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Synthesis and characterization of poly(amide-imide)s derived from a new *ortho*-functional unsymmetrical dicarboxylic acid†

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A new diacid monomer containing an imide ring and a methoxy pendant group, 3-trimellitimido-4-methoxybenzoic acid **TMBA**, was synthesized and characterized. The diacid was used to synthesize six novel poly(amide-imide)s, (**PAI**s), through a polycondensation reaction with different diamines in the presence of triphenylphosphite, calcium chloride, and pyridine in *N*-methyl-2-pyrrolidinone. The chemical structures of the diacid monomer and poly(amide-imide)s were confirmed by FTIR and ^{1}H NMR spectroscopy. All **PAI**s were obtained in high yield with inherent viscosities ranging from 0.32 to 0.54 dL g^{-1}. They were soluble in aprotic solvents, and exhibited film forming ability. The **PAI** films displayed glass transition temperatures between 281 and 377 °C, as determined by dynamic mechanical analysis, and they show high thermal stability. Gas permeability results for **TMBA-6FDA** film show that this **PAI** could be an interesting material for polymeric membranes aimed to CO$_2$ separation process.

1. Introduction

Poly(amide-imide)s (**PAI**)s combine the superior mechanical properties associated with the amine group, and the high thermal stability of the imide ring allowing a combination intended to attain high-performance polymers.[1] These properties make them appropriate for different applications as substitutes for some high performance polyamides and polyimides. Generally, the synthesis of **PAI**s is carried out through two main routes: (a) polycondensation through amide-bond formation utilizing monomers containing a preformed imide-bond; and (b) polycondensation through imide-bond formation utilizing monomers containing a preformed amide-bond.[2] Based on these two approaches, the **PAI**s have been prepared using trimellitic anhydride (**TMA**), as a strategy to synthesize symmetric monomers with either preformed amide- or imide-bond.[3–7]

The synthesis of novel **PAI**s with specific functionalities in the backbone may provide a way of controlling certain physical properties or special functions. Feng *et al.*[8] have reported the preparation of biodegradable **PAI**s based on diacid monomers

containing amino acids. On the other hand, Rafiee[7] synthesized a triptycene-containing dicarboxylic acid monomer, which was polymerized to obtain organosoluble **PAI**s with high performance properties. Sarkar *et al.*,[9] reported the synthesis of **PAI**s based on aromatic diamine monomers with preformed amine bonds and pendent *n*-alkyloxy side chains, these **PAI**s exhibited good properties to align liquid crystals (LC). Typically, **PAI**s are synthesized from symmetrical monomers.[10,11] However, the incorporation of unsymmetrical monomers into the polymer backbone decreases packing density and crystallinity which allows obtaining soluble high performance polymers.[12] Moreover, the incorporation of chemical functionalities into the **PAI**s backbone could lead to preparation of thermally rearranged polymers that may find use in polymer membrane technology.[13–15]

This study reports the synthesis and characterization of a new *ortho*-functional unsymmetrical dicarboxylic acid containing an imide ring and a methoxy pendant group, 3-trimellitimido-4-methoxybenzoic acid. This low cost monomer is easy to obtain from a condensation reaction between trimellitic anhydride and a non-conventional aminoacid. Furthermore, to the best of our knowledge, there are not reports in the literature of its synthesis and application for polymer preparation. Additionally, the synthesis, characterization and some physical properties of six novel **PAI**s derived from the new diacid monomer are described. Moreover, the effect of **PAI** structure on pure gas permeability coefficients for the six different **PAI**s films was also investigated and discussed.

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2. Experimental

2.1 Materials

All reactants used for the nonconventional aminoacid monomer and **PAI**s synthesis were purchased from Sigma-Aldrich. The reactants 3-amino-4-methoxybenzoic acid (**AMA**), trimellitic anhydride (**TMA**), 2,4,6-trimethyl-1,3-phenylenediamine (**3MPD**), 2,3,5,6-tetramethyl-1,4-phenylenediamine (**4MPD**), 4,4′-hexa-fluoroisopropylidenedianiline (**6FDA**), 4,4′-(hexafluoroiso-propylidene)bis(p-phenyloxy)dianiline (**BAPHF**), 4,4′-(9-fluo-renylidene)diamine (**FND**), 4,4′-(1,4-phenylenediisopropylidene) bisaniline (**PDBI**), N-methyl-2-pyrrolidinone (**NMP**), triphenyl-phosphite (**TPP**), and pyridine (**Py**) were used as received. Calcium chloride (CaCl₂) was dried under vacuum at 200 °C overnight prior to use. All other solvents and reagents were used as received without further purification.

