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Correlation between the *ortho*-Positronium Pick-off Annihilation Lifetime and the Free Volume in Molecular Liquids and Polymers

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A good correlation between the *ortho*-positronium (*o*-Ps) pick-off annihilation lifetime and the free volume, computed as the difference between the specific volume at room temperature and that at 0 K, is reported for molecular liquids and polymers. Bondi's group contribution approach was employed for estimating the specific volume at 0 K. The *o*-Ps lifetimes in molecular solids, such as phenanthrene deviate considerably from the correlation. It is suggested that a *bubble* may be formed around Ps in liquids and polymers, but not in the low-molecular-weight crystalline solids. A correlation is presented between the diffusion coefficients of Ar and the lifetimes of *o*-Ps in both liquids and polymers.

The behavior of a gas molecule in molecular substances such as polymers has been studied rather extensively these days in relation to the technology of gas separation. In a recent paper, Haraya and Hwang[1)] showed that the diffusivity of O_2, Ar, and N_2 in various polymers can be well correlated with the amount of free volume (v_f) present in the polymers. These authors computed the free volume as the difference between the specific volume at room temperature (v) and that at 0 K (v_0). Following Lee,[2)] the latter specific volume was estimated as

$$v_0 = 1.3\, v_w,$$

where v_w is the specific van der Waals volume of the substance; it was computed based on the group contribution approach of Bondi.[3)] The gas-diffusion coefficients (D) were successfully fitted to the following equation predicted by the free volume theory:

$$D = A \exp(-B/v_f).$$

Here A and B are constants for a given gas.

One of the problems associated with this method of evaluating the free volume is that the substance must have a known chemical structure comprising only atomic groups with known van der Waals volumes. Thus, for an extended test of the free volume theory of diffusion, a more direct and convenient means of numerically determining the free volume is desired.

Positrons have been used for materials research since it was discovered that the positron lifetime in a variety of substances is very sensitive to the presence of defects and other inhomogeneities. The usefulness of positrons in studies of molecular substances is enhanced by the fact that a positron can capture an electron form a bound system, a positronium (Ps).[4,5)] *ortho*-Positronium (*o*-Ps), where the spins of the two particles are parallel, has a lifetime of 142 ns in vacuum. *para*-Positronium (*p*-Ps), where the spins are antiparallel, has a lifetime of only 123 ps. In condensed matter the lifetime of *o*-Ps is reduced to a few nanoseconds or less, because of pick-off of the positron by electrons with antiparallel spin in the surrounding medium. Since the annihilation rate of *o*-Ps is proportional to the overlap of the positron and the pick-off electron wave functions, it is possible to determine the cavity size around Ps from the measured *o*-Ps lifetime.

In this paper, we report that there is a good correlation between the *o*-Ps annihilation lifetime and the free volume computed by Bondi's group contribution method and suggest that the positron technique may become a new convenient means for evaluating the free volume not only in polymers but also in liquids.

Experimental

Positron lifetime measurements were performed with the spectrometer[6)] described previously. The time resolution of the spectrometer was approximately 240 ps FWHM. Lifetime spectra were fitted to a sum of three exponential functions and the *o*-Ps lifetime was determined as the lifetime of the longest-lived component, τ_3. As before, the POSITRON FIT EXTENDED routine[7)] was employed for the data analysis. All of the measurements were performed at room temperature.

Results and Discussion

Figure 1 shows a plot of the *o*-Ps lifetimes versus the free volume determined by the method described above. The open circles indicate data for molecular liquids (saturated and aromatic hydrocarbons, alcohols, ethers, pyridine, and hexafluorobenzene)[8)] and the squares indicate those for glassy polymers, poly(4-methyl-1-pentene), poly(vinylidene difluoride), polypropylene, polystyrene, polycarbonate, polysulfone, poly(vinyl acetate)[9)], poly(methyl methacrylate), poly(ethersulfone), poly(aryl ether-ether-ketone), and poly(phenylene sulfide). The points represented by closed circles are data for low-molecular-weight crystalline solids

