Migration of *ortho*-Positronium in Polymer Films

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Positron-annihilation measurements were performed for polymer films containing quenchers of *ortho*-positronium (*o*-Ps) in order to obtain information about the migration of *o*-Ps. The diffusion coefficients of *o*-Ps, estimated from the quenching-rate constants, were $(1—2)\times10^{-6}$ cm^2 s^{-1} at 298 K, which lead to root-mean-square distances of 1.5—2.4 nm during its lifetime. *o*-Ps is considered to migrate through more than several free-space holes until pick-off annihilation, suggesting that the size estimated from the lifetime of *o*-Ps corresponds to an average size weighted to the larger size because *o*-Ps is more stable in larger holes. The diffusion coefficients of *o*-Ps were compared with those of gas molecules, leading us to conclude that the migration of *o*-Ps follows a different mechanism from that of the diffusion of gas molecules. The quenchers also had the effect of inhibiting *o*-Ps formation in the polymers, and the inhibition coefficients were determined to be 6—17 M^{-1}, which are as high as the corresponding values in benzene solutions.

The position annihilation lifetime (PAL) has attracted attention as a technique to probe the microstructure of polymer solids.[1] The PAL spectra of most polymers have a long-lived component, which is attributed to pick-off annihilation of *ortho*-positronium (*o*-Ps) formed in amorphous regions. The lifetime of the long-lived component (τ_3) is a measure of the size of interstitial spaces among polymer chains, which are referred to as "free space holes" in this paper. The intensity of the component (I_3) is considered to contain information about the concentration of the free space holes. PAL spectra have been applied to investigate the variation in free space holes with temperature,[2—4] pressure,[5] physical aging,[6] vapor sorption,[7] CO$_2$ conditioning,[8] and irradiation with γ-rays.[9] There are also reports on the correlations between the gas diffusion coefficients and τ_3 in rubbery and glassy polymers.[10—13]

The average size of the free space holes probed by *o*-Ps, $v_{\mathrm{h,Ps}}$ $[=(4/3)\pi R^3]$ is often calculated from the following equation:[14,15]

$$\tau_3=(1/2)[1-R/R_0+(1/2\pi)\sin(2\pi R/R_0)]^{-1},$$
$$R_0=R+\Delta R. \quad \Delta R=0.166\,\mathrm{nm}. \qquad (1)$$

where R is the radius of spherical cavity trapping *o*-Ps. The thus-calculated $v_{\mathrm{h,Ps}}$ is often used in quantitative discussions. However, it should be carefully examined whether $v_{\mathrm{h,Ps}}$ represents the real free space holes. For instance, it is quite probable that *o*-Ps probes preferentially larger free space holes, and thus the $v_{\mathrm{h,Ps}}$ should be regarded as the average size weighted to the larger size. Therefore, it is important to clarify the processes of *o*-Ps formation and their trapping in free space holes.

It is important to know how far and how many free space holes an *o*-Ps can migrate and cover, respectively, during its lifetime. Assuming that the migration of *o*-Ps can be described in terms of diffusion, Ito et al. estimated the diffusion coefficient of *o*-Ps (D_{Ps}) to be $(0.6—1.8)\times10^{-5}$ cm^2 s^{-1} for polyethylene with specially low density being synthesized by gas-phase radiation polymerization from quenching with the free radicals formed by γ-ray irradiation.[16] Recently, Hirata et al. have evaluated D_{Ps} to be $(2.6—3.2)\times10^{-6}$ cm^2 s^{-1} for polysulfone, polycarbonate, and polystyrene at 298 K using 2,2′-dinitrobiphenyl as a quencher.[17] Based on the relationship between D_{Ps} and fractional free volume, they suggested that the free volume model is valid for *o*-Ps diffusion, as in the case of gas diffusion.[17] Using Hirata's data, Jean evaluated the migration length of *o*-Ps to be 2.0 nm, and claimed that an *o*-Ps is trapped in, or near to, a single free-space hole in an amorphous polymer during its entire lifetime.[18] This view is strongly opposed in a paper published by Yu et al.,[19] where it is suggested that rapid *o*-Ps migration is ensured by tunneling.

