The Effects of Vapor Sorption in Polymers Observed by Positron Annihilation

Yasuo ITO,* Victor SANCHEZ,[†,#] Rafael LOPEZ,[†] Luz A. FUCUGAUCHI,[†] Kazuhiro TANAKA,[††] and Kenichi OKAMOTO[††]
Research Center for Nuclear Science and Technology, The University of Tokyo, Tokai, Ibaraki 319-11
[†] Instituto Nacional de Investigaciones Nucleares, A. P. 18-1027, Mexico 11 801, D.F.
[††] Faculty of Engineering, Yamaguchi University, Ube, Yamaguchi 755

(Received October 5, 1992)

Positron lifetime measurements were performed for two different kinds of polymers (low density polyethylene and a polyimide 6FDA-TMPD) during sorption of various vapors (hexane, cyclohexane, benzene, acrylic acid, methyl acrylate, water, and oxygen). The vapor sorption affected the long-lived component (ortho-positronium component) in a systematic way regardless of the kind of the vapor molecules, i.e. for the polyethylene both the lifetime and the intensity of the long-lived component were enhanced, while for the polyimide they were decreased significantly. These different effects are interpreted in terms of different states of sorbed molecules in rubbery (the polyethylene) and in glassy (the polyimide) polymers.

It is well-recognized that positron annihilation lifetime (PAL) spectra in polymers have a long-lived component that can be ascribed to ortho-positronium (*o*-Ps).[1)] The lifetime, τ_3, is considered to be a measure of the size of the microvacancies in which *o*-Ps is trapped and is annihilated through pick-off annihilation with the rate which depends on the size of the vacancy. But it is not clear whether the size estimated from τ_3 exactly reflects that of the preexisting microvacancies, or whether *o*-Ps is equally sampling all of the different sizes of the microvacancies. Another important problem concerns the correlation between free volume fraction and the *o*-Ps intensity, I_3, which has often been noted to exist experimentally, i.e. I_3 is usually larger in polymers having larger free volume fraction. But the mechanism underlying such correlation has not yet been understood properly.

The present study was motivated by our program to use the PAL technique for the study of microvacancies in polymers modified by graft polymerization. Before dealing with graftpolymers, however, we tried to see how PAL parameters change when vapor molecules are introduced into microvacancies, and have found interesting results which are important for understanding interactions between Ps and polymers.

Experimental

Two different kinds of polymers, low density polyethylene (LDPE) and a polyimide (6FDA-TMPD PI), were used. An important difference is that LDPE (T_g=-27°C) is in a rubbery state and the polyimide (T_g=377°C) is in a glassy state at room temperature. LDPE pellets were supplied from Sumitomo Chemicals, Co. and were from the same batch that was used for our previous experiments.[2)] The pellets were melted at 110 °C, and discs of 10 mmϕ ×1 mm in size were cut. Two identical discs were put together with a positron source (15 μCi of ^{22}Na) in the sandwich geometry and were placed in one arm of the glass tube as shown in Fig. 1, evacuated at 110°C for 30 min, and then slowly cooled down to room temperature. After cooling, the sample was kept at room temperature for 2—3 d to allow the polymer chains to become stable by aging. The conditions for this aging may not be repeatable, since the values of τ_3 and I_3 varied for different samples. (Thus we have to evaluate the data for LDPE only qualitatively.) Liquids of hexane, cyclohexane, benzene, acrylic acid, methyl acrylate, or water was put in another arm of the glass tube and was evacuated. The PAL was measured several times before starting the vapor sorption, and then the stop cock connecting the two arms was opened to let the vapor into the sample. The PAL measurements were performed continuously and the data were recorded every 1 or 2 h. The data analysis was performed

