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Scaling behavior of free-volume holes in polymers probed by positron annihilation

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Positron lifetimes in polybutadiene (PB) and polypropylene (PP) are measured as functions of temperature in the range 95–305 K and 95–370 K, respectively. From the variations of *ortho*-positronium (o-Ps) lifetime τ_3, we have determined the glass transition temperatures T_g in PB and PP and the excluding temperature T_e in PB, beyond which the o-Ps lifetime τ_3 in PB is saturated. From the analogy of the temperature-dependent o-Ps intensity I_3 in PB and PP, high- and low-density polyethylene (HDPE and LDPE), we propose that above the glass transition temperature T_g the o-Ps intensity I_3 exhibits the scaling relation $I_3 \sim (T - T_g)^\beta$ in these polymers. The data also indicate the existence of a crossover temperature T_c, located above T_g, where the β value changes greatly. When $T_g < T \le T_c$, β has the order of magnitude of 10^{-2}. When $T_c \le T < T_e$, $\beta = 0.346 \pm 0.035$ and 0.297 ± 0.037 for linear polymers PB and PP. Similar features are also observed for previous results of HDPE and LDPE [D. Lin and S. J. Wang, J. Phys. Condens. Matter **4**, 3331 (1992)]. The β values in the region of $T_c \le T < T_e$ are found to be 0.336 ± 0.038 and 0.507 ± 0.059 for linear polymers HDPE and branched LDPE, respectively. These results reveal a common picture of hole creation above T_g in polymers, however, the concrete value of β may be associated with the branching structure of macromolecules.

I. INTRODUCTION

The macroscopic properties of polymers strongly depend on time and temperature in comparison with those of other materials such as metal and ceramics, which has been extensively investigated for decades.[1] One of the interesting observations on these viscoelastic properties is that the viscosity, modulus, heat capacity, and thermal expansion coefficient of polymers undergo dramatic changes when temperature is raised or lowered through the glass-transition region. These phenomena have been satisfactorily explained by the free-volume theory.[1–4] It has been proposed that the ease of local chain segment rotation and diffusion depends on the amount of "excess or empty volume" available locally, and the increase in free volume available to a segment is carried out by rearrangement of its neighborhood as temperature increases. In recent years the free-volume holes have been experimentally found to play an important role in understanding the mechanical properties,[5–7] the glass transition,[8–10] and physical aging[11] of polymers. As for the glass transition, some theoretical developments have been made to predict the changes of free-volume properties and in turn the observable quantities in the vicinity of glass-transition temperature T_g. For instance, the free-volume theory has been extended by incorporating the ideas from the percolation theory[12] and has proved the average size of free-volume hole $v_f \propto (T - T_g)$ as temperature is well above T_g. On the other hand, some authors have performed the Monte Carlo simulation to understand the variations of size and concentration of free-volume holes with temperature.[13]

As a nondestructive probe, the positron annihilation lifetime spectroscopy[8] (PALS) has been widely used to detect the properties of free-volume holes with a size of few Å, on the basis that the ortho-positronium (o-Ps) "atom" is preferentially localized in the free-volume hole, where the o-Ps lifetime is relevant to the hole size[8] and it is considered that the o-Ps formation probability is proportional to the concentration of holes.[14,15]

The scaling concept has been extensively applied to various polymer systems including the polymer solution, melts,[16] and glasses,[2] e.g., the scaling treatment on the free-volume hole in polymer glasses has given a reasonable explanation of the relaxation time spectrum.[2] Furthermore, the scaling theory has been proposed to analyze the behavior of measurable quantities near the ideal glass-transition temperature T_0.[17,18] Due to the existence of analogous behaviors of physical quantities, the scaling concept has been preferentially used to analyze the "universal" properties of polymers. However, to the authors' knowledge, very few works on the scaling behavior of free-volume-hole properties of polymers have been reported. Based on the free-volume model, the results of PALS measurements on several polymers with simple structures have clearly demonstrated the similar variations of o-Ps intensity versus temperature, which indicates the existence of a possible scaling behavior of free-volume concentration.

In this work we present the result of positron lifetime measurement of polybutadiene (PB) and polypropylene (PP) as a function of temperature. We will show that the hole creation above T_g is universal in several polymers with a simple structure of chains, i.e., PB, PP, high- and low-density polyethylene (HDPE, LDPE).[9] We will formulate a scaling relation of o-Ps intensity as a function of temperature.

