Polymer Bulletin 60, 137–147 (2008)
DOI 10.1007/s00289-007-0841-2

Polymer Bulletin

The gas permeation properties of 6FDA-2, 4, 6-trimethyl-1, 3-phenylenediamine (TMPDA)/1, 3-phenylenediamine (mPDA) copolyimides

Lina Wang[a, b], Yiming Cao[a] (✉), Meiqing Zhou[a], Xiaoli Ding[a, b], Qinhua Liu[a], Quan Yuan[a]

[a]Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China
[b]China Graduate University of Chinese Academy of Sciences, Beijing 100049, China
E-mail: ymcao@dicp.ac.cn; Fax: 86 411 84379329

Received: 20 March 2007 / Revised version: 18 September 2007 / Accepted: 18 September 2007

Summary

The gas permeation behavior of 2, 2'-bis (3, 4'dicarboxyphenyl) hexafluoropropane dianhydride(6FDA)-2, 4, 6-Trimethyl-1, 3-phenylenediamine (TMPDA)/1,3-phenylenediamine (mPDA) polyimides was investigated by systematically varying the diamine ratios. The physical properties of the copolyimides were characterized by IR, DSC and TGA. All the copolyimides were soluble in most of the common solvents. The gas permeabilities and diffusion coefficients decreased with increasing mPDA content; however, the permselectivity of gas pairs such as H_2/N_2, O_2/N_2, CO_2/CH_4 was enhanced with the incorporation of mPDA moiety. The permeability coefficients of H_2, O_2, N_2, CO_2 and CH_4 were found to decrease with the increasing order of kinetic diameters of the penetrant gases. Moreover, all of the copolyimides studied in this work exhibited performance near, lying on or above the existing upper bound trade-off line between permselectivity and permeability.

Keywords

6FDA copolyimide; permeability; gas separation

Introduction

Aromatic polyimides are considered to be one of the most important classes of high-performance polymers because of their excellent thermal, mechanical, and electrical properties, chemical resistance as well as outstanding gas selectivities for gas pairs such as O_2/N_2 and CO_2/CH_4 [1-3]. Commercially viable materials must have both high permeability and high selectivity for the gas separations of interest. However, there still exists a tradeoff relationship between gas permeability and permselectivity for polyimide membranes [4-6]. In recent years, the structure/permeability/selectivity relationships of polymers have become the objective of systematic studies in order to achieve a high permeability and a high selectivity [7-10]. Many studies indicate that the following structural modifications are required in order to enhance the selectivity and permeability of polyimides, and possibly also of other glassy polymers, toward light gases:

1) The backbone chains must be stiffened by inhibiting their intrasegmental (rotational) mobility.
2) Intersegmental packing of the polymer chains must be simultaneously prevented.
3) Interchain interactions must be weakened and, if possible, eliminated [11].

Some aromatic polyimides that contain $–C(CF_3)_2–$ groups in their dianhydride moieties (e.g., the 6FDA-based polyimides) have been found to be considerably more gas-selective than other glassy polymers with comparable permeabilities. 6FDA (hexafluorodianhydride)- based polyimides consistently deviate from the general relationship between permeability and permselectivity by showing systematically higher selectivities at values of permeability equivalent to other polymers [12].

Fluorinecontaining polyimides have received a great deal of attention also because fluorine often lowers the thermal-expansion coefficient and gives increased solubility and lowers the dielectric constant. The most practical approach is to introduce flexible linkages between the aromatic rings in the diamine and dianhydride. Modified polyimides with flexible bonds that provide improved solubility have been successfully commercialized. Some of 6FDA polyimides have been employed to fabricate high performance membranes [13-18].