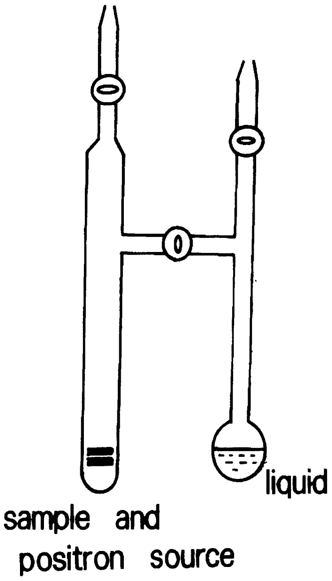

Fig. 1. The sample tube for the vapor sorption experiment. The sample polymer together with the positron source was placed in the left arm, and the sample liquid was put into the right arm. After evacuating the whole system, the stop cock connecting the two arms was opened to start contact of the vapor with the polymer.

[#] Visiting research fellow to RCNST, The Univ. of Tokyo, 1991.

using the program PATFIT[3] for each set of data, but for the case where the changes were small several succeeding sets of data were summed together and were analyzed.

Polyimides have numerous chemical structures depending on the combination of the acid anhydrides and the diamine moieties. For the present experiment 6FDA-TMPD PI (the chemical structure is shown in Fig. 2) has been selected because it is one of the polyimides that show substantial *o*-Ps intensity.[4] The polyimide sample was prepared as thin films of about 20 μm thickness,[5] and was dried in a vacuum at 200°C for 20 h prior to the experiments. Several tens of sheets thus prepared were stacked together with a positron source in the middle of the stack. All of the other procedures were the same as for LDPE. Contrary to LDPE, the values of τ_3 and I_3 did not vary significantly after the heat treatment at 110°C. This is probably because the heat treatment was carried out far below T_g.

Results

The *o*-Ps parameters, τ_3 and I_3, are shown in Figs. 3 and 4 for LDPE and in Figs. 5, 6, and 7 for 6FDA-TMPD PI as a function of the contact time with the vapors. Apparently there is a systematic difference between the results for LDPE and 6FDA-TMPD PI. For LDPE both τ_3 and I_3 increased after starting contact with the vapors. For 6FDA-TMPD PI both τ_3 and I_3 decreased significantly. It is important to note that these qualitative changes did not depend on the type of vapor molecules. The influence of the vapors on 6FDA-TMPD PI was so large that I_3 decreased down to about 5% in most cases. The effect of cyclohexane sorption in 6FDA-TMPD PI (Fig. 5, middle) was exceptionally slow compared to the other vapors. It is also noted for 6FDA-TMPD PI that I_3 and λ_3 respond differently in time, i.e. the increase in λ_3 was delayed in time compared to the decrease in I_3. This is typical for cyclohexane (Fig. 5) and H_2O (Fig. 7), but is also seen for hexane and benzene (Fig. 5).

In addition to the basic changes mentioned above, there were additional delayed ones. One is the gradual decrease in λ_3 and the gradual increase in I_3 for the polyimide that occurred after the basic rapid changes. This is particularly evident for methyl acrylate, hexane, and benzene. Another additional change can be seen in the I_3 value for acrylic acid and methyl acrylate vapors in LDPE, where I_3 increased at first but decreased fairly significantly at later times.

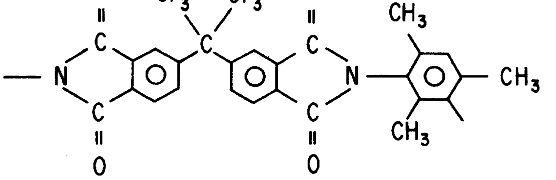

Fig. 2. The chemical structure of the polyimide 6FDA-TMPD used in the present experiment. symbol: 6FDA-TMPD PI 6FDA: 4,4′-[bis(trifluoromethyl)methylene]bis[phthalic anhydride] TMPD: 2,4,6-trimethyl-1,3-phenylenediamine.

