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Gas transport properties of novel aromatic poly- and copolyamides bearing bulky functional groups

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ABSTRACT

The synthesis and properties of novel aromatic poly- and co-polyisopthalamides bearing –OH, -tert-butyl (TERT) and 3,5-bis(trifluoromethyl) benzoyl (BTFB) groups are reported. All synthesized aramides are highly soluble in aprotic solvents, thermally stable up to 400 °C and present good film forming ability. The combination at random of -OH group with TERT or BTFB groups in copolymers **CPA 1** and **CPA 2** is highly effective for improving gas permeability (*P*) for all tested gases (CO_2, O_2, N_2, CH_4) and selectivity (α) for CO_2/CH_4 and CO_2/N_2. Copolymer **CPA 2b** containing OH and BTFB groups exhibited high gas permeability and good selectivity (P_{CO2}=60.17 and P_{CH4}=2.67, α=22.53) in comparison with analogous polyamides and some polyimides. These results are well correlated with both the increase in fractional free volume (FFV) and interchain *d*-spacing.

1. Introduction

Over the years, aromatic polyamides or aramides have been widely studied due to their outstanding thermal and mechanical resistance [1–5]. The properties arise from their aromatic structure and amide linkages, which result in rigid-rod polymer chains that interact with each other via strong hydrogen bonding. These bonds often create effective crystalline microdomains, resulting in high-level intermolecular packing and cohesive energy [6]. As a result, they tend to exhibit low solubility in common organic solvents and very low processability. Intensive efforts have been made to enhance their processability and solubility, as well as to increase some properties for applications that require high thermal and mechanical stability. These studies include the modification of their chemical structure, reducing hydrogen bonding by N-substitution, introducing flexible segments, replacing symmetrical aromatic rings for unsymmetrical ones, copolymerization with the introduction of an appropriate second monomeric unit sequence and the incorporation of bulky pendant groups [3,7–16]. Another interesting approach that has been studied is the introduction of functional polar groups into the polymer chain, such as hydroxyl (–OH) or carboxyl (–COOH) groups, because they can be used to impart special functionality to high performance polymers. For example, the relationship between polymers with functional polar groups and their solubility in organic solvents and in some cases the modification of their gas permeability has been studied for polymers such as polyimides [17–24], poly(ether ether ketone) [25], polyesters [26] and poly(diphenylacetylenes) [27].

Wholly aromatic polyisophthalamides (PIPAs) containing reactive free -OH groups and the subsequent incorporation of side poly(ethylene oxide) (PEO) sequences have been studied in recent years [28,29]. The results confirmed that OH-*p*-PIPA and OH-*m*-PIPA are quite hydrophilic compared with non-hydroxylated aromatic polyamides. They were proposed as an alternative approach in the preparation of ultrafiltration (UF) membranes with high flux and antifouling properties [29]. It was also reported that the presence of –OH groups in membranes from highly aromatic polymers increases the solubility coefficient of condensable gases, although a decrease in gas diffusivity is observed [19]. The incorporation of –COOH in the aromatic

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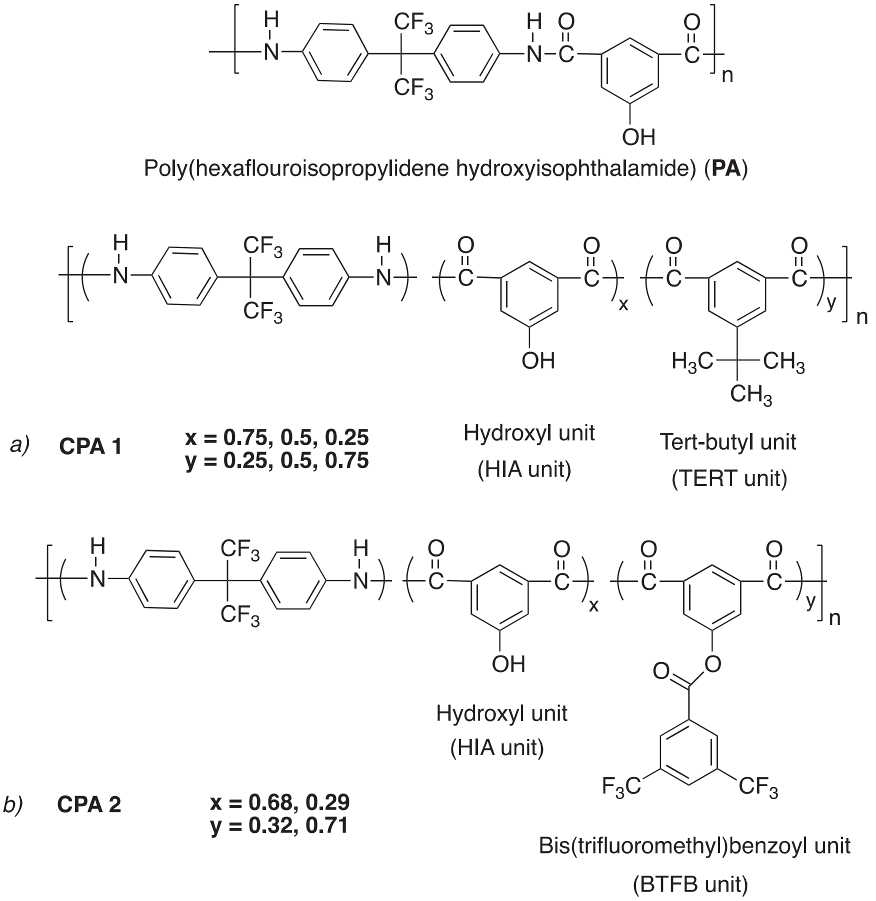


Fig. 1. Chemical structure of **PA** and copolyaramides with different bulky pendant groups.

polymers leads to strongly reduced permeability, but CO_2-induced plasticization can be reduced due to hydrogen bonding crosslinks [20]. The -OH group can be thermally converted to polybenzoxazole group and shows excellent CO_2 separation compared to conventional membranes [21–23]. Moreover, polyimides containing a free polar –COOH group were used as precursor to introduce bulky pendant groups [24].

In this work, we present the synthesis and characterization of a novel polyaramide poly(hexafluoroisopropylidene hydroxyisophthalamide) (**PA**) which contains a free hydroxyl pendant group in its repeating unit. Two syntheses of random copolyaramides were carried out: a) by direct polycondensation of the diamine 4,4′-(hexafluoroisopropylidene) dianiline (HFA) with different comonomer ratios of 5-*tert*-butylisophthalic acid (TERT) and 5-hydroxyisophthalic acid (HIA); which lead to a random copolymer **CPA 1** (Fig. 1a, where X, Y indicate the feed molar percent of HIA and TERT, respectively), and b) by a consecutive esterification reaction of **PA** polyamide to introduce 3,5-bis(trifluoromethyl) benzoyl (BTFB) bulky pendant groups via reaction with the free –OH groups in **PA** main chain, which lead to **CPA 2** random copolymers (Fig. 1b, where X, Y indicate the level of chemical modification).

The structure and general properties of the polymers obtained, and their gas transport characteristics and separation properties are reported.

2. Experimental

2.1. Materials

4,4′-(Hexafluoroisopropylidene)dianiline (HFA, 98%), 5-*tert*-butylisophthalic acid (TERT, 98%), pyridine (Py, 99%), triphenyl phosphite (TPP, 97%), triethylamine (TEA, ≥99%), 3,5-bis(trifluoromethyl) benzoyl chloride (BTFBC, 97%), *N,N*-dimethylacetamide (DMAc, 99.8%), *N*-methylpyrrolidinone (NMP, 99.5%) and methanol (MeOH, 99%) were supplied by Aldrich and were used as received. Anhydrous calcium chloride ($CaCl_2$, Baker) was dried under vacuum at 180 °C. 5-hydroxyisophthalic acid (HIA, Aldrich 98%) was recrystallized from MeOH.

2.2. Synthesis of poly(hexafluoroisopropylidene hydroxyisophthalamide) (PA)

Poly(hexafluoroisopropylidene hydroxyisophthalamide) (**PA**) homopolymer was synthesized by direct polycondensation of HFA and HIA. The reaction was carried out in a 1:1 mol ratio between the diamine and the diacid using the method reported by Yamazaki [30]. In a typical polyamide synthesis, a 50 mL three-neck flask equipped with mechanical stirrer and a nitrogen inlet was charged with (2.5 mmol) HFA, (2.5 mmol) HIA, (15% w/w) $CaCl_2$, Py (1.44 mL) and TPP(1.42 mL) in NMP (5.5 mL). The reaction mixture was heated with stirring at 105 °C for 24 h. The resultant polymer was poured slowly into MeOH and the fibrous product obtained was filtered and washed several times with MeOH. Finally, the PA was dried in a vacuum oven at 200 °C for 24 h.

