Accepted Manuscript

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PII: S0032-3861(16)30350-0

DOI: [10.1016/j.polymer.2016.04.068](https://doi.org/10.1016/j.polymer.2016.04.068)

Reference: JPOL 18655

To appear in: *Polymer*

Received Date: 24 February 2016

Revised Date: 25 April 2016

Accepted Date: 30 April 2016

Please cite this article as: Ghanem B, Alaslai N, Miao X, Pinnau I, Novel 6FDA-based polyimides derived from sterically hindered Tröger's base diamines: Synthesis and gas permeation properties, *Polymer* (2016), doi: 10.1016/j.polymer.2016.04.068.

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**Novel 6FDA-based polyimides derived from sterically hindered Tröger's base diamines:
Synthesis and gas permeation properties**

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Abstract

Two novel Tröger's base-based di-*o*-substituted diamine monomers were synthesized and used to prepare two intrinsically microporous 6FDA-based polyimides (PIM-PI-TB-1 and PIM-PI-TB-2) with high molecular weight, high thermal stability and excellent solubility in common organic solvents. Compared to previously reported methods for preparing TB-based diamines, which are based on reduction of dimerized nitro-substituted anilines or condensation of phenylenediamine derivatives with dianhydrides, the novel protocol can be used to prepare different functionalized TB-based diamine monomers from a wide variety of aniline derivatives. PIM-PI-TB-1 (made from 6FDA and dibromo-tetramethyl-substituted TB diamine) and PIM-PI-TB-2 (made from 6FDA and tetramethyl-substituted TB diamine) are intrinsically microporous polymers with high BET surface areas of 440 m²/g and 580 m²/g, respectively. Pure-gas permeability coefficients of He, H₂, N₂, O₂, CH₄, and CO₂ were measured at 35 °C and 2 bar for fresh and 180 days aged films. Both TB-based polyimides exhibited high gas permeability with moderate selectivity. The gas permeability dropped significantly coupled with a moderate increase in selectivity after long-term physical aging of 180 days.

Keywords: Tröger's base polyimides, methyl/bromine-substituted diamines, gas permeation

1. Introduction

High free volume microporous ladder-type polymers, named polymers of intrinsic microporosity (PIMs), were introduced as promising materials for membrane-based gas separation applications in 2004 [1, 2]. The microporosity in PIMs is created by introduction of highly rigid and contorted molecular building blocks, which inhibit efficient molecular chain packing of the polymer matrix [3]. Aromatic polyimides (PIs) have been used as high performance materials in a variety of applications, including adhesives, composite materials, aerospace, electronic industries and gas separation membranes due to their exceptional thermal and chemical stability, mechanical robustness, film-forming ability and structural diversity [4-10]. Thus, an effective integration of the ladder-type, kinked monomers characteristic of PIM-1 into polyimide structures was used to produce intrinsically microporous polyimides with membrane-based gas separation performance close to the 2008 permeability/selectivity upper bounds [11-13]. Further developments with optimized structural designs by McKeown's and Pinnau's groups using ethanoanthracene- and 9,10-bridgehead-substituted triptycene moieties resulted in PIM-PIs that significantly exceeded the 2008 upper bounds for several gas pairs [14-18]. Recently, a new structural modification incorporating Tröger's base (TB) units into PIMs was first reported by McKeown [19] and followed subsequently by Guiver's group [20] and by Wang et al. [21, 22]. The TB moiety is a nitrogen-containing kinked heterocycle with V-shape bridged bicyclic linking group as a site of contortion that can rigidify polymers and generate microporosity. Therefore, incorporating TB units into ladder-type polymers (**Fig. 1a**) [23], TB-PIM polyimides (**Fig. 1 b, c and d**) [20-22] and insoluble network PIMs [24, 25] proved to be an efficient strategy for gas separation membranes and adsorption-based CO₂ capturing applications.

Fig. 1. Structure of soluble, amorphous TB-based (a) ladder polymers and (b-d) polyimides.

