Gas Permeability and Selectivity of Hexafluoroisopropylidene Aromatic Isophthalic Copolyamides

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ABSTRACT: The synthesis, thermal, and gas transport properties of poly(hexafluoro-isopropylidene isophthalamide), HFA/ISO homopolymer, and HFA/TERT-*co*-HFA/ISO copolyamides with different poly(hexafluoroisopropilydene-5-*t*-butylisophthalamide), HFA/TERT, ratios are reported. The results indicate that the glass transition temperatures of the copolyamides increase as the concentration of HFA/TERT in the polyamide increases. The gas permeability coefficients in the polyamides and copolyamides are independent of pressure or decrease slightly particularly with CO_2, N_2, and CH_4. It was seen that HFA/TERT is 2–6 times more permeable than HFA/ISO, depending on the gas being considered. This was assigned to the presence of the bulky lateral substituent, *t*-butyl group in HFA/TERT and HFA/TERT-*co*-HFA/ISO copolyamides. This substituent increases fractional free-volume, as expected. Therefore, the gas permeability and diffusion coefficients generally increase with increasing fractional free-volume. The experimental results for the gas permeability and permselectivity for the copolyamides was well represented by a logarithmic mixing rule of the homopolyamides permeability coefficients and their volume fraction. The selectivity of gas pairs, such as O_2/N_2, CO_2/CH_4, and N_2/CH_4 decreased slightly with the addition of HFA/TERT. The temperature dependence of permeability for homopolyamides and copolyamides can be described by an Arrhenius type equation. © 2005 Wiley Periodicals, Inc. J Polym Sci Part B: Polym Phys 43: 2625–2638, 2005
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INTRODUCTION

The separation of gases by polymeric membranes is used in a wide variety of applications, such as the removal of helium from natural gas, hydrogen recovery from ammonia, carbon dioxide recovery from natural gas and biogas, or concentration of oxygen from air among others.[1]

In the last years, special attention has been focused on the development of high glass transition temperature amorphous polymers, such as polyarylates,[2] poly(aryl-eteres),[3] polyaramides,[4–6] polysulfones,[7,8] polycarbonates,[9] and polyimides,[10–14] which have lead to a new generation of gas separation membrane materials. However, it is only in recent years that the relationship between structure and gas permeability and selectivity of polymers has become the object of several systematic studies. On the basis of these systematic investigations, several criteria have been proposed for polymer structures that might

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exhibit a high gas permeability as well as a high selectivity and show high thermal and mechanical stability.[10] The ideal polymeric material for gas separation applications should be highly permeable and highly selective. It has also been observed that both permeability and selectivity may be enhanced by incorporation of bulky pendant groups in glassy membrane-forming polymers that simultaneously decrease chain packing efficiency and hinder torsional mobility.[5]

Recent studies indicate that the packing density and segmental mobility of the polymer chain are two dominant factors that affect gas transport properties. High permeabilty is primarily related to high free-volume, while significant increases in gas permselectivity may be due to restricted segmental motion. On the basis of these facts, one can design new polymers to combine the two favorable factors, thus preparing polymers with both high permeabilty and high permselectivity.[15]

In this regard, aromatic polyamides are an interesting class of polymeric materials for the preparation of membranes for gas separation. These polymers offer excellent thermal and mechanical properties, and they also show good chemical resistance. Because polyamides commonly have high cohesive energy density and show a strong propensity for very efficient polymer chain packing, they normally tend to exhibit crystallinity and low permeability to small molecules.[5] However, Ghosal et al.[4] observed that the addition of bulky pendant groups to aromatic polyamides renders them wholly amorphous and moderately permeable. The same observation was made by Singh et al.[5] who studied the effect that backbone and pendant group modifications induce on the gas solubility, diffusivity, and permeability coefficients, as well as the selectivity of a series of aromatic polyisophthalamides (PIPAs) based on isophthaloyl chloride (IPC) derivatives that bear a pendant phenyl group and a hexafluoroisopropylidene (6F) linkage in the main chain. The addition of pendant phenyl groups hinders chain packing in the SO_2-bearing polymer in a stronger manner than in the 6F-containing PIPAs. As a result, the former has a greater permeability coefficient on the addition of a pendant phenyl group than the latter.

Morisato et al.[6] determined the effect of systematic chemical structure variation on gas permeability properties of a family of amorphous PIPAs, based on the condensation of IPC derivatives containing pendant groups and 4,4'-(hexafluoroisopropylidene) dianiline (HFA). In this work, bulky *t*-butyl groups, substituted at the 5th position of the diacid moiety and bulky, hexafluoropropylidene linkages in HFA were introduced into the PIPA backbone to disrupt chain packing in an attempt to improve the gas separation characteristics relative to those of unmodified PIPA analogs.

Lin et al.[16] measured the gas transport properties for 6FDA-durene homopolymer and their copolyimides 6FDA-durene/*p*PDA at several compositions, synthesized from 2,2'-bis (3,4'-dicarboxyphenyl) hexafluoropropane diandydride (6FDA), 2,3,5,6-tetramethyl-1,4-phenylenediamine (durene diamine), and 1,4-phenylenediamine (*p*PDA). They observed that 6FDA-durene exhibited the highest permeability with the lowest selectivity and that the permeability of the copolymers decreased with increasing 6FDA-*p*PDA content, while permselectivity increased with an increase in 6FDA-*p*PDA content. A similar behavior was observed in the study by Liu et al.[17] about the physical and gas transport properties of homopolyimides, 6FDA-durene, an 6FDA-2,6 diaminotoluene (2,6-DAT), and their copolyimides, 6FDA-durene/2,6-DAT with different diamine ratios. The gas permeability of 6FDA-durene/2,6-DAT decreased with increasing 6FDA-2,6-DAT content. However, the selectivity of gas 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.

In the present study, we have synthesized polyamides and copolyamides based on the direct polycondensation of isophtalic diacid (ISO), 5 *t*-butylisophthalic diacid (TERT), and 4,4'-(hexafluoroisopropylidene) dianiline (HFA), with different comonomers ratios. The copolymerization lead to obtain copolyamides with lower density, larger fractional free-volume (FFV), and a rise in glass transition temperatures as HFA/TERT content increase in the copolymer. These highly aromatic copolyamides will offer the possibility of preparing membranes for gas separation with gas permeabilities and selectivities that are located between those of the homopolyamides. In this way, with the copolymerization, one may be able to tailor their gas separation properties, as well as other thermal and physical properties, by varying in a controlled form, the comonomer ratio.
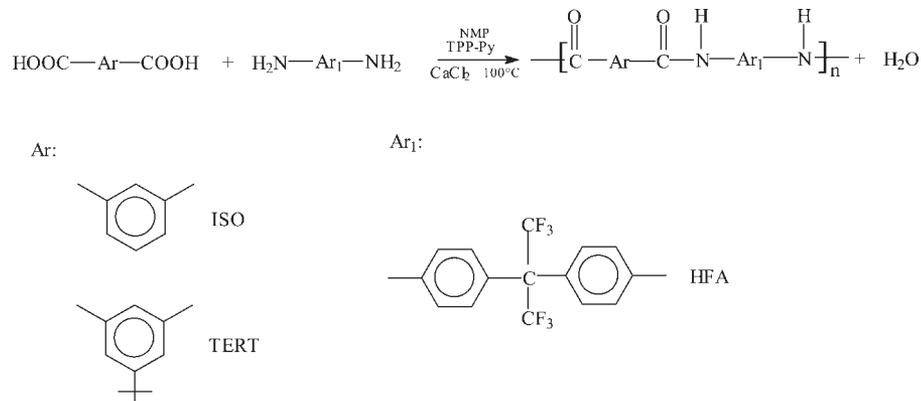
Figure 1. Yamazaki's reaction scheme for synthesis of isophthalic homopolyamides and copolyamides.[18]

EXPERIMENTAL

Materials

The monomers 4,4′-(hexafluoroisopropylidene) dianiline (HFA), the aromatic dicarboxylic acids isophthalic acid (ISO), and 5-*tert*-butylisophthalic acid (TERT) were obtained from Aldrich Chemical, Co. (St. Louis, MO) and used as received.

