The Effects of CO_2-Conditioning of Polymers on Positron Annihilation and Gas Permeation Properties

Kazuhiro Tanaka, Masamichi Ito, Hidetoshi Kita, Ken-ichi Okamoto,* and Yasuo Ito[†]

Department of Advanced Materials Science and Engineering, Faculty of Engineering, Yamaguchi University, Yamaguchi 755

[†]Research Center for Nuclear Science and Technology, The University of Tokyo, Ibaraki 319-11

(Received January 23, 1995)

The effects of CO_2-conditioning, i.e. exposing a polymer film to high pressure CO_2 and degassing it in vacuo, on positron annihilation and gas permeation properties of polyimides and polyethylene were investigated. Both lifetime and intensity of ortho-positronium (o-Ps) (τ_3 and I_3, respectively) increased for polyimides by the CO_2-conditioning. The size distribution of free space holes, which was evaluated from annihilation rate distribution of o-Ps, became broader and shifted to larger size. Permeability, diffusion, and solubility coefficients of gases for polyimides increased by the CO_2-conditioning. The increases in diffusion coefficient are attributed to increases in volume fraction of free space holes, V_F. The increases in τ_3 and in I_3 were much larger than those expected from the increases in V_F. This may be explained by a model based on an interplay between electron affinity and size of free space holes for Ps formation. In the CO_2-conditioned films, permeability and diffusion coefficients, V_F, and I_3 gradually decreased with lapse of time but after five months they were still larger than those in the as-cast films, whereas τ_3 remained almost constant. No effect of the CO_2-conditioning was observed for polyethylene.

Positron annihilation lifetime (PAL) has attracted attention as a technique to probe microstructure of polymers.[1)] PAL spectra of polymers have a long-lived component which is attributed to pick-off annihilation of ortho-positronium (o-Ps) formed in amorphous regions. The lifetime and intensity of the long-lived component, τ_3 and I_3, in polymer films are considered to be measures of the size and concentration, respectively, of interstitial spaces among polymer chains, which are referred to as "free space holes" in this paper. PAL spectra have been applied to investigate variations of free space holes in polymers with temperature[2,3)] and pressure,[4)] isothermal relaxation,[5)] and mechanical deformation.[6,7)]

The permeability coefficient for gas in a polymer film is expressed by the product of the solubility coefficient and the diffusion coefficient. The diffusion coefficient is closely related to the volume fraction and the size distribution of free space holes. The volume fraction of free space holes, V_F, is estimated by the method of van Krevelen and Bondi.[8,9)]

$$V_F = (V_T - V_0)/V_T, \qquad (1)$$

where V_T is the molar volume at temperature T K calculated from the density data, V_0 the volume occupied by the molecules at 0 K per mole of repeat unit of polymer estimated by a group contribution method.[9)] The V_F refers to the ratio of the so-called "expansion volume"[10)] to the observed volume. For many glassy polymers,[11)] a rough correlation has been observed between the logarithm of diffusion coefficient of gas and the reciprocal of V_F. On the other hand, polyimides having tri- or tetramethylphenylenediamine moieties have about 10 times larger diffusion coefficients than the other polyimides having similar values of V_F[11)] (see Fig. 5). This may be attributed to the difference in the size distribution of free space holes. The polyimides having tri- or tetramethylphenylenediamine moieties have larger τ_3 than the other polyimides having the similar V_F, suggesting that the former polyimides have a higher fraction of large free space holes than the latter.[12)] A higher fraction of free space holes large enough for a penetrant molecule to pass through leads to a larger diffusion coefficient. Furthermore, there has been observed the tendency that the polyimides with larger τ_3 have larger diffusion coefficients for CO_2 and CH_4.[12)] It is considered that τ_3 reflects the average size of free space holes large enough for the gas molecules to pass through because the minimum size of free space holes to accommodate o-Ps (0.033 nm^3) is similar to the molecular size of CO_2 and CH_4.

It is well-known that gas permeability of glassy polymers increases by CO_2-conditioning, done by exposing a polymer film to high pressure CO_2 and then degassing it in vacuo.[13—18)] This is due to increases in solubility and diffusion coefficients. A small increase in specific volume has also been observed and related to the CO_2 exposure pressure.[13,18] This indicates that the volume fraction of free space holes increases by the CO_2-conditioning. When a polymer film is exposed to high pressure CO_2, the polymer chains are plasticized by the CO_2 molecules sorbed at a high concentration, leading to volume dilation of the polymer. A little part of the volume dilation is supposed to remain as "penetrant-scale defects" in polymer matrix after evacuating CO_2 because the segmental motion is frozen in glassy state.[13—15,18] Even for polyimides having rigid polymer backbone the CO_2-conditioning effect on gas permeability has been observed.[16,17] CO_2 permeability for fluorinated polyimides was found to increase largely with increasing upstream pressure in the region of relatively low pressure, suggesting that they are susceptible to plasticization.[19] PAL is the best method to investigate the changes in average size and size distribution of free space holes caused by the CO_2-conditioning. To the author's knowledge, however, such investigations have not been reported. In this study, PAL and gas permeation properties of polyimides and polyethylene were measured to investigate the effects of CO_2-conditioning on their free space holes.

