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The physical and gas permeation properties of 6FDA-durene/2,6-diaminotoluene copolyimides

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Abstract

The physical and gas transport properties of homo-polyimides, 6FDA-durene and 6FDA-2, 6-diaminotoluene (2,6-DAT), and their copolyimides, 6FDA-durene/2,6-DAT with different diamine ratios, were characterized. The glass transition temperatures of the copolyimides obtained from DSC experiments were about 6–10°C lower than that calculated from the Fox equation. The experimental results for the gas permeability, diffusivity and solubility of this series of polyimides fitted well with that predicted from the logarithm of property versus volume fraction. The gas permeability of 6FDA-durene/2,6-DAT decreased with increasing 6FDA-2,6-DAT content. However, the selectivity of gases pairs, such as CO_2/N_2, O_2/N_2 and H_2/N_2, increased with the addition of 6FDA-2,6-DAT. The permeability coefficients of H_2, He, O_2, N_2 and CO_2 decreased with the kinetic molecular diameters of the gas molecules, with an exception of helium. The diffusion coefficients for the gases of O_2, N_2 and CO_2 were found to decrease with the effective diameters of the penetrant molecules. The solubility coefficients of the gases increased with the condensability of the gas molecules. By decoupling the permselectivity of gas pairs of CO_2/N_2, O_2/N_2, it was found that the permselectivity of CO_2/N_2 was mainly controlled by the solubility selectivity, while in the gas pair of O_2/N_2, the permselectivity was dominated by the diffusivity selectivity.

Keywords: 6FDA copolyimide; Gas transport properties; Polyimides

1. Introduction

Polyimides have attracted much attention as gas separation membrane materials because of their good gas transport properties, thermal and chemical stability, as well as mechanical properties [1]. A lot of research works have been done on polyimide membrane materials to explore the relationship between the chemical structures and the gas transport properties [2–10]. Among the homopolyimides synthesized from various dianhydrides, 6FDA (hexafluoro-dianhydride) based polyimides exhibit good gas transport properties and solubility which favors dense film formation through solution casting and facilitates the intrinsic gas transport property study [11].

Stern et al. [2] studied the relationships among chain structure, physical properties, gas permeability, diffusivity and solubility of polyimides with different side-chain lengths in the diamines. They indicated that the permeability was not related to the length of side groups in diamine moieties. Kim and Koros et al. [4] compared the permeability and selectivity of polyimides synthesized from 6FDA and PMDA (pyromellitic dianhydride) dianhydrides and attributed the higher permeability and selectivity of the 6FDA based polyimides to the presence of the bulky $-C(CF_3)_2-$ groups which hinder intra-segmental mobility, disrupt inter-chain packing and stiffen the backbones. Tanaka et al. [7] investigated the gas permeability, diffusivity and solubility in a number of fluorinated and non-fluorinated polyimides. The results showed similar observations in the polyimides with $-C(CF_3)_2-$ in the dianhydrides. A noticeable permeability increase was observed in the polyimides derived from $-C(CF_3)_2-$ containing diamines. However, the selectivity of the polyimides containing $-C(CF_3)_2-$ in the diamine was lower.

There are two widely used approaches to tailor the properties of polymers: blending [12–19] and copolymerization [20–26]. For membrane applications, blending modification would involve complicated phase behavior in membrane fabrication, as most polymers are immiscible. In contrast,

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copolymerization would be a simple and easy way as the polycondensation reaction for the formation of poly(amid acid), which is the precursor of polyimide, requires moderate conditions [27]. Compared with the large amount of work done on the gas transport behavior of homopolyimides, few investigations were reported on the gas permeability, diffusivity, and solubility of copolyimides by varying the ratios of diamines or dianhydrides.

Block copolymers with micro-phase separation morphology would be expected to exhibit a sigmoid relationship of the logarithm of permeability versus volume fraction of monomer due to different phase continuities at different volume fractions. This was demonstrated in the polysulfone-polydimethylsiloxane block copolymers and ethylene-vinyl acetate copolymer-modified poly(dimethylsiloxane) membranes [21,22]. Random copolymers without micro-phase separation morphology would show a linear relationship of the logarithm of permeability versus volume fraction of monomer. In the case of random copolyimides of 6FDA-3,3′-DDS/6FAP (3,3′-diaminodiphenylsulfone/2,2′-bis(4-aminophenoxy) hexafluoropropane) [23], the logarithm of permeability and selectivity of O_2/N_2 and CO_2/CH_4 versus 6FAP volume fraction showed a positive deviation. However, a linear relationship between the logarithm of gas permeability and the spin-lattice relaxation time of the carbon atom in $-CF_3$ was found. In the case of random copolyimides from 6FDA-durene/*p*PDA (2,3,5,6-tetramethyl-1,4-phenylenediamine/1,4-phenylenediamine), a large positive deviation in the logarithm of permeability versus volume fraction was also found [24], which was attributed to the larger gas solubility caused by the excessive free volume in the copolyimides. The excessive free volume in the copolyimide of 6FDA-durene/*p*PDA should be resulted from the structural difference in the two diamines used. The permeability coefficients of 6FDA-durene for different gases are about 30–50 times higher than that of 6FDA-*p*PDA. To further understand the relationship between the gas permeation behavior and the composition in copolyimides, 2,6-DAT (2,6-diaminotoluene) was used to replace *p*PDA so that the structural difference of the two diamines (durene and 2,6-DAT) becomes smaller. 6FDA-2,6-DAT exhibits higher gas permeability but similar CO_2/CH_4 and O_2/N_2 permselectivity compared with 6FDA-*p*PDA. It is hoped that the chemical combination of 6FDA-durene and 6FDA-2,6-DAT could yield membrane materials having both high intrinsic permeability and selectivity.

