

# Gas-Sorption Properties of 6FDA–Durene/1,4-Phenylenediamine (pPDA) and 6FDA–Durene/1,3-Phenylenediamine (mPDA) Copolyimides

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**ABSTRACT:** We investigated the sorption isotherms of O<sub>2</sub>, N<sub>2</sub>, CH<sub>4</sub>, and CO<sub>2</sub> gases in 6FDA–durene, 6FDA–1,4-phenylenediamine (6FDA–pPDA), and 6FDA–1,3-phenylenediamine (6FDA–mPDA) homopolymers and 6FDA–durene/pPDA and 6FDA–durene/mPDA copolyimides. The solubilities decrease in the order of the inherent condensabilities of the penetrant gases, namely, CO<sub>2</sub>, CH<sub>4</sub>, O<sub>2</sub>, and N<sub>2</sub>. The chemical structures of the polymer, as well as the chain packing, determine the sorption properties of these homopolymers and copolymers. The FDA–durene homopolymer has the highest solubility for all gases because of its high specific free volume and fractional free volume. The solubilities of the copolymers increase with an increasing 6FDA–durene content, while the solubility selectivities of

the copolymers only vary slightly. The values of  $K_D$  (Henry's law constant) and  $C_H'$  (Langmuir site capacity) of these copolyimides decrease with a decreasing 6FDA–durene content. To our surprise, contradictory to the previous known fact that the *meta*-connected materials tend to have denser molecular packing than that of the *para*-linked materials for homopolymers, the 6FDA–durene/mPDA 80/20 copolymer has higher gas solubilities than those of the 6FDA–durene/pPDA 80/20 copolymer. The random moiety sequence within the copolymer may be the main cause for the abnormal phenomenon. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 2187–2193, 2003

**Key words:** polyimides; gas permeation; copolymerization

## INTRODUCTION

To use polymeric membranes for the applications of gas separation, the inherent polymeric properties such as permeability, spinnability, thermal stability, and mechanical strength should be evaluated. The permeation of a penetrant in a polymer occurs through a solution–diffusion mechanism, where the gas molecules dissolve into the polymer on the feed side, diffuse through the polymer, and desorb from the low-pressure permeate side. The permeability is a product of the solubility coefficient and diffusivity coefficient. The permselectivity is a product of the solubility selectivity and diffusivity selectivity. By improving the solubility selectivity or diffusivity selectivity, the polymers can be modified and achieve a high gas-separation performance.<sup>1,2</sup>

The intersegmental chain packing and intrasegmental mobility of chain segments are two important factors determining the gas-transport properties in glassy polymers. Bulky groups incorporated into the polymer backbone can inhibit intersegmental packing and create pathways for gas diffusion and the space for gas sorption. As a result, permeability is increased. Rigid polymeric segments that restrict mobile linkages in the polymer backbones tend to enhance gas permselectivity.<sup>1,2</sup> Among the polymers developed for gas separation, some of polyimides satisfy these requirements and possess high gas selectivities, thus attracting much research interest.<sup>3–6</sup> One of the examples is the introduction of —C(CF<sub>3</sub>)<sub>2</sub>— linkages into 2,2'-bis(3,4'-dicarboxyphenyl)hexafluoropropane diandrydride (6FDA)-based polyimides.<sup>1,3,6,7–10</sup> The —C(CF<sub>3</sub>)<sub>2</sub>— linkages hinder the rotation of neighboring phenyl rings and enhance the permselectivity. So, the polymers show higher selectivities and maintain relatively high permeabilities.

However, there still exists a trade-off relationship between gas permeability and permselectivity for polyimides. Copolymerization is one of the approaches to further improve the gas-separation performance for polymeric materials. It may potentially combine the advantages of the base polymers and