Reagent-grade calcium chloride was dried under vacuum at 180 °C before use. *N*-methyl-2-pyrrolidinone (NMP) 99.5%, *N*, *N*-dimethylacetamide (DMAc) 99.8%, pyridine (Py) 99%, and triphenyl phosphite (TPP) 97% were used as received. All reactants were purchased from Aldrich Chemical Co.

Polymer and Copolymer Preparation

The hompolyamides and copolyamides were synthesized by direct polycondensation of the diamine (HFA) with the appropriate aromatic dicarboxilic acid, following the reaction scheme described by Yamazaki,[18] which is schematically shown in Figure 1. The reaction was carried out in a 1:1 mol ratio between the diamine and the diacid for the homopolyamides or mixture of diacids for the copolyamides.

As an example, the synthesis of the homopolymer poly(hexafluoroisopropylidene isophthalamide), HFA/ISO, was performed by adding 2.5 mmol of HFA and 2.5 mmol of ISO in a round-necked flask equipped with a mechanical stirrer and inlet and outlet for N_2, to keep inert atmosphere. The monomers were diluted in NMP (4.4 mL). Pyridine (1.6 mL) and triphenyl phosphite (1.6 mL), which catalyze the reaction,

were added when the monomers dissolved completely. Finally 8% by weight of calcium chloride was added. The system was heated to 100 °C for 3 h. At the end of this time, the polymer solution was precipitated slowly into methanol (200 mL) with constant stirring. The product was a fibrous precipitate, which was washed thoroughly with methanol and hot water, collected on a filter, and dried at 120 °C under vacuum for 24 h.

The structures of the homopolymers poly(hexafluoroisopropylidene isophthalamide), HFA/ISO, and poly(hexafluoroisopropylidene-5-*t*-butylisophthalamide), HFA/TERT, are shown in Figure 2. The copolymers were prepared by reacting HFA with different mixtures of ISO and TERT monomers to produce a copolymer series containing 20, 50, and 80 mol % of HFA/TERT, following the same reaction scheme. These copolymers will be identified as IHT82, IHT55, and IHT28, respectively.

Films of all polyamides and copolyamides were cast by dissolving 0.5 g of each polymer in 6 mL of dimethyl acetamide, DMAc. The solution was filtered and poured on a glass plate with an aluminum ring, and the solvent was evaporated slowly at 70 °C. Once the film was strong enough, it was dried in a vacuum oven by increasing the temperature gradually up to 200 °C. The films were kept at this temperature for 48 h to eliminate the solvent completely.

Onset of thermal descomposition, T_d, measurements for homopolymers and copolymers were performed in a Perkin-Elmer thermogravimetrical analyzer (TGA-7). The tests were carried out on 5-mg samples, between 50 and 600 °C, at a heating rate of 10 °C/min under
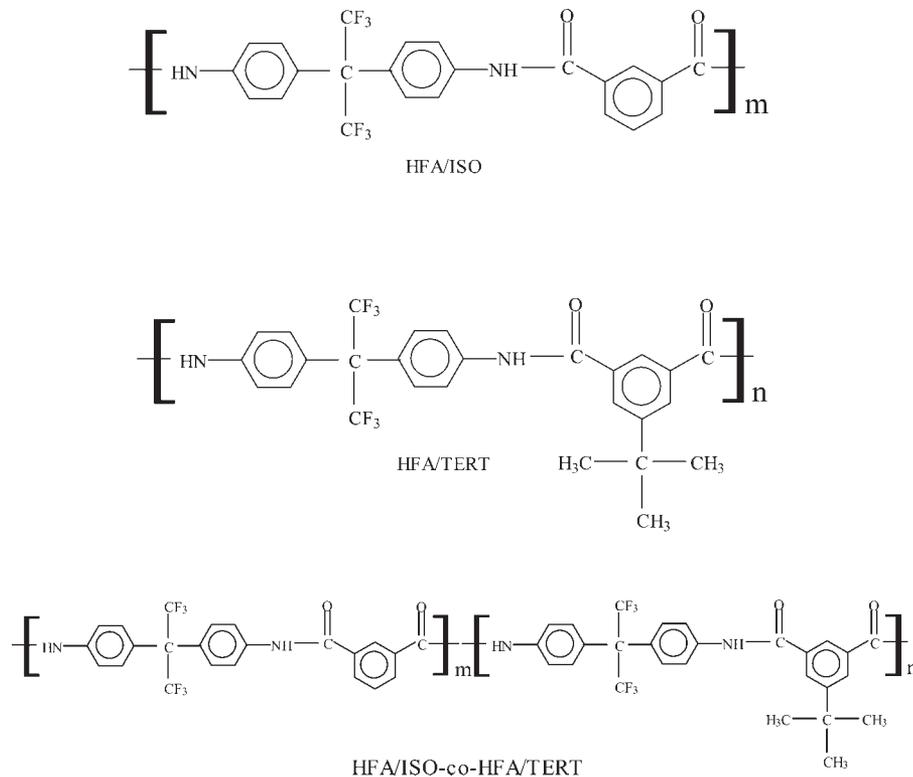
Figure 2.   Structures of the aromatic homopolyamides and copolyamides synthesized.

nitrogen atmosphere. Glass transition temperatures for the polyamides were determined using differential scanning calorimetry in a DSC-7 (PerkinElmer, Boston, MA), using 10-mg samples, between 50 °C and 350 °C, at a heating rate of 20 °C/min under nitrogen atmosphere. The density gradient column method was used to determine the density of all polymers synthesized. The column was prepared at 23 °C, using calcium nitrate solutions between 1.3 and 1.42 g/cm³. Inherent viscosities of all polymer samples were measured using an Ubbelohde viscosimeter, N° 50, with a polymer concentration of 0.5 g/dL in DMAc at 25 ± 0.1 °C.

For all polyamides and copolyamides, the infrared spectrum was obtained using a Fourier transform infrared spectrophotometer, NICOLET Protege 460, taking an average of 50 scans per sample, using 2% (w/w) polymer on KBr pellets.

Gas permeability coefficients for five different pure gases, He, O_2, N_2, CH_4, and CO_2, were measured in a permeation cell of the constant volume type as described elsewhere.[19] The test temperature was maintained at 35 °C, and the feed pressures were 2, 5, 7.5, and 10 atm for each pure gas. For safety reasons, O_2 permeabil-

ities were not determined at high pressures. Gas permeability coefficients were also measured at 2 atm and four temperatures between 35 and 65 °C for He, CO_2, and CH_4.