There are some methods to tailor the properties of polymers: blending, surface modification and copolymerization. Blending has been widely used in polymer modification. In heterogeneous blends, the morphology of the biphasic structure and the nature of the interface are the governing factors that affect the gas transport properties. In homogenous miscible blends, the gas transport properties are, however, highly dependent on the strength of the interactions between the two components. For membrane applications, blending modification would involve complicated phase behavior in membrane fabrication, as most polymers are immiscible [19-24]. Membranes formed from crosslinked polyimides have improved environmental stability and superior gas selectivity than the corresponding uncrosslinked polyimide [25,26]. But crosslinking reaction usually results in decreased solubility in organic solvents as well as very high glass-transition bemperatures. These properties make the materials difficult to fabricate by means of conventional techniques [27]. Therefore, special fabrication methods such as compression molding or sintering molding must be applied. Films are fabricated from polyamic acid solutions followed by imidization. To overcome these limitations, several kinds of structural modifications have been adopted. One direction was structural modifications of the polymer backbone such as the addition of bulky lateral substituents, flexible alkyl side chains, non-coplanar biphenylene moieties, and kinked comonomers have been utilized to modify the polymer properties, either by lowering the interchain interactions or by reducing the stiffness of the polymer backbone. Copolyimides offer the possibility of preparing membranes with gas permeabilities and selectivities not obtainable with homopolyimides. One may be able to tailor their gas separation properties by varying the monomer ratio [28-33].

This study is to investigate the relationship between the permeabilities and component ratio of 6FDA-TMPDA and 6FDA-mPDA. The reason for choosing these polyimides is that 6FDA-TMPDA has a higher permeability, but a relatively low selectivity for a specific gas pair, while 6FDA–mPDA has a higher selectivity with a relatively low permeability. The advantages of these two homopolymers may be taken to develop a copolyimide with a better combination of permeability and selectivity than both of homopolymers for gas separation applications.

Experimental

Syntheses of polyimides

The dianhydride monomer used in this study was 2, 2'-bis (3, 4'dicarboxyphenyl) hexafluoropropane dianhydride (6FDA). This monomer was obtained from Clariant Chemicals Co., Ltd., which was purified by vacuum sublimation. The diamine monomers used were: 2, 4, 6-Trimethyl-1, 3-phenylenediamine (TMPDA) obtained from Zhejiang dragon chemical Co., Ltd., which was purified by vacuum sublimation, and 1, 3-phenylenediamine (m-PDA) obtained from Acros, which was recrystallized from toluene. N-Methyl-2-pyrrolidone (NMP) was purchased from Acros Organics Ltd. NMP was purified by vacuum distillation. Acetic anhydride and triethylamide were received from Shenyang chemical reagent factory and Shantou Xilong chemical factory respectively, which were purified by distillation under nitrogen. Methanol was obtained from Shenyang chemical reagent factory used as received. The monomers used to synthesize homo- and copolymers are shown as Figure 1.

The homo- and co-polyimides were synthesized by a two-step method. Polyamic acids (PAA) were prepared by stoichiometric addition of solid 6FDA in portion wise to the diamine(s) contained in NMP. PAA solutions were made up to 20% solids. Reaction mixtures were stirred with a mechanical EUROSTAR power control-visc stirrer in a nitrogen atmosphere at RT overnight. Then polyamic acids were imidized to form polyimides. The cyclization was achieved by chemical imidization under nitrogen purge at RT for 24h through the addition of acetic anhydride (dehydrating agent) and triethylamide (catalyst). Polymer solution was precipitated with methanol and then washed three times by methanol and dried at 200°C in vacuum oven for 24h.

Preparation of dense membranes

All polyimides were prepared as dense films. These films were obtained by a casting method. The appropriate amount of polyimides were dissolved in dry NMP to form 10 wt% solutions, then filtered using filters to remove nondissolved materials and dust particles. After being degassed, the polyimides solutions were poured into a casting ring on a leveled clean glass plates at 80°C, the whole plate was covered with a hood with a small gap to allow the solvent to slowly evaporate for about 24h at room temperature. Subsequently, the films were removed from the glass plates; the nascent films were dried in a vacuum oven at 80°C for 24 h to remove residual solvent. The temperature was gradually increased at a heating rate of 1°C/ min from 80 to 250°C, and each membrane was annealed at 250°C for 24 h. The films were slowly cooled in an oven from 250°C to room temperature then were stored in a desiccator for further tests and study.

