Microscopic basis of free-volume concept as studied by quasielastic neutron scattering and positron annihilation lifetime spectroscopy

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We have reexamined the free-volume concept presented by Cohen and Turnbull on the basis of two microscopic quantities: the excess mean-square displacement $\langle u^2 \rangle_f$ and the total free volume $V_{PA,t}$, of poly- butadiene evaluated from the quasielastic neutron scattering and the positron annihilation lifetime spectroscopy (PALS) data, respectively. Comparing with the viscosity η we found two relations, $\eta = \eta_0 \exp u_0^2/\langle u^2 \rangle_f$ and $\eta = \eta_0 \exp V_{PA,0}*/V_{PA,t} = \eta_0 \exp V_{PA,0}*/v_{PA,f}$, where u_0^2, $V_{PA,0}*$ and $v_{PA,0}*$ are the critical values for the mean-square displacement, the total PALS free volume, and the PALS free volume per molecule, respectively, and further $v_{PA,0}* = V_{PA,0}*/N$, N being the total number of molecules or segments. On the basis of these relations, we discuss the microscopic basis of the free-volume theory. The experimentally evaluated critical values u_0^2 and $v_{PA,0}*$ are much larger than the average values of $\langle u^2 \rangle_f$ and $v_{PA,f}$ calculated from the distributions. This has been explained from the low probability of escaping motions from a molecular cage. The free volume per monomer and the free-volume fraction were calculated from the excess mean-square displacement $\langle u^2 \rangle_f$. The former was compared with the free-volume hole obtained by PALS, suggesting that 22 monomers are required for one PALS free-volume hole. The free-volume fraction obtained from the excess mean-square displacement was found to be 6.4% at 250 K, which is in reasonable agreement with that evaluated from the rheological data (9.0%). [S1063-651X(99)00308-6]

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I. INTRODUCTION

Extensive studies have been performed in the last decade on dynamics of glass-forming materials including polymers as well as organic and inorganic small molecules using many kinds of techniques such as quasielastic neutron scattering, light scattering, dielectric relaxation, NMR, fluorescence depolarization, and mechanical relaxation, which shed light on the substantial nature of the dynamics from a microscopic point of view [1]. Of these techniques the contribution of the quasielastic neutron scattering is outstanding that directly gives microscopic quantities like mean-square displacements, characteristic times, and so on.

In the previous studies [2–4], we have investigated the dynamics of polybutadiene near the glass transition temperature T_g using quasielastic neutron scattering (QENS) and positron annihilation lifetime spectroscopy (PALS). It was found in the QENS studies [2,3] that the so-called *fast process* with characteristic times of the order of a picosecond sets in at around the Vogel-Fulcher temperature T_{VF}, suggesting that the *fast process* is directly related to the glass transition, and that the *slow process* with temperature-

dependent characteristic times of several ten to several hundred picoseconds setting in near T_g is an elementary process connecting to the conformational transition or structural relaxation of polymer chains. It is worth noting that the onset of the *fast process* at T_{VF} is not universal for all amorphous polymers as shown by Colmenero and Arbe [5]. In accordance with the onset of these processes, the mean-square displacement shows an excess value, suggesting that the excess volume is required for these motions. On the other hand, PALS studies [4] have revealed that the free-volume hole drastically begins to increase above T_g, suggesting directly that the excess free volume is necessary for the structural relaxation. These observations remind us of the phenomenological free-volume theory [6] dealing with the flow process or the viscosity of supercooled liquids near T_g, which is often applied to polymer melts [7].

In the free-volume theory [6], viscosity η is related to free volume through

$$\eta = \eta_0 \exp\left(\frac{\gamma V_0}{V_f}\right) = \eta_0 \exp\left(\frac{\gamma v_0}{v_f}\right), \tag{1}$$

where V_f and V_0 are the total free volume and the critical value for the free volume, respectively, and further, $v_f = V_f/N$ and $v_0 = V_0/N$ are the free volume per molecule and its critical value, respectively, N being the total number of molecules. γ is a numerical factor that was introduced by taking into account the overlap of free volume. In the con-

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ventional theories, the free volume per molecule is phenomenologically defined based on the total free volume V_f, which is determined from the macroscopic measurements of thermal expansion of specific volume. Microscopic interpretation of the free volume per molecule is still open to question. In this paper, therefore, we reexamine the free-volume theory from a microscopic point of view. As microscopic quantities, we employ mean-square displacement and free-volume hole (or some kind of cavity) measured by QENS and PALS, respectively. It should here be noted that the relation between the free volume observed in PALS and that defined in the theory is not obvious at present. Hence, in this paper, we call the free volume observed by PALS as PALS *free volume* or PALS *free-volume hole* in order to distinguish it from the free volume defined in the theory.

