Relationship Between Gas Transport Properties and Fractional Free Volume Determined from Dielectric Constant in Polyimide Films Containing the Hexafluoroisopropylidene Group

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ABSTRACT: The dielectric constant and gas transport properties (i.e., permeability, diffusivity, and solubility) in 2,2′-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA)-based polyimides were systematically investigated in terms of their polymer fractional free volumes (FFVs) at 30°C. The permeability and diffusion coefficients of the 6FDA-based polyimide films to hydrogen, oxygen, nitrogen, methane, and carbon dioxide were correlated with their FFVs estimated using van Krevelen's group contribution method. There appeared, however, small linear correlation coefficients. Linear correlations were also observed between the gas transport properties and dielectric constant of these polyimides. This study described FFV as a function of the dielectric constant based on the Clausius-Mossotti equation. It was found that the gas permeability and diffusion coefficients of these 6FDA-based polyimide films increased as their dielectric constant-based FFV increased. A better linear relationship was observed between the gas transport properties and the FFV determined from the polymer dielectric constant in comparison to that estimated using the group contribution method. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 107: 3933–3944, 2008

Key words: permeability; diffusivity; dielectric constant; polyimide; free volume

INTRODUCTION

The dielectric constant of polymer materials is a very important property in designing electric materials and is used for dielectric evaluation. A low dielectric constant is necessary for a faster signal propagation in microelectronic devices without crosstalk for new multilevel high-density and high-speed electronic circuits.[1] The dielectric constant is a relative value of the vacuum state or air. The dielectric constant, ε, of a general polymer material is larger than three.[2] If the ε value is less than three, the polymer is expected to be applied as an interlayer insulation film in large scale integration (LSI) or in integrated circuits (IC).[3] To approximate the ε value of air (i.e., ε = 1), some macro voids were purposely created in electric materials (e.g., ceramic materials and polymer materials).[4]

The permeability of small molecules is also a very important property for LSI applications. In particular, oxygen and water vapor sorbed in a film induce the change in electronic properties of insulation polymer layers; for example, the absorption of water vapor and oxygen causes an increase in the dielectric constant. Thus, in designing high-performance polymer materials with superior dielectric characteristics, it is very important to consider the relationship between its dielectric constant and gas transport properties (i.e., permeability, diffusivity, and solubility).

The polymers with a larger fractional free volume (FFV) have greater permeabilities and diffusivities. On the basis of the free-volume theory, the logarithm of the permeability and diffusion coefficients of small molecules in a polymer are linearly correlated with the reciprocal of its FFV.[5] However, it is a fact that even though polymers have the same FFVs, their gas permeabilities and diffusivities are not exactly the same each other. For instance, the carbon dioxide diffusion coefficient in various types of polymers with an FFV value of 0.18 varies from 10^{-6} to 10^{-8} cm^2/s.[6] Only in the estimates among a family of polymers, such as polycarbonates and polysulfones, do gas permeability and diffusivity provide a good correlation to their FFVs. This illustrates the limited usage of the current free-volume theory in comparison of various types of polymers.

Among polymer materials, polyimides have higher heat and chemical resistance properties. They are, therefore, widely used as electronics materials, such as overcoats of semiconductors and interlayer insula-

tion films.[7–9] Polyimides containing the 2,2′-bis(3,4-dicarboxyphenyl) hexafluoropropane dianhydride (6FDA) group have lower dielectric constant properties compared with nonfluorine polymers. Hence, the 6FDA-based polyimides have a high potential as materials in electronics applications.[1,10–12]

Matsumoto et al. reported a linear relationship between carbon dioxide permeability and dielectric constant in several polymers.[13] However, there is no physical chemistry-based linkage between mass transport and dielectric constant. Hence, this study systematically investigated the dielectric constants and permeabilities of various gases (i.e., hydrogen, oxygen, nitrogen, and methane as well as carbon dioxide) in a family of 6FDA-based polyimides in terms of their polymer FFVs. On the basis of the Clausius-Mossotti equation, we newly described the FFV of a polymer as a function of its dielectric constant. Then, we investigated the relationships between the gas transport properties (i.e., permeability, diffusivity, and solubility) and the dielectric constant-based polymer FFV.

EXPERIMENTAL

Materials

The 6FDA was obtained from Aldrich Chemical. The dianhydride was stored in a desiccator that was dried with phosphorus pentoxide and was used without further purification. The 1,3-phenylene diamine (mPD), 4-methyl-1,3-phenylene diamine (MPD), 2,4,6-trimethyl-1,3-phenylene diamine (TMPD), and 2,3,5,6-tetramethyl-1,4-phenylene diamine (TeMPD) were obtained from the Tokyo Chemical Industry. These diamines were recrystallized from some alcohols (e.g., ethanol and 2-propanol) prior to their use. Meanwhile, the solvent used in the polymerization and casting, N,N-dimethylacetoamide (DMAc), was obtained from Junsei Chemical and was dehydrated with well-dried 3A molecular sieves. Finally, the other reagents, pyridine and acetic anhydride, were obtained from the Tokyo Chemical Industry as well, and were used without further purification.

Polymer preparation

The synthesis scheme of the 6FDA-based polyimides used in this study is shown in Figure 1. These polyimides, 6FDA-mPD, 6FDA-MPD, 6FDA-TMPD, and 6FDA-TeMPD, were prepared through the two-step method followed by chemical imidization with pyridine and acetic anhydride in DMAc. The diamine and DMAc were placed in a completely dried four-necked round-bottomed flask equipped with a mechanical stirrer, a thermometer, and a nitrogen inlet-outlet system. After about half an hour of stirring, an equimolar amount of 6FDA was added to the flask. The mixture
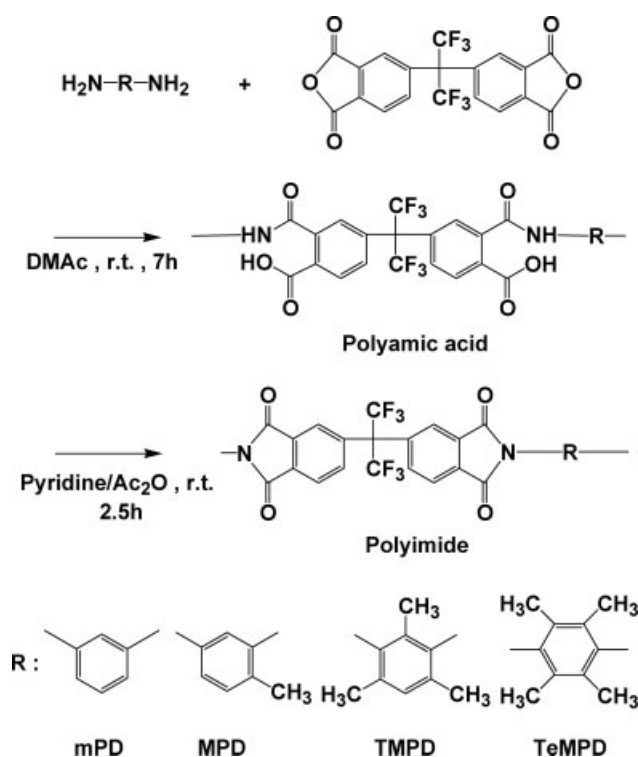