Physical properties

The densities of the polyimide dense films were measured by the buoyancy method. The weights of the film in air and in high purity ethanol (99.9%) were measured and

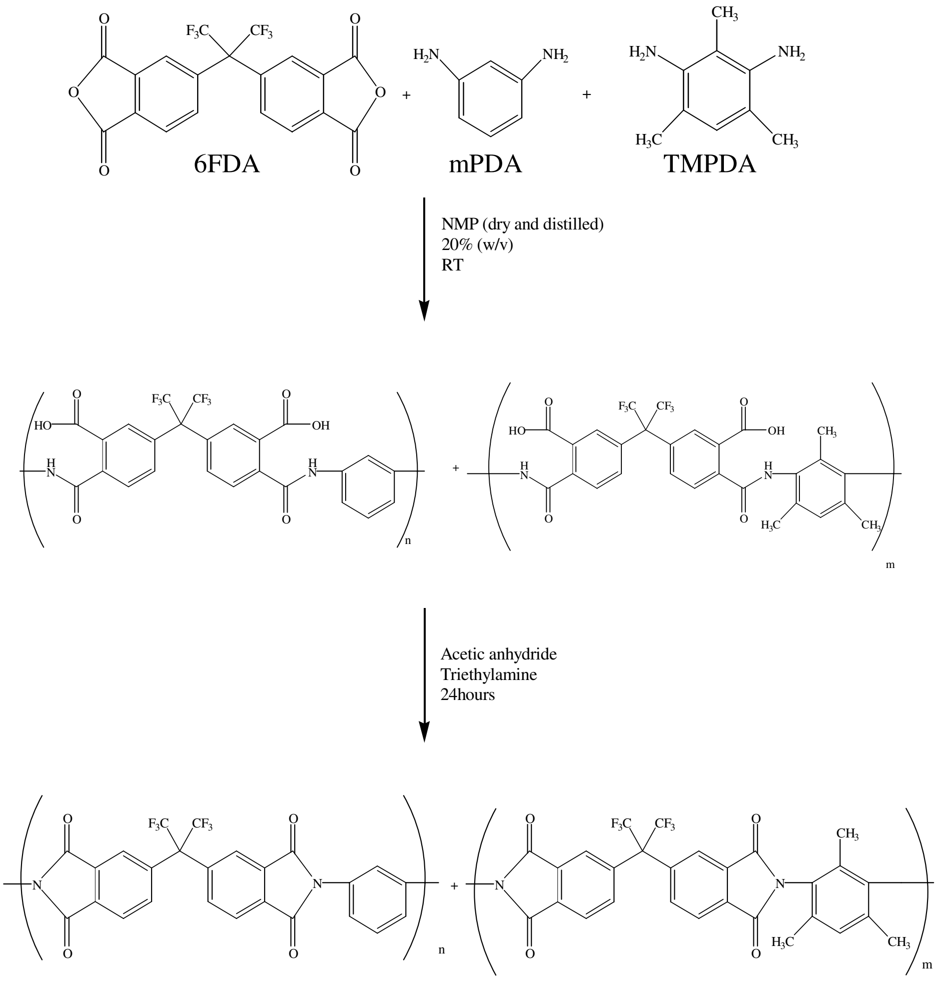

Figure 1. Reaction scheme of copolyimides

the density was calculated as follows: $\rho_{\text{polyimide}} = \dfrac{w_0}{w_0 - w_1}\rho_{\text{liquid}}$, where w_0 and w_1 are the polyimide weights in air and in ethanol, respectively. FTIR-ATR is applied to confirm the formation of imide ring using polyimide dense films, which were determined by a Thermo Nicolet NEXUS FTIR spectrometer. The scanning range was from 4000 to 400 cm^{-1}. Tg was determined from the second heating cycle using a Mettler Toledo DSC822 differential scanning calorimetry (DSC). Temperature scanned was in the range of 100–400°C in the heating cycle and from 400 to 100°C in the cooling cycle at a heating rate of 5°C/min. Weight loss of copolyimides in dense film form examined at a heating rate of 10°C/min in the range of 20–900°C using a SHIMADZU DT-20B thermogravimetric analyzer in nitrogen atmosphere and a sample size of 10±1 mg was used.