Discussion

Polymers contain microvacancies in which *o*-Ps can be trapped. If these vacancies could be considered as "rigid holes", the penetrating vapor molecules would simply fill them, and the number and the size of the holes would be reduced. The consequence on PAL would be a decrease in τ_3 and I_3. The initial changes in τ_3 and I_3 for the polyimide appear to agree with this picture, but those for LDPE are contradictory. Undoubtedly the penetrating molecules are not looking at the microvacancies simply as "rigid holes". There should be strong interactions between the penetrating molecules and the polymer chains, which can affect the aggregation states of the latter.

An important difference between the polyimide and LDPE is that they are in glassy and rubbery states, respectively, at room temperature. In the rubbery state the polymer chains are allowed extensive segmental motions. In the glassy state most of the segmental motions are frozen.

We will first consider the case of the rubbery state. The relaxation time of the segmental motions in the amorphous regions measured by dielectcric constant or NMR ranges from 10^{-6} to 10^{-2} s. This is too long compared to the lifetime, ca. 2 ns, of *o*-Ps in polymers, and such slow relaxations may look almost as frozen on the time scale of *o*-Ps lifetime. *Ortho*-Ps may simply sit in the vacancies that exist at thermal equilibrium. Vapor sorption in rubbery polymers takes place mainly by the Henry-type dissolution.[6] In this sorption mechanism the vapor molecules dissolved in the polymer can expand the inter-chain separations and also get into synchronous motions with the chains. As a result T_g is lowered and the polymer becomes more susceptible to plastic deformation, the so-called "plasticization" effect. It is commonly recognized that the free volume fraction is expanded by the plasticization. The equilibrium distribution of the free volume elements is thus shifted toward a larger number and size, and it becomes possible for *o*-Ps to find larger microvacancies and hence to live longer.

One may imagine that *o*-Ps is able to expand the size of the vacancy just as it makes "Ps bubbles" in liquids.[7] In liquids the Ps bubble is formed because Ps pushes aside the surrounding molecules to make a free space around itself. The bubble size is determined by the conditions that gives the minimum of the bubble energy. Because of the very high viscosity of polymers, Ps may not form "bubble" with the same ease as it does in liquids, but it will nevertheless be able to push aside nearby segments. The energy required to expand the space may be supplied from the binding energy of Ps (6.8 eV in vacuum) which is released during the Ps formation process. It is interesting to consider in this rela-