2. Experimental

2.1. Materials

The homo- and co-polyimides used in this study were synthesized in our lab via a generally used two-step synthesis route and are shown in Chart 1. Before chemical synthesis, 2,2′-bis(3,4′-dicarboxyphenyl) hexafluoro-propane dianhydride (6FDA) and 2,6-diaminotulene (2,6-DAT) were purified by sublimation, and 2,3,5,6-tetramethyl-1,4-phenylenediamine (durene) was purified by re-crystallization in methanol. The solvent, *N*-methyl-2-pyrolidone (NMP), was distilled at 42°C and 1 mbar after drying with molecular sieve. The polyamic acid was synthesized by mixing equal-mole dianhydride and diamine in NMP and stirred for 24 h at room temperature. The polyamic acid in NMP was then imidized by the addition of acetic anhydride and triethylamine with a mole ratio of acetic anhydride/triethylamine to 6FDA of 4:1. The polyimides were precipitated in methanol and the polymer was washed in methanol and filtered and finally dried at 150°C under vacuum for 24 h prior to use.

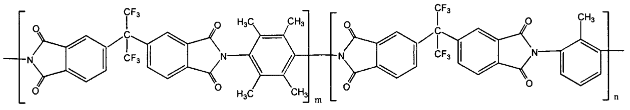
where m/n = 100/0; 75/25; 50/50; 25/75 and 0/100.

Chart 1. Chemical structure of 6FDA-durene/2,6-DAT polyimides.

2.2. Preparation of polymer dense films

A 2–3% w/v solution of polymer in methylene chloride (used as received) was prepared and filtered through a 1 μm filter to remove the non-dissolved materials and dust particles. The solution was then poured into a casting ring on a leveled clean glass plate. The casting ring was covered with a piece of glass and a small gap was kept for slow solvent evaporation. The casting process took about 4 days at room temperature. To obtain dense films, the cast films were dried in an oven at 60°C for 24 h without vacuum and for another 24 h with vacuum, and then the oven temperature was increased from 60 to 250°C at a heating rate of 12°C/20 min. The dense films were annealed at 250°C for 24 h and then cooled down slowly within the oven.

2.3. Physical properties characterization

The thermal stability of the dense films was evaluated by a Perkin–Elmer thermogravimetric analyzer (TGA-7) in air environment with a heating rate of 20°C min^{-1}. The polyimides exhibit good thermal stability. They begun to decompose when heated to 500°C, and the 5% decomposition temperatures for all these polyimides were higher than 530°C. There was no obvious weight loss before 300°C, indicating that no further imidization took place during TGA experiments. In other words, the polyamic acids were fully converted to polyimides. The glass transition temperatures shown in Fig. 1 were measured by a TA 2920 differential scanning calorimetry (DSC) at a heating rate of 20°C and under a dry nitrogen purge.

The densities of the polyimide dense films were measured by the buoyancy method. The film weights in air and in high

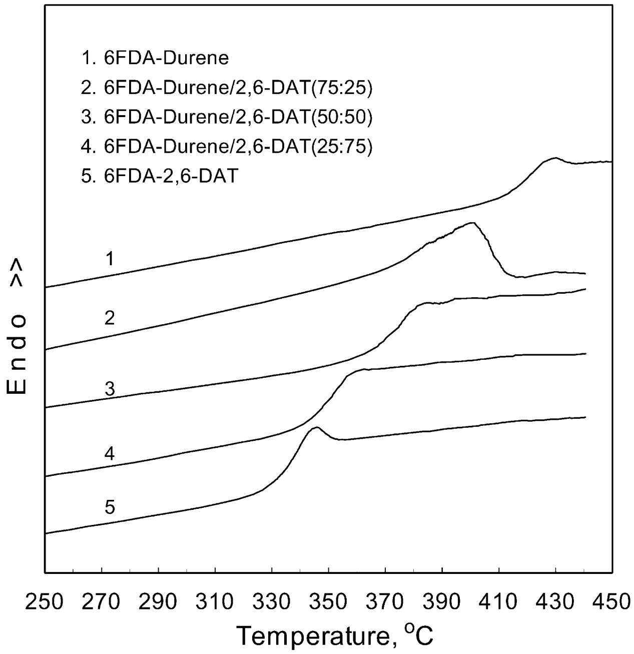

Fig. 1. DSC curves for 6FDA-durene/2,6-DAT polyimides at a heating rate of 20°C min^{-1}.

purity ethanol (99.9%) were measured and the density was calculated as follows:

$$\rho_{\text{polymer}} = \frac{w_0}{w_0 - w_1}\rho_{\text{liquid}} \tag{1}$$

where w_0 and w_1 are the polymer weights in air and in ethanol, respectively.

