

Novel Aromatic Polyimides Derived from 5'-*t*-Butyl-2'-pivaloylimino-3,4,3",4"-*m*-terphenyltetracarboxylic Dianhydride with Potential Application on Gas Separation Processes

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ABSTRACT: A new family of polyimides having two bulky groups in the central ring of a *m*-terphenyl moiety has been obtained. These polyimides have been synthesized by reaction of four commercial diamines with the electrophilic monomer, 5'-t-butyl-2'-pivaloylimino-3,4,3",4"-*m*-terphenyltetracarboxylic acid dianhydride (**PTPDA**). This monomer has been obtained by a modern C-H-activated arylation method with good yield and purity. The attained polymers showed T_g values ranging from 300 to 430 °C, thermal stability > 500 °C, and excellent solubility in a broad range of solvents, including tetrahydrofuran. Despite having an amide group, uptake of water was low and comparable to that of classical aromatic polyimides. Mechanical properties of polymer films were good enough to permit the use of these polyimides on gas separation applications at high pressures. Films obtained by casting offered a good balance of permeability and permselectivity with values close to the Robeson upper-bound, in particular for the O_2/N_2 gas pair.

Introduction

Aromatic polyimides are considered to be relevant materials for advanced technologies because of their outstanding thermal, mechanical, and chemical stability. However, it is known that fully aromatic polyimides are very often insoluble in most organic solvents, which highly limits their application in many fields.¹⁻⁶ To overcome this drawback, different approaches have been outlined, most of them based on the modification of their chemical structure. Flexible links such as -O-, -SO₂-, or -CH₂-, or bulky groups (hexafluoroisopropylidene, isopropylidene, etc.) are commonly employed as solubilizing moieties, 7^{-9} but it often brings about a loss of thermal stability and chain stiffness of polyimides. Alternatively, tractable aromatic polyimides can be obtained from nonplanar monomers where the nonplanarity provides the conformational freedom to lower chain regularity and rigidity.^{7,10} With the purpose of improving the tractability, polyimides derived from *m*-terphenyl dianhydride have been synthesized, yet they still showed limited solubility in organic solvents.¹¹ Furthermore, it has been observed that the incorporation of a t-butyl pendent group in the 5' position of the *m*-terphenyl moiety improves their solubility. Therefore, polyimides from 5'-t-butyl-m-terphenyl-3,4,3",4"-tetracarboxylic acid dianhydride (BTPDA) were soluble in m-cresol, N-methylpyrrolidinone (NMP), and N,N-dimethylacetamide (DMAc).¹² These soluble *m*-terphenyl polyimides are promising materials in different fields, including gas separation applications, because they exhibit a combination of desirable properties such as high thermal resistance, high glass-transition temperatures, and good mechanical properties. In addition, the effective chain separation effect caused by the presence of the bulky t-butyl pendant group, results in a hindered molecular packing affording high free volume, and hence, they have an excellent permeability to low M_w molecules.¹³ However, these polyimides exhibit a moderated permselectivity and a moderated gas separation capacity owing to the trade-off between permeability and selectivity.¹⁴⁻¹⁶

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In view of that, the major goal of this ongoing research has consisted of further improving the gas separation capacity of these versatile aromatic polyimides from **BTPDA** as well as their processability from different organic solvents without impairing their whole outstanding properties by means of an adequate, tailormade modification.

This article reports the synthesis of a novel dianhydride derived from **BTPDA**, which in addition contains a bulky substituent in position 2' such as the pivalamide group (pivalamide or pivaloylimino: C(CH₃)₃CONH–). It has been prepared by a suitable, economical, and original route involving C–H activation methodology.¹⁷ The incorporation of the pivaloyl substituent in position 2' has simultaneously brought about a noteworthy improvement in polymer chain rigidity and solubility relative to those polyimides derived from **BTPDA**. Additionally, the improvement in polymer chain rigidity has led to a better gas separation capacity. Polycondensation of this dianhydride with four aromatic diamines, characterization of the resulting polyimides, and a preliminary evaluation as gas separation membranes are described and compared with some polyimides derived from **BTPDA**.