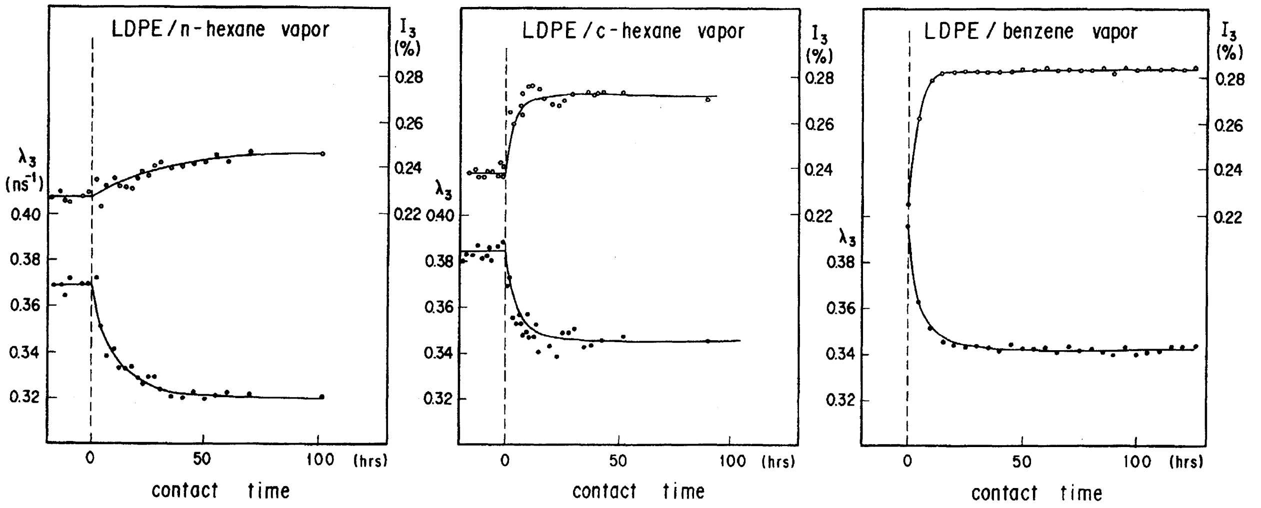

Fig. 3. The changes of the o-Ps parameters, λ_3 and I_3, in LDPE as a function of the contact time with the vapor of nonpolar molecules: hexane, cyclohexane and benzene. In each figure, the upper data is for I_3 and the lower is for λ_3.

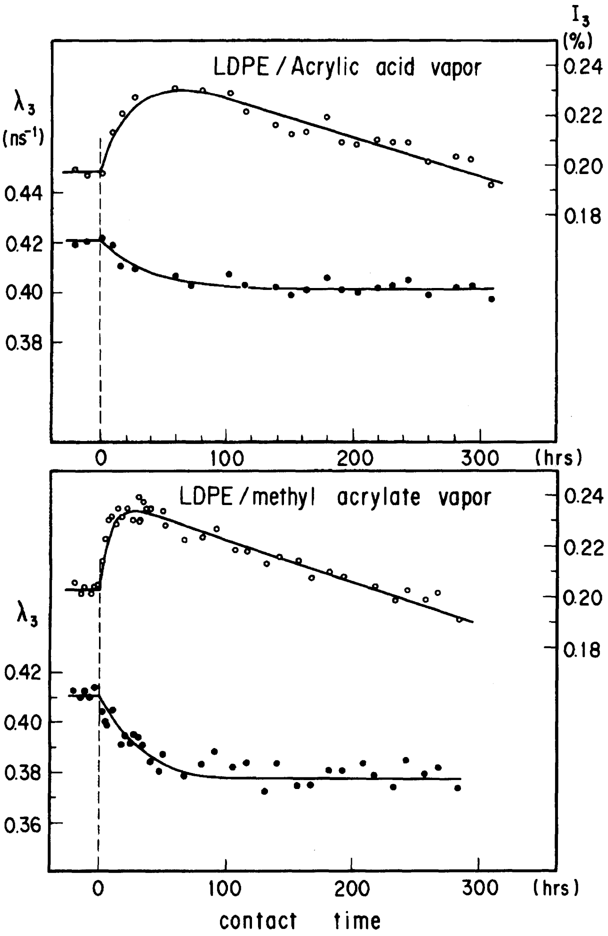

Fig. 4. The changes of the o-Ps parameters, λ_3 and I_3, in LDPE as a function of the contact time with the vapor of polar molecules: acrylic acid and methyl acrylate. The upper data is for I_3 and the lower is for λ_3.

tion that the phase change (α-relaxation) of the LDPE observed at 312 K[2] corresponds to the onset of the bubble formation. Since LDPE containing dissolved vapor molecules will become soft by the plasticization effect, the bubble formation will be promoted and enhancement of o-Ps lifetime is quite probable.

We have presented two views concerning the o-Ps states in LDPE, i.e. o-Ps entering microvacancy at thermal equilibrium and o-Ps expanding the microvacancy. They are not exclusive to each other, and may take place depending on the rigidity of the polymer chains.

The increase in I_3 in LDPE due to vapor sorption needs some consideration. It should be correlated with the plasticization effect by which the free volume fraction is enhanced, but the detailed mechanism connecting the free volume fraction and I_3 should differ depending on the origin of the long-lived o-Ps state. It is often considered[8] that o-Ps must diffuse some distance before it encounters and be trapped in a microvacancy. In this case I_3 corresponds to o-Ps trapped in the microvacancies, and is the measure of the density of free volume elements. There can be another view that considers density fluctuation in the polymer. It is quite probable that some structure among the density fluctuation can act as a trapping site of the precursors of Ps, e^- and/or e^+, and inhibits Ps formation. The plasticization due to vapor sorption promotes segmental motions, and this might release some of the trapping sites, resulting in an enhanced Ps formation. In this case the free volume fraction and Ps intensity is indirectly correlated through the number of trapping sites. At present we do not have enough knowledge about such trapping sites in polymers, but the viewpoint based on the trapping sites may not be disregarded.

