

Gas separation properties of pendent phenyl substituted aromatic polyamides containing sulfone and hexafluoroisopropylidene groups

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Abstract

The synthesis and gas transport properties of aromatic polyisophthalamides (PIPAs) based on isophthaloyl chloride (IPC) derivatives bearing a pendent phenyl group and a hexafluoroisopropylidene (6F) linkage in the main chain are reported. The properties of these polymers are compared with the properties of similar PIPAs containing sulfonyl (SO₂) rather than 6F in the main chain. Polymers containing a phenyl pendent group at the five position of the isophthaloyl linkage are more permeable than those bearing only a hydrogen atom at this position, although increases in permeability are generally accompanied by decreases in selectivity. In the SO₂-bearing polymer, the addition of a phenyl pendent group hinders chain packing more than in the 6F containing PIPAs. Consequently, permeability coefficients increase more upon addition of a pendent phenyl group in SO₂-containing rather than 6F-containing PIPAs. The effect of amide linkage reversal on the gas transport properties of a polymer containing 6F linkages in the chain backbone and a hydrogen atom at the five position of the isophthaloyl linkage was minimal. All the PIPAs considered in this study were more permeable to nitrogen than to methane, some with nitrogen/methane selectivities of more than two. © 1999 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Polymeric materials for gas separation applications should be highly permeable and highly selective [1]. Typically, there is a tradeoff between permeability and selectivity in polymeric materials [2,3]. However, recent studies have demonstrated that both permeability and selectivity may be enhanced by incorporation of bulky pendent groups in glassy membrane-forming polymers that simultaneously decrease chain packing efficiency and hinder torsional mobility [4–7]. Gas separation properties of polycarbonates, [4] polysulfones, [5,6] and polyimides [7] have been optimized using this heuristic. Typically, frustrating chain packing efficiency increases permeability while reductions in torsional mobility improve selectivity [1].

As a class, aromatic polyamides offer excellent thermal and mechanical properties, good chemical resistance, and are easily spun into hollow fibers appropriate for gas

separation modules [8,9]. Because polyamides commonly have high cohesive energy density and show a strong propensity for very efficient polymer chain packing, they normally exhibit low permeability to small molecules [10]. However, Ghosal et al. observed that the addition of bulky pendent groups to aromatic polyamides renders them wholly amorphous and moderately permeable [3,11]. This report describes the synthesis and gas transport properties of aromatic polyisophthalamides (PIPAs) based on isophthaloyl chloride (IPC) derivatives bearing a pendent phenyl group and hexafluoroisopropylidene (6F) linkage in the main chain. The properties of these polymers are compared with those of similar PIPAs containing sulfonyl (SO₂) rather than 6F in the main chain. The effect of amide linkage reversal on the gas transport properties of a 6F containing polyamide with no pendent groups is also presented.

2. Experimental

2.1. Monomer and solvent purification

N,N-dimethylacetamide (DMAc) was vacuum distilled twice, the first time over phosphorous pentoxide and the

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second time over calcium hydride. Subsequently, it was stored in a dark glass bottle over molecular sieves (4D). Trimethylchlorosilane (TMSCl) was distilled twice at normal pressure under nitrogen. Isophthaloyl chloride (IPC) was distilled at reduced pressure. 2,2-bis(4-carboxyphenyl) hexafluoropropane (6F*DA) was obtained from Chriskev Co. (Kansas City, KS). *m*-Phenylenediamine (MPD) and 4,4'-sulfonyldianiline (DDS) were obtained commercially from Fluka (Ronkonkoma, NY) and were sublimed twice before use. 4,4'-hexafluoroisopropylidene dianiline (6FDA) was kindly supplied by Hoechst Celanese and was used as received. Other commercially available reagents were used as received.

2.2. Monomer synthesis: Synthesis of 5-phenylisophthaloyl chloride (PHC)

A solution of 0.36 mol of phenylboronic acid and 1.0 mol of Na₂CO₃ in 400 ml of water was added to a vigorously stirred solution of 0.15 mol of 3,5-dimethylbromobenzene and 1.5 mmol of tetrakis (triphenyl-phosphine) palladium (0) in 300 ml of toluene under a nitrogen atmosphere. The stirred mixture was refluxed for 24 h and then cooled and partitioned between dichloromethane (200 ml) and a 2 M aqueous solution of Na₂CO₃ (100 ml) containing 25 ml of concentrated NH₄OH. The organic layer was dried over magnesium sulfate, filtered through Celite 7, and then concentrated to dryness under reduced pressure. Pure 3,5-dimethylbiphenyl was obtained by vacuum distillation (yield 95%, b.p. 128°C/7 mm Hg).