PA: FTIR (cm^{-1}): 3000–3600 (O–H, N–H), 1665 (C=O), 1175, 1205 (C–F). ^1H NMR (600 MHz, DMSO-d_6, δ): 10.66 (s, 2H; NH), 10.30 (s, 1H; OH), 8.05 (s, 1H; Ar H), 7.98 (d, 4H; Ar H), 7.61 (s, 2H; Ar H), 7.42 (d, 4H; Ar H). ^{19}F NMR: (600 MHz, DMSO-d_6, δ): −63.3 (s, 6F; C–CF_3).

2.3. Synthesis by direct polycondensation of random copolyaramides bearing –OH and tert-butyl groups (CPA 1)

Copolyaramides bearing tert-butyl (TERT) pendant groups and hydroxyl groups were synthesized by direct polycondensation of HFA diamine with the corresponding amounts of HIA and TERT monomers to produce copolymers containing 25, 50 and 75 mol% of HIA. These polymers will be identified as **CPA 1a**, **CPA 1b** and **CPA 1c.**

2.4. Synthesis of random copolyaramides (CPA 2) by chemical modification of PA

The synthesis of copolyaramides bearing 3,5-bis(trifluoromethyl) benzoyl (BTFB) groups and hydroxyl groups were carried out through an esterification reaction at 25 °C and 60 °C. A typical PA esterification reaction is described as follows: (0.81 g) **PA** (corresponding to 1.7 mequivalents of –OH) was dissolved in NMP (11 mL) in a 50 mL three-necked round-bottom flask equipped with magnetic stirrer under nitrogen atmosphere. The homogenous solution was cooled and 1.7 mmol of TEA were added drop-wise. After complete addition of TEA, (1.7 mmol) BTFBC dissolved in NMP (4 mL) was added and the reaction mixture was stirred for 10 min. The temperature was then raised to 60 °C (a second reaction was carried out under the same conditions at 25 °C) and the mixture was stirred at this temperature for 24 h. Finally, the polymer solution was precipitated in MeOH. The precipitate was filtered and then washed several times with MeOH and dried in a vacuum oven at 200 °C for 24 h. The synthesis of the **CPA 2b** copolyaramides was carried out by triplicate. According to the modification grade of the –OH groups, the copolyaramides were identified as **CPA 2a** (32%) and **CPA 2b** (71%).

CPA 2: FTIR (cm^{-1}): 3000–3600 (O–H, N–H), 1752 (C=O ester), 1665 (C=O), 1100–1300 (C–F, C–O–C ester). ^{1}H NMR (600 MHz, DMSO-d_6, δ): 10.80 (s, 2H; NH), 10.63 (s, 2H; NH), 10.25 (s, 1H; OH), 8.75 (s, 2H; Ar H), 8.61 (s, 1H; Ar H), 8.25 (s, 2H; Ar H), 8.02 (s, 2H; Ar H), 7.96 (d, 8H; Ar H), 7.58 (s, 2H; Ar H), 7.40 (d, 8H; Ar H). ^{19}F NMR: (600 MHz, DMSO-d_6, δ): −63.3 (s, 12F; C–$(CF_3)_2$), −61.5 (s, 6F; C_6H_3–$(CF_3)_2$).

2.5. Preparation of dense films

All dense films of the polyaramide and copolyaramides obtained were prepared by casting a 4% (w/v) polymer solution in DMAc. The solution was poured into an aluminum ring and the solvent was evaporated slowly at 70 °C. The films obtained were dried in a vacuum oven at 200 °C for 24 h to remove the residual solvent. Complete removal of solvent was monitored using thermogravimetric (TGA) analysis.

2.6. Characterization

^{1}H NMR and ^{19}F NMR spectra were recorded on a Varian NMR spectrometer operating at 600 MHz using deuterated dimethylsulfoxide (DMSO-d_6) as the solvent. The solubility of each polymer was determined by mixing 5 mg of polymer in 1 mL of solvent, followed by stirring for 24 h at room temperature. Inherent viscosities were measured using an Ubbelohde viscometer No. 50 at 30 ± 0.1 °C with DMAc as solvent at a concentration of 0.5 g/dL. Polymer films density was measured in a density gradient column (Techne Corp) based on aqueous calcium nitrate solutions between 1.22 and 1.47 (g/cm^3) at 23 °C. Based on the density data, the fractional free volume (FFV) was calculated from van der Waals Volumes (V_w) obtained from Bondi's group contribution method [31] using the following equation

$$FFV = \frac{V_{sp} - V_o}{V_{sp}} \tag{1}$$

Where V_{sp} is the specific volume ($V_{sp}=1/\rho$) and V_o is the chain occupied specific volume ($V_o=1.3V_w$). For copolymers, the occupied volume was calculated assuming that there exists additivity of each polyamide occupied volume using the following equation

$$V_{OC} = w_1 V_{01} + w_2 V_{02} \tag{2}$$

where w_1 and w_2 are the weight fractions of each aromatic polyamide in the copolyamide; V_{01} and V_{02} are the occupied volume of the homopolymers.

X-ray diffraction (XRD) measurements were performed with a Siemens 5000 X-ray diffractometer using Cu-K_α radiation (λ=1.54 Å) at 34 kV and 25 mA in all polymer films. The measurements were made between 0 and 60° 2θ at a step rate of 0.04°. Thermogravimetric analysis (TGA) was carried out using a Thermogravimetric balance (Perkin Elmer TGA-7) under nitrogen atmosphere at a heating rate of 10 °C/min between 50 and 700 °C. Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectra of the polymer films were measured on a Nicolet 8700 FTIR in the wavenumber range from 4000 to 400 cm^{-1}. Mechanical properties under uniaxial tension were determined in a universal testing machine (Shimadzu AGS-X) with a load cell of 100 N at a crosshead speed of 1 mm/min. Samples with dimension 0.5 cm×2 cm and 50 µm thickness were used for the measurements. Molecular weight measurements, M_n and M_w, were performed by gel permeation chromatography (GPC) in a HP Agilent 1100 HPLC system equipped with a differential refractive index detector (IR). DMF containing 0.5% LiBr was used as the mobile phase (flow rate 1.0 mL min^{-1}) at 30 °C. Two columns Zorbax PSM 60-S and PSM 1000-S were used for molecular weight determination and calibration was carried out with polystyrene standards. Glass transition temperatures for the polyamides were determined using differential scanning calorimetry (TA Instrument 2920 DSC). The measurements were made between 30 °C and 350 °C at a heating rate of 10 °C/min under nitrogen atmosphere.

2.7. Gas transport properties

Pure gas permeability (*P*), diffusion (*D*), and solubility (*S*) coefficients for four different gases: oxygen (O_2), nitrogen (N_2), methane (CH_4), and carbon dioxide (CO_2), were determined in a gas permeation cell using the constant volume method and a film area of 1.15 cm^2. All gases used in the study were obtained from Praxair Corp. with purities > 99.99%. *P* coefficients were determined from the slope of the downstream pressure versus time plot $(dp/dt)_{ss}$, under steady-state conditions at 2.02 bar upstream pressure and 35 °C for each pure gas, by using the following equation:

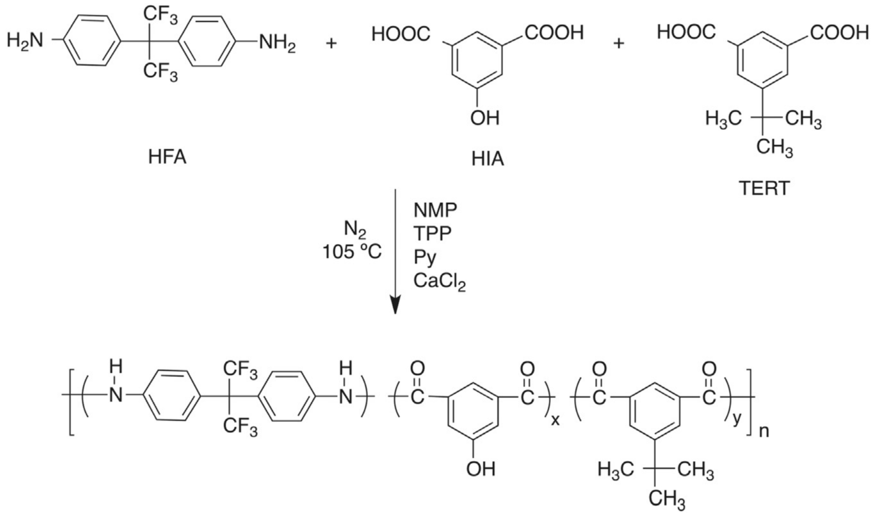
$$P = \frac{VR^{N}l}{ART\Delta p}\left(\frac{dp}{dt}\right)_{ss} \tag{3}$$

where *V* is the downstream volume (cm^3) of the cell, R^N volume of a gas mole at standard conditions (STP), *l* and *A* are the film thickness (cm) and the effective area of the film exposed to the gas (cm^2), respectively. *R* is the gas constant, *T* is the absolute temperature (°K), Δp is the pressure difference between upstream and downstream (cm Hg) where downstream pressure is considered low enough that the pressure difference across the membrane is essentially the value of the upstream pressure. $(\frac{dp}{dt})_{ss}$ is the steady state increase of pressure in the downstream (cm Hg/s). Gas permeability coefficients, *P*, are reported in Barrer [1 Barrer=1×10^{-10} (cm^3 (STP) cm cm^{-2} s^{-1} cm Hg^{-1})].

Apparent diffusion coefficients, *D*, are determined using the time lag method as described by Eq. (4), where *l* is the film thickness (cm), and θ is the time lag before reaching steady state permeation.

$$D = \frac{l^2}{6\theta} \tag{4}$$

The solubility coefficient, *S*, was determined as the ratio of *P* and *D* using the following equation:



Scheme 1. Synthesis of random copolyaramides **CPA 1** by direct polycondensation.

$$S=P/D \tag{5}$$

The ideal permselectivity, $\alpha_{A/B}$, of the film for a given pair of gases A and B is defined as the ratio of the individual gas permeability coefficients.

$$a=P_A/P_B \tag{6}$$

3. Results and discussion

3.1. Synthesis and characterization of PA and random copolyaramides CPA 1

The **PA** and the copolymers **CPA 1** were synthesized by direct polycondensation (see Scheme 1) with a yield over 97%, which indicates that it is possible to control the amount of –OH groups present by copolymerization and that the –OH groups do not give rise to side reactions in these polymerization conditions [32]. The latter is due to differences in reactivity as a nucleophile of the amino group (–NH_2) and the hydroxyl group (–OH). The chemical structure of the **PA** and **CPA 1** series were confirmed by FTIR.

FT-IR spectra show characteristic absorption peaks of the **PA** homopolymer and **CPA 1** copolyaramides. A carbonyl (C=O) absorption band at 1665 cm^{-1} and the absorption bands at 1175 and 1205 cm^{-1}, corresponding respectively to the symmetric and asymmetric stretching bands of the C–F bonds in the hexafluoroisopropylidene group. A broad absorption band between 3000 and 3600 cm^{-1} attributed to the O–H group, this band overlaps with the absorption of the N–H amide group. Meanwhile, the appearance of a new absorption band was observed at 2966 cm^{-1}, which is representative of the –C–$(CH_3)_3$ tert-butyl groups present in the copolyamides **CPA 1**, which does not appear in the spectrum of **PA**. Moreover, this band was more intense as the concentration of the TERT monomer increases in the copolymer (see FT-IR spectra in Supplementary material).

Inherent viscosities (η_{inh}) of **PA** and **CPA 1** copolyaramides obtained were in the range of 0.49–0.61 dL/g. The inherent viscosity decreased with increasing amounts of tert-butyl monomer. This decrease was attributed to a difference in conformation due to the steric effect produced by the bulky tert-butyl groups that decrease interchain interaction present in **PA** (see Table 1). The number average molecular weights (M_n) of the **PA** and **CPA 1** random copolyamides were in the range of 48,000–82,000 with polydispersity index (PDI) ranges from 1.79 to 2.18. Due to the fact that random copolymerization of two different diacids, TERT and HIA, could have some reactivity differences the molecular weight are in the expected range.

3.2. Synthesis and characterization of random copolyaramides CPA 2

One of the advantages from synthesizing polymers with functional reacting groups, such as –COOH or as in **PA** case –OH, is that they can be used for subsequent modifications. In this particular polyaramide, **PA**, the –OH groups are able to react under mild conditions to attach other functional groups [32].

It has been shown that the introduction of lateral substituents containing trifluoromethyl –CF_3 groups considerably improves some properties of polymers for a wide range of applications [33]. The introduction of CF_3 groups improves properties such as solubility, thermal stability, optical transparency and they are expected to present higher gas permeability and flame-resistance, while simultaneously decreasing the crystallinity, dielectric constant and water absorption in the polymer [34]. Thus, due to the proven advantages of –CF_3 substituted polymers, in this case, 3,5-bis(trifluoromethyl) benzoyl was selected as the substituent for **PA** chemical modification.

The chemical modification was carried out based on the Schotten-Baumann synthetic route [35], making acid chlorides react with the free –OH groups of the **PA** in the presence of triethylamine (see Scheme 2). This reaction is an efficient and irreversible method for the formation of esters. Usually, this reaction is quite rapid and exothermic, and proceeds well at low temperatures for small molecules. For comparison, we carried out the reaction at room temperature (25 °C) and at 60 °C. As will be shown later, NMR spectroscopy confirmed a different level of modification 32% and 71%, for reaction at 25 °C and 60 °C respectively. In principle, any organic reaction that has been applied for small molecules can be applied to modify chemically polymers. However, the reactivity of a functional group attached to a polymer chain may not be the same as when it is attached to a small molecule thus a 100% substitution was not achieved. Also, we observed that the solubility of the reaction mixture (**PA**, TEA, BTFBC in NMP) improved with increasing temperature. This enhanced solubility level of the reactants with temperature is favorable to increase the substitution of –OH groups attached to the polyamide, **PA**. In further experiments, a possible addition of a BTFBC molar excess in the reaction at 60 °C is expected to allow a higher substitution level.

The incorporation of 3,5-bis(trifluoromethyl) benzoyl into the chemical structure of the **PA** was confirmed by NMR and FTIR spectroscopy. In FTIR spectrum can be clearly seen that the broad absorption band in the 3200–3600 cm^{-1} range (O–H stretching) decreases as the percentage of chemical modification of **PA** increases, which indicates that the introduction of 3,5-bis(trifluoromethyl) ben-

Table 1
Yield, inherent viscosity and molecular weight of the **PA** and **CPA 1**.

Polyamide	HIA (%mmol)	TERT (%mmol)	η_{inh} (dL/g)	$M_n \times 10^{-3}$ (g mol^{-1})[a]	$M_w \times 10^{-3}$ (gmol^{-1})[a]	PDI[b]	Yield (%)
PA	100	0	0.61	51.3	91.8	1.79	97.0
CPA 1a	75	25	0.57	82.0	176.7	2.15	98.5
CPA 1b	50	50	0.55	54.0	117.8	2.18	98.3
CPA 1c	25	75	0.49	48.5	92.2	1.90	97.1

[a] Molecular weights; polystyrene calibration.
[b] Polydispersity Index.

zoyl was effectively taking place by esterification. Moreover, the appearance of the absorption band at 1752 cm^{-1} (ester C=O stretching) in **CPA 2a** and **CPA 2b** indicates the conversion of the hydroxyl groups into an ester moiety. Another important characteristic in the **CPA**'s **2a** and **2b** are the bands in the 1100–1300 cm^{-1} region, which are broadened (see Supplementary information). This behavior is attributed to the superposition of the C–O–C stretching and C–F stretching of the ester group and trifluoromethyl moieties, respectively.

The **PA** and modified polyaramides, **CPA 2a** and **2b** were characterized by ^{1}H NMR. **PA** exhibited peaks around of 8.05, 7.98, 7.61 and 7.4 ppm corresponding to aromatic protons; the signals at 10.66 and 10.30 ppm are assigned to the amide protons (C(=O)–NH–) and OH protons, respectively. The ^{1}H NMR spectrum of the modified polymers shows the presence of new peaks in the aromatics region around of 8.75, 8.61 and 8.25 ppm, corresponding to protons of the 3,5-bis(trifluoromethyl) benzoyl (H: 6 y 7) and to protons of hydroxyl isophthalic acid (H: 5) which was modified (see Fig. 2). It also shows the presence of a signal at 10.80 ppm due to the amide protons (H: c) that are influenced by their proximity to the pendant group. The level of modification was estimated by comparing the area of peaks **a** (10.80 ppm) and **b** (10.63 ppm) or the area of peaks **6** (8.75 ppm) and **4** (7.58 ppm) (see NMR spectra with the peak integrals in Supplementary information). The polyaramide modified at room temperature, **CPA 2a**, reached a level of reaction where 32% –OH groups were modified, while the esterification reaction carried out at 60 °C rose to 71% –OH groups modified (**CPA 2b**).