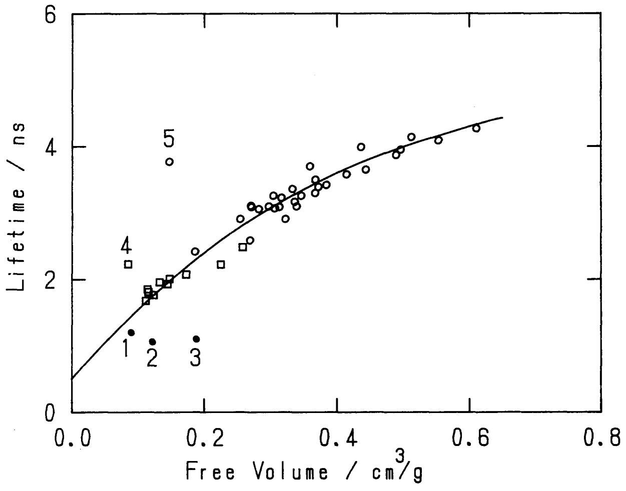

Fig. 1. Plot of the *o*-Ps lifetime versus the free volume computed by the group contribution method of Bondi. The open circles indicate data for liquids and the squares indicate data for polymers. The *o*-Ps lifetimes in liquids were determined in a previous study.[8] Closed circles indicate data for molecular solids, adamantane (1), phenanthrene (2), and biphenyl (3). Points 4 and 5 are data for poly(vinylidene difluoride) and hexafluorobenzene, respectively. The *o*-Ps lifetimes in poly(vinyl acetate), adamantane, phenanthrene, and biphenyl were taken from references.[9-12] The solid line is a visual fit under the assumption that the lifetime in a sample with no free volume is 0.5 ns.

(biphenyl, phenanthrene and adamantane).[10-12] The free volume of semicrystalline polymers, such as polypropylene, was computed from the densities expected for completely amorphous samples.[1,13] From Fig. 1 it is clearly seen that there is a strong correlation between the *o*-Ps lifetimes and the amounts of free volume present in liquids and polymers. Furthermore, the points for these two kinds of substances, except those for a couple of fluorine-containing compounds, are well reproduced by a single line. This suggests that the Ps state in the amorphous region of polymers is similar to that in liquids.

Ps in liquids is believed to be localized in a large cavity called a *bubble*. The Ps bubble is formed as a result of the large zero-point energy of a light particle confined within a small cavity. A simple bubble model[14] states that the equilibrium bubble size is determined by the energy minimum condition for the total bubble energy, given as the sum of the zero-point energy of Ps and the energy required to make a cavity with a certain radius in liquid. Since the latter energy is related to molecular cohesion, good correlations have been found between the equilibrium bubble size and various liquid parameters, such as surface tension,[15] solubility parameter (cohesive energy density),[16] and the molar free volume computed from the sound velocity.[17] Recent studies[6,18] on the effect of external pressure on the chemical reactivity of *o*-Ps provide strong supporting evidence to the presence of bubbles in organic liquids.

Thus, the fact that the points for polymers are almost on the same line as the points for liquids in Fig. 1 appears to indicate that a bubble is formed around Ps, not only in liquids but also in polymers. If this is the case, the time necessary for bubble formation must be shorter than the *o*-Ps lifetime; the good correlation in Fig. 1 suggests that the energy required to make a cavity in liquids and polymers is well correlated to the free volume. The considerable downward deviation of the closed circles in the same figure may show that a bubble is not formed in the low-molecular-weight crystalline solids. Although the possibility of Ps bubble formation in noncrystalline glassy solids was suggested by Tao[15] about 20 years ago, most authors of subsequent publications concerning positron annihilation have implicitly assumed that Ps is trapped by preexisting free-volume holes in polymers.