Experimental

Polyimides were prepared from 4,4′-(hexafluoroisopropylidene)diphthalic anhydride (6FDA) with 2,3,5,6-tetramethyl-1,4-phenylenediamine (TeMPD), 4,4′-(hexafluoroisopropylidene)dianiline (6FAN), and 1,3-phenylenediamine (mPD). The chemical structures of the polyimides are shown in Fig. 1. The methods of polymerization and film preparation of the polyimides have been described elsewhere.[11] Polyethylene films were supplied from Ube Industries Ltd.

The CO_2-conditioning was carried out by exposing as-cast or as-received films to CO_2 gas uniformly in a chamber at 50 atm and room temperature for 24 h and then by degassing them in vacuo.

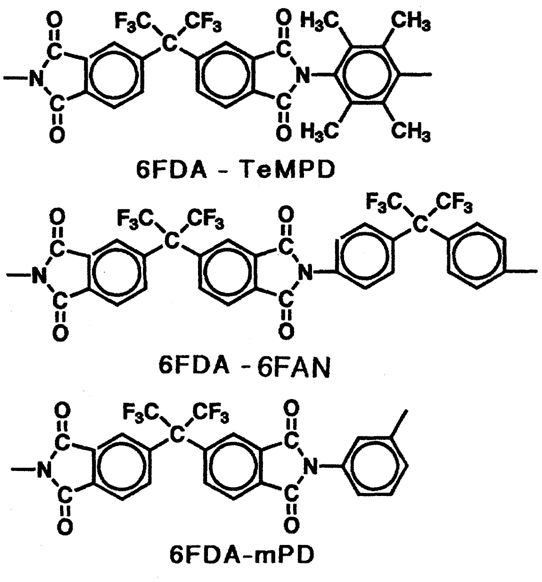

Fig. 1. Chemical structures of polyimides.

The PAL measurement was carried out at the Inter-University Laboratory for the Common Use of JAERI facilities.[20] Positron source used was about 25 μCi of ^{22}NaCl sandwiched between thin nickel foils. 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 at room temperature (298 K). The PAL spectrometer was the fast–fast coincidence equipment with the 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. Annihilation rate distribution was also determined with the program CONTIN (PALS-2)[22] from a spectrum with total counts of about 1.3×10^7 and was sampled at 75 grid points over the range $0.1<\lambda<20$ ns^{-1}, where λ is the annihilation rate. Aluminum sample with an annihilation rate of 6.02 ns^{-1} was used as the reference.

Permeability and solubility coefficients, P and S, were measured by means of the vacuum time-lag method, and a dual-volume type sorption cell,[23] respectively. They were measured at 308 K and at 2 or 10 atm for H_2, CO_2, N_2, and CH_4. The average diffusion coefficient, D, was calculated from the equation

$$D = P/S. \tag{2}$$

Results

Characteristics of the polyimides and polyethylene are listed in Table 1. PAL and CO_2 gas permeation data for as-cast films of the polyimides are listed in Table 2. P, D, S, τ_3, and I_3 are in the order 6FDA-TeMPD>6FDA-6FAN>6FDA-mPD, whereas V_F is in the order 6FDA-TeMPD=6FDA-6FAN>6FDA-mPD. 6FDA-mPD polyimide has more efficient polymer-chain packing among 6FDA-based polyimides because of the meta-oriented and no-substituted diamine moiety, and as a result it has lower V_F and smaller D and P. 6FDA-TeMPD and 6FDA-6FAN polyimides have less efficient packing and as a result larger V_F, because of the rigidity and non-planar structure of the polymer chain due to methyl substituents and $-C(CF_3)_2-$ linkages, respectively. 6FDA-TeMPD polyimide has higher fraction of large free space holes than 6FDA-6FAN polyimide, judging from the larger τ_3 for the former. This is the reason that P and D are larger for 6FDA-TeMPD than

Table 1. Characteristics of Polymers [a]

Polymers	T_g / K	Density / $g\,cm^{-3}$	V_F / —
6FDA-TeMPD	693	1.326	0.184
6FDA-6FAN	578	1.476	0.184
6FDA-mPD	571	1.474	0.160
Polyethylene[b]	251	0.910	0.192

a) Density and V_F are at 298 K. b) Semicrystalline sample, amorphous fraction=0.65.