2.4. Gas permeation measurements

The pure gas permeability coefficients were measured by using a constant volume method. The testing temperature was maintained at 35°C and the feed pressure was 10 atm. The details of the apparatus design and testing procedures could be found in the publications from this group [24]. In short, the gas permeability coefficient was calculated from the following equation when the permeation reaches a steady state:

$$P = \frac{273.15\times 10^{10}}{760}\frac{VL}{AT((p_2\times 76)/14.7)}\frac{\mathrm{d}p_1}{\mathrm{d}t} \tag{2}$$

where V is the downstream volume (cm^3), L the membrane thickness (cm), A the membrane effective area (cm^2), p_2 the upstream pressure (psia), T the absolute temperature (K), and $\mathrm{d}p_1/\mathrm{d}t$ is the pressure increase rate at the down stream (mmHg s^{-1}).

The apparent diffusion coefficient (cm^2 s^{-1}) was estimated from the time lag method by using the following equation:

$$D_{\text{app}} = \frac{L^2}{6\theta} \tag{3}$$

where θ is the time lag and L is the membrane thickness.

The transport of gases in glassy polymers occurs through a solution-diffusion mechanism [28]. The gas molecules dissolve at the high-pressure side, diffuse through the material due to the concentration gradient, and re-emerge into the gas at the low-pressure side. The permeability is a product of a kinetics parameter, D_{app}, which is called diffusion coefficient and a thermodynamic parameter, S_{app}, which is called solubility. Therefore, the solubility coefficient, S_{app} (cm^3 (STP) cm^{-3} cmHg^{-1}), can be obtained from the ratio of permeability coefficient to diffusion coefficient:

$$S_{\text{app}} = \frac{P}{D_{\text{app}}} \tag{4}$$

The various selectivities for gas A relative to gas B for permeability, diffusivity and solubility were calculated from

$$\alpha^P_{\text{A/B}} = P_{\text{A}}/P_{\text{B}} \tag{5}$$

$$\alpha^D_{\text{A/B}} = D_{\text{A}}/D_{\text{B}} \tag{6}$$

$$\alpha^S_{\text{A/B}} = S_{\text{A}}/S_{\text{B}} \tag{7}$$

3. Results and discussion

3.1. Physical properties

The FTIR spectra of the homo- and copolyimides studied are shown in Fig. 2. The existence of the absorption bands at 1785 (C=O asymmetric stretching) and 1716 (C=O symmetric stretching), 1351 (C–N stretch) and 718 cm^{-1} (deformation of imide ring) confirmed the formation of imide group. The systematic increase of the absorption at 1476 cm^{-1} from spectrum 1–5 in Fig. 2, which is the absorption from the aromatic C–H bond, agreed well with the increase of 2,6-DAT diamine content in the copolyimides. There were no obvious weight losses before 400°C in the TGA experiments when the films were heated at 20°C min^{-1} in air, which confirmed the complete conversion from poly(amid acid) to polyimide during the course of chemical imidization and further thermal treatment.

The basic physical properties of this series of polyimides are presented in Table 1. Both 6FDA-Durene and 6FDA-2,6-DAT homopolymers are amorphous due to the non-linear and the non-coplanar nature of the molecular chains. The incorporation of –C(CF_3)– group in the dianhydride destroys the molecular linearity and co-planarity. The stick models show that both repeating units of 6FDA-durene and 6FDA-2,6-DAT have similar molecular shape as shown in Fig. 3. As 6FDA-durene contains four methyl groups and connects at the *para* position in the diamine, which hinders

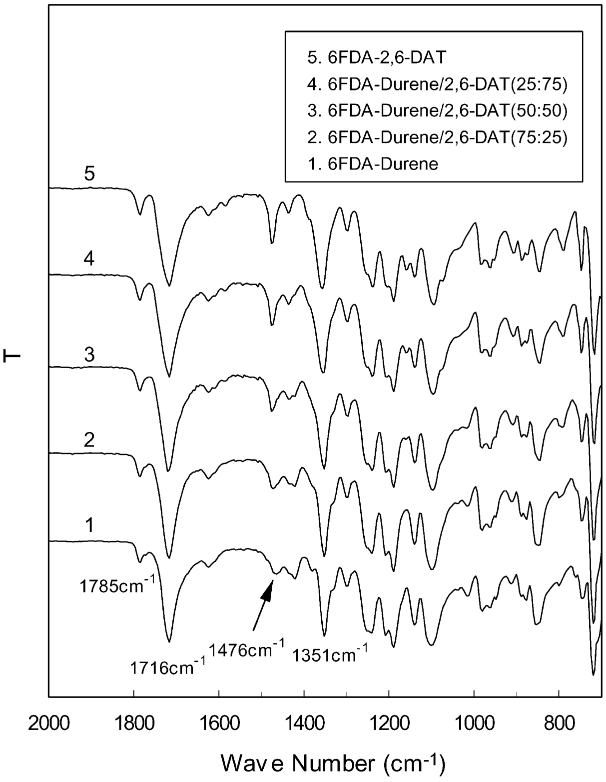

Fig. 2. FTIR spectra of 6FDA-durene/2,6-DAT polyimides.