In this study, we report on the results of our experiments similar to those of Hirata et al.[17] using different polymers and quenchers, and show that the smallness of the *o*-Ps diffusion constant in polymers appears to be a common phenomenon. Although small, the *o*-Ps diffusion constants are still large enough so that *o*-Ps can migrate several free-space holes during its lifetime. Contrary to the previous arguments,[18,19] *o*-Ps is neither localized in a single hole nor efficiently mobile. We present a discussion on how *o*-Ps migrates through amorphous polymers.

Experimental

The polymers used were PC [polycarbonate; poly(oxycarbonyloxy-1,4-phenyleneisopropylidene-1,4-phenylene)], Poly(butyl methacrylate) (PBMA), and polyimide from 4,4′-(hexafluoroisopropylidene)diphthalic anhydride (6FDA) and 2,4,6-trimethyl-1,3-phenylenediamine (TrMPD). The *o*-Ps quenchers used were 2,2-Diphenyl-1-picrylhydrazyl (DPPH) and *N*,*N*′-dibutylpyromellitimide (BPMI). Their chemical structures are shown in Fig. 1.

A 5 wt% polymer solution containing a known amount of an *o*-Ps quencher was cast onto glass Petri dishes at room temperature. The solvents were benzene for PBMA and dichloromethane for PC and 6FDA–TrMPD polyimide. The films were peeled off the dishes and dried in vacuo at 50 °C for 40 h.

The PAL measurement was carried out at the Inter-University Laboratory for the Common Use of JAERI facilities.[20)] The positron source used was about 25 μCi of ^{22}NaCl sandwiched between thin nickel foils. The sample films were stacked to make 1 mm thickness, and two equivalent stacks were placed in a glass tube together with the positron source in the sandwich geometry. The sample tube was evacuated and the PAL was measured in the temperature range of 298 to 353 K. The PAL spectrometer was a fast–fast coincidence equipment with a time resolution of 0.30 ns (FWHM). The τ_3 and I_3 were obtained with the computer program PATFIT[21)] from a spectrum with total counts of about 1×10^6.

Results and Discussion

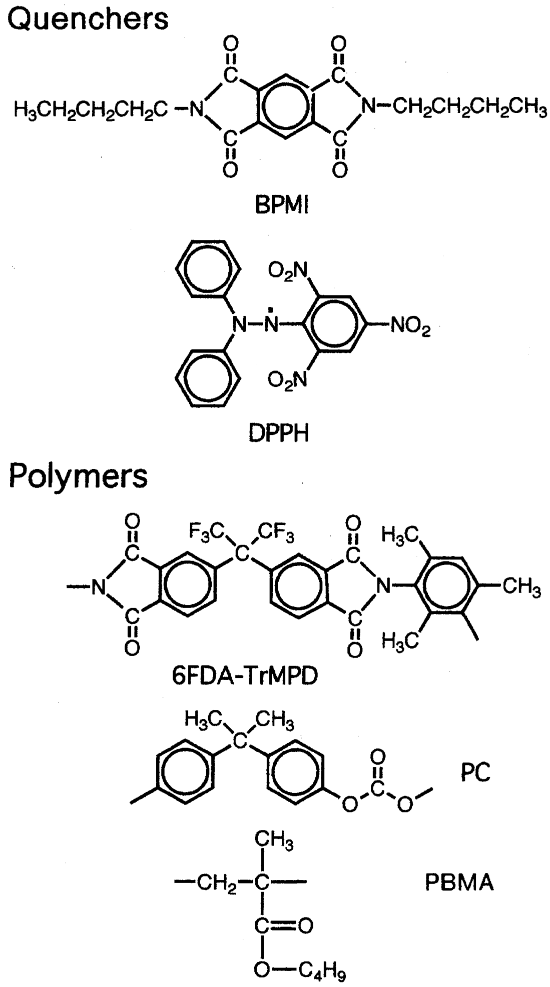

Fig. 1. Chemical structures of *o*-Ps quenchers and polymers.