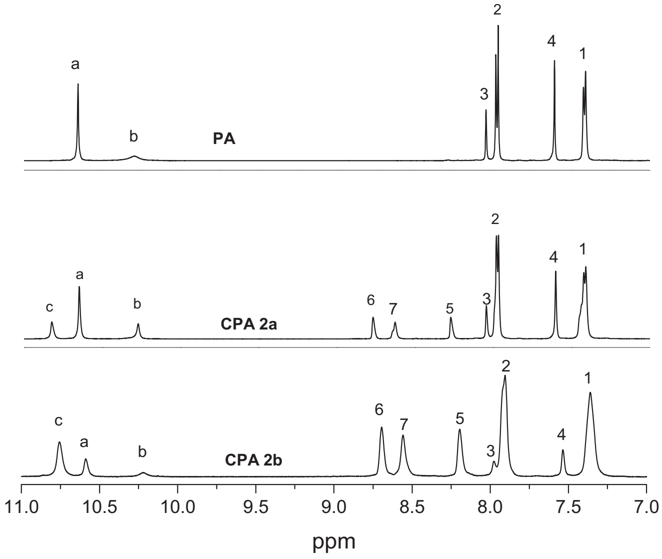
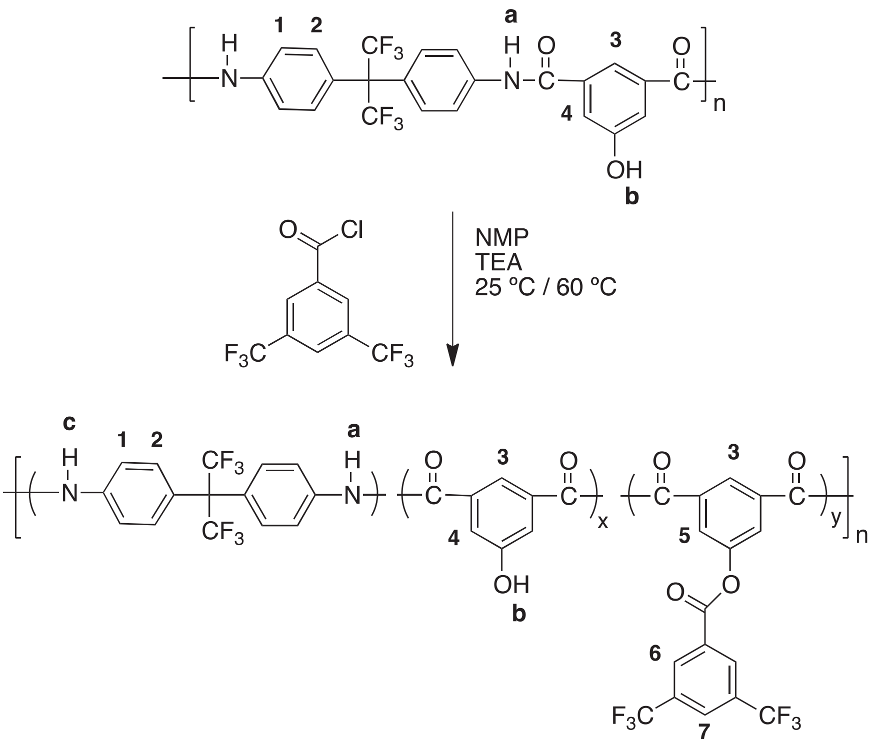


Fig. 2. ^{1}H-RMN spectra of **PA** and modified polyaramide **CPA 2**.

The incorporation of the fluorinated pendant groups and the degree of modification of **CPA 2b** were confirmed by ^{19}F NMR. The ^{19}F NMR spectrum for the **PA** (Fig. 3b) presents a single signal at −63.3 ppm corresponding to the fluorine atoms of the two (–CF$_3$) groups on the



Scheme 2. Synthesis of random copolyaramides **CPA 2a** and **CPA 2b** by chemical modification of **PA** at 25 °C and 60 °C.

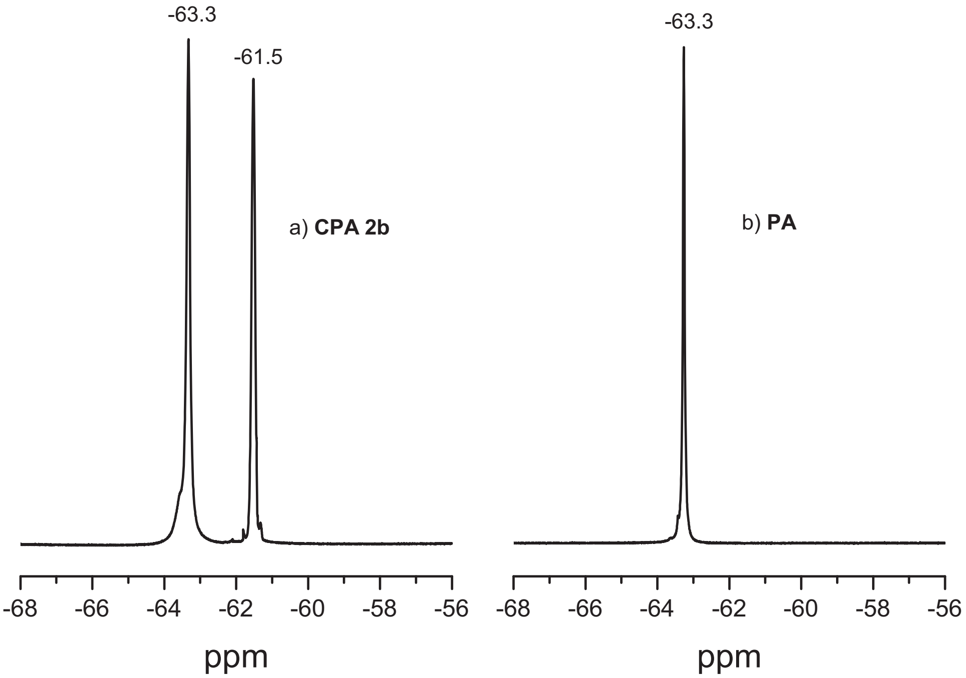


Fig. 3. ^{19}F NMR spectrum of (a) **CPA 2b** and (b) **PA** in DMSO-d_6.

HFA. In the **CPA 2b** copolymer (Fig. 3a), two signals were observed at −63.3 and −61.5 ppm, the latter is due to the fluorine atoms in the 3,5-bis(trifluoromethyl) benzoyl pendant group. The areas of the two signals were integrated and they match the modification level estimated by ^{1}H NMR.

3.3. Solubility

All polyaramides were readily soluble in different organic solvents such as NMP, DMF, DMSO and DMAc. However, the solubility of the polymers in THF decreases as the number of –OH groups in the polymer chain decreases. For example, the **CPA 2b** and **CPA 1c** were partially soluble and the previously reported HFA/TERT polymer was insoluble [11]. Thus, the solubility results confirmed that crosslinking reactions did not occur, a possibility that could be expected due to the presence of –OH group in the polyaramides main chain. On the other hand, none of the aramides were soluble in chlorinated solvents.

3.4. Thermal and mechanical properties

Thermal characterization of polymer films by TGA revealed a higher thermal stability up to 400 °C. **PA** and **CPA 1** showed a single decomposition temperature (T_d) with a 10% loss between 488 and 496 °C. According to Fig. 4, a slight increase in thermal stability was observed as the concentration of the tert-butyl monomer increased up to 496 °C, while **PA**, without the presence of tert-butyl groups, has an onset at 488 °C (with 10% weight loss).

On the other hand, **CPA 2** showed an additional decomposition stage (see Fig. 4). The first stage is detected at 415 °C with a weight loss at around 10% for **CPA 2a** and 15% for **CPA 2b**, which is attributed to degradation of the units containing ester groups, and points out to the loss of pendant groups [24]. This result indicates that the presence of ester groups slightly reduces the thermal stability respect to **PA**. The second decomposition stage occurs around 490 °C with a weight loss around 30% for **CPA 2a** and 40% for **CPA 2b**, and can be attributed to the generalized polymer backbone degradation. The weight losses of **CPA 2a** due to degradation of the ester units at 350–460 °C are lower than that of **CPA 2b**. This result agrees with the fact that **CPA 2a** has lower amounts of ester groups than **CPA 2b**.