the rotation of phenyl groups and increases the chain rigidity, the length of the repeating unit of 6FDA-durene is slightly longer (~17.15 Å) than that of 6FDA-2,6-DAT (~16.66 Å). Therefore, 6FDA-durene homopolymer should have a higher glass transition temperature but a looser chain packing compared with 6FDA-2,6-DAT. It is expected that 6FDA-durene has a higher permeability but a lower permselectivity than 6FDA-2,6-DAT.

The glass transition temperature of random copolymers and miscible polymer blends changes with monomer or polymer compositions. A simple way to estimate the glass transition temperatures of random copolymers by the Fox equation is shown below [29]:

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \tag{8}$$

where w_1 and w_2 are the weight fractions and T_{g1} and T_{g2} are the glass transition temperatures of homopolymers. The weight fraction can be obtained from Eq. (9)

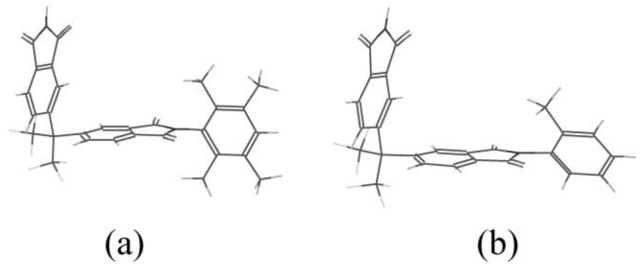

Fig. 3. The repeating unit of (a) 6FDA-Durene; and (b) 6FDA-2,6-DAT.

$$w_i = \frac{m_i M_i}{\sum m_i M_i} \tag{9}$$

where m_i is the molar fraction and M_i is the molecular weight of the repeating unit.

Fig. 4 compares the glass transition temperatures obtained from the DSC experiments and calculated from Eq. (8). For the homopolymers, the T_gs are quite close to those reported in the literature [8,24], while for the copolymers, the T_gs from experiments are about 6–10°C lower than those obtained from the calculation. This indicates that the existence of 6FDA-durene moiety in the copolymers contributes to a slightly larger free volume than the polymer chains should have, which has been confirmed from Table 1. As a result, the copolymers may have a higher permeability, but a lower permselectivity. The trend of our T_gs results is similar to that of 6FDA-3,3-DDS/4,4′-DDS [30], while differs from that of 6FDA-durene/*p*PDA [24] and 6FDA-6FAP/3,3′-DDS [23]. Another important contribution to T_g is from the intermolecular interaction. The strong intermolecular interactions which were confirmed by fluorescence emission experiments in the 6FDA-3,3′-DDS/6FAP copolymers could be the reason for positive contribution to T_g in the copolymers of 6FDA-3,3′-DDS/6FAP.

Table 1 also gives the fraction of free volume (FFV), which is the ratio of the expansion volume $(V - V_0)$ to the observed volume (V) and was calculated from the following equation:

$$\mathrm{FFV} = \frac{V - V_0}{V} \tag{10}$$

where V and V_0 are the specific volume and the chain occupied volume, respectively. V_0 is calculated from the van der Waals volume $(V_0 = 1.3V_w)$ which can be obtained

Table 1
Some physical properties of 6FDA-durene/2,6-DAT polyimides

Polymer	ρ (g cm^{-3})	V (cm^3 g^{-1})	V_{ideal} (cm^3 g^{-1})	V_0 (cm^3 g^{-1})	V_f (cm^3 g^{-1})	V_{fmix} (cm^3 g^{-1})	FFV
6FDA-Durene	1.334	0.750	0.750	0.615	0.135	0.135	0.180
6FDA-Durene/2,6-DAT (75:25)	1.329	0.752	0.740	0.609	0.143	0.132	0.190
6FDA-Durene/2,6-DAT (50:50)	1.349	0.741	0.730	0.602	0.139	0.128	0.188
6FDA-Durene/2,6-DAT (25:75)	1.377	0.726	0.720	0.595	0.131	0.125	0.180
6FDA-2,6-DAT	1.410	0.709	0.709	0.588	0.121	0.121	0.171