2.2 Characterizations

FTIR spectra were recorded on with a Nicolet 8700 (Thermo-Scientific) FTIR spectrometer. The diacid monomer and poly(amide-imide)s were analysed using KBr pellets and films, respectively. The spectra were obtained in the transmittance mode on the range of 4000 to 400 cm⁻¹, with 32 scans using a resolution of 4 cm⁻¹. ¹H NMR spectra were acquired on a 600 MHz Varian VNMRS spectrometer using deuterated dimethylsulfoxide (DMSO-d_6) as solvent with tetramethylsilane as an internal reference. Solubility tests were carried out placing 5 mg of **PAI**s into 1 mL of solvent at room temperature followed by stirring during 24 h. Thermogravimetric analyses (**TGA**) were performed using a TGA-8000 (Perkin Elmer, Inc) thermogravimetric balance. 5 to 8 mg film samples were analysed between 50 and 800 °C, at a heating rate of 10 °C min⁻¹ under nitrogen atmosphere. Dynamic mechanical analysis (DMA) of **PAI**s films was performed on a DMA-Q800 (TA Instruments) the measurements were carried out using rect-angular films 20 mm long × 1 mm wide × 0.1 mm thick in the tension mode. Measurements were performed as a function of temperature between 50 and 400 °C at a heating rate of 5 °C min⁻¹ using a static force of 110 mN and an 88 mN dynamic force at 1 Hz. A Shimadzu AGS-X universal testing machine was employed to determine the tensile properties of the films. Stress–strain curves were obtained with a 100 N load cell using a 1 mm min⁻¹ strain rate according to ASTM-D882-02. Inherent viscosity (η_{inh}) was determined with an Ubbelohde viscometer, size 50, on 0.5 g dL⁻¹ polymer solutions in dime-thylacetamide (DMAc) at 30 °C. **PAI**s films density was deter-mined by the density gradient column method (Techne Corp) using calcium nitrate solutions (1.22 to 1.47 g cm⁻³). Pure gas permeability coefficients were determined using a constant volume, variable pressure permeation cell, at 35 °C and 2 atm. The effective film area was 1.13 cm². Before each permeation test, the film was degassed for 24 h. Gas permeability coeffi-cients, P, were determined from the slope of the downstream pressure versus time plot under steady-state conditions $(dp/dt)_{ss}$, from the following equation:

$$P = \frac{VR^N}{ART} \frac{l}{\Delta p} \left[\frac{dp}{dt}\right]_{ss}$$

where V is the cell downstream volume (cm³), R^N is the molar volume of a gas molecule at standard conditions (STP), l and A are the thickness (cm) and effective area (cm²) of the film exposed to the gas. R is the gas constant, T is the absolute temperature in K, and Δp is the pressure differential (cm Hg) between the feed gas and the downstream of the permeation cell.

2.3 Monomer synthesis

2.3.1 3-Trimellitimido-4-methoxybenzoic acid (TMBA).