Figure 1 Synthesis and chemical structure of the 6FDA-based polyimides.

was diluted by DMAc into a solution with a concentration of 20 wt %. The solution was then stirred at room temperature for about 7 h under nitrogen, and the polyamic acid solution was obtained. Pyridine ([pyridine]/[6FDA] = 7/1) and acetic anhydride ([acetic anhydride]/[6FDA] = 5/1) were added into the polyamic acid solution as cyclodehydration catalysts. The solution was again stirred at room temperature for about 2.5 h under nitrogen.

To precipitate the product, the polyimide solution was poured into about 800 mL of methanol. The solid product was collected and dried for 72–96 h under vacuum at room temperature. After drying, the solid product was dissolved in 5.0 wt % DMF solution. The polymer solution was precipitated into about 800 mL of methanol solution and stirred for 3 h again for the extraction of residual solvents in the polymer. This solution-reprecipitation purification process was repeated three times. Any impurities could no longer be detected using ^{1}H-NMR.

The chemical structure of each product, as shown in Figure 1, was confirmed by infrared (IR) and nuclear magnetic resonance (NMR) analyses. These analyses also confirmed that the imidization was quantitatively completed, that is, there were no residual polyamic acid structures in the polyimides. 6FDA-mPD: IR (neat); 1783 cm^{-1} and 1728 cm^{-1} (C=O stretching), 1360 cm^{-1}(C—N stretching), 720 cm^{-1} (C—N defor-

mation), ^{1}H-NMR (in CDCl$_3$ with TMS); 7.46–7.66 ppm (4H, aromatic ring of mPD), 7.85–8.12 ppm (6H, aromatic ring of 6FDA). 6FDA-MPD: IR (neat); 1785 cm^{-1} and 1730 cm^{-1} (C=O stretching), 1360 cm^{-1} (C—N stretching), 722 cm^{-1} (C—N deformation), ^{1}H-NMR (in CDCl$_3$ with TMS); 2.28 ppm (3H, methyl group of MPD), 7.35–7.55 ppm (3H, aromatic ring of MPD), 7.83–8.18 ppm (6H, aromatic ring of 6FDA). 6FDA-TMPD: IR (neat); 1785 cm^{-1} and 1729 cm^{-1} (C=O stretching), 1358 cm^{-1} (C—N stretching), 724 cm^{-1} (C—N deformation), ^{1}H-NMR (in CDCl$_3$ with TMS); 1.98 ppm (3H, methyl group of TMPD), 2.22 ppm (6H, methyl group of TMPD), 7.23–7.29 ppm (1H, aromatic ring of TMPD), 7.92–8.06 ppm (6H, aromatic ring of 6FDA). 6FDA-TeMPD: IR (neat); 1784 cm^{-1} and 1724 cm^{-1} (C=O stretching), 1354 cm^{-1} (C—N stretching), 723 cm^{-1} (C—N deformation), ^{1}H-NMR (in CDCl$_3$ with TMS); 2.13 ppm (12H, methyl group of TeMPD), 7.95–8.09 ppm (6H, aromatic ring of 6FDA).

Film preparation

Isotropic, dense nonporous polyimide films were fabricated by casting a 5–8 wt % DMAc solution onto a glass petri dish and then dried under vacuum at room temperature for two weeks to gradually evaporate the solvent. These dried films were peeled off from the plate and then immersed in methanol to eliminate the mechanical stress and to completely remove residual solvents (i.e., extraction of DMAc from the films) until all experiments began. The films were dried under vacuum at 80°C for 12 h to completely remove methanol prior to use. Any solvents (i.e., DMAc and methanol) could not be detected in the films by ^{1}H-NMR analysis.

The thickness of the films used in the experiments varied from 30 to 40 μm for the permeation tests and from 110 to 115 μm for the dielectric constant measurements. Each film had an uncertainty of ±2 μm in thickness. To quantify the comparison of a series of polymers, the film preparation protocols were exactly followed.

Polymer characterization

The IR spectra were recorded with an Fourier transform infrared (FTIR) 460+ spectrometer (JASCO Tokyo Japan) at a 4.0 cm^{-1} resolution. The ^{1}H-NMR spectra were recorded at 25°C on a Bruker AVANCE-500 (500 MHz) spectrometer with CDCl$_3$ and tetramethylsilane (TMS) as solvent and internal reference, respectively. Polymer density was determined by flotation of film samples in a density gradient column at 23°C. Wide angle X-ray diffraction (WAXD) patterns were taken by a RINT1200 X-ray diffractometer (Rigaku, Tokyo Japan) with a scanning speed of

TABLE I
Physical Properties of the Gases Tested in this Study[14]

Gas	Kinetic diameter (Å)	V_c (cm^3/mol)	T_c (K)
H$_2$	2.89	65.0	33.3
CH$_4$	3.80	98.6	191
N$_2$	3.64	90.1	126
O$_2$	3.46	73.4	155
CO$_2$	3.30	94.1	304

2°/min, using Cu Kα radiation at 40 kV and 20 mA in a dispersion angle of 3–50°. The glass transition temperature (T_g) was determined with a Perkin-Elmer Pyris 1 differential scanning calorimeter (DSC) at a heating rate of 10°C/min.

Gas transport measurement

The gas transport properties of polymer films were determined by a constant volume-variable pressure method at 30°C ± 1°C. The gases employed in this study were hydrogen (H$_2$), oxygen (O$_2$), nitrogen (N$_2$), carbon dioxide (CO$_2$), and methane (CH$_4$). The physical properties of these gases are summarized in Table I.[14] The upstream pressure was maintained at about 40 cmHg. This pressure ensured no hysteresis (e.g., plasticization) during the permeation measurements of glassy polymer films with these five gases.[5] Meanwhile, the downstream pressure was maintained under vacuum. The gas permeability coefficient, P (cm^3(STP)cm/(cm^2 s cmHg)), was determined from

$$P = \frac{dp}{dt}\frac{273V}{760(273+T)}\frac{1}{A}\frac{1}{p_1}\ell \qquad (1)$$

where dp/dt is the pressure increase over time at a steady-state, V (cm^3) is the downstream volume, T (°C) is the temperature, A (cm^2) is the film area, p_1 (cmHg) is the upstream pressure, and ℓ (cm) is the film thickness.