Table 2. CO_2 Gas Permeation, Fraction of Free Space Holes, and PAL Data before and after CO_2-Conditioning [a)]

Polymer	P	D	S	V_F	τ_3	I_3	$v_{h,Ps}$
				—	ns	%	nm^3
6FDA-TeMPD							
As-cast	740	31	24	0.184	3.8	21	0.29
Conditioned	1340	47	28	0.189	4.9	22	0.43
6FDA-6FAN							
As-cast	51	8.1	6.3	0.184	3.1	15	0.22
Conditioned	84	12	7.1	0.194	3.9	18	0.31
6FDA-mPD							
As-cast	8.8	1.8	4.8	0.160	2.4	7.8	0.14
Conditioned	18	2.7	6.5	0.164	2.9	12	0.18

a) P is in 10^{-10} cm^3 (STP) $cm^{-1}s^{-1}$ $cmHg^{-1}$, D is in 10^{-8} $cm^2 s^{-1}$, and S is in 10^{-2} cm^3 (STP) cm^{-3} $cmHg^{-1}$. The data are at 308 K and 2 atm for 6FDA-TeMPD and 10 atm for 6FDA-6FAN and 6FDA-mPD polyimides. (1 cmHg=1333.22 Pa).

for 6FDA-6FAN in spite of the same V_F.

Figure 2 shows variations in τ_3 and I_3 with time elapsed after the CO_2-conditioning for polyimides and polyethylene. The τ_3 and I_3 for the polyimides increased by the CO_2-conditioning. For 6FDA-TeMPD and 6FDA-mPD polyimides the τ_3 slightly increased with the elapse of time until 100 h after the conditioning and then leveled off, whereas no such increase in τ_3 was observed for 6FDA-6FAN polyimide. For every polyimide the I_3 gradually decreased with the elapse of time after the conditioning. However, the I_3 values after four months were still larger than the values before the conditioning. No such variations in τ_3 and I_3 with time were observed for the as-cast films. Contrary to the polyimides, τ_3 and I_3 for polyethylene did not change by the CO_2-conditioning.

PAL data of the polyimides at about 200 h after the CO_2-conditioning are listed in Table 2. The increase in I_3 by the conditioning is larger for the polyimide having smaller τ_3 and is in the order 6FDA-mPD>6FDA-6FAN>6FDA-TeMPD. The order of increase in τ_3 is reversed, that is, it is larger for the polyimide having larger τ_3.

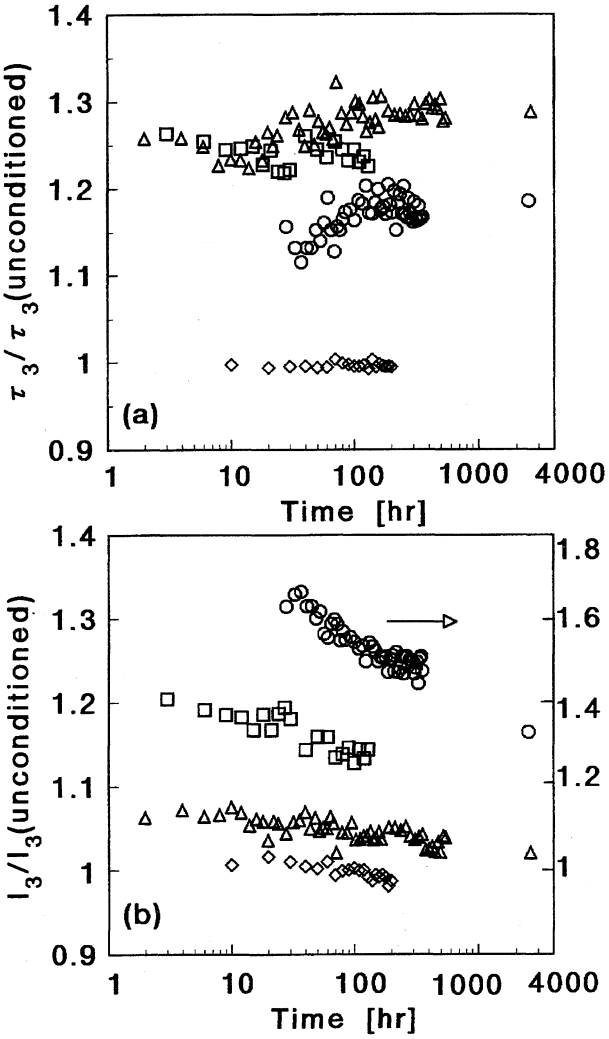

Fig. 2. Variations in (a) lifetime and (b) intensity of ortho-positronium with time elapsed after the CO_2-conditioning for 6FDA-TeMPD (△), 6FDA-6FAN (□), and 6FDA-mPD (○) polyimides and polyethylene (◇).

Figures 3 and 4 show variations in P and S with time elapsed after the CO_2-conditioning for 6FDA-mPD and 6FDA-TeMPD polyimides. The increases in P by the conditioning were larger for the gas with larger molecular size ($CH_4>N_2>CO_2>H_2$), whereas the increases in S were independent of gases. As can be seen from Table 2, the increases in P, D, and S for CO_2 at about 200 h after the conditioning were 70—100, 50, and 10—35%, respectively. The increases in P are attributed mainly to the increases in D. After the conditioning, P gradually decreased with the elapse of time due to the decrease in D, whereas S remained almost constant. However, the P and D values after five months were still larger than the values before the conditioning. Such variations in P and D with time were not observed for the unconditioned films in the same time scale.