In glassy polymers vapor sorption can take place both by the Henry-type and by the Langmuir-type sorp-

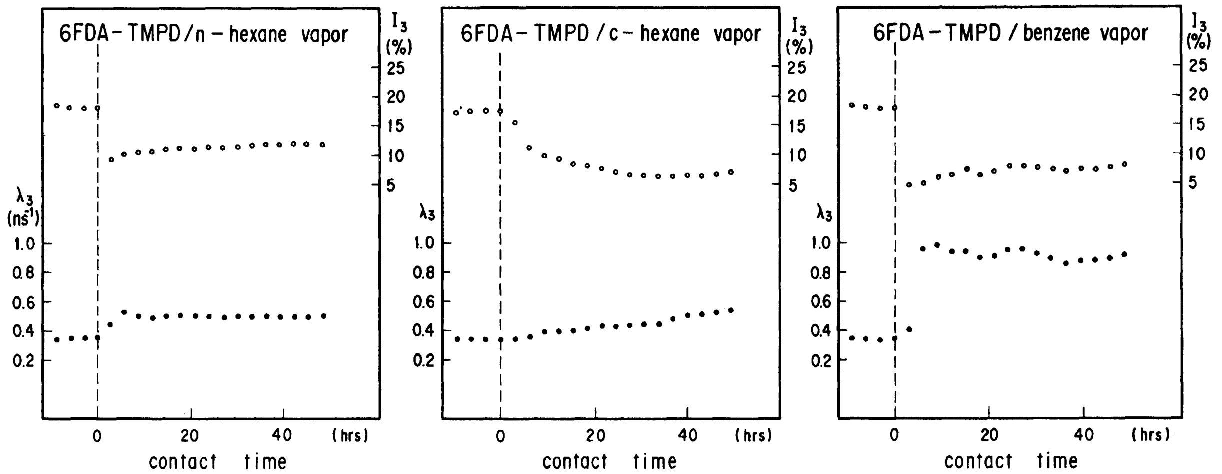

Fig. 5. The changes of the o-Ps parameters, λ_3 and I_3, in 6FDA-TMPD PI as a function of the contact time with the vapor of nonpolar molecules; hexane, cyclohexane, and benzene. The upper data is for I_3 and the lower is for λ_3.

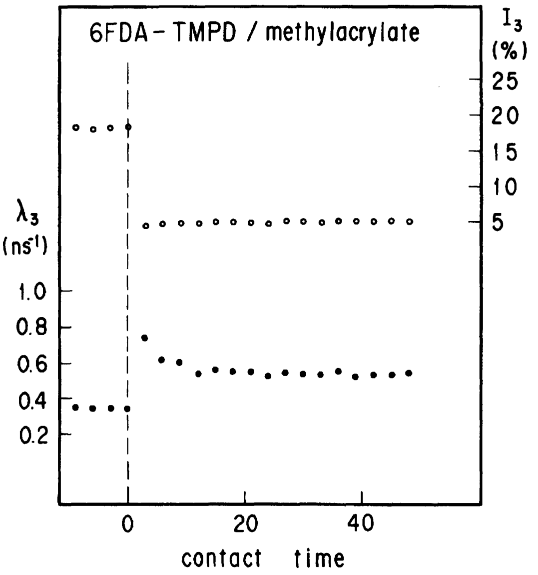

Fig. 6. The changes of the o-Ps parameters, λ_3 and I_3, in 6FDA-TMPD PI as a function of the contact time with the vapor of methyl acrylate. The upper data is for I_3 and the lower is for λ_3.

tions. As in LDPE the former type of sorption induces plasticization which leads to expansion of the volume fraction. However in glassy polymers the plasticization proceeds slowly because the relaxation times are long. Thus only the effects of filling the microvacancies by the vapor molecules (the Langmuir-type sorption) are observed at the beginning of the sorption, which are the rapid increase in λ_3 and the rapid decrease in I_3. The later gradual decrease in λ_3 and the gradual increase in I_3 for 6FDA-TMPD PI should be correlated with the plasticization as in the case of LDPE.