Here we discuss the free volume in three parts. In the first part, we discuss the microscopic basis of the free-volume theory and the critical value of the mean-square displacement for structural relaxation on the basis of the relation between the mean-square displacement obtained by the QENS measurements and the viscosity. In the second part, we discuss the microscopic basis of the free-volume theory from the relation between the PALS *free volume* and the viscosity. In the final part, we calculate the free volume per monomer and the free-volume fraction from the excess mean-square displacement, and then discuses them in relation to the PALS *free-volume hole* and the free-volume fraction evaluated from the rheological data, respectively.

II. EXPERIMENT

In this paper we mainly reanalyzed the data previously reported; the details are found in the reported papers [2–4]. Here, only brief explanations are made for the samples, the measurements, and the data analyses.

A. Samples

The samples used in the experiments were *cis*-1,4-polybutadiene (*cis*-PB) [2–4] and *cis-trans*-polybutadiene (*cis-trans*-PB) [8] with microstructure of *cis*:*trans*:vinyl = 95.7:2:2.3 and 41:52:7, respectively. The weight-average molecular weight M_w and the polydispersity M_w/M_n are 8.1×10^5 and 2.8 for *cis*-PB and 2.1×10^3 and 1.07 for *cis-trans*-PB, respectively. The glass transition temperatures T_g of *cis*-PB and *cis-trans*-PB are 170 and 178 K, respectively.

B. Quasielastic neutron scattering (QENS)

In quasielastic neutron scattering measurements we observe the dynamic scattering law $S(Q,\omega)$, which is dominated by incoherent scattering from hydrogens because the incoherent atomic scattering cross section of hydrogen is much larger than the coherent and incoherent atomic scattering cross sections of carbon as well as the coherent cross section of hydrogen [9]. The incoherent dynamic scattering law $S_{\text{inc}}(Q,\omega)$ is given by the Fourier transform of the self part of the van Hove time-space correlation function $G_s(\mathbf{r},t)$ [10], which gives the probability of finding the same particle at a position $\mathbf{r}$ at time t if there is a particle at the position $\mathbf{r}=0$ at time $t=0$ in equilibrium.

The observed incoherent elastic scattering intensity $I_{\text{el}}(Q)$ $[\propto S(Q,\omega=0)]$ is related to the Debye-Waller factor w through $I_{\text{el}}(Q)=\exp[-2w]$. Under the Gaussian approximation [11] it is written by

$$I_{\text{el}}(Q)=\exp[-\langle u^2 \rangle Q^2], \qquad (2)$$

where $\langle u^2 \rangle$ is the mean-square displacement [12]. Using this equation, we evaluated $\langle u^2 \rangle$ from the Q dependence of the elastic scattering intensity $I_{\text{el}}(Q)$.

The Gaussian approximation in Eq. (2) is often broken down in high Q ranges due to the effect of the higher-order terms of Q. By analyzing such non-Gaussian behavior, one can evaluate the distribution of $\langle u^2 \rangle$, termed $g_{msd}(\langle u^2 \rangle)$ and the average value $\overline{\langle u^2 \rangle}$ [13–15].

QENS measurements were carried out with an inverted geometry time-of-flight spectrometer (LAM-80) at the National Laboratory for High-Energy Physics (KEK), Tsukuba, and a conventional triple-axis spectrometer (GP-TAS) at the JRR-3M reactor, Tokai. The energy resolutions $\delta\varepsilon$ of LAM-80 and GP-TAS are about 0.02 and 1.1 meV and hence the evaluated $\langle u^2 \rangle$'s may be related to motions in time ranges faster than 2×10^{-10} and 3.8×10^{-12} s, respectively. The magnitude of scattering vector Q ($Q=4\pi \sin\Theta/\lambda$: 2Θ and λ being scattering angle and wavelength of neutrons, respectively) ranges from 0.2 to 1.64 and 0.4 to 6.4 Å^{-1} for LAM-80 and GP-TAS, respectively. The details of the measurements were described in Refs. [2, 14, 15].