According to Nakanishi et al.,[19] the relation between the *o*-Ps lifetime and the Ps cavity size can be written as

$$\tau_3{}^{-1} = 2(\mathrm{ns}^{-1})\,(1 - [R/R_0] + 0.159\,[\sin(2\pi R/R_0)]), \qquad (1)$$

where R is the cavity (bubble) radius and R_0 is equal to $R + 1.656$ Å. This equation gives a bubble volume ranging from 150 to 330 Å^3 for common liquids, which corresponds to a molar bubble volume of 90—200 cm^3 mol^{-1}. The actual bubble volume may by larger, since the volume change upon the reaction of Ps with nitrobenzene in hexane (determined from the pressure dependence of the rate constant[6]) is more than 300 cm^3 mol^{-1}. Since Ps can be regarded as being a gas molecule, it may be helpful to compare the estimated bubble size with the cavity size around a gas molecule in liquids. The partial molar volume of CO_2 in organic solvents is known to be about 46 cm^3 mol^{-1}.[20] This indicates that the volume occupied by Ps is at least twice as large as that occupied by a CO_2 molecule in liquids.

Gas dissolution in a polymer system occurs in different manners, depending on whether the polymer is in a flexible rubbery state or in a glassy state.[21,22] In the rubbery state, gas dissolution follows Flory–Huggins' law. Dissolution following Henry's law can be treated as a special case of this type of dissolution. The Flory–Huggins' dissolution in a polymer accompanies a fairly large volume expansion and is assumed to be accomplished through the formation of a hole by a gas molecule, as in dissolution in liquids. In the case of rubbery Poly(ethyl methacrylate), the partial molar volume of Ar and CO_2 is approximately 40 cm^3 mol^{-1}, which means that a cavity of 65 Å^3 is formed upon the dissolution of one gas molecule. The size of a Ps cavity in rubbery poly(vinyl acetate) at temperatures between 45 and 75 °C is calculated from the data by Kobayashi et al.[9] to be 100—135 Å^3 by Eq. 1 and, hence, is probably larger than the cavity size around the gas molecules. Since the molecular chain should be flexible above the glass-transition temperature (T_g), it seems unlikely that a sufficient number of cavities (as large as 100 Å^3 to trap all Ps formed) exist in a rubbery polymer.[17] Therefore, the above statment that the cavity size around Ps is larger than that around the gas molecules appears to point to Ps bubble formation in rubbery polymers.

In the case of a glassy polymer, some part of the gas dissolution occurs according to Langmuir's law. The rest of the gas dissolution follows Flory–Huggins' law, as in the case of a rubbery polymer. The cavity size around a dissolved gas molecule in a glassy polymer is almost the same as that in a rubbery polymer, that is, several tens of cubic angstroms.[21,22] From the lifetime data given in Fig. 1 and Eq. 1 the Ps cavity size is estimated to be 65—135 Å^3 in glassy polymers. In Langmuir dissolution, it has been postulated that the gas molecule goes into a preexisting microvoid. Kamiya and co-workers[21,22] carefully measured the elongation of a poly(ethyl methacrylate) film upon the dissolution of Ar and CO_2 and determined the size of the microvoid to be 25—129 Å^3. Since this size is comparable to that of the Ps cavity, our question is now whether Ps formed in glassy polymers goes into the preexisting microvoids as the Langmuir species (Ps trapping) or dissolves by making a cavity, as does the Flory–Huggins species (Ps bubble formation).

The energy required to make a cavity in a polymer can be estimated from its cohesive energy density. Let us consider the case of poly(methyl methacrylate) as an example. According to the data of solubility parameters by Mangaraj et al.,[23] the cohesive energy density of this polymer is about 90 cal cm^{-3}. Thus, the energy required to make a hole of, for example, 80 Å^3 is only 0.19 eV. This energy is lower than the energy needed to make a Ps bubble with a radius of 5 Å in hexane, estimated either from the cohesive energy density (0.72 eV) or from the surface tension as surface energy (0.36 eV). Since the cohesive energy density does not vary much from one polymer to another, we can say that Ps bubble formation in glassy polymers should be possible, at least, energetically.