Thus the primary differences in the effects of vapor sorption on PAL in LDPE and 6FDA-TMPD PI are understood as due to their different aggregation states.

In the followings we discuss secondary effects observed in the experimental results.

The delayed response of λ_3 compared to that of I_3 in 6FDA-TMPD PI is typically observed for cyclohexane (Fig. 5) an H_2O (Fig. 7), and to a lesser extent but evidently for hexane and benzene (Fig. 5). When the amount of vapor sorption is small, some of the vacancies would remain unfilled. Thus o-Ps lifetimes can remain unaffected until all of the vacancies become smaller with filled molecules.

The slow effect of cyclohexane on the polyimide (Fig. 5) may simply be due to its slow penetration into the polymer, because the diffusion cross section of cyclohexane molecule (0.313 nm^2) is the largest of the molecules used in the experiments (cf. 0.248 nm^2 for benzene, 0.239 nm^2 for hexane).

At the beginning of sorption of acrylic acid and methyl acrylate I_3 increased, but at later times it decreased after passing a maximum (Fig. 4). The interpretation is not straightforward. It is known that Ps yield is small in polar liquids[9)] due to solvation of Ps precursors in clusters of polar molecules. The decrease in I_3 in Fig. 4 may be understood in a similar way since the dissolved molecules at high content, i.e. at the conditions of swelling, would have been gathering together to form clusters. It must be noted, however, that these molecules are monomers. Thus it is probable that their polymerization inside free volume holes cause reduction in the size and number of the holes. Detailed investigation into the role of the polar molecules is under way and will be reported elsewhere.

Water vapor is surprisingly efficient for 6FDA-TMPD PI, where I_3 rapidly goes down as low as to 3%, and there is no gradual delayed change (Fig. 7). Similar strong water effect on I_3 has also been observed by others for polyimide[10)] and for polyamide.[11)] The amount of water (4.6 wt%[12)]) sorbed in 6FDA-TMPD PI is far

