Relationship Between the Gas Transport Properties and the Refractive Index in High-Free-Volume Fluorine-Containing Polyimide Membranes

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ABSTRACT: The refractive index and gas transport properties (i.e., permeability, diffusivity, and solubility) in the 2,2′-bis(3,4-dicarboxyphenyl) hexafluoropropane dianhydride (6FDA)-based polyimides were systematically investigated in terms of their polymer fractional free volumes (FFVs). The permeability and diffusion coefficients of the 6FDA-based polyimide membranes to hydrogen, oxygen, nitrogen, methane, and carbon dioxide were correlated with their FFVs, which were estimated with van Krevelen's group contribution method. Linear correlations were also observed between the gas transport properties and the refractive index of these polyimides. We described FFV as a function of the refractive index based on the Lorentz–Lorenz equation. Linear correlations were observed between their refractive-index-based FFVs and the gas permeability, diffusivity, and solubility coefficients of these 6FDA-based polyimides membranes. However, the FFVs of the 6FDA-based polyimides calculated from refractive index were 1.16–1.37 times larger than their FFV values. This FFV was dependent on the free-volume space and optical factors, such as the refractive index and molar refraction, which affected the electronic structure and the interactions between the gas molecules and the polymer segments. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 121: 2794–2803, 2011

Key words: diffusion; films; gas permeation; polyimides; refractive index

INTRODUCTION

The optical properties of polymer materials are very important in designing optic devices. Amorphous transparent polymer components are indispensable for such applications because they are used for the manufacture of optical fibers,[1] compact discs,[2] and display materials.[3] As a factor contributing to transparency, the reflection/absorption/dispersion properties of photons are necessary for designing polymer materials for optics, particularly, for the development of antireflection films that possess surfaces that are able to prevent optical reflection from the outside. The material characteristic of reflectance is important in next-generation displays. The effect of reflectance on the refractive index of materials may be evaluated by Fresnel's equation:[4]

$$R = \left(\frac{n-1}{n+1}\right)^2 \quad (1)$$

where R is the reflectance and n is the refractive index of the materials. A low refractive index is necessary for next-generation antireflection films. The refractive index is the ratio of the velocity of the photon in the vacuum and material. In material properties, this is the standard of diffusivity of the photon. The refractive index is one of the important parameters for clarifying the material structure.[5]

The permeability of small molecules is also a very important property for next-generation antireflection films for preventing material degradation (e.g., oxidation) caused by air exposure during use. The barrier properties of carbon dioxide (CO_2) are necessary for packing materials. In designing antireflection films, consideration of the relationship between its refractive index and its gas transport properties (i.e., the permeability, diffusivity, and solubility) is crucial. However, there is no physical chemistry-based linkage between the mass transport and the refractive index.

Among polymer materials, polyimides have higher heat and chemical resistance properties; thus, they are widely used as electronics materials, such as in overcoats of semiconductors and interlayer insulation films. The refractive index of general polyimides is more than 1.6, and Kapton is 1.78.[6–9] However, fluorine-containing polyimides are expected to show

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higher heat resistances and lower dielectric constants and refractive indices. The fluorine atom has a high electronegativity, whereas the C—F combination has a high binding energy and a low polarizability. Thus, fluorine-containing polyimides have high potential as materials in electronic applications.[10,11] Furthermore, the fractional free volume (FFV), which is the standard of the space between polymers segments, increases with the introduction of substituents that have a high volume among atoms, such as fluorine atoms.

Polymers with higher FFVs have greater permeabilities and diffusivities. On the basis of the free-volume theory, the logarithm of the permeability and the diffusion coefficients of small molecules in a polymer is linearly correlated with the reciprocal of its FFV.[12] However, although polymers have the same FFVs, their gas permeabilities and diffusivities are not identical. This is one of the reasons FFV is calculated with the group contribution method. For instance, the CO_2 diffusion coefficients in various types of polymers with an FFV value of 0.18 vary from 10^{-6} to 10^{-8} cm^2/s.[13]

Hence, in this study, we systematically investigated the refractive index and permeabilities of various gases (i.e., hydrogen, oxygen, nitrogen, methane, and CO_2) in a family of 2,2′-bis(3,4-dicarboxyphenyl) hexafluoropropane dianhydride (6FDA)-based polyimides in terms of their FFVs. On the basis of the Lorentz–Lorenz equation, the FFV of the polymer as a function of its refractive index is described. The relationship between the gas transport properties (i.e., permeability, diffusivity, and solubility) and the refractive index-based polymer FFV was also investigated.

EXPERIMENTAL

Membrane preparation

The chemical structure of each product, as shown in Figure 1, was confirmed by IR and NMR analyses. The 6FDA-based polyimides were 6FDA–1,3-phenylene diamine (mPD), 6FDA–4-methyl-1,3-phenylene diamine (MPD), 6FDA–2,4,6-trimethyl-1,3-phenylene diamine (TMPD), and 6FDA–2,3,5,6-tetramethyl-1,4-phenylene diamine (TeMPD).

The 6FDA-based polyimides membranes used in this research were the same samples that we used in a previous study.[14] We fabricated isotropic, dense, nonporous polyimide membranes by casting a 5–8 wt % *N,N*-dimethylacetamide (DMAc) solution onto a glass Petri dish and then drying it *in vacuo* at room temperature for 2 weeks to gradually evaporate the solvent. These dried membranes were peeled off of 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 membranes) until all of the experiments began. The films were dried *in vacuo* at 80°C for 12 h to completely remove methanol before use. No solvent (i.e., DMAc or methanol) could be detected in the membranes by ^{1}H-NMR analysis. The thickness of the membranes varied from 30 to 40 μm for permeation tests, with an uncertainty of ±2 μm. To quantify the comparison of a series of polymers, the membrane preparation protocols were followed exactly.