5-Phenylisophthalic acid was prepared from 3,5-dimethylbiphenyl by treatment with an excess of KMnO₄ in H₂O/pyridine (vol. ratio 1/1) at 90°C. The diacid was isolated by precipitation with dilute HCl from the alkaline solution. It was recrystallized from acetic acid (yield 85%, m.p. 346°C–347°C).

5-Phenylisophthaloyl chloride (PHC) was synthesized from phenylisophthalic acid by refluxing it with a tenfold molecular excess of thionyl chloride. Once the excess thionyl chloride was stripped off, the diacid chloride was recrystallized from hexane and finally distilled at reduced pressure (yield 80%, m.p. 119°C–120°C) [12].

2,2-bis(4-chloroformylphenyl) hexafluoropropane (6F*DC) was synthesized from 2,2-bis(4-carboxyphenyl) hexafluoropropane by refluxing it with a tenfold molecular excess of thionyl chloride. Once the excess thionyl chloride was removed, the diacid chloride was recrystallized from hexane and finally sublimed under high vacuum just prior to use (yield 75%, m.p. 105°C–106°C).

2.3. Polymer synthesis

The following example illustrates the general procedure employed for polyamide synthesis. A flask equipped with a mechanical stirrer and blanketed with dry nitrogen was flame dried and charged with 15 ml of DMAc and 0.01 mol of diamine (i.e. 4,4'-diaminodiphenylsulfone

(DDSO) or 6FDA). The mixture was stirred at room temperature until all solids had dissolved. Then the solution was cooled to –5°C and the required amount of TMSCl was slowly injected through a serum cap. The temperature was raised to room temperature and the solution was stirred for 15 min. to assure the formation of the silylated diamine. The solution was then cooled to –5°C, and 0.01 mol of the acid chloride (IPC or PHC) was rapidly added using a funnel that was subsequently rinsed with 5 ml of DMAc. The reaction mixture was stirred for 1 h at this temperature, after which it was heated to room temperature and left for a further 3 h. The resulting polymer solution was poured into 500 ml water. The precipitate was washed with hot water and hot methanol and extracted in a Soxhlet extractor with acetone to remove solvent and oligomers. The polymer from 6FDA and IPC required extraction in methanol since it swelled in acetone. All of the polymers were dried overnight under vacuum at 120°C. Essentially quantitative yields were obtained.

2.4. Polymer characterization

Elemental analysis and nuclear magnetic resonance (NMR) spectroscopy were used to identify intermediates, monomers and polymers. ¹H and ¹³C NMR spectra were recorded on a Varian Gemini-200 spectrometer tuned at 200 and 50.38 MHz respectively, using chloroform-*d* or dimethyl sulfoxide-*d*₆ as solvents. Inherent viscosities (IV) were determined in an automated Ubbelohde viscometer using 0.5% (w/v) polymer solutions in DMAc at 25 ± 0.1°C. Glass transition temperatures (*T*_g) were determined using a Perkin-Elmer DSC-7 calorimeter at a heating rate of 10°C/min. The differential scanning calorimetry (DSC) measurement cell was purged with nitrogen during these measurements.

Polymer density was determined by flotation of small film samples in a density gradient column, which was maintained at 23 ± 0.1°C, using a method described previously [11]. The density data were used to characterize chain packing by estimating the fractional free volume (FFV) according to the following relation [11]

$$\text{FFV} = \frac{V - 1.3V_w}{V}, \quad (1)$$

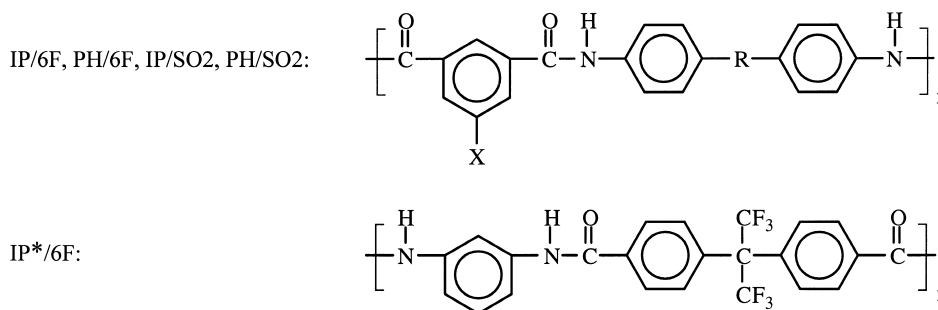
where *V* is the polymer specific volume, and *V*_w is the specific Van der Waals volume calculated using the group contribution method of Bondi [13].