C. Positron annihilation lifetime spectroscopy (PALS)

In PALS measurements, lifetime τ_3 of orthopositronium (*o*-Ps) and its intensity I_3 are evaluated. The lifetime τ_3 is related to the radius R of a spherical PALS *free-volume hole* with an electron layer of thickness ΔR on the basis of a simple quantum-mechanical model [16],

$$\tau_3 = \frac{1}{2}\left(1 - \frac{R}{R_0} + \frac{1}{2\pi}\sin\frac{2\pi R}{R_0}\right)^{-1}, \qquad (3)$$

where $R_0 = R + \Delta R$. The parameter $\Delta R = 1.66$ has been determined from the fitting of the experimental values of τ_3 with the known hole size of one of the standards such as molecular crystals and zeorites. The intensity I_3 is considered to be a measure of the PALS *free-volume hole* density.

The distribution of inverse lifetime $h(1/\tau_3)$ can be obtained by analyzing the PALS spectra and is related to the distribution of the radius of the PALS *free-volume hole* $f(R)$ through

$$f(R) = 2\Delta R\left(\cos\frac{2\pi R}{R+\Delta R} - 1\right)\frac{h(1/\tau_3)}{(R+\Delta R)^2}. \qquad (4)$$

Then, the distribution of the volume of the PALS *free-volume hole* $v_{\text{PA},h}$ is given by

$$g_{\text{PA},h}(v_{\text{PA},h}) = \frac{f(R)}{4\pi R^2}. \qquad (5)$$

The details of the measurements and the analysis were described in Ref. [4].

D. Evaluation of temperature dependence of viscosity

In this paper, we have evaluated the temperature dependence of the viscosity from the rheological data as follows.

In rheological measurements, it is well known that storage G' and loss G'' moduli are rescaled to a single master curve using horizontal and vertical shift factors, a_T and b_T, respectively,

$$G'(\omega,T) = b_T G'(a_T\omega,T_0), \tag{6}$$

$$G''(\omega,T) = b_T G''(a_T\omega,T_0), \tag{7}$$

where T_0 is a reference temperature. In the so-called rubbery region, vertical shift factor b_T is given by $T\rho/T_0\rho_0$, ρ and ρ_0 being the densities of the system at T and T_0, respectively. Usually, the temperature dependence of b_T is much smaller than that of a_T. Then, assuming that b_T is independent of T, it follows that the shift factor is proportional to the viscosity η: $a_T \propto \eta$. The temperature dependence of η or the shift factor a_T is usually described by the Williams-Landel-Ferry (WLF) equation,

$$\log_{10} a_T = \frac{-c_1^0(T-T_0)}{c_2^0+T-T_0}, \tag{8}$$

where c_1^0 and c_2^0 are parameters depending on T_0. The WLF equation is often used to describe the polymer melts while in some cases it is preferable to use the Vogel-Fulcher (VF) equation for the viscosity, although both the equations are equivalent.

$$\eta = A \exp\left(\frac{B}{T-T_{VF}}\right), \tag{9}$$

where T_{VF} is the Vogel-Fulcher temperature. At higher temperatures where viscosity is dominated by entanglements in high molecular weight systems, the relation is not held any longer. Usually, the relation is valid for temperature ranges below about $T_g+100\,K$ [7]. The comparison between the WLF and VF equations gives

$$T_{VF} = T_0 - c_2^0, \quad B = 2.303 c_1^0 c_2^0. \tag{10}$$

The VF parameter A cannot be determined from the WLF parameters because it requires information about the absolute value of the viscosity. In this paper we estimated A by assuming that the viscosity at T_g is $10^{12}\,Pa\,s$, which is commonly accepted for many kinds of glass-forming materials [17] though the absolute value is not essential for our discussion in this report. For the calculation of the viscosity, the WLF parameter was taken from Refs. [18, 19] for cis-PB and cis-trans-PB, respectively.