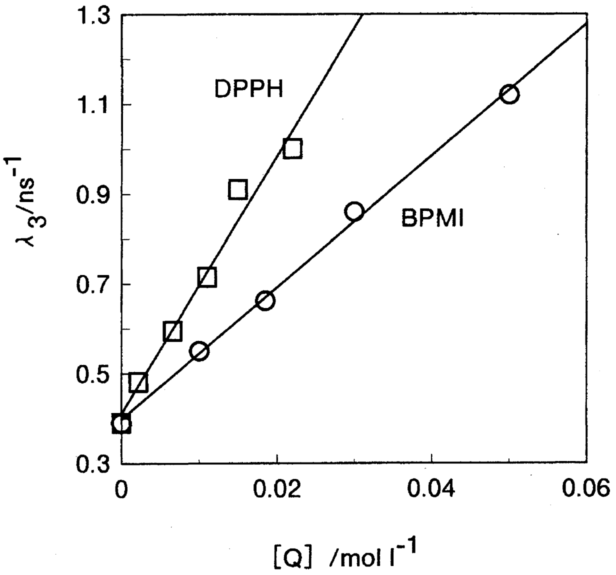

Fig. 2. Variations in annihilation rate of *o*-Ps in benzene solutions with concentrations of the quenchers at 298 K. The data were cited from Refs. 21 and 22.

Figure 2 shows variations in the annihilation rates of *o*-Ps, λ_3 $(=1/\tau_3)$ in benzene solutions with the concentration of the quenchers [Q].[22,23)] The λ_3 observed is the sum of pick-off annihilation and quenching rates,

$$\lambda_3=\lambda_p+k[\mathrm{Q}], \tag{2}$$

where *k* is the quenching rate constant. λ_3 increased linearly with increasing [Q] for both quenchers. From the slopes of the straight lines, the *k* values were calculated to be 1.5×10^{10} and 3.0×10^{10} [$\mathrm{M}^{-1}\,\mathrm{s}^{-1}$] for BPMI and DPPH, respectively. These values are comparable to the value (2.6×10^{10}) for nitrobenzene in benzene, which is known to correspond to a diffusion-controlled reaction.[24)] This indicates that their reactivities are so high that quenching occurs on every encounter with an *o*-Ps.

Figure 3 shows the variations in λ_3 in polymer films with [Q]. For every polymer-quencher system λ_3 increased linearly with [Q]. The *k* values calculated from the slopes are listed in Table 1. The *k* values for the polymers were 1/20—1/50 of those for benzene solutions. Although it is not clear whether the migration of *o*-Ps in polymer films can be described in terms of diffusion, we adopt the following equation, simply because there is no other appropriate treatment:

$$k=4\pi N(D_{\mathrm{Ps}}+D_{\mathrm{Q}})(R_{\mathrm{Ps}}+R_{\mathrm{Q}}), \tag{3}$$

where *N* is Avogadro's number, *D* is the diffusion coefficient, *R* is the critical radius for quenching, and the subscripts Ps and Q designate the quantity for *o*-Ps and quencher, respectively. Since the quencher molecules hardly migrate in polymers, we take $D_{\mathrm{Q}}=0$. The R_{Ps} value was taken to be 0.05 nm, which is half of the Bohr diameter of *o*-Ps. The R_{Q} values were estimated to be 0.58 nm for DPPH and 0.36 nm for BPMI, respectively, by using a Stuart-type molecular model. For BPMI, only the acid anhydride moiety was assumed to be effective for quenching. The calculated D_{Ps} values are listed in Table 1.