A mixture of 1.67 g (10 mmol) of 3-amino-4-methoxybenzoic acid (**AMA**), 1.92 g (10 mmol) of trimellitic anhydride (**TMA**), and 20 mL of dimethylformamide (**DMF**) was refluxed at 160 °C during 18 h. After cooling at room temperature, the reaction mixture was poured into 500 mL of cold water. The resulting precipitate was filtered off, and then washed thoroughly with water. The crude product obtained was recrystallized from iso-propanol obtaining a creamy solid. (2.2 g, yield: 64.5%) Mp: 312 °C. FT-IR: (KBr: cm⁻¹) 3400–3300 (O–H stretch, broad), 1780 (C=O asymm. stretch), 1700 (C=O symm. stretch), 1380 (C–N stretch), 740 (C–N bending), and 1090 (C–O–C stretch). ¹H-NMR (600 MHz, DMSO-d_6) δ 8.43 (d, J = 8.0 Hz, H_a, 1H), 8.32 (s, H_b, 1H), 8.09 (m, H_c, H_d, 2H), 8.01 (d, J = 8.0 Hz, H_e, 1H), 7.34 (d, J = 8.0 Hz, H_f, 1H), 3.84 (s, H_g, 3H). ¹³C NMR (600 MHz, DMSO-d_6) δ 166.29 (C_a), 165.91 (C_1), 165.90 (C_b), 165.74 (C_3), 158.73 ($C_{2'}$), 136.65 (C_8), 135.60 (C_6), 134.84 (C_9), 132.42 ($C_{4'}$), 132.04 ($C_{1'}$), 131.64 ($C_{6'}$), 123.95 (C_5), 123.52 (C_7), 123.20 (C_4), 119.91 ($C_{5'}$), 112.23 ($C_{3'}$), 56.37 (C_c) (Fig. S1†).

2.4 Poly(amide-imide)s synthesis

PAIs were synthesized by direct polycondensation of **TMBA** with six aromatic diamines (**3MPD**, **4MPD**, **6FDA**, **FND**, **PDBI**, **BAPFH**) using Yamazaki's method.[16] A typical synthesis proce-dure for trimellitimido-methoxy-carboxylic hexa-fluorisopropylidene poly(amide-imide), **TMBA-6FDA**, was carried out as follows: a mixture of 0.68 g (2 mmol) of **TMBA**, 0.67 g (2 mmol) of **6FDA**, previously sublimated, 0.8 g CaCl₂ previously dried at 200 °C overnight, 1.4 mL (17.31 mmol) of pyridine (**Py**), 1.4 mL (5.34 mmol) of triphenylphosphite (**TPP**), and 8.8 mL of **NMP** were charged into a three neck round bottom flask equipped with a nitrogen inlet/outlet, and a mechanical stirrer. The reaction mixture was stirred, and heated at 105 °C during 24 h. After cooling at room temperature, the resulting viscous solution was poured slowly into 700 mL of a water/ethanol mixture (1 : 3 v/v). The resulting fibrous precipitated was recuperated by filtration, washed thoroughly with methanol and hot water and dried at 100 °C under vacuum for 24 h.

2.5 PAIs films preparation

PAIs dense films were prepared using a solvent casting method. Briefly, 0.3 g of **PAI** were placed in 6 mL of **DMF**; next, they were stirred until a homogeneous solution was obtained. The

polymeric solution was filtered and poured into an aluminium mould. The solvent was slowly evaporated at 80 °C during 24 h. After that, the dense films were peeled off and subsequently dried under vacuum at 150 °C for 24 h. Solvent elimination was verified by **TGA** in the interval of temperature between 50 and 250 °C. Dense films for all **PAI**s were obtained with thicknesses ranging from 65 to 80 μm.

3. Results and discussion

3.1 Monomer synthesis

Fig. 1 shows the synthetic route for the *ortho*-functional unsymmetrical dicarboxylic acid, **TMBA**. This strategy is a simple one-pot reaction where 3-amino-4-methoxybenzoic acid was reacted with trimellitic anhydride under dimethylformamide reflux to obtain a preformed imide ring.[17,18] The FTIR spectrum of **TMBA** monomer (Fig. 2A) showed the characteristic absorption of carboxylic acid bands (3400–3300 cm^{-1}, OH–stretch), and imide heterocyclic ring (1780 cm^{-1} C=O symm, 1700 cm^{-1} C=O asymm, and 1380 cm^{-1} C–N stretch). Other important signal was observed at 1090 cm^{-1} corresponding to the methoxy group ether bond (C–O–C stretch). The ^{1}H NMR spectrum of **TMBA** was used to confirm the proposed chemical structure (Fig. 2B). First, no signal from amine groups was detected. Second, the proton signals of carboxylic acids were detected at 13.0 ppm. Finally, the signals in the range of 7.3–8.4 ppm were assigned to aromatic protons and the singlet at 3.84 ppm corresponds to methoxy group protons present in the *ortho*-position of **AMA**. On the basis of these spectroscopic data, the synthesis of a new monomer, **TMBA**, was successfully

achieved; thus, the new monomer was employed for the synthesis of several novel **PAI**s.