The presence of the microvoids has been assumed to be related to the unrelaxed volume of a glassy polymer. Then, the number of the microvoids in a glassy polymer quenched from a temperature above T_g to another temperature below T_g may gradually decrease with time after the quench. In dual-mode sorption theory,[21,22] the number of the microvoids can be related to the hole saturation constant, $C_H{}^{0\prime}$. It has been reported for several polymers[9,24] that during isothermal annealing below T_g or physical aging, the yield of *o*-Ps (I_3) gradually decreases to a certain value, while the *o*-Ps lifetime (τ_3) remains almost unchanged. This result may show that the microvoids act as Ps formation centers and extra Ps formed in the unrelaxed microvoids disappears during isothermal annealing. In this connection it may be interesting to study the relation between the Ps yield and the hole saturation constant for a glassy polymer as a function of the aging time. The observation that the lifetime is nearly constant may be explained by considering that the energy required to make the Ps bubble is not much affected by the presence of microvoids, and hardly changes in the process of physical aging.

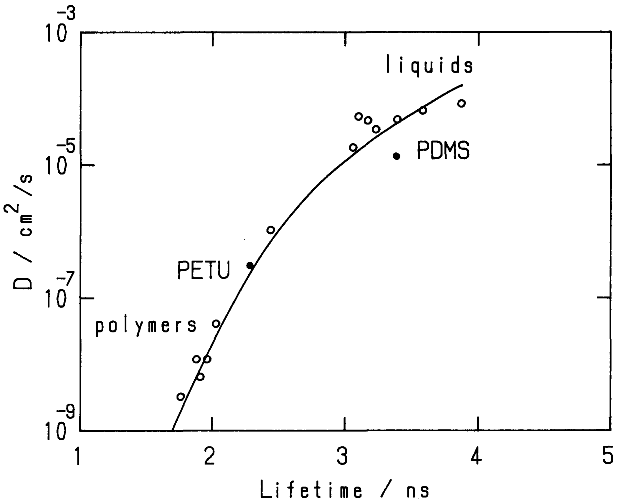

Fig. 2. Plot of the diffusion coefficients of Ar in liquids and polymers against *o*-Ps lifetime. The diffusion coefficients in polymers except poly(dimethylsiloxane) (polysulfone, poly(ether-sulfone), polycarbonate, polystyrene, poly(vinyl acetate), poly(4-methyl-1-pentene), and poly(ether-urethane)) are those reported by Haraya and Hwang,[1] and the values in liquids (hexane, octane, benzene, decane, cyclohexane, 1-butanol, and 1-octanol) were those by Evans et al.[25,26] The diffusivity of Ar in poly(dimethylsiloxane) was determined in this study. The solid line is a visual fit to the data.

Returning to Fig. 1, the considerable upward deviation of the points for poly(vinylidene fluoride) and hexafluorobenzene suggests that in fluorine-containing substances the Ps cavity is larger than that expected from the free volume. Perhaps there is some interaction between the fluorine atoms and Ps in these substances, thus making the cavity size larger. A similar interaction might be present between fluorine atoms and gas molecules, since Mohr and Paul[13] reported that the gas permeabilities through flrorine-containing polymers are higher than expected from a general correlation between the permeabilities and the free volume.

Since the *o*-Ps lifetime is well correlated with the free volume, it may be possible to relate the lifetime to diffusivity to some extent. Figure 2 shows a plot of the diffusion coefficient of Ar against the *o*-Ps lifetimes for liquids and polymers. Obviously there is a fairly good correlation between these two quantities. It should be noted that the points for rubbery poly(ether-urethane) (PETU) and poly(dimethylsiloxane) (PDMS) are almost on the correlation. The free volume of these polymers cannot be computed from the group contribution method because of the unknown chemical structure or the unknown van der Waals volume. The fact that the points almost fall on the correlation in Fig. 2 suggests that the positron technique may be a useful and convenient means for evaluating the free volume in cases where the group contribution method cannot be applied.

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