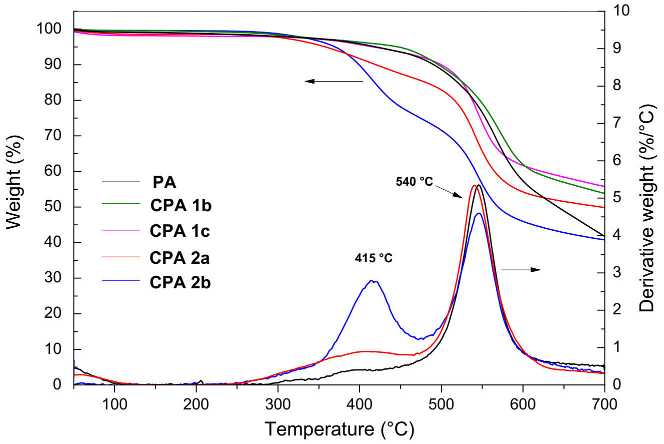


Fig. 4. TGA thermograms of **PA** and modified polyaramides **CPA1** and **CPA 2**.

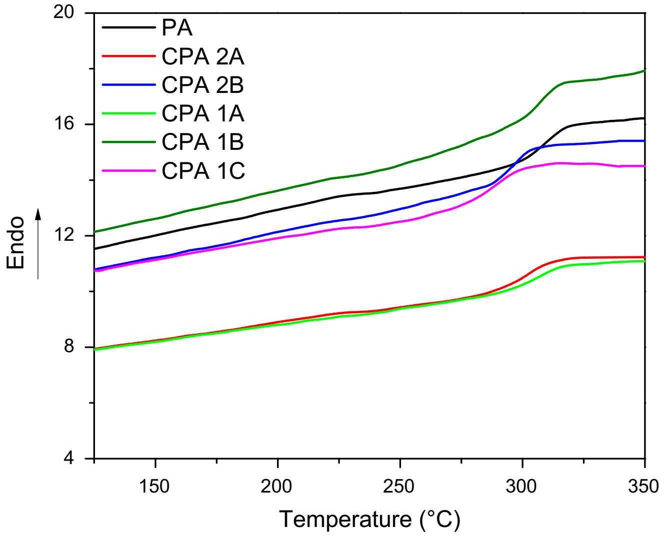


Fig. 5. DSC curves of **PA** and modified polyaramides **CPA1** and **CPA 2**.

Table 2
Molecular weight, thermal and mechanical properties of the polyaramides and their comparison with some polymers.

Polymer	M_n×10^{-3} (g mol^{-1})[a]	$T_{10\%}$ (°C)	T_g (°C)	TS (MPa)	Elongation break (%)	Modulus (GPa)
PA[b]	51.3	488	309	63.89 ± 4.4	12.32 ± 2.25	1.21 ± 0.11
CPA 1a[b]	82.0	489	308	74.58 ± 6.02	8.76 ± 1.35	1.43 ± 0.11
CPA 1b[b]	54.0	493	307	67.50 ± 3.99	9.35 ± 0.87	1.48 ± 0.17
CPA 1c[b]	48.5	496	289	59.46 ± 11.99	6.95 ± 1.53	1.16 ± 0.08
CPA 2a[b]	57.4	415	303	57.27 ± 4.63	9.97 ± 0.01	1.39 ± 0.04
CPA 2b[b]	54.9	398	297	45.19 ± 5.79	4.81 ± 0.89	1.49 ± 0.05
HFA/TERT[b] [11]	–	494	306	31.35 ± 0.1	3.05 ± 0.3	1.24 ± 0.02
PA 9B [36][c]	50.0	438	235	81 ± 2.00	7 ± 2.00	1.8 ± 0.01
6FDA-SADAF [37][d]	56.8	480	370	80	10	1.8
APA 5 [38][d]	–	–	268	88	–	2.23

[a] Number average molecular weight; polystyrene calibration.
[b] Mechanical properties evaluated at a crosshead speed of 1 mm/min.
[c] Mechanical properties evaluated at a crosshead speed of 1.25 mm/min.
[d] Mechanical properties evaluated at an crosshead speed of 5 mm/min.

The glass transition temperatures (T_g) of **PA**, **CPA 1** and **CPA 2** were in the range of 289–309 °C (Fig. 5 and Table 2). A decrease in T_g was observed as the concentration of the tert-butyl or 3,5-bis(trifluoromethyl) benzoyl groups increased. The high T_g values of **PA**, **CPA 1a**, **CPA 1b** and **CPA 2a** were attributed to a combination of interchain interactions and the presence of bulky pendant groups, which hinders molecular motions. On the other hand, when the substitution is above 50 mol% of OH groups in the copolymers the T_g decreases an indication that bulky groups had diminished the interchain interactions.

Under uniaxial tension test, **PA** and **CPA 1** and **CPA 2** membranes exhibited tensile strength (TS) in the range 45.19–74.58 MPa, and elastic modulus above 1.0 GPa with elongation at break that ranges between 4% and 12%. A reduction of elongation at break and tensile strength were observed in random copolyamides **CPA 1** and **CPA 2** with the introduction of tert-butyl group or 3,5-bis(trifluoromethyl) benzoyl groups. A tendency of improving mechanical properties with increasing molecular weight was found. In general, the combination of thermal and mechanical properties exhibited by these polyaramides fit well the requirements to meet the demands of separation processes and they are comparable with some polymers reported recently [11,36–38]. Table 2 summarizes the thermal decomposition and mechanical properties of **PA**, **CPA 1** and **CPA 2** and their comparison with some polyamides and polyimides reported in the literature [11,36–38].

3.5. X-ray diffraction, density and FFV

X-ray diffraction patterns showed a behavior typical of amorphous polymers for **PA** and copolyamides **CPA 1** and **CPA2**. The values (*d*-spacing) of the maxima are taken as the average intersegmental distance between polymer chains and were calculated using Bragg's equation ($n\lambda$=2dsin θ). Fig. 6 shows the X-ray diffraction patterns of **CPA 1c** and **CPA 2b** which presented some differences as compared with the **PA** homopolymer.

The presence of tert-butyl and 3,5-bis(trifluoromethyl) benzoyl bulky pendant groups has effects on chain packing. **CPA 2b** copolyamide shows 3 maximum in the amorphous halo corresponding to 3.75 Å (2θ=23.6), 4.84 Å (2θ=18.3) and 6.67 Å (2θ=13.8). **CPA 1c** shows 3 maximum in the amorphous halo corresponding to 3.94 Å (2θ=22.5), 5.45 Å (2θ=17) and small shoulder at 6.67 Å (2θ=13.8). **PA** shows only 2 maximum in the amorphous halo with *d*-spacing at 3.75 Å (2θ=23.6) and 5.31 Å (2θ=16.6). In general, the appearance of several intersegmental distances is associated with a certain degree of irregularity in the packing of polymer chains [24]. In here the emergence of a third maxima at *d*-spacing 6.67 Å for **CPA 2b** and for **CPA 1c** that is not present in **PA** is assigned to the presence of the 3,5-bis(trifluoromethyl) benzoyl and tert-butyl groups respectively which restrict the mobility of the polymer chains and increase the interchain distance.

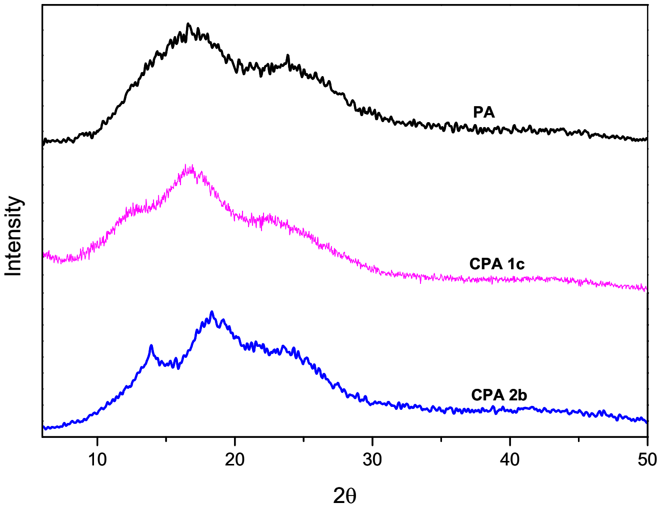


Fig. 6. XRD patterns of **PA**, **CPA 1c** and **CPA 2b**.

