

Enhanced Gas Transport Performance of Polyamide Membranes by Postpolymerization Modification

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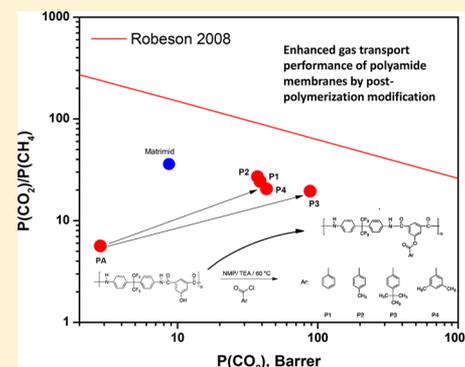
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Supporting Information

ABSTRACT: A novel series of aromatic polyamides was synthesized by postpolymerization modification using a simple strategy to introduce different bulky pendant groups into a precursor polymer. The polyamides possess high thermostability with T_g values in the range of 298–312 °C and good mechanical properties. These polyamide membranes also exhibit enhanced gas separation performance, especially for CO₂ and H₂ separations, with plasticization resistance in the range tested (2.02–10.13 bar). The most remarkable result for gas permeability is attained with P3 bearing 4-*tert*-butylbenzoyl (TBB) as pendant group ($P_{CO_2} = 88.1$, $P_{H_2} = 101$ with selectivity (α) for CO₂/CH₄ = 19.2 and H₂/N₂ = 21.5). The highest permselectivity is obtained for P2 containing *p*-toluoyl (*p*-T) as pendant group (CO₂/CH₄ = 26.1 and H₂/CH₄ = 38.1).



1. INTRODUCTION

Separation process in various sectors of energy, chemical industries, and especially in the separation of gaseous species is a high-energy consumption technology.¹ In comparison to conventional methods such as cryogenic distillation and condensation, polymeric membranes can offer potentially low energy consumption for the separation of industrial gases of interest, coupled to high adaptability, compact size, and lower capital cost for the separation of several important gases.^{2,3} Thermostable polymers have been investigated as materials for gas separation membranes because of their excellent chemical, thermal, and mechanical properties. Although polyamides are one promising material in this topic,^{4–8} many of them are known to be materials with limited solubility in common solvents and difficult to process, as a consequence of their hydrogen-bonding capacity.⁷ The incorporation of bulky pendant groups and voluminous lateral substituents into polyamides is an efficient way to modify packing density and solubility. In particular, this strategy has the advantage of improving solubility, fractional free volume, and gas permeability while retaining thermal and mechanical properties.^{4,7–16}

A recently reported synthetic route to introduce different pendant groups into poly- and copolyamide backbone by postpolymerization modification, using an esterification reaction with acid chlorides at 60 °C, offers a way to obtain a great variety of polymeric structures, otherwise not

obtainable by simple polycondensation.¹⁴ A simple pendant group exchange may significantly modify some of the polymer properties, such as thermostability, solubility in organic solvents, glass transition temperature, mechanical properties, and gas transport.^{4,15} In the present study, we used this approach to introduce a variety of structurally different pendant groups into poly(hexafluoroisopropylidene hydroxyisophthalamide) (PA) backbone to assess the effect that carefully chosen pendant group modification has on polymer properties as compared to the base PA polyamide. We discuss the modified polyamide structure–property correlation in relation to their precursor, and also report variations on gas transport properties associated with the small modification on the bulky pendant groups.

2. EXPERIMENTAL SECTION

2.1. Materials. The diamine 4,4'-(hexafluoroisopropylidene)dianiline (HFA) was purified by sublimation. The diacid 5-hydroxyisophthalic acid (HIA) was recrystallized from methyl alcohol. Benzoyl chloride (B), *p*-toluoyl chloride (*p*-T), 3,5-dimethylbenzoyl chloride (DMB),

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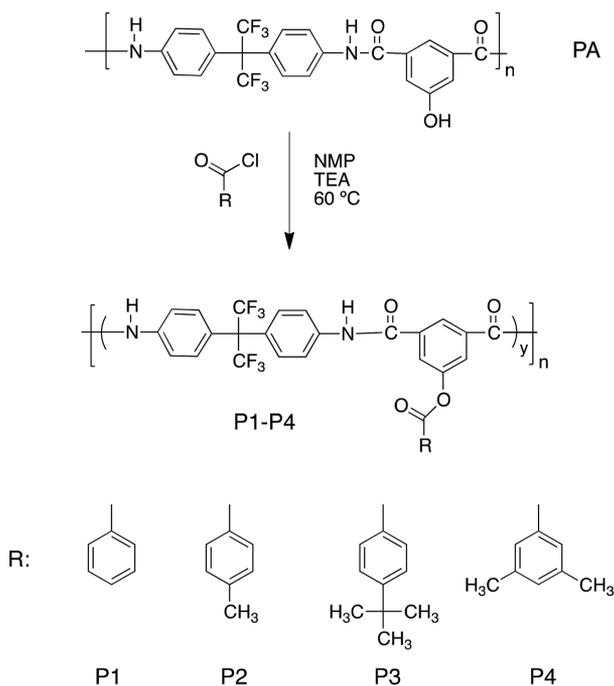
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4-*tert*-butylbenzoyl chloride (TBB), pyridine (Py), triphenoxyposphine (TPP), and triethylamine (TEA) were obtained commercially (Aldrich Chemical) and used without further purification. *N,N*-Dimethylacetamide (DMAc), methyl alcohol (MeOH), dimethyl sulfoxide (DMSO), *N*-methyl-2-pyrrolidone (NMP), *N,N*-dimethylformamide (DMF), and the chlorinated solvents acetylene tetrachloride (TCE), ethylene dichloride (DCE), and trichloromethane (CF) also were obtained from Aldrich Chemical and used as received. Calcium chloride (CaCl₂) was dried at 180 °C in a vacuum oven overnight. The pure gases CO₂, CH₄, O₂, N₂, He, and H₂ (purity >99.9%) were purchased from Praxair Corp.