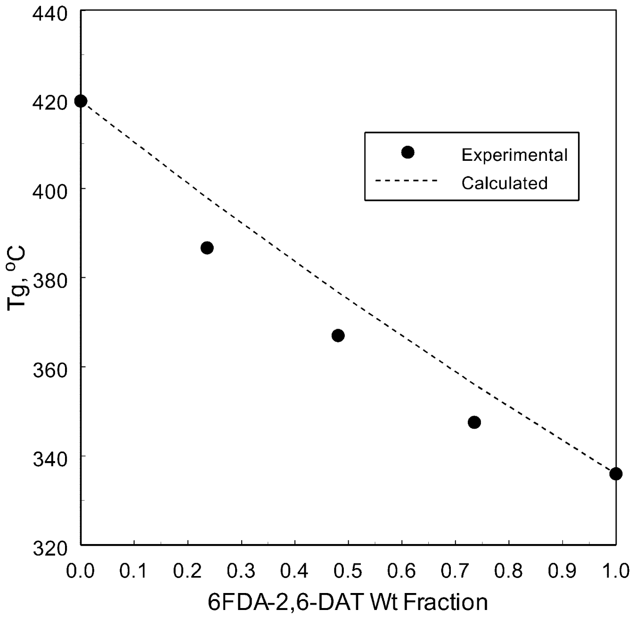

Fig. 4. Comparison of T_gs obtained from DSC experiments and calculated from the Fox equation.

from Bondi's group contribution. For the copolyimides, $V_w = m_1 V_{w1} + m_2 V_{w2}$, where m_1 and m_2 are the molar fractions and V_{w1} and V_{w2} refer to the Van der Waals volumes of the homo-polyimides [15,31]. As shown in Table 1, the specific free volume, V_f, is close to that calculated specific free volume V_{fmix} by using the addition method ($V_{fmix} = w_1 V_{f1} + w_2 V_{f2}$, where w_1 and w_2 are the weight fractions, and V_{fi} is the specific free volume of homopolymers), indicating that the permeability and selectivity may be consistent with the rule of semi-logarithmic addition.

3.2. Gas transport properties

The gas permeability coefficients and ideal selectivity of 6FDA-durene/2,6-DAT series polyimides for different gases measured at 35°C and 10 atm are tabulated in Table 2. From Table 2 it can be noted that the gas permeability of this series polyimides decreases in the following order: $P(H_2) > P(He) > P(CO_2) > P(O_2) > P(N_2)$, which, with an exception of helium gas, is well consistent with the kinetic diameters (σ_k) of the penetrant molecules (Table 3). The exception for helium gas may be because helium is a single-atom molecule. It can also be seen from Table 2 that the permeability coefficients for all the gases tested decrease with increasing the content of 6FDA-2,6-DAT. This can be explained by the smaller free volume fraction and denser chain packing of 6FDA-2,6-DAT polyimide.

Table 3
The physical constants of various gases

Gas	He	H_2	CO_2	O_2	N_2	CH_4
σ_k (Å)	2.60	2.89	3.30	3.46	3.64	3.80
σ_c (Å)	2.58	2.92	4.00	3.43	3.68	3.82
σ_{eff} (Å)	2.59	2.90	3.63	3.44	3.66	3.81
T_c (K)	5.26	33.3	304.2	154.4	126.2	190.7
ϵ/k (K)	10.2	38.0	190.	113	91.5	137

The permeability coefficients of copolyimides is calculated from that of the parent homopolymers as follows [22]:

$$\ln P = \phi_1 \ln P_1 + \phi_2 \ln P_2 \qquad (11)$$

where ϕ is the volume fraction, P is the permeability coefficient and subscripts 1 and 2 indicate the two homopolymers. A comparison for the permeability coefficients obtained from experiments and calculated from Eq. (11) is given in Fig. 5. The experimental results were in good accordance with those calculated from Eq. (11), within 10% difference.

The permselectivity of the interested gas pairs CO_2/N_2, O_2/N_2 and H_2/N_2 for the copolyimides can be estimated by using the following equation:

$$\ln\left(\frac{P_A}{P_B}\right) = \phi_1 \ln\left(\frac{P_A}{P_B}\right)_1 + \phi_2 \ln\left(\frac{P_A}{P_B}\right)_2 \qquad (12)$$

The experimental results for the selectivity of gas pairs of CO_2/N_2, O_2/N_2 and H_2/N_2 are also in good agreement with the calculated values for all the copolyimides studied as shown in Fig. 6.

Since gas permeation through glassy polymers is a solution-diffusion process, it is necessary to decouple the contributions from diffusivity and solubility to the gas permeability. The apparent diffusion coefficients of O_2, N_2 and CO_2 obtained from time-lag method and the diffusivity

Table 2
Permeability coefficients and permselectivity of 6FDA-durene/2,6-DAT polyimides

Polymer	Permeability, barrer					Ideal selectivity		
	He	H_2	O_2	N_2	CO_2	CO_2/N_2	O_2/N_2	H_2/N_2
6FDA-Durene	362	589	125	35.5	456	12.8	3.52	16.6
6FDA-Durene/2,6-DAT (75:25)	273	374	64.8	16.2	220	13.6	3.99	23.1
6FDA-Durene/2,6-DAT (50:50)	196	243	36.9	8.44	117	13.8	4.38	28.8
6FDA-Durene/2,6-DAT (25:75)	153	169	21.3	4.33	67.3	15.5	4.91	39.1
6FDA-2,6-DAT	109	102	10.3	1.83	34.0	18.6	5.64	59.7
6FDA-2,6-DAT[a]	–	106	11.3	2.24	40.1	17.9	5.04	47.3

[a] Data from Ref. [8].