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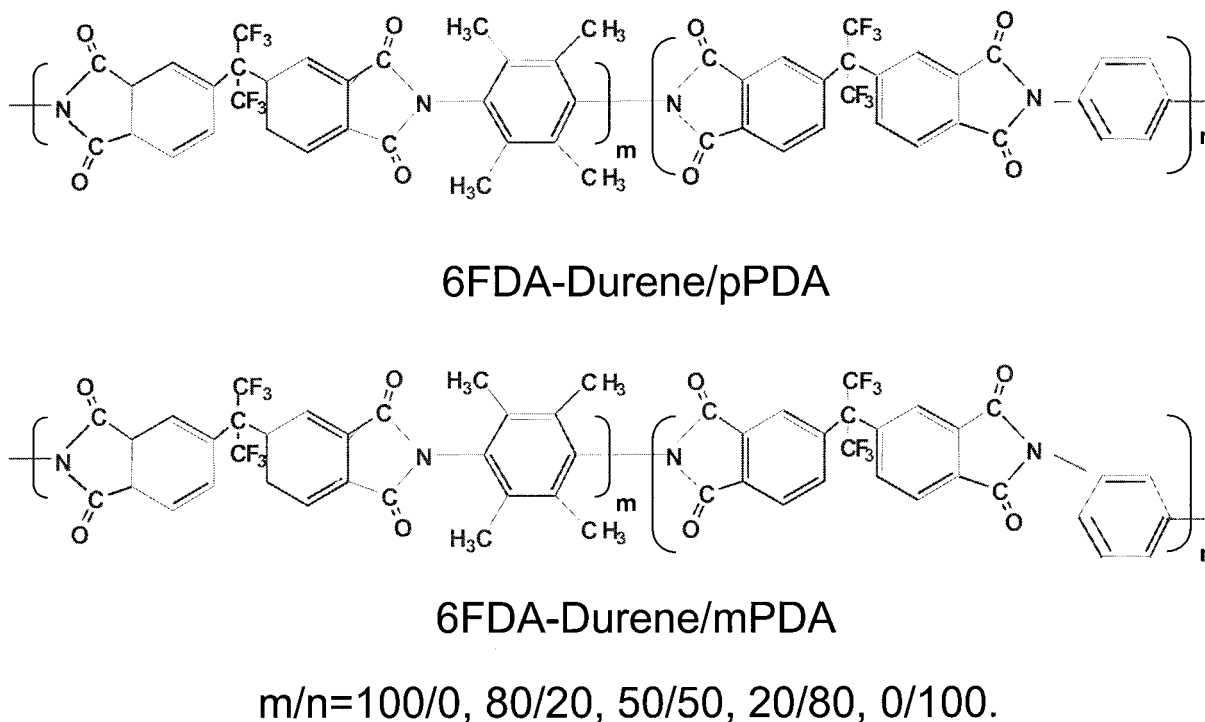


Figure 1 Chemical structures of polyimides.

eliminate their deficiencies. In terms of gas permeability, copolymers generally exhibit a linear relationship between the log of permeability and the volume fraction of a specific comonomer.<sup>11</sup> However, some copolyimides exhibit a positive deviation in gas permeability from the additional rule of the semilogarithmic equation.<sup>9</sup> This phenomenon may be due to the higher solubility coefficients resulting from the generation of the excess free volume. The objective of this work was to study the gas sorption of copolyimides synthesized from (1) 6FDA, 2,3,5,6-tetramethyl-1,4-phenylenediamine (durene diamine), and 1,4-phenylenediamine (pPDA), and (2) 6FDA, durene diamine, and 1,3-phenylenediamine (mPDA) with a dianhydride-to-diamine molar ratio of 1:1. The gas-transport properties of O<sub>2</sub>, N<sub>2</sub>, CH<sub>4</sub>, and CO<sub>2</sub> of these two series of materials were investigated as a function of the composition, pressure, and temperature using the constant volume-variable pressure method.<sup>9,10</sup> Here, we employ a microbalance to study their sorption behaviors and quantitatively characterize their Henry and Langmuir sites.

## EXPERIMENTAL

### Polyamide materials and dense flat membranes

The homopolyimides and copolyimides were synthesized from 6FDA, durene diamine, and pPDA or mPDA by addition and imidization reactions reported elsewhere.<sup>12</sup> The chemical structures of these copoly-

imides are illustrated in Figure 1. The molecular weights of the polyimides were measured using a gel permeation chromatograph (GPC) (Waters 2690) with tetrahydrofuran (THF) as the carrier solvent. The glass transition temperatures were determined using a Perkin-Elmer Pyris 1 differential scanning calorimeter (DSC) with a heating rate of 20°C/min.

Dense films for the sorption tests were prepared by a solution-casting method published elsewhere.<sup>9,10</sup> The films were programmed to be thermally dried with specific heating rates and, finally, vacuum-dried at 250°C for 24 h and cooled to room temperature naturally. Film densities were determined using a top-loading electronic Mettler Toledo balance with a density kit by weighing samples in air and ethanol at room temperature.