Figure 5 shows plots of $\log D_{CO_2}$ versus V_F^{-1} for as-cast and CO_2-conditioned films of the polyimides investigated here together with other glassy polymers.[11)] As shown by the solid line, there is a rough correlation between $\log D_{CO_2}$ and V_F^{-1} for most glassy polymers, except for the polyimides having tri- or tetramethylphenylenediamine moieties. Another correlation shown by the broken line holds for the latter polyimides. The plots for the CO_2-conditioned films of 6FDA-mPD and 6FDA-6FAN polyimides are on the former correlation line as in the as-cast films, whereas those of 6FDA-TeMPD polyimide are on the latter correlation line. This suggests that the variations in D_{CO_2} by the CO_2-conditioning and with the elapse of time after it are attributed to the corresponding variations in V_F.

Figure 6 shows plots of permselectivity of CO_2

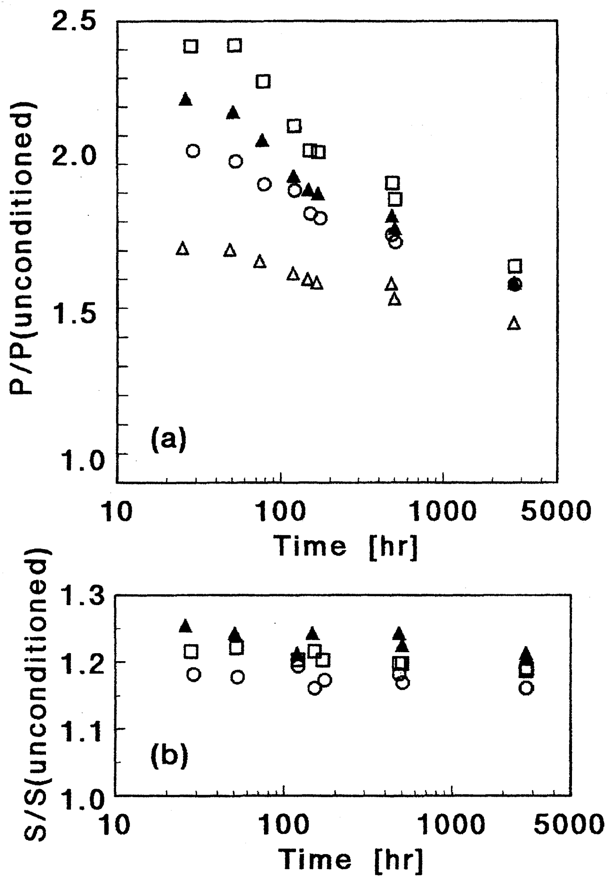

Fig. 3. Variations in (a) permeability and (b) solubility coefficients of gases with time elapsed after the CO_2-conditioning for 6FDA-TeMPD polyimide at 308 K and 2 atm. □: CH_4, ▲: N_2, ○: CO_2, △: H_2.

over CH_4 (ratio of each permeability coefficient, P_{CO_2}/P_{CH_4}) versus P_{CO_2} for the polyimides used here together with other polyimides.[11] The permselectivity is expressed by the product of the diffusivity and solubility selectivities.

$$P_{CO_2}/P_{CH_4} = (D_{CO_2}/D_{CH_4})(S_{CO_2}/S_{CH_4}). \quad (3)$$

As the fraction of free space holes large enough for gas molecule to pass through increases, diffusion coefficient of the gas increases. The rate of the increase is larger for gas with larger molecular size, resulting in a decrease in diffusivity selectivity.[11] Consequently, there is a tendency in Fig. 6 that permselectivity generally decreases with increasing permeability. However, the permselectivity for 6FDA-mPD polyimide did not decrease with an increase in permeability by the CO_2-conditioning. The permselectivity for 6FDA-6FAN and 6FDA-TeMPD polyimides slightly decreased with an increase in permeability by the conditioning. With the elapse of time after the conditioning, the permselectivity then gradually increased and the permeability decreased. Figure 6 shows the upper-bound line denoting the limit of separating ability of polymers at the present time for CO_2/CH_4 system, which was deduced by analyzing the literature data and reported by Robeson.[24] The data points for the conditioned samples were nearer to the line or on the right of the line. The performance of the polyimide films for CO_2/CH_4 separation was slightly improved by the conditioning.