In this study, we report the synthesis of two novel sterically hindered TB-based-diamine monomers (TBDA1 and TBDA2, **Scheme 1a**) with *di-ortho*-substituted groups and explore their incorporation into novel 6FDA-based microporous polyimides *via* high temperature polycondensation mechanism (**Scheme 1b**). The two polyimides were fully characterized by ^1H NMR, FTIR, GPC, TGA and BET surface area measurements. Moreover, pure-gas permeation data for fresh and 180 days aged membranes are reported.

Scheme 1. Synthetic route of TB-based (a) diamine monomers TBDA1 and TBDA2 and (b) polyimides (PIM-PI-TB1 and PIM-PI-TB2).

2. Experimental

2.1. Materials

Trifluoroacetic acid, potassium nitrate, hydrazine monohydrate, paraformaldehyde, 4-bromo-2,5-dimethylaniline, 2,4-dimethylaniline, Pd/C catalyst (10 wt%) and isoquinoline were obtained from Aldrich and used without further purification. 4,4'-(Hexafluoroisopropylidene) diphthalic anhydride (6FDA) was purchased from Aldrich and purified by sublimation under vacuum prior to use. *m*-Cresol was purchased from Aldrich and was dried over 4 Å molecular sieves and kept

under nitrogen in the dark. All other solvents were obtained from various commercial sources and used as received.

2.2. Characterization methods

^1H and ^{13}C NMR (400 MHz) was recorded on a Bruker DRX 400 spectrometer in a suitable solvent. Chemical shifts (δ) are reported in ppm. Column chromatography was performed on silica gel 60A using suitable solvents. Fourier transform infrared (FTIR) measurements were carried out using a Varian 670-IR FTIR spectrometer. Gel permeation chromatography (GPC, Viscotek) analyses were performed using chloroform as an eluent. High-resolution mass spectroscopy (HRMS) was conducted on a Thermo LC/MS system with LTQ Orbitrap Velos detectors. Thermogravimetric analysis (TGA, TA Q-5000) measurements were carried out under nitrogen atmosphere. The BET surface area of the polyimides was determined by N_2 sorption at -196°C using a Micromeritics ASAP-2020. Powder polymer samples were degassed under high vacuum at 150°C for 24 hours prior to analysis. Analysis of the pore size distributions was performed using the NLDFT (Non-Local Density Functional Theory) model using N_2 (at -196°C) sorption isotherms for carbon slit pore geometry provided by ASAP 2020 version 4.02 software.

2.3. Monomer synthesis

2.3.1. Synthesis of 2,8-dibromo-1,4,7,10-tetramethyl-6,12-dihydro-5,11-methanodibenzo[b,f][1,5]-diazocine (TB1)

TB-1 was prepared according to the previously reported procedure by Œturala et al. [26] as follows: 4-bromo-2,5-dimethylaniline (5 g, 24.9 mmol) and paraformaldehyde (1.5 g, 50 mmol) were added in portions to trifluoroacetic acid (50 ml) at 15°C . The mixture was left in the ice-salt bath and allowed to slowly reach room temperature. After stirring for 24 hours, the mixture was poured into excess of cold aqueous ammonia and the PH was adjusted to 9-10 using ammonia solution and stirred vigorously for 2 hours before the precipitate was collected by filtration. The solid was washed with water and methanol, dried in a vacuum oven at 80°C to

give a white powder (7.91 g, 73% yield). ^1H NMR (CDCl_3 , δ): 2.11 (s, 6H), 2.36 (s, 6H), 3.92 (d, 2H), 4.22 (s, 2H), 4.44 (d, 2H), 7.30 (s, 2H).