The transport of gases in glassy polymers is known to occur through a solution-diffusion mechanism. In the approach used here, it is possible to determine the permeability coefficient under steady-state conditions. In this case, the mechanism for gas permeation and diffusion is that the gas molecules dissolve at the high-pressure side, diffuse through the material due to the concentration gradient, and re-emerge at the low-pressure side. The permeability coefficient is taken as the product of a diffusion coefficient, D, and the solubility coefficient, S. The gas permeability coefficient, P, can be expressed as:

$$P = D \cdot S \qquad (1)$$

where P is the permeability coefficient of a membrane for the permeant gas, which is usually expressed in Barrer $= 1 \times 10^{-10} \left[\frac{cm^3 \, (STP) \, cm}{cm^2 \, s \, cmHg} \right]$.

The apparent diffusion coefficient, D_{app} (cm^2/s) was estimated by the time lag (θ) method as described elsewhere,[10,20] under steady-state conditions, applying the following equation

Table 1. Thermal Properties, Inherent Viscosity, Density, and FFV as a Function of Concentration of the TERT Moiety in HFA/TERT-*co*-HFA/ISO Random Copolyamides

Polyamide	m (mol %)	n (mol %)	T_g (°C)	T_d (°C)	Weight Loss at 500 °C (%)	η_{inh} (dL/g)	Density (g/cm^3)	FFV
HFA/ISO	100	0	294	492	19	0.514	1.422	0.143
IHT82	80	20	296	485	11	0.439	1.395	0.146
IHT55	50	50	300	492	10	0.390	1.360	0.150
IHT28	20	80	304	477	9	0.411	1.327	0.153
HFA/TERT	0	100	306	494	11	0.404	1.305	0.156

$$D_{app} = \frac{l^2}{6\theta} \qquad (2)$$

where θ is the time lag, and l is the membrane thickness.

The apparent solubility coefficient, S_{app} (cm^3(STP)/cm^3-cmHg), was obtained from the ratio of permeability coefficient to the apparent diffusion coefficient.

$$S_{app} = \frac{P}{D_{app}} \qquad (3)$$

The ideal permselectivity of the polyamides and copolyamides films for gas A relative to gas B was defined as follows

$$\alpha_{A/B} = \frac{P_A}{P_B} \qquad (4)$$

RESULTS AND DISCUSSION

Physical Properties

The properties of the homopolyamides and random copolyamides synthesized here are summarized in Table 1. The polyamide prepared with the bulky nonpolar *tert*-butyl substituent (HFA/TERT) has a glass transition temperature, T_g, which is 12 °C higher than that of the unsubstituted analogue (HFA/ISO). These results are consistent with the notion that the addition of bulky substituents to polymer backbones can inhibit local-scale segmental polymer motions that are important in the glass to rubber transition and, therefore, lead to an increase in T_g values.[4] The T_g's of homopolyamides, HFA/ISO and HFA/TERT, were similar to those reported elsewhere in the literature.[5,6,21] The T_g of the HFA/ISO-*co*-HFA/TERT copolyamides increase with an increase in HFA/TERT content,

and the presence of a single glass transition temperature indicates that there is no phase separation in these materials, a fact that was expected for random copolymers. The glass transition temperature of random copolymers and miscible blends changes with comonomer compositions. A simple way to estimate the glass transition temperatures of random copolymers is applying the Fox equation, which is shown below[16,17,22]

$$\frac{1}{T_{gC}} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \qquad (5)$$

where w_1 and w_2 are the weight fractions of homopolymers in the copolymer, and T_{g1} and T_{g2} are the glass transition temperatures of homopolymers, and T_{gC} is the glass transition temperature of the copolymer.

Figure 3 compares the glass transition temperatures obtained from the DSC experiments and those calculated from the Fox equation. The results show good agreement between the exper-
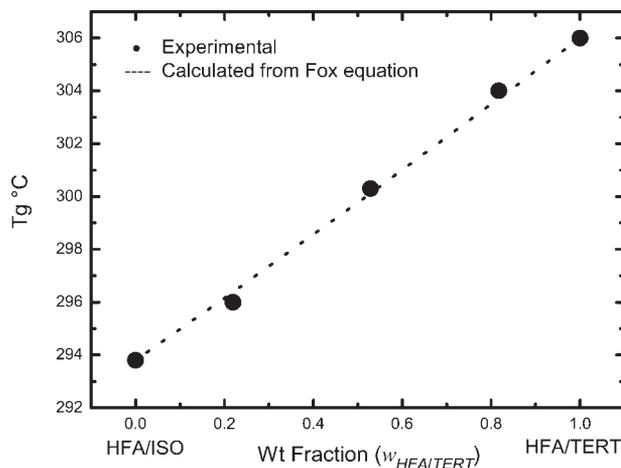
Figure 3. Comparison of T_g's obtained experimentally and those calculated from the Fox equation.

imental values and those predicted by eq 5. This trend implies that the thermal properties of the aromatic copolyamides can be tailored by controlling the amount of comonomer present in the copolymer.

In Figure 4(a), the infrared spectra of the synthesized homopolyamides and copolyamides are shown. These spectra show, among other bands, several bands that are expected for the formation of the polyamides, a carbonyl absorption band at 1660 cm^{-1} and a broad absorption band attributed to the amide group at 3300 cm^{-1}. The polyamides containing the *tert*-butyl group also show the representative band of the methyl groups at 2960 cm^{-1}. The infrared spectra have been normalized respect to the carbonyl absorption band (1660 cm^{-1}). The normalized values will allow the comparison of the methyl absorption band at 2960 cm^{-1}, which increases as TERT moiety content increases in the copolymer, (see Fig. 4(b)). From this normalization and a comparison of the absorption height of the 2960 cm^{-1} band for HFA/TERT and the different copolymers, the amount of this moiety was calculated. The values obtained for IHT82, 17%, IHT55, 46%, and IHT28, 83%, are very close with those expected from the molar percentage feed of monomers.

The onset of descomposition temperature, T_d, is shown in Table 1, for these aromatic polyamides and copolyamides is above 470 °C. The results indicate that homopolyamides and copolyamides have T_d's that are high and similar. The weight loss at 500 °C was recorded to compare the thermal stability of the polyamides after descomposition has started. The results indicate that the homopolyamide, HFA/TERT, and the copolyamides have similar stability with a mass loss around 10 wt % at this temperature, while HFA/ISO shows a slightly larger decrease in mass, up to 19 wt %. This implies that *tert*-butyl group, incorporated into the copolymers, produces a slight increase in thermal stability once the descomposition has started.