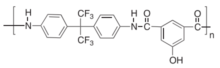
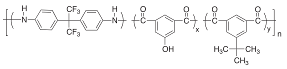
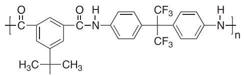
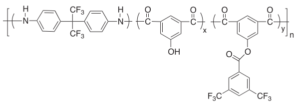
Table 3 shows the data from the experimentally measured density and those from calculated fractional free volume (FFV) of the **PA**, **CPA 1** and **CPA 2**. These results support the fact of an interchain distance increase in the tert-butyl and bis(trifluoromethyl) benzoyl copolymers since there is a larger FFV than in **PA**. It is also seen that as the concentration of either group increases in **CPA 1** or **CPA 2** the FFV also increases.

3.6. Gas transport properties of PA and CPA films

It is known that the incorporation of strong polar groups in polymer structures reduces permeability [19]. Based on XRD and *FFV* results, it is expected that the copolyamides **CPA 1** and **CPA 2** will present higher permeability coefficients than **PA**. Therefore, experimental permeability coefficient (*P*) for pure gases CO_2, O_2, N_2 and CH_4 were performed at 2.02 bar and 35 °C for **PA** and the copolyaramide series **CPA 1** and **CPA 2**. The results are summarized in Table 3.

In all polyaramide films the gas permeability coefficients showed the following behavior $PCO_2 > PO_2 > PN_2 \sim PCH_4$, this sequence is related to the order of kinetic diameters of the tested gases (CO_2, 3.30 Å; O_2, 3.46 Å; N_2, 3.64 Å; CH_4, 3.80 Å) [39]. This trend is commonly observed in most glassy polymer films [40–42]. The incorporation of tert-butyl and 3,5-bis(trifluoromethyl) benzoyl in the **PA** structure not only renders copolyaramide films more permeable but also shows increase in $\mathbf{CO_2/CH_4}$ selectivity up to four times as compared to **PA** for **CPA 2b**. Gas permeability coefficient increased

Table 3
Density, fractional free volume, gas permeability coefficient (*P*), and permselectivities (α) of **PA**, **CPA 1** and **CPA 2** films.

Membrane		**ρ (g/cm^3)**	**FFV**	[a]**Permeability, *P* (Barrer)**				**Selectivity, α**	
				CO_2	**O_2**	**N_2**	**CH_4**	**CO_2/CH_4**	**CO_2/N_2**
	PA	1.456	0.131	2.82	0.66	0.30	0.50	5.64	9.40
	CPA 1b	1.376	0.143	11.85	1.53	0.63	0.96	12.34	18.80
 HFA-TERT	CPA 1c	1.335	0.151	23.69	3.77	0.97	1.10	21.34	24.42
	HFA-TERT[b]	1.305	0.156	26.08	5.8	1.1	0.86	31.18	23.12
	CPA 2a	1.442	0.160	11.9	2.50	0.69	0.55	21.63	17.25
	CPA 2b	1.451	0.174	**60.17**	**12.54**	**3.28**	**2.67**	**22.53**	**18.64**

[a] Permeability coefficient evaluated at 2.02 bar and 35 °C; Barrer: 1×10^{-10} cm^3 (STP) cm/cm^2 s cm Hg.
[b] From Ref. [11].

with decreasing -OH groups presence in the random copolyaramides backbone, indicating that the suppression of hydrogen bonding in PA is promoted by the replacement of the –OH groups with the tert-butyl or 3,5-bis(trifluoromethyl) benzoyl groups. These results agree with calculated FFV and increase in X-ray diffraction *d*-spacing. In particular, the polymer **CPA 2b** shows an order of magnitude increase in gas permeability coefficients and almost two times selectivity increase for **CO_2/CH_4** pair as compared to **PA**, which is ascribed to the presence of 3,5-bis(trifluoromethyl) benzoyl moiety in the backbone which presents the largest fractional free volume (FFV) of all copolyaramides studied.

Moreover, it was observed that ideal selectivity (CO_2/CH_4 and CO_2/N_2) in the modified films (**CPA 2**) would not follow the expected trade-off of diminishing selectivity with increasing permeability coefficients since both permeability coefficients and ideal selectivity increase with the -OH substitution. This result can be explained analyzing the solution diffusion model for gas transport through polymer films ($P=D\cdot S$), permeability coefficients are the result of the product of a diffusion, *D*, and solubility, *S*, coefficients.

Table 4 lists the diffusion and solubility coefficients of **PA**, **CPA 1** and **CPA 2**. The introduction of tert-butyl or 3,5-bis(trifluoromethyl) benzoyl shows improving diffusion coefficient, *D*, for all gases. This improvement in *D* is attributed to an increase in fractional free volume, in particular for **CPA 2b** copolymer that is larger than the one of **CPA 1 b,c** tert-butyl copolymers. Furthermore, the introduction of 3,5-bis(trifluoromethyl) benzoyl resulted in a CO_2 increase in solubility coefficient, *S*, while *S* decreases or remains constant for the other gases. Since for CO_2 both *D* and *S* increase, the overall result is that CO_2 permeability coefficient, *P*, improves more than the ones observed for CH_4 and O_2 which show a decrease in solubility coefficient. In general, the introduction of tert-butyl or 3,5-bis(trifluoromethyl) benzoyl groups, inhibits close chain packing and helps mitigate the selectivity loss associated with the increasing *FFV* for CO_2/CH_4 and CO_2/N_2 gas pairs [42].

Table 4
Diffusion (*D*) and solubility (*S*) coefficients for **PA**, **CPA 1** and **CPA 2** evaluated at 2.02 bar and 35 °C.

Membrane	**CO_2**		**O_2**		**N_2**		**CH_4**	
	D[a]	***S***[b]	***D***[a]	***S***[b]	***D***[a]	***S***[b]	***D***[a]	***S***[b]
PA	0.35	8.05	0.79	0.70	0.03	9.23	0.04	12.5
CPA 1b	2.50	4.74	2.72	0.55	0.05	12.82	0.12	8.01
CPA 1c	2.95	8.03	5.21	0.73	0.23	4.34	0.41	2.70
CPA 2a	1.28	9.35	13.00	0.19	0.23	3.05	0.12	3.88
CPA 2b	7.95	7.57	71.85	0.17	1.84	1.78	1.01	2.62

[a] Diffusion coefficients (D×10^{-8}) cm^2 s^{-1}.
[b] Solubility coefficients (S×10^{-2}) cm^3 (STP) cm^3 cm Hg.

3.7. Comparison with some aromatic polymers previously reported

The performance of the modified copolymers **CPA 1** and **CPA 2** as compared to **PA** and some commercial polymers (Matrimid, Trogamid and cellulose acetate) [38,43,44] and some polyaramides and polyimides bearing large pendant moieties reported in the literature is shown in Supplementary information (Table 1S) [11,36, 37, 45–48]. The correlation between CO_2 permeability and selectivity for CO_2/CH_4 gas pair and CO_2/N_2 pair in terms of a Robeson plot for polyamides and polyimides is shown in Figs. 7 and 8.