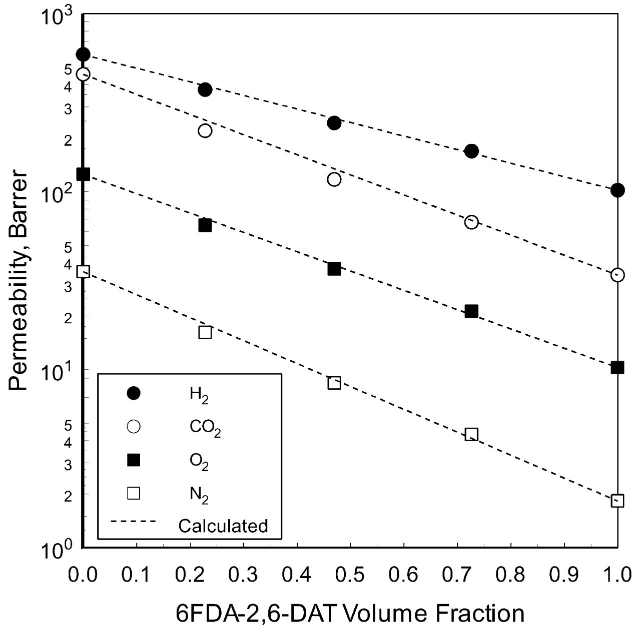

Fig. 5. Effect of 6FDA-2,6-DAT content on the permeability coefficients of 6FDA-durene/2,6-DAT polyimides.

selectivity for O_2/N_2 and CO_2/N_2 are presented in Table 4. In order to compare the experimental results with those predicted from group contribution method, the diffusion coefficients of the above gases were calculated by using

$$\ln D = \phi_1 \ln D_1 + \phi_2 \ln D_2 \tag{13}$$

where ϕ is the volume fraction, D is the diffusion coefficient and subscripts 1 and 2 indicate the two homopolymers.

From Fig. 7 it can be seen that the diffusion coefficients for a single polymer follow this trend: $D(O_2) > D(CO_2) > D(N_2)$. This trend is different from that of the permeability in that $P(CO_2)$ is greater than $P(O_2)$, while $D(O_2)$ is much greater than $D(CO_2)$. Generally, diffusivity of gas molecules permeating through glassy polymers decreases with the kinetic diameters of penetrant gases. Stern et al. [2] explained that the inconsistency could be caused by the strong quadrupole of the CO_2 molecule. Another explanation for the inconsistency in the diffusivity with penetrant diameters may be associated with the 'true size' of CO_2 molecule. In fact, there are two sets of molecules' diameters: collision diameter (σ_c) and kinetic diameter (σ_k) [11,32]. For gas molecules such as He, H_2, O_2, N_2 and CH_4, the two sets of diameters are very close to each other as shown in Table 3. However, for CO_2 molecule, σ_c (4.00 Å) is much bigger than σ_k (3.30 Å). The collision diameter is determined based on the molecular interactions and is used as a correlating parameter for diffusivity in relatively highly mobile rubber or liquid medium, while the kinetic diameter is close to the molecular sieving dimension. It is reported that the effective molecular diameter of CO_2 diffusing through the glassy polymer matrix is underestimated by the kinetic diameter and is overestimated by the collision diameter. A compromised method was proposed, which uses the square root of the product of collision and kinetic diameter and is called 'effective diameter' (σ_{eff}) [33]

$$D = K_1\, e^{-K_2(\sigma_{\text{eff}})^2} \tag{14}$$

where K_1 and K_2 are constants. The diffusion coefficients decrease with increasing the effective diameters (σ_{eff}) of the penetrant molecules. However, it seems that the CO_2

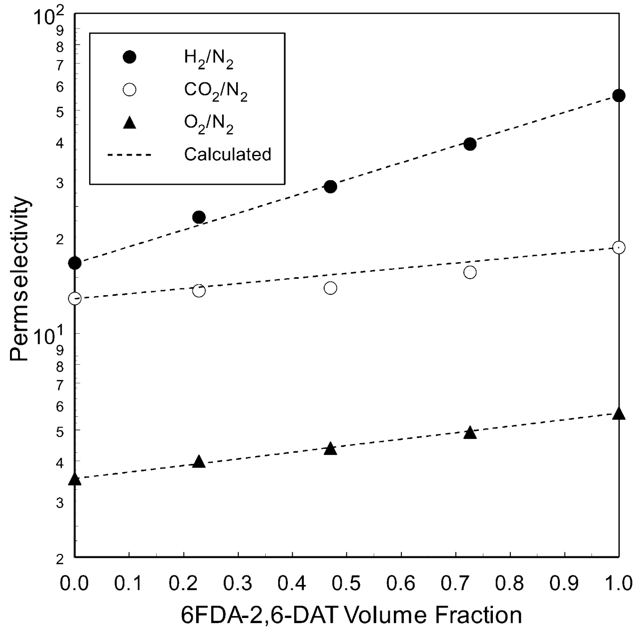

Fig. 6. Effect of 6FDA-2,6-DAT content on the permselectivity of 6FDA-durene/2,6-DAT polyimides.