II. EXPERIMENT

The PALS measurements are performed on two kinds of polymers consisting only of a backbone basically without side chains, i.e., polybutadiene (PB) and polypropylene (PP). The individual samples of PB and PP are obtained from Hubei Provincial Institute of Chemistry Research and the Institute of Chemistry, Chinese Academy of Sciences, respectively. The PB sample (density=0.890 g/cm^3) has no detectable crystallinity at 77 K and at room temperature as measured by means by wide-angle x-ray scattering.[19] The crystallinity of the PP sample (melt flow index=3 g/10 min) is estimated to be 54% from the density of 0.905 g/cm^3. The dynamic mechanical analysis (DMA) measurement shows that $T_g=188$ K for PB, and $T_g=286$ K for PP as the increase rate of temperature is 5 K/min. The sample for positron lifetime measurements has a size of $8\times8\times1.5$ mm.

A conventional fast-fast coincident lifetime spectrometer is used for PALS measurement. The time resolution is found to be a sum of two Gaussians with FWHM$_1$=270 ps (91%) and FWHM$_2$=240 ps (9%). The positron source is 30 μCi ^{22}NaCl, deposited on a Ni foil (1 mg cm^{-2}), folded and then sandwiched between two identical samples. The temperature of samples is controlled by the apparatus as described elsewhere.[9] After the sample is annealed at 95 K for about 12 h, the collection of positron lifetime spectrum begins. Half a million counts are collected for each spectrum in about 60 min when temperature increases in intervals of 4–5 K. The temperature ranges for PALS measurements on PB and PP are 95–305 and 95–370 K, respectively.

III. RESULTS AND DISCUSSION

The positron lifetime spectra are resolved into three components using the computer program PATFIT.[20] After the background and source correction are subtracted, variance of fit is less than 1.2. The two short components $\tau_1\sim0.13$ ns and $\tau_2\sim0.4$ ns are attributed to para-positronium (*p*-Ps) atoms and "free" positron annihilation, and are found to exhibit no correlation with the free-volume properties.[11] The third component ($\tau_3=1.2$–3.0 ns, $I_3=10$–30 %) arises from *o*-Ps pick-off annihilation, and is correlated with the properties of free-volume holes.[13] The variations of *o*-Ps lifetime τ_3 and intensity I_3 in PB and PP are shown in Figs. 1 and 2.

A. Structural transitions

From Fig. 1, the *o*-Ps lifetime τ_3 increases with temperature, which demonstrates the expansion of hole size with temperature.[8] However, the detailed increasing slope $d\tau_3/dT$ is obviously different in different temperature ranges, suggesting the existence of structural transitions in PB and PP. We use the least-squares linear fitting technique to approximate the τ_3-T curves in several different temperature ranges, therefore the intercepting points can be determined by joining the equations of neighboring lines and are considered as the structural transition temperatures.[8–10] For PP, the τ_3-T curve can be better linearly fitted within two temperature regions, i.e.,

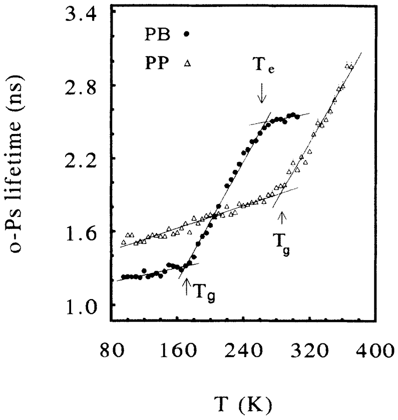

FIG. 1. The variations of *o*-Ps lifetime τ_3 for PB and PP as a function of temperature. The error limits of PB are the same size of the symbols. The straight lines are drawn according to Eqs. (1) and (2).

$$\tau_3(T)=(2.330\pm0.070)\times10^{-3}T+(1.259\pm0.014)\ \text{(ns)}\quad(95\le T\le285\ \text{K})\ ,\qquad\text{(1a)}$$

$$\tau_3(T)=(11.900\pm0.030)\times10^{-3}T-(1.473\pm0.097)\ \text{(ns)}\quad(290\le T\le370\ \text{K})\ ,\qquad\text{(1b)}$$