The apparent diffusion coefficient, D (cm^2/s), was determined from time lag, θ (s), the period of time for reaching the steady state:

$$D = \frac{\ell^2}{6\theta} \qquad (2)$$

The apparent solubility coefficient, S (cm^3(STP)/(cm^3 cmHg)), can be evaluated by a solution-diffusion mechanism.

$$S = \frac{P}{D} \qquad (3)$$

Dielectric constant measurement

A thin platinum electrode (about 600 nm in thickness) was formed on each polyimide film by vapor deposition. The films were dried at room temperature for

TABLE II
Physical and Electric Properties of the
6FDA-Based Polyimides

Polyimide	Density (g/cm^3)	FFV	T_g (°C)	ε
6FDA-mPD	1.47 ± 0.01	0.162 ± 0.01	298	3.08
6FDA-MPD	1.42 ± 0.01	0.171 ± 0.01	335	2.82
6FDA-TMPD	1.36 ± 0.01	0.177 ± 0.01	380	2.59
6FDA-TeMPD	1.34 ± 0.01	0.177 ± 0.01	427	2.46

24 h before vapor deposition to eliminate the effects of moisture. The dielectric constant, ε, was determined by.

$$\varepsilon = \frac{\ell'}{\varepsilon_0 A'} \times C \qquad (4)$$

where C (F) is the electrostatic capacity, A' (m^2) is the electrode area, ℓ' (m) is the film thickness, and ε_0 (8.85 × 10^{-12} F/m) is the dielectric constant of air. The C of the polyimide films was measured by using an LCR meter (Toyo) at 1 kHz frequency, 23°C, and 55% RH.

RESULTS AND DISCUSSION

Characterizations

Table II summarizes the physical and electrical properties of the 6FDA-based polyimides. The film density of these polyimides varied from 1.34 to 1.47 g/cm^3. This density value strongly depended on the number of methyl groups in the diamine moiety. As the number of methyl groups increased, the density decreased.

The FFV can be determined by:

$$\text{FFV} = \frac{V - V_0}{V} \qquad (5)$$

where V is the polymer molar volume and V_0 is the occupied volume at 0 K. The occupied volume can be estimated from:

$$V_0 = 1.3 V_w \qquad (6)$$

where V_w is the van der Waals volume, which was calculated from the group contribution method of van Krevelen.[15] The free-volume theory for gas transport is usually applied to rubbery polymers. However, it is also applied to various families of glassy polymers, such as polycarbonates, polysulfones, and polyimides.[5] The FFV value of these polymers varied from 0.162 to 0.177. As the number of the methyl group in the diamine moiety increased from one to three, the FFV also increased. The FFV values of 6FDA-TMPD and 6FDA-TeMPD were the same for both types of polymers.

The WAXD patterns of the 6FDA-based polyimide films are presented in Figure 2. One broad halo appeared in all films, indicating that all polyimide films were completely amorphous. The 2θ value in a polymer film showed a distance between its polymer segments. In this regard, the 6FDA-based polyimide films had a wide distribution in the distance between polymer segments, which could contribute to gas diffusion in a film. In general, the *d*-spacing value is estimated as the distance between polymer segments on the basis of the maximum 2θ intensity value. However, as is evident from Figure 2, it was difficult for these 6FDA-based polyimide films to accurate indication of the maximum 2θ intensity value.

The T_g value was much higher than the temperature employed in all the permeation and dielectric constant measurements. The T_g value of 6FDA-mPD was 298°C. As the number of the methyl group in the diamine moiety increased, the T_g value also increased. The addition of four methyl groups provided an increase of 129°C in T_g. Thus, it seemed that the methyl groups restricted the mobility of polymer segments.

Gas transport properties

The gas permeation properties in the 6FDA-based polyimides were determined in a glassy state. In general, the gas permeation properties in glassy polymer films are strongly affected by film preparation procedures (e.g., solvent, solvent evaporating speed) and permeation test conditions (e.g., feed gas pressure, ex-
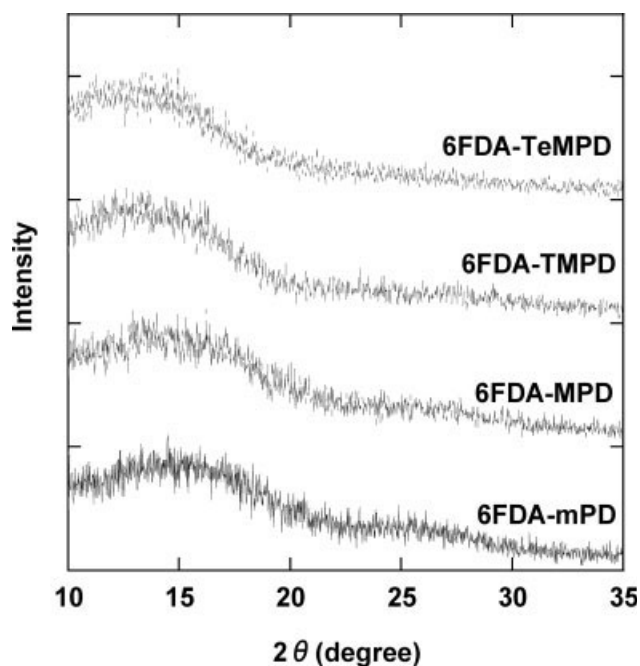

Figure 2 Wide-angle X-ray diffraction patterns of the 6FDA-based polyimide films.

TABLE III
Permeability (*P*), Diffusion (*D*), and Solubility (*S*) Coefficients in the
6FDA-Based Polyimides at 30°C

Polyimide	Gas	$P \times 10^{10}$ $(cm^3(STP)cm/$ $(cm^2 \, s \, cmHg))$	$D \times 10^8$ (cm^2/s)	$S \times 10^2$ $(cm^3(STP)/$ $(cm^3 \, cmHg))$
6FDA-mPD	H_2	43	–	–
	O_2	3.1	2.3	1.3
	N_2	0.47	0.41	1.1
	CO_2	12	0.30	40
	CH_4	0.18	0.046	3.9
6FDA-MPD	H_2	63	–	–
	O_2	6.7	5.0	1.3
	N_2	1.2	1.0	1.2
	CO_2	43	0.99	43
	CH_4	0.92	0.22	4.2
6FDA-TMPD	H_2	239	–	–
	O_2	46	22	2.1
	N_2	11	6.5	1.7
	CO_2	309	5.2	59
	CH_4	9.8	1.8	5.4
6FDA-TeMPD	H_2	529	–	–
	O_2	130	52	2.5
	N_2	31	15	2.1
	CO_2	615	9.9	62
	CH_4	28	4.2	6.7

perimental temperature). Even though several permeation data were already reported for various 6FDA-based polyimides,[16–18] their values were slightly different from each other. Hence, the gas permeability, diffusion, and solubility coefficients of various gases in the four 6FDA-based polyimide films were systematically determined at the same experimental conditions and summarized in Table III.