### Gas-sorption tests

Gas solubilities of O<sub>2</sub>, N<sub>2</sub>, CH<sub>4</sub>, and CO<sub>2</sub> were measured by a microbalance (CAHN D200) sorption cell under different pressures. The microbalance consists of two empty pans hooked to the strings in the sample chamber and reference chamber, respectively. The empty microbalance was first calibrated to 350 psi with individual gas. Films with a thickness of approximately 10–20 μm and a weight of about 50–200 mg were folded and placed in the sample pan. The system was placed under a vacuum for at least 12 h before conducting the sorption tests. The gas testing se-

TABLE I  
Properties of the Polyimides

Polyimides	$M_w$	Density (g/cm <sup>3</sup> )	$T_g$ (°C)	$V$ (cm <sup>3</sup> /g)	$V_0$ (cm <sup>3</sup> /g)	$V_f$ (cm <sup>3</sup> /g)	FFV
6FDA-durene	226,809	1.3278	424	0.7531	0.615	0.1381	0.183
6FDA-durene/pPDA 80/20	85,279	1.3430	422	0.7446	0.607	0.1376	0.185
6FDA-durene/pPDA 50/50	109,506	1.3864	406	0.7213	0.594	0.1273	0.176
6FDA-durene/pPDA 20/80	101,299	1.4080	397	0.7102	0.580	0.1302	0.183
6FDA-pPDA	228,417	1.4620	350	0.6840	0.570	0.1140	0.167
6FDA-durene/mPDA 80/20	199,989	1.3520	399	0.7396	0.607	0.1326	0.178
6FDA-durene/mPDA 50/50	124,410	1.3722	378	0.7287	0.594	0.1347	0.185
6FDA-durene/mPDA 20/80	273,319	1.4199	319	0.7043	0.580	0.1243	0.176
6FDA-mPDA	172,511	1.4648	301	0.6827	0.570	0.1127	0.165

quence was in the order of O<sub>2</sub>, N<sub>2</sub>, CH<sub>4</sub>, and CO<sub>2</sub>. The amount of sorption at a specific pressure was collected until the sorption behavior reached its equilibrium. The equilibrium sorption value obtained should be corrected by the buoyancy force.

## RESULTS AND DISCUSSION

### Polymer properties

Table I lists the  $M_w$ , density, and  $T_g$  of the two series of polyimides. The 6FDA-durene homopolymer has the lowest density. The density of the copolyimides increased with an increasing 6FDA-pPDA or 6FDA-mPDA content, indicating denser chain packing for

systems containing higher percentages of either 6FDA-pPDA or 6FDA-mPDA.

The glass transition temperature,  $T_g$ , is an indicator of the cooperative motion of polymeric chains. The glass transition temperature of the 6FDA-durene homopolymer is higher than those of the 6FDA-pPDA and 6FDA-mPDA copolymers. This arises from that 6FDA-durene has —(CH<sub>3</sub>) substitutions on the phenyl ring in the diamine moiety, which hinder the phenyl ring rotation and result in an increase in chain stiffness. The presence of a single glass transition temperature for the copolyimides indicates that there is no phase separation in these polymers. The  $T_g$  of these