The results of inherent viscosity, η_{inh}, reported in Table 1, are an indirect measurement of molecular weight. Relatively reasonable inherent viscosities, around 0.45 dL/g, were obtained for all polymers. These values of inherent viscosity correspond to comparatively medium molecular weight polymer similar to those reported before.[21] As can be seen, the inherent viscosity increases as the content of the ISO moiety increase in the copolymer, except for IHT55.
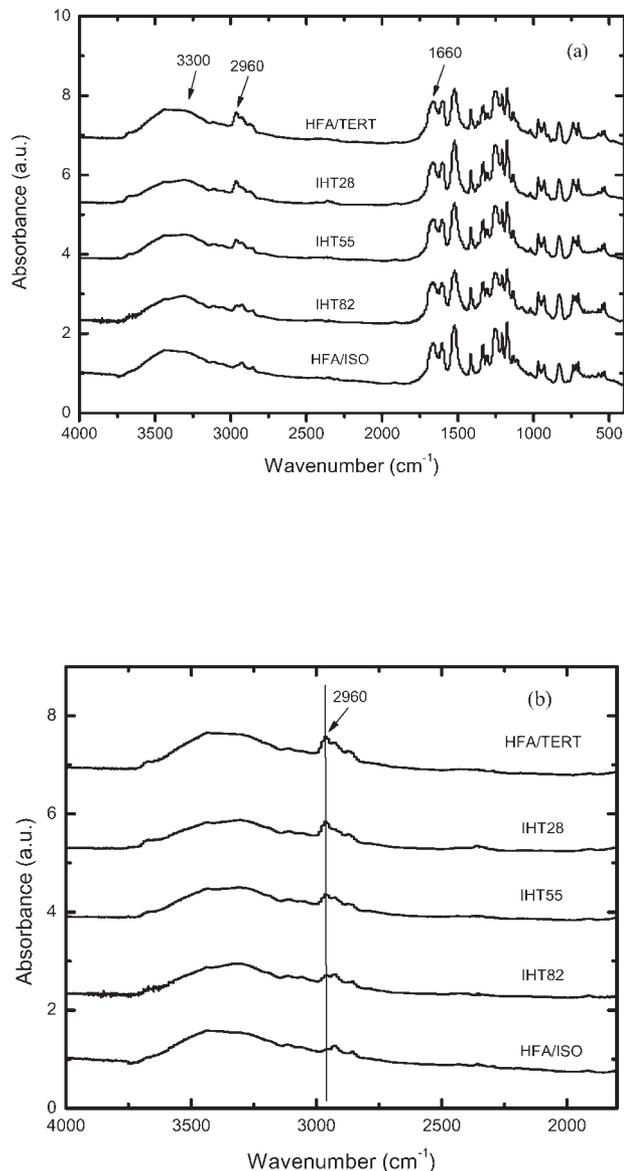
Figure 4. Infrared spectra of the aromatic homopolyamides and copolyamides synthesized.

Density measurements show that the aromatic polyamide containing the large *tert*-butyl group substitution in the phthalic moiety, HFA/TERT, has the lowest density while the polyamide, HFA/ISO, shows the largest density of these aramides. These results are because the polyamide containing the large *tert*-butyl substitution in the meta connected phthalic moiety, HFA/TERT, hinders the packing of the polyamide chains, decreasing the density as compared to the other polyamide, HFA/ISO. The different copolyamides, HFA/ISO-*co*-HFA/TERT, show density values that are between those of

the homopolyamides and they depend on the relative concentrations of the TERT and ISO moieties in the copolyamide. It is also clear that they show a decrease in density as the amount of the TERT moiety increases. This in turn has the effect of increase in the fractional free-volume as the concentration of the TERT moiety in the copolyamides increases. The fractional free-volume, FFV, was calculated as the ratio of the expansion volume (V-V_0) to the experimental volume (V) using the following equation

$$\text{FFV} = \frac{V - V_0}{V} \tag{6}$$

where V and V_0 are the specific volume and the chain occupied specific 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 method.[23] For copolymers, it has been reported that the occupied volume can be calculated assuming that there exists additivity of each polyamide occupied volume using the following equation

$$V_{0C} = w_1 V_{01} + w_2 V_{02} \tag{7}$$

where w_1 and w_2 are the weight fractions of each aromatic polyamide in the copolyamide, and V_{01} and V_{02} refer to the occupied volumes of the homopolyamides.[16,17] However, for these copolyamides, the occupied volume was calculated by an inverse additivity rule of each polyamide occupied volume, using the equation

$$\frac{1}{V_{0C}} = \frac{w_1}{V_{01}} + \frac{w_2}{V_{02}} \tag{8}$$

Figure 5(a) shows the relationship between the weight fraction of the HFA/TERT moiety and the specific volume, V [1/density], and occupied specific volume, V_0. The V correlates linearly with the HFA/TERT weight fraction as well as V_0, as expected from the additivity rule. The result is similar to that found in the T_g measurement and implies volume additivity in the copolymers. In Figure 5(b), the FFV is plotted as a function of HFA/TERT weight fraction. In this graph, the FFV correlates linearly as expected as the TERT moiety concentration increases in the copolymer when FFV is calculated by eq 8. If eq 7 is used, the FFV shows a negative desviation from volume additivity as the HFA/TERT weight fraction increases. This implies that an
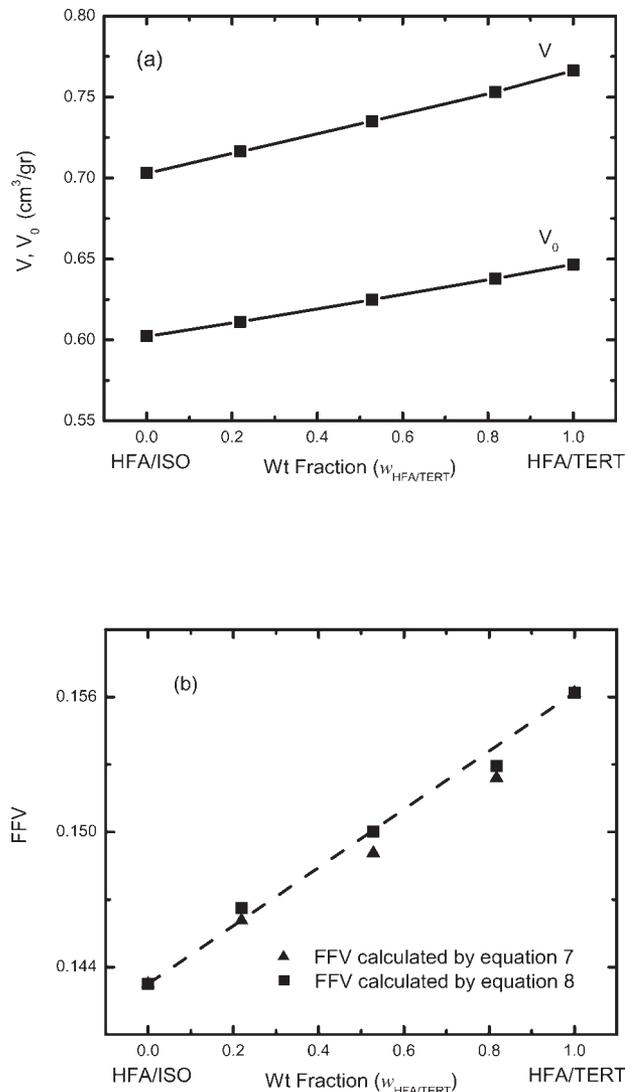
Figure 5. Change of (a) specific volume, V, and occupied specific volume, V_0, and (b) fractional free-volume, FFV, for the copolyamide series as a function of HFA/TERT weight fractions.

additivity rule such as eq 8 describes better the interaction of occupied volumes, V_0, in the copolymer than the one on eq 7, at least for the FFV found in these particular copolyamides.