III. RESULTS AND DISCUSSION

A. Relation between mean-square displacement $\langle u^2\rangle$ and viscosity η

In this subsection, we examine the relation between the mean-square displacement $\langle u^2\rangle$ and the viscosity, and discuss the microscopic basis of the free-volume theory. For this purpose, we first describe the temperature dependence of
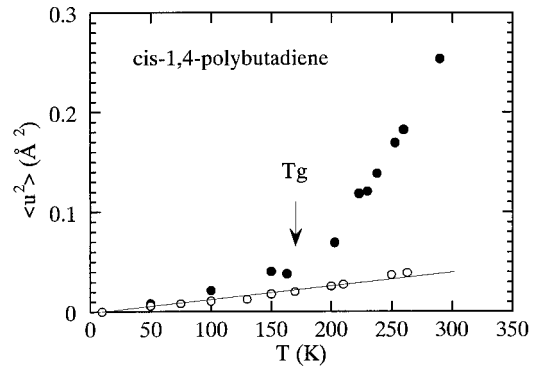

FIG. 1. Temperature dependence of the mean-square displacement $\langle u^2\rangle$ of cis-1,4-polybutadiene measured with the energy resolution $\delta\varepsilon$ of 0.02 meV (●) and 7 meV (○).

the mean-square displacement. The critical value of the mean-square displacement for structural relaxation is also discussed on the basis of the distribution of the mean-square displacement $g_{msd}(\langle u^2\rangle)$.

Temperature dependence of $\langle u^2\rangle$. In Fig. 1, temperature dependence of the mean-square displacement $\langle u^2\rangle$ evaluated from the measurements on cis-PB by LAM-80 ($\delta\varepsilon = 0.02$ meV) is shown by solid circles. The data points were mainly taken from the previously reported papers [2,3] though they contain some unpublished data [20]. In the temperature range below about the Vogel-Fulcher temperature T_{VF}, which is usually ~50 K below the glass-transition temperature T_g [7], $\langle u^2\rangle$ increases linearly with T, suggesting that the motion observed here is approximately a harmonic vibration. Above ~T_{VF}, however, some amount of excess $\langle u^2\rangle$ deviating from the linear relationship is observed [2]. In what follows we will discuss this point. As shown in the previous investigations [2,3], there exist two kinds of modes of motions near T_g: one is the *fast process* with T-independent characteristic time in the energy range below ~2 meV, and the other is the *slow process* in the energy range below ~0.2 meV, which is related to an elementary process of conformational transition or structural relaxation. The excess $\langle u^2\rangle$ appearing above T_{VF} is caused by these motions.

In Fig. 1, $\langle u^2\rangle$ values evaluated for the low-energy resolution $\delta\varepsilon = 7$ meV are also displayed by open circles, which were obtained from the Q dependence of the integrated intensity in an energy region between 0 and 7 meV. The $\langle u^2\rangle$ for $\delta\varepsilon = 7$ meV increases linearly with T even above T_g. Judging from the fact that the temperature dependence of $\langle u^2\rangle$ does not change below and above T_g, the $\langle u^2\rangle$ for $\delta\varepsilon = 7$ meV may be regarded as the mean-square displacement owing to vibrational motions similar to those in crystals. It is also supported by the fact that, even below T_{VF}, the $\langle u^2\rangle$ for $\delta\varepsilon = 7$ meV is slightly smaller than that for $\delta\varepsilon = 0.02$ meV. Although we did not observe the $\langle u^2\rangle$ of the true crystalline state as it could be done for selenium [21], which is impossible for amorphous cis-PB, we define the difference in $\langle u^2\rangle$ between $\delta\varepsilon = 0.02$ and 7 meV as excess mean-square displacement $\langle u^2\rangle_f$ for the structural relaxation above T_{VF}.

Relation between $\langle u^2\rangle_f$ and η. If logarithm of the viscosity is plotted against the inverse of the excess mean-square displacement $\langle u^2\rangle_f$ in the temperature range from 200 to 290
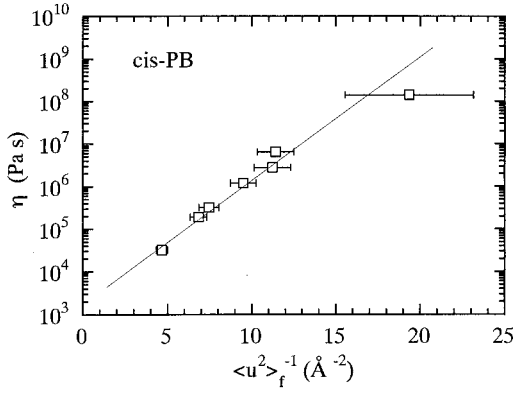
FIG. 2. Relation between logarithm of the viscosity log η and the excess mean-square displacement $\langle u^2 \rangle_f$.