Experimental Section

Materials. Solvents and reactants were of reagent-grade quality and used without further purification. Pivaloyl chloride, 4-*t*-butylaniline, and palladium acetate were purchased from Aldrich and silver acetate to Fluka. 2,2-Bis-(4-aminophenyl)hexafluoro-propane (Criskev Co., Kansas) (**6FpDA**), 2,2-bis-(3-amino-4-methylphenyl)hexafluoro-propane (Apollo, U.K.) (**m6FMe**), 2,4,6-trimethyl-*m*-phenylendiamine (Aldrich) (**3MemPD**), and 2,3,5,6-tetramethyl-*p*-phenylendiamine (Aldrich) (**4MepPD**) were sublimed just before being used. Dimethyl 4-iodophthalate was synthesized by oxidation of 4-iodo-*ortho*-xylene using potassium permanganate in a mixture of pyridine/water,¹⁸ followed by Fisher esterification of the obtained diacid with methanol.¹⁹

Monomer Synthesis. Elemental analyses and spectroscopic characterization (¹H and ¹³C NMR) data of intermediates and monomers is included in the Supporting Information

4-t-Butylpivanilide. Pivaloyl chloride (78 mmol, 9.6 mL) was added dropwise to a cooled solution (0 °C) of chloroform (150 mL), 4-t-butylaniline (67 mmol, 10.7 mL), and pyridine (67 mmol, 5.4 mL). After stirring for 15 min at 0 °C, the mixture was allowed to warm up to room temperature and stirred for 2 h. The solvent was removed, and the solid residue was washed with water and recrystallized from EtOH/H₂O (1/1) to give a white product. Yield: 95%. mp 189 °C.

5'-t-Butyl-2'-pivaloylimino-tetramethyl-3.4,3'',4''-m-terphenylcarboxilate. A solution of 4-t-butylpivanilide (2.92 g, 12.5 mmol), dimethyl 4-iodophthalate (20 g, 62.4 mmol), palladium acetate (0.14 g, 0.62 mmol), and silver acetate (5.8 g, 50.0 mmol) in trifluoroacetic acid (40.0 mL) was heated under nitrogen at 120 °C. The reaction was followed by TLC until it was completed. During this time, a dark-yellow precipitate was formed, and the supernatant became clear dark red. The reaction mixture was diluted with toluene (60 mL) and filtered through Celite, and the solvent was evaporated under reduced pressure. The residue was purified by flash chromatography on silica gel (CH₂Cl₂/AcOEt (10/1)) to give the product after solvent evaporation as a white solid. Yield (5 runs): 80%. mp 167 °C.

5'-t-Butyl-2'-pivaloylimino-3,4,3",4"-m-terphenyltetracarboxylic Acid. The tetramethyl-m-terphenylcarboxilate (20.0 g, 32.4 mmol) and a solution of 10.4 g of sodium hydroxide in 150 mL of water were charged into a 500 mL round-bottomed flask equipped with a reflux condenser. The mixture was boiled until the ester disappeared, as checked by TLC. The reaction solution was diluted with an equal volume of water, and after cooling, it was poured with vigorous stirring onto 120 mL of hydrochloric acid 1 N. The crude acid precipitated as a clear solid, which was filtered, dissolved in a NaOH solution, and poured again into concentrated HCl for further purification. The tetracarboxylic acid was then obtained as a white solid, which was thoroughly washed with water and dried under vacuum at 90 °C for 24 h. Yield: 18 g (90%). mp 283 °C (cyclization).

5'-t-Butyl-2'-pivaloylimino-3,4,3'',4''-m-terphenyltetracarboxylic Dianhydride. The dianhydride **PTPDA** was prepared by refluxing the tetraacid precursor (20 mmol) in acetic anhydride (50 mL) and a small amount of AcONa for 3 h. The solution was filtered and cooled to room temperature, and the monomer crystallized off as a white solid, which was filtered, washed with toluene, and dried at 120 °C under vacuum. Yield: 95%. mp 292 °C.