2.2. Polyamides Synthesis and Membrane Casting. Polyamides were synthesized by the esterification reaction of poly(hexafluoroisopropylidene hydroxyisophthalamide) (PA) previously synthesized via polycondensation^{14,17,18} and four structurally different pendant groups using NMP as solvent and TEA as a base at 60 °C (see Scheme 1) as follows. PA

Scheme 1. Schematic Reactions for the Synthesis of Polyamides P1–P4



(800 mg, 1.6 mmol of –OH) was dissolved in *N*-methyl-2-pyrrolidone (10 mL) under nitrogen atmosphere. TEA (0.89 mL, 6.4 mmol) and 1.09 mL (6.4 mmol) of the monomer (acid chloride), which had been previously dissolved in NMP (3 mL), were added. The mixture was heated at 60 °C for 20 h. At the end, the highly viscous polymeric solution was precipitated in a large amount of methyl alcohol (400 mL) and dried under vacuum at 180 °C for 24 h. The other polyamides were prepared using the same steps and conditions.

The polyamide membranes were prepared by casting solution (4.6% w/v) in DMAc at 70 °C. After 24 h, the membranes were immersed in methyl alcohol to exchange the residual DMAc. Finally, the membranes were dried under vacuum at 200 °C for 24 h. Membrane thickness was maintained between 30 and 50 μm.

2.3. Characterization. A Varian-600 spectrometer was used to obtain ¹H NMR spectra of the polymeric samples

dissolved in DMSO-*d*₆. Polyamide membranes FT-IR spectra were obtained with a Nicolet 8700 spectrometer (between 4000 and 650 cm⁻¹). Polymer inherent viscosity (η_{inh}) and membrane samples density measurements were determined using an Ubbelohde viscometer no. 50 (at 30 ± 0.1 °C and 0.5 g/dL polyamide in DMAc) and a density gradient column Techne Corp. (filled with aqueous solution of calcium nitrate at 22 °C), respectively. Thermal stability of the membrane samples was studied using a PerkinElmer TGA-7 in the temperature range of 50–800 °C at 10 °C/min, under N₂ atmosphere. Membranes X-ray diffraction (XRD) measurements were carried out on a D8-Advance diffractometer (Bruker) with CuK α radiation (λ = 1.54 Å) at a 0.02° step rate over a 2 θ range of 10–60°. Mechanical properties were determined in a Shimadzu AGS-X universal tester at a crosshead speed of 1 mm/min using a 1000 N load cell. The average value of at least three membrane samples (2 cm × 0.5 cm with 30–50 μm thickness) is reported. Glass transition temperature (T_g) of each membrane was determined with a TA Instruments differential scanning calorimeter (DSC-2920) between 30 and 320 °C at a rate of 10 °C/min under N₂ atmosphere.

2.4. Gas Transport Measurements. Pure He, H₂, O₂, N₂, CH₄, and CO₂ permeation measurements were evaluated at 2.02 bar and 35 °C in a permeation cell by the constant volume method, as described in the literature.¹⁴ For some membrane (P2 and P3), the upstream pressure was increased to 2.02, 5.06, 7.59, and 10.13 bar at 35 °C for each pure gas, except for O₂ (up to 7.59 bar) for safety reasons. Gas permeability coefficients, P , were determined by the slope of the downstream pressure (dp/dt)_{ss} (cm Hg s⁻¹) when it reached steady-state conditions as described before¹⁸ and as calculated by eq 1:

$$P = \frac{VR^N l}{ART \Delta p} \left(\frac{dp}{dt} \right)_{ss} \quad (1)$$

where l and A are the thickness and the effective area of the membrane, R^N is the volume of a gas mole at standard conditions (STP), V is the downstream volume of the cell, R is the gas constant, Δp is the pressure difference between upstream and downstream (cm Hg), and T is the absolute temperature.¹⁴

The time lag method (θ) was used to calculate the diffusion coefficient, D , and the solubility coefficients, S , were obtained from the P/D ratio. The ideal permselectivity, $\alpha_{X/Y}$, of the polyamide membranes was estimated from the P coefficients ratio for a given gas pair X and Y .

3. RESULTS AND DISCUSSION

3.1. Polyamide Membranes Characteristics.

3.1.1. Spectroscopic Analysis. The most remarkable features shown in ATR-FTIR spectra (Figure 1) of P1–P4 were the bands of amide groups at 3420–3170, 1662, and 1512 cm⁻¹ assigned to N–H, C=O stretching, combined N–H bending, and C–N stretching vibrations, respectively.^{14,19,20} The absorption bands of the ester moiety at 1728 and 1240 cm⁻¹ corresponding to C=O and C–O–C indicate the successful bulky pendant groups' incorporation in the PA backbone.²⁰ Last, the band at 1597 cm⁻¹ is representative of aromatic C–C stretching vibration,²¹ and at 2990–2820 cm⁻¹ the bands of aromatic C–H stretching, –C–CH₃ groups, or, in the case of P3, the *tert*-butyl group –C–(CH₃)₃. More detailed chemical