Gas Transport Properties

The effect of pressure on gas transport properties in the homopolyamides and copolyamides can be observed in Figure 6. This figure presents permeability coefficients for polyamides and copolyamides to five pure gases CO_2, CH_4, N_2, O_2, and He at 35 °C as a function of upstream pressure. Penetrant permeability coefficients in the poly-
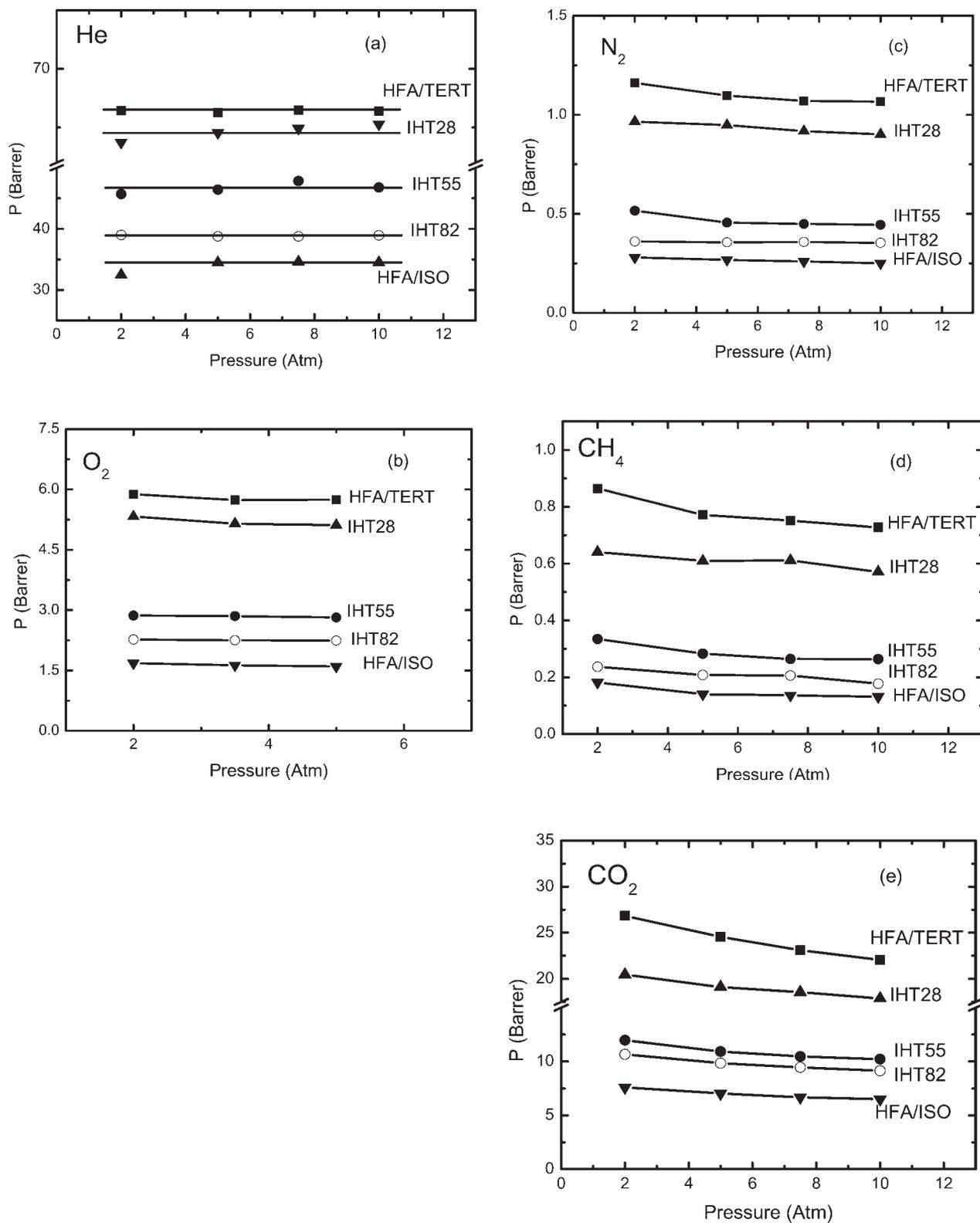
Figure 6. The effect of upstream pressure on permeability coefficients of HFA iso-phthalic and 5-*tert*-butylishophthalic polyamides and copolyamides for (a) He, (b) O_2, (c) N_2, (d) CH_4, and (e) CO_2 at 35 °C.

Table 2. Gas Permeability Coefficients[a] and Permselectivities of HFA-Based Polyamides and Copolyamides at 35 °C and 10 atm

Polyamide	P_{He}	P_{CO_2}	P_{O_2}[b]	P_{N_2}	P_{CH_4}	P_{O_2}/P_{N_2}	P_{CO_2}/P_{CH_4}	P_{N_2}/P_{CH_4}
HFA/ISO	34.5	6.5	1.68	0.25	0.13	6	50	1.9
IHT82	38.9	9.13	2.25	0.35	0.17	6.26	51.58	1.97
IHT55	46.7	10.21	2.86	0.44	0.26	5.60	39.26	1.69
IHT28	65.3	17.87	5.32	0.90	0.57	5.52	31.35	1.58
HFA/TERT	66.4	22.05	5.88	1.06	0.72	5.06	30.31	1.46

[a] Permeability values are expressed in Barrer, where 1 Barrer = 10^{-10} [cm^3 (STP) cm]/[cm^2 s cmHg].
[b] Oxygen Permeability coefficients are reported at 2 atm.

amides and copolyamides are independent of pressure in the range measured for He and O_2. On the other hand, the CO_2, N_2, and CH_4 permeability coefficients decrease slightly with increasing pressure, over the pressure range tested here. None of the polymers exhibits gas-induced plasticization, which would be signaled by an increase in permeability with increasing upstream pressure. Typically, CO_2 is used as a probe gas for induced plasticization, since CO_2 is often the most soluble gas examined in gas transport studies, and the propensity of a penetrant to plasticize a polymer increases as the amount of penetrant dissolved in the polymer increases.[4] Resistance to plasticization is an important property for membrane materials, particularly in high-pressure applications, such as CO_2 stripping from natural gas streams, since plasticized polymers exhibit markedly reduced selectivity to penetrant mixtures.[4,10]

An examination of the permeability coefficient values found that HFA/TERT is 2 to six times more permeable than HFA/ISO depending on the gas being considered. Also, on the basis of the data presented in Figure 6, it can be seen that the permeability coefficients of HFA-based isophthalamides, polyamides, and copolyamides decrease in the order PHe > PCO$_2$ > PO$_2$ > PN$_2$ > PCH$_4$, which follows closely the order of increasing kinetic diameters of the penetrant molecules.[10,17] Table 2 provides a summary of permeability coefficients at 35 °C and 10 atm, except for O_2 permeability, which is reported at 2 atm. This table shows that permeability coefficients for all the gases tested increases with increasing HFA/TERT content. This can be explained by the presence of the bulky backbone substituent, the *tert*-butyl group in HFA/TERT, and in HFA/TERT-*co*-HFA/ISO random copolyamides. This bulky substituent disrupt chain packing in the polymers, thereby increasing free-volume and, in turn, increasing permeability coefficient as pointed out elsewhere.[4,5]

Table 2 shows the ideal selectivities for the gas pairs CO_2/CH_4, O_2/N_2, and N_2/CH_4. From these results, it can be seen that HFA/ISO is the most selective homopolymer, and HFA/TERT exhibits the lowest selectivity. The aromatic copolymers selectivities are found in between those of the homopolymers depending on the relative concentration of TERT and ISO moieties in the copolymer. It is also observed that as the permeability coefficients values for the HFA-based polyamides and copolyamides increases the ideal selectivities decrease. This result is consistent with the trade-off between permeability and selectivity commonly found for gas separation in polymeric membranes.[4,5]