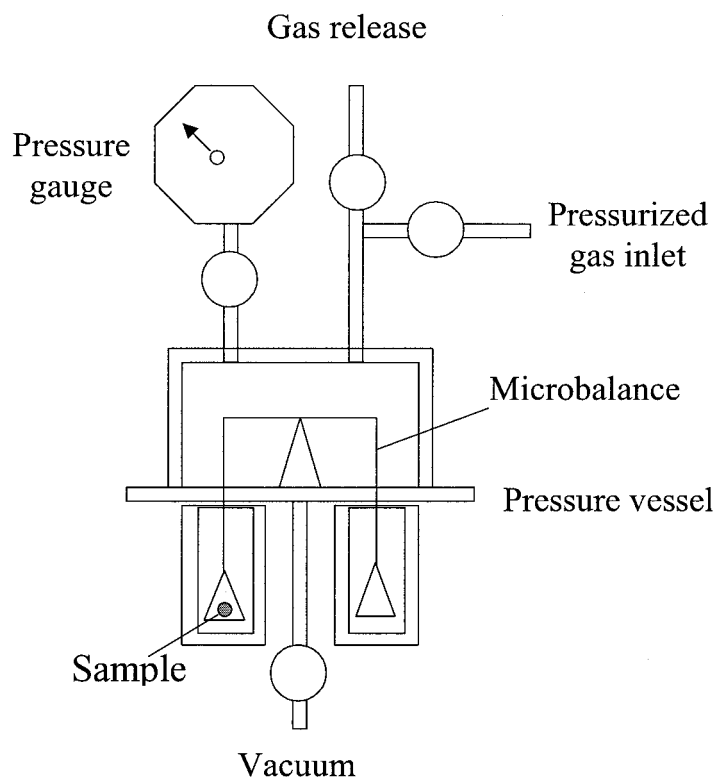
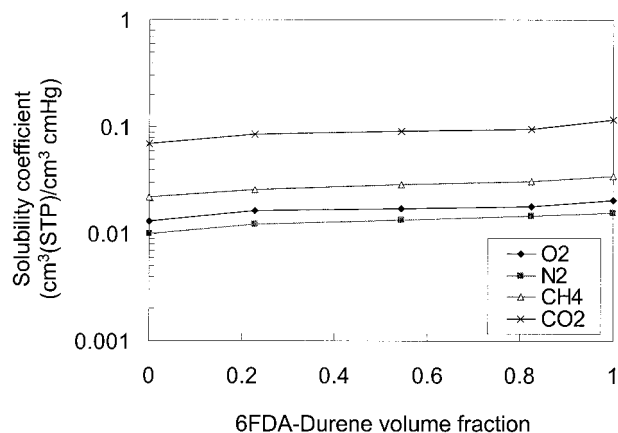
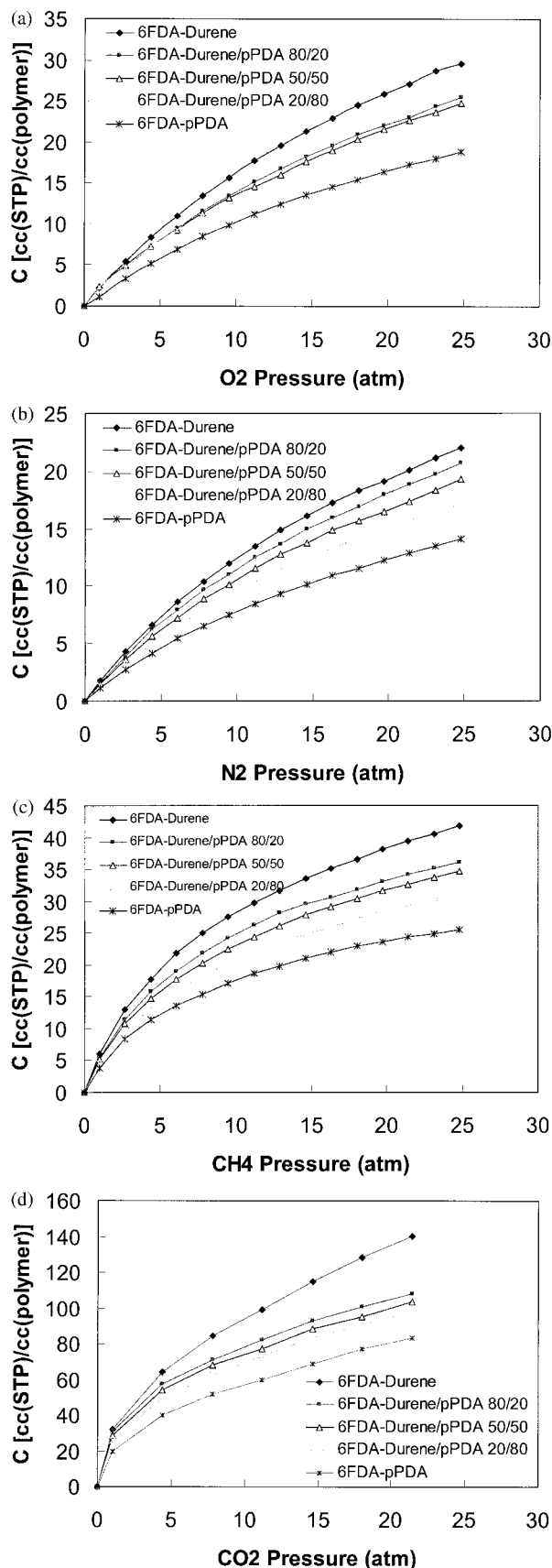


Figure 2 Schematic diagram of microbalance sorption apparatus.



**Figure 4** Dependence of solubility coefficients of 6FDA-durene/pPDA polyimides on the 6FDA-durene volume fraction at 11.2 atm and 23°C.

copolyimides decreases with an decreasing 6FDA-durene content.