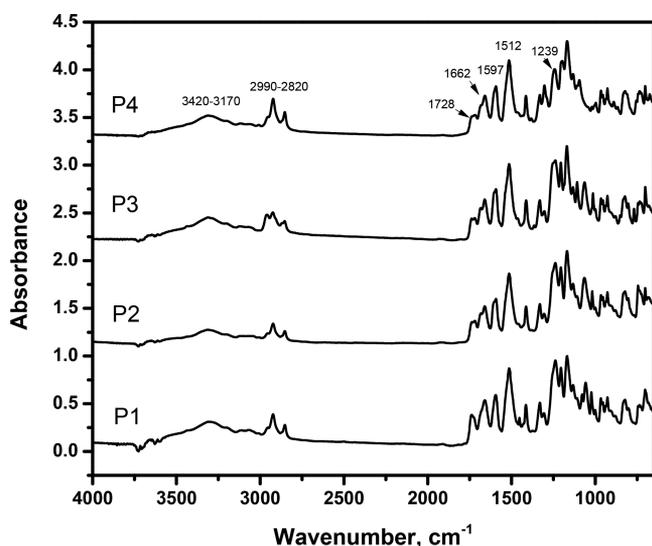


Figure 1. Infrared spectra of polyamides P1–P4.

structural information for the synthesized polyamides was obtained by ^1H NMR spectroscopy. Figure 2 shows the peak labeling in the P3 ^1H NMR spectrum (for NMR spectra of P1, P2, and P4, see the Supporting Information). The region from 8.52 to 7.35 ppm clearly shows the proton signals from the aromatic rings of the backbone chain and the pendant group. The two amide protons from $(-\text{C}(=\text{O})-\text{NH}-)$ at 10.71 ppm and the nine protons belonging to the $-\text{C}(\text{CH}_3)_3$ group are observed at 1.30 ppm.

3.1.2. Solubility Test. Polyamides solubility was verified in several aprotic and chlorinated solvents (see results in Table S1). The four polyamides were soluble in DMF, NMP, DMSO, and DMAc, and insoluble in chlorinated solvents and THF even upon heating. The high polyamides solubility in the first four solvents may be due to the presence of CF_3 and bulky pendant groups, which reduced chain interactions.

3.1.3. Inherent Viscosity (η_{inh}), Density, FFV, and XRD. Table 1 shows the polyamides inherent viscosity (η_{inh}) ranging between 0.73 and 1.07 dL/g. The inherent viscosity decreases

Table 1. η_{inh} , Density, and FFV of the Polyamides

polymer	η_{inh} (dL/g)	density (g/cm^3)	FFV
PA ¹⁴	0.61	1.456	0.131
P1	0.73	1.402	0.155
P2	0.81	1.385	0.152
P3	1.07	1.314	0.167
P4	1.02	1.357	0.156

in the following order: P3 > P4 > P2 > P1. This decrease could be associated with a difference in chain packing induced by the different bulky groups that inhibit the macromolecular chain interactions.¹⁴ Fractional free volume (FFV) is often used for a correlation and possible prediction for membrane materials gas separation performance.^{22,23} FFV calculation requires experimental density measurement of the polymers and an estimation of polymer occupied volume ($V_o = 1.3V_w$) that was obtained from the predictive method using group contribution established by Bondi.²⁴ Table 1 shows the density values and occupied volume of the synthesized polyamides.

FFV increases in the following order: P3 > P4 > P1 > P2, attributed to the chemical structure of the bulky groups. Regarding P2, P4, and P3, the benzoyl pendant group bearing methyl (in *para*-position to the ester bond), dimethyl (in *meta*-position), and *tert*-butyl group (in *para*-position), respectively, provide higher chain separation and a decrease in chain packing density in comparison with P1 (using benzene as pendant group), with a subsequent increase in the FFV.²⁵ However, P1, P2, and P4 presented little difference in their FFV values, which might be due to similar macromolecular rearrangement and conformational freedom caused by pendant groups on the polyamide backbone. On the other hand, P3 presented the highest FFV as a consequence of segmental mobility restriction produced by the pendant benzene bearing the bulky *tert*-butyl group.

The XRD characterization showed an amorphous halo in polyamides membranes (Figure 3). Polymer P3 presents the highest *d*-spacing (6.75 Å), attributed to the 4-*tert*-butylbenzoyl (TBB) voluminous group, which has a more pronounced effect of diminishing chain packing than the other pendant groups in P1, P2, and P4, according to FFV results.

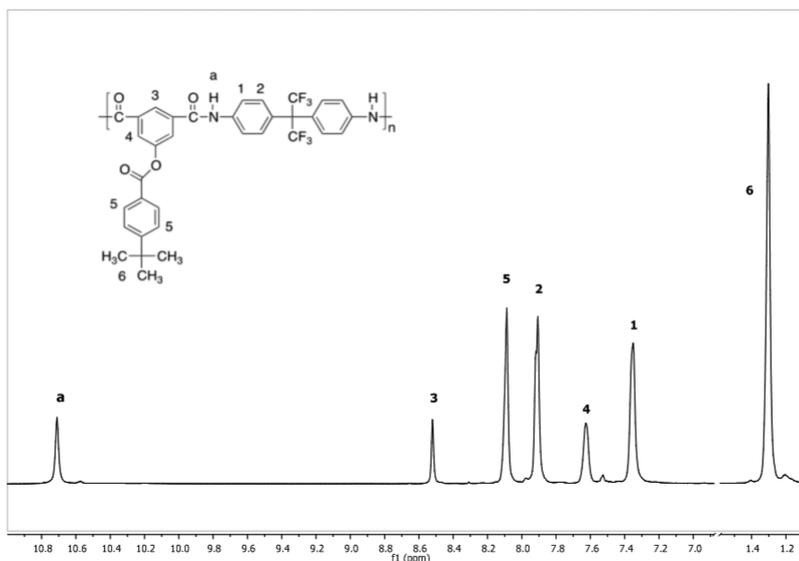


Figure 2. ^1H NMR spectrum of P3 polyamide.