K, a linear relation is obtained as shown in Fig. 2. This relation can be described by

$$\eta = \eta_0 \exp\left(\frac{u_0^2}{\langle u^2 \rangle_f} \right), \qquad (11)$$

where η_0 and u_0^2 are constants. This relation is close to the equation derived from the free-volume concept [6] in which the random distribution of an average free volume per atom is assumed. A similar relation between $\langle u^2 \rangle_f$ and η has been reported for amorphous selenium Se by Buchenau and Zorn [21].

Theoretically the relation of Eq. (11) can be derived from the following picture [21]: a given atom or atomic group performs back-and-forth motions, i.e., rather oscillatory than jumping, in a cage (the *fast process*). It seems reasonable to consider that its probability distribution in the cage motion (the *fast process*) is a Gaussian with the mean-square displacement $\langle u^2 \rangle_f$. If the amplitude of the *fast process* exceeds, by chance, a critical displacement u_0, local structural relaxation or conformational transition (the *slow process*) takes place. Assuming that the characteristic time of the *fast process* is independent of temperature, which was experimentally confirmed for many amorphous polymers [22], the waiting time for the occurrence of the *slow process* (or structural relaxation) at a given atom is proportional to the probability of finding an atom or an atomic group outside the sphere with radius u_0. Then, one gets the relation of Eq. (11) theoretically [23].

The present results may suggest that the excess mean-square displacement $\langle u^2 \rangle_f$ behaves as a free volume and is closely connected to an elementary step of the structural relaxation or the conformational transition of PB.

Critical value of mean-square displacement. The slope of the linear relation in Fig. 2 provides u_0^2 in Eq. (11), which may be considered to be a critical value of the excess mean-square displacement required for the structural relaxation as will shown later: $u_0^2 = 0.32 \, \text{Å}^2$. In order to see if the value is reasonable we have evaluated the distribution $g_{\text{msd}}(\langle u^2 \rangle)$ of $\langle u^2 \rangle$. For this purpose, we employed the data obtained by the GP-TAS spectrometer because it can access the higher Q range up to $6.4 \, \text{Å}^{-1}$. The excess mean-square displacement $\langle u^2 \rangle_f$ evaluated from the GP-TAS data also fulfilled the relation of Eq. (11) and the slope of log η vs $1/\langle u^2 \rangle_f$ gives a
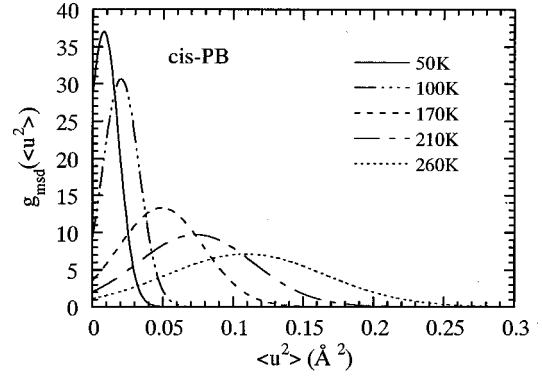

FIG. 3. Distribution of the mean-square displacement for *cis-trans*-polybutadiene measured with the energy resolution $\delta \varepsilon$ of 1.1 meV for 50, 100, 170, 210, and 260 K.

critical value u_0^2 of 0.60 Å^2. This value is larger than that evaluated by the LAM-80 data because the energy resolution of GP-TAS is lower than that of LAM-80 as mentioned in Sec. II [24].

By analyzing the non-Gaussian behavior of the GP-TAS data [14] we evaluated the distribution functions of $\langle u^2 \rangle$ (not $\langle u^2 \rangle_f$) at various temperatures, which are shown in Fig. 3. From the distribution function, the average value of $\langle u^2 \rangle$ was calculated to be 0.11 Å^2 at 260 K which is much smaller than the critical value of 0.60 Å^2. Here, it should be noted that even the tail of the distribution at 260 K does not reach the critical value of 0.60 Å^2 although the distribution of $\langle u^2 \rangle$ is rather wide. This result is not surprising because the free-volume theory [6] predicts that the critical value is in order of 10 times as large as the average one. A microscopic interpretation of this large critical value may be provided by taking into account the characteristic times of the *fast* and the *slow processes* as is explained below.