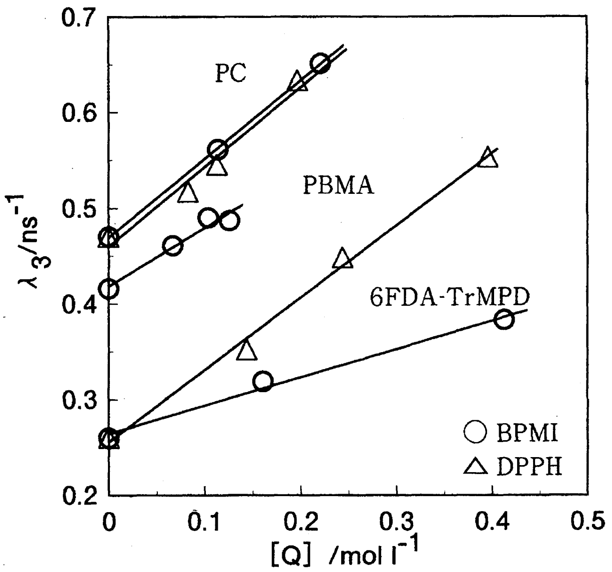

Fig. 3. Variations in annihilation rate of o-Ps in polymer films with concentrations of the quenchers at 298 K.

Table 1. Quenching Rate Constant (k), Diffusion Coefficient of o-Ps (D_{Ps}), and Average Migration Distance (x) of o-Ps in Polymer Films at 298 K

Polymers /Quencher	k M^{-1} ns^{-1}	D_{Ps} 10^{-6} cm^2 s^{-1}	x nm
6FDA–TrMPD			
/BPMI	0.31	1.0	1.5
/DPPH	0.77	1.6	1.9
PC			
/BPMI	0.81	2.6	2.4
/DPPH	0.85	1.8	2.0
PBMA			
/BPMI	0.62	2.0	2.1

$D=k/(4\pi R^*L)$, R^*: 0.36 nm (BPMI), 0.58 nm (DPPH). $x=\sqrt{6D\tau_3}$, τ_3: 3.7 ns (6FDA–TrMPD), 2.1 ns (PC), 2.4 ns (PBMA).

The D_{Ps} values for BPMI differed from those for DPPH by 40—60%. This might be attributed to a possible difference in the dispersion state of the quencher molecules and the uncertainty in the R_Q values. Information concerning the dispersion of DPPH was obtained from electron spin resonance (ESR). The ESR spectra of DPPH in PC and polyimide films had a structure similar to that in benzene solutions, indicating that DPPH molecules were well dispersed in the polymer films. We have no information about the dispersion of BPMI in polymer films. The R_Q value estimated for DPPH is about two times larger than that for BPMI. This is consistent with the result that the observed k values in benzene solutions are two times larger for DPPH than for BPMI. This difference in the k values is reasonably considered to be due to the difference in the R_Q values on the basis of the fact that the D_Q values for the quenchers, which are estimated to be 1×10^{-5} cm^2 s^{-1} in benzene solutions, are much less than D_{Ps}, ca. 2×10^{-4} cm^2 s^{-1}.[25,26]

As can be seen from Table 1, the D_{Ps} values for polymer films ranged from 1×10^{-6} to 3×10^{-6} cm^2 s^{-1} and were hardly dependent on the kinds of polymer. These values are smaller than those in solutions by two orders of magnitude.[25,26] The D_{Ps} values estimated here are close to Hirata's values,[17] although being much smaller than the D_{Ps} values of 0.6—1.8×10^{-5} cm^2 s^{-1} for polyethylene estimated from the quenching with free radicals formed by γ-ray irradiation.[16]

Assuming a three-dimensional random hopping walk model for the diffusion, we can estimate the average migration distance (x) of o-Ps in polymer films during the lifetime (τ_3) to be

$$x=\sqrt{6D\tau_3}\,. \tag{4}$$

The x values are listed in Table 1. They range from 1.5 to 2.4 nm. The average migration distance (x) means that an o-Ps goes out from a sphere with radius x during its lifetime with a probability of 32%.[27] We estimated the number of free space holes in the sphere based on a simple cubic model as follows.