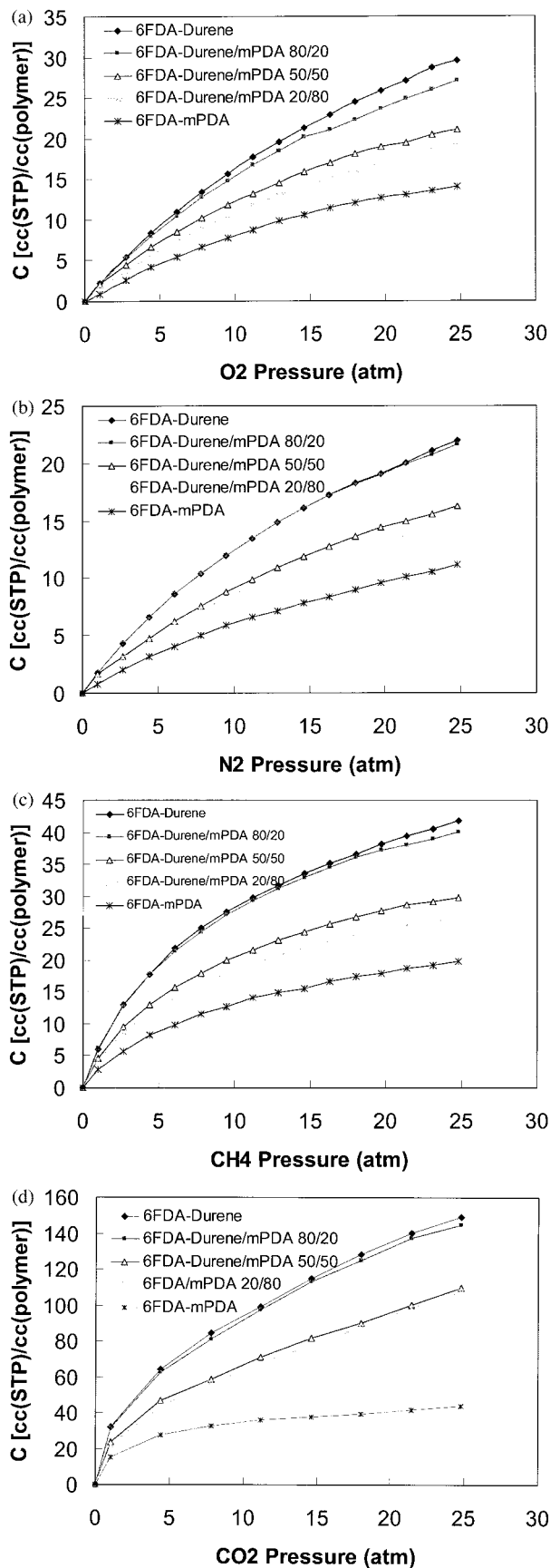
The fractional free volume (FFV) is defined as the difference between the observed specific volume and the occupied volume divided by the observed specific volume as follows:

$$\text{FFV} = \left( \frac{V - V_0}{V} \right)$$

The FFV was used to indicate the relative chain packing. Here, the observed specific volume,  $V$ , is calculated from the measured density, and the occupied volume,  $V_0$ , is calculated from the correlation,  $V_0 = 1.3 V_w$ , where  $V_w$  is the van der Waals volume, which is estimated using the Bondi's group contribution method.<sup>13</sup> For the copolyimides,  $V_w$  is estimated by the equation  $V_w = m_1 V_{w1} + m_2 V_{w2}$ , where  $m_1$  and  $m_2$  are the molar fractions and  $V_{w1}$  and  $V_{w2}$  are the van der Waals volumes of homopolymers 1 and 2, respectively. The difference between the observed specific volume and the occupied volume is also called the specific free volume and is expressed as  $V_f = V - V_0$ . Both  $V_f$  and FFV are useful parameters for interpreting permeation characteristics.