An atom or an atomic group performs the *fast motion* having a characteristic time of an order of a picosecond in a cage within an average time, but it makes a jump (the *slow process*) to escape from the cage if the mean-square displacement exceeds a critical value by chance, which is much larger than the average value of $\langle u^2 \rangle$ as observed here. This critical value may be considered to correspond to the so-far-discussed critical value u_0^2. For molecules (or segments) to make such a large jump, they must move cooperatively, giving a very small jump probability. This probability is approximately given by the ratio of the characteristic time of the *fast process* to that of the *slow process* (conformational transition or structural relaxation), which is between 0.001 and 0.01 in a temperature range of $T_g + 40$ to $T_g + 80 \, \text{K}$ for *cis*-PB [2]. The small probability of the jump may explain the large difference between the average value $\langle u^2 \rangle$ and the critical value of u_0^2, and vice versa.

B. Relation between PALS *free volume* V_f and viscosity η

In this subsection, we examine the relation between the PALS *free volume* (or some kind of cavity) and the viscosity to have an insight into the free-volume theory from microscopic point of view. For this purpose, we first describe the temperature dependence of the PALS *free volume*. Similarly, to Sec II A, we also discuss the critical value of the PALS *free volume*.
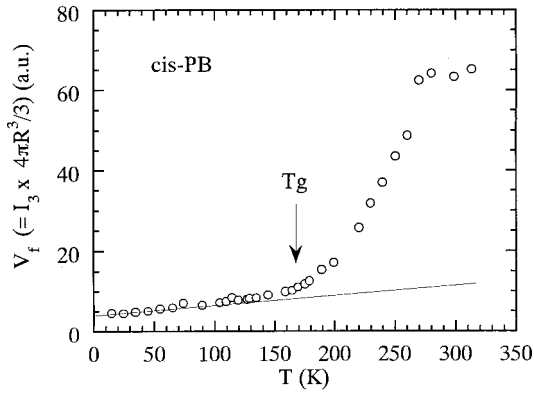
FIG. 4. Temperature dependence of the total PALS *free volume* $V_{PA,f}$ defined as $I_3 \times 4\pi R^3/3$, where R and I_3 are the radius of the PALS *free-volume hole* and its intensity. For details, see text.

Temperature dependence of PALS *free volume.* In the previous paper [4] we have evaluated the temperature dependence of the radius R of the PALS *free-volume holes* and the intensity I_3, which is proportional to the number of the PALS *free-volume holes*, for *cis*-PB. On the basis of these data, the total amount of the PALS *free volume* $V_{PA,t}$, which is defined as $I_3 \times 4\pi R^3/3$, can be calculated, and it is plotted as a function of temperature in Fig. 4. As seen from the figure, the total PALS *free volume* $V_{PA,t}$ is observed even at low temperatures far below T_g. This may be originated from some vacancies frozen in the glassy state. At temperatures above ~ 290 K it is seen that $V_{PA,t}$ is almost independent of temperature. This phenomenon is explained by formation of the so-called bubble state [25–27], and is not connected with the concept of free volume, and hence we excluded the two data points above ~ 290 K from the analysis.

Relation between PALS *free volume and viscosity.* In Fig. 5, the logarithm of the viscosity is plotted against the inverse of $V_{PA,t}$ for *cis*-PB in a temperature range of 180 to 280 K, giving a linear relation,

$$\eta = \eta_0 \exp\left(\frac{V_{PA,0}^*}{V_{PA,t}} \right), \qquad (12)$$

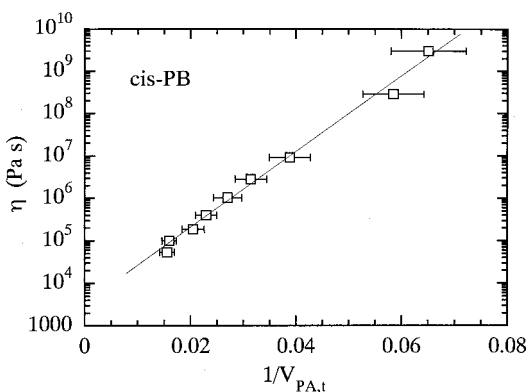where η_0 and $V_{PA,0}^*$ are constants. Equation (12) can be rewritten as