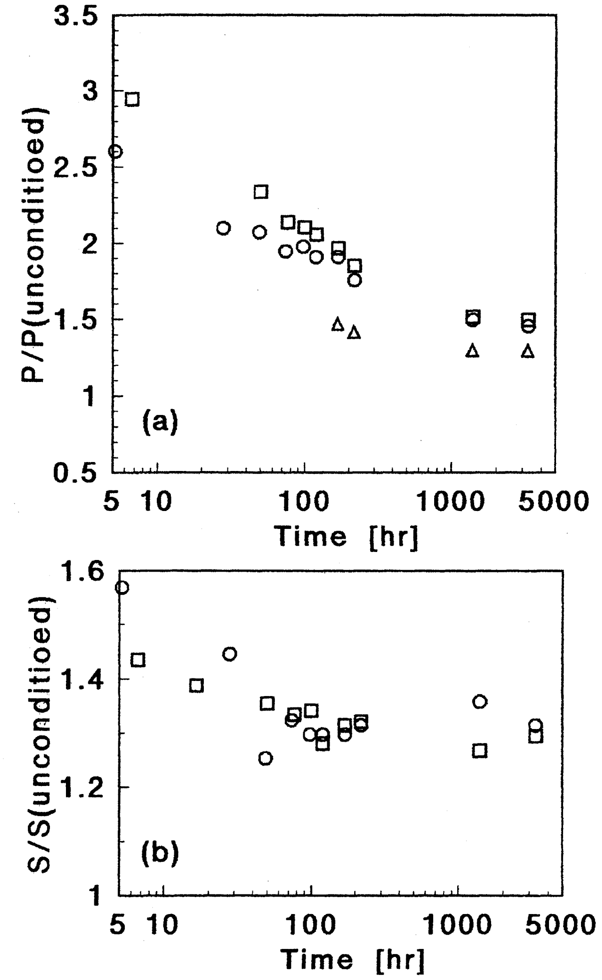

Fig. 4. Variations in (a) permeability and (b) solubility coefficients of gases with time elapsed after the CO_2-conditioning for 6FDA-mPD polyimide at 308 K and 10 atm for H_2 and CH_4, and at 2 atm for CO_2. The symbols are as in Fig. 3.

Discussion

The average size of free space holes probed by o-Ps, $v_{h,Ps}$ [$=(4/3)\pi R^3$], was calculated by the following expression for τ_3 in a spherical microvacancy of radius, R [nm].[25,26]

$$\tau_3 = (1/2)[1 - R/R_0 + (1/2\pi)\sin(2\pi R/R_0)]^{-1}, \quad (4)$$

where $R_0 = R + \Delta R$. $\Delta R = 0.1656$ nm. By the CO_2-conditioning the $v_{h,Ps}$ increased by 30—50% as listed in Table 2.

The size distribution of free space holes, $g(V)$, was estimated by transformation of the annihilation rate distribution of o-Ps, $\alpha(\lambda)$, using the following

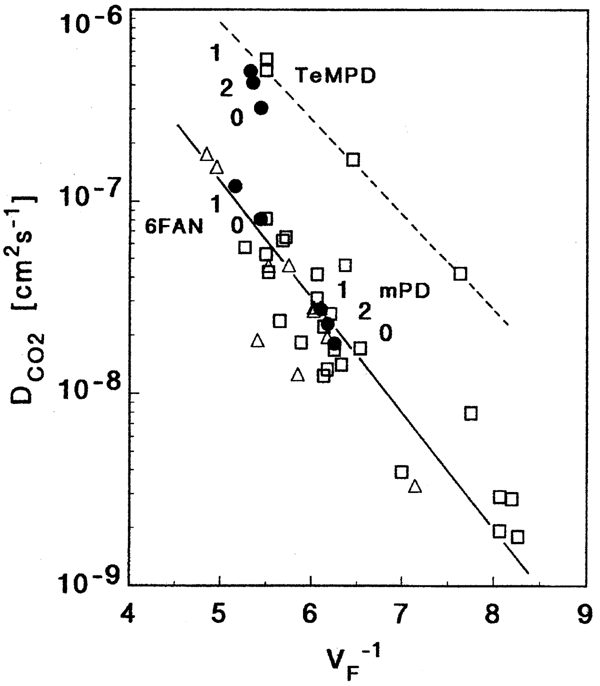

Fig. 5. Plots of logarithm of D of CO_2 at 308 K and 10 atm versus V_F^{-1} for as-cast and CO_2-conditioned films of the polyimides used here (●) together with other polyimides (□) and glassy non-polyimide polymers (△). 0: as-cast films; 1 and 2: at 200 h (120 h for 6FDA-6FAN polyimide) and five months, respectively, after the CO_2-conditioning.

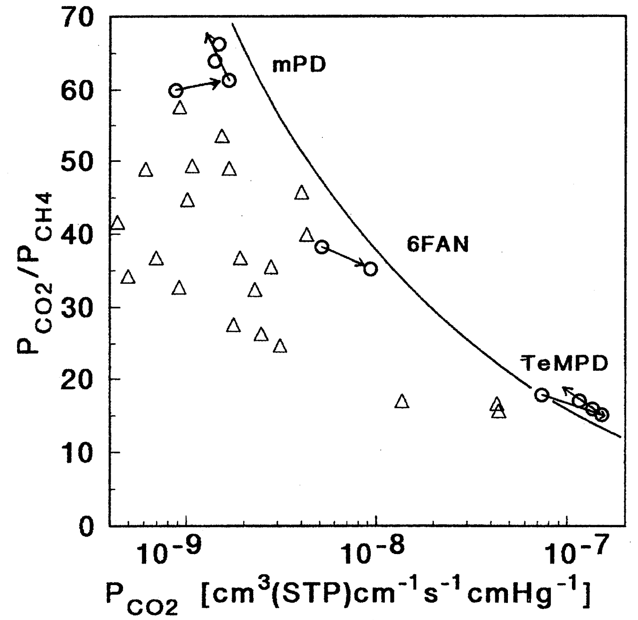

Fig. 6. Plots of P ratios of CO_2 over CH_4 versus P of CO_2 at 308 K and 2 atm for 6FDA-TeMPD and at 10 atm for 6FDA-6FAN and 6FDA-mPD polyimides (○) together with the data for other polyimides (△). The solid line denotes the upper limit of separating ability of polymers at the present (see text).