The volume fraction of free-space holes (V_F) was estimated by the method of van Krevelen and Bondi,[28,29] and listed in Table 2.

$$V_F=(V_T-V_0)/V_T, \tag{5}$$

where V_T is the molar volume at temperature T K, calculated from the density data; V_0 is the volume occupied by the molecules at 0 K per mole of repeat unit of polymer, and can be estimated by a group-contribution method.[29] V_F refers to the ratio of the so-called "expansion volume"[30] to the observed volume. The average number (N_h) of free-space holes within a sphere with a radius of x was calculated using $(V_F/v_{h,Ps})(4/3)\pi x^3$, where the volume of a free space hole was assumed to be $v_{h,Ps}$ for convenience. The calculated N_h values, which are also listed in Table 2, ranged from 14 to 74. In view of the crudeness of the treatment, although no absolute meaning should be attached to these numbers, we may at least infer that an o-Ps migrates through many free space holes.

Hirata et al. estimated the migration length of o-Ps to be ca. 0.8 nm.[17] However, this value is misleadingly too small, because they used a one-dimensional random-hopping model. Using Hirata's data, Jean estimated the migration length to be 2.0 nm using the same equation as Eq. 4.[18] This value is similar to the present values (1.5—2.4). Jean compared this value with the distance from one hole to the nearest-neighbor hole (d) of 1.75 nm, and claimed that an

Table 2. Estimated Values of Average Distance between Free Space Holes in Polymer Films

Polymers	V_F	$v_{h,Ps}$ nm^3	N_h	d nm
6FDA–TrMPD	0.182	0.273	14	1.1
PC	0.165	0.100	74	0.9
PBMA	0.163	0.133	48	0.9

$N_h=(V_F/v_{h,Ps})(4/3\pi x^3)$.

o-Ps is trapped in, or near to, a single free-space hole in an amorphous polymer during its entire lifetime.[18] The *d* value of 1.75 nm was calculated for a cubic lattice consisting of free space holes with a radius of 0.4 nm and a fractional free space of 5%, according to Yu et al.[19] However, this is an unusual case, dealing with a very large size and a very low volume fraction of free space holes. The *d* values calculated from the V_F and $v_{h,Ps}$ values of each polymer, assuming a cubic lattice, which are listed in Table 2, ranged from 0.9 to 1.1 nm. The migration length of *o*-Ps (ca. 2.0 nm) is larger than the *d* values. Even if we assume a much smaller V_F value of 5%, the *d* and N_h values are 1.3 nm and 22, respectively, for polycarbonate ($v_{h,Ps}=0.100$ nm^3, $R=0.29$ nm). Therefore, we may conclude that an *o*-Ps migrates through more than several free space holes, not a few holes as was claimed by Jean.

Figure 4 shows the correlation between D_{gas} in PC and 6FDA–TrMPD polyimide and collision diameters (d_c) of the gases.[10,31] The plots of log (D_{gas}) versus d_c lie on a straight line for each polymer. The D_{Ps} values estimated above are situated far below this correlation at the Bohr diameter of *o*-Ps (0.106 nm). Furthermore, the D_{gas} values are more than one order of magnitude different between PC and 6FDA–TrMPD, whereas the D_{Ps} values are similar between them.

The results mentioned above suggest that the diffusion of *o*-Ps is different from that of a gas molecule, resulting from repeated collisions between the gas molecules and the polymer chains. A gas molecule can travel from one free space hole to a neighboring one which is larger than the size of the gas molecule. It would be easy for *o*-Ps to travel from one free space hole to a neighboring one if only its diameter were to be considered. However, since the mass of *o*-Ps is extremely small, the zero-point energy (E_0 [eV]) of *o*-Ps in a free space hole is much larger than the thermal energy and strongly dependent on the size of the free space hole. The E_0 value in a sphere is crudely evaluated by the following equation for a spherical potential well of infinite height:

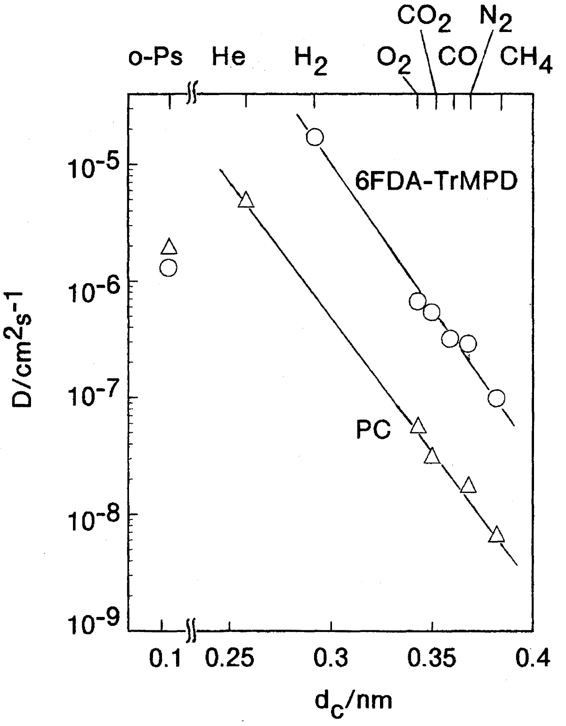

Fig. 4. Plots of diffusion coefficients of gas molecules versus collision diameters of the gases for polycarbonate and 6FDA–TrMPD polyimide at 308 K and 10 atm.

$$E_0 = 0.188/{R_0}^2 . \tag{6}$$

It is not possible for an *o*-Ps to obtain sufficient excess energy to travel from one free space hole to smaller ones. As a result of this energy restriction, an *o*-Ps migrates through only larger ones and is trapped at the largest free space hole among several neighboring holes until it decays, resulting in a much lower diffusion coefficient of *o*-Ps compared with that expected from Fig. 4.

We suggest that *o*-Ps probes preferentially the larger free space holes, and that $v_{h,Ps}$ is regarded as the average size weighted to the larger size. This view is experimentally supported by the effects of CO_2-conditioning of polymers on positron annihilation and the gas permeation properties;[8] it was shown that the size distribution of free space holes evaluated from the annihilation rate distribution of *o*-Ps became broader and shifted to a larger size. However, this change was too large to be expected from other experimental data, such as V_F and the sorption and diffusion coefficients of gases. There is no doubt that the volume information from positron annihilation tends to overestimate the real size of free space holes.

Figure 5 shows the temperature dependence of D_{Ps} for PC. The activation energy of diffusion (E_D) for *o*-Ps was 6 kJ mol^{-1}. As shown in Fig. 6, E_D for PC was linearly correlated with the square of the molecular diameter (d_c^2) of gases.[32] The E_D for *o*-Ps is much smaller than those for gas molecules, and seems to correspond to a diameter of 0.14 nm, which is rather close to the Bohr diameter of *o*-Ps. However, this small E_D may not be due to its small diameter, because the migration of *o*-Ps is different from the simple diffusion of small particles, as described above. In a case where an *o*-Ps

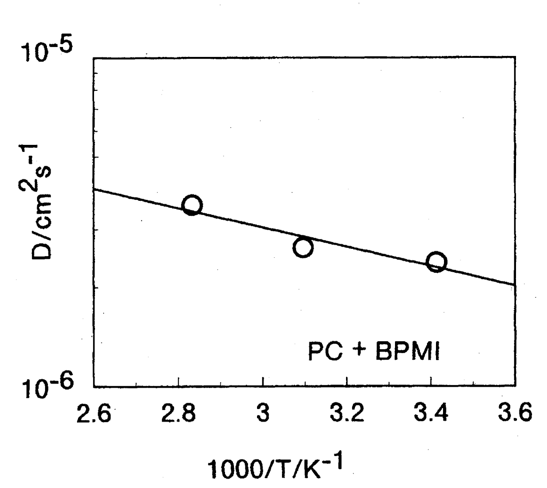

Fig. 5. Temperature dependence of diffusion coefficient of *o*-Ps in polycarbonate.