As previously explained, based on the solution-diffusion mechanism, gas permeability is the product of gas solubility and gas diffusivity. Gas solubility is correlated with gas condensability. On the basis of the systematic data in this table, the ranking of the gas solubility coefficients in the 6FDA-based polyimide films was $CO_2 > CH_4 > O_2 > N_2$. This is the same order as the critical temperature, T_c, in Table I, which is a measure of gas condensability. The gas with a higher T_c dissolved in these polymers more than the gas with a lower T_c.

Gas diffusivity depends on gas size. The kinetic diameter indicates the diameter of the smallest cross section of a gas molecule, while the critical volume shows the average size of a gas molecule considering its three-dimensional structure. The ranking of the gas diffusion coefficient was $O_2 > N_2 > CO_2 > CH_4$. This is the same order as the critical volume, V_c, as shown in Table I. This is probably because gas diffusion among polymer segments depended on both the size of the cross section of a gas molecule and the distance of the diffusion pass.

As a result, the ranking of the gas permeability coefficients was $H_2 > CO_2 > O_2 > N_2 > CH_4$ for 6FDA-mPD and 6FDA-MPD films and $CO_2 > H_2 > O_2 > N_2 > CH_4$ for 6FDA-TMPD and 6FDA-TeMPD films. These orders were provided by a combination of the solubility and diffusivity factors.

As the number of the methyl side chain groups in the diamine moiety increased, the gas permeability, diffusion, and solubility coefficients increased. The ranking of their gas permeabilities, diffusivities, and solubilities was 6FDA-TeMPD > 6FDA-TMPD > 6FDA-MPD > 6FDA-mPD. On the basis of the free-volume theory, the gas permeability, diffusion, and solubility coefficients are plotted as a function of the reciprocal FFVs as presented in Figure 3. As expected, overall the gas permeability and diffusion coefficients increased as the FFV increased. The gas solubility coefficient also increased slightly as the FFV increased.

The free-volume theory provides gas permeability, diffusivity, and solubility as a function of FFV:[19,20]

$$P = A_{\mathrm{P}} \exp\left(\frac{-B_{\mathrm{P}}}{\mathrm{FFV}}\right) \qquad (7)$$

$$D = A_{\mathrm{D}} \exp\left(\frac{-B_{\mathrm{D}}}{\mathrm{FFV}}\right) \qquad (8)$$

$$S = A_{\mathrm{S}} \exp\left(\frac{-B_{\mathrm{S}}}{\mathrm{FFV}}\right) \qquad (9)$$

where A_p, A_D, A_S, B_p, B_D, and B_S are adjustable constants. The free-volume theory was initially proposed for gas diffusion. A_D and B_D are inherent diffusion pa-
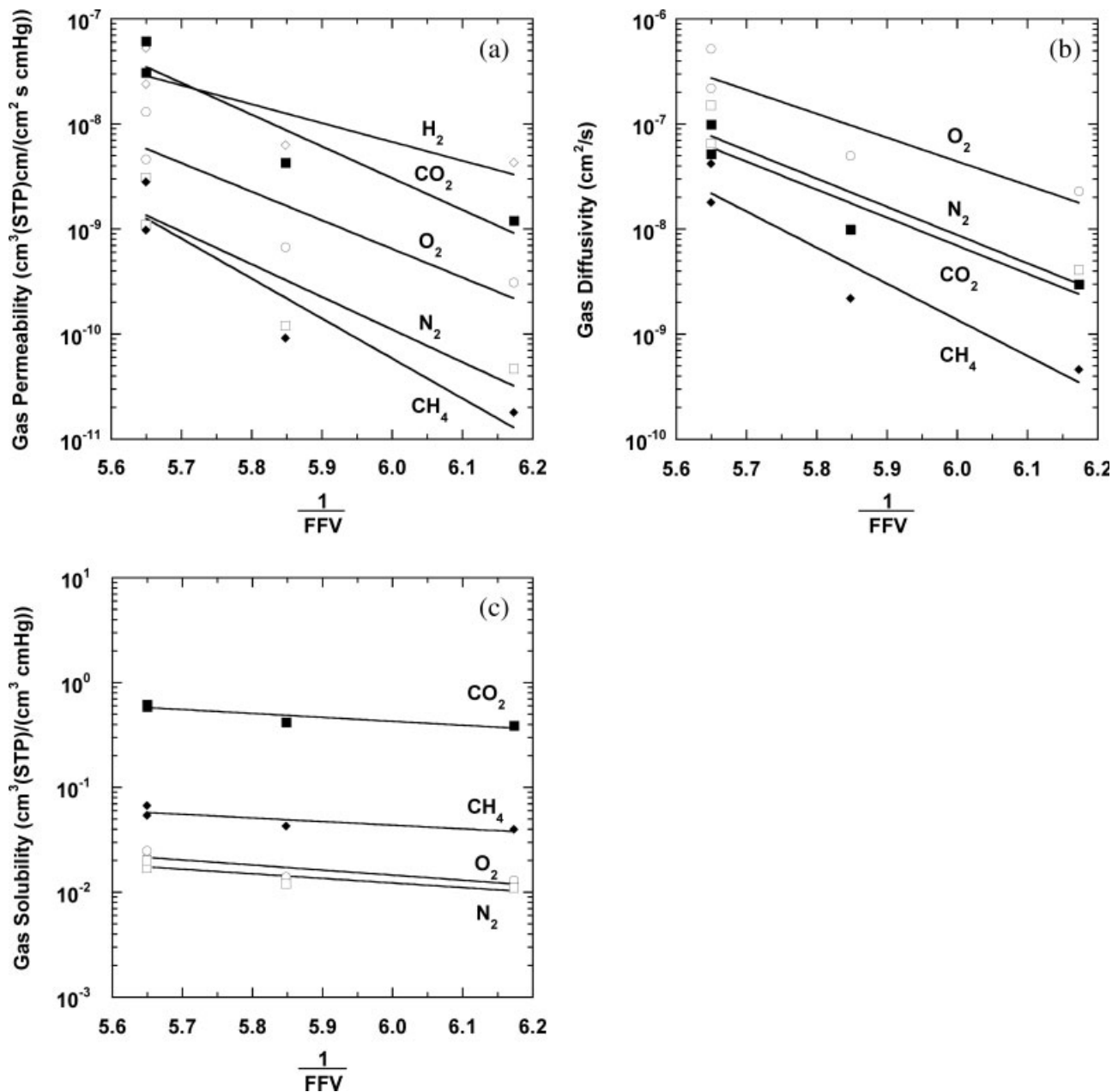
Figure 3 Permeability (a), diffusivity (b), and solubility (c) of various gases at 30°C in the 6FDA-based polyimides as a function of reciprocal fractional free volume (1/FFV). Gases; hydrogen ($\diamond$), nitrogen ($\square$), oxygen ($\bigcirc$), methane ($\blacklozenge$), carbon dioxide ($\blacksquare$).