Solubility

Solubility of copolyimides was evaluated using the following method: copolyimide powder of 20 mg was added into 1 ml of the solvent and dispersed thoroughly. After the mixture was swayed continuously for 24 h at room temperature, solubility was characterized.

Measurement of gas permeability

The gas transport properties were measured using variable pressure (constant volume) method. Permeation properties of H_2, O_2, N_2, CO_2 and CH_4 were measured. Ultrahigh-purity gases (99.99%) were used for all experiments. The membrane was mounted in a permeation cell prior to degassing the whole apparatus. Permeant gas was then introduced on the upstream side, and the permeant pressure on the downstream side was monitored using a MKS-Baratron pressure transducer. From the known steady-state permeation rate, pressure difference across the membrane, permeable area and film thickness, the permeability coefficient was determined (pure gas tests). The permeability coefficient, P (cm^3 (STP) cm/cm^2 s cmHg), was determined by the following equation:

$$P = \frac{22414}{\mathrm{A}} \times \frac{\mathrm{V}}{\mathrm{R}T} \times \frac{\mathrm{L}}{p} \times \frac{dp}{dt}$$

Where A is the membrane area (cm^2), L is the membrane thickness (cm), p is the upstream pressure (cmHg), V is the downstream volume (cm^3), R is the universal gas constant (6236.56 cm^3 cmHg/mol K), T is the absolute temperature (K), and dp/dt is the permeation rate (cmHg/s). The gas permeabilities of polymer membranes were characterized by a mean permeability coefficient with units of Barrer. 1Barrer= 10^{-10}cm^3 (STP) ·cm/ (cm^2·s·cmHg).

The gas permeability coefficient can be explained on the basis of the solution-diffusion mechanism, which is represented by the follwing equation: $P = D \times S$ where D (cm^2/s) is the diffusion coefficient and S (cm^3 (STP)/cm$^3_{\text{polym.}}$cmHg) is the solubility coefficient. The diffusion coefficient was calculated by the time-lag method, represented by the following equation $D = \frac{\mathrm{L}^2}{6\theta}$ where θ(s) is the time-lag. Once P and D were calculated, the apparent solubility coefficient S (cm^3 (STP)/cm^3 cmHg) may be calculated by the following expression:

$$S = \frac{P}{D}$$

The ideal permselectivity of a dense membrane for gas A to gas B is defined as follows:

$$\alpha_{A,B} = \frac{P_A}{P_B}$$

Results and Discussion

Polymer Characterization

Figure 2 shows the FTIR-ATR spectra of the 6FDA-TMPDA/mPDA polyimides dense films. It can be seen that the formation of peaks at 1720 and 1786 cm^{-1} which

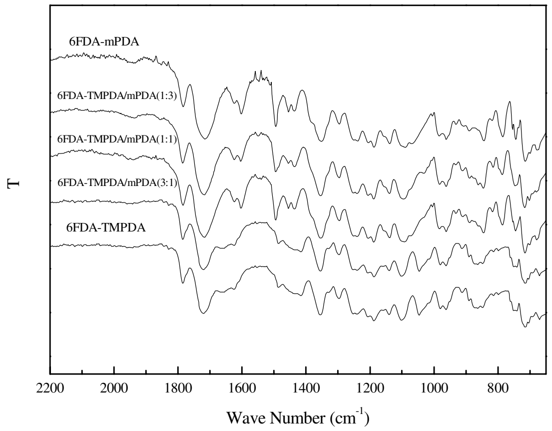

Figure 2. FTIR-ATR spectra

corresponds to the symmetric and asymmetric $\nu_{C=O}$ of imide respectively. The peak observed at 1356 cm^{-1} was assigned to $\nu_{C\text{-}N}$. All the copolyimides were assumed to be random compolymers because of the presence of single glass transition temperature in DSC traces (Table 1). Glass transition temperature increased with increase in TMPDA content. The presence of three methyl groups in TMPDA moiety hinders the rotation of the phenyl ring of TMPDA whereas the phenyl ring of comonomer mPDA rotates freely as there are no methyl groups in its phenyl ring. Temperature at which 5% weight loss observed in nitrogen atmosphere is given in Table 1. Copolyimides exhibit a single decomposition starting at a temperature above 450°C. The thermal stability generally decreases with increasing TMPDA content. This observation may be attributed to polymetric ring strain, which has been shown to decrease stability.