To understand the gas permeation mechanism, free-volume is often applied to glassy amorphous polymers. According to this theory, which was developed by Cohen and Turnbull, gas diffusivity D is assumed to depend on free-volume following the equation[4,11,24]

$$D = A \exp\left(-\frac{B}{FFV}\right) \qquad (9)$$

where A and B are characteristic constants of the polymer-penetrant system, which are independent of the penetrant concentration. This relation typically provides a good description of gas diffusivity in a family of polymers.[4,5,8,11] Lee suggested that solubility would not be a strong function of free-volume and, therefore, the gas permeability P and FFV should be related to fractional free-volume by the equation[4,11]

$$P = A' \exp\left(-\frac{B'}{FFV}\right) \qquad (10)$$

where A' and B' are constants. The easy of FFV estimation makes this a useful relationship. As
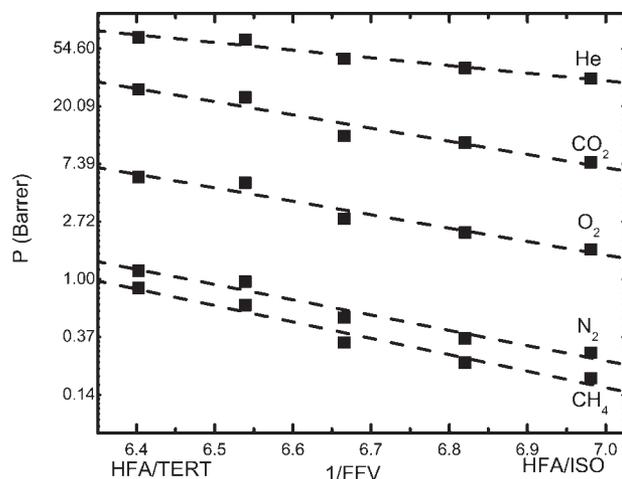
Figure 7. Dependence of pure gas permeability coefficients on fractional free-volume for HFA isophthalic and 5 *tert*-butylisophthalic polyamides and copolyamides.

explained earlier, the FFV can be calculated from density data and estimations of van der Waals volume (V_w) by a group contribution method.

Figures 7 and 8 present the dependence of permeability coefficients and diffusion coefficients on FFV, respectively, for HFA homopolyamides and copolyamides. In many amorphous polymer systems, the logarithm of permeability as well as diffusivity decrease roughly linearly with increasing reciprocal fractional free-volume.[5] As can be seen, for the polyamides considered in this study, gas permeability and diffusion coefficients generally follow this trend. These results suggest that the assumption of volume additivity from each homopolymer moiety contained in the copolymer holds in the aromatic copolyamides studied here.

Table 3 and Table 4 present gas apparent diffusion coefficients, diffusivity selectivities, solubility coefficients, and solubility selectivities for HFA-based polyamides and copolyamides at 35 °C and 2 atm, respectively. These data show that in all these polymers the apparent diffusion coefficients decrease in the following order: $D_{app}O_2 > D_{app}CO_2 > D_{app}N_2 > D_{app}CH_4$. It is well-known that the diffusion process depends on the size and shape of the molecule. Therefore, a general trend should be that the diffusion coefficients in a given polymer decrease with increasing kinetic diameter of the penetrant molecule. However, the diffusion coefficients for CO_2 and O_2 obtained in this study depart from this trend because $D(O_2) > D(CO_2)$, whereas the

kinetic diameter of the oxygen is higher than carbon dioxide. Similar behavior has also been observed for other types of glassy polymers including polyimides, polycarbonates, and polysulfones.[10] Stern et al.[25] interpreted that this inconsistency could be caused by the strong quadrupole of the CO_2 molecule. Another possible reason for the anomaly mentioned above is the difficulty in estimating an accurate diameter for the CO_2 molecule because of its nonspherical nature, however, the CO_2 molecule may have a larger effective size, possibly between its kinetic diameter of 3.3 Å and its collision diameter of 3.94 Å.[17,25] For all polymers and copolymers, the apparent diffusion coefficients, D_{app}, obtained for O_2, CO_2, N_2, and CH_4 have a significant increase with increasing upstream pressure in the low-pressure region, between 2 and 5 atm. At upstream pressures above 5 atm, the diffusion coefficients maintain an almost constant value with a small increase in D_{app}.

The above results are consistent with the notion that the bulky nonpolar *tert*-butyl group inhibits chain packing, thereby increasing polymer free-volume and, in turn, gas diffusion coefficients in HFA/TERT relative to HFA/ISO. These results are consistent with calculated fractional free-volume values reported in Table 1. In these, the free-volume of HFA/TERT is greater than that of HFA/ISO, and gas diffusion coefficients are commonly understood to be quite sensitive to polymer free-volume.[4]
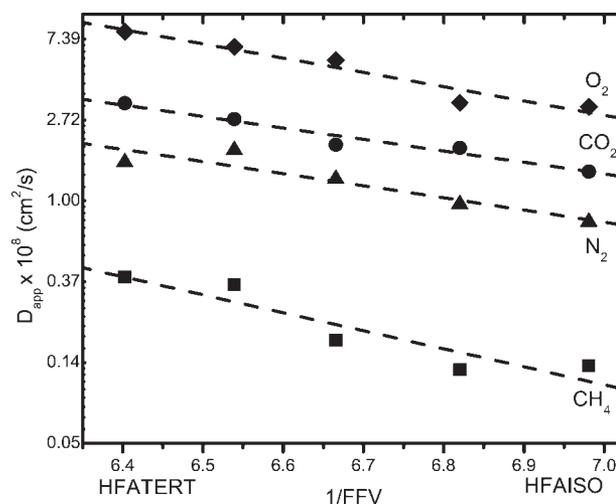
Figure 8. Dependence of gas apparent diffusion coefficients on fractional free-volume for HFA isophthalic and 5 *tert*-butylisophthalic polyamides and copolyamides.

Table 3. Apparent Gas Diffusion Coefficients and Diffusivity Selectivities of HFA-Based Polyamides and Copolyamides at 2 atm and 35 °C

Polyamide/gas	D_{app}[a]				D_A/D_B		
	O_2	CO_2	N_2	CH_4	O_2/N_2	CO_2/CH_4	N_2/CH_4
HFA/ISO	3.20	1.43	0.77	0.13	4.15	11	5.9
IHT82	3.37	1.92	0.96	0.12	3.51	15.48	7.74
IHT55	5.70	2	1.31	0.17	4.35	11.23	7.36
IHT28	6.70	2.75	1.87	0.35	3.58	7.74	5.26
HFA/TERT	8.10	3.35	1.61	0.39	5.03	8.59	4.12

[a] D_{app} has units of 10^{-8} cm^2 / s and was determined from time lag measurements.

From the data in Table 4, the gas solubility coefficients of polyamides and copolyamides can be seen to change 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. Typically, in the absence of strong polymer-gas 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.[5,8] However, there is a tendency to increasing solubilities of CO_2, N_2, and CH_4 as the HFA/TERT content increases in the copolymers indicating that the higher permeabilities for the HFA/TERT containing membrane are due to the higher gas solubility and apparent diffusion coefficients allowed by the HFA/TERT moiety. As can be seen from Table 4, the solubilities of CO_2 and CH_4 in HFA/TERT are 2.3 and 1.6 times greater, respectively, than those found in HFA/ISO. For all polymers and copolymers, the apparent solubility coefficients, S_{app}, obtained for O_2, CO_2, N_2, and CH_4 have a significant decrease with increasing upstream pressure in the low-pressure region between 2 and 5 atm. At upstream pressures above 5 atm, the solubility coefficients maintain an almost constant value

with a small decrease in S_{app}. Generally, the solubility coefficient of a gas is thermodynamic in nature and is determined by the inherent condensability of the gas, the polymer-gas interactions, and the amount and distribution observed of the excess free-volume in the glassy polymers.[10]

It is also possible to predict the gas permeability coefficients of copolymers if those of the parent homopolymers are known using the simple rule of mixing[16,17,26]

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

where ϕ_1 and ϕ_2 are the volume fraction of the homopolymers in the copolymer, P_1 and P_2 are the permeability coefficients of the two homopolymers, P_C is the permeability coefficient of the copolymer. A comparison of the permeability coefficients found experimentally and those calculated from eq 11 is given in Figure 9. The experimental results show good agreement with those calculated from eq 11. As can be seen from this figure, the copolymers that contain volume fractions of 0.23 and 0.54 of the HFA/TERT moiety show permeability coefficients slightly below those predicted by eq 11.