TABLE IV
Parameter A_P and B_P in eq. (7)[a]

Gas	Temperature (°C)	Upstream pressure	Number of polymers	A_P (cm^3(STP) cm/(cm^2 s cmHg))	B_P	Liner correlation coefficient (r^2)	Reference
CO$_2$	30	40 cmHg	4	4.20×10^9	6.96	0.888	This study
CO$_2$	35	10 atm	181	2.41×10^5	1.62	0.802	6
CH$_4$	30	40 cmHg	4	3.92×10^{12}	8.75	0.815	This study
CH$_4$	35	10 atm	158	2.85×10^3	1.43	0.720	6
N$_2$	30	40 cmHg	4	4.69×10^8	7.15	0.810	This study
N$_2$	35	2 atm	121	4.32×10^4	1.88	0.929	6
O$_2$	30	40 cmHg	4	1.40×10^7	6.26	0.801	This study
H$_2$	30	40 cmHg	4	3.88×10^2	4.13	0.821	This study

[a] There values were determined from the least-squares fit analyses in Figure 3(a).

TABLE V
Parameter A_D and B_D in eq. (8)[a]

Gas	Temperature (°C)	Upstream pressure	Number of polymers	A_D (cm²/s)	B_D	Liner correlation coefficient (r^2)	Reference
CO_2	30	40 cmHg	4	7.15×10^7	6.14	0.892	This study
CO_2	35	10 atm	162	4.90×10^3	1.21	0.675	6
CH_4	30	40 cmHg	4	5.77×10^{11}	7.92	0.856	This study
CH_4	35	10 atm	144	3.26×10^2	1.11	0.609	6
N_2	30	40 cmHg	4	1.17×10^8	6.19	0.846	This study
N_2	35	2 atm	101	1.53×10^2	1.19	0.722	6
O_2	30	40 cmHg	4	1.83×10^6	5.23	0.823	This study

[a] There values were determined from the least-squares fit analyses in Figure 3(b).

rameters which are correlated with the penetrant size and shape. However, these parameters have not been clearly discussed so far. One reason is that although there are varieties of measures of gas size and shape, the optimum measure of the penetrant size and shape has not been defined for this theory. Other parameters, A_p, A_S, B_p, and B_S might be also correlated with the penetrant size and shape. However, like A_D and B_D, these parameters have not been discussed in details.

On the basis of the least-squares fit analysis in Figure 3, the A_p, A_D, A_S, B_p, B_D, and B_S values for each gas are summarized in Tables IV–VI. So far, the gas solubility coefficients have been rarely discussed with FFV and it is very difficult to compare values among the literature. Kanehashi and Nagai reported these types of relationships for gas permeation and diffusion in more than 100 glassy polymers.[6] These 6FDA-based polyimides were filed in the same group, which indicated that these polyimides showed the common permeation properties.

Many sample numbers provided large uncertainties and the smallest linear correlation coefficient r^2 was 0.720 for CH_4 in eq. (7) and 0.609 for CH_4 in eq. (8) On the basis of this literature, although polymers have similar FFVs, their gas permeabilities and diffusivities are sometimes different by two orders of magnitude.[6] This indicates the limited usage of the current free-volume theory in comparing various types of polymers. This fact would result to an existence of a distribution of the size and volume of free-volume elements. In a polymer family (e.g., polysulfone), the linear correlation coefficient for gas permeability and diffusivity tends to be a larger value. Even though the number of polymers is four in the 6FDA-based polyimides, the r^2 value was around 0.8. The main reason is that the 6FDA-TeMPD and 6FDA-TMPD films have the same FFV value of 0.177, but their permeability and diffusivity values are different from each other. This result suggests a difference in the size/volume distribution of the FFV elements between these two polyimides, producing a smaller linear correlation coefficient. In fact, as previously mentioned, a wide distribution of the distance between polymer segments appeared in the WAXD patterns in Figure 2.

Relationship between gas transport properties and dielectric constant

The ε value of the 6FDA-based polyimides varied from 2.46 to 3.08 in Table II. As the number of the methyl group in the diamine moiety increased, the ε value decreased. Matsumoto et al. reported a linear relationship between carbon dioxide permeability and dielectric constant in several polymers.[13] Figure 4 presents the gas permeability, diffusion, and solubility coefficients of the 6FDA-based polyimides as a function of the dielectric constant. For the 6FDA-based polyimides, linear relationships also appeared among the gas permeability, diffusivity, and solubility of hydrogen, oxygen, nitrogen, and methane as well as carbon dioxide.

Unfortunately, there is no physical chemistry-based linkage between mass transport and dielectric constant. Hence, we described FFV as a function of the dielectric constant based on the Clausius-Mossotti equation, and investigated the relationships between gas transport properties and the dielectric constant-based polymer FFV. Equation (10) is derived from the Clausius-Mossoti equation, which is used to calculate the dielectric constant of a polymer material.[15]

$$\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{P_{LL}}{V} \qquad (10)$$

where P_{LL} is the molar polarization (cm³/mol) and V is the polymer molar volume (cm³/mol). When polymer samples are isotropic dense homopolymer films

TABLE VI
Parameter A_S and B_S in eq. (9) at 30°C[a]

Gas	A_S (cm³(STP)/ (cm³ cmHg))	B_S	Liner correlation coefficient (r^2)
CO_2	73.7	0.86	0.914
CH_4	5.22	0.80	0.829
N_2	5.26	1.01	0.882
O_2	11.4	1.11	0.875