As shown in Table I, among the three homopolyimides that we studied, the 6FDA-durene homopolymer has the highest  $V_f$  and FFV, whereas the 6FDA-pPDA and 6FDA-mPDA homopolymers have the lowest  $V_f$  and FFV values in their corresponding series. For each series, both  $V_f$  and FFV tend to increase with an in-

**Figure 3** (a) O<sub>2</sub> sorption isotherm in 6FDA-durene/pPDA polymers. Temperature, 23°C. (b) N<sub>2</sub> sorption isotherm in 6FDA-durene/pPDA polymers. Temperature, 23°C. (c) CH<sub>4</sub> sorption isotherm in 6FDA-durene/pPDA polymers. Temperature, 23°C. (d) CO<sub>2</sub> sorption isotherm in 6FDA-durene/pPDA polymers. Temperature, 23°C.



creasing 6FDA-durene content. Surprisingly, in a few cases, because of unfavorable intersegmental chain packing, copolyimides even have higher FFV values than those of 6FDA-durene. A similar phenomenon was observed by Lin et al.<sup>9</sup> For the reader's information, the density,  $V_f$ , and FFV values reported here may be slightly different from those of the previous data<sup>9,10</sup> because of different synthesis conditions and batches of materials.

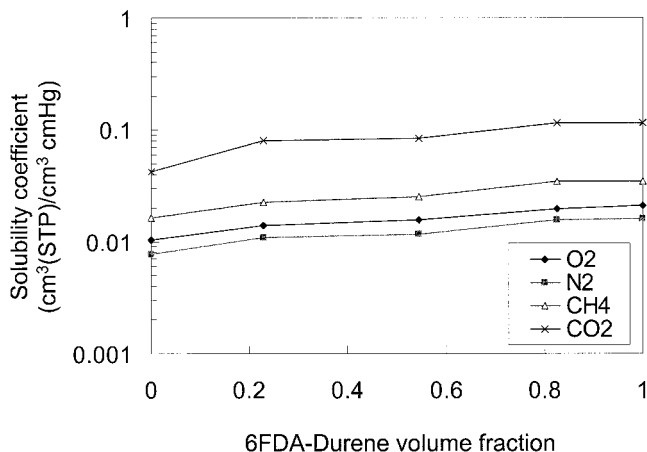
**Effect of composition on gas-sorption properties**

Figures 2(a-d) show the sorption isotherms of  $O_2$ ,  $N_2$ ,  $CH_4$ , and  $CO_2$  gases for the 6FDA-durene/pPDA copolyimides. The gas-sorption measurements for these materials were carried out from 0 to 24.8 atm. The highest solubility values for all gases are seen for the 6FDA-durene homopolymer, which has the highest  $V_f$ . With an increase in 6FDA-pPDA content, the solubility decreases, possibly because of the reduction of  $V_f$  and FFV.

For each polymer, the solubilities of different gases decrease in the order of  $CO_2 > CH_4 > O_2 > N_2$ , which is in agreement with the decreasing order of inherent condensabilities of these gases.  $CO_2$  possesses a higher inherent condensability, resulting in a greater solubility. Figure 3 shows the solubility coefficients of the 6FDA-durene/pPDA polymers with different percentages of the 6FDA-durene moiety. The solubility coefficient increases with an increase in the 6FDA-durene volume fraction. The previous work<sup>9</sup> reported that the 20/80 6FDA-durene/pPDA polymers have gas permeabilities greater than those calculated from the addition rule of the semilogarithmic equation. The high deviation from the additional rule of the semilogarithmic equation is attributed mainly to the fact that this polymer has higher  $V_f$  and FFV values than those from the rule of addition, which was defined elsewhere.<sup>9</sup>

The sorption isotherms of 6FDA-durene/mPDA polyimides are exhibited in Figure 4(a-d). Similarly, we can find that the 6FDA-durene homopolymer has the highest solubility and the 6FDA-mPDA homopolymer has the lowest one, as shown in Figure 5. The solubility increase sequence is the same as that of the 6FDA-durene/pPDA series. However, the solubility coefficients of the 6FDA-durene/mPDA 80/20 and 6FDA-durene/mPDA 20/80 copolymers are higher than are the theoretical values obtained from

**Figure 5** (a)  $O_2$  sorption isotherm in 6FDA-durene/mPDA polymers. Temperature, 23°C. (b)  $N_2$  sorption isotherm in 6FDA-durene/mPDA polymers. Temperature, 23°C. (c)  $CH_4$  sorption isotherm in 6FDA-durene/mPDA polymers. Temperature, 23°C. (d)  $CO_2$  sorption isotherm in 6FDA-durene/mPDA polymers. Temperature, 23°C.



**Figure 6** Dependence of solubility coefficients of 6FDA-durene/mPDA polyimides on the 6FDA-durene volume fraction at 11.2 atm and 23°C.

the additional rule of the semilogarithmic equation, especially for the 6FDA-durene/mPDA 80/20 copolymer which has values close to those of the 6FDA-durene homopolymer. The possible reasons are that (1) the copolymer has an excess free volume resulting from nonperfect intersegmental packing and it has a different distribution of the free volume from that of the other compositions.