FIG. 5. Relation between logarithm of the viscosity $\log \eta$ and the total PALS *free volume* $V_{PA,f}$ defined as $I_3 \times 4\pi R^3/3$.
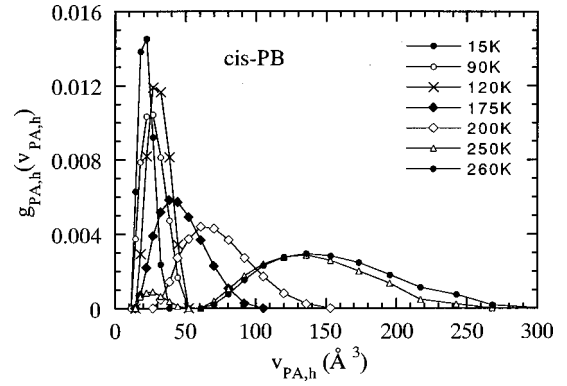

FIG. 6. Distribution of the PALS *free volume hole* $v_{PA,h}$ for *cis*-1,4-polybutadiene for 15, 90, 120, 175, 200, 250, and 260 K.

$$\eta = \eta_0 \exp\left(\frac{v_{PA,0}^*}{v_{PA,t}} \right), \qquad (13)$$

where $v_{PA,t} = V_{PA,t}/N$ and $v_{PA,0}^* = V_{PA,0}^*/N$, N being the total number of molecules (or the segments). Equation (13) is formally the same as the relation predicted in the free-volume theory [6] if we neglect the numerical factor γ in Eq. (1), which was introduced by taking into account the overlap of free volume. Hereafter, we call $v_{PA,0}^*$ as effective critical value of the PALS free volume.

In the free volume theory it is assumed that the free volume is linearly proportional to temperature and vanishes at the VF temperature T_{VF}. However, in the measurements, the PALS free volume is still observed even below T_{VF}. If we subtract the frozen PALS free volume $V_{PA,g}$ observed below T_{VF} (solid line in Fig. 4), we can no longer obtain the linear relation between $\log \eta$ and $1/(V_{PA,f} - V_{PA,g})$, but a convex curve. This may suggest that the PALS free volume can only be considered as the free volume in the theory above T_g. At present, the relation between the PALS free volume and the theoretical free volume is not established below T_{VF}.

Critical value of PALS *free volume.* The critical free volume $V_{PA,0}^*$ cannot be obtained from the slope of the solid line in Fig. 5 since the relation between the number of holes and I_3 is unknown. If we assume that the PALS *free-volume hole* corresponds to the free volume per monomer ($I_3 = 1$) at T_g [28], we get an effective critical value $v_{PA,0}^* = V_{PA,0}^*/N = 797 \text{ Å}^3$. The distribution $g_{PA,h}(v_{PA,h})$ of the PALS *free-volume hole* $v_{PA,h}(= 4\pi R^3/3)$ is displayed in Fig 6 for various temperatures below and above T_g. The average value of the PALS *free-volume hole* $\overline{v_{PA,h}}$ is calculated from the distribution, e.g., $\overline{v_{PA,h}} = 137 \text{ Å}^3$ at 250 K. The effective critical value $v_{PA,0}^*$ of 797 Å^3 is 5.8 times as large as the average one, which is within the ordinary range ($v_0 \approx 10 v_f$) of the free-volume theory [6]. As in the discussion on $\langle u^2 \rangle$ and u_0^2, this large difference between $v_{PA,f}$ and $v_{PA,0}^*$ also implies that cooperative motions of surrounding molecules are required for the structural relaxation. It seems worthy to point out that the effective critical value $v_{PA,0}^*$ ($= 797 \text{ Å}^3$) is comparable to the size of the cooperatively rearranging region [29] for the primary α process in glass-forming materials.

C. Free volume per monomer and free-volume fraction

In this subsection we calculate the free volume per monomer and the free-volume fraction from the excess mean-square displacement $\langle u^2 \rangle_f$, and compare it with the PALS *free-volume hole* and free-volume fraction evaluated from the macroscopic rheological data, respectively.