From Eqs. (1a) and (1b), the inflection point at $T_g=(285.5\pm13.8)$ K is identified as the glass transition in PP. However, the empirical relation between τ_3 and T for PB is best described within three temperature regions, i.e.,

$$\tau_3(T)=(1.300\pm0.150)\times10^{-3}T+(1.089\pm0.021)\ \text{(ns)}\quad(95\le T\le170\ \text{K})\ ,\qquad\text{(2a)}$$

$$\tau_3(T)=(12.520\pm0.150)\times10^{-3}T-(0.827\pm0.033)\ \text{(ns)}\quad(175\le T\le270\ \text{K})\ ,\qquad\text{(2b)}$$

$$\tau_3(T)=(1.530\pm0.820)\times10^{-3}T+(2.085\pm0.237)\ \text{(ns)}\quad(275\le T\le305\ \text{K})\ .\qquad\text{(2c)}$$

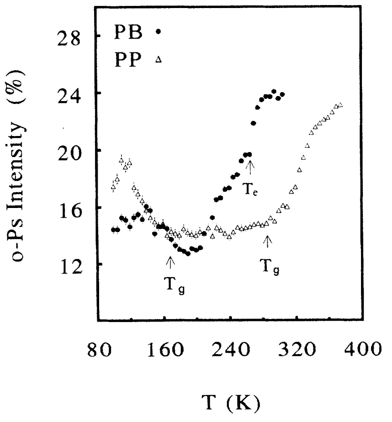

FIG. 2. The variations of *o*-Ps intensity I_3 for PB and PP as a function of temperature.

Therefore, $T_g = (170.8 \pm 4.7)$ K can be evaluated by joining Eqs. (2a) and (2b), while another inflection point at 265.0 ± 29.6 K can be derived from Eqs. (2b) and (2c), which was previously denoted as the excluding temperature T_e of PB.[8] From Fig. 1, the *o*-Ps lifetime τ_3 at $T_g \leq T < T_e$ rapidly increases with temperature, indicating the free-volume holes in the rubbery polymer undergoes a dramatic thermal expansion. Above T_e, the τ_3 is saturated. This fact clearly demonstrates that T_e corresponds to a structure transition temperature, and the variation of τ_3 above T_e does not crucially depend on the expansion of holes as below T_e.[8] However, above T_e, what the structural characteristic is and whether a Ps-bubble state is formed are still two interesting and open questions.

The obtained values of structural transition temperatures T_g and T_e in PB, PP, HDPE, and LDPE (Ref. 9) are listed in Table I, where the glass transition at T_g characterizes the onset of correlating main-chain segmental motions, e.g., the micro-Brownian motion or the short-range diffusion of chains.[8,9] It deserves mentioning that the T_g values of PB and PP measured by PALS are somewhat lower than those by the dynamic mechanical analysis, which results from the duration of measurement being about 1 h for PALS and only a few minutes for DMA.[8,9] As shown in Fig. 1, τ_3 above T_g increases more rapidly with temperature than at $T < T_g$ since the activity of short-range diffusion of segments needs the much larger size of hole. As temperature increases through the glass-transition region (within the vicinity of T_g),[1,3] the polymer is in the rubbery state characterized by much lower modulus and viscosity than in the glassy state. Above the excluding temperature T_e, the *o*-Ps lifetime τ_3 of PB tends to a saturated level and demonstrates another characteristic of microstructure which is significantly different from that at $T < T_e$. However,the saturation effect of the *o*-Ps lifetime in our PP in the temperature range of 285–370 K is not observed, so we deduce that the T_e value in our PP sample is near[10] or somewhat larger than 370 K.

B. The scaling analysis of free-volume-hole concentration

The variation of *o*-Ps intensity I_3 in Fig. 2 provides some interesting information on the change in free-volume concentration. In the initial stages, i.e., 95–120 K for PP and 95–140 K for PB, we can see the *o*-Ps intensity I_3 increases with temperature. This observation is attributed to a time-dependent effect.[21] The time effect results from structural relaxation[21] because the annealing time of PB and PP samples from room temperature to 95 K before PALS measurement is only about 12 h, which is not long enough for PB and PP to reach an equilibrium or more precisely a quasiequilibrium state.[22] Moreover, when the glassy polymer undergoes expansion, the hole concentration at the quasiequilibrium state for the glassy polymer is higher than that at the nonequilibrium state.[21,23] So, the increase of I_3 with temperature in the initial stage more likely reflects the process that the microstructure of free-volume holes approaches the quasiequilibrium state. When $120 < T \leq 165$ K for PP or $140 < T \leq 170$ K for PB, we can see the *o*-Ps intensity I_3 decreases steeply with temperature. This trend can be assigned to the crankshaft motion.[8,24] In the glassy polymer, the rearrangement of molecules is impossible, so the larger holes that the local crankshaft motion needs may arise from the coalescence of small holes, which leads to the decrease of I_3 with temperature. When $170 \leq T < 285$ K for PP, the I_3 generally keeps a constant level. This phenomenon probably arises from the dynamic equilibrium between the coalescence and the creation of holes.[15]