Films for permeation studies were prepared by casting 10%–15% (w/v) polymer solutions onto a glass plate. The solvent was a 1/1 (v/v) mixture of DMAc and *N,N*-dimethylformamide for all 6FDA-containing polymers. The films were cast in an oven at 100°C and left for 48 h to dry. Afterwards, the films were cooled, lifted from the glass plate, and further annealed for 48 h in a vacuum oven at 160°C to remove residual solvent. All polymer films were between 1 and 2 mils (25–50 μm) thick.

Table 1
Physical Property Characterization

Polymer	X	R	Density (g/cm ³)	FFV	T _g (°C)	IV (dl/g)
IP/6F	–H	–C(CF ₃) ₂ –	1.411	0.149	297	1.94
IP*/6F	–H	–C(CF ₃) ₂ –	1.407	0.146	303	1.54
PH/6F ^a	Phenyl	–C(CF ₃) ₂ –	1.361	0.152	311	1.07
IP/SO ₂	–H	–SO ₂ –	1.378	0.100	323	1.01
PH/SO ₂ ^a	Phenyl	–SO ₂ –	1.341	0.107	328	1.03

^a PH/6F and PHSO₂ are semicrystalline and contain approximately 10 weight percent crystallinity based on WAXD estimates:



A barometric permeation method was used to determine steady state pure gas permeability at 35°C at pressures up to 20 atm [14]. The downstream pressure was kept below 10 mmHg, while the upstream pressure was maintained at super-atmospheric pressures. N₂ and He were purchased from National Specialty Gases (Durham, NC). CO₂, O₂ and H₂ were obtained from Linde (Danbury, CT), and CH₄ was bought from Air Products (Allentown, PA). CH₄ and O₂ purity was > 99.5%; all other gases had purities >99.99%. All permeability measurements were performed on films which had first been “vector conditioned” with CO₂ at 20 atm for 24 h [15]. Gas diffusivities, *D*, were estimated from time lag data at an upstream pressure of 3 atm using the relation: $D = l^2/6\theta$, where *l* is film thickness, and θ is the time lag [16]. Apparent solubility coefficients, *S*, were estimated using the relation: $S = P/D$, where *P* is the apparent steady state permeability coefficient [16]. Time lags for H₂ and He were too short to permit accurate diffusion coefficient determination. For safety reasons, H₂ permeabilities were not determined at pressures greater than approximately 3 atm.

Wide angle X-ray diffraction (WAXD) spectra of the PIPA films were obtained using a Siemens Kristalloflex 4 X-ray generator and a Siemens type $F\theta/2\theta$ goniometer. The X-rays were generated using a CuK _{α} (wavelength = 1.54 Å) source.

3. Results and discussion

3.1. Polymer synthesis

PIPAs containing sulfone and hexafluoroisopropylidene groups were prepared by a modification of the low temperature method in DMAc as described in the experimental part.

The synthesis was achieved by using in situ silylated aromatic diamines as described elsewhere [17]. By means of this modification it was possible to obtain PIPAs from aromatic diamines with electron withdrawing groups attached to the aromatic rings. Moreover, polymers prepared by this route had much higher molecular weight than those obtained by the classical low temperature method [3,11].

3.2. Polymer characterization

Table 1 presents the chemical structure and selected physical properties of PH/6F, PH/SO₂ and IP*/6F. For comparison, relevant data for unsubstituted PIPAs, IP/6F and IP/SO₂ are also included in the table [3]. No indications of crystallinity were observed in DSC scans or wide angle X-ray diffraction (WAXD) spectra for IP/6F, IP*/6F and IP/SO₂ [3]. However, DSC and WAXD spectra of PH/6F and PH/SO₂ indicated the presence of crystallinity in each polymer sample, which was estimated to be approximately 10 wt.% from WAXD results. The polymer physical properties reported for PH/6F and PH/SO₂ in Table 1 are for the as-cast, semicrystalline polymer samples. Transport property results presented in subsequent tables and figures of this article are not corrected for crystallinity.