Polymer Synthesis. Two Steps Polymerization Method. A three-necked flask, equipped with a mechanical stirrer and gas inlet and outlet, was charged with 3.0 mmol of diamine and 3.0 mL of NMP. The mixture was stirred at room temperature under a blanket of nitrogen until the solid was entirely dissolved. Then, the solution was cooled to 0 °C, and pyridine (6.0 mmol) and trimethylchlorosilane (6.0 mmol) were slowly added. The solution was allowed to warm up to room temperature and stirred for 15 min to ensure the formation of the silvlated diamine. After this time, the solution was cooled again to 0 °C, and pivaloyl dianhydride (3.0 mmol) was added, followed by 3.0 mL of NMP. The reaction mixture was stirred for 15 min at 0 °C; then, the temperature was raised up to room temperature and left overnight. Acetic anhydride (30 mmol) and pyridine (30 mmol) were then added, and the viscous solution was stirred at room temperature for 6 h, followed by heating for a further 1 h at 60 °C to promote imidation. The flask was cooled down to room temperature, and the polymer solution was poured dropwise on 500 mL of water, washed several times with water, and extracted in a Soxhlet with ethanol to remove traces of solvent and oligomers. The polymer was dried overnight under vacuum at 120 °C. Yield was quantitative.

One-Step Polymerization Method. m-Cresol (12 mL) and 3.0 mmol of diamine were mixed in a 50 mL three-necked flask with mechanical stirring and blanketed by dry nitrogen. After the diamine was dissolved, 3.0 mmol of dianhydride was added, and the mixture was heated to 80 °C. Then, pyridine (2.0 mmol) was added, and the solution was kept at that temperature for 1 h.

Afterward, benzoic acid (2.0 mmol) was added, and the mixture was stirred at 180 °C for 8 h. After cooling, the solution was poured slowly into a 1/2 (v/v) mixture of water/ethanol. The obtained polymer was filtered off and washed thoroughly with a 1/1 (v/v) mixture of water/ethanol, extracted with ethanol in a Soxhlet apparatus, and finally dried in a vacuum oven at 120 °C overnight. Yields were virtually quantitative in every case.

Measurements. Elemental analyses were performed with a Carlo Erba EA1108 elemental analyzer. ¹H and ¹³C NMR spectra were recorded on a Varian Gemini spectrometer tuned at 299,95 and 75,43 MHz, respectively. FT-IR spectra were recorded on a Perkin-Elmer RX-1 device on powder for monomers and intermediates and on films $(50-60 \,\mu\text{m})$ for polymers. An attenuated total reflection accessory (ATR) was used in all cases. Differential scanning calorimetry (DSC) analyses were performed on a TA instruments Q-2000 calorimeter at a heating rate of 20 °C/min under nitrogen. Thermogravimetric analyses (TGAs) were performed on a TA Q-500 thermobalance, heating under controlled flux of nitrogen at 10 °C/min. Inherent viscosities were measured at 25 °C with an Ubbelohde viscometer with NMP as a solvent on polymer solutions with a concentration of 0.3 g/dL. Melting points of intermediates and monomer were measured by DSC. Qualitative solubility was determined with 10 mg of polymer in 1 mL of solvent at room temperature after 24 h or heating until dissolution for samples soluble on heating. Measurements of mechanical properties were conducted on a MTS Synergie 200 Universal Testing dynamometer of vertical extension on 30 mm length, 5 mm width film strips using mechanical clamps with an initial separation of 12 mm and 5 mm/min extension rate.

Weight-average molecular weights (M_w) and number-average molecular weights (M_n) were determined by gel permeation chromatography (GPC) with Perkin-Elmer Series 200 pump, oven, and UV-vis detector. Wavelength was 271 nm, oven temperature was 70 °C, and solvent flow was 0.3 mL/min. Polyethyleneglycol standards were used as references. The samples were prepared by dissolving 1 mg of polymer in 1 mL of *N*,*N*-dimethylformamide. The software TotalChrom from Perkin-Elmer was used for data acquisition and analysis. Two Polymer Laboratories Resipore columns (3 μ m, 300 × 4.6 mm², molecular weights range from 200 to 400 000) were used. Eluent was *N*,*N*-dimethylformamide containing 0.1% (w/v) LiBr.