2.3.2. Synthesis of 2,4,8,10-tetramethyl-6,12-dihydro-5,11-methanodibenzo[*b,f*][1,5]diazocine (TB2)

Following the above procedure used for the synthesis of TB-1, TB-2 was prepared from 2,4-dimethylaniline in 38% yield as white crystals after purification by silica gel column chromatography using DCM as eluent and recrystallization from dichloromethane/methanol mixture. ^1H NMR (CDCl_3 , δ): 2.17 (s, 6H), 2.36 (s, 6H), 3.91 (d, 2H), 4.28 (s, 2H), 4.51 (d, 2H), 6.54 (s, 2H), 6.84 (s, 2H). ^{13}C NMR (CDCl_3 , δ): 17.13, 20.91, 55.22, 67.90, 124.92, 127.83, 129.85, 132.64, 133.15, 143.51. HRMS(ESI): (m/z) calc. for $\text{C}_{19}\text{H}_{22}\text{N}_2$: 278.18; found 279.18 $[\text{M}+\text{H}]^+$, 280.19 $[\text{M}+2\text{H}]^+$, 281.19 $[\text{M}+3\text{H}]^+$.

2.3.3. Synthesis of 2,8-dibromo-1,4,7,10-tetramethyl-3,9-dinitro-6,12-dihydro-5,11-methanodibenzo[*b,f*][1,5]diazocine (TBDN1)

Following the procedure reported by Œturala et al. [26], TBDN1 was prepared as follows: Potassium nitrate (2.96 g, 29.3 mmol) was slowly added to a stirred solution of TB-1 (5.8 g, 13.30 mmol) and conc. H_2SO_4 (100 ml). After stirring at room temperature for 3 h, the reaction mixture was added to 500 ml cold water. The pH was adjusted to 8-9 using ammonia solution (30%) and the resulting beige precipitate was collected, washed with water, methanol and ether. The product was purified by column chromatography on silica gel with hexane/DCM 1:1 (v/v) as an eluent to give the dinitro product. ^1H NMR (CDCl_3 , δ): 2.23 (s, 6H), 2.32 (s, 6H), 4.03 (d, 2H), 4.21 (s, 2H), 4.55 (d, 2H). FTIR (powder, ν , cm^{-1}): 1519 (asym N-O, str), 1361 (sym N-O, str).

2.3.4. Synthesis of 2,4,8,10-tetramethyl-1,7-dinitro-6,12-dihydro-5,11-methanodibenzo[*b,f*][1,5]-diazocine (TBDN2)

Following the above procedure used for the synthesis of TBDN1, TBDN2 was prepared from 2,4,8,10-tetramethyl-6,12-dihydro-5,11-methanodibenzo[*b,f*][1,5]diazocine in 51% yield as yellow crystals after purification by column chromatography on silica gel with hexane/DCM 2:3 v/v as an eluent and recrystallization from dichloromethane/methanol mixture. ^1H NMR

(CDCl₃, δ): 2.23 (s, 6H), 2.38 (s, 6H), 3.87 (d, 2H), 4.26 (s, 2H), 4.62 (d, 2H), 7.02 (s, 2H). ¹³C NMR (CDCl₃, δ): 12.24, 18.15, 54.17, 65.03, 108.81, 124.32, 131.03, 135.22, 146.6, 151.42. FTIR (powder, ν , cm⁻¹): 1518 (asym N-O, str), 1360 (sym N-O, str). HRMS(ESI): (m/z) calc. for C₁₉H₂₀N₄O₄: 368.15; found 369.15 [M+H]⁺; 370.15 [M+2H]⁺, 371.16 [M+3H]⁺.

2.3.5 Synthesis of 2,8-dibromo-1,4,7,10-tetramethyl-3,9-diamino-6,12-dihydro-5,11-methanodibenzo[b,f][1,5]diazocine (TBDA1)