3.2 Poly(amide-imide)s synthesis

Traditionally, the phosphorylation polycondensation reaction is reported for condensation of diamines and diacids to obtain polyamides.[16] Using this approach **TMBA** was reacted with six commercial diamines as shown in Fig. 3. **3MPD** and **4MPD** were considered due to the fact that they have a short and stiff structure. **6FDA** and **FND** were selected because they present bulky pendant groups that hinder rotations of the polymer chain. On the other hand, **PDBI** and **BAPHF** were taken into account to understand the effect that long and flexible sections have on the **PAI**s. All polymerization reactions produce homogeneous and highly viscous solutions with up to 95% yield.

The main disadvantage of both polyamides and polyimides is their insolubility, which difficults their processing. The poly(amide-imide)s synthesized from the monomer **TMBA** were soluble in polar aprotic solvents at a concentration of 5 mg mL^{-1}, and in some cases partially soluble in THF. They were insoluble in chlorinated solvents (Table 1). Based on these solubility results, their inherent viscosities were determined in DMAc. Inherent viscosity values range from 0.32 to 0.54 dL g^{-1} which is indicative of polymers formation with moderate molecular weights.[7,19] These values were acceptable to elaborate flexible dense films by the solution casting method.

All **PAI**s chemical structures were confirmed by FTIR and ^{1}H NMR spectroscopy. FTIR spectra of all **PAI**s (Fig. S2†) show the formation of the amide bond that was easily identified due to
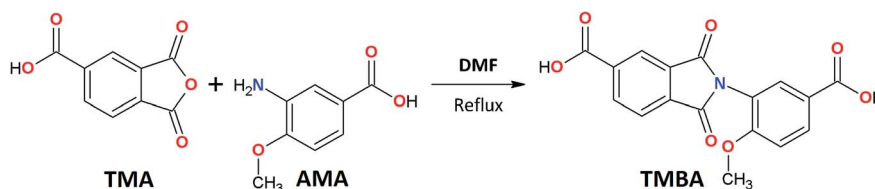

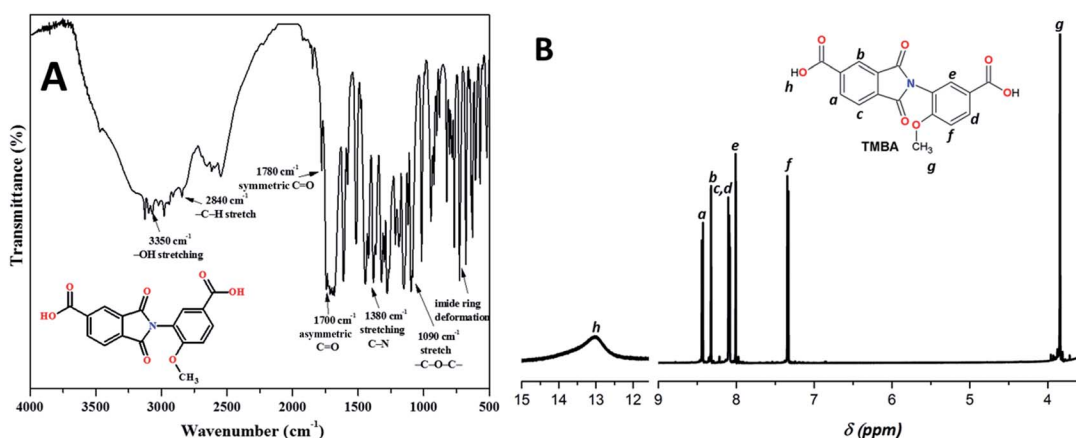Fig. 1   Scheme of **TMBA** monomer synthesis.