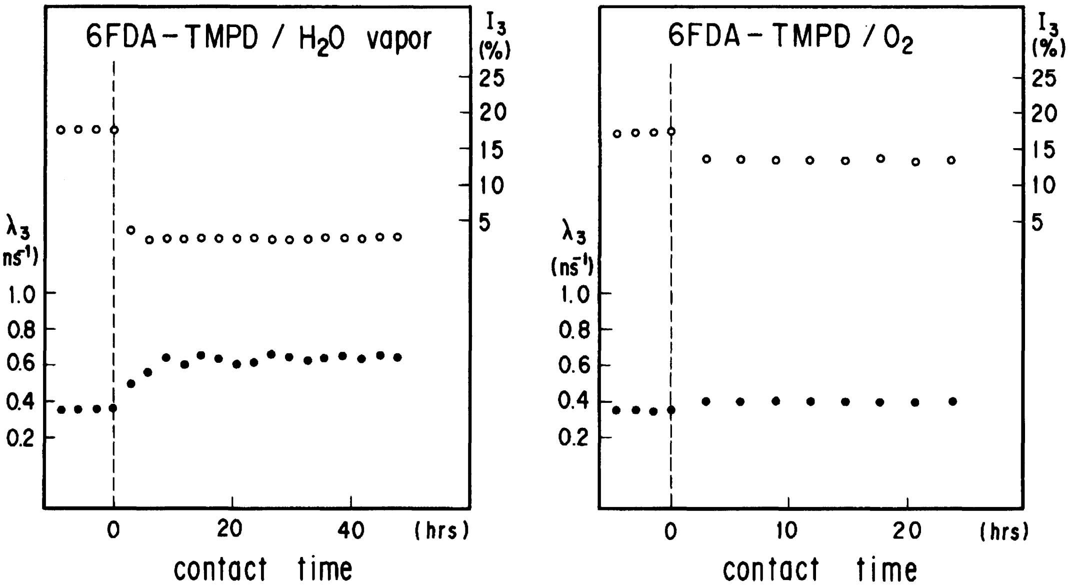

Fig. 7. The changes of the *o*-Ps parameters, λ_3 and I_3, in 6FDA-TMPD PI as a function of the contact time with water vapor and oxygen. The upper data is for I_3 and the lower is for λ_3. Although not shown, water and oxygen had no effect on LDPE.

smaller than the amount of benzene sorption (43 wt%). In order to explain this particularly efficient effect of water, it is important to remind the special aspect in water sorption by 6FDA-TMPD PI. 6FDA-TMPD PI has both hydrophilic (imide groups) and hydrophobic ($-CF_3$ groups) functional groups. As a consequence water molecules absorbed to 6FDA-TMPD PI may stick to the imide groups and, through clustering, condense in the voids. This explains why water is very efficient to influence Ps yield and lifetime in spite of the small amount of sorption. The water effect was absent for LDPE, and this is due to far smaller water solubility ($<$ 0.007 wt%) caused by the strong hydrophobic nature of polyethylene.

The amount of water, 4.6 wt%, sorbed to 6FDA-TMPD PI corresponds to 0.063 cm^3 of liquid water in 1 cm^3 of the polymer (density=1.35). For a crude estimation we assume that the vacancies are the same for Ps and for water clusters. We will also take the drop of I_3 from 18 to 3% as being due to filling roughly 83% of the microvacancies with water. The average size of the microvacancies can be estimated from τ_3 using the empirical equation given by Tao[13] and Eldrup,[14] and is v_p=0.18 nm^3 for 6FDA-TMPD PI. Thus the number of the microvacancies occupied by water is calculated to be 3.5×10^{20} cm^{-3}. This value agrees in the order of magnitude with the values, 1.5—3×10^{20} cm^{-3}, for various rubbery polymers estimated by dividing the fractional WLF free volume by v_p.[4]

The strong water effect may further be explained as the consequence of associative effects of the imide groups and the water clusters. The imide groups are electron-withdrawing groups. In our systematic PAL measurements of various polyimides, we have found that Ps formation is mainly controlled by the electron affinity of the imide groups.[4] Thus the polyimides having large electron affinities do not show Ps formation while those having small affinities have an *o*-Ps component, with 6FDA-TMPD PI belonging to the latter group. Our explanation for the *o*-Ps formation in 6FDA-TMPD PI is similar to the explanation for the "anti-inhibition" effect,[15] i.e. because of the small electron affinity e^- is loosely captured at the imide groups, and e^+ can pick it off to form Ps. When there are water clusters sticking to the imide groups, however, the captured e^- should then be solvated into the water cluster. Solvation is in effect a deep trap of e^- and Ps formation is inhibited. It is not clear whether the strong water effect is due simply to the effect of filling the pores or whether the solvation effect is important, but water has many reasons for becoming an efficient inhibitor of Ps formation in 6FDA-TMPD PI.

Oxygen in 6FDA-TMPD PI has effects similar to other vapors but to a lesser extent (Fig. 7). The amount of oxygen absorption, 0.14 wt% for 1 atm oxygen, is far smaller compared to other vapors. This corresponds to about 3.5×10^{19} O_2 molecules/cm^3 -polymer, or in other words only about 10% of the microvacancies would contain O_2. Therefore it is difficult to attribute the oxygen effect simply to the filling effect, and we have to consider that chemical effects are operating here. Oxygen is known to be particularly efficient in inhibiting Ps formation and in quenching *o*-Ps lifetimes in the studies of porous materials like zeolites,[15] and the previous oxygen effect may be considered in a similar way. Assuming that the increment in λ_3 (Fig. 7 right) is due to the chemical reaction with the sorbed O_2, the rate constant of reaction between *o*-Ps and O_2 is calculated to be 1.46×10^{-12} cm^3 s^{-1}. This value can be compared to 3×10^{-12} cm^3 s^{-1} for the same reaction in MS-3A.[15] Although the data is not shown, no effect was observed when LDPE was subjected to oxygen. The absence of the oxygen effect in LDPE is plausible, since the amount of O_2 sorption in LDPE is far smaller (0.007 wt%).