To a stirred mixture of TBDN1 (3.37 g, 6.4 mmol) and palladium/carbon 10% (0.40 g) in a mixture of 60 ml THF and 40 ml ethanol was added dropwise hydrazine hydrate (5.4 ml, 293 mmol) under N₂ atmosphere. After refluxing for 15 h, the cooled mixture was filtered into stirred water (800 ml). The resulting white powder was dried under vacuum at 130 °C for 20 h to give the diamine in 92% yield. ¹H NMR (DMSO-d₆, δ): 2.05 (s, 6H), 2.19 (s, 6H), 3.68 (d, 2H), 4.09 (s, 2H), 4.33 (d, 2H), 4.78 (s, 4H). ¹³C NMR (CDCl₃, δ): 12.50, 18.30, 54.82, 66.15, 108.44, 115.17, 116.36, 131.34, 142.68, 145.92. HRMS(ESI): (m/z) calc. for C₁₉H₂₂Br₂N₄: 464.02; Found 465.03 [M+H]⁺; 464.03 [M+2H]⁺, 467.03 [M+3H]⁺, FTIR (powder, ν , cm⁻¹): 3449, 3363 (NH₂ str.).

2.3.6 Synthesis of 2,4,8,10-tetramethyl-1,7-diamino-6,12-dihydro-5,11-methanodibenzo[b,f][1,5]diazocine (TBDA2)

Following the above procedure used for the synthesis of TBDA1, TBDA2 was prepared from 2,4,8,10-tetramethyl-1,7-dinitro-6,12-dihydro-5,11-methanodibenzo[b,f][1,5] diazocine in 72% yield as a white powder. ¹H NMR (DMSO-d₆, δ): 2.45 (s, 6H), 2.72 (s, 6H), 4.32 (d, 2H), 4.37 (s, 4H), 4.57 (s, 2H), 4.69 (d, 2H), 7.14 (s, 2H). ¹³C NMR (CDCl₃, δ): 16.80, 17.61, 52.63, 66.54, 112.99, 116.02, 119.39, 130.14, 140.87, 144.86. HRMS(ESI): (m/z) calc. for C₁₉H₂₄N₄: 308.20; Found 309.17 [M+H]⁺, 309.17 [M+H]⁺; 310.17 [M+H]⁺; 310.178 [M+2H]⁺. FTIR (powder, ν , cm⁻¹): 3448, 3363 (NH₂ str.).

2.4. Synthesis of TB-based polyimides (PIM-PI-TB): General procedure

To a solution containing diamine monomer (1.0 mmol) in 3 ml freshly distilled *m*-cresol was added 1.0 mmol of the dianhydride monomer in one portion. After stirring for 15 minutes under a flow of nitrogen, the temperature was raised to 80 °C. Catalytic amount of isoquinoline (3

drops) was added and the temperature was raised to 200 °C gradually and kept at this temperature for 2 h before being poured into methanol (200 ml). The resulting fibrous polymer was collected by filtration, purified by reprecipitation from chloroform/methanol mixture and dried under vacuum at 130 °C for 20 h.

2.4.1 Synthesis of PIM-PI-TB-1

Following the above procedure, polyimide PIM-PI-TB-1 was prepared from 6FDA and TBDA1 in 87% yield. ^1H NMR (DMSO-d_6 , δ): 2.26 (s, 6H), 2.36 (s, 6H), 3.99 (d, 2H), 4.30 (s, 2H), 4.55 (d, 2H), 7.93-8.08 (m, 6H). FTIR (Membrane, ν , cm^{-1}): 1789 (asym C=O, str), 1725 (sym C=O, str), 1367 (C-N, str), 885 (imide ring deformation). Analysis by GPC (CHCl_3): $M_n = 35500 \text{ g mol}^{-1}$, $M_w = 55600 \text{ g mol}^{-1}$ relative to polystyrene, PDI = 1.57. BET surface area = $440 \text{ m}^2 \text{ g}^{-1}$, total pore volume = $0.3495 \text{ cm}^3 \text{ g}^{-1}$ at ($p/p_o = 0.98$, adsorption). TGA analysis: (Nitrogen), initial weight loss due to thermal degradation commences at $T_d = 400 \text{ }^\circ\text{C}$.