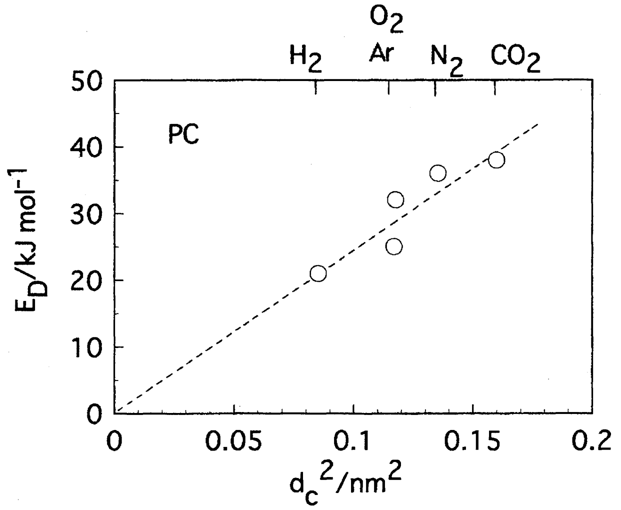

Fig. 6. Plots of activation energy of diffusion for gas molecules versus square of collision diameters in polycarbonate.

is trapped in a large hole, the apparent diffusion coefficient of *o*-Ps may be controlled by the size distribution of free space holes in the sense that it is difficult for *o*-Ps to find neighboring holes having a similar size, which is necessary for quantum mechanical energy matching for tunneling. The small E_D may be the consequence of a small dependence of the size distribution on the temperature.

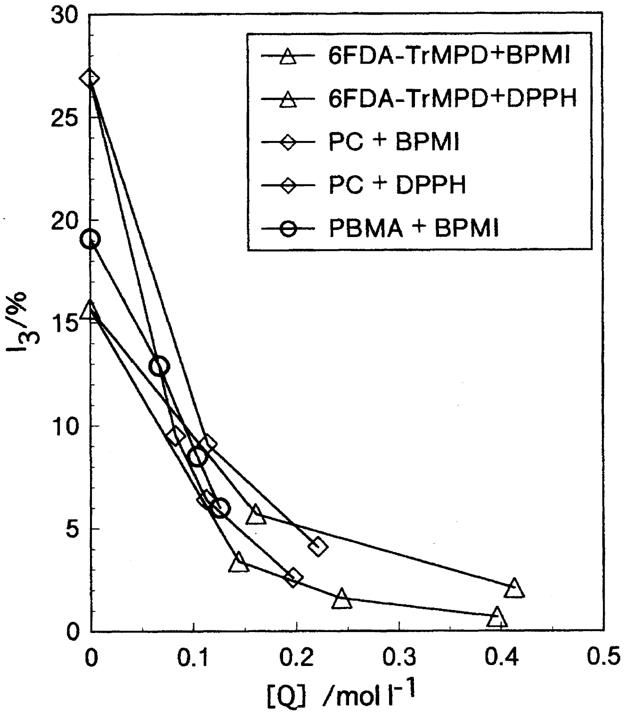

Fig. 7. Variations in intensities of *o*-Ps in polymer films with concentrations of the quenchers at 298 K.

Figure 7 shows the variations in I_3 with [Q]. When a quencher strongly reacts with *o*-Ps, the observed I_3 (I_3(obsd)) is estimated to be larger than the true probability of *o*-Ps formation (I_3(true)), as expressed by the following equation:[25)]

$$I_3(\text{obsd}) = (\lambda_c - \lambda_p)/(\lambda_c - \lambda_p - k[X])I_3(\text{true})\,, \qquad (7)$$

where λ_p is the pick-off annihilation rate and λ_c is the annihilation rate of the positron in a *o*-Ps/quencher complex. Although the λ_c values are not known precisely for the quenchers used here, they are generally estimated to be about 2.5 ns^{-1}. Using this value, the difference between I_3(obsd) and I_3(true) are estimated to be less than 16% in every case. As shown in Fig. 7, the observed I_3 decreased with increasing [Q] for both quenchers, indicating that the quenchers also inhibit the formation of *o*-Ps. This inhibition is interpreted in terms of the spur reaction model of Ps formation.[33)] The spur is a group of reactive intermediates formed during the slowing-down process of an injected positron. Ps is considered to be formed as a result of a spur reaction between a positron and one of the electrons in the spur. The Ps formation competes with the recombination of the electrons and parent ions. A reaction of the electrons in the spur with scavengers also decreases the Ps formation probability. The quenchers used here have a sufficient electron affinity to act as scavengers and to inhibit Ps formation. The inhibition curves in solutions have often been quantified by using the following equation:[34)]