From Table 1, the fractional free volume values (FFV) of the 6F polymers are markedly higher than those of the corresponding SO₂ analogs. These results are consistent with earlier observations of an increase in polymer free volume upon incorporation of bulky hexafluoroisopropylidene (6F) linkages into the chain backbone [3]. The addition of a pendent phenyl group to the unsubstituted PIPAs (IP/6F and IP/SO₂) to form PH/6F and PH/SO₂, respectively, slightly increases the average FFV in the polymers, even though the phenyl-bearing polymers contain low levels of

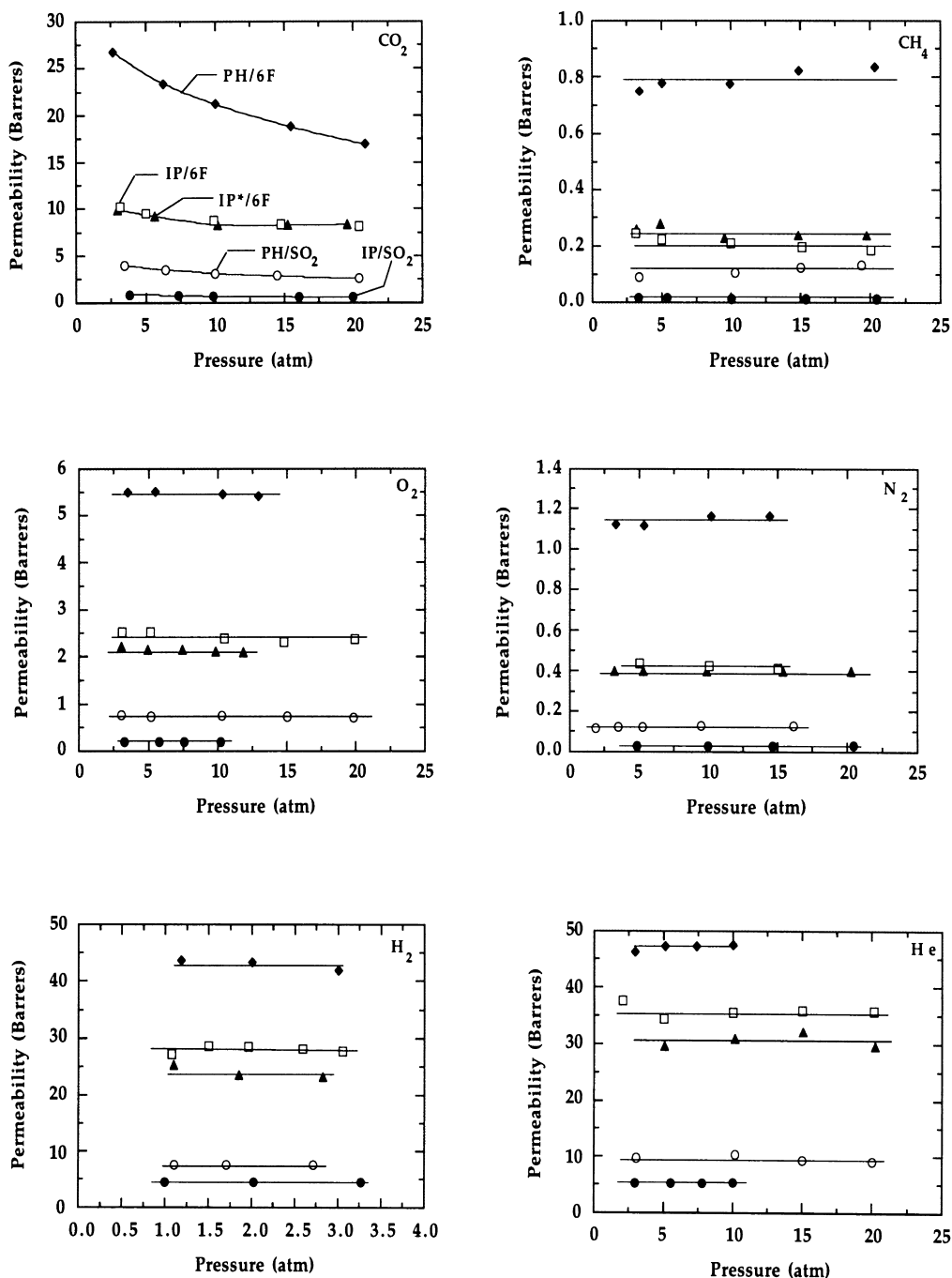


Fig. 1. The effect of upstream pressure on permeability at 35°C. Permeability coefficients presented for PH/6F and PH/SO₂ are for semicrystalline samples.

crystallinity while the unsubstituted analogs are wholly amorphous. The addition of a pendent phenyl group to IP/6F increases the glass transition temperature, T_g , suggesting that the phenyl group hinders backbone motions important in the glass–rubber transition. This effect is more pronounced for the 6F containing polymers than the SO₂ polymers. In fact, the increase in T_g in PH/SO₂ relative to IP/SO₂ is small and near the uncertainty limits of the T_g measurement. The unsubstituted SO₂-bearing polymer, IP/SO₂, is more rigid than its 6F-containing analog,

IP/6F, (based on glass transition temperature, which is 26°C higher in IP/SO₂ than in IP/6F). The addition of a phenyl substituent to the more rigid, sulfone-rich matrix appears to have only a modest effect on glass transition temperature, while incorporation of phenyl substituents in the more flexible (i.e. lower T_g) 6F-containing polymer has a greater impact on torsional mobility.