[a] There values were determined from the least-squares fit analyses in Figure 3(c). The number of polymers was 4.
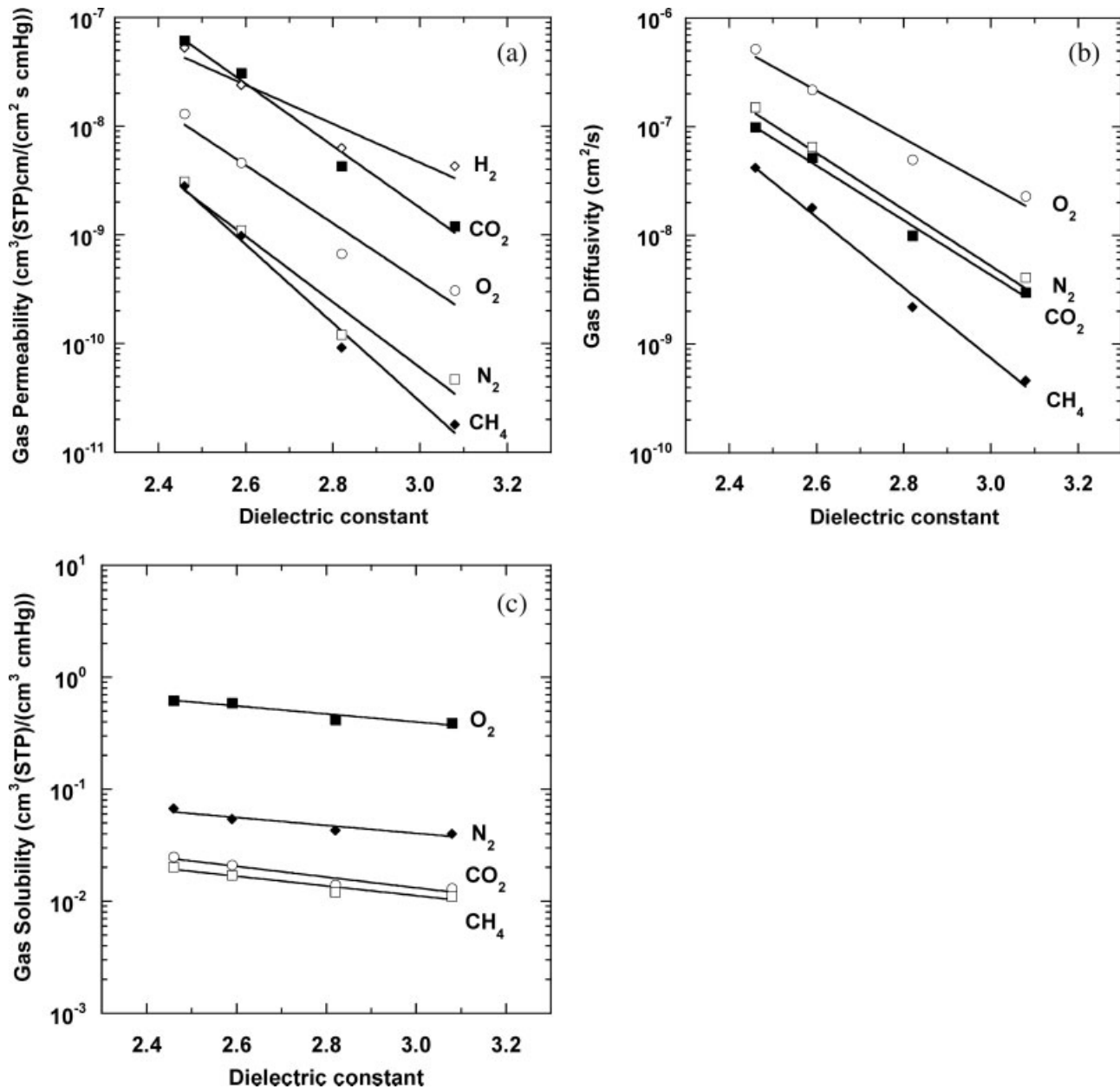
Figure 4 Permeability (a), diffusivity (b), and solubility (c) of various gases at 30°C in the 6FDA-based polyimides as a function of the dielectric constant. Gases; hydrogen ($\diamondsuit$), nitrogen ($\square$), oxygen ($\bigcirc$), methane ($\blacklozenge$), carbon dioxide ($\blacksquare$).

without any additives, the V in eq. (5) is equal to the V in eq. (10). Hence, eq. (5) can be rewritten in eq. (11) as a function of ε.

$$\text{FFV} = 1 - \alpha \quad \alpha = 1.3 \frac{V_{\text{w}}}{P_{\text{LL}}} \frac{\varepsilon - 1}{\varepsilon + 2} \tag{11}$$

Equations (7–9) can be described with eq. (11) as a function of the dielectric constant-based FFV, $1-\alpha$

$$P = \gamma_P \exp\left(\frac{-\beta_P}{1 - \alpha}\right) \tag{12}$$

$$D = \gamma_D \exp\left(\frac{-\beta_D}{1 - \alpha}\right) \tag{13}$$

$$S = \gamma_S \exp\left(\frac{-\beta_S}{1 - \alpha}\right) \tag{14}$$

where γ_P, γ_D, γ_S, β_P, β_D, and β_S are adjustable constants.