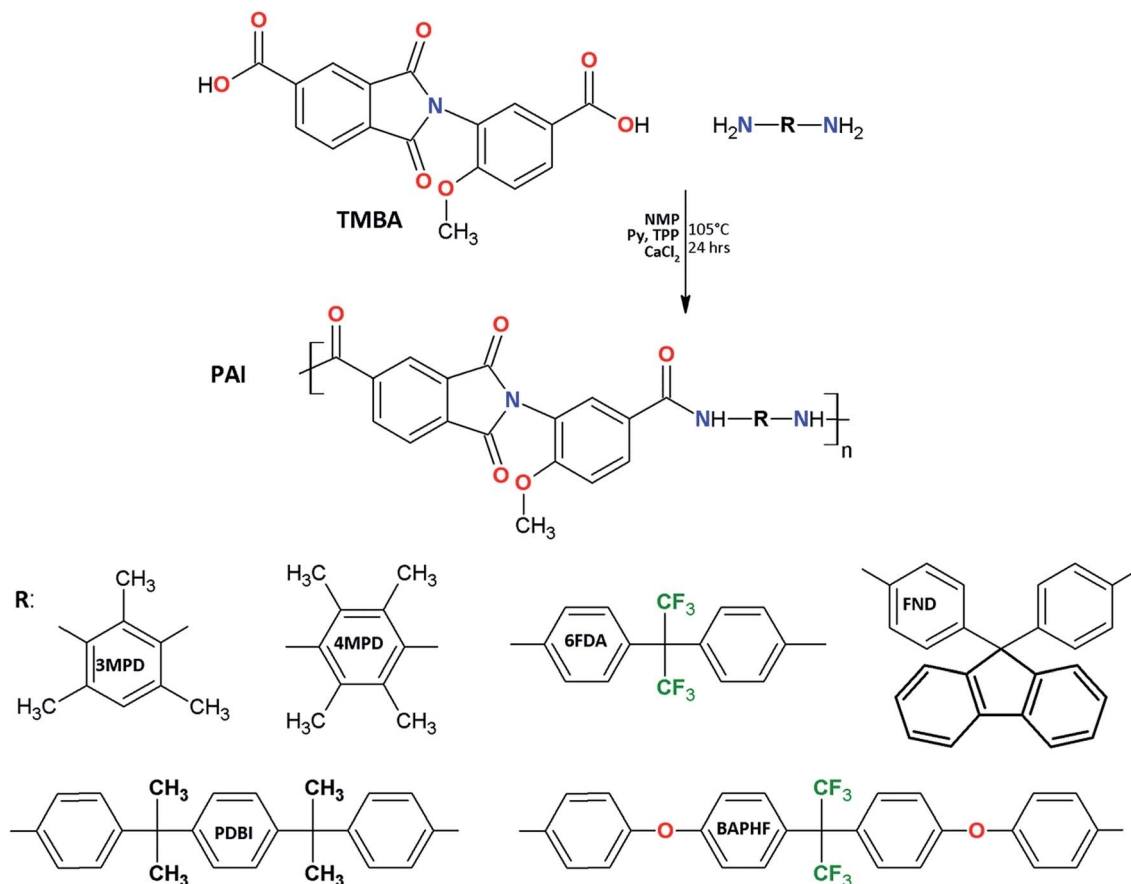Fig. 2   (A) FTIR and (B) ^{1}H NMR **TMBA** spectra.

Fig. 3 Synthesis of poly(amide-imide)s.

Table 1 PAIs solubility and inherent viscosity[a]

| PAI | Solvents | | | | | | | | η_{inh} (dL g^{-1}) |
	NMP	DMAc	DMF	DMSO	THF	DCM	TCE	CHCl$_3$	
TMBA-3MPD	+	+	+	+	−	−	−	−	0.47
TMBA-4MPD	+	+	+	+	−	−	−	−	0.46
TMBA-6FDA	+	+	+	+	±	−	−	−	0.54
TMBA-FND	+	+	+	+	−	−	−	−	0.47
TMBA-PDBI	+	+	+	+	±	−	−	−	0.32
TMBA-BAPHF	+	+	+	+	±	−	−	−	0.34

[a] Measured in DMAc (0.5 g dL^{-1}) at 30 °C. Solubility (5 mg mL^{-1}): +, soluble, −, insoluble, ±, partially soluble at room temperature.