Above T_g, the increase of *o*-Ps intensity I_3 in PB and PP with temperature is generally due to the increase in hole concentration or the creation of free-volume holes.[8,9] However, the variation of I_3 above T_g may contain more detailed information on the short-range diffusion of segments in the rubbery state. As shown in Fig. 2 and the plots $I_3 \sim T$ in Ref. 9, the I_3 in the temperature range from T_g to about $T_g + 30$ K does not increase pronouncedly as when $T > T_g + 30$ K, so I_3 has no linear relation with T. In order to demonstrate the detailed variation of hole concentration versus temperature, we have calculated the values of $\ln[I_3(T)/I_{3g}]$, where I_{3g} is denoted as the *o*-Ps intensity at T_g and is evaluated under the assumption that I_3 varies linearly with T in the temperature range of $T_g \pm 5$ K. We use the T_g determined by PALS as the reference temperature instead of the ideal glass-transition temperature T_0 (Ref. 25) (usually $T_0 \sim T_g - 50$ K for most polymers[2]) based on the following reasons. First, the *o*-Ps intensity I_3 near T_g basically reaches a minimum value, so the glass-transition temperature T_g can be treated as a thermodynamic anomaly at which the most stable configuration is reached under the close packing of holes and flex bonds.[2] Second, the theoretically predicted ideal glass transition at T_0 is unobservable since astronomical waiting times are required to maintain the equilibrium of supercooled polymers below the observed glass-transition temperature.[25]

TABLE I. List of characteristic temperatures and constant β measured by means of positron lifetime spectroscopy.

Samples	T_g (K)	T_c (K)	T_e (K)	β $(T_g < T \leq T_c)$	β $(T_c \leq T < T_e)$
PB	170.8	198.4	265.0	-0.016 ± 0.017	0.346 ± 0.035
PP	285.5	309.3	>370	0.038 ± 0.015	0.297 ± 0.037
HDPE	249.2	285.0	360.2	0.015 ± 0.010	0.336 ± 0.038
LDPE	240.9	265.2	309.6	-0.003 ± 0.015	0.507 ± 0.059

At $T > T_g$, the variations of $\ln(I_3/I_{3g})$ in PB and PP as a function of $\ln[(T-T_g)/T_g]$ are plotted in Fig. 3, where we do not consider the other behaviors because the variation of $\ln[I_3/I_{3g}]$ has no linear relation with T^{-1} and I_3 does not obey the Arrhenius behavior[26] and more fundamentally, above T_g the analogy of $I_3(T)$ for PB , PP, HDPE, and LDPE indicates the existence of scaling behavior, i.e., $I_3 \sim (T-T_g)^{\beta}$. This behavior is suitable for further renormalization-group analysis[17,18] on the creation of free-volume holes.

As shown in Fig. 3, above T_g the variations of $\ln(I_3/I_{3g})$ as a function of $\ln[(T-T_g)/T_g]$ can be properly fitted by two lines in the range $T_g < T \leq T_c$ and $T_c \leq T < T_c$, respectively. Here T_c is another intercepting temperature at which the slope

$$\beta = \frac{d[\ln(I_3/I_{3g})]}{d[\ln(T-T_g)/T_g]} \tag{3}$$

shows an abrupt increase. We have calculated the β values in the temperature ranges from T_g to T_c and from T_c to T_e, where the characteristic temperatures T_c of PB and PP are determined and also listed in Table I.

This interesting feature of *o*-Ps intensity I_3 suggests that we consider the temperature dependence of I_3 in other polymers, especially those with simple structure of chain such as polyethylene. The high- and low-density polyethylene (HDPE, LDPE) are basically linear and branched polymers[9] respectively, which can provide a comparison for the linear structure of PB and PP. The T_c and β values of HDPE and LDPE have been similarly determined by utilizing the positron lifetime results[9] and are listed in Table I, and the plots of $\ln(I_3/I_{3g})$ versus $\ln[(T-T_g)/T_g]$ for HDPE and LDPE are shown Fig. 4. From Table I, we can see that $T_c \approx T_g + 30$ K, and when $T_c \leq T < T_e$, β values (average $\beta = 0.326$) are nearly the same for PB, PP, and HDPE within the error ranges, while $\beta = 0.507$ in LDPE is much larger than those in PB, PP, and HDPE.