2.4.2. Synthesis of PIM-PI-TB-2

Following the above procedure, polyimide PIM-PI-TB-2 was prepared from 6FDA and TBDA2 in 93% yield. ^1H NMR (400MHz, CDCl_3) δ (ppm): 2.10 (s, 6H), 2.34 (d, 6H), 3.94 (t, 2H), 4.34 (s, 2H), 4.47 (d, 2H), 7.12 (d, 2H), 8.01-8.12 (m, 6H). FTIR (Membrane, ν , cm^{-1}): 1787 (asym C=O, str), 1723 (sym C=O, str), 1369 (C-N, str). Analysis by GPC (CHCl_3): $M_n = 65900 \text{ g mol}^{-1}$, $M_w = 105100 \text{ g mol}^{-1}$ relative to polystyrene, PDI = 1.59. BET surface area = $580 \text{ m}^2 \text{ g}^{-1}$, total pore volume = $0.5442 \text{ cm}^3 \text{ g}^{-1}$ at ($p/p_o = 0.98$, adsorption). TGA analysis: (Nitrogen), initial weight loss due to thermal degradation commences at $T_d = 440 \text{ }^\circ\text{C}$.

2.5. Polymer film preparation

Solutions of PIM-PI-TB-1 and PIM-PI-TB-2 in chloroform (5 w/v %) were filtered through $0.45 \mu\text{m}$ polypropylene filters and isotropic films were obtained by slow evaporation of the solvents at room temperature from a levelled and covered glass Petri dish. To remove any traces of residual solvent, the dry membranes were soaked in methanol for 12 h, air-dried, and finally dried at $120 \text{ }^\circ\text{C}$ in a vacuum oven for 24 h. TGA was used to check that all solvent was completely removed from the films. The resulting tough films with thickness of $65 \pm 5 \mu\text{m}$ were used for gas permeability measurements. Film thickness and effective areas for gas permeation

measurement were determined by a digital micrometer and scanner, respectively. The fresh film samples used for the initial permeation tests were stored for 180 days under dry conditions in a desiccator. These aged films were subsequently used for gas permeation studies.

2.6. Physisorption measurement

Nitrogen sorption measurements were performed up to 1 bar using a Micromeritics ASAP-2020 apparatus equipped with a micropore upgrade. Powder samples of PIM-PI-TB-1 and PIM-PI-TB21 were dried at 150 °C under high vacuum for 24 h prior to measurement. All data were collected and analyzed using ASAP 2020 software version 4.02. The BET surface area was obtained from the N₂ isotherm at relative pressures of $0.1 < p/p_o < 1.0$, where $p_o = 1$ bar is the saturation pressure for N₂ and p is the gas pressure. Maximum pore volumes were identified at $p/p_o < 0.98$ of the N₂ isotherm. Analysis of the pore size distributions was performed using the NLDFT (non-local density functional theory) model for carbon slit pore geometry.

2.7. Gas permeation measurements

The pure-gas permeability of the polyimides was determined with a custom-designed permeation system using the constant-volume/variable-pressure method. The permeability was calculated from the steady-state rate of increase in pressure of the gas (dp/dt) in the permeate reservoir using the following equation:

$$P = \frac{VL}{ATp_{up} \times 0.278} \times \frac{dp}{dt} \times 10^{10}$$

where P , V , L , A , T , p_{up} are the permeability coefficient in barrers (1 barrer = 10^{-10} cm³(STP) cm/cm² s cmHg), volume of the downstream gas reservoir, membrane thickness, membrane area, operating temperature and the upstream pressure, respectively. The pure-gas permeability of He, H₂, N₂, O₂, CH₄, and CO₂ was measured at 35 °C and 2 bar. The apparent diffusion coefficient D (cm²/s) of the polymer membrane was calculated by $D = L^2/6\theta$, where θ is the time lag of the permeability measurement. The solubility coefficient S (cm³(STP)/cm³ cmHg) was obtained from the relationship $S = P/D$. The pure-gas selectivity was calculated as: $\alpha_{A/B} = P_A/P_B$.