The solubility selectivities of various gas pairs for these two series of polyimides at 11.2 atm were calculated and the results are tabulated in Table II. The solubility selectivities of O<sub>2</sub>/N<sub>2</sub> and CO<sub>2</sub>/CH<sub>4</sub> for the copolymers with different compositions are almost the same. Clearly, for these two series of 6FDA copolyimides, the solubility selectivity is largely determined by the relative condensabilities of the test gases.

The dual-mode sorption has been widely used to describe the nonlinear sorption isotherms of gases in most glassy polymers.<sup>1,2,7,14-18</sup> It assumes that there are two kinds of sorbed molecules contributing to the penetrant concentration,  $C$ , in glassy polymers as follows:

**TABLE II**  
Solubility Selectivities of the Polyimides

Polyimides	Solubility selectivities	
	O <sub>2</sub> /N <sub>2</sub>	CO <sub>2</sub> /CH <sub>4</sub>
6FDA-durene	1.32	3.32
6FDA-durene/pPDA 80/20	1.21	3.12
6FDA-durene/pPDA 50/50	1.26	3.17
6FDA-durene/pPDA 20/80	1.34	3.35
6FDA-pPDA	1.32	3.20
6FDA-durene/mPDA 80/20	1.24	3.34
6FDA-durene/mPDA 50/50	1.34	3.28
6FDA-durene/mPDA 20/80	1.27	3.50
6FDA-mPDA	1.34	3.55

Temperature, 23°C.

**TABLE III**  
Dual-mode Parameters of Polyimides

O <sub>2</sub>	$K_D$	$C_H'$	$b$
6FDA-durene	0.143	54.1	0.0378
6FDA-durene/pPDA 80/20	0.349	28.4	0.0584
6FDA-durene/pPDA 50/50	0.481	19.1	0.0848
6FDA-durene/pPDA 20/80	0.289	21.9	0.0846
6FDA-pPDA	0.00188	43.2	0.0310
6FDA-durene	0.143	54.1	0.038
6FDA-durene/mPDA 80/20	0.149	43.1	0.0474
6FDA-durene/mPDA 50/50	0.0536	36.6	0.0476
6FDA-durene/mPDA 20/80	0.0572	36.0	0.0399
6FDA-mPDA	0.00651	28.5	0.0395
N <sub>2</sub>			
6FDA-durene	0.158	32.3	0.0509
6FDA-durene/pPDA 80/20	0.261	23.6	0.0603
6FDA-durene/pPDA 50/50	0.262	20.9	0.0617
6FDA-durene/pPDA 20/80	0.130	25.8	0.0474
6FDA-pPDA	0.201	14.8	0.0646
6FDA-durene	0.158	32.3	0.0509
6FDA-durene/mPDA 80/20	0.00154	42.5	0.0415
6FDA-durene/mPDA 50/50	0.113	24.9	0.0475
6FDA-durene/mPDA 20/80	0.198	16.6	0.0670
6FDA-mPDA	0.195	10.0	0.0677
CH <sub>4</sub>			
6FDA-durene	0.455	38.1	0.164
6FDA-durene/pPDA 80/20	0.306	36.2	0.151
6FDA-durene/pPDA 50/50	0.449	29.1	0.178
6FDA-durene/pPDA 20/80	0.421	25.6	0.182
6FDA-pPDA	0.237	24.8	0.162
6FDA-durene	0.455	38.1	0.164
6FDA-durene/mPDA 80/20	0.311	41.4	0.148
6FDA-durene/mPDA 50/50	0.272	29.7	0.151
6FDA-durene/mPDA 20/80	0.279	24.6	0.176
6FDA-mPDA	0.218	18.3	0.149
CO <sub>2</sub>			
6FDA-durene	3.53	68.1	0.675
6FDA-durene/pPDA 80/20	2.45	60.0	0.867
6FDA-durene/pPDA 50/50	2.38	56.4	0.859
6FDA-durene/pPDA 20/80	2.35	51.6	0.823
6FDA-pPDA	2.16	40.0	0.785
6FDA-durene	3.53	68.1	0.675
6FDA-durene/mPDA 80/20	3.42	67.0	0.662
6FDA-durene/mPDA 50/50	2.78	42.9	0.957
6FDA-durene/mPDA 20/80	2.87	38.3	0.981
6FDA-mPDA	0.459	33.8	0.779