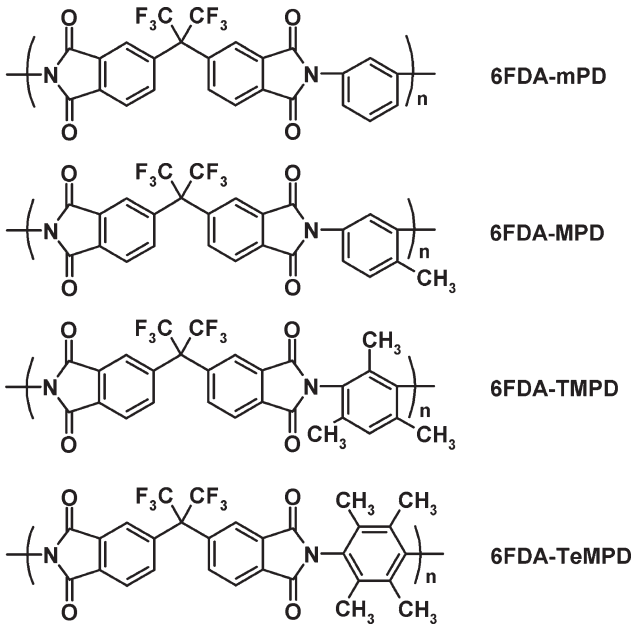

Figure 1 Chemical structures of the fluorine-containing polyimides: 6FDA–mPD, 6FDA–MPD, 6FDA–TMPD, and 6FDA–TeMPD.

Membrane characterization

All of the characterization data were determined in the membrane state for at least three samples to confirm the reproducibility of the experimental results. The membrane density was determined by flotation of the small membrane samples in a density gradient column, which was maintained at 23 ± 1°C. FFV is given by the following equation:

$$\mathrm{FFV} = \frac{V_t - 1.3V_W}{V_t} \tag{2}$$

where V_t is the polymer specific volume and V_W is the van der Waals volume, which is calculated from the group contribution method of van Krevelen.[4]

The thermal analysis data were measured with a Diamond DSC differential scanning calorimeter (PerkinElmer, Inc., Shelton, Nebraska, United State) at a heating rate of 10°C/min.

Wide-angle X-ray diffraction measurements were performed on a Rint 1200 X-ray diffractometer (Rigaku, Co., Ltd., Tokyo, Japan) with a Cu Kα radiation source. The wavelength of the radiation was

1.54 Å, and the maximum intensity in the halo peak was 2θ.

Gas transport measurement

The gas permeability coefficient [*P;* cm^3(STP)cm/(cm^2 s cmHg)] of each membrane was determined by a constant volume-variable pressure method at 30 ± 1°C, which was described in the previous study.[14] The gases used in this study were hydrogen (H_2), oxygen (O_2), nitrogen (N_2), CO_2, and methane (CH_4). The upstream pressure was maintained at about 40 cmHg, whereas the downstream pressure was maintained *in vacuo.* The apparent diffusion coefficient [*D* (cm^2/s)] was determined from time lag method. Finally, the apparent solubility coefficient [*S* (cm^3(STP)/(cm^3 cmHg)] was evaluated by a solution–diffusion mechanism (i.e., $S = P/D$). Because the time lag of only hydrogen was shorter, which made it difficult to detect with high accuracy, hydrogen was omitted from the diffusion and solubility coefficients.

Optical property measurement

Refractive index measurements were performed on a UVISEL ellipsometer (Jobin Yvon S. A. S., Longjumeau, France) at 23 ± 1°C. The Abbe number (v_D) is given by the following equation:[15]

$$\nu_D = \frac{n_D - 1}{n_F - n_c} \tag{3}$$

where n_D is the refractive index at 589 nm, n_F is the refractive index at 486 nm, and n_C is the refractive index at 656 nm. All of the optical properties were determined for at least three samples to ensure reproducibility of the experimental results.

RESULTS AND DISCUSSION

Membrane characterization

The density (ρ) values of the isotropic, dense nonporous 6FDA–mPD, 6FDA–MPD, 6FDA–TMPD, and 6FDA–TeMPD polyimide membranes were 1.47, 1.42, 1.36, and 1.34 g/cm^3, respectively. The FFV values of the 6FDA–mPD, 6FDA–MPD, 6FDA–TMPD, and 6FDA–TeMPD polyimide membranes determined from eq. (2) were 0.162, 0.171, 0.177, and 0.177, respectively. The glass-transition temperature values of the 6FDA–mPD, 6FDA–MPD, 6FDA–TMPD, and 6FDA–TeMPD polyimide membranes were 298, 335, 380, and 427°C, respectively. The glass-transition temperature value was much higher than the temperature used in all of the permeation measurements. Under the gas permeation conditions, all of the 6FDA-based polyimides were glassy and completely amorphous.

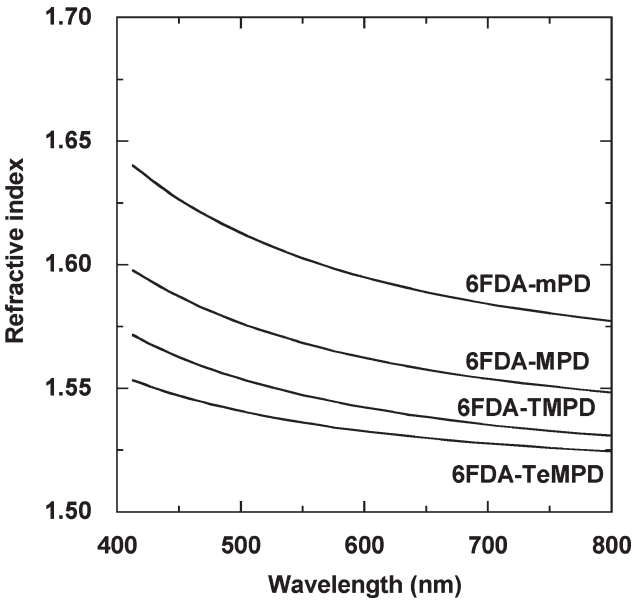

Figure 2 Wavelength dispersion of the refractive index for various polyimides: 6FDA–mPD, 6FDA–MPD, 6FDA–TMPD, and 6FDA–TeMPD.