Permeability to pure gases was studied on polymer films, made by casting 10% (w/v) DMAc solutions of polymers onto a leveled glass plate and by heating at 80 °C for 12 h and at 180 °C under vacuum overnight. A barometric method was used to determine steady-state pure gas permeability at 30 °C, applying a pressure of 3 bar and an initial pressure in the expansion chamber < 0.1 mbar.

Water sorption measurements were determined gravimetrically at 25 °C in a 65% relative humidity atmosphere. Films of 100 mg, previously dried at 120 °C for 24 h over P_2O_5 , were placed in a closed desiccator containing a saturated aqueous solution of NaNO₂. The films were weighed periodically during 12 h and then were allowed to humidify for 3 more days until they had equilibrated with their surroundings, as denoted by no weight change.

Results and Discussion

Monomer Synthesis. The synthetic route for dianhydride **PTPDA** is shown in Scheme 1. Intermediates were not commercially available, so they had to be prepared. 4-*t*-Butylpivalanilide 1 was obtained by facile acylation of 4-*t*-butylaniline with pivaloyl chloride. Dimethyl 4-iodophthalate 2 was synthesized by oxidation of 4-iodo-*ortho*-xylene using potassium permanganate^{12,18} in a mixture of pyridine/ water, followed by Fisher esterification of the obtained diacid with methanol.¹⁹ The overall yield was ~85%.

The key step of this synthetic route was the coupling reaction to give the *m*-terphenyl moiety. We have previously

Scheme 1. Synthesis of Dianhydride PTPDA



described the preparation of *m*-terphenyl dianhydrides by means of a Suzuki catalyzed coupling reaction of arylbromides with arylboronic acid.^{11,12} This highly efficient and selective methodology involves the use of a dibromo derivative and an ulterior oxidation of four methyl groups to give finally a tetraacid compound. This step can represent very often a drawback in the synthetic process because achieving a whole oxidation is cumbersome and, moreover, the yield in terms of pure tetracarboxylic compound can be not very high. In view of that, we have now developed a new procedure based on a double arylation by C-H activation methodology.¹⁷ In this method, the presence of a directing group, such as pivalamide, allows the direct *ortho*-arylation of the benzene ring. Besides, doing the reaction on an acid derivative is an additional advantage because no oxidation is needed. Therefore, the reaction of the 4-t-butylpivalanilide 1 with dimethyl 4-iodophthalate 2, in combination with silver acetate and palladium acetate as catalysts, yielded the *m*-terphenyltetraester derivative 3 in a clean and selective mode. The next steps, saponification and dehydratation, afforded the dianhydride **PTPDA** in high yield and purity. Saponification of the tetraester precursor was carried out by refluxing with NaOH solution,²⁰ and its completion was determined by TLC. The tetracarboxylic acid 4 was cyclodehydrated by means of acetic anhydride and NaOAc to give PTPDA in quantitative yield and pure enough for preparing polymers of high molecular weight. The obtained intermediates in each step as well as the structure of the novel monomer were confirmed by spectroscopic techniques. As an example, FT-IR and ¹H NMR spectra of dianhydride PTPDA have been reproduced in Figure 1.

The melting point for **PTPDA** crystallized from Ac_2O was determined by DSC (Figure 2). On heating, **PTPDA** showed a melting endotherm at 292 °C. However, when the sample was quenched from the melt, it was possible to detect the glass transition of the amorphous phase at 134 °C, followed by a cold crystallization at 186 °C, and finally the melting endotherm at 292 °C.