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: $FFV = \frac{V - V_0}{V}$, where V and V_0 are the specific volume and chain occupied volume, respectively. V_0 is calculated from the van der Waals volume $(V_0 = 1.3V_w)$ which can be obtained from Bondi's group contribution. For the copolyimides, $V_w = \mathrm{m}_1 V_{w1} + \mathrm{m}_2 V_{w2}$, where m_1 and m_2 are the molar fractions, $V_{\mathrm{w}1}$ and $V_{\mathrm{w}2}$ refer to the Van der Waals volumes of the homo-polyimides.

Table 1 Physical properties of 6FDA-TMPDA/mPDA copolyimides

PI	Tg (°C)	5% wt. loss (°C)	ρ(g.cm^{-3})	FFV
6FDA-TMPDA	383	465	1.352	0.182
6FDA-TMPDA/mPDA(3:1)[a]	358	478	1.372	0.176
6FDA-TMPDA/mPDA(1:1)[a]	339	485	1.408	0.170
6FDA-TMPDA/mPDA(1:3)[a]	330	502	1.444	0.163
6FDA-mPDA	315	519	1.474	0.156

[a] In a molar ratio of diamines in a diamine mixture

Gas transport properties

The gas permeability coefficients, ideal selectivity of 6FDA-TMPDA/mPDA series polyimides for different gases measured at 35°C and 0.2MPa are summarized in Table 2. It can be seen that the gas permeability coefficients decrease with the addition of mPDA, while the permselectivity of the gas pairs such as H_2/N_2, O_2/N_2 and CO_2/CH_4 increased considerably. The gas permeability coefficients decrease in the following sequence: $P(H_2)>P(CO_2)>P(O_2)>P(N_2)>P(CH_4)$, which agrees well with the increasing order of kinetic diameters of the gas molecules (Table 3).

In addition, Table 1 suggests that the FFV of 6FDA-TMPDA/mPDA (1:3) equals to that of 6FDA-mPDA, but 6FDA-mPDA has the lower permeability coefficients (Table 2) and diffusion coefficients (Table 4). This may arise from the fact that fractional free volume alone cannot determine the permeability. 6FDA-TMPDA/mPDA (1:3) copolyimide may have different free volume distributions, and the effective contribution of its large fractional free volume on permeability and diffusivity values is larger than that of 6FDA-mPDA polyimide. The similar phenomenon was 6FDA-durene/pPDA copolymides reported by Chung et al [31].

Table 2 Permeability coefficients and permselectivity of 6FDA-TMPDA/mPDA polyimides

PI	P (Barrer)					α		
	H_2	O_2	N_2	CO_2	CH_4	H_2/N_2	O_2/N_2	CO_2/CH_4
6FDA-TMPDA	476.36	100.30	28.20	511.94	22.42	16.89	3.56	22.84
6FDA-TMPDA/mPDA(3:1)	239.19	38.87	8.86	195.16	5.79	26.99	4.39	33.72
6FDA-TMPDA/mPDA(1:1)	139.69	18.08	3.59	88.25	2.07	38.91	5.04	42.66
6FDA-TMPDA/mPDA(1:3)	47.86	3.64	0.58	15.66	0.29	82.53	6.27	54.73
6FDA-mPDA	27.32	2.08	0.31	6.55	0.07	89.31	6.81	96.73