The wavelength dispersions of the refractive index of the 6FDA-based polyimides in this study are shown in Figure 2. As the wavelength increased, the refractive index decreased. In the whole range of wavelength, the ranking of the refractive index was 6FDA–mPD > 6FDA–MPD > 6FDA–TMPD > 6FDA–TeMPD. The n_F, n_D, n_C, and v_D values of the 6FDA-based polyimides, other polyimides, and general polymers are summarized in Table I.[6–9,15,16] As the number of methyl side-chain groups in the diamine moiety increased, the refractive index decreased from 1.616 to 1.543 for n_F, from 1.598 to 1.534 for n_D, and from 1.589 to 1.530 for n_C. Additionally, the v_D value increased from 22.13 to 41.14 as the number of methyl side-chain groups in the diamine moiety increased. The refractive index of the nonfluorine polyimides showed values from 1.595 to 1.78. Hence, polyimides containing the 6FDA group had lower refractive index properties compared with the nonfluorine polyimides.

v_D as a function of the refractive index (n_D) of 6FDA-based polyimides and general polymers is presented in Figure 3. The n_D of the 6FDA-based polyimide in this study showed the error of the value determined from at least three samples. Generally, as the refractive index increased, v_D decreased. Moreover, a linear correlation between the refractive index and v_D was also observed.[7,16] As is evident from Figure 3, the relationship between the refractive index and v_D of the 6FDA-based polyimides in this study was similar to that of general polymers. This result indicates that the optical data of the 6FDA-based polyimides was reliable.

TABLE I
Optical Properties of the 6FDA-Based Polyimides, Nonfluorine Polyimides, and General Polymers

		Refractive index				
	Polymer	n_F	n_D	n_C	v_D	Reference
Polyimides with F atom	6FDA–mPD	1.616 ± 0.001	1.597 ± 0.001	1.589 ± 0.001	22.13 ± 2.63	This study
	6FDA–MPD	1.579 ± 0.015	1.572 ± 0.010	1.558 ± 0.008	27.24 ± 9.54	This study
	6FDA–TMPD	1.556 ± 0.002	1.544 ± 0.003	1.538 ± 0.003	30.22 ± 1.78	This study
	6FDA–TeMPD	1.543 ± 0.012	1.534 ± 0.013	1.530 ± 0.009	41.14 ± 6.19	This study
Polyimides without F atom	Kapton	—	1.78	—	—	6
	Poly[2,2′-bis(methyl)-4,4′-biphenylene pyromellitimide]	—	1.723	—	—	7
	Poly(*p*-phenylene-4,4′-oxydiphthalitimide)	—	1.691	—	—	7
	Poly(*p*-phenylene biphenyltetracarboximide)	—	—	1.771	—	8
	Poly(4,4′-biphenylene pyromellitimide)	—	—	1.764	—	9
	Poly(*p*-phenylene pyromellitimide)	—	—	1.743	—	8
	Poly[2,2′-bis(fluoro)-4,4′-biphenylene pyromellitimide]	—	—	1.729	—	9
	Poly(4,4′-oxydiphenylene pyromellitimide)	—	—	1.700	—	8
	Poly[2,2′-bis(methyl)-4,4′-biphenylene pyromellitimide]	—	—	1.695	—	9
	Poly[2,2′-bis(methoxy)-4,4′-biphenylene pyromellitimide]	—	—	1.693	—	9
	Poly(4,4′-oxydiphenylene benzophenonetetracarboximide)	—	—	1.684	—	8
	Poly[2,2-bis(trifluoromethyl)-4,4-biphenylene pyromellitimide]	—	—	1.595	—	9
General polymers	Polystyrene	—	1.590	—	30.9	15
	Polycarbonate	—	1.586	—	29.8	15
	Styrene–methyl methacrylate copolymer	—	1.562	—	34.7	15
	Epoxy resin	—	1.56	—	36.0	16
	Poly(vinyl chloride)	—	1.55	—	42.0	16
	Poly(methyl methacrylate)	—	1.491	—	57.2	15
	Poly(4-methyl-1-pentene)	—	1.466	—	56.4	15

The gas permeability, apparent diffusion, and solubility coefficients at 30°C of the 6FDA-polyimides were similar to the data in the previous study.[14] Free-volume theory and solution–diffusion theory provided the gas permeability, diffusivity, and solubility as a function of FFV:[17,18]

$$P = A_P \exp\left(\frac{-B_P}{\mathrm{FFV}}\right) \quad (4)$$

$$D = A_D \exp\left(\frac{-B_D}{\mathrm{FFV}}\right) \quad (5)$$

$$S = \frac{P}{D} = \frac{A_P}{A_D}\exp\left(\frac{-(B_P - B_D)}{\mathrm{FFV}}\right) = A_S \exp\left(\frac{-B_S}{\mathrm{FFV}}\right) \quad (6)$$

where A_P, A_D, A_S (i.e., A_P/A_D), B_P, B_D, and B_S (i.e., $B'_P - B'_D$) are adjustable constants. Free-volume theory was initially proposed for gas diffusion. Here, A_D and B_D are inherent diffusion parameters that are correlated with the penetrant size and shape. However, these parameters have not been clearly discussed thus far. Other parameters (i.e., A_P, A_S, B_P, and B_S) might be also correlated with the penetrant size and shape. However, similar to A_D and B_D, these parameters have not been discussed in detail. Generally, polymers with larger FFVs have greater diffusivities. However, although polymers have the same FFVs, their gas diffusivities are not exactly the same. For instance, the CO_2 diffusion coefficients in various types of polymers with an FFV value of 0.18 vary from 10^{-6} to 10^{-8} cm^2/s.[13] This illustrates the limited use of the current free-

