Vh,g}$ instead of the more correct the expansion coefficient of the free volume hole fraction $\alpha_{fh,g}$, Thus we have arrived to the other outputs and consequently, to the other coefficient K_{Vh}, but the total picture of the fit does not change . In the present application the free volume hole fractions $f_h(T)$ are more realistic in comparison with the previous ones over the entire temperature interval studied.
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