the presence of characteristic bands at 3300 cm^{-1} (N–H stretching) and at 1660 cm^{-1} (C=O stretching). Moreover, the resulting **PAIs** also showed signals at 1780 cm^{-1} and 1720 cm^{-1} (C=O symmetrical and asymmetrical stretching), and at 1370 cm^{-1} (C–N stretching) corresponding to the imide ring, and at 2930 cm^{-1} (C–H stretching) of methyl groups present in **TMBA**. Fig. 4 shows, as an example, the FTIR spectrum of the poly(amide-imide) **TMBA-6FDA**. Furthermore, in the ^{1}H NMR spectra of all **PAIs** (Fig. S3A and S3B†) there were observed two signals in the region between 10.2 and 10.9 ppm and 9.8 to 10.5 ppm, these signals were attributed to amide protons (–CO–NH–) formed by the condensation reaction between diacids and

diamines; moreover, these results confirmed the unsymmetrical structure of **TMBA**, where the amide proton downfield corresponds to **TMA**, while the amide proton observed upfield corresponds to the **AMA** moiety. Fig. 5 shows, as an example, the assignments of protons for the repeating unit from poly(amide-imide) **TMBA-6FDA**.

3.3 Thermal properties

Thermal behaviour of all **PAIs** was evaluated by DMA and **TGA** techniques under nitrogen atmosphere the results are summarized in Table 2. Glass transition temperature (T_g) was
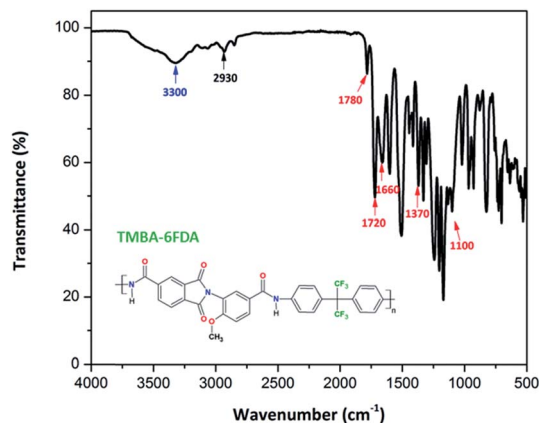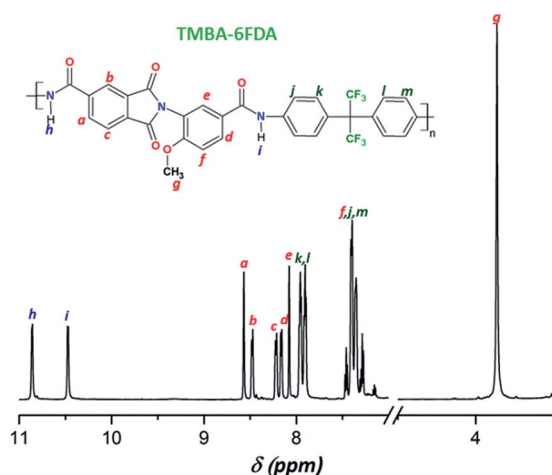
Fig. 4   FTIR spectrum of PAI TMBA-6FDA.

Fig. 5 ^{1}H NMR spectrum of PAI TMBA-6FDA.

obtained from the peak in tan delta curves from DMA analysis (Fig. S4†).[20] T_g's of poly(amide-imide)s were in the range of 281 to 377 °C. The T_g depended on the diamine moiety structure. When the diamine is rigid and bulky, such as **FND**, the poly(amide-imide) **TMBA-FND** displayed the highest T_g; whereas when the diamine has flexible linkages, as is the case of the poly(amide-imide) **TMBA-BAPHF**, T_g was the lowest due to a higher flexibility associated with the ether (C–O–C) groups

present in this diamine moiety. On the other hand, all aromatic **PAI**s exhibited two thermal degradation steps (Table 2, Fig. 6, and Fig. S5†). The first weight loss was observed around 368 up to 426 °C and it was ascribed to the elimination of the methoxy pendant groups present in the **TMBA**, which could be converted to benzoxazole rings by thermal rearrangement;[22–24] meanwhile the second weight loss in the range of 496 to 592 °C was ascribed to the polymer backbone degradation. Moreover, the char yield at 800 °C was found in the range of 53 to 56 wt%. The later data were employed to calculate the limiting oxygen index (LOI). Based on LOI values obtained on **PAI**s these polymers can be classified as auto-extinguishing materials.[7,25,26]