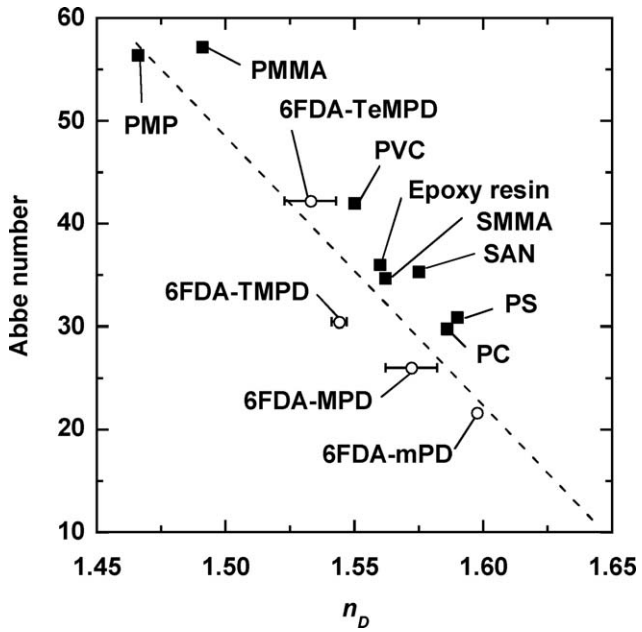

Figure 3 v_D as a function of the refractive index: (○) 6FDA-based polyimides and (■) refs. 15 and 16. PMMA = poly(methyl methacrylate), PMP = poly(4-methyl-1-pentene), PVC = poly(vinyl chloride), SMMA = styrene-methyl methacrylate copolymer, SAN = styrene-acrylonitrile copolymer, PS = polystyrene, PC = polycarbonate.

volume theory in 6FDA–TMPD and 6FDA–TeMPD with the same FFV value 0.177.

Relationship between the gas transport properties and the refractive index

Figure 4 presents the gas permeability, diffusion, and solubility coefficients in the 6FDA-based polyimides as a function of the refractive index, which mainly used general n_D. As the refractive index increased, the gas permeability, diffusion, and solubility coefficients decreased.

Unfortunately, there is no physical chemistry-based linkage between mass transport and photon transport properties. Hence, we described FFV as a function of the refractive index based on the Lorentz–Lorenz equation and investigated the relationships between the gas transport properties and the refractive index-based polymer FFV. Equation (7) is derived from the Lorentz–Lorenz equation, which is used to calculate the refractive index of polymer material.[4]

$$\frac{n_D^2 - 1}{n_D^2 + 2} = \frac{R_{LL}}{V} \tag{7}$$

where V is the polymer molar volume (cm^3/mol) and R_{LL} is the molar refraction (cm^3/mol), which was determined with the group contribution method.[4] When polymer samples are isotropic dense homopolymer membranes without any additives, the V in eq. (2) is equal to the V in eq. (7). Hence, eq. (2) can be rewritten in eq. (7) as a function of the refractive index (n_D):

$$\mathrm{FFV} = 1 - 1.3\frac{V_W}{R_{LL}}\frac{n_D^2 - 1}{n_D^2 + 2} = 1 - \varphi \tag{8}$$

Equations (4–6) can be described with eq. (8) as a function of the refractive index-based FFV ($1 - \varphi$). Hence, eqs. (4–6) can be rewritten as eqs. (9–11):

$$P = A'_P \exp\left(\frac{-B'_P}{1-\varphi}\right) \tag{9}$$

$$D = A'_D \exp\left(\frac{-B'_D}{1-\varphi}\right) \tag{10}$$

$$S = \frac{P}{D} = \frac{A'_P}{A'_D}\exp\left(\frac{-\left(B'_P - B'_D\right)}{1-\varphi}\right) = A'_S \exp\left(\frac{-B'_S}{1-\varphi}\right) \tag{11}$$

where A'_P, A'_D, A'_S (i.e., A'_P/A'_D), B'_P, B'_D, and B'_S (i.e., $B'_P - B'_D$) are adjustable constants.

Figure 5 presents the gas permeability, diffusion, and solubility coefficients in the 6FDA-based polyimides as functions of the reciprocal of $1 - \varphi$. As the $1 - \varphi$ value increased, the gas permeability and diffusivity values also increased. However, gas solubility showed a slight increase with increasing $1 - \varphi$ value. Linear correlations were also observed between $1 - \varphi$ and the gas permeability, diffusivity, and solubility; thus, the gas transport properties could be described as a function of the refractive index.

On the basis of the least-squares fit analysis in Figure 5, the A'_P, A'_D, A'_S, B'_P, B'_D, and B'_S values for each gas are summarized in Table II. The r^2 value of the solubility parameter of $1 - \varphi$ varied from 0.823 to 0.916, and that of the diffusivity and permeability varied from 0.872 to 0.974. Free-volume theory provides gas permeability, diffusivity, and solubility as a function of the FFVs of glassy polymer membranes.[17,18] Because there is a linear relationship between the gas transport properties and FFVs on the basis of the refractive index, this parameter adapts to various types of polymers. Therefore, we systematically studied the A'_P, A'_D, A'_S, B'_P, B'_D, and B'_S values of various gases.

The B'_P values (i.e., the slope of the lines of gas permeability) were 3.23 for CO_2, 4.07 for CH_4, 3.37 for N_2, 2.97 for O_2, and 1.98 for H_2. These values were similar for the different gases. The difference in B'_P among these gases was much smaller than that in A'_P (i.e., the intercept of the lines of gas permeability). In Table II, for example, the largest value is 3.64×10^{-2} cm^3(STP)cm/(cm^2 s cmHg) for CH_4, whereas the smallest one is 1.20×10^{-4} cm^3(STP)cm/(cm^2 s cmHg) for H_2. Therefore, the