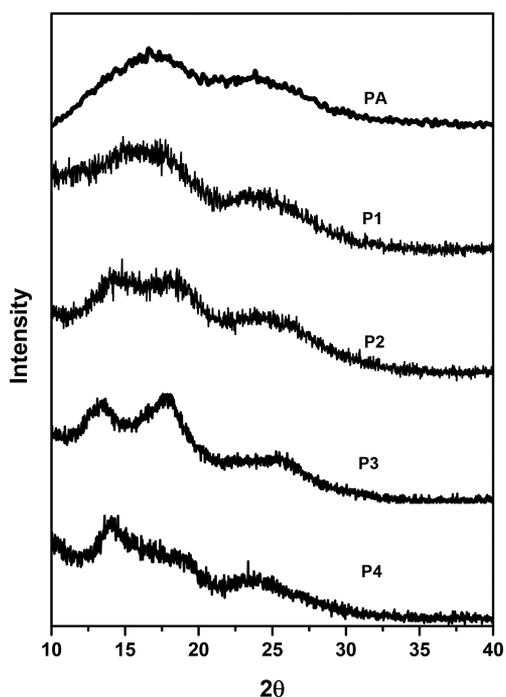


Figure 3. Polyamide P1–P4 XRD patterns.

Moreover, the d -spacing values of P1–P4 exhibit little differences as compared to those of the precursor, as shown in Figure 3 and Table 2S. For example, PA presents two amorphous halos corresponding to 3.75 and 5.31 Å, while P1–P4 show a third maxima around a d -spacing of 6 Å with a decrease in d -spacing between maxima at 3.75 and 5.31 Å, a fact that is ascribed to the incorporation of the B, *p*-T, DMB, and TBB groups, respectively, which increase the interchain distance.¹⁴ On the other hand, there is no correlation between d -spacing and FFV for P1 and P2, where the latter has lower FFV.

3.1.4. Thermal and Mechanical Behavior. The thermal stability of these polyamides was estimated by thermogravimetric analysis and their glass transition by DSC. Figure 4 shows the degradation profiles for the synthesized polyamides

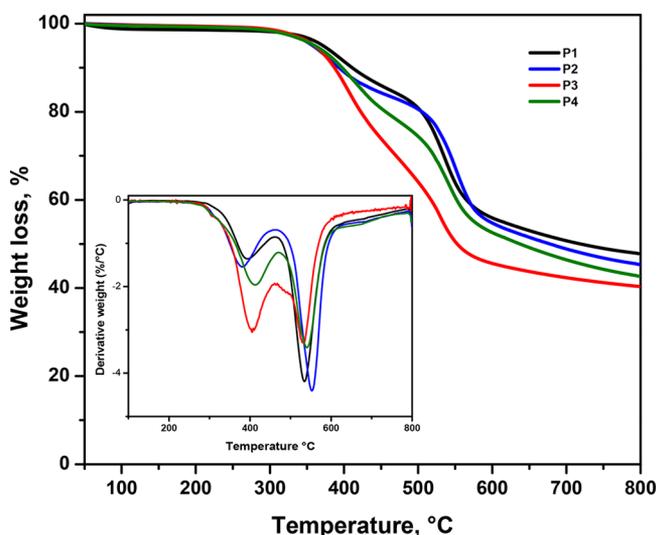


Figure 4. Thermograms of polyamide membranes P1–P4.

P1, P2, P3, and P4. The polyamides underwent a 10% weight loss ($T_{10\%}$) close to 400 °C, showing that they possess a high thermal stability. This first degradation stage is associated with the loss of pendant groups.^{14,26} A second degradation stage takes place between 470 and 610 °C, which is due to the generalized polymer backbone degradation, where the char yield, around 40–48%, obtained for each synthesized polyamide evidenced once again their high aromaticity. On the other hand, the DSC thermograms indicate that P1 and P2 have a T_g at 298 and 302 °C, respectively, followed by P3 at 312 °C, which are the highest T_g of all of the polyamides synthesized here, while P4 exhibits a T_g at 308 °C. These polyamides T_g increased as FFV increases, which could be attributed to chain packing restrictions produced by the introduction of bulky phenyl and phenyl-substituted groups and to an increase in rotational barrier energy.²⁷ It must also be noticed that T_g 's for these polyamides show a difference of 12 °C between the highest and the lowest as they present only small differences in the pendant groups.

Mechanical properties of polyamide membranes under uniaxial tension tests are presented in Table 2. P1–P4 exhibit

Table 2. T_g and Stress–Strain Values of PA and Modified Polyamides

polymer	T_g (°C)	TS (MPa)	elongation at break (%)	modulus (GPa)
PA ¹⁴	309	63.8 ± 4.4	12.32 ± 2.25	1.21 ± 0.11
P1	298	39.3 ± 0.55	2.71 ± 0.69	1.88 ± 0.08
P2	302	44.2 ± 0.21	3.76 ± 0.58	1.61 ± 0.12
P3	312	46.7 ± 2.54	3.01 ± 0.45	1.85 ± 0.34
P4	308	45.7 ± 5.30	3.10 ± 0.64	2.16 ± 0.12

mechanical properties with elongation at break ranging from 2.7% to 3.76%, and tensile strength (TS) and Young's modulus values are in the range of 39.3–46.7 MPa and 1.6–2.1 GPa, respectively. Although the presence of different pendant groups into poly(hexafluoroisopropylidene hydroxyisophthalamide) (PA) precursor (with FFV = 0.131, TS = 63.89 ± 4.4 MPa) leads to polymeric structures with higher FFV, they still show higher tensile modulus as compared to PA. Moreover, P1–P4 show a tensile modulus increase that is almost twice in comparison to that reported for PA, which could have originated from differences in polymer structures rigidity caused by the introduction of pendant groups with the ester linkage and differences in molecular weight.¹⁴