3.4   Mechanical properties

Mechanical properties of **PAI**s films, obtained by the solvent casting method, were characterized by the tensile test and the results are summarized in Table 3. Tensile properties of the **PAI TMBA-3MPD** were not measured because the film was highly brittle. The other **PAI**s films present tensile strengths ranging from 52 to 71 MPa. Tensile modulus was found to be between 1.3 and 1.8 GPa while elongation at break percent lies in between 3.5 and 9.0%. These results are consistent with data previously reported in the literature for aromatic **PAI**s and suggest that the **PAI**s dense films based on **TMBA** present high mechanical properties.[6,7,10,17]

3.5   Gas permeability coefficient

Polymeric gas separation membranes have great potential for industrial gas separation process because of their cost-effectiveness and lower energy requirements in applications such as natural gas sweeting.[27–29] The potential application of different poly(amide-imide)s as gas separation membranes has been previously reported.[30–32] In here, pure gas permeability coefficients of the novel **PAI**s films prepared were tested using a constant-volume, variable pressure gas permeation cell at 35 °C and 2 atm. Results of pure gas permeability coefficients for He, O_2, CO_2, CH_4 and N_2 for the six **PAI**s and a commercial **PAI** (Torlon) for comparison are given in Table 4. Gas permeability coefficients for the **TMBA**-based **PAI**s decrease in the order $P_{He} > P_{CO_2} > P_{O_2} > P_{N_2} > P_{CH_4}$. This behaviour agrees with the kinetic diameter order of the gases evaluated: He (2.6 Å) > CO_2 (3.3 Å) > O_2 (3.46 Å) > N_2 (3.64 Å) > CH_4 (3.8 Å).

Table 2   Thermal properties of PAIs

PAIs	T_g (°C), DMA[a]	T_{max1}[b] (°C)	T_{max2} (°C)	Char yield[c] (%)	LOI[d]
TMBA-3MPD	353	373	516	59.7	41.3
TMBA-4MPD	367	368	496	59.7	41.3
TMBA-6FDA	347	423	578	53.5	38.9
TMBA-FND	377	426	592	66.3	44.0
TMBA-PDBI	286	419	541	55.0	39.4
TMBA-BAPHF	281	419	575	56.6	40.1

[a] Measured by DMA at heating rate of 5 °C min^{-1} and 1 Hz. [b] T_{max}, onset of decomposition temperature of the two events observed. [c] At 800 °C in N_2 atmosphere. [d] Limiting oxygen index (LOI) calculated from equation LOI = 17.5 + 0.4 (char yield).[21]
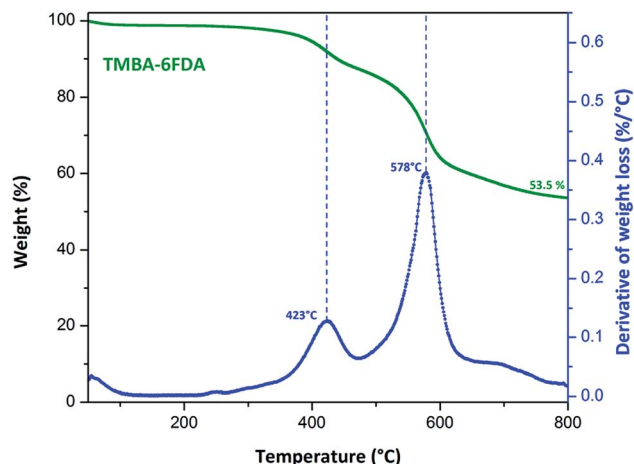
Fig. 6 TGA and DTGA curves of PAI TMBA-6FDA.