In Robeson plots, Figs. 7 and 8, Trogamid shows CO_2 permeability at least one order of magnitude lower than the polyamides **PA** and **CPA's** and it is the lowest of these polymers. Trogamid is a partially aliphatic polyaramide with a bulky tert-butyl pendant group that can be seen as a good comparison base since it follows the usual trade off of higher selectivity with lower permeability. If we compare Trogamid with the 6 FDA polyamides **PA**, **CPA 1**, **CPA 2**, HFA-TERT, DAIA-6F, PA-9B and 3 h, they clearly show higher permeability in all cases but selectivity for PA is lower due to higher packing as discussed above. The introduction of bulky pendant groups to the main chain, this is particularly true for bulky adamantyl (PA-9B) and **CPA 2b** with 3,5-bis(trifluoromethyl) benzoyl polyamides increase both P and α one order of magnitude compared to **PA** values for CO_2/CH_4 separation. In comparison with some previously reported polymer, it can be observed that **CPA 2b** film show one of the highest CO_2 permeability coeffi-

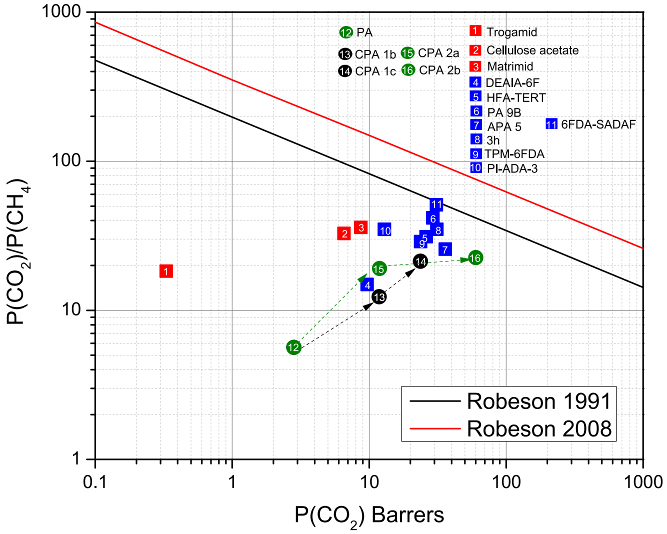


Fig. 7. Robeson plot for a comparison of CO_2/CH_4 selectivity vs. CO_2 permeability of the **PA**, **CPA 1** and **CPA 2** with some other polymers [11,36–38, 43–48].

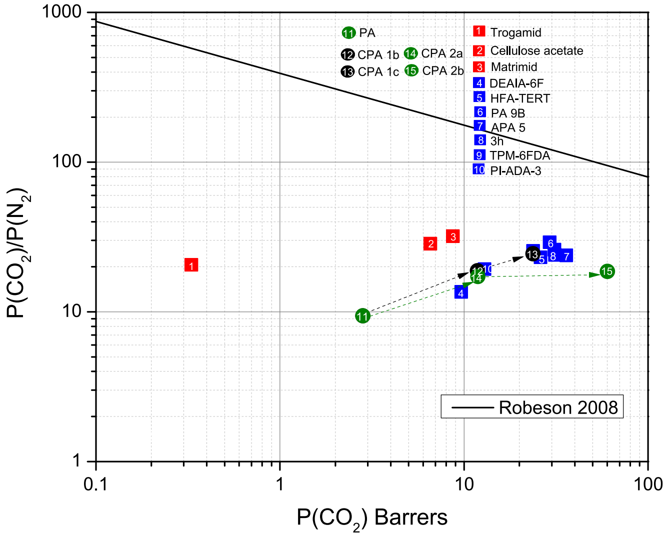


Fig. 8. Robeson plot for a comparison of CO_2/N_2 selectivity vs. CO_2 permeability of the **PA**, **CPA 1** and **CPA 2** with some other polymers [11,36–38, 43–48].

cients. Furthermore, the increase in CO_2 permeability is accompanied by an increase in CO_2/CH_4 selectivity. A further review shows that 6 F polyimides TPM-6FDA, PI-ADA-3 and 6FDA-SADAF with bulky pendant groups to the main chain have the same tendency of increasing CO_2 permeability coefficient and improving or very similar selectivity for CO_2/CH_4 and CO_2/N_2 pairs depending on the pendant group substitution. In this case Matrimid shows a CO_2 permeability around 9 Barrer and selectivity of 36 and 32 for CO_2/CH_4 and CO_2/N_2, the bulky pendant group substituted 6F polyimides show increased CO_2 permeability with very similar or higher selectivity. Overall pendant bulky groups substitution in this high rigidity polyamides and polyimides (modulus above 1 GPa) shows both and increase in P and α with a strong tendency to move to the right quadrant of the permeability-selectivity trade off curve. The inclusion of these bulky groups does not reach yet the upper limit of the trade off curve but the tendency indicates that these bulky substituents such as those on **CPA 1** and **CPA 2** are advantageous modifications that with further improvement could became high performance high selectivity membranes.

4. Conclusions

A novel poly(hexafluoroisopropylidene hydroxyisophthalamide) (**PA**) with −OH groups in the backbone and two different random copolymers with tert-butyl and 3,5-bis(trifluoromethyl) benzoyl by substitution of PA −OH groups were synthesized. To the best of our knowledge, the syntheses of **PA** and their subsequent reaction with the 3,5-bis(trifluoromethyl) benzoyl chloride have not been previously reported. The reaction between the −OH and acid chlorides is a promising and versatile synthetic route for anchoring different groups to a polyaramide backbone, under mild conditions and it can be temperature controlled. This procedure is simpler than a direct copolymerization reaction as shown here by a tert-butyl bearing monomer and offers the same or better advantages in the copolymer final properties. All the synthesized polyaramides and copolyaramides are readily soluble in organic solvents and present high thermal stability up to 400 °C. The substitution at random of the -OH groups in **PA** for tert-butyl and 3,5-bis(trifluoromethyl) benzoyl groups was very effective for increasing polymer interchain distance and improving gas permeability (*P*) for all tested gases. It also increases gas selectivity for CO_2/CH_4 and CO_2/N_2. In particular, the copolyaramide **CPA 2b** shows a sharp enhancement in gas permeability with respect to **PA**. This result is attributed to the fact that the incorporation of 3, 5-bis(trifluoromethyl) benzoyl groups increases the FFV and interchain *d*-spacing.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.memsci.2016.09.035.

References

[1] L. Soon-Chien, F.J. Vankelecom, Impact of preparation method on physical properties and gas separation performance of fluorinated copolymer membranes, React. Funct. Polym. 86 (2015) 117–124.

[2] J.K. Adewole, A.L. Ahmad, S. Ismail, C.P. Leo, Current challenges in membrane separation of CO_2 from gas natural: a review, Int. J. Greenh. Gas Control 17 (2013) 46–65.

[3] J.J. Ferreiro, J.G. de la Campa, A.E. Lozano, J. de Abajo, J. Preston, Effect of pendant oxyethylene moieties on the properties of aromatic polyisophthalamides, J. Polym. Sci. Part A: Polym. Chem. 45 (2007) 4671–4683.

[4] J.M. Garcia, F.C. Garcia, F. Serna, J.L. de la Peña, High-performance aromatic polyamides, Prog. Polym. Sci. 35 (2010) 623–686.

[5] B.J.M. Flaconnèche, M.H. Klopffer, Permeability, diffusion and solubility of gases in polyethylene, polyamide 11 and poly(vinylidene fluoride), Oil Gas Sci. Technol. 56 (2001) 261–278.

[6] A. Gómez-Valdemoro, N. San-José, F. Clemente-Garcia, J.L. de la Peña, F. Serna, J.M. Garcia, Novel aromatic polyamides with main chain and pendant 1,2,4-triazole moieties and their application to the extraction/elimination of mercury cations from aqueous media, Polym. Chem. 1 (2010) 1291–1301.

[7] Y. Imai, N. Hamaoka, M. Kakimoto, Preparation and properties of N-phenylated aromatic polyamides from N, N′-diphenyl-p-phenylenediamine and aromatic diacid chlorides, J. Polym. Sci. Part A: Polym. Chem. 22 (1984) 1291–1297.

[8] M. Takayanagi, T. Katayose, N-substituted poly(p-phenylene terephthalamide, J. Polym. Sci. Part A: Polym. Chem. 19 (1981) 1133–1145.

[9] P. Carretero, S. Molina, R. Sandín, J. Rodríguez-Hernández, A.E. Lozano, J. de Abajo, Hydrophilic polyisophthalamides containing poly(ethylene oxide) side chains: synthesis, characterization, and physical properties, J. Polym. Sci. Part A: Polym. Chem. 51 (2013) 963–976.

[10] M.I. Loría-Bastarrachea, M. Aguilar-Vega, Synthesis and gas transport properties of rigid block copolyaramides, J. Membr. Sci. 329 (2011) 40–48.