3.2. Pure Gas Transport Properties. **3.2.1. Chemical Structure Modification Influence on Gas Transport Properties.** Bulky ester phenyl and phenyl-substituted pendant groups introduction in the polyamides is expected to increase FFV, enhance gas permeability, and/or hinder chain rotation, increasing gas selectivity through the membranes.^{9,14,15} In this case, the polyamides share the same backbone structure and differ only in the nature of the substitution on the phenyl in the bulky pendant groups, such as benzoyl (B), *p*-toluoyl (*p*-T), 3,5-dimethylbenzoyl (DMB), and 4-*tert*-butylbenzoyl (TBB). To establish the influence of the molecular structure on transport properties, the P coefficients for the polyamide membranes were evaluated for H₂, He, CO₂, N₂, O₂, and CH₄ gases. The results of pure gas permeability (P), apparent diffusion (D), and solubility (S) coefficients at 35 °C and 2.02 bar are listed in Tables 3 and 4.

Table 3. Gas Permeation Properties and Ideal Selectivity of P1–P4 Membranes

membrane	permeability, ^a <i>P</i> (barrer)						selectivity, α			
	He	H ₂	CO ₂	O ₂	N ₂	CH ₄	CO ₂ /CH ₄	CO ₂ /N ₂	H ₂ /CH ₄	H ₂ /N ₂
PA ¹⁴	19	24.8	2.82	0.66	0.4	0.5	5.64	7.0	49.6	62.0
P1	62	56.3	38.9	7.3	1.9	1.6	24.3	20.5	35.2	29.6
P2	57	53.4	37.2	7.0	1.7	1.4	26.6	21.9	38.1	31.4
P3	95	101	88.1	17.5	4.7	4.6	19.2	19.0	18.9	21.5
P4	62	60.4	43.1	8.5	2.2	2.1	20.5	19.8	28.8	27.5

^a1 barrer = 1×10^{-10} cm³ (STP) cm/cm² s cm Hg.

Table 4. Apparent *D* and *S* Coefficients of P1, P2, P3, and P4 Membranes

membrane	<i>D</i> (10 ⁻⁸ cm ² /s)				<i>S</i> (10 ⁻² cm ³ (STP)/cm ³ cm Hg)			
	O ₂	N ₂	CH ₄	CO ₂	O ₂	N ₂	CH ₄	CO ₂
PA	0.79	0.10	0.04	0.35	0.7	3.7	12.5	8.05
P1	13.6	4.1	0.9	6.2	0.5	0.5	1.8	6.2
P2	8.4	2.5	0.6	4.2	0.8	0.7	2.5	8.9
P3	24	7.7	2.4	15	0.7	0.6	2.0	6.0
P4	16.8	5.2	1.3	7.8	0.5	0.4	1.7	5.5

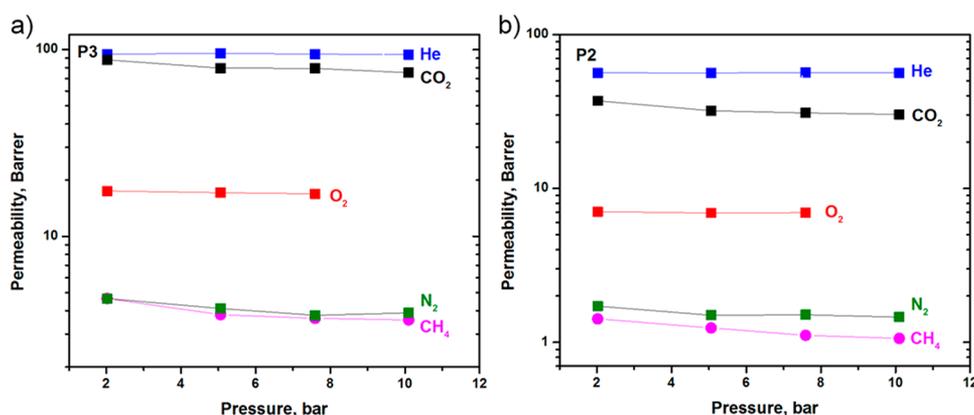


Figure 5. Gas permeability up to 10.17 bar at 35 °C: (a) P3 and (b) P2.

Depending on the bulky pendant group, the synthesized polyamides were highly permeable (13.2–31.4 times higher for CO₂) and more selective (3.4–4.5 times higher for CO₂/CH₄ and 2.0–2.3 times higher CO₂/N₂) in comparison with the precursor PA (see Table 3), confirming that bulky pendant groups hinder the chain packing and increase the *P* coefficients.²³ The order observed in polyamides *P* values was P3 > P4 > P1 > P2 with a sequence in the gas permeability coefficients according to the gas kinetic diameter size of the analyzed gases. P1 is similar in polymeric structure to P2 except for an additional methyl group at the *para*-position to the ester link in the bulky pendant group. Because of the additional methyl, one could expect that P2 would present higher FFV and therefore a greater permeability coefficient to gases, in comparison with P1. However, this was not reflected in the FFV values, and P2 was slightly less permeable than P1. Apparently, the aforementioned substitution –CH₃ at *para*-position is only effective for increasing its H₂/CH₄, H₂/N₂, CO₂/CH₄, and CO₂/N₂ ideal separation capacity due to the increase in the rigidity of the macromolecular chain, as indicated by its glass transition temperature value. P3 and P4 exhibited an increase in permeability, maintaining or slightly diminishing the selectivity depending on the gas pairs. In particular, P3 containing 4-*tert*-butylbenzoyl (TBB) as pendant group clearly exhibits higher

P coefficients for the six gases tested with respect to the precursor polymer PA (31–10 times higher depending on the gas analyzed) and in comparison with P1, P2, and P4 (2–2.3 times higher) with a slight decrease in H₂/CH₄ and H₂/N₂ permselectivity, maintaining constant those for CO₂/CH₄ and CO₂/N₂. These results agree with the FFV increase, attributed to the voluminous pendant group introduction. Thus, the presence of the bulky substitutions (B, *p*-T, DMB, and TBB) clearly disrupts initial PA polymeric structures and influences significantly gas transport properties, *T*_g and FFV.