Amide linkage reversal slightly decreases FFV and increases T_g in IP*/6F relative to IP/6F. However, these effects are subtle and near the uncertainty limits of the

Table 2

Pure Gas Permeabilities and Permselectivities at 10 atm and 35°C. Permeability coefficients are reported in Barrers, where 1 Barrer = 10^{-10} cm³(STP) cm/(cm² s cmHg)

Polymer	P_{He}	$P_{\text{H}_2}^a$	P_{O_2}	P_{N_2}	P_{CO_2}	P_{CH_4}	$P_{\text{CO}_2}/P_{\text{CH}_4}$	$P_{\text{O}_2}/P_{\text{N}_2}$	$P_{\text{H}_2}/P_{\text{CH}_4}$	$P_{\text{N}_2}/P_{\text{CH}_4}$
IP/6F	35	29	2.4	0.42	9.0	0.20	45	5.7	145	2.1
IP*/6F	31	23	2.2	0.40	8.4	0.24	35	5.5	96	1.7
PH/6F	48	42	5.5	1.2	21	0.78	27	4.6	54	1.5
IP/SO ₂	5.2	4.3	0.19	0.031	0.78	0.014	56	6.1	310	2.2
PH/SO ₂	10	7.6	0.75	0.13	3.2	0.11	29	5.8	69	1.2

^a Hydrogen permeability coefficients are reported at 3 atm.

density and T_g measurements. IP/6F is synthesized from the condensation of isophthaloyl chloride (IPC) and 4,4'-hexafluoroisopropylidene dianiline (6FDA) in an in-situ silylation reaction as described previously [3]. IP*/6F is synthesized from m-phenylenediamine (MPD) and 6F*DC using TMSCl as a catalyst. Both syntheses can be performed easily and produce polymer in high yield with high molecular weight. However, the presence of electron releasing groups in the diamine moiety improves the oxidative resistance of aromatic polyamides [18]. Therefore, IP/6F would probably have better chemical resistance towards, for example, chlorine. In the absence of significant differences in physical and transport properties, IP/6F would be more attractive as a potential membrane material than IP*/6F because: (1) the synthesis cost is lower, (2) in-situ silylation makes it possible to synthesize somewhat higher molecular weight polymer (based on the IV values reported in Table 1), and (3) the presence of electron withdrawing groups attached to the diamine moiety should improve the oxidative behavior of the polymer.

Solvent cast films with good mechanical properties were fabricated from the polymers listed in Table 1. Relatively

high inherent viscosities, greater than 1.0 dl/g, were obtained for all polymers. These high IV values indicate that the synthesis resulted in relatively high-molecular-weight polymers.

3.3. Gas transport

Fig. 1 presents permeabilities of the PIPAs to CO₂, CH₄, N₂, O₂, H₂ and He at 35°C as a function of upstream pressure. Permeability coefficients of PH/6F and PH/SO₂ presented in Fig. 1 have not been corrected for crystallinity. Based on literature correlations between gas permeability and crystalline content and a crystallinity level of approximately 10% in these samples, the permeability of wholly amorphous PH/6F and PH/SO₂ might be expected to be approximately 20% higher than the values reported in Fig. 1 [19]. Penetrant permeability coefficients in all of the polymers are independent of pressure, except for CO₂, where permeability coefficients decrease with increasing pressure. This behavior is typical for the permeation of gases in glassy polymers over the moderate pressure ranges considered in this study [1]. Based on the data presented in Fig. 1, the permeabilities are in the following order: PH/6F > IP/6F ≈ IP*/6F > PH/SO₂ > IP/SO₂. An increase in the permeability coefficients of the semicrystalline samples (PH/6F and PH/SO₂) of 20% or so would not change this order.