Polymer Synthesis and Characterization. Four commercial diamines were combined with **PTPDA** to attain polyimides bearing the *m*-terphenyl unit (Scheme 2). The polyimide from diamine 2,2-bis-(4-aminophenyl) hexafluoro-propane, **6FpDA**, was prepared by the two-step low-temperature polycondensation method, using trimethylsilyl chloride and pyridine as polycondensation promoters and NMP as solvent.²¹ The molecular weight achieved for this polyimide was high enough to prepare creasable films by casting from

polymer solutions. However, when this two-step procedure was tried out with diamine 2,2-bis-(3-amino-4-methylphenyl) hexafluoro-propane (m6FMe), very low viscosities were achieved because of the premature precipitation of the poly(amic acid) precursor. In contrast, it was found out that the use of the one-pot method in *m*-cresol solution at high temperature²²⁻²⁴ led to viscosities up to 1.26 dL/g for PTPDA-m6FMe polyimide and up to 0.65 dL/g when the sterically hindered 2,4,6-trimethyl-*m*-phenylendiamine (3MemPD) was employed. These results confirmed that the one-step procedure seems to be a more suitable and convenient method for this dianhydride when the polyimide is soluble in the reaction solvent. Only when the 2,3,5,6-tetramethyl-p-phenylendiamine (4MepPD) was employed, a modest value of viscosity was achieved ($\eta = 0.41 \text{ dL/g}$), presumably because of the higher steric hindrance and rigid character of this tetramethylated diamine.

The results of polymerization are compiled in Table 1. From GPC measurements, it was confirmed that polymers had high molecular weights in the range of $46\,800-301\,000\,\text{g/mol}$ for M_w and $14\,300-77\,500\,\text{g/mol}$ for M_n . The elemental analyses agreed quite well with calculated values for the proposed structures of polyimides. The chemical composition of the polymers was also confirmed by IR and ¹H NMR spectroscopies. As an example, the ¹H NMR spectrum of **PTPDA-6FpDA** is showed in Figure 3. The IR spectra supported the complete imidation; characteristic absorption bands of polyimides appeared at 1780 (asym C=O str), 1718 (sym C=O str), 1364 (C-N str), and 750 cm⁻¹ (imide ring deformation), whereas no signals associated with polyamic acid (higher than 3000 cm⁻¹) were observed.

The solubility of polyimides was studied in different solvents (Table 2). Satisfactorily, all polymers were soluble in aprotic polar solvents and even in common organic solvents such as THF and chloroform. Taking into account the limited solubility showed by classical aromatic polyimides and the related polyimides from 5'-t-butyl-m-terphenyl-3,4,3",4"-tetracarboxylic acid dianhydride,¹² it is clear that the incorporation of the pivalamide group on the dianhydride moiety significantly enhances the solubility, and hence the processability. This improvement is most likely due to the combination of the steric and polar nature of the pivaloyl substituent and the t-butyl placed in 5' position, which greatly favors the solution in polar organic media. Also, the steric hindrance of this bulky group in the 2' position of the *m*-terphenyl moiety twists the rings dramatically out of plane, resulting in a noncoplanar, rigid, and



Figure 1. FT-IR and ¹H NMR spectra of dianhydride PTPDA.

contorted conformation capable of efficiently hindering the chain packing. This highly contorted conformation can be seen in the simulated structure of the **PTPDA** diimide, as calculated by the semiempirical AM1 method (Figure 4). In addition, it can be noticed from this model that the amide group is not very accessible because it is shielded by the *t*-butyl and the side phenyl groups of the *m*-terphenyl moiety. This may explain the good chemical stability of this group, which does not easily undergo hydrolysis reaction as well as the moderate moisture absorption showed by these polyimides, as commented below, despite having an amide function.

Furthermore, the introduction of this substituent should bring about an improvement in the polymer chain stiffness, as predicted by molecular modeling. Therefore, a theoretical study using the semiempirical AM1 method was carried out to calculate the torsional mobility and rotational energy barrier around the bonds that join the aromatic rings of the *m*-terphenyl unit. The calculations were performed on the repeating unit of **PTPDA-6FpDA** and also on **BTPDA-6FpDA** for comparative purposes. Figure 5 presents the AM1 enthalpy barriers calculated by rotating the dihedral angle, Φ , in 10° increments for X = H and NHCOtBu, respectively. The maximum value of the rotational barrier was \sim 9.8 kcal/mol for X = NHCOtBu, whereas for X = H, it was only 2.4 kcal/mol. Therefore, the presence of the pivalamide group did greatly heighten the rotational barrier of the aryl moieties, resulting in a much more restricted torsional mobility and consequently in a much higher chain rigidity. The effect of this group on the mobility of the chains could also be observed upon looking at the glasstransition temperatures (Table 3), which were higher for **PTPDA** polymers than those reported for polyimides from