Conclusion

The different effects of vapor sorption on *o*-Ps parameters in low density polyethylene and 6FDA-TMPD polyimide can be explained by considering different aggregation states, i.e. rubbery for the former and glassy for the latter. The plasticization effect of the Henry-type sorption which occurs for both rubbery and glassy polymers assists *o*-Ps formation and enhances its lifetime. For the glassy polymer the Langmuir-type sorption also occurs and this causes filling in the preexisting microvacancies leading to a decrease in *o*-Ps intensity and lifetime. The strong effect of water in the polyimide is particularly important, since it suggests efficient condensation of water molecules in the microvacancies of the polymer.

Although simple this kind of experiment appears important not only for the fundamental understanding of positronium states in polymers but also for understanding the vacancies and sorption of molecules in polymers. In the previous experiments the *o*-Ps parameters have been presented in terms of the contact time, but it would be more fruitful if we measure them as a function of the absolute amount of the sorbed vapor.

This work was supported by the exchange program between Japan Society of Promotion of Science (JSPS, Japan) and the National Council of Science and Technology (CONACYT, Mexico).

References

1) For a general reference, see: Y. C. Jean, in "Positron and Positronium Chemistry," World Scientific, 1990; pp. 1—29.

2) Z. C. Zhang and Y. Ito, *Radiat. Phys. Chem.*, **38**, 221 (1991).

3) P. Kirkegaard, N. J. Pedersen, and M. Eldrup, "PATFIT-88, Risø-M-2740."

4) K. Okamoto, K. Tanaka, M. Katsube, O. Sueoka, and Y. Ito, *Int. J. Radiat. Phys. Chem.*, in press.

5) K. Tanaka, M. Okano, H. Toshino, H. Kita, K. Okamoto, *J. Polym. Sci., Polym. Phys. Ed.*, **30**, 907 (1992).

6) More precisely, sorption of molecules by dissolution in polymer matrix may be described both by the Henry-type and the Flory–Huggins dissolution isotherm. However we will simply call it the Henry-type in order to contrast with the Langmuir-type sorption which is mainly by deposition in preexisting sites: W. R. Vieth, J. M. Howell, and J. H. Hsieh, *J. Membr. Sci.*, **1**, 177 (1976).

7) Y. C. Jean, as in Ref. 1, pp. 159—192.

8) G. G. Aleksayan, A. A. Berlin, A. V. Goldanskii, N. S. Grineva, V. A. Onishuk, V. P. Shantarovich, and G. P. Safonov, *Khim. Fiz.*, **5**, 1225 (1986).

9) Y. Ito and Y. Tabata, *Chem. Phys. Lett.*, **15**, 584 (1972).

10) J. V. Dolveck, G. H. Dai, P. Moser, M. Pineri, P. Aldebert, M. Escoubes, R. Avrillon, and J. C. Mileo, *Materials Science Forum*, **105—110**, 1549 (1992).

11) M. Welander and F. H. J. Maurer, *Materials Science Forum*, **105—110**, 1815 (1992).

12) K. Okamoto, et al., *J. Polym. Sci., Polym. Phys. Ed.*, **30**, 1223 (1992).

13) S. J. Tao, *J. Chem. Phys.*, **56**, 5499 (1972).

14) M. Eldrup, D. Lightbody, and J. N. Sherwood, *Chem. Phys.*, **63**, 51 (1981).

15) Y. Ito, as in Ref. 1, pp. 577—582.