Gas permeability coefficients at 10 atm (except for H₂ permeability, which is reported at 3 atm) are recorded in Table 2. Polymers bearing phenyl substituents are more permeable than their unsubstituted analogs to all penetrants tested. For example, permeability coefficients are 1.5–4 times higher in PH/6F than in IP/6F. Similarly, the permeability coefficients of the gases considered in this study are 2–9 times higher in PH/SO₂ than in IP/SO₂. Pendent phenyl group substitution has a greater impact on permeability coefficients of SO₂-containing polymers than on those of 6F-bearing polymers. This phenomenon may be related to the much higher FFV in the 6F-bearing polymers. Introducing a bulky pendent substituent into a high FFV environment may inhibit chain packing and, therefore, increase permeability to a lesser extent than introducing the same substituent into a low free volume matrix where such groups could disrupt chain packing strongly. Consistent with this point of view, the addition of a pendent phenyl group to

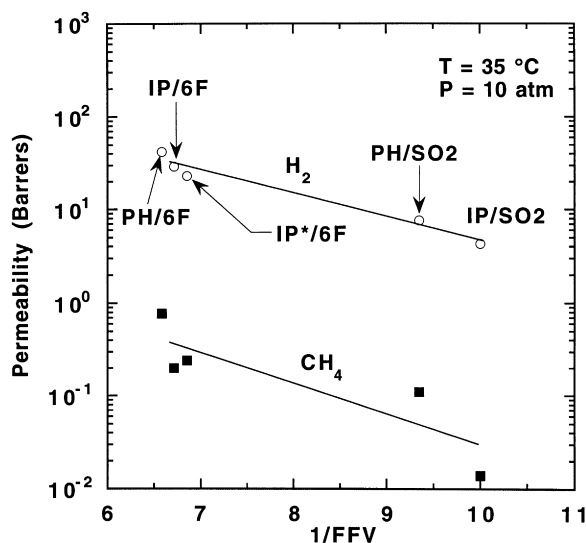


Fig. 2. The dependence of gas permeabilities on fractional free volume. Permeability coefficients and FFV presented for PH/6F and PH/SO₂ are for semicrystalline samples.

Table 3
Gas Solubility and Diffusivity at 3 atm and 35°C^a

Polymer	S_{O_2}	S_{N_2}	S_{CO_2}	S_{CH_4}	S_{O_2}/S_{N_2}	S_{CO_2}/S_{CH_4}	S_{N_2}/S_{CH_4}	D_{O_2}	D_{N_2}	D_{CO_2}	D_{CH_4}	D_{O_2}/D_{N_2}	D_{CO_2}/D_{N_2}	D_{N_2}/D_{CH_4}
IP/6F	0.29	0.32	5.26	1.2	0.9	4.4	0.27	6.3	1.0	1.3	0.13	6.3	10	7.7
IP*/6F	0.42	0.49	9.1	1.5	0.9	6.1	0.33	4.0	0.62	0.83	0.13	6.4	6.4	4.8
PH/6F	0.79	0.56	9.8	3.2	1.4	3.1	0.18	5.3	1.5	2.1	0.18	3.5	12	8.3
IP/SO ₂	0.56	0.58	7.5	1.2	1.0	6.2	0.48	0.26	0.04	0.09	0.01	6.5	9.0	4.0
PH/SO ₂	0.69	0.40	7.1	1.0	1.7	7.1	0.40	0.86	0.23	0.43	0.07	3.7	6.1	3.3

^a S in cm^3 (STP)/(cm^3 polymer atm); D has units of $10^{-8}\text{cm}^2/\text{s}$ and was determined from time lag measurements.

IP/6F resulted in a 2% increase in FFV whereas the addition of the phenyl group to IP/SO₂ increased FFV by 7%.

Except for CH₄, permeability coefficients in IP/6F are slightly higher than in IP*/6F, consistent with the marginally higher FFV in IP/6F. The effect is, however, subtle and the observed differences are near the resolution of the experimental methods used. Therefore, reversal of the amide linkage does not have an easily detectable effect on the permeation properties of IP/6F and IP*/6F.

Fig. 2 presents the dependence of CH₄ and H₂ permeability on FFV for these aromatic polyamides. The dependence of permeability on FFV was similar for the other gases considered. In many amorphous polymer systems, the logarithm of permeability decreases roughly linearly with increasing reciprocal fractional free volume [20]. As is evident from Fig. 2, for the PIPAs considered in this study, permeability coefficients generally follow this trend. This result suggests that the impact of crystallinity on the permeation properties of these materials is a minor effect. Increases in permeability were generally accompanied by decreases in selectivity, estimated as the ratio of pure penetrant permeability. This result is consistent with the trade-off between permeability and selectivity observed

by Robeson et al. for gas separation membrane polymers [2]. Therefore, reversal of amide linkage or addition of a pendent phenyl substituent does not result in unusual trade-offs between permeability and selectivity.