BTPDA dianhydride. For instance, the T_g of polyimide **PTPDA-6FpDA** is 340 °C, whereas for the homologous polyimide without pivalamide substituent (**BTPDA-6FpDA**) is 325 °C.¹² It is worth remarking the very high glasstransition temperatures of **PTPDA-3MemPD** and **PTPDA-4MepPD**, 420 and 430 °C, respectively, which are among the highest values ever reported for lineal, soluble polyimides.



Figure 2. DSC curve of PTPDA dianhydride after being quenched from the melt state.

The results of TGA showed an excellent thermal stability of the new polyimides, even though they bear a pivalamide side group. They exhibited values of decomposition temperatures (T_d , taken as the temperature at initial weight loss onset in the TGA curves) > 500 °C. Therefore, the introduction of the amide substituent did not seem to impair largely the thermal resistance, and thus **PTPDA-3MemPD** showed a T_d of ~510 °C, whereas its homologous without the pivaloyl group has a T_d of 525 °C.¹²

The mechanical properties of polymers films by solution casting from DMAc are summarized in Table 3. Polyimide PTPDA-4MepPD could not be cast into flexible films because of their moderate molecular weight and elevated chain stiffness ($T_g = 430$ °C), so we were not able to evaluate its mechanical properties. It was not the case for **PTPDA**-6FpDA, which even having a low inherent viscosity could be processed into good quality films. Polyimide films had tensile strengths of 50-80 MPa, elongations at break of 5-8%, and tensile moduli of 1.5 to 1.8 GPa. These values of tensile strengths and tensile modulus are acceptable for highmolecular-weight polyimides, although they did not match the mechanical resistance of classical wholly, unmodified polyimides. It may result from low intermolecular interaction because of the presence of the bulky pendant t-butyl group and the highly twisted molecular structure. Furthermore, these results do confirm that the pivalamide group, as could be presumed from molecular modeling of the diimide of **PTPDA** (Figure 4), is hindered by the *t*-butyl and imide



Table 1. Properties and Elemental Analyses of Polyimides

polymer		$\eta_{\rm inh} \left({\rm dL/g} ight)^a$	$M_{\rm n}({ m GPC})^b$	$M_{\rm w} \left({ m GPC} ight)^b$	PDI $(M_{\rm w}/M_{\rm n})$	elemental analysis (%)			
	yield (%)						С	Н	Ν
PTPDA-6FpDA	95	0.39	14 300	46 800	3.3	calcd	67.07	4.28	5.10
						found	66.85	4.41	5.22
PTPDA-m6FMe	96	1.26	77 500	301 000	3.9	calcd	67.67	4.61	4.93
						found	67.59	4.71	4.80
PTPDA-3MemPD	96	0.65	62 600	136 000	2.2	calcd	75.10	5.83	6.57
						found	74.89	6.08	6.36
PTPDA-4MepPD	93	0.41	16200	76 300	4.7	calcd	75.32	6.01	6.43
						found	75.08	6.22	6.70

^a Inherent viscosity measured at a concentration of 0.3 g/dL in NMP at 25 °C. ^b Relative to polyethylenglycol.



Figure 3. ¹H NMR spectrum of PTPDA-6FpDA polyimide.

 Table 2. Solubility of Polyimides

polyimide	<i>m</i> -cresol	NMP	DMAc	DMSO	CHCl_3	THF	toluene
PTPDA-6FpDA	+ +	+ +	+ +	+ +	+ -	++	+ -
PTPDA-m6FMe	+ +	+ +	+ +	+ +	+ +	+ +	+ -
PTPDA-3MemPD	+ +	+ +	+ +	+ +	+ +	+ +	
PTPDA-4MepPD	+ +	+ +	+ +	+ +	+ -		+ -
a + +: soluble.	+ -: par	tially s	oluble	: ins	oluble.		