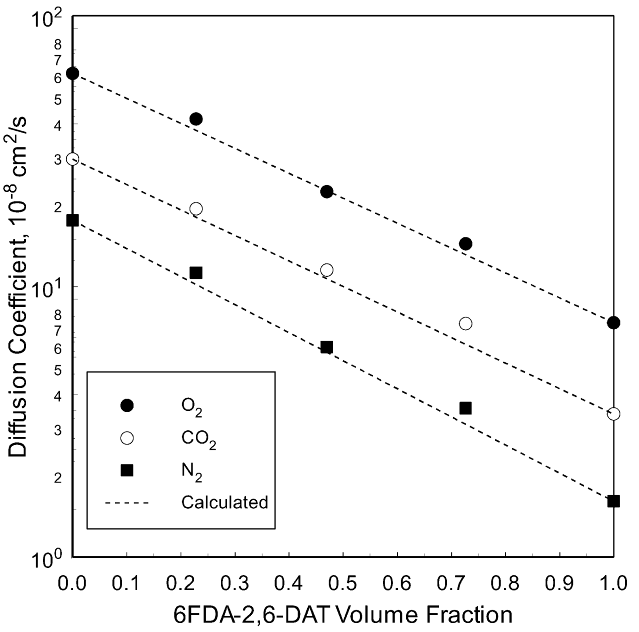

Fig. 7. Effect of 6FDA-2,6-DAT content on the diffusion coefficients of 6FDA-durene/2,6-DAT polyimides.

Table 4
Diffusion coefficients and diffusivity selectivity of 6FDA-durene/2,6-DAT polyimides

Polymer	Diffusion coefficient (10^{-8} cm^2 s^{-1})			Diffusivity selectivity	
	O_2	N_2	CO_2	CO_2/N_2	O_2/N_2
6FDA-Durene	61.3	17.6	29.7	1.69	3.49
6FDA-Durene/2,6-DAT (75:25)	41.6	11.3	19.4	1.72	3.69
6FDA-Durene/2,6-DAT (50:50)	22.4	5.99	11.5	1.92	3.74
6FDA-Durene/2,6-DAT (25:75)	14.4	3.55	7.3	2.06	4.06
6FDA-2,6-DAT	7.36	1.61	3.4	2.11	4.57
6FDA-2,6-DAT[a]	7.5	1.9	6.2	3.26	3.95

[a] Data from Ref. [8].

Table 5
Solubility coefficients and solubility selectivity of 6FDA-durene/2,6-DAT polyimides

Polymer	Solubility coefficient (cm^3 (STP) cm^{-3} cmHg^{-1})			Solubility selectivity	
	O_2	N_2	CO_2	CO_2/N_2	O_2/N_2
6FDA-Durene	0.0204	0.0202	0.154	7.62	1.01
6FDA-Durene/2,6-DAT (75:25)	0.0156	0.0144	0.113	7.85	1.08
6FDA-Durene/2,6-DAT (50:50)	0.0165	0.0141	0.102	7.23	1.17
6FDA-Durene/2,6-DAT (25:75)	0.0148	0.0122	0.092	7.54	1.21
6FDA-2,6-DAT	0.0141	0.0114	0.100	9.09	1.27
6FDA-2,6-DAT[a]	0.015	0.012	0.065	5.41	1.30

[a] Data from Ref. [8].

diffusivity deviates from the straight line if a plot of $\ln D$ versus $(\sigma_{\mathrm{eff}})^2$ is drawn.

It is also observed from Fig. 7 that the diffusivity coefficients of the copolyimides obtained from experiments are slightly higher than that calculated from Eq. (13). This could be due to the looser chain packing in the copolyimides, which can be reflected from the specific free volume (V_f), as shown in Table 1.

The solubility coefficients for O_2, N_2 and CO_2 are given in Table 5. The solubility of all the polyimides studied follows the trend: $S(CO_2) > S(O_2) > S(N_2)$. The change of solubility with composition was estimated from the equation below:

$$\ln S = \phi_1 \ln S_1 + \phi_2 \ln S_2 \tag{15}$$

where ϕ is the volume fraction, S is the solution coefficient and subscripts 1 and 2 refer to the two homopolymers. From Fig. 8 it can be seen that the solubility of O_2 and N_2 in all the five polyimides studied changes very little, while the solubility of CO_2 is much higher than that of O_2 and N_2. This could be related to the high condensability of CO_2 molecules in the polymer matrix. The solubility selectivity for gas pair of CO_2/N_2 is much greater than that of O_2/N_2. From Fig. 8 it is noted that the solubility coefficients for CO_2, N_2 and O_2 in the copolyimides are slightly lower than the predicted values. In glassy polymers, the gas solubility consists of contributions from both Henry-type sites and Langmuir-type sites. The lower solubility coefficients suggest that, with the replacement of durene by 2,6-DAT in the copolyimides, the intrasegmental packing could be slightly improved, while the intersegmental packing is still poor, which can be evidenced from the lower T_g (Table 2) and higher diffusion coefficients (Table 4).