expression.[22]

$$f(R) = 2\Delta R[\cos(2\pi R/(R+\Delta R)) - 1]\alpha(\lambda)/(R+\Delta R)^2, \quad (5)$$

$$g(V) = f(R)/4\pi R^2. \quad (6)$$

Figure 7 (a) and (b) show the results for 6FDA-6FAN and 6FDA-mPD polyimides, respectively. The distribution of free space holes in the polyimides became broader and shifted to a larger size by the CO_2-conditioning, indicating that preexisting free space holes were enlarged and/or new larger free space holes were formed by the CO_2-conditioning.

The $v_{h,Ps}$ and I_3 increased by 30—50% and 5—50%, respectively by the CO_2-conditioning as listed in Table 2. The rates of increase in $v_{h,Ps}$ and I_3 are much larger than those in V_F (3—5%), suggesting that $v_{h,Ps}$ and I_3 don't directly reflect the real changes in the number and the size of all free space holes. For the interpretation of this inconsistency it is necessary to consider positronium (Ps) formation mechanism.

Recently, a model for Ps formation in polymers has been proposed.[27] The model is based on an interplay between electron affinity of polymer moiety and size of free space holes. The energetics of Ps formation is described as:

$$-E(e^+) - P_{sol}(e^+) - E(e^-) - P_{sol}(e^-) + E(Ps_{hole}) < 6.8 \text{ eV}, \quad (7)$$

where $E(e^+)$ and $E(e^-)$ are the energies of Ps precursors (e^+ and e^-) in the matrix, $E(Ps_{hole})$ is the energy of Ps in the hole, and P_{sol} is the solvation energy of e^+ and e^-. It is preferable for Ps formation that $E(Ps_{hole})$ is small. $E(Ps_{hole})$ may be represented by the zero point energy of Ps in the pores of radius $R[E(Ps_{hole}) = 0.188 \text{ eV}/R^2$, R:nm]. The energetic consideration leads to a concept that there is a cut-off level on the size of free space holes which are available for Ps formation. The cut-off level depends on interactions between e^+ or e^- and moieties of polymer chains, which are not changed by the CO_2-conditioning. The change in I_3 reflects the change in the amount of free space holes larger than the cut-off level, rather than the total amount of free space holes. When the free space holes are enlarged and/or new larger free space holes are formed by the CO_2-conditioning, the fraction of free space holes above the cut-off level increases, and I_3 increases even if the total number of free space holes remains constant. It is considered that a change in I_3 is larger than a change in the total number of free space holes. The result that the increase in I_3 was larger for the polyimide with smaller τ_3 is consistent with the above consideration. The rate of increase in the number of free space holes above the cut-off level may be larger for the polyimides with smaller τ_3 where number of such free space holes is originally smaller. When Ps probes free space holes larger than the cut-off level, τ_3 reflects an average size of the larger free space holes. Moreover, if Ps diffuses from one free space hole to connected neighboring ones, it is prefer-