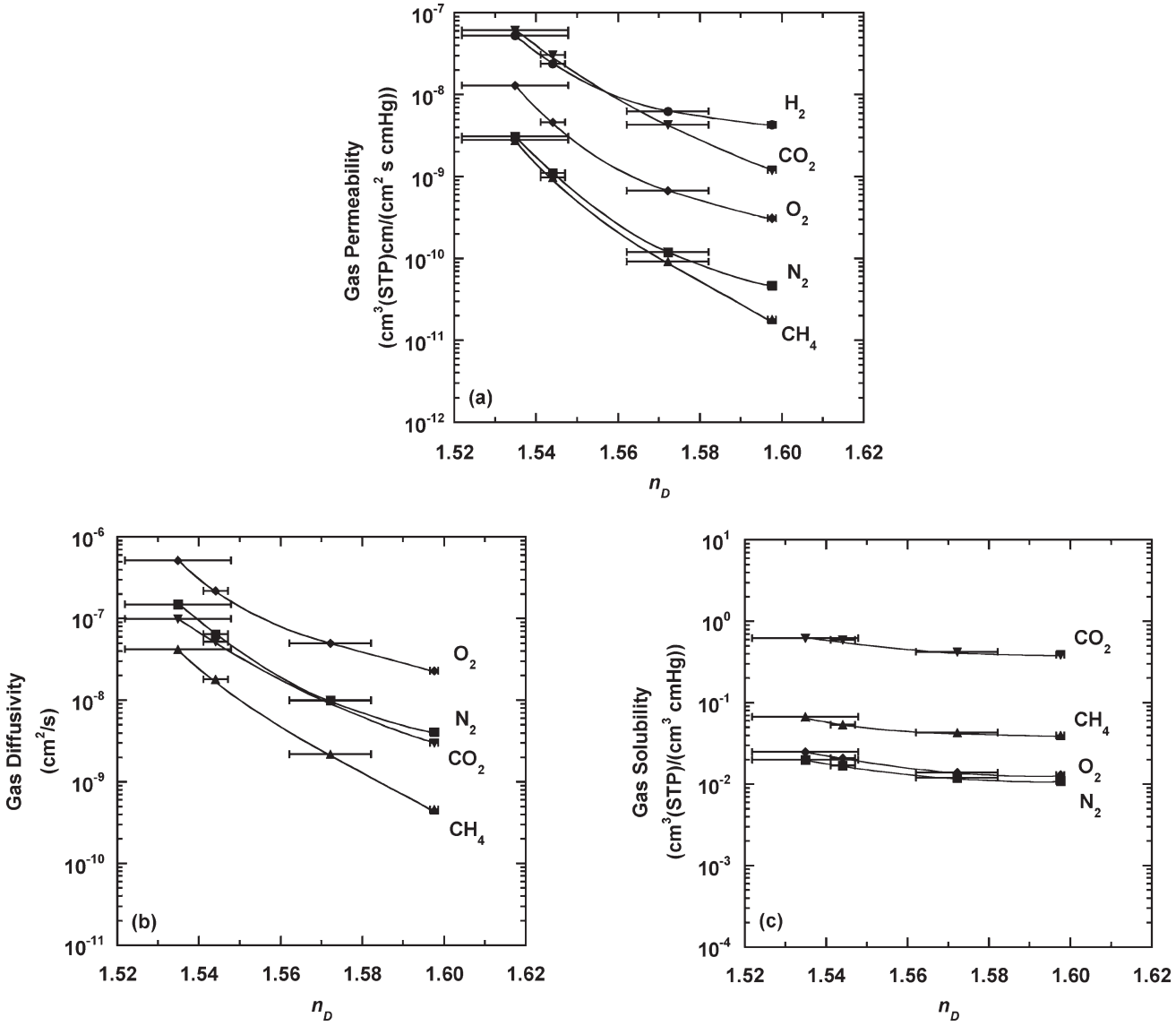

Figure 4 (a) Permeability, (b) diffusivity, and (c) solubility of various gases at 30°C in the 6FDA-based polyimides as a function of the refractive index: (●) hydrogen, (■) nitrogen, (◆) oxygen, (▲) methane, and (▼) CO_2. The gas transport data were taken from ref. 14.

differences in the permeability values in the 6FDA-based polyimides resulted from the A'_P values.

The B'_D values (i.e., the slope of the lines of gas diffusivity) were 2.84 for CO_2, 3.66 for CH_4, 2.91 for N_2, and 2.46 for O_2. These values were similar for the different gases. The difference in B'_D among these gases was much smaller than that in A'_D (i.e., the intercept of the lines of gas diffusivity). In Table II, for example, the largest value is 1.12×10^{-1} cm^2/s for CH_4, and the smallest one is 9.11×10^{-3} cm^2/s for O_2. Therefore, differences in the diffusivity values in the 6FDA-based polyimides also resulted from the A'_P values.

The B'_S values (i.e., the slope of the lines of gas solubility) were 0.39 for CO_2, 0.41 for CH_4, 0.46 for N_2, and 0.51 for O_2. These values were similar for the different gases. The difference in B'_S among these gases was much smaller than that in A'_S (i.e., the intercept of the lines of gas solubility). In Table II, for example, the largest value is 2.93 $cm^3(STP)/(cm^3\ cmHg)$ for CO_2, whereas the smallest one is 0.126 $cm^3(STP)/(cm^3\ cmHg)$ for N_2. Therefore, differences in the solubility values in the 6FDA-based polyimides also resulted from the A'_S values, similar to the gas permeability and diffusivity.

On the basis of the results in Table II, the parameters A'_P, A'_D, A'_S, B'_P, B'_D, and B'_S seemed to be dependent on the penetrant size, shape, and condensability. The order of these parameters was correlated with that of the critical volume (V_c), which is a standard of penetrant size, and that of critical temperature (T_c), which is a standard of penetrant condensability.[19,20] The parameters A'_P, A'_D, and A'_S were plotted as functions of V_c in Figure 6 and T_c in