Figure 5 presents the gas permeability, diffusion, and solubility coefficients in the 6FDA-based polyimides as a function of the reciprocal of $1-\alpha$. As the $1-\alpha$ value increased, their gas permeability and diffusivity values also increased. Their gas solubility showed a slight increase with the increase in $1-\alpha$ value. A better linear relationship between the gas transport properties and the reciprocal of $1-\alpha$ was observed as compared to the data in Figure 3.
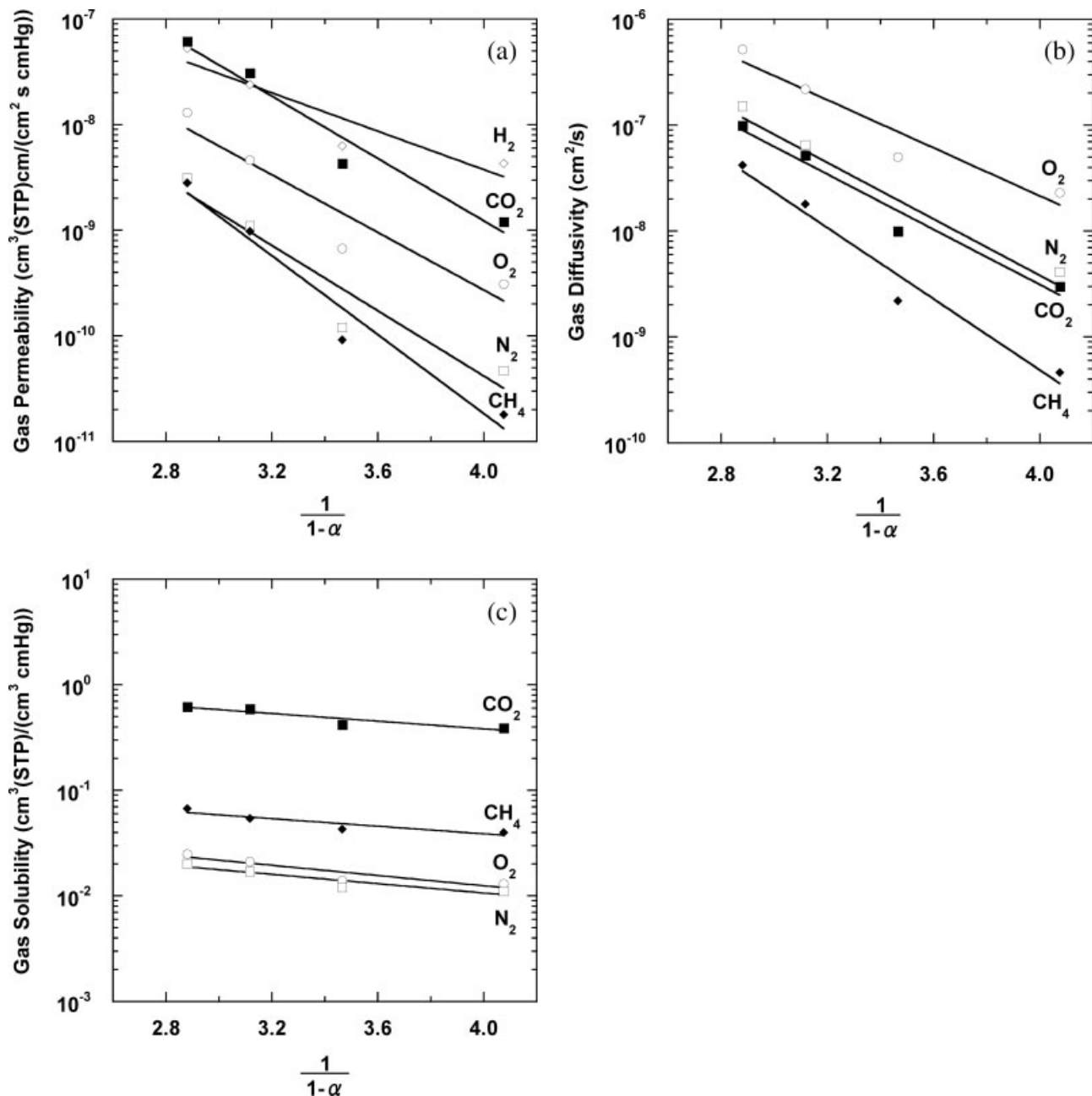
Figure 5 Permeability (a), diffusivity (b), and solubility (c) of various gases at 30°C in the 6FDA-based polyimides as a function of reciprocal $1-\alpha$. Gases; hydrogen ($\diamond$), nitrogen ($\square$), oxygen ($\bigcirc$), methane ($\blacklozenge$), carbon dioxide ($\blacksquare$).

Like in Figure 3, based on the least-squares fit analysis in Figure 5, the γ_P, γ_D, γ_S, β_P, β_D, and β_S values for each gas are summarized in Tables VII–IX. The r^2 value of all parameters was found to be greater than 0.92. The β_P value (i.e., slope of the lines) for each gas was 3.40 for CO_2, 4.30 for CH_4, 3.56 for N_2, 3.14 for O_2, and 2.09 for H_2. These values were similar for the different gases. The difference in β_P among these gases was much smaller than that in γ_P (i.e., intercept of the lines). In Table VII, for example, the largest value was 9.85×10^{-4} for CO_2, and the smallest one was 1.62×10^{-5} for H_2. Therefore, differences in the

permeability values in the 6FDA-based polyimides resulted from the γ_P values. The β_D values were 3.00 for CO_2, 3.87 for CH_4, 2.72 for N_2, and 2.61 for O_2. These values were similar for the different gases. In the case of γ_D, the largest value was 5.11×10^{-4} for CO_2, and the smallest one was 7.37×10^{-5} for O_2. Hence, the differences in diffusivity in the 6FDA-based polyimides resulted from the γ_D values. Like permeability and diffusivity, the β_S values were similar to each other; 0.42 for CO_2, 0.41 for CH_4, 0.51 for N_2, and 0.56 for O_2. In Table IX, the largest value of γ_S was 2.04 for CO_2, and the smallest one was 0.081 for

TABLE VII
Parameter γ_P and β_P in eq. (12) at 30°C[a]

Gas	γ_P (cm^3(STP)cm/ (cm^2 s cmHg))	β_P	Liner correlation coefficient (r^2)
CO_2	9.85×10^{-4}	3.40	0.994
CH_4	5.47×10^{-4}	4.30	0.999
N_2	6.32×10^{-5}	3.56	0.995
O_2	7.79×10^{-5}	3.14	0.989
H_2	1.62×10^{-5}	2.09	0.975

[a] There values were determined from the least-squares fit analyses in Figure 5(a). The number of polymers was 4.

TABLE IX
Parameter γ_S and β_S in eq. (14) at 30°C[a]

Gas	γ_S (cm^3(STP)/(cm^3 cmHg))	β_S	Liner correlation coefficient (r^2)
CO_2	2.04	0.42	0.936
CH_4	0.20	0.41	0.925
N_2	0.081	0.51	0.946
O_2	0.12	0.56	0.941

[a] There values were determined from the least-squares fit analyses in Figure 5(c). The number of polymers was 4.

N_2. Hence, the differences in solubility in the 6FDA-based polyimides resulted from the γ_S values.

Table X summarizes the group contribution-based FFV in eq. (5) and the dielectric constant-based FFV, $1-\alpha$ in eq. (11) in the 6FDA-based polyimides. The $1-\alpha$ values of the 6FDA-based polyimides were 1.6 (1.6–2.2 times larger than their FFV values. As expected from eq. (5), the FFV was mainly dependent only on the free-volume space in a film. On the other hand, the $1-\alpha$ (i.e., FFV determined from eq. (11)) was dependent on free-volume space and electric factors such as molar polarization, which affected the interactions between the gas molecules and the polymer segments. This factor would provide a more actual adjustment for gas transport in a free volume of a polymer film in a comparison among a family of polymers.

As previously mentioned, the parameters, A_p, A_D, A_S, B_p, B_D, and B_S, of the free-volume theory are thought to be correlated with only the penetrant size and shape. Although there are varieties of measures of gas size and shape, the optimum measure of the penetrant size and shape has not been defined for this theory. In fact, the orders of the parameter values in Tables IV–VI were not correlated with that of kinetic diameter or critical volume, V_c.

On the basis of the results in Table X, the parameters, γ_P, γ_D, γ_S, β_P, β_D, and β_S, were not simply dependent on the penetrant size and shape. The order of these parameters was not correlated with that of kinetic diameter or V_c, because these parameters were

also affected by the interactions between the gas molecules and the polymer segments. One of the measures of such interactions is critical temperature, T_c.[14,15] As previously discussed in Table III, V_c was a better measure of penetrant size than kinetic diameter. Therefore, the $V_c T_c$ value is used as a simple measure of the combined factors of the penetrant size and shape and the interactions.