Table 4. Apparent Gas Solubility Coefficients and Solubility Selectivities of HFA-Based Polyamides and Copolyamides at 2 atm and 35 °C

Polyamide/gas	S_{app}[a]				S_A/S_B		
	O_2	CO_2	N_2	CH_4	O_2/N_2	CO_2/CH_4	N_2/CH_4
HFA/ISO	0.39	4.03	0.27	0.98	1.4	4.11	0.27
IHT82	0.50	4.22	0.28	1.45	1.75	2.90	0.19
IHT55	0.38	4.55	0.3	1.43	1.26	3.18	0.20
IHT28	0.60	6.46	0.39	1.37	1.53	4.71	0.28
HFA/TERT	0.55	6.07	0.54	1.65	1	3.68	0.32

[a] S_{app} in cm^3 (STP)/(cm^3 polymer atm).
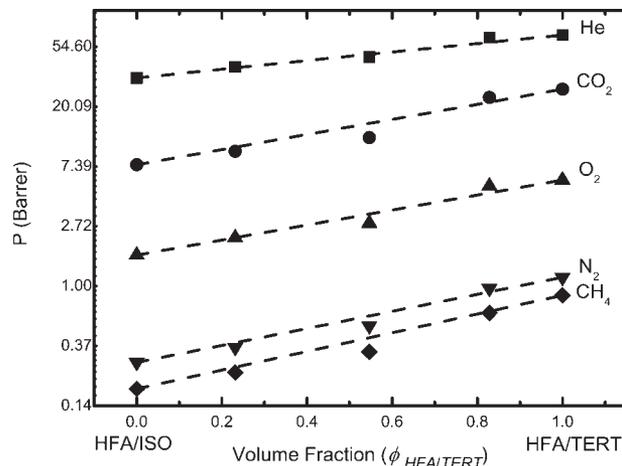
Figure 9. Effect of increasing HFA/TERT volume fraction on gas permeability coefficients for copolymers HFA/TERT-*co*-HFA/ISO.

The permselectivity of the gas pairs O_2/N_2, CO_2/CH_4, and N_2/CH_4 for the copolyamides can be estimated by using the following equation[16,17]

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

The experimental results for the selectivity of gas pairs O_2/N_2, CO_2/CH_4, and N_2/CH_4 are also in good agreement with the values obtained from eq 12 for all the copolyamides studied here (see Fig. 10). From these results, it follows that in the case of the copolyamides tested here it is possible to predict the permeability coefficients and permselectivity from a knowledge of that of the homopolyamides and the volume fraction of the homopolyamide present in the copolymer.

Effect of Temperature on Gas Transport Properties

Within a temperature range in which no thermal transitions of the polymer occur, gas permeability coefficients generally follow an Arrhenius relationship[10,11]

$$P = P_0 \exp(-E_P/RT) \qquad (13)$$

where P_0 is a pre-exponential factor, E_P is the activation energy for permeation, R is the ideal gas constant, and T is the temperature. This relation can be used as a convenient method to calculate permeabilities at different temperatures within the range of validity. On the other hand, the parameters obtained may also provide a better insight into the basic processes involved

in gas permeability. Figure 11 shows the effect of temperature on permeability coefficients for He, CO_2, and CH_4 at 2 atm upstream pressure over the temperature range 35–65 °C in HFA-based homopolyamides and copolyamides. From this figure, it is clear that the temperature dependence of P for the HFA/ISO-*co*-HFA/TERT copolyamides can be described by the Arrhenius equation, as with other polymers reported in the literature.[10,11] The general trend is that the gas permeabilities increase with temperature. Activation energies calculated from these plots are shown in Table 5. As can be seen, the HFA/TERT homopolyamide shows a lower E_P than HFA/ISO homopolyamide, and in HFA/ISO-*co*-HFA/TERT random copolyamides, the E_P's decrease with increasing HFA/TERT content. The HFA/ISO homopolyamide and IHT82 and IHT55 random copolyamides show activation energies that are very similar for the CO_2 gas indicating a similar interaction when 50 mol % or above of TERT moiety is present in the polyamide, while IHT28 shows a lower value, tending to that of HFA/TERT homopolymer, which can be due to gas condensability. In general, it has been found that a glassy polymer with a higher T_g and fractional free-volume tends to have a lower E_P within a family of polymers.[11]

CONCLUSIONS

The synthesis and thermal characterization of highly aromatic homopolyamides, HFA/ISO and HFA/TERT, and several of their copolymers indi-
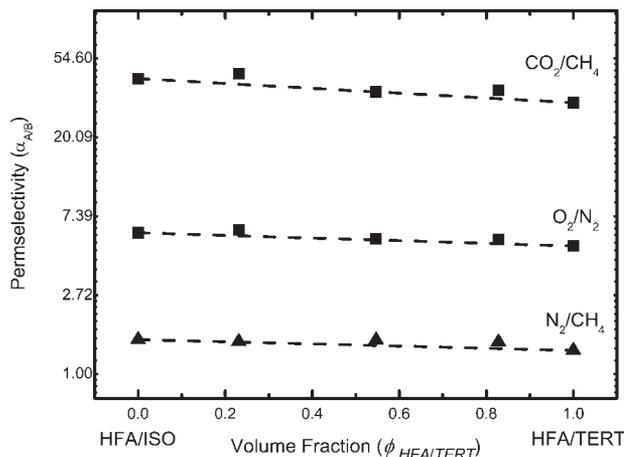
Figure 10. Effect of increasing HFA/TERT volume fraction on gas permselectivity for copolymers HFA/TERT-*co*-HFA/ISO.
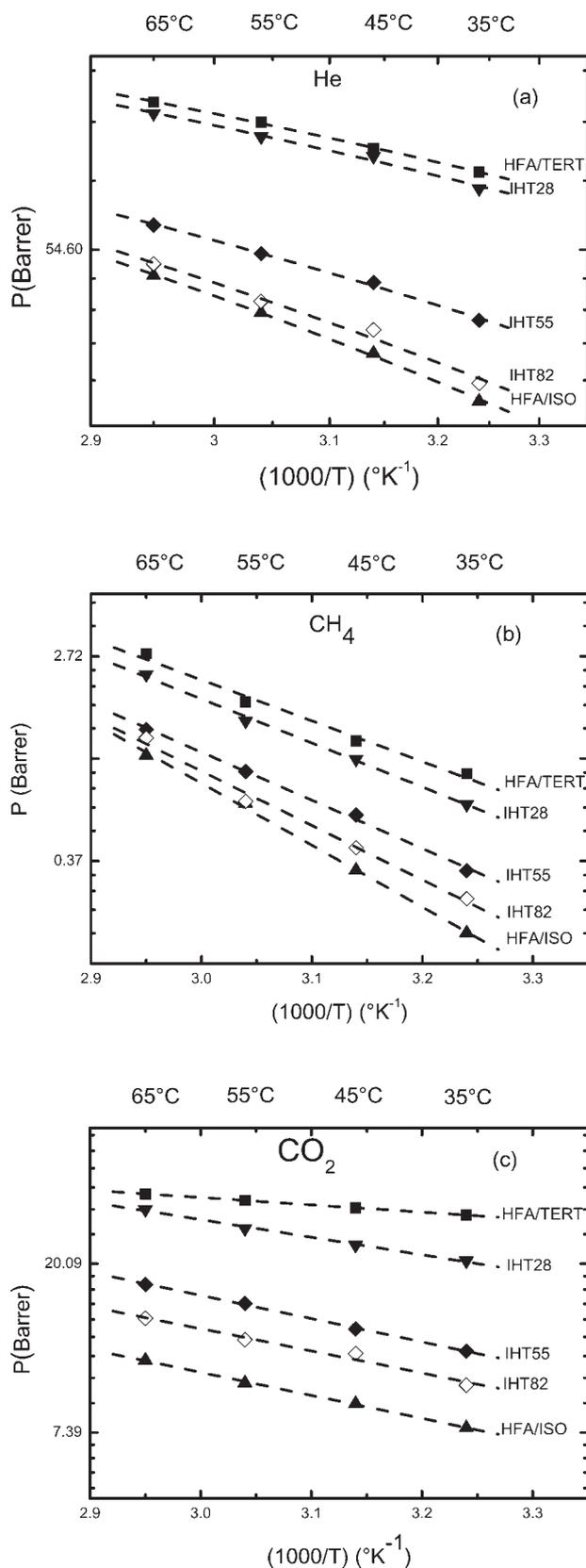
Table 5. Activation Energies for Permeation for He, CO_2, and CH_4 in the HFA-Based Polyamides and Copolyamides