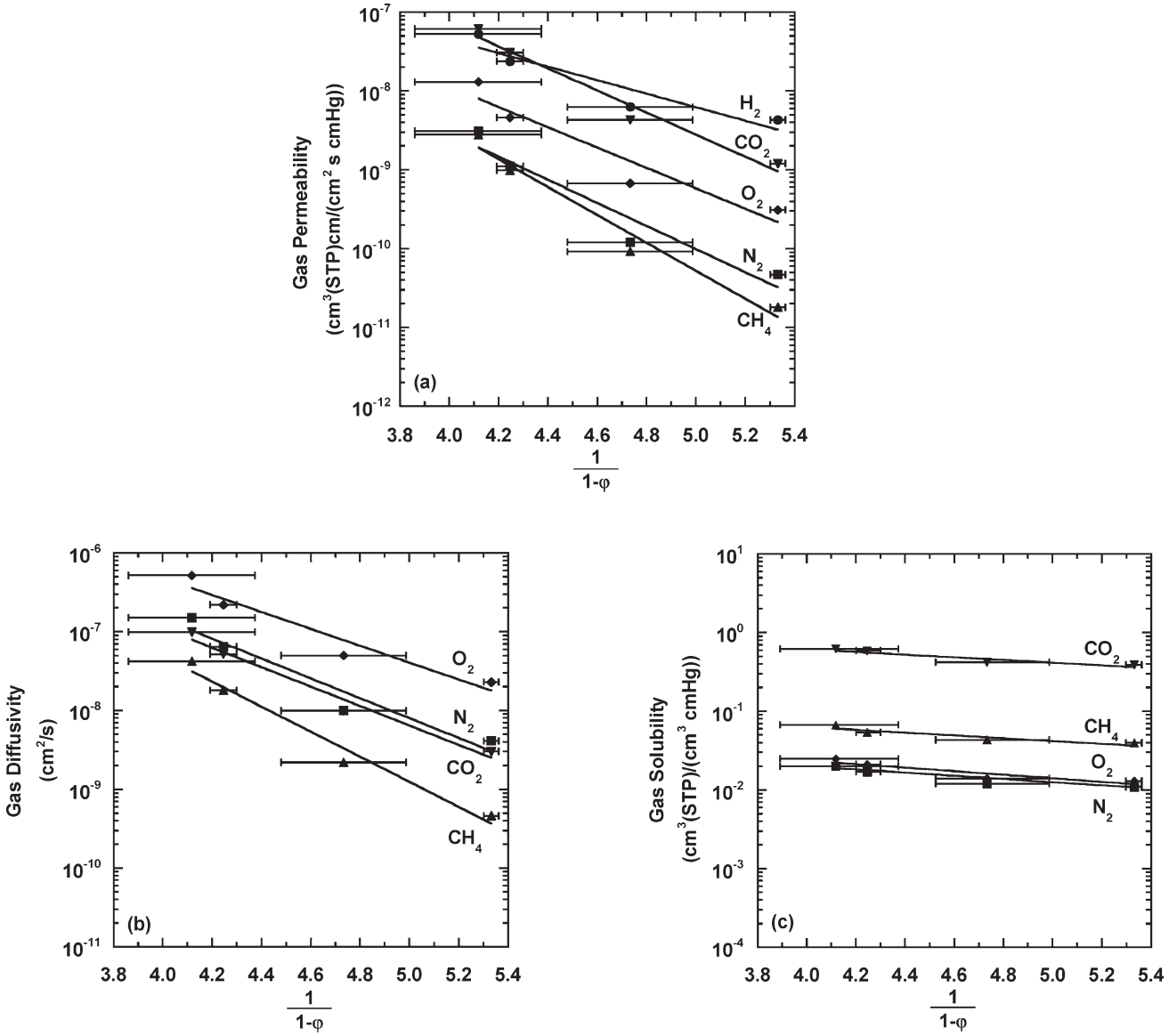

Figure 5 (a) Permeability, (b) diffusivity, and (c) solubility of various gases at 30°C in the 6FDA-based polyimides as a function of $1 - \varphi$: (●) hydrogen, (■) nitrogen, (◆) oxygen, (▲) methane, and (▼) CO_2. The gas transport data were taken from ref. 14.

Figure 7. The parameters B'_P, B'_D, and B'_S are not presented in the figure because, as previously explained, these values were similar to each other, which indicated that they were independent of any penetrant properties. The linear correlations between the parameter of permeation (A'_P) and V_c and T_c are shown in Figures 6 and 7, respectively. The parameter increased as V_c and T_c increased. The gas

TABLE II
Parameter A' and B' in Eqs. (9–12) at 30°C[a]

Gas	A'_P [cm^3(STP) cm/(cm^2 s cmHg)]	B'_P	A'_D (cm^2/s)	B'_D	A'_S [cm^3(STP)/(cm^3 cmHg)]	B'_S
CO_2	2.85×10^{-2}	3.23	9.74×10^{-3}	2.84	2.93	0.39
CH_4	3.64×10^{-2}	4.07	1.12×10^{-1}	3.66	0.325	0.41
N_2	2.08×10^{-3}	3.37	1.65×10^{-2}	2.91	0.126	0.46
O_2	1.65×10^{-3}	2.97	9.11×10^{-3}	2.46	0.181	0.51
H_2	1.20×10^{-4}	1.98	—	—	—	—

[a] There values were determined from the least-squares fit analyses in Figure 5.