3. Results and discussion

3.1. Synthesis of Tröger's base-containing diamine monomers

Two new TB-containing diamines, TBDA1 and TBDA2, were synthesized *via* a three-step synthetic route (Scheme 1a). The key intermediates, 2,8-dibromo-1,4,7,10-tetramethyl-6,12-dihydro-5,11-methanodibenzo[*b,f*][1,5]-diazocine (TB1) and 2,4,8,10-tetramethyl-6,12-dihydro-5,11-methanodibenzo[*b,f*][1,5]diazocine (TB2) were prepared by the conventional acid-catalyzed condensation of 4-bromo-2,5-dimethylaniline or 2,4-dimethylaniline with paraformaldehyde, respectively, using a previously reported procedure [26]. Selective nitration of TB1 and TB2 using potassium nitrate and sulfuric acid followed by reduction of the nitro groups using hydrazine hydrate and Pd/C gave the TB-diamine monomers. The molecular structures of all products and two diamines were confirmed by ^1H and ^{13}C NMR, FTIR and mass spectroscopic analysis. In addition, the molecular structure of 2,4,8,10-tetramethyl-1,7-dinitro-6,12-dihydro-5,11-methanodibenzo[*b,f*][1,5]-diazocine (TBDN2) was confirmed by single-crystal x-ray crystallography (**Fig. SI-1**). In the ^1H NMR spectra the signals at 2.05 - 2.73 ppm were assigned to the protons of methyl groups and the three signals in the range of 3.63 - 4.69 ppm confirmed the presence of TB units in the diamines. The amine group protons for TBDA1 and TBDA2 appeared at 4.37 and 4.78 ppm, respectively. The FTIR spectra for both diamines exhibited characteristic double absorption bands in the range of 3363-3448 cm^{-1} due to N-H stretching vibrations of the amine groups. The exact molecular mass of both diamines was confirmed by HRMS analyses.

3.2. Synthesis and characterization of TB-based polyimides

Two novel TB-based polyimides with intrinsic microporosity (PIM-PI-TB-1 and PIM-PI-TB-2) were synthesized via the high-temperature one-step cycloimidization reaction between equimolar amounts of the commercially available 6FDA and the novel diamine monomers in *m*-cresol (**Scheme 1b**). The molecular structures of the two polymers were confirmed by FTIR and ^1H NMR spectroscopy. The characteristic absorption bands of the imide groups were observed at about 1780 and 1720 cm^{-1} (imide asymmetric and symmetric C=O, stretching), and 1370 cm^{-1} (C-N, stretching frequency). ^1H NMR spectra of the two polymers were consistent with their proposed chemical structures (**Fig. 2a** and **Fig. 2b**, as representative example). The three signals

in the range of 3.94 - 4.55 confirmed the presence of the TB unit in the polymer backbone. No signals above 10 ppm were observed indicating complete imidization. The two polyimides were further characterized by GPC, TGA, and BET surface area. High average molecular weights and narrow polydispersities of the polyimides were obtained by GPC (**Table 1**).

Fig. 2. (a) FTIR spectrum and (b) ^1H NMR spectrum of PIM-PI-TB-1.

Table 1

Physical properties of PIM-PI-TB-1 and PIM-PI-TB-2 and related TB polyimides.

Polymer	BET ($\text{m}^2 \text{g}^{-1}$)	M_n (g mol^{-1})	M_w (g mol^{-1})	PDI	T_d ($^{\circ}\text{C}$)	Max pore volume ($\text{cm}^3 \text{g}^{-1}$)
PIM-PI-TB-1	440	35500	55600	1.57	400	0.3495
PIM-PI-TB-2	580	65900	105100	1.59	440	0.5442
PI-TB-1 [20]	544	52500	151000	2.86	487	0.431
TBDA2-6FDA-PI [21]	325	23000	52000	2.3	449	-

The TB-based PIs showed excellent solubility in low-boiling point solvents, such as acetone, chloroform etc. and high-boiling point polar aprotic solvents, such as DMF, DMAc etc. (**Table 2**). The excellent solubility can be attributed to the contorted V-shape of the TB moieties, the

restricted rotation of the imide linkages resulting from *o*-substituents and the nonplanar bulky CF₃-groups [27-29], which reduce the interchain interactions.