Table 3 presents gas solubilities, diffusivities, diffusivity selectivities and solubility selectivities for 6F and SO₂-containing polymers at 35°C and 3 atm. Diffusion coefficients are estimated from the time lag at 3 atm. Penetrant diffusivities in the 6F-bearing polymers are substantially higher than those in the SO₂-bearing polymers, consistent with the higher free volume in the 6F polymers. Also, diffusion coefficients are higher in the phenyl-substituted polymers (PH/6F and PH/SO₂) than in their unsubstituted analogs (IP/6F and IP/SO₂). This trend is also consistent with the higher free volume in the unsubstituted analogs. However, there is no systematic trend in diffusivity selectivity that is easily rationalized based on primary chemical structure. Therefore, the replacement of a SO₂ linkage by a 6F linkage apparently increases FFV without increasing large scale, non-discriminant backbone molecular motion commonly understood to reduce diffusivity selectivity [11]. With the exception of CH₄, the diffusion coefficients are higher in IP/6F than in IP*/6F, consistent with the slightly higher free volume in IP/6F. These differences in diffusivity, are however, small and near the resolution of the measurement. With the exception of O₂, increases in permeability were accompanied by an increase in diffusivity. For SO₂-containing polymers, most of the change in permeability could be attributed to a change in the diffusion coefficient, and therefore to changes in chain torsional mobility and chain packing.

For many polymer families, the logarithm of penetrant diffusivity decreases linearly with reciprocal fractional free volume [1]. Qualitatively, models of the effect of free volume on penetrant diffusion coefficients predict this trend [1]. Fig. 3 presents several penetrant diffusion coefficients as a function of reciprocal fractional free volume. The diffusion coefficients generally decrease with increasing reciprocal fractional free volume, as expected.

From the data in Table 3, gas solubility changes in the following order: $S_{CO_2} > S_{CH_4} > S_{O_2} \approx S_{N_2}$. This trend is consistent with the decreasing condensability of the penetrants (as measured by, for example, critical temperature) [21,22]. Gas solubility generally increases with increasing critical temperature in the absence of specific

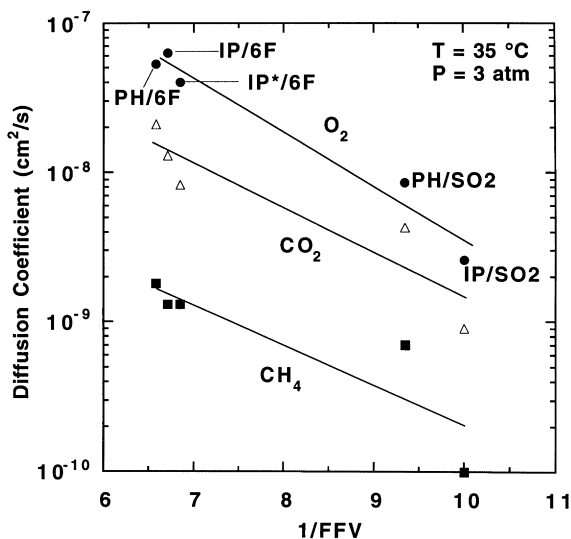


Fig. 3. The dependence of gas diffusivities on fractional free volume. Diffusion coefficients and FFV presented for PH/6F and PH/SO₂ are for semicrystalline samples.

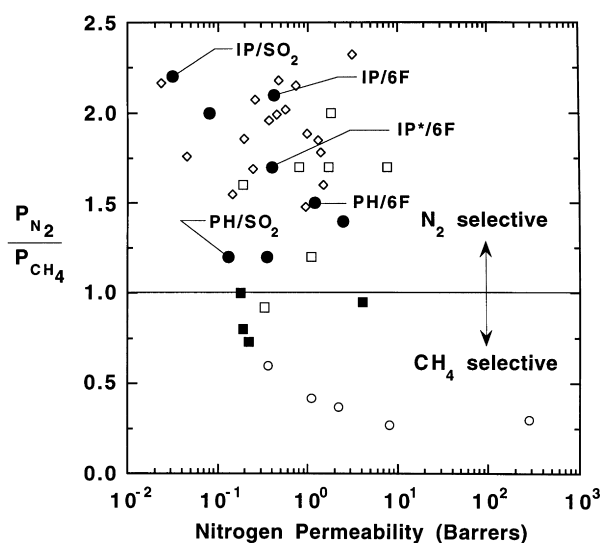


Fig. 4. Comparison of nitrogen/methane separation performance of conventional rubbery (○)²⁴ and glassy polymers (■)²⁴, polycarbonates (□)⁴, polyimides (◇)⁷ and aromatic polyamides (●)³.