[11] C. Carrera-Figueiras, M. Aguilar-Vega, Gas permeability and selectivity of hexafluoroisopropylidene aromatic isophthalic copolyamides, J. Polym. Sci. Part B: Polym. Phys. 43 (2005) 2625–2638.
[12] W. Chun-Shan, Y. Rong-Wen, Novel perfluorononenyloxy group containing aromatic polyamides, Polym 38 (1997) 6109–6114.
[13] H. Sheng-Huei, C. Chien-Wei, L. Guey-sheng, Novel aromatic polyamides bearing pendent diphenylamino or carbazolyl groups, J. Polym. Sci. Part A: Polym. Chem. 42 (2004) 3302–3313.
[14] R.P. Pal, P.S. Patil, M.M. Salunkhe, N.N. Maldar, P.P. Wadgaonkar, Synthesis, characterization and constitutional isomerism study of new aromatic polyamides containing pendant groups based on asymmetrically substituted meta-phenylene diamines, Eur. Polym. J. 45 (2009) 953–959.
[15] Y. Ohta, Y. Kamijio, S. Fujii, A. Yokoyama, T. Yokozawa, Synthesis and properties of a variety of well-defined hyperbranched N-alkyl and N-H polyamides by chain-growth condensation polymerization of AB_2 monomers, Macromolecules 44 (2011) 5112–5122.
[16] H. Behniafar, F. Zardoozi, A. Rastkar, Fluoro-containing poly(amide-imide)s with sterically hindered pendants: synthesis and characterization, J. Fluor. Chem. 138 (2012) 34–41.
[17] K.J. Kim, S.H. Park, W.W. So, D.J. Ahn, S.J. Moon, CO_2 separation performances of composite membranes of 6FDA-based polyimides with a polar group, J. Membr. Sci. 211 (2003) 41–49.
[18] D. Likhatchev, C. Gutierrez-Wing, I. Kardash, R. Vera-Graziano, Soluble aromatic polyimides based on 2,2-bis(3-amino-4-hydroxyphenyl)hexafluoropropane: synthesis and properties, J. Appl. Polym. Sci. 59 (1996) 725–735.
[19] C. Staud-Bickel, W.J. Koros, Improvement of CO_2/CH_4 separation characteristics of polyimides by chemical crosslinking, J. Membr. Sci. 155 (1999) 145–154.
[20] C. Jung-Ho, Y.M. Lee, Gas permeation properties of hydroxyl-group containing polyimide membranes, Macromol. Res. 16 (2008) 555–560.
[21] H.B. Park, C.H. Jung, Y.M. Lee, A.J. Hill, S.J. Pas, S.T. Mudie, E.V. Wagner, B.D. Freeman, D.J. Cookson, Polymers with cavities tuned for fast selective transport of small molecules and ions, Science 318 (2007) 254–258.
[22] M. Calle, Y.M. Lee, Thermally rearranged (TR) poly(ether-benzoxazole) membranes for gas separation, Macromolecules 44 (2011) 1156–1165.
[23] C.A. Scholes, C.P. Ribeiro, S.E. Kentish, B.D. Freeman, Thermal rearranged poly(benzoxazole-co-imide) membranes for CO_2 separation, J. Membr. Sci. 450 (2014) 71–80.
[24] E.M. Maya, A.E. Lozano, J. de Abajo, J.G. de la Campa, Chemical modification of copolyimides with bulky pendent groups: effect of modification on solubility and thermal stability, Polym. Degrad. Stab. 92 (2007) 2294–2299.
[25] S. Feng, Y. Shang, Y. Wang, G. Liu, X. Xie, W. Dong, J. Xu, K.K. Mathur, Synthesis and crosslinking of hydroxyl-functionalized sulfonated poly(ether ether ketone) copolymer as candidates for proton exchange membranes, J. Membr. Sci. 352 (2010) 14–21.
[26] T. Nishikubo, A. Kameyama, A. Suzuki, A novel synthesis of polyesters with pendant hydroxyl groups by polyaddition of bis(oxetane) with dicarboxylic acids catalyzed by quaternary onium salts, React. Funct. Polym. 37 (1998) 19–25.
[27] Y. Hu, T. Sakaguchi, M. Shiotsuki, F. Sanda, T. Masuda, Synthesis and gas permeation properties of poly(diphenylacetylenes) having bulky alkyl/silyl and hydroxyl groups, J. Membr. Sci. 282 (2006) 423–429.
[28] P. Carretero, R. Sandín, S. Molina, J.G. Martínez, J.G. de la Campa, A.E. Lozano, J. de Abajo, Linear polyisophthalamides from the trifunctional monomer 5-hydroxyisophthalic acid. A convenient approach towards functionalized aromatic polymers, Eur. Polym. J. 47 (2011) 1054–1064.
[29] S. Molina, P. Carretero, S.B. Teli, J.G. de la Campa, A.E. Lozano, J. de Abajo, Hydrophilic porous asymmetric ultrafiltration membranes of aramid-g-PEO copolymers, J. Membr. Sci. 454 (2014) 233–242.
[30] N. Yamazaki, M. Matsumoto, F. Higashi, 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. Part A: Polym. Chem. 13 (1975) 1373–1380.
[31] D.W. Van Klevelen, K.T. Nijenhuis, In Properties of Polymers, Elsevier, Amsterdam, 1976.
[32] M.A. Gauthier, M.I. Gibson, H.A. Klok, Synthesis of functional polymers by post-polymerization modification, Angew. Chem. Int. Ed. 48 (2009) 48–58.
[33] M.G. Dhara, S. Banerjee, Fluorinated high-performance polymers: poly(arylene ether)s and aromatic polyimides containing trifluoromethyl groups, Prog. Polym. Sci. 35 (2010) 1022–1077.
[34] H. Behniafar, F. Zardoozi, A. Rastkar, Fluoro-containing poly(amide-imide)s with sterically hindered pendants: synthesis and characterization, J. Fluor. Chem. 138 (2012) 34–41.
[35] R.N. Boyd, R.T. Morrison, In Organic Chemistry, 6th ed., Prentice Hall, Englewood Cliffs, N.J., 1992.
[36] D. Bera, P. Bandyopadhyay, S. Ghosh, S. Banerjee, Gas transport properties of aromatic polyamides containing adamantyl moiety, J. Membr. Sci. 453 (2014) 175–191.
[37] D. Plaza-Lozano, B. Comesaña-Gándara, M. de la Viuda, J.G. Seong, L. Palacio, P. Prádanos, J.G. de la Campa, P. Cuadrado, Y.M. Lee, A. Hernández, C. Alvarez, A.E. Lozano, New aromatic polyamides and polyimides having an adamantane bulky group, Mater. Today Commun. 5 (2015) 23–31.
[38] J. Espeso, A.E. Lozano, J.G. de la Campa, J. de Abajo, Effect of substituents on the permeation properties of polyamide membranes, J. Membr. Sci. 280 (2006) 659–665.
[39] L.M. Robeson, Correlation of separation factor versus permeability for polymeric membranes, J. Membr. Sci. 62 (1991) 165–185.
[40] D. Bera, P. Bandyopadhyay, S. Gosh, S. Banerjee, V. Padmanabhan, Highly gas permeable aromatic polyamides containing adamantine substituted triphenylamine, J. Membr. Sci. J. Membr. Sci. 474 (2015) 20–31.
[41] H. Tong, C. Hu, S. Yang, Y. Ma, H. Guo, L. Fan, Preparation of fluorinated polyamides with bulky structure and their gas separation performance correlated with microstructure, Polymer 69 (2015) 138–147.
[42] M.L. Jue, R.P. Lively, Targeted gas separation through polymer membrane functionalization, React. Funct. Polym. 86 (2015) 88–110.
[43] M.D. Guiver, G.P. Robertson, Y. Dai, F. Bilodeau, Y.S. Kang, K.J. Lee, J.Y. Jho, J. Wong, Structural characterization and gas-transport properties of brominated matrimid polyamide, J. Polym. Sci. Part A: Polym. Chem. 40 (2002) 4193–4204.
[44] A.C. Puleo, D.R. Paul, The effect of degree of acetylation on gas sorption and transport behavior in cellulose acetate, J. Membr. Sci. 47 (1989) 301–332.
[45] J.L. Santiago-García, J.M. Pérez-Francisco, M.I. Loría-Bastarrachea, M. Aguilar-Vega, Synthesis and characterization of novel polyamides containing dibenzobarrelene pendant groups, Des. Monomer Polym. 18 (2015) 350–359.
[46] Y. Ding, B. Bikson, Soluble aromatic polyamides containing the phenylindane group and their gas transport characteristics, Polymer 43 (2002) 4709–4714.
[47] C. Aguilar-Lugo, J.L. Santiago-García, M.I. Loría-Bastarrachea, D. Guzmán-Lucero, L. Alexandrova, M. Aguilar-Vega, Synthesis, characterization, and structure-property relationships of aromatic polyimides containing 4, 4′-diaminotriphenylmethane, J. Polym. Res. 23 (49) (2016) 1–8.
[48] E.M. Maya, I. García-Yoldi, A.E. Lozano, J.G. de la Campa, J. de Abajo, Macromolecules 44 (2011) 2780–2790.