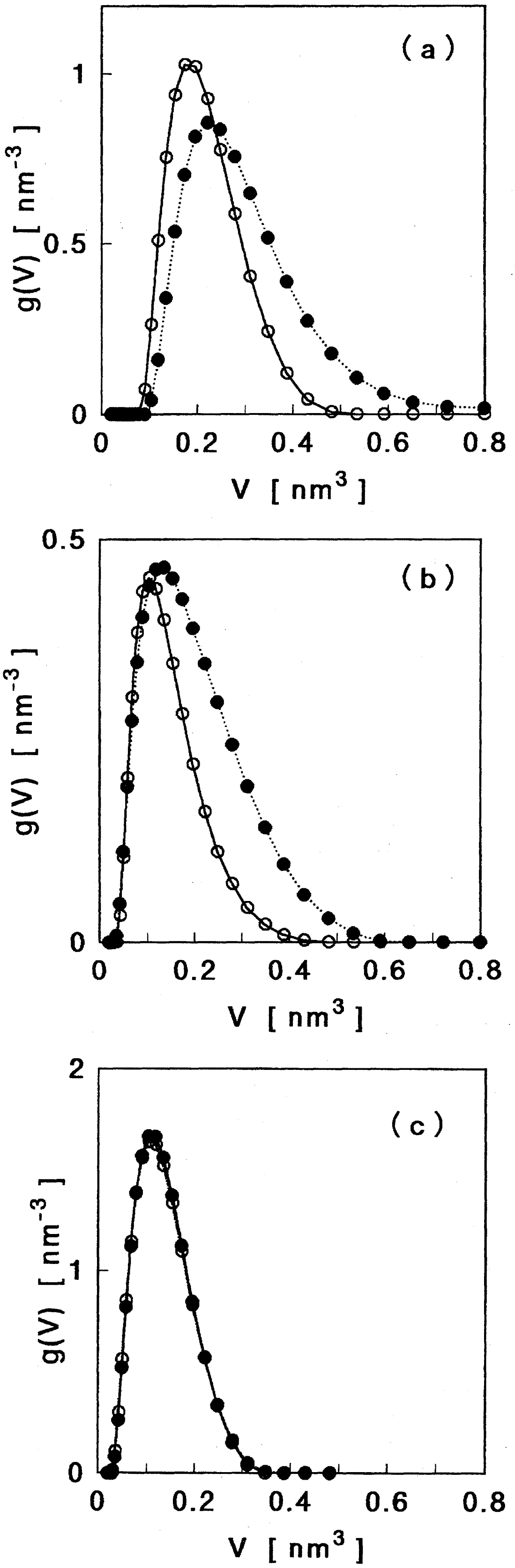

Fig. 7. Size distributions of free space holes for (a) 6FDA-6FAN polyimide, (b) 6FDA-mPD polyimide, and (c) polyethylene. ○: as cast films, ●: conditioned films at 200 h after the conditioning.

ably trapped at a larger free space hole and τ_3 more sensitively varies with a change in the size of larger free space holes. The increase in $v_{\mathrm{h,Ps}}$ by the conditioning is therefore considered to be larger than the real increase in average size of all free space holes.

For PC samples exposured to CO_2 at 308 K and 60 atm for 24 h, the CO_2 sorption amount and the volume dilation have been reported to be 62 [cm^3(SPT)cm^{-3}] and 7.6%, respectively.[18,28] After the removal of CO_2, the PC samples have been reported to display a residual excess volume of 0.8% of the original volume.[18] The sorption amounts of CO_2 for 6FDA-mPD, 6FDA-6FAN, and 6FDA-TeMPD polyimides were 87, 125, and 180 [cm^3(STP)cm^{-3}], respectively, at 308 K and 50 atm.[29] The volume dilations of the polyimides caused by the CO_2 sorption are estimated to be about 13, 18, and 24%, respectively, based on the idea that the volume dilation is due only to the Henry's law sorption according to the dual-mode sorption model.[28] The residual excess volumes for these polyimides were 0.6, 1.2, and 0.5%, respectively, at 200 h after the CO_2-conditioning.

The polyimides are still in glassy state under exposure to CO_2 at 50 atm, judging from much higher T_{g} as compared with PC and the decrease in T_{g} (about 90 K) of PC under exposure to CO_2 at 60 atm.[30] Although the segmental motion is frozen, local motion of polymer chains is enhanced to some extent by the plasticization effect of sorbed CO_2. As a result, the polymer chains irreversibly relax to a new state with looser chain packing. Upon the CO_2 desorption, the volume dilation due to the Henry's law sorption of CO_2 almost disappear, whereas the volume dilation caused by the CO_2-induced relaxation process remains as a residual excess volume. After the CO_2-conditioning, P and D gradually decreased with the elapse of time as a result of gradual decrease in V_{F}. This behavior is a kind of isothermal relaxation and the similar result has been obtained for CO_2-conditioned films of other polyimide.[17] In the CO_2-conditioned films the polymer chains relax to a new stable of their packing being different from the original one. This is supported by the variation in the relation between the permselectivity and permeability for CO_2/CH_4 system shown in Fig. 6 and by the fact that I_3 decreased with time but τ_3 hardly changed.

On the contrary, for polyethylene the size distribution of free space holes was not changed by the CO_2-conditioning as shown in Fig. 7(c), nor τ_3 and I_3 were changed, as shown in Fig. 2. This is because the polymer chain segments in rubbery state are in thermodynamic equilibrium state, that is, the size of free space holes enlarged by the sorbed CO_2 can go back to the original size spontaneously upon the CO_2 desorption.

Conclusion

It was demonstrated from the PAL technique, i.e., variations in τ_3, I_3, and annihilation rate distribution of o-Ps that the size distribution of free space holes in the polyimides became broader and shifted to larger size by the CO_2-conditioning. The rates of increase in $v_{\mathrm{h,Ps}}$ and I_3 by the conditioning were much larger than that in V_F, suggesting that the variations in $v_{\mathrm{h,Ps}}$ and I_3 tend to overestimate the real variations in the average size and the number of all free space holes, respectively. This may be explained by an interplay model for Ps formation, which is based on an interplay between electron affinity of polymer moiety and size of free space holes. In the CO_2-conditioned films I_3, P, D, and V_F decreased with the elapse of time, whereas τ_3 remained constant and $P_{\mathrm{CO_2}}/P_{\mathrm{CH_4}}$ increased, indicating the relaxation of polymer chain packing to a different state from the original one.