polymer-penetrant interactions. Gas solubility was observed to be a much weaker function of free volume than diffusivity, with gas solubility increasing slightly with increasing free volume [1]. In these polyamides, there was no obvious correlation between penetrant solubility coefficients and FFV. Subtle variations in gas solubility with polymer structure and, in turn, free volume may be masked by experimental uncertainty. As the solubility coefficients are estimated indirectly from penetrant permeability and diffusivity, experimental errors associated with each of these quantities additively influence the precision of the calculated solubility coefficients. In this regard, an oxygen/nitrogen solubility selectivity of less than 1 (cf. Table 3) is very unusual and is probably an experimental artifact because of limitations in the accuracy of determination of solubility by permeability and time lag measurements of diffusion coefficients. In general O₂ is more soluble than N₂ in both glassy and rubbery polymers [5,23].

The removal of nitrogen from methane in natural gas processing could be a commercially important and challenging membrane separation [24]. For polymer membranes to be useful for this separation, they should be more permeable to nitrogen than to methane [24]. This property permits the selective removal of nitrogen while maintaining the natural gas product at or near feed pressure. Fig. 4 presents the N₂/CH₄ selectivity of PIPAs as a function of nitrogen permeability. For comparison, the selectivities of conventional rubbery and glassy polymers [24], polyimides [7] and polycarbonates [4,25] have also been included in the figure. All PIPAs considered in this study are more permeable to nitrogen than to methane and the N₂/CH₄ selectivity varies from 1.2 to 2.3. For many polymers, nitrogen permeability is lower than methane permeability, and consequently, such conventional polymers are methane selective [24].

However, Kim et al. [24] and Stern [7] have observed aromatic polyimides to be more permeable to nitrogen than to methane. Similarly, Koros et al. have reported several nitrogen-selective polycarbonates [4,25].

The selectivity of a polymer for N₂ over CH₄, α_{N_2/CH_4} can be expressed as

$$\alpha_{N_2/CH_4} = \frac{P_{N_2}}{P_{CH_4}} = \frac{D_{N_2}}{D_{CH_4}} \times \frac{S_{N_2}}{S_{CH_4}}, \quad (2)$$

where P_{N_2} and P_{CH_4} are the permeability coefficients of N₂ and CH₄ respectively, D_{N_2}/D_{CH_4} is the diffusivity selectivity and S_{N_2}/S_{CH_4} is the solubility selectivity. Diffusivity selectivity always favors the smaller penetrant while solubility selectivity often favors the larger (and generally more condensable) penetrant [26]. Consequently, for N₂/CH₄ mixtures, $D_{N_2}/D_{CH_4} > 1$ while $S_{N_2}/S_{CH_4} < 1$. Therefore, there is usually a tradeoff between diffusivity and solubility selectivity, and the permselectivity, α_{N_2/CH_4} , can be larger or smaller than one depending on the relative magnitude of these terms [26]. For typical glassy polymers, such as polysulfone, diffusivity selectivity is not high enough to offset solubility selectivity, and therefore, polysulfone is more permeable to methane than to nitrogen [27,28]. However, for the PIPAs considered in this study, the diffusivity selectivity in favor of nitrogen is large enough to more than counterbalance the solubility selectivity (cf. Table 3). Kim et al. have observed similar effects in aromatic polyimides, and attributed the strong size-selective behavior of the polyimides to the limited mobility of the polymer backbone segments [24]. The restricted mobility of the main chain segments is presumed to reduce the distribution of intersegmental gap sizes that are responsible for penetrant diffusion, thereby increasing diffusivity selectivity [24]. Similar effects are probably responsible for the observed nitrogen-selective behavior in PIPAs.

4. Conclusions

The effect of backbone and pendent group modifications on the gas solubility, diffusivity, permeability and selectivity of a series of aromatic polyamides is reported. The addition of pendent phenyl substituents increased permeability of the polymers relative to the unsubstituted polymers. However, increases in permeability were accompanied by decreases in selectivity. Penetrant diffusivities were generally higher in the phenyl substituted polymers, consistent with the higher free FFVs of these PIPAs. The addition of a pendent phenyl group to the unsubstituted polymer modestly increases the fractional free volume in 6F and SO₂ containing polyamides. Introduction of such bulky pendent substituents into a high FFV environment seems to have less influence on transport properties than introducing the same substituents into low free volume matrices.

Reversal of the amide linkage direction of IP/6F has a very small effect on FFV, and the transport properties of the

two polymers (i.e. IP/6F and IP*/6F) were similar. These PIPAs are more permeable to nitrogen than to methane because of high diffusivity selectivity (which favors nitrogen).

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