Gas apparent diffusion (*D*) and solubility (*S*) coefficients are presented in Table 4. As can be seen, there is a similar trend between the gas *D* coefficients, the gas permeability coefficients (*P*), and FFV, which is an indication of the opening between macromolecular chains through which gases can diffuse easily.²⁸ Thus, the *D* increase in bulky substituted polyamide membranes, P1–P4 in comparison with PA (*D*_{CO₂} = 0.35, *D*_{N₂} = 0.10, *D*_{CH₄} = 0.04, *D*_{O₂} = 0.79), is due to the improvement on FFV (see Table 1). With regard to solubility coefficients (*S*), the values were lower for polyamides P1–P4 as compared to PA. They were similar in the case of O₂ and show a small decrease in CO₂ solubility. In the case of N₂ and CH₄, they show around 1 order of magnitude lower solubility in polyamides P1–P4 as compared to those of the precursor PA (*S*_{CO₂} = 8.05, *S*_{N₂} = 3.7, *S*_{CH₄} = 12.5, *S*_{O₂} = 0.70).¹⁴ The

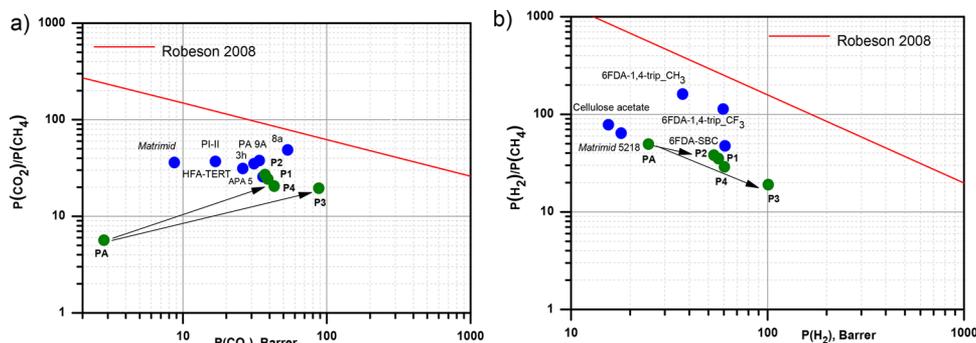


Figure 6. (a) CO_2 permeability versus CO_2/CH_4 selectivity and (b) H_2 permeability versus H_2/CH_4 selectivity of P1–P4 as compared to some polymers.

large difference in solubility for N_2 and CH_4 gives an increase in solubility selectivity (in Table 3S) and, if it is combined with the increase in diffusivity selectivity (Table 3S) for CO_2/CH_4 and CO_2/N_2 , contributes to the observed increase in overall selectivity for these gas pairs. Moreover, the CO_2 solubility values in these polyamides are high as compared to those of N_2 , O_2 , and CH_4 , which is attributed to the condensability of the CO_2 molecule.^{15,29}

A disadvantage of high performance polymers in gas separation is a possible plasticization phenomenon.^{30,31} In gas separation applications, carbon dioxide is frequently the most soluble gas and the one that tends to induce membrane plasticization, a fact that is widely reported in natural gas purification.^{31,32} Thus, the effect of upstream pressure (2.02–10.13 bar) on P coefficients through the membranes P2 and P3 was evaluated at 35 °C. Membranes P2 and P3 were selected for this study due to their high CO_2 permeability and permselectivity performance in the pure gas analysis, respectively. In both membranes (P2 and P3), He, CH_4 , N_2 , O_2 , and CO_2 permeability remains constant or slightly decreases with increasing pressure (Figure 5a,b). Thus, gas-induced plasticization over the pressure range tested was not observed.

Figure 6a and b exhibits CO_2 and H_2 separation performance in a 2008 Robeson plot for the polyamides P1–P4 as compared to PA, Matrimid, and some polymers bearing bulky moieties.^{8,9,15,16,25,31–36} As can be seen, all synthesized polyamides significantly improve their P coefficients and gas CO_2/CH_4 permselectivity, while the gas pair H_2/CH_4 follows the usual trade-off because it decreases selectivity as H_2 permeability increases in comparison with PA. In general, in glassy polymers, substitution of bulky pendant groups will often increase FFV accompanied by an increase in diffusion coefficients and finally gas permeability; in here, the TBB group was the most efficient chain packing disrupting moiety and contributed to a larger increase in permeability coefficients, allowing also an increase in permselectivity when they are compared to the unsubstituted precursor PA. The comparison between P1–P4 and Matrimid shows CO_2 and H_2 permeabilities for the polyamides are at least one order of magnitude higher. Moreover, it can be observed that P3 membrane shows a favorable increase on CO_2 and H_2 permeability coefficients in comparison with recently reported HFA-TERT and APA-5 containing *tert*-butyl moieties. This enhanced gas transport in P3 is ascribed to a FFV increase, caused by the TBB bulky pendant groups, while CO_2/CH_4 and H_2/CH_4 ideal selectivity follows the usual trade-off of

decreasing selectivity as permeability increases, a fact that is attributed to the *tert*-butyl groups in the main chain, which have lower rotational freedom than the TBB bulky pendant group containing a linking ester group to the backbone chain.²⁵