Table 2

Solubility of the Tröger's base PIM-PIs in various organic solvents.

Polymer	Acetone	CHCl ₃	DCM	THF	DMAc	DMF	DMSO	NMP	Methanol
PIM-PI-TB-1	+	+	+	+	+	+	+	+	-
PIM-PI-TB-2	+	+	+	+	+	+	+	+	-

+ completely dissolved; - insoluble. CHCl₃: chloroform; NMP: N-methyl-2-pyrrolidone; DMAc: N,N-dimethylacetamide; DCM: dichloromethane; THF: tetrahydrofuran; DMSO: dimethylsulfoxide.

The thermal stability of PIM-PI-TB-1 and PIM-PI-TB-2 was evaluated by TGA (**Fig. 3**). As expected for polyimides, both polymers exhibited good thermal stability with decomposition temperatures exceeding 400 °C (**Table 2**) in N₂ atmosphere.

Fig. 3. Thermal gravimetric analysis of PIM-PI-TB-1 and PIM-PI-TB-2 under N₂ atmosphere.

3.3 Physisorption properties.

Recently, the introduction of a *single ortho*-substituted methyl group to the C-N imide linkages in rigid TB-based PIs was reported by McKeown and Carta and later Wang et al. [19, 21]. The *ortho*-methyl group restricts the rotation around these linkages – hence leading to high chain rigidity and poor chain packing. For example, TBDA2-6FDA-PI (**Fig. 1c**) with a single *o*-substituted methyl group to each imide linkage possessed a surface area of 325 m² g⁻¹. The pore structures of PIM-PI-TB-1 and PIM-PI-TB-2 powders were qualitatively determined by N₂ adsorption measurements at -196 °C (**Fig. 4a**) and displayed rapid nitrogen uptake at very low relative pressure indicating a typical microporous texture. The apparent BET surface areas for PIM-PI-TB-1 and PIM-PI-TB-2 were 440 m²/g and 580 m²/g, respectively. Moreover, the pore size distribution (PSD) deduced from N₂ adsorption isotherms (**Fig. 4b**) using NLDFT showed a major narrow pore size in the range of 5 to 7 Å indicating ultramicroporous voids for both polymers. This may be due to the enhanced rigidity of the sterically hindered imide linkages caused by the two *o*-methyl groups or one *o*-methyl- and *o*-bromine group to each imide linkage. The surface area of TB-PIs obtained by our protocol may be further tuned by the choice of the aniline derivatives.

Fig. 4. (a) Physisorption isotherms using N₂ at -196 °C and (b) NLDFT-based estimated pore size distribution obtained from N₂ isotherms (assuming carbon slit-pore geometry) for PIM-PI-TB-1 and PIM-PI-TB-2.

3.4. Gas transport properties

Pure-gas permeation experiments were performed at 2 bar and 35 °C on fresh and 180 days aged samples of PIM-PI-TB-1 and PIM-PI-TB-2. For fresh samples, both polyimides exhibited high permeabilities and moderate selectivities, as shown in **Table 3**. The gas permeabilities and selectivities of the two TB-based polyimides were similar; for example the O₂ permeabilities of PIM-PI-TB1 and PIM-PI-TB2 were 133 and 123 barrer with moderate O₂/N₂ selectivities of 3.2 and 3.6, respectively. This result indicates that caging the imide linkage either between two *ortho* positioned methyl groups or methyl/bromine substituents has only a small effect on the permeability or selectivity of the TB polyimides. The gas permeabilities of both polyimides decreased in the order: CO₂~H₂>He>O₂>N₂~CH₄, a trend that indicates that the TB polyimides have only moderate size-sieving properties. The gas diffusion and solubility values of PIM-PI-TB-1 and PIM-PI-TB-2 are provided in the supplementary information (Table **SI-1** and **SI-2**).

Table 3

Pure-gas permeabilities and selectivities for fresh and 180 days aged PIM-PI-TB-1 and PIM-PI-TB-2 (at 2 bar; 35 °C) compared to related TB-based polyimides (at 1 bar; 35 °C).