$$I_3/I_3^0 = 1/(1+(\alpha C)^{\beta})\,, \qquad (8)$$

where α is the inhibitor constant and β is an adjustable parameter. The α and β values were obtained by fitting the changes in I_3 to Eq. 8. Although the values listed in Table 3 were obtained from the I_3(true) values of Eq. 7, they do not differ significantly, even if a correction by Eq. 7 is not applied. As shown in Fig. 8, there is a linear relationship between α and k, suggesting that the quenching is due to the electron affinity of the quenchers. The α values are equal to or larger than the corresponding values in benzene solutions (6.1 for BPMI,[22)] and the value for DPPH was not reported in reference,[23)]) suggesting that electrons in polymer films can migrate as fast as in solutions. However, the β values in polymer films are fairly larger than unity, whereas the β values in solutions have been reported to be less than unity.[34)] This may reflect the difference in the mechanism of electron scavenging, although the physical meaning of β has not yet been clarified.

Table 3. Positronium Inhibition Parameters According to Eq. 8

System	α/M^{-1}	β
6FDA–TrMPD		
/BPMI	6	1.7
/DPPH	14	1.8
PC		
/BPMI	14	1.6
/DPPH	17	1.9
PBMA		
/BPMI	11	2.3

Conclusion

The diffusion coefficients of *o*-Ps ($D_{\text{Ps}}=(1-2)\times10^{-6}$

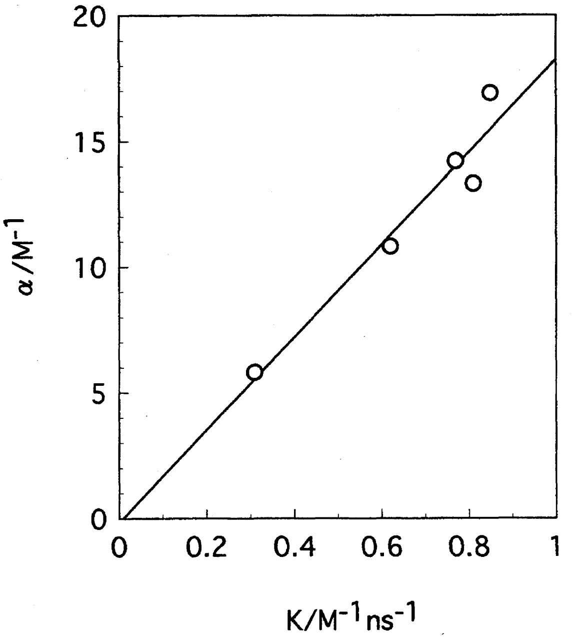

Fig. 8. Correlation between α and k for polymer films.

cm^2 s^{-1}), if interpreted by a three-dimensional random hopping model, indicate that *o*-Ps migrates through more than several free space holes. The D_{Ps} values are much smaller than those (more than 10^{-4} cm^2 s^{-1}) expected from a simple size extrapolation of the relationship between the diffusion coefficients of the gas molecules and their diameters. The activation energy of the diffusion for *o*-Ps (about 6 kJ mol^{-1}) is much smaller than those for gas molecules. These facts suggest that the migration of *o*-Ps is different from the diffusion of gas molecules. We propose that an *o*-Ps in a free space hole can not travel into a smaller one, because of its very large zero point energy. Once an *o*-Ps enters one of the largest holes, it tends to be trapped there. Its migration is limited by the fact that there are few holes around having the same size into which *o*-Ps can move by quantum mechanical tunneling. The volume information brought forth by *o*-Ps should be weighted to larger size. There is some experimental evidence for this view, as described in the text.

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