The scaling relation $I_3 \sim (T-T_g)^{\beta}$ for four polymers provides some interesting information about the segmental motion and creation of free-volume holes. In the stage of $T_g < T \leq T_c$, the value of β ($\approx 10^{-2}$) is almost zero within the ranges of experimental error, so new holes are not obviously created and the structure change probed by PALS is mainly the enlargement of free-volume holes. From Figs. 2–4, only above T_c can we observe that a great number of new holes are created and the intensive short-range diffusion of polymer segments begins. Here it is mentioned that the identification of $T_c = 198.4$ K for PB by PALS is very close to the reported $T_c = 205$ K from the measurement of Debye-Waller factor by using neutron spin echo (NSE).[27]

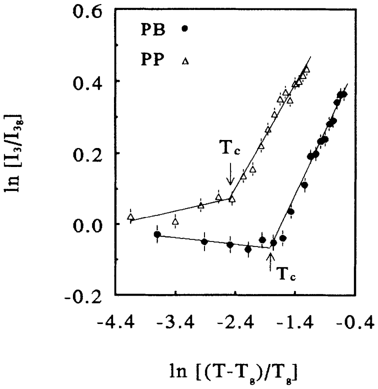

FIG. 3. The plots of $\ln[I_3(T)/I_{3g}]$ vs $\ln[(T-T_g)/T_g]$ for PB and PP.

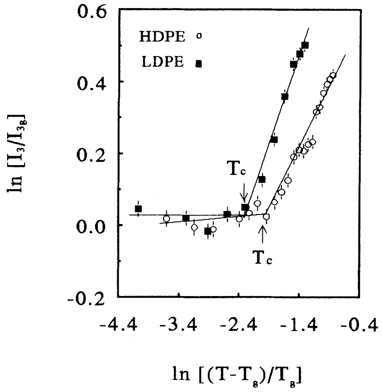

FIG. 4. The plots of $\ln[I_3(T)/I_{3g}]$ vs $\ln[(T-T_g)/T_g]$ for HDPE and LDPE.

The magnitude of β above T_c characterizes the degree of excitation for the free-volume-hole creation. In the region of $T_c \leq T < T_e$, the β values of PB, PP, and HDPE are basically identical, indicating that the common picture of hole creation and the short-range diffusion of segments may be associated with these linear polymers consisting of a backbone basically without the side chains.[28] This dedication is supported by the fact that the β value in the region of $T_c \leq T < T_e$ for linear polymer HDPE is smaller than that for the branched polymer LDPE, so the mechanism of hole creation is probably correlated with the branching structures of chains. In comparison with linear polymers, the branched ones have more chain ends and side chains which may degrade the average rigidity of segments, therefore the short-range diffusion of segment would become easier. From this consideration, when temperature increases, the hole creation in the branched polymer LDPE would be more dramatic than in linear HDPE, and the β value of LDPE should be higher than that of HDPE as shown in Fig. 4.

IV. CONCLUSION

In summary, we have measured the positron lifetimes in polybutadiene (PB) and polypropylene (PP) as functions of temperature, and determined the structural transition temperatures from the variations of *o*-Ps lifetime τ_3. Especially, by comparing the behavior of *o*-Ps intensity I_3 versus temperature in PB, PP, HDPE, and LDPE, we have noticed the similarity of I_3 above T_g which may reveal a scaling behavior, i.e., $I_3 \sim (T-T_g)^{\beta}$. The plots of $\ln[I_3(T)/I_{3g}]$ versus $\ln[(T-T_g)/T_g]$ for PB, PP, HDPE, and LDPE indicate a crossover temperature T_c, where the β changes greatly. When $T_g < T \leq T_c$, β has the order of magnitude of 10^{-2} for these polymers, suggesting that the microstructural change is mainly the enlargement of free-volume holes rather than the creation of new holes. In the range of $T_c \leq T < T_e$, where the intensive hole creation accompanying the short-range diffusion of segments occurs, the average β value is 0.326 for linear polymers PB, PP, and HDPE and $\beta = 0.507$ for the branched polymer LDPE. The scaling analysis of the o-Ps intensity I_3 in PB, PP, HDPE, and LDPE provides a common feature on short-range diffusion of segments in the polymers with rather simple structure of chains, and the magnitude of β values characterizes the activities for free-volume-hole creation, however, quantitative understanding this scaling behavior needs future theoretical analysis.

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