Overall, this postpolymerization method to introduce voluminous pendant groups into polyamides offers a way to modify a low permeability and low FFV polymer with a variety of pendant groups whose polymeric structures would lead to high permeability, and moderate selectivity for gas separation process. Thus, an adequate choice of the lateral group substitution in the polymeric structures significantly influences gas transport properties increasing permeability up to two orders of magnitude. In this case, PA has lower gas permeability and selective values because it presents high intermolecular packing caused by high hydrogen bonding coming from both amide linkages and $-\text{OH}$ groups.¹⁸ However, the introduction of bulky ester phenyl and phenyl-substituted pendant groups in the polyamides dilutes the interaction and increases FFV markedly because a jump from 0.131 to 0.152 will enhance permeability by at least one order of magnitude. An extra reward is that it is increasing gas selectivity for CO_2/CH_4 and CO_2/N_2 . In the case of *d*-spacing, there is a new third maxima around 6 Å for all bulky group substituted polyamides, which also support the permeability increases. Moreover, the increases in selectivity could be supported by the associated decreases in *d*-spacing between 3.54 and 5.3 Å in the new modified polyamides. Finally, the T_g in these polyamides seems to be more related to the backbone chain rigidity because it does not change appreciably with the substitution.

4. CONCLUSIONS

Four new polyamides have been efficiently prepared by postpolymerization modification via a simple esterification reaction of poly(hexafluoroisopropylidene hydroxyisophthalamide) (PA) with acid chlorides under mild conditions. In this approach, a wide variety of acid chlorides with bulky pendant groups can be employed to tailor a variety of polymeric structures otherwise not obtainable. Furthermore, the synthesized polyamides exhibit good solubility and processability for film preparation in most common aprotic solvents, and they also show high mechanical and thermal stability. Depending on the bulky pendant group, the synthesized polyamides were highly permeable (13.2–31.4 times higher for CO_2) and more permselective (3.4–4.5 times higher for CO_2/CH_4 and 2.0–2.3 times higher CO_2/N_2) in comparison with the precursor polyamide, PA. Gas-induced plasticization over the pressure

range up to 10.17 bar tested was not observed. Thus, the postpolymerization method will be useful in the evaluation of structure–property relationship, incorporating more bulky and rigid pendant groups, to enhance gas transport through the membranes.

■ ASSOCIATED CONTENT

📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.iecr.8b01772.