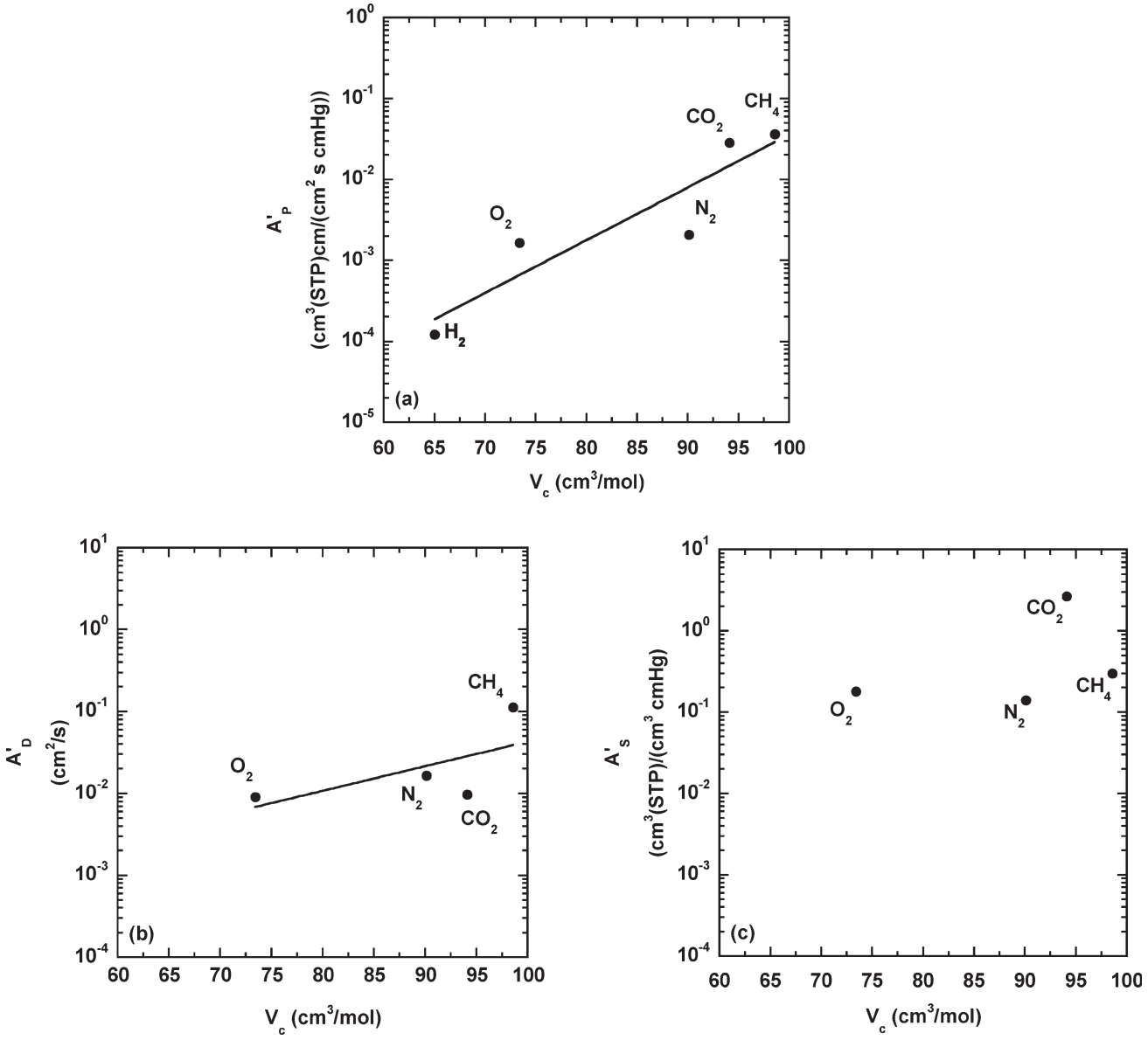

Figure 6 Parameters (a) A'_P, (b) A'_D, and (c) A'_S at 30°C in the 6FDA-based polyimides as a function of V_c of gases.[19,20]

permeability did not depend on either the penetrant size or condensability; rather, it was dependent on the balance between them. Additionally, when the gas diffusion and solution parameters were analyzed on the basis of the solution–diffusion mechanism, the parameter A'_D increased as V_c increased (Fig. 6). There was no relationship between A'_D and T_c (Fig. 7). However, the parameter A'_S showed the opposite properties. There was no relationship between A'_D and V_c (Fig. 6). The parameter A'_S increased as T_c increased (Fig. 7).

The results in Figures 6 and 7 indicate that A'_D depended on the penetrant size, and A'_S depended on the penetrant condensability. Therefore, A'_P (i.e., $A'_D \times A'_S$) was dependent on the penetrant size or condensability factor or on the balance between them.

Table III summarizes the group contribution-based FFV in eq. (2) and the refractive index-based FFV, $1 - \varphi$ in eq. (8), in the 6FDA-based polyimides. The $1 - \varphi$ values of the 6FDA-based polyimides were 1.16–1.37 times larger than their FFV values. As expected from eq. (2), FFV was mainly dependent on the free-volume space in a membrane. In contrast, $1 - \varphi$ [i.e., the FFV determined from eq. (8)] was dependent on the free-volume space and optical factors, such as the refractive index and molar refraction, which affected the electronic structure and the interactions between the gas molecules and the polymer segments. This factor provided a more precise adjustment for gas transport in a free volume of a polymer membrane among a family of polymers.