Table 3 The kinetic diameters of the gas molecules

	H_2	CO_2	O_2	N_2	CH_4
σ_k (Å)	2.89	3.30	3.46	3.64	3.80
T_C (K)	33.3	304.2	154.4	126.2	190.7

There is a general relationship reported in the literatures that as the permeability of gas A increases, its selectivity decreases. This behavior is easily understood if the matrix is capable of tightly packing since the free volume, or unoccupied space, is reduced thereby decreasing its ability to transport permeants. In 1991, Robeson reported trends that he found to be applicable to all permeation measurements. He observed that, regardless of the repeat unit, polymer gas transport properties did not exceed a certain boundary level when viewed on a log ($\alpha_{A/B}$) verses log (P_A) plot, where A is the faster permeating gas. This boundary is defined as the “upper bound”, which is the upper limit of gas separation performance for current state of the art membranes. The performances of 6FDA-TMPDA/mPDA copolyimides are compared to the “upper bound” trade-off lines (Figure 3~5). As shown, all of the copolyimides exhibit high gases separation performance, near, lying on or above the upper bound limit. 6FDA-TMPDA exhibits the highest permeability and lowest selectivity of the five polyimides investigated in this work. It is because the interchain spcings are so large that the chains fail to effectively discriminate between similarly sized molecules. As mPDA content is gradually added to the polymer backbone, the selecivities are higher with the permeabilities decreasing. The low permeabilities result from the significant reduction in interchanin spacing.

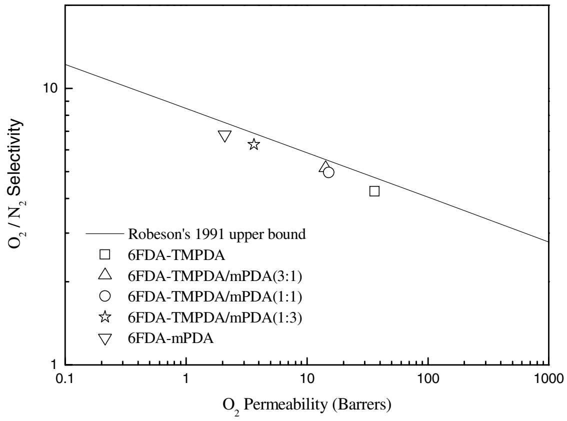

Figure 3. Performances of 6FDA-TMPDA/mPDA copolyimides compared to O_2/N_2 trade-off limit

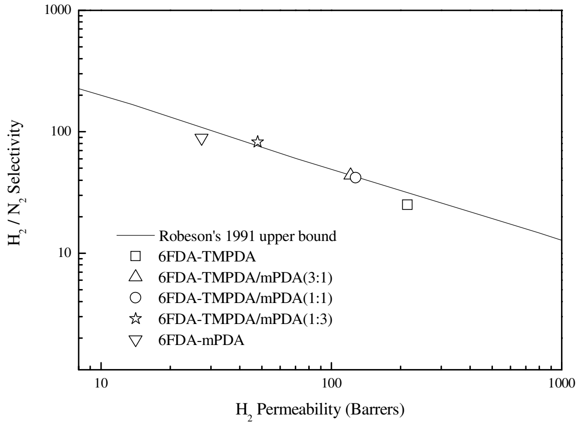

Figure 4. Performances of 6FDA-TMPDA/mPDA copolyimides compared to H_2/N_2 trade-off limit

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 diffusion coefficients of O_2, N_2, CO_2 and CH_4 obtained from the time-lag method, together with the diffusion selectivity of O_2, N_2, CO_2 and CH_4, are presented in table 4. It can be seen that the diffusion coefficients for the polyimides follow the trend: $D(O_2)>D(CO_2)>D(N_2)>D(CH_4)$. However, it is different from that of the permeability coefficients in that $P(CO_2)$ is much greater than $P(O_2)$, while $D(CO_2)$ is smaller than $D(O_2)$. It results from the specific interactions between CO_2 and the polar groups in the 6FDA-based polyimides, e.g., the -$(CF_3)_2$- and C=O in their dianhydride moieties [32, 33]. The interactions may hinder the mobility of CO_2