Polyamides ¹H NMR spectra for P1, P2, and P4 (Figures S1–S3), Table 1S gives solubility test information, Table 2S gives occupied volume (V_o), 10% weight loss ($T_{10\%}$), and d -spacing data of the polyamides, and Table 3S contains diffusion and solubility selectivity of polyamide membranes (PDF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) Sholl, D. S.; Lively, R. P. Seven separations to change the world. *Nature* **2016**, *532*, 435–437.
- (2) Koros, W. J. Evolving beyond the thermal age of separation processes: membranes can lead the way. *AIChE J.* **2004**, *50*, 2326–2334.
- (3) Bernardo, P.; Drioli, E.; Golemme, G. Membrane gas separation: a review/state of the art. *Ind. Eng. Chem. Res.* **2009**, *48*, 4638–4663.
- (4) Bisoi, S.; Mandal, A. K.; Padmanabhan, V.; Banerjee, S. Aromatic polyamides containing trityl substituted triphenylamine: Gas transport properties and molecular dynamics simulations. *J. Membr. Sci.* **2017**, *522*, 77–90.
- (5) Adewole, J. K.; Ahmad, A. L.; Ismail, S.; Leo, C. P. Current challenges in membrane separation of CO₂ from gas natural: A review. *Int. J. Greenhouse Gas Control* **2013**, *17*, 46–65.
- (6) Bera, D.; Padmanabhan, V.; Banerjee, S. Highly gas permeable polyamides based on substituted triphenylamine. *Macromolecules* **2015**, *48*, 4541–4554.
- (7) Garcia, J. M.; Garcia, F. C.; Serna, F.; de la Peña, J. L. High-performance aromatic polyamides. *Prog. Polym. Sci.* **2010**, *35*, 623–686.
- (8) Ding, Y.; Bikson, B. Soluble aromatic polyamides containing the phenylindane group and their gas transport characteristics. *Polymer* **2002**, *43*, 4709–4714.
- (9) Bera, D.; Bandyopadhyay, P.; Ghosh, S.; Banerjee, S.; Padmanabhan, V. Highly gas permeable aromatic polyamides containing adamantane substituted triphenylamine. *J. Membr. Sci.* **2015**, *474*, 20–31.
- (10) Behniafar, H.; Zardoozi, F.; Rastkar, A. Fluoro-containing poly(amide-imide)s with sterically hindered pendants: Synthesis and characterization. *J. Fluorine Chem.* **2012**, *138*, 34–41.
- (11) Bandyopadhyay, P.; Bera, D.; Banerjee, S. Synthesis, Characterization and gas transport properties of semifluorinated new aromatic polyamides. *Sep. Purif. Technol.* **2013**, *104*, 138–149.
- (12) Maji, S.; Banerjee, S. Synthesis, characterization and properties of novel fluorine containing aromatic polyamides. *J. Appl. Polym. Sci.* **2008**, *108*, 1356–1364.
- (13) Singh, A.; Ghosal, K.; Freeman, B. D.; Lozano, A. E.; de la Campa, J. G.; de Abajo, J. Gas separation properties of pendant phenyl substituted aromatic polyamides containing sulfone and hexafluoroisopropylidene groups. *Polymer* **1999**, *40*, 5715–5722.
- (14) Santiago-Garcia, J. L.; Pérez-Francisco, J. M.; Zolotukhin, M. G.; Vázquez-Torres, H.; Aguilar-Vega, M.; González-Díaz, M. O. Gas transport properties of aromatic poly- and copolyamides bearing bulky functional groups. *J. Membr. Sci.* **2017**, *522*, 333–342.
- (15) Bera, D.; Bandyopadhyay, P.; Ghosh, S.; Banerjee, S. Gas transport properties of aromatic polyamides containing adamantyl moiety. *J. Membr. Sci.* **2014**, *453*, 175–191.
- (16) Guiver, M. D.; Robertson, G. P.; Dai, Y.; Bilodeau, F.; Kang, Y. S.; Lee, K. J.; Jho, J. Y.; Wong, J. Structural characterization and gas-transport properties of brominated matrimid polyamide. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 4193–4204.
- (17) Yamazaki, N.; Matsumoto, M.; Higashi, F. Studies on reactions of the N-phosphonium salts of pyridines. XIV. Wholly aromatic polyamides by the direct polycondensation reaction by using phosphites in the presence of metal salts. *J. Polym. Sci., Polym. Chem. Ed.* **1975**, *13*, 1373–1380.
- (18) González-Díaz, M. O.; Pérez-Francisco, J. M.; Herrera-Kao, W.; González-Díaz, A.; Montes-Luna, A.; Aguilar-Vega, M. Novel copolyamides with bulky flexible groups for pure and mixed-gas separation. *Sep. Purif. Technol.* **2017**, *189*, 366–374.
- (19) Zou, F.; Wen, H.; Yan, T.; Cai, M. Synthesis and properties of novel soluble aromatic polyamides containing 4-aryl-2,6-diphenylpyridine moieties and pendant fluorinated phenoxy groups. *J. Polym. Res.* **2016**, *23*, 225.
- (20) Kwon, Y.-N.; Leckie, J. O. Hypochlorite degradation of crosslinked polyamide membranes II. Changes in hydrogen bonding behavior and performance. *J. Membr. Sci.* **2006**, *282*, 456–464.
- (21) Askari, M.; Xiao, Y.; Li, P.; Chung, T.-S. Natural gas purification and olefin/paraffin separation using cross-linkable 6FDA-Durene/DABA co-polyimides grafted with α , β and γ -cyclodextrin. *J. Membr. Sci.* **2012**, *390–391*, 141–151.
- (22) Park, J. Y.; Paul, D. R. Correlation and prediction of gas permeability in glassy polymer membrane materials via a modified free volume based group contribution method. *J. Membr. Sci.* **1997**, *125*, 23–39.
- (23) Nagel, C.; Günther-Schade, K.; Fritsch, D.; Strunskus, T.; Faupel, F. Free volume and transport properties in highly selective polymer membranes. *Macromolecules* **2002**, *35*, 2071–2077.
- (24) Van Klevelen, D. W.; Nijenhuis, K. T. *Properties of Polymers*; Elsevier: Amsterdam, 1976.
- (25) Espeso, J.; Lozano, A. E.; de la Campa, J. G.; de Abajo, J. Effect of substituents on the permeation properties of polyamide membranes. *J. Membr. Sci.* **2006**, *280*, 659–665.
- (26) Maya, E. M.; Lozano, A. E.; de Abajo, J.; de la Campa, J. G. Chemical modification of copolyimides with bulky pendent groups: effect of modification on solubility and thermal stability. *Polym. Degrad. Stab.* **2007**, *92*, 2294–2299.
- (27) Lu, Y.; Xiao, G.; Chi, H.; Dong, Y.; Hu, Z. Effects of *tert*-butyl substitutes of fluorinated diamine on the properties of polyimides. *High Perform. Polym.* **2013**, *25*, 894–900.
- (28) Yampolskii, Y.; Pinnau, I.; Freeman, B. D. *Materials Science of Membranes for Gas and Vapor Separation*; John Wiley & Sons, Ltd.: New York, 2006.
- (29) Morisato, A.; Ghosal, K.; Freeman, B. D.; Chern, R. T.; Alvarez, J. C.; de la Campa, J. G.; Lozano, A. E.; de Abajo, J. Gas separation

properties of aromatic polyamides containing hexafluoroisopropylidene groups. *J. Membr. Sci.* **1995**, *104*, 231–241.

(30) Maya, E. M.; García-Yoldi, I.; Lozano, A. E.; de la Campa, J. G.; de Abajo, J. *Macromolecules* **2011**, *44*, 2780–2790.

(31) Sanders, D. F.; Smith, Z. P.; Guo, R.; Robeson, L. M.; McGrath, J. E.; Paul, D. R.; Freeman, B. D. Energy-efficient polymeric gas separation membranes for a sustainable future: A review. *Polymer* **2013**, *54*, 4729–4761.

(32) Carrera-Figueiras, C.; Aguilar-Vega, M. Gas permeability and selectivity of hexafluoroisopropylidene aromatic isophthalic copolyamides. *J. Polym. Sci., Part B: Polym. Phys.* **2005**, *43*, 2625–2638.

(33) Kothawade, S. S.; Kulkarni, M. P.; Kharul, U. K.; Patil, A. S.; Vernekar, S. P. Synthesis, Characterization, and gas permeability of aromatic polyimides containing pendant phenoxy group. *J. Appl. Polym. Sci.* **2008**, *108*, 3881–3889.

(34) Puleo, A. C.; Paul, D. R. The effect of degree of acetylation on gas sorption and transport behavior in cellulose acetate. *J. Membr. Sci.* **1989**, *47*, 301–332.

(35) Zhang, C.; Li, P.; Cao, B. Effects of the side groups of the spirochroman-based diamines on the packing and gas separation properties of the polyimides. *J. Membr. Sci.* **2017**, *530*, 176–184.

(36) Wiegand, J. R.; Smith, Z. P.; Liu, Q.; Patterson, C. T.; Freeman, B. D.; Guo, R. Synthesis and characterization of triptycene-based polyimides with tunable high fractional free volume for gas separation membranes. *J. Mater. Chem. A* **2014**, *2*, 13309–13320.