Figure 4. Molecular modeling of 5'-*t*-butyl-3,4,3'',4''-*m*-terphenyl dimethylimide (top) and 5'-*t*-butyl-2'-pivaloylimino-3,4,3'',4''-*m*-terphenyl dimethylimide (bottom) resulting of the reaction of methyl amine with **BTPDA** and **PTPDA**, respectively.

groups, preventing interchain hydrogen bonding and hence avoiding an enhancement of the intermolecular attractions between polymer chains.

Interestingly, even having an amide function, these polyimides showed low water uptake, similar to other commercial



Figure 5. Dihedral angle rotation enthalpy by AM1 molecular modeling.

polyimides without polar groups (Table 4). This fact is again explained by the protection of the amide group for the *t*-butyl and the edge phenyl groups of the *m*-terphenyl unit. As expected, **PTPDA-6FpDA** and **PTPDA-m6FMe** had significantly lower moisture uptake than polyimides from **3MemPD** and **4MepPD** diamines because of the well-known hydrophobic effect of the trifluoromethyl groups. Nevertheless, the water uptake values were slightly higher than those not having the pivaloyl imide moiety and used as references in this article.

Gas Transport Properties of Polyimides. The permeability coefficients for five gases and ideal separation factors for some interesting gas pairs are given in Table 5. For comparative purposes, the permeability and selectivity data for related polyimides from 5'-t-butyl-m-terphenyl-3,4,3",4"tetracarboxylic acid dianhydride, BTPDA-6FpDA and BTPDA-3MemPD, without the pivalamide group have also been included. As it was previously reported,¹³ these latter exhibit outstanding permeabilities with moderate selectivity values for gas pairs O₂/N₂ and CO₂/CH₄. Therefore, because of the convenient synthesis route and high molecular volume of the pivalamide group, we rationalized that this new monomer could bring about materials with enhanced properties for gas separation. Accordingly, the newly synthesized membranes derived from the PTPDA dianhydride showed higher ideal selectivity values based on ratios of pure gas permeability coefficients when compared with polymers from **BTPDA** dianhydride. Therefore, polyimide **PTPDA-**6FpDA showed an enhancement of 9 and 12% in CO₂/CH₄ and O₂/N₂ selectivities, respectively, regarding BTPDA-**6FpDA**. The improvement was even greater for the more permeable PTPDA-3MemPD polyimide, namely, the 24% increase for O2/N2 and 26% enhancement for CO2/CH4 ideal selectivity values when compared with BTPDA-3MemPD.

Because the well-established trade-off between permeability and selectivity^{14–16} in size-sieving polymers such as those considered in this study, this enlarged selectivity is certainly accompanied by a decrease in the permeability coefficients for every gases studied.^{25,26} Therefore, from the permeability/selectivity map presented in Figure 6 for O_2/N_2 separation, it can be noticed the improved separation performance of polyimides from **PTPDA** dianhydride relative to the performance of the best materials for this separation is characterized by the so-called upper bound line established by Robeson.^{14,15} Although all materials in this study fall below the recently established upper bound, **PTPDA** polyimides

Table 3. Thermal and Mechanical Properties of Polyimides

				-	•	
polyimide	$T_{\rm g}(^{\circ}{\rm C})^a$	$T_{\rm d}(^{\circ}{\rm C})^b$	char yield $(\%)^c$	tensile strength (MPa)	elongation at break (%)	tensile modulus (MPa)
PTPDA-6FpDA	340	500	54	55	5.0	1.8
PTPDA-m6FMe	300	526	57	64	4.7	1.8
PTPDA-3MemPD	420	510	58	80	8.0	1.5
PTPDA-4MepPD	430	500	56	d	d	d

^{*a*} From the second trace of DSC measurements conducted with a heating rate of 20 °C/min under a nitrogen atmosphere. ^{*b*} Onset weight loss temperature in TGA at 20 °C/min heating rate. ^{*c*} Residual yield in TGA at 800 °C under a nitrogen atmosphere. ^{*d*} Brittle polymer.