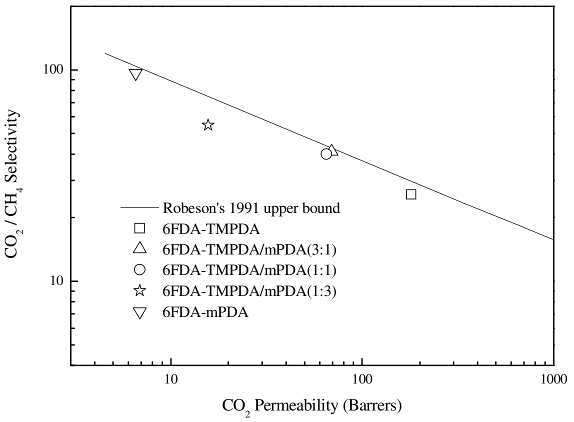

Figure 5. Performances of 6FDA-TMPDA/mPDA copolyimides compared to CO_2/CH_4 trade-off limit

molecules in the polyimide matrix. The distance between the chain segments provides a relative measure of diffusion resistance, where this resistance is reduced as the average center-to-center intersegmental spacing is increased. For all gases, 6FDA-TMPDA exhibits the highest diffusion coefficients due to its containing only the TMPDA diamine moiety results in the largest intersegmental spacing. As mPDA replaces TMPDA in the backbone, the greater chain packing leads to diffusion coefficients decrease. The diffusivity selectivities also increase upon mPDA incorporation, and as the polymer matrix becomes more tightly packed, it simultaneously becomes more selective.

Table 4 Diffusion coefficients and diffusivity selectivities for 6FDA-TMPDA/mPDA Polyimides at 35°C and 0.2Mpa

PI	Diffusion Coefficient, 10^{-8} cm^2/s				Diffusivity Selectivity	
	O_2	N_2	CO_2	CH_4	O_2/N_2	CO_2/CH_4
6FDA-TMPDA	40.87	12.63	15.33	3.38	3.23	4.53
6FDA-TMPDA/mPDA (3:1)	17.41	4.80	6.31	0.98	3.62	6.41
6FDA-TMPDA/mPDA (1:1)	8.92	2.29	3.17	0.41	3.90	7.71
6FDA-TMPDA/mPDA (1:3)	2.36	0.44	0.84	0.093	5.38	9.04
6FDA-mPDA	1.85	0.33	0.43	0.035	5.63	12.21

Table 5 shows the solubility coefficients and solubility selectivities of O_2, N_2, CO_2 and CH_4. The solubility coefficients of these gases decrease in the order of $CO_2 > CH_4 > O_2 > N_2$, which agrees well with the order of critical temperature of the gas molecules (Table 3). It can be seen that the solubility coefficients of O_2, N_2, CO_2 and CH_4 show much less change with diamine composition as compared with the diffusion coefficients. The higher condensability of CO_2 molecules in the polymer matrix contributed to the higher solubility of CO_2. The possible explanation is that the copolyimides of 6FDA-TMPDA/mPDA may have excess free volume resulting from imperfect intersegmental packing due to conformation difference between 6FDA-TMPDA and 6FDA-mPDA. This excess free volume enhances Langmuir-mode sorption and leads to higher solubility. Therefore, the solubility selectivity for CO_2/CH_4 is much greater than that of diffusion selectivity.

Table 5 Solubility coefficients and diffusivity selectivities for 6FDA-TMPDA/mPDA copolyimides at 35°C and 0.2MPa

PI	Solubility Coefficient, $cm^3(STP)/(cm^3.cmHg)$				Solubility Selectivity	
	O_2	N_2	CO_2	CH_4	O_2/N_2	CO_2/CH_4
6FDA-TMPDA	0.025	0.022	0.334	0.066	1.10	5.04
6FDA-TMPDA/mPDA (3:1)	0.022	0.018	0.309	0.059	1.21	5.26
6FDA-TMPDA/mPDA (1:1)	0.020	0.016	0.279	0.050	1.29	5.53
6FDA-TMPDA/mPDA (1:3)	0.015	0.013	0.186	0.031	1.17	14.06
6FDA-mPDA	0.011	0.0093	0.151	0.019	1.21	16.21

Conclusion

6FDA-TMPDA/mPDA copolyimides were investigated by systematically varying the diamine ratios. All the copolyimides were soluble in most of the common solvents. The gas permeability, diffusion coefficients decreased with increasing mPDA content; however, the permselectivity of gas pairs such as H_2/N_2, O_2/N_2, CO_2/CH_4 was enhanced with the incorporation of mPDA moiety. The permeability coefficients of H_2, O_2, N_2, CO_2 and CH_4 were found to decrease with the increasing order of kinetic diameters of the penetrants gases. Moreover, all of the prepared copolyimides in this work exhibited performance close to, lying on or above the existing upper bound trade-off line between permselectivity and permeability. Therefore, it is suggested that dual-layer asymmetric hollow fiber membranes made from these copolyimides can be utilized for commercial gas separation membranes.