Table 3 PAIs mechanical properties under tension

PAI	Tensile modulus (GPa)	Tensile strength (MPa)	Elongation at break (%)
TMBA-3MPD	—	—	—
TMBA-4MPD	1.3	64.1	6.4
TMBA-6FDA	1.6	63.9	6.4
TMBA-FND	1.8	55.9	3.5
TMBA-PDBI	1.4	52.0	4.5
TMBA-BAPHF	1.4	71.9	9.0

Table 4 PAIs pure gas permeability coefficients

PAI	Permeability[a], P, (Barrer)					α^b
	He	CO_2	O_2	N_2	CH_4	CO_2/CH_4
TMBA-3MPD	14.5	**2.4**	0.73	0.38	0.37	6.5
TMBA-4MPD	27.3	**5.8**	1.35	0.56	0.52	11.1
TMBA-6FDA	**46.5**	**12.3**	**3.10**	**0.73**	**0.64**	**19.2**
TMBA-FND	29.6	**9.1**	2.43	1.12	1.11	8.2
TMBA-PBDI	19.0	**7.4**	1.63	0.48	0.48	15.4
TMBA-BAPHF	28.3	**10.9**	2.41	0.64	0.58	**18.8**
Torlon[33]	3.73	**0.54**	0.13	0.018	0.013	41.5

[a] 1 Barrer = 10^{-10} cm^3 (STP) cm s^{-1} cm^{-2} $cmHg^{-1}$, evaluated at 35 °C and 2 atm. [b] Ideal separation factor.

PAIs films showed significant changes on pure gas permeability coefficient depending on the kind of diamine used for its preparation. For example, CO_2 permeability coefficients, P_{CO_2} decrease in the order **TMBA-6FDA** > **TMBA-BAPHF** > **TMBA-FND** > **TMBA-PDBI** > **TMBA-4MPD** > **TMBA-3MPD**. Interestingly, **TMBA-6FDA** film also shows the highest ideal selectivity for the gas pair CO_2/CH_4. However, its selectivity was lower than the one reported for Torlon.[33] Gas permeability in a dense polymeric film is related with structural parameters which are responsible of molecular packing such as fractional free volume.

The concept of fractional free volume (FFV) has been helpful to explain the gas permeability behaviour in polymeric membranes. FFV is defined as:

Table 5 PAIs density and fractional free volume

PAI	ρ (g cm^{-3})	V (cm^3 mol^{-1})	V_{wd} (cm^3 mol^{-1})	FFV
TMBA-3MPD	1.279	356.14	240.58	0.122
TMBA-4MPD	1.278	367.37	254.25	0.100
TMBA-6FDA	1.420	450.35	288.77	0.166
TMBA-FND	1.288	507.53	332.77	0.148
TMBA-PDBI	1.248	520.59	347.57	0.132
TMBA-BAPHF	1.391	592.16	386.37	0.152

$$FFV = \frac{(V - V_o)}{V}$$

in which, V is the specific volume of the polymer, calculated as:

$$V = \frac{1}{\rho}$$

where ρ is the measured density given in Table 5, and V_o is the polymer chain occupied volume that was calculated from:

$$V_o = 1.3V_W$$

where, V_W is the van der Waals volume of the polymer chain repeating unit, that was calculated by Bondi's group contribution method.[34,35]

In the present work, **PAIs** gas permeability coefficients show a good correlation with FFV. In particular, **TMBA-6FDA** and **TMBA-BAPHF**, that contain the bulky $-CF_3$ group, presented higher FFV which is associated to higher pure gas permeability. They also show the best CO_2/CH_4 ideal selectivity which is linked to the presence of $-CF_3$ groups.

4.   Conclusions

In summary, a new *ortho*-functional unsymmetrical dicarboxylic acid, 3-trimellitimido-4-methoxybenzoic acid (**TMBA**) was successfully synthesized and its chemical structure confirmed. Moreover, novel poly(amide-imide)s were prepared from **TMBA** with six aromatic diamines by a direct polycondensation reaction using triphenyl phosphite and pyridine. The **PAIs** were soluble in polar aprotic solvents. They were able to form dense films with good mechanical properties and they present high thermal stability and LOI. They have pure gas permeability coefficient one order of magnitude larger than those of commercial poly(amide-imide) Torlon. **TMBA-6FDA** films show both higher pure gas permeability coefficients and higher ideal selectivity for the gas pair CO_2/CH_4 in the evaluated membranes; thus, this particular poly(amide-imide), **TMBA-6FDA**, shows a potential for application as a membrane for gas separation processes.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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