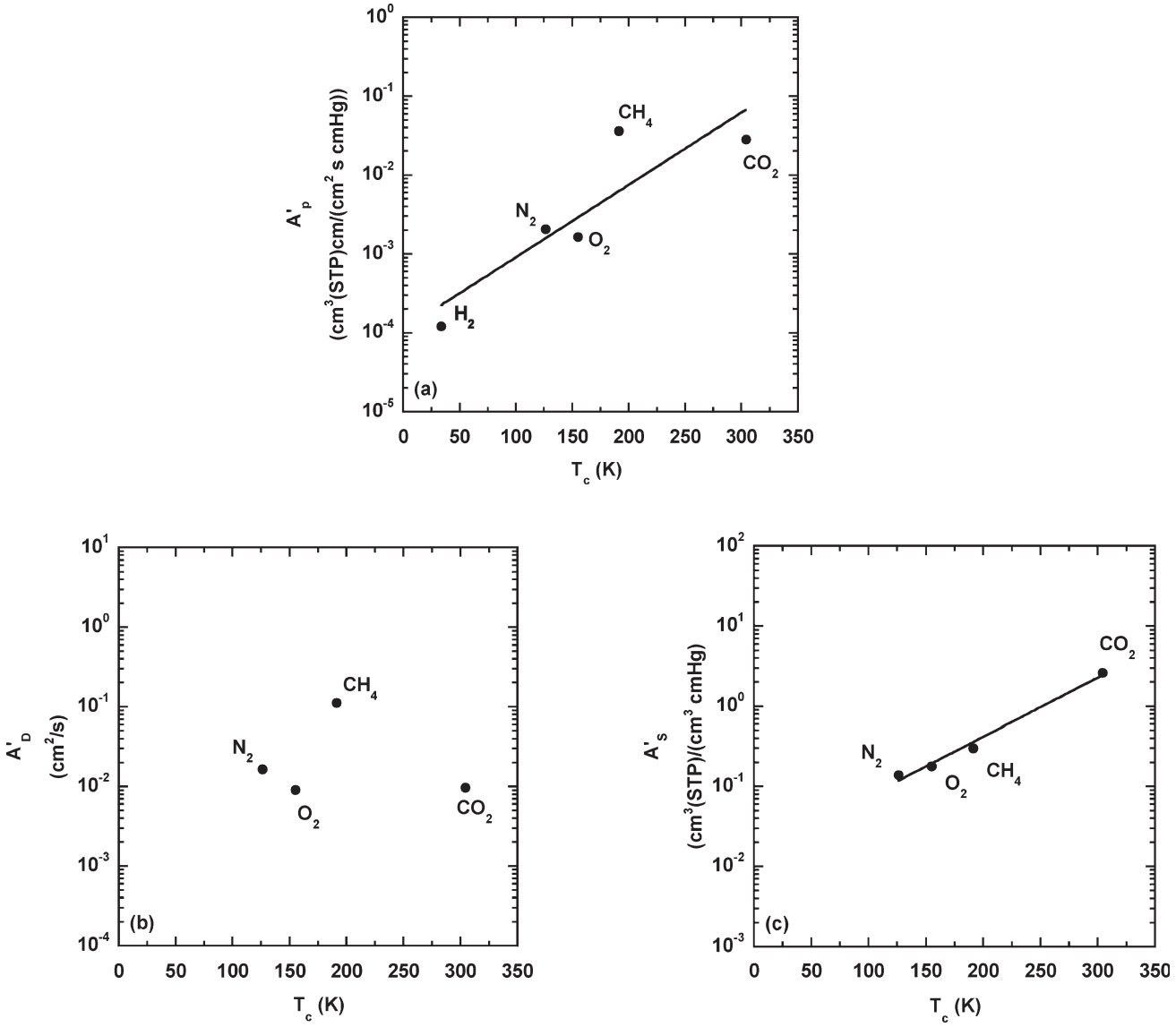

Figure 7 (a) A'_P, (b) A'_D, and (c) A'_S at 30°C in the 6FDA-based polyimides as a function of T_c of gases.[19,20]

The photon has two properties: waviness and elementary particles. The photon elementary particle size was not clarified in this study; however, it was classified as one of the elementary particles, and the size was about 1.0×10^{-5} Å, which is about 10,000 times smaller than a molecule or an atom. This result indicates that the photon can analyze in detail the polymer segment structure as a high-performance probe. Tanio and Nakanishi[21] reported the effect of thermal treatment on the polymer density on the basis of the difference in the refractive indices. This free-volume model considers the electronic structures and the interactions between the gas molecules and polymer segments on the basis of the refractive index.

TABLE III
FFV Values Determined from the Group Contribution Method and the Refractive Index of the 6FDA-Based Polyimides

Polyimide	FFV From eq. (2)	$1 - \varphi$ From eq. (8)	$(1 - \varphi)$/FFV
6FDA–mPD	0.162 ± 0.01	0.188 ± 0.001	1.16
6FDA–MPD	0.171 ± 0.01	0.211 ± 0.011	1.24
6FDA–TMPD	0.177 ± 0.01	0.236 ± 0.003	1.33
6FDA–TeMPD	0.177 ± 0.01	0.243 ± 0.015	1.37

The relationship between the observed and calculated densities on the basis of the optical properties, such as the refractive index and molar refraction of 6FDA-based polyimides, was also studied. The density was calculated by the refractive index on the basis of the Lorentz–Lorenz equation [eq. (12)]:

$$\rho_{cal} = \frac{M}{R_{LL}} \frac{n_D^2 - 1}{n_D^2 + 2} \tag{12}$$

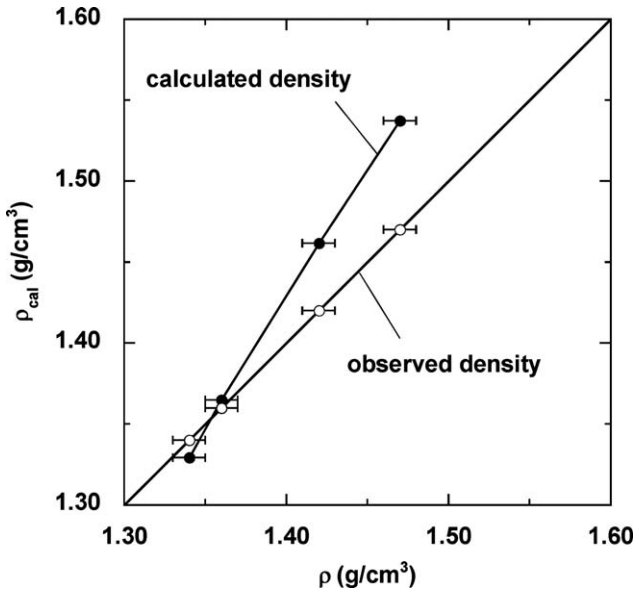

Figure 8 (●) Calculated density as a function of (○) the observed density for the 6FDA-based polyimides.

The density (ρ_{cal}) values calculated from the refractive index were 1.54 for 6FDA–mPD, 1.46 for 6FDA–MPD, 1.36 for 6FDA–TMPD, and 1.33 for 6FDA–TeMPD. The ρ_{cal} value calculated from the refractive index as a function of the observed density is presented in Figure 8. As the observed density increased, the ρ_{cal} value increased. The difference in the density between the observed value and the value calculated from the refractive index increased as the density of polyimide increased. This result indicates that the dense polyimide affected the influence of the electronic structures and the interactions between the gas molecules and polymer segments. The reason for the difference in the density values was also dependent on the electronic structures, which were affected by the refractive index. This result indicates that this free-volume model took into consideration the electronic structures.

CONCLUSIONS

The refractive-index 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. As the refractive index decreased, the gas permeability increased. On the basis of the Lorentz–Lorenz equation, the permeability, diffusivity, and solubility as a function of FFV, as determined from optical constants, such as the refractive index and molar refraction, were examined. From this model, the gas permeability and diffusion coefficients of the 6FDA-based polyimide membranes were found to increase as their refractive index-based FFVs increased. The gas permeability did not depend on either the molecular size or cohesiveness but was dependent on the balance between them. This was because the gas diffusivity was dependent on the penetrant size, whereas the gas solubility was dependent on the interactions between gas molecules and polymer segments. The FFVs of the 6FDA-based polyimides calculated from the refractive index were 1.16–1.37 times larger than their FFV values. This result indicates that the polyimide density affected the influence of the electronic structures and the interactions between the gas molecules and polymer segments. This finding led us to conclude that the electronic structure of the polyimide changed depending on the polymer chemical structure.

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