The γ_P, γ_D, and γ_S are plotted as a function of $V_c T_c$ in Figure 6. The β_P, β_D, and β_S are not presented in the figure, because, as previously explained, these values were similar to each other, indicating that they were independent on any penetrant properties. The linear correlation coefficient r^2 was greater than 0.93 for the permeability, diffusivity, and solubility in Figure 6. As is evident from this figure, the logarithm of γ_P, γ_D, and γ_S increased linearly with an increase in $V_c T_c$ (i.e., an increase in the combined factors of the penetrant size and shape and the interactions). This result suggests that these parameters are the inherent transport parameters which are combined with several penetrant properties such as the penetrant size and shape and the interactions.

CONCLUSION

The dielectric constant and gas transport properties (i.e., permeability, diffusivity, and solubility) in the 6FDA-based polyimides were systematically investigated in terms of their polymer FFVs at 30°C. On the basis of Clausius-Mossottii equation, we newly described the permeability, diffusivity, and solubility

TABLE VIII
Parameter γ_D and β_D in eq. (13) at 30°C[a]

Gas	γ_D (cm^2/s)	β_D	Liner correlation coefficient (r^2)
CO_2	5.11×10^{-4}	3.00	0.995
CH_4	2.54×10^{-4}	3.87	0.997
N_2	8.09×10^{-5}	2.72	0.994
O_2	7.37×10^{-5}	2.61	0.988

[a] There values were determined from the least-squares fit analyses in Figure 5(b). The number of polymers was 4.

TABLE X
FFV Values Determined from the Group Contribution Method and the Dielectric Constant of the 6FDA-Based Polyimides

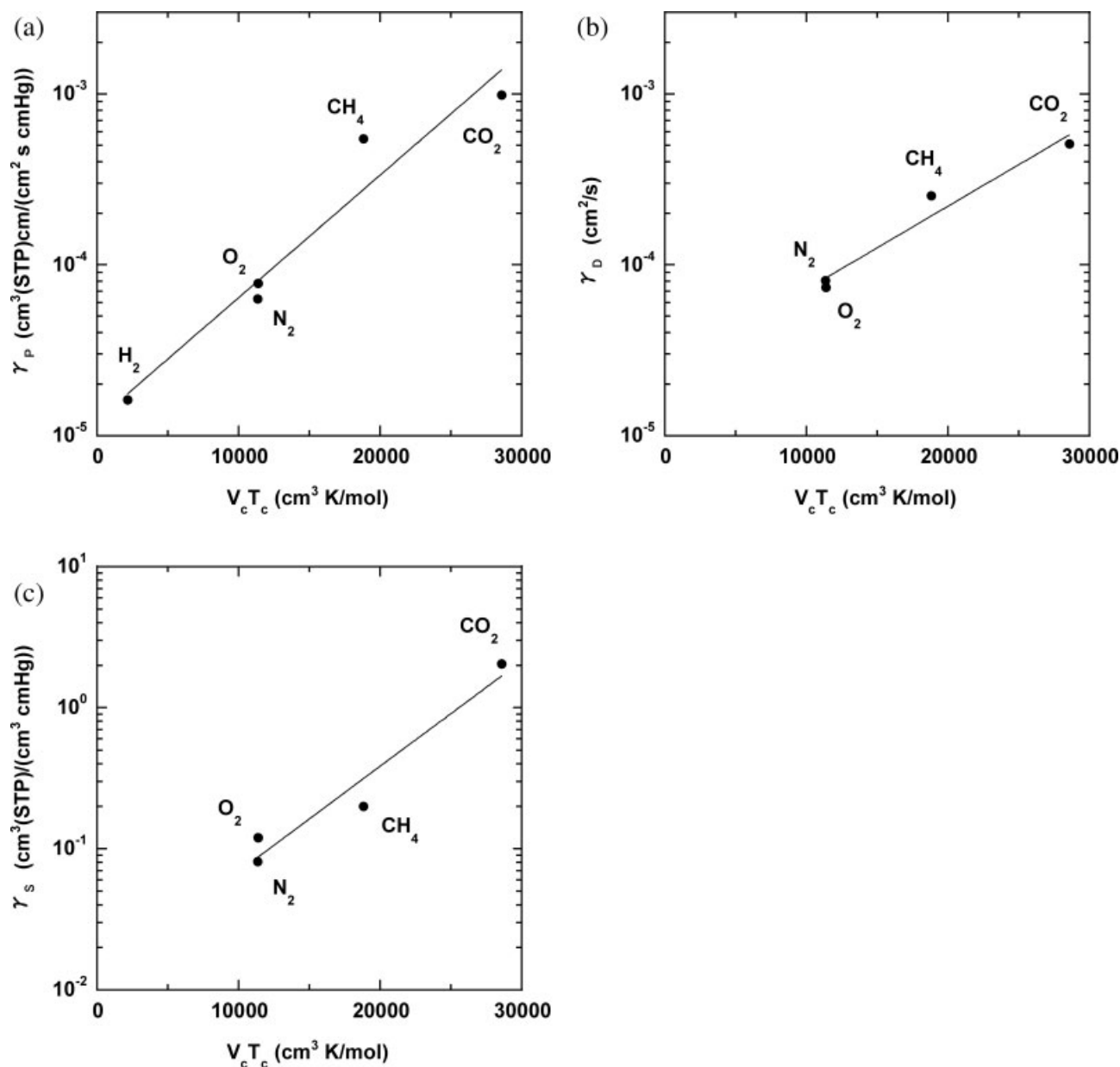| Polyimide	FFV from eq. (5)	$1-\alpha$ from eq. (11)
6FDA-mPD	0.162	0.263
6FDA-MPD	0.171	0.293
6FDA-TMPD	0.177	0.347
6FDA-TeMPD	0.177	0.381

Figure 6 Parameter γ_P (a), γ_D (b), and γ_S (c) at 30°C in the 6FDA-based polyimides as a function of V_cT_c of gases.

as a function of the FFV determined from dielectric constant. It was found that the gas permeability and diffusion coefficients of these 6FDA-based polyimide films increased as their dielectric constant-based FFV increased. A better linear relationship was observed between the gas transport properties and the FFV determined from the polymer dielectric constant in comparison to that estimated using the group contribution method. This free-volume model considered the interactions between the gas molecules and the polymer segments. This factor would provide a more actual adjustment for gas transport in a free volume of a polymer film in a comparison among a family of polymers.

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