Table 4. Water U	Up	take	ot.	Po	lvim	ides
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moisture uptake	(%)
PTPDA-6FpDA	2,3
PTPDA-m6FMe	1,5
PTPDA-3MemPD	4,5
PTPDA-4MepPD	3.1
BTPDA-6FpDA	0.3
RTPDA-3MemPD	3.2

^{*a*} Moisture uptake (%) = $100(W - W_0)/W_0$; W = weight of polymer sample after standing in a 65% relative humidity atmosphere. W_0 = weight of polymer sample after being dried at 120 °C for 24 h over P₂O₅.

Table 5. Gas Transport Properties of Polyimides

	permeability (barrers) ^a					ideal separation factors		
polyimide	He	CO_2	O ₂	N_2	CH_4	O_2/N_2	$\mathrm{CO}_2/\mathrm{CH}_4$	
PTPDA-6FpDA	104.3	86.2	18.3	3.9	3.5	4.7	24.9	
PTPDA-m6FMe	89.1	58.5	14.2	2.7	2.3	5.2	25.2	
PTPDA-3MemPD	187	276	58.5	12.7	17.4	4.6	15.9	
BTPDA-6FpDA	115	114	24.2	5.8	5.0	4.2	22.9	
BTPDA-3MemPD	270	600	130	35.1	47.6	3.7	12.6	
	10 2							

^{*a*} 1 barrer = 10^{-10} cm³ (STP) cm/(s cm² cmHg).



Figure 6. Permeability/selectivity plot for the polyimides of this study. The upper bound calculated by Robeson (1991) and Robeson (2008)^{5,6} are also included.

show the best combination of permeability and selectivity because they are placed closer to the upper bound line. Also, and more interestingly, the gas productivity of these materials is much better than those derived from **BTPDA**, showing values of gas separation comparable to the best materials used for gas separations.^{27,28}

Conclusions

By using methods of molecular simulations, it was observed that a very bulky group placed in the 2' position of *m*-terphenyl dianhydride could bring about a very rigid monomer owing to the high rotational barrier caused by the strong steric hindrance of that bulky group with the lateral phenyl groups of *m*-terphenyl. In this way, the bulky group, computationally designed and selected to provide good properties, was the pivalamide moiety.

The new dianhydride monomer with a *m*-terphenyl group, 5'-t-butyl-2'-pivaloylimino-3,4,3",4"-m-terphenyltetracarboxylic dianhydride (**PTPDA**), has been obtained by a regioselective, efficient, and cost-effective synthesis using a modern C-H aryl coupling methodology. In addition, this route of synthesis involves the use of reactants bearing acid groups, which overcomes the necessity and drawback of oxidizing tetramethyl derivatives. The monomer was attained with good yield and high purity. Upon using the one- and two-step methods of polyimidation, a new set of polyimides was obtained, which could be processed into flexible and creasable films (except for the polymer derived from 4MepPD). These films were thoroughly characterized, showing good solubility in polar aprotic solvents and also in less common solvents for aromatic polyimides as chloroform and THF in some cases. Thermal stability was only slightly lower than reference polyimides from **BTPDA**, and T_{g} values were quite high with values higher than most of the literature-referenced polyimides. Polymer films exhibited a low water uptake and average mechanical properties good enough to allow their use on gas separation processes at high pressures. The increase in rigidity brought about a decrease in permeability with a concurrent augment of permselectivity, which is translated into a better balance of gas separation properties than those of polymers from BTPDA because these novel materials are closer to the Robeson limit, and thus they could be used on specific gas applications as air or natural gas purification.²

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Supporting Information Available: More detailed experimental section with elemental analyses and spectroscopic characterization (¹H and ¹³C NMR) data of intermediates and monomers, along with the description and bibliography of the computational methods employed in this article. This material is available free of charge via the Internet at http://pubs.acs.org.

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