Temperature, 23°C.  $K_D$ : cm<sup>3</sup>/(STP)/cm<sup>3</sup> (polymer) atm;  $C_H'$ : cm<sup>3</sup>/(STP)/cm<sup>3</sup> (polymer);  $b$ : 1/atm.

$$C = C_D + C_H = K_D P + C_H' b P / (1 + b P)$$

One ( $C_D$ ) follows Henry's law for the sorption in the amorphous densely packed regions of the polymer and the other ( $C_H$ ) follows Langmuir sorption in the packing defects or microvoids in the polymer.  $K_D$  is the Henry's law constant;  $C_H'$ , the Langmuir capacity constant; and  $b$ , the Langmuir affinity constant. These

constants are treated as independent of the pressure but dependent on the temperature. For most glassy polymers at low-pressure environments, gas molecules are sorbed into Langmuir mode sites more easily than into Henry's mode sites. The situation changes at high-pressure environments. Henry's mode of sorption becomes predominant because of the easy saturation of the Langmuir sites. The constant values can be obtained by fitting the equation to the experimental data. Normally, a nonlinear least-square analysis is required.<sup>15,16</sup> The reliability of the results depends on the number of data points, the data accuracy, and the pressure range.

The sorption data were fitted by the dual-mode sorption model using a nonlinear least-square method and the fitting results of CH<sub>4</sub> and CO<sub>2</sub> gases are summarized in Table III. For each polymer, their  $K_D$  and  $C_H'$  increase in the order of CO<sub>2</sub> > CH<sub>4</sub> > O<sub>2</sub> > N<sub>2</sub>, which is consistent with the sequence of solubility increase. Compared with the polyimides with different contents of 6FDA-durene, generally, the values of  $K_D$  and  $C_H'$  of the copolyimides decrease with an decreasing 6FDA-durene content. Since  $C_H'$  is the saturation concentration of Langmuir sites, which implies the amount of excess free volume below the glass transitional temperature ( $T_g$ ), a comparison of  $C_H'$  in Table III versus  $T_g$  in Table I shows that the amount of the excess free volume decreases with an increase in  $T_g$  of the copolyimides. In addition, *meta* linkage (6FDA-durene/mPDA series) appears to have a steeper decrease than that of the *para* linkage (6FDA-durene/pPDA series). However, it is important to point out that the  $C_H'$  of 6FDA-durene/mPDA 80/20 copolymer is very close to that of 6FDA-durene homopolymer. The high Langmuir sorption capacity is possibly due to the nonperfect intersegmental chain packing introduced by copolymerization. These fitting results are in good agreement with the experimental data.

The lower  $T_g$  of the 6FDA-mPDA homopolymer (Table I) indicates that 6FDA-mPDA has a higher chain mobility and thus may be more likely to have dense chain packing if compared to the 6FDA-pPDA. Although the *meta*-connected materials are known to have denser packing than that of the *para*-linked materials for homopolymers,<sup>1,3,7</sup> the status for copolymers may be different. Even though the 6FDA-mPDA homopolymer has lower solubility than that of the 6FDA-pPDA homopolymer, the 6FDA-durene/mPDA 80/20 copolymer has higher solubilities than those of the 6FDA-durene/pPDA 80/20 copolymer. The random moiety sequence within the copolymer may be the main cause of the nonperfect molecular packing.

## CONCLUSIONS

The sorption properties of 6FDA-durene/pPDA and 6FDA-durene/mPDA copolyimides with different

compositions were studied in detail. In each specific polymer, the solubilities decreased in the order of CO<sub>2</sub> > CH<sub>4</sub> > O<sub>2</sub> > N<sub>2</sub>, which is in agreement with the inherent condensabilities of the penetrant gases. The chemical structures and polymeric chain packing determine the sorption properties of these homopolymers and copolymers. The homopolymer 6FDA-durene has the highest solubility for all gases because of its high free volume. The solubilities of copolymers increase with an increasing 6FDA-durene content, while the solubility selectivities of the copolymers are similar. The dual-mode sorption model-fitting results show that the 6FDA-durene/mPDA 80/20 copolymer has higher gas solubilities than those of the 6FDA-durene/pPDA 80/20 copolymer; the nonperfect packing induced by the copolymerization may cause the abnormal excess solubilities for the 6FDA-durene/mPDA 80/20 copolymer.

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