Calculation of free volume per monomer from mean-square displacement. The excess mean-square displacement $\langle u^2 \rangle_f$ evaluated here is related to that of hydrogen atoms as mentioned in Sec. II. Hence the excess volume per monomer is approximately calculated from the $\langle u^2 \rangle_f$ values in the following way. The contribution from hydrogen atoms is given as $6 \times (4\pi/3)\langle u^2 \rangle_f^{3/2}$ per monomer because one monomer has six hydrogen atoms and that from carbon atoms is given by $4 \times (4\pi/3)\{\langle u^2 \rangle_f (M_H/M_C)\}^{3/2}$, where M_H and M_C are atomic masses of hydrogen and carbon atoms, respectively, because the mean-square amplitude of motions is approximately proportional to inverse mass. Then the total excess volume per monomer is the sum of both the contributions, e.g., 6.22 Å^3 at 250 K for *cis*-PB if the three-dimensional isotropic motions are assumed. This value is much smaller than the PALS *free-volume hole*, $V_{PA,h} = 137$ Å^3 at 250 K, implying that 22 ($=137/6.22$) monomers are required for one PALS *free-volume hole* at 250 K.

Fraction of free volume. In order to calculate the fraction of the free volume we have to evaluate the total volume of a monomer including both the occupied and free volumes, which is easily calculated from the molar density and molar mass. Referring to the thermal expansion coefficient and the density from the literature [30], we calculated the total volume of a monomer as 97.8 Å^3 for *cis*-PB at 250 K($=T_g$ $+80$ K), leading to a free-volume fraction f_f of 6.4%.

We have also estimated free-volume fraction f_f for *cis*-PB from the rheological data [31]. Assuming that the fraction of free volume f_f increases linearly with temperature as

$$f_f = f_0 + \alpha_f(T - T_0), \tag{14}$$

where α_f and f_0 are the thermal expansion of free volume relative to the total volume and the fractional free volume at a reference temperature T_0, respectively; the following equation for the shift factor a_T can be derived from the free-volume theory,

$$\log_{10} a_T = -\frac{(B'/2.303 f_0)(T - T_0)}{f_0/\alpha_f + T - T_0}, \tag{15}$$

where B' is a constant. Equation (15) is identical to the WLF equation [Eq. (8)] when c_1^0 and c_2^0 are $B'/2.303 f_0$ and f_0/α_f, respectively. Taking the glass-transition temperature as the reference temperature, the parameters f_g/B' and α_f/B' can be evaluated from the WLF parameters [18]. Putting unity into B', we have evaluated the free-volume fraction f_f through Eq. (14) to be $f_f = 9.0\%$ at 250 K. The 6.4% from the neutron data is in reasonable agreement with this value.

IV. CONCLUSIONS

In this paper we have re-examined the free-volume concept on the basis of microscopic quantities: the mean-square displacement and the PALS *free-volume hole* obtained in the QENS and PALS measurements. Comparing the temperature dependence of both the quantities with that of the viscosity η, we found linear relations between $\log \eta$ and $1/\langle u^2 \rangle_f$ as well as between $\log \eta$ and $1/V_{PA,t}$ above T_g. Here, $\langle u^2 \rangle_f$ and $V_{PA,t}$ are the excess mean-square displacement and the total PALS *free volume*, evaluated from the QENS and PALS data, respectively. These results support the concept of the free volume theory by Cohen and Turnbull above T_g. It is worth noting that the PALS *free volume* is still observed below T_{VF} and, hence the linear relation between $\log \eta$ and $1/V_{PA,t}$ is limited to temperatures above T_g. The critical values for the excess mean-square displacement u_0^2 and for the PALS *free volume hole* $v_{PA,0}^*$ are 5.5 and 5.8 times as large as the corresponding average values at 250 K, respectively. This has been explained by a small jump probability for conformational transition or structural relaxation (the slow process) occurring during the cage motion (the fast process), implying that cooperative motions are necessary for structural relaxation. The free volume per monomer and the free-volume fraction were calculated from the excess mean-square displacement, and an obtained fraction of 6.4% at 250 K for *cis*-PB is fairly reasonable and in good agreement with that evaluated from the rheological data (9.0%).

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[24] As described in Sec. II, the mean-square displacement observed by LAM-80 and GP-TAS are related to motions in time ranging faster than 2×10^{-10} and 3.8×10^{-12} s, respectively. The slower motions are observed in the LAM-80 measurements, so that the mean-square displacement observed by LAM-80 is larger and the temperature dependence is stronger than those observed by GP-TAS, respectively. Hence the apparent critical value u_0^2 evaluated from the LAM-80 data is smaller than that from GP-TAS.

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