An equation correlating the gas solubility in polymers

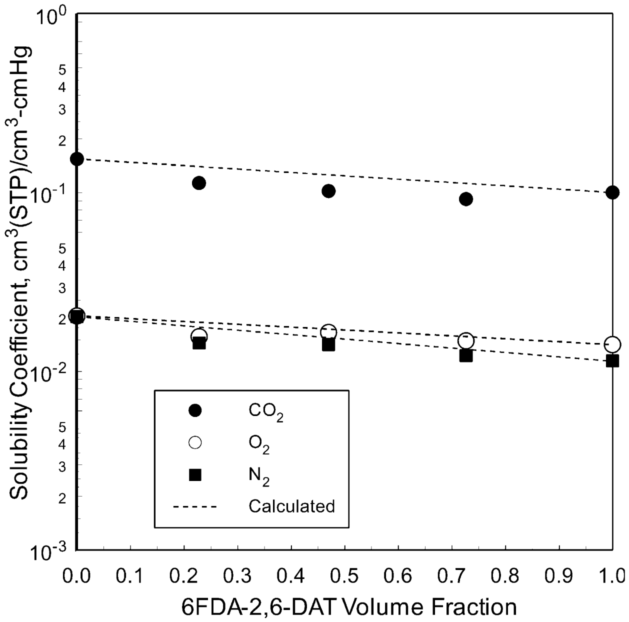

Fig. 8. Effect of 6FDA-2,6-DAT content on the solution coefficients of 6FDA-durene/2,6-DAT polyimides.

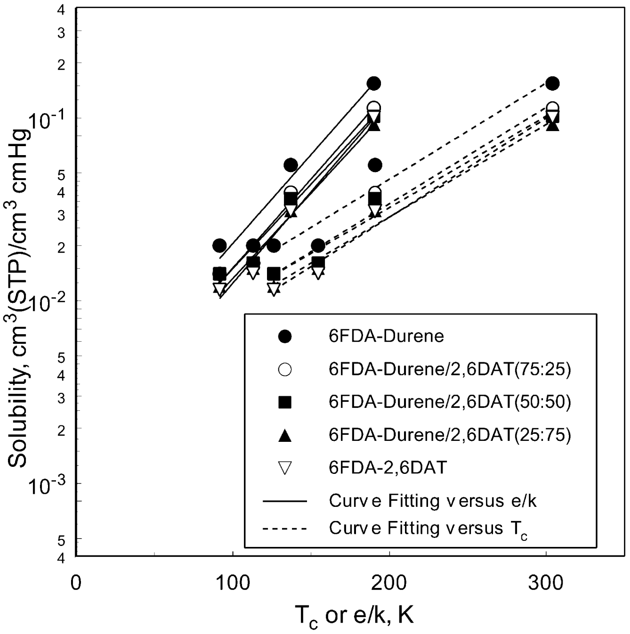

Fig. 9. Solubility as a function of critical temperature (T_c) or Lennard–Jones force constant (ϵ/k).

with critical temperature (T_c) or Lennard–Jones force constant (ϵ/k) was given below [28]:

$$\ln S = \ln S_0 + K_c T_c = \ln S_0 + K_e(\epsilon/k) \qquad (16)$$

where S_0, K_c and K_e are constants. This equation suggests that the gas solubility in polymer matrix parallels to T_c, or ϵ/k. The results shown in Fig. 9 follow this trend fairly.

4. Conclusions

The physical and gas transport properties of homo- and co-polyimide membranes synthesized from 6FDA, durene and 2,6-DAT were studied. It was found that the permeability, diffusivity and solubility coefficients followed well with the predictions from the logarithm of property versus volume fraction. The permeability coefficients of He, H_2, O_2, N_2 and CO_2 decreased with the molecular kinetic diameter with an exception of helium. The gas permeability coefficients for all gases studied decreased with increasing 6FDA-2,6-DAT content. The permselectivity of gas pairs of CO_2/N_2, O_2/N_2 and H_2/N_2 was found to increase with increasing 6FDA-2,6-DAT content. The diffusion coefficients for the copolyimides were found to be slightly higher than the predicted values. This could be resulted from the looser chain packing in the copolymers. The diffusion coefficients for the gases of O_2, N_2, CO_2 decreased with the effective diameters of the penetrant gases. The solubility coefficients of the gases increased with the condensability of the gas molecules. A slightly smaller solubility was found than the prediction in the copolymers, which could be resulted from the slightly improved intrasegmental packing. The permselectivity of the gas pairs of CO_2/N_2 and N_2/O_2 was contributed by different mechanisms. In the gas pair of CO_2/N_2, permselectivity was largely controlled by the solubility selectivity, while in the gas pair of O_2/N_2, the permselectivity was mainly attributed from the diffusivity permselectivity.

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