Polymer	Pure-gas permeability (barrer)						Selectivity (α)		
	He	H ₂	N ₂	O ₂	CH ₄	CO ₂	CO ₂ /CH ₄	H ₂ /CH ₄	O ₂ /N ₂
Di- <i>o</i> -substituted PIs									
PIM-PI-TB-1	300	612	42	133	44	662	15	14	3.2
Aged PIM-PI-TB-1	(241)	(380)	(19)	(70)	(16)	(361)	(23)	(24)	(3.7)
PIM-PI-TB-2	328	582	34	123	31	595	19	19	3.6
Aged PIM-PI-TB-2	(269)	(405)	(19)	(77)	(18)	(376)	(21)	(23)	(4.1)
Single- <i>o</i> -substituted PIs									
PI-TB-1 [20]	376	607	31	119	27	457	17	22	3.8
PI-TB-3 [30]	221	299	9.5	42	6.7	218	33	45	4.5
TBDA1-6FDA-PI [21]	199	253	6.5	28	3.3	155	47	77	3.9
TBDA2-6FDA-PI [21]	223	390	12	47	8	285	36	49	4.0

Like most microporous glassy polymers, the two TB PIs undergo significant physical aging, where the chains gradually assume a tighter packing arrangement towards their equilibrium state [31, 32]. The gas permeation properties of PIM-PI-TB-1 and PIM-PI-TB-2 aged for 180 days are reported in **Table 3** (values in parentheses). The freshly prepared films exhibited about 18–60% reductions in gas permeability with only small to moderate increase in selectivity. The decrease in permeability resulted from a simultaneous decrease in gas diffusion and solubility coefficients due to densification of the polyimides. A possible solution to the physical aging process in glassy polymer membranes has recently been proposed by Lau et al. wherein incorporation of a porous aromatic framework (PAF-1) in an intrinsically microporous polymer (PIM-1) showed significantly inhibited aging and essentially no loss in permeability over time [33]. Compared to previously reported single-ortho-substituted TB polyimides [20, 21, 30], shown in Table 3, the di-ortho-substituted TB polyimides of this study showed lower selectivity, specifically for CO₂/CH₄ and H₂/CH₄ separations. A similar trend was reported in an earlier study for 6FDA-based polyimides in a series of methyl-substituted phenylenediamines, where permeability increased and selectivities decreased with increasing degree of substitution [34].

4. Conclusions

An efficient approach to the synthesis of novel Tröger's base-containing aromatic diamines was developed, which involves the selective nitration of substituted 6,12-dihydro-5,11-methanodibenzo[*b,f*][1,5]diazocines, prepared by the condensation of aniline derivatives with paraformaldehyde in acidic medium, followed by reduction of the dinitro groups. The two diamines of this study, TBDA1 and TBDA2, were used to prepare two intrinsically microporous TB-based polyimides by the high-temperature polycondensation reaction with commercially available 6FDA. The two polyimides exhibited good thermal stability, high molecular weight and excellent solubility in common organic solvents. The BET surface area results showed that the TB moiety with *di-ortho* functionalization can introduce rigidity and significant microporosity to the PIs, which consequently provided high permeability. However, the selectivities of the 6FDA-derived TBDA1 and TBDA2 polyimides were only moderately attractive for commercial gas separation membrane applications.

Acknowledgments

The research reported in this publication was supported by funding from King Abdullah University of Science and Technology (KAUST).

Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.polymer.2016.xx.xxx>.

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Highlights

- Two novel sterically hindered Tröger's base based-polyimides were synthesized.
- PIM-PI-TB-1 and PIM-PI-TB-2 showed BET surface areas of 440 and 580 m²/g, respectively.
- PIM-PI-TB-1 and PIM-PI-TB-2 demonstrated high gas permeability and moderate selectivity.
- PIM-PI-TB-1 and PIM-PI-TB-2 exhibited reductions in gas permeability due to physical aging.