This work was supported partly by a Grand-in-Aid for Scientific Research No. 06651056 from the Ministry of Education, Science and Culture. The authors also gratefully acknowledge financial support provided by a research grant from Iketani Science and Technology Foundation (No. 042053B) and by a research grant from Ube Industries Ltd.

References

1) Y. C. Jean, "Positron and Positronium Chemistry," ed by Y. C. Jean, World Scientific, New Jersey (1990), p. 1.

2) A. D. Kasbekar, P. L. Jones, and A. Crowson, *J. Polym. Sci., Polym. Chem. Ed.*, **27**, 1373 (1989).

3) J. Liu, Q. Deng, and Y. C. Jean, *Macromolecules*, **26**, 7149 (1993).

4) Y. C. Jean and Q. Deng, *J. Polym. Sci., Polym. Phys. Ed.*, **30**, 1359 (1992).

5) A. J. Hill, P. L. Jones, J. H. Lind, and G. W. Pearsall, *J. Polym. Sci., Polym. Chem. Ed.*, **26**, 1541 (1988).

6) M. Y. Ruan, H. Moaddel, A. M. Jamieson, R. Simha, and J. D. McGervey, *Macromolecules*, **25**, 2407 (1992).

7) O. A. Hasan, M. C. Boyce, X. S. Li, and S. Berko, *J. Polym. Sci., Polym. Phys. Ed.*, **31**, 185 (1993).

8) D. W. Van Krevelen, "Properties of Polymers," Elsevier, Amsterdam (1976).

9) A. Bondi, *J. Phys. Chem.*, **68**, 441 (1964); A. Bondi, "Physical Properties of Molecular Crystals, Liquids, and Glasses," John Wiley & Sons, New York, N.Y. (1968).

10) R. N. Haward, *J. Macromol. Sci., Rev. Macromol. Chem.*, **C4**, 191 (1970).

11) K. Tanaka, M. Okano, H. Toshino, H. Kita, and K. Okamoto, *J. Polym. Sci., Polym. Phys. Ed.*, **30**, 907 (1992); K. Tanaka, H. Kita, M. Okano, and K. Okamoto, *Polymer*, **33**, 585 (1992).

12) K. Tanaka, M. Katsube, K. Okamoto, H. Kita, O. Sueoka, and Y. Ito, *Bull. Chem. Soc. Jpn.*, **65**, 1891 (1992).

13) A. G. Wonders and D. R. Paul, *J. Membr. Sci.*, **5**, 63 (1979).

14) S. M. Jordon, W. J. Koros, and G. K. Fleming, *J. Membr. Sci.*, **30**, 191 (1987).

15) J. S. Chiou and D. R. Paul, *J. Membr. Sci.*, **32**, 195 (1987).

16) H. Hachisuka, Y. Tsujita, A. Takizawa, and T. Kinoshita, *Polym. J.*, **21**, 1019 (1989).

17) K. Okamoto, K. Tanaka, T. Shigematsu, H. Kita, A. Nakamura, and Y. Kusuki, *Polymer*, **31**, 673 (1990).

18) G. K. Fleming and W. J. Koros, *Macromolecules*, **23**, 1353 (1990).

19) W. J. Koros and D. R. B. Walker, *Polym. J.*, **23**, 481 (1991).

20) T. Suzuki, Y. Ito, K. Endo, S. Fujita, Y. Masuda, and T. Egusa, *Int. J. Appl. Radiat. Isot.*, **39**, 53 (1988).

21) P. Kirkegaard, N. J. Pederson, and M. Eldrup, "PATFIT-88, Riso-M-2740."

22) R. B. Gregory, *J. Appl. Phys.*, **70**, 4665 (1990).

23) K. Tanaka, H. Kita, K. Okamoto, A. Nakamura, and Y. Kusuki, *Polym. J.*, **21**, 127 (1989); K. Tanaka, O. Yokoshi, H. Kita, and K. Okamoto, *Mem. Fac. Eng. Yamaguchi Univ.*, **38**, 277 (1988).

24) L. M. Robeson, *J. Membr. Sci.*, **62**, 165 (1991).

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

26) M. Eldrup, L. Lightbody, and J. N. Sherwood, *J. Chem. Phys.*, **63**, 51 (1984).

27) Y. Ito, K. Okamoto, and K. Tanaka, "The Proceedings of 4th International Workshop on Positron and Positronium Chemistry," Vol. 3, p. 241 (1993).

28) G. K. Fleming and W. J. Koros, *Macromolecules*, **19**, 2285 (1986).

29) K. Tanaka, H. Kita, and K. Okamoto, *J. Polym. Sci., Polym. Phys. Ed.*, **31**, 1127 (1993).

30) H. Hachisuka, T. Sato, T. Imai, Y. Tsujita, A. Takizawa, and T. Kinoshita, *Polym. J.*, **22**, 77 (1990).