	E_P (kJ/mol)		
Polyamide/gas	He	CO_2	CH_4
HFA/ISO	9.03	11.36	50.27
IHT82	8.37	10.92	44.20
IHT55	6.80	11.46	39.13
IHT28	5.31	8.66	35.75
HFA/TERT	5.10	3.60	33.24

cates that the presence of the *tert*-butyl moiety in these isophthalamides increases the glass transition temperature, T_g, with a minimum effect on the onset of the descomposition temperature. It was also found that an increase in the concentration of the *tert*-butyl moiety in the isophthalic polyamides and copolyamides produces a decrease in density. This decrease in density in turn increases the fractional free-volume available for gas transport in these polymers.

These results indicate that the larger gas permeability coefficients are found for the polyamides and copolyamides that bear the largest concentration of the *tert*-butyl group in their structure. It was also found the gas permeability coefficients and ideal gas separation factors can be predicted with a reasonable accuracy from the simple logarithmic mixing rule that take into account the volume fraction and permeability coefficients of each homopolyamide in the copolymer.

Finally, the results show that gas permeability coefficients for these polyamides increase with temperature, and the temperature dependence of P for the HFA/ISO-*co*-HFA/TERT copolyamides is well described by an Arrhenius type equation.

Overall, it was found that the copolymerization in these highly aromatic aramides allows a control of their properties that follows closely simple rules of mixing. This fact would permit to obtain aramides with controlled applicability specially for preparation of membranes for gas separation.

Figure 11. Effect of temperature on permeability coefficients for (a) He, (b) CH_4, and (c) CO_2 at 2 atm for copolymers HFA/TERT-*co*-HFA/ISO.

REFERENCES AND NOTES

1. Teo, L. S.; Kuo, J. F.; Chen, C. Y. Polymer 1998, 39, 15, 3355.

2. Kharul, U. K.; Kulkarni, S. S.; Kulkarni, M. G.; Houde, A. Y.; Charati, S. G.; Joshi, S. G. Polymer 1998, 2011, 39, 10.

3. Aguilar-Vega, M.; Paul, D. R. J Polym Sci Part B: Polym Phys 1993, 31, 1577.

4. Ghosal, K.; Freeman, B. D.; Chern, R. T.; Alvarez, J. C.; de la Campa, J. G.; Lozano, A. E.; de Abajo, J. Polymer 1995, 36, 793.

5. Singh, A.; Ghosal, K.; Freeman, B. D.; Lozano, A. E.; de la Campa, J. G.; de Abajo, J. Polymer 1999, 40, 5715.

6. Morisato, A.; Ghosal, K.; Freeman, B. D.; Chern, R. T.; Alvarez, J. C.; de la Campa, J. G.; Lozano, A. E.; de Abajo, J. J Membr Sci 1995, 104, 231.

7. Pixton, M.; Paul, D. R. Polymer 1995, 36, 3165.

8. Ghosal, K.; Chern, R. T.; Freeman, B. D.; Daly, W. H.; Negulescu, I. I. Macromolecules 1996, 29, 4360.

9. Aguilar-Vega, M.; Paul, D. R. J Polym Sci Part B: Polym Phys 1993, 31, 991.

10. Xu, Z. K.; Böhning, M.; Springer, J.; Steinhauser, N.; Mülhaupt, R. Polymer 1997, 38, 581.

11. Xu, Z. K.; Böhning, M.; Schultze, J. D.; Li, G. T.; Springer, J.; Glatz, F. P.; Mülhaupt, R. Polymer 1997, 38, 1573.

12. Coleman, M. R.; Koros, W. J. Macromolecules 1999, 32, 3106.

13. Alentiev, A. Y.; Loza, K. A.; Yampolskii, Y. P. J Membr Sci 2000, 167, 91.

14. Staudt-Bickel, C.; Koros, W. J. J Membr Sci 2000, 170, 205.

15. Wang, Z.; Chen, T.; Xu, J. Macromolecules 2000, 33, 15, 5672.

16. Lin, W. H.; Vora, R. H.; Chung, T. S. J Polym Sci Part B: Polym Phys 2000, 38, 2703.

17. Liu, S. L.; Wang, R.; Liu, Y.; Chung, M. L.; Chung, T. S. Polymer 2001, 42, 8847.

18. Yamazaki, N.; Matsumoto, M.; Higashi, F. J Polym Sci Part A: Polym Chem 1975, 13, 1373.

19. Koros, W. J.; Paul, D. R.; Rocha, A. A. J Polym Sci Part B: Polym Phys 1976, 14, 687.

20. Crank, J. The Mathematics of Diffusion; 2nd ed.; Oxford University Press: New York, 1975.

21. Palí, R.; Loría-Bastarrachea, M.; Angulo, J. L.; Vázquez, H.; Aguilar-Vega, M. High Perform Polym 2002, 14, 77.

22. Mark, J. E.; Eisenberg, A. Physical Properties of Polymers; American Chemical Society: Washington, D.C., 1984.

23. Van Krevelen, D. W.; Hoftyzer, P. J. Properties of Polymers; Elsevier: Amsterdam, 1976.

24. Chun, B-W.; Ishizu, C.; Itatani, H.; Haraya, K.; Shindo, Y. J Polym Sci Part B: Polym Phys 1994, 32, 1009.

25. Stern, S. A.; Liu, Y.; Feld, W. A. J Polym Sci Part B: Polym Phys 1993, 31, 939.

26. Barnabeo, A. E.; Creasy, W. S.; Robeson, L. M. J Polym Sci Part A: Polym Chem 1979, 1975, 13.