Acknowledgements. The authors are grateful to Honeywell International, Inc. (Project Number: DICP-001-2005) for funding this study. Dr. Shaojun James Zhou, Senior Principal Engineer of Advanced Technology Honeywell International, is acknowledged for his help in this work.

References

1. Koros WJ, Fleming GK, Jordan SM, Kim TH, Hoehn HH. Prog Polym Sci 1988; 13: 339.
2. Chung TS, Kafchinski ER, Vora R. J Membr Sci 1994; 88: 21.
3. Wang WY, Ugomori T, Tanaka K, Kita H, Okamoto K, Suma Y. J Polym Sci Polym Phys 2000; 38: 2954.
4. Robeson LM. J Membr Sci 1991; 62: 165.
5. Robeson LM, Smith CD, Langsam M. J Membr Sci 1997; 132: 33.
6. Koros WJ, Fleming GK. J Membr Sci 1993; 83:1.
7. Park JY, Paul DR. J membr Sci 1997;125:23.
8. Stern SA, Liu Y, Feld WA. J Polym Sci Polym Phys 1993; 31: 939.
9. Mi Y, Stern SA, Trohalaki S. J Membr Sci 1993; 77: 41.
10. Hirayama Y, Yoshinaga T, Kusuki Y, Ninomiya K, Sakakibara, T, Tamari T. J Membr Sci 1996; 111: 169.
11. Stern SA. J Membr Sci 1994; 94: 1.
12. Tanaka K, Kita H, Okano M, Okamoto K. Polymer 1992; 33: 585.
13. Hiroyoshi K, Mikawa M, Nagaka S. J Membr Sci 1997; 137: 241.

14. Hachisuka H, Ohara T, Ikeda K. J Membr Sci 1996; 116: 265.
15. Chung TS, Kafchinski ER, Vora RH. J Membr Sci 1994; 88: 21.
16. Chung TS, Kafchinski ER, Foley P. J Membr Sci 1992; 75: 181.
17. Chung TS, Lin WH, Vora RH. J Membr Sci 2000; 167: 55.
18. Li DF, Chun TS, Wang R, Liu Y. J Membr Sci 2002; 198:211.
19. Chun BW, Ishizu C, Itatani H, Haraya K, Shindo Y. J Polym Sci, Part B Polym Phys 1994;32:1009.
20. Chiou JS, Paul DR. J Appl polym Sci 1987;34:1037.
21. Paul DR. J Membr Sci 1984;18:75.
22. Toy LG, Freeman BD, Spontak RJ, Morisato A, Pinnau I. Macromolecules1997;30:4766.
23. Kapantaidakis GC, Kaldis SP, Sakellaropoulos GP, Chira E, Loppinet B, Floudas G. J Polym Sci Part B Polym Phys 1999;37:2788.
24. Suzuki T, Yamada Y. J Polym Sci Part B Polym Phys 2006;44:291.
25. Richard A, Hayes HD. US pat4717393.
26. Staudt-Bickel C, Koros WJ. J Membr Sci 1999;155:145.
27. Chung TS, Shao L, Tin PS. Macromol Rapid Commun 2006;27:998.
28. Mikawa M, Nagaoka S, Kawakami H. J Membr Sci 1999;163:167.
29. Coleman MR, Koros WJ. J Membr Sci 1990;50:285.
30. Chung TS, Lin WH, Vora RH. J Applied Polym Sci 2001;81:3552.
31. Lin WH, Vora RH, Chung TS. J Polym Sci Part B Polym Phys 2000;38:2703.
32. Liu SL, Wang R, Chung TS, Chng ML, Liu Y, Vora RH. J Membr Sci 2002;202:165.
33. Liu SL, Wang R, Liu Y, Chng ML, Chung TS. Polymer 2001;42:8847.