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Synthesis, Characterization, and Gas Permeation Properties of a Novel Group of Polymers with Intrinsic Microporosity: PIM-Polyimides

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ABSTRACT: A range of polyimides with characteristics similar to a polymer of intrinsic microporosity (PIM) were prepared by reaction with various aromatic diamines of a bis(carboxylic anhydride) incorporating a spiro-center. The polymers exhibited high surface area, as determined by nitrogen adsorption, and high thermal stability. Membrane gas permeation experiments showed PIM-polyimides to be among the most permeable of all polyimides and to have selectivities close to the upper bound for several important gas pairs. A group contribution method was used to predict permeability coefficients and separation factors for further PIM-polyimide structures, revealing worthwhile targets for future synthetic efforts.

Introduction

A polymer of intrinsic microporosity (**PIM-1**, Scheme 1) discovered several years ago[1,2] has attracted great interest as a novel and rather unusual material for membrane gas separations. It has been prepared by several groups of researchers, and its transport properties and free volume have been described in detail.[3−9] The most important features of this polymer are (i) relatively high gas permeability, with a good permselectivity, so the data points are above Robeson's 1991 upper bound[10] for several important gas pairs, and help to define the recently revised upper bounds;[11] (ii) strong sensitivity of the transport parameters to the protocol of film-forming procedure; (iii) extremely high solubility coefficients, the largest among all the polymers studied; (iv) large free volume as measured by independent probe methods; (v) low activation energies of permeation; and (vi) a weak tendency to aging.

Some of these properties could be explained[8] by the peculiarities of its structure, specifically the presence of spirobisindane and dibenzodioxane moieties in the repeat units of this polymer. It is interesting, therefore, to study other polymers that are structurally akin to **PIM-1**. With this aim in mind, we prepared and studied a series of polyimides (Scheme 2), called below PIM-PIs, whose "dianhydride" component is very similar to **PIM-1** and whose diamine components vary significantly. Preliminary data for three of these PIM-PIs, namely **PIM-PI-1**, **PIM-PI-3**, and **PIM-PI-8**, have been reported previously.[12] Zhang et al.[13] have also prepared the polymer designated **PIM-PI-1**, and similar polyimides, following a different synthetic scheme. In this paper we give a detailed description of our procedures for preparation of monomers and polymers. The gas permeation properties of this series of PIM-PIs were tested first for six gases using a barometric technique. Then, for two polymers, namely **PIM-PI-1** and **PIM-PI-8**, a detailed gas chromatographic study of the effects of film-forming protocol on gas permeability was performed. In addition, an analysis of the permeability of this group of polyimides was carried out using the group contribution method, and some predictions are made for polymers not yet prepared.

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Experimental Section

Materials. Bisphthalonitrile **2** was synthesized according to the procedure of Maffei et al.[14] from 5,5′,6,6′-tetrahydroxy-3,3,3′,3′-tetramethyl-1,1′-spirobisindane and 4,5-dichlorophthalonitrile in anhydrous DMF. 4,5-Dichlorophthalonitrile was prepared according to the procedure of Wohrle et al.[15] The compounds 2,3,5,6-tetramethyl-1,4-phenylenediamine (Aldrich) and 1,5-diaminonaphthalene (Lancaster) were purified by recrystallization from ethyl acetate/petroleum ether (40−60). The compounds 5,5′-(hexafluoroisopropylidene)-di-*o*-toluidine (Aldrich), 4,4′-(hexafluoroisopropylidene)dianiline (Apollo), 2,2′-bis(trifluoromethyl)-4,4′-diaminobiphenyl (Apollo), 3,3′-dimethylnaphthidine (TCI), 5,5′,6,6′-tetrahydroxy-3,3,3′,3′-tetramethyl-1,1′-spirobisindane (Alfa Aesar), anhydrous potassium carbonate (K_2CO_3; Fisher Scientific), acetic anhydride (Aldrich), quinoline (Aldrich), and *N,N*-dimethylformamide (DMF; Aldrich) were used as received. *m*-Cresol (Lancaster) was purified by drying over calcium chloride followed by distillation under reduced pressure over molecular sieves. All other solvents were obtained from various commercial sources and used without further purification.

Synthesis of Dianhydride Monomer (An-1). To a solution of potassium hydroxide (28.2 g, 0.5 mol) in a mixture of ethanol−water (1:1 volume; 280 mL) was added bisphthalonitrile **2** (14.7 g, 0.025 mol). The reaction mixture was then refluxed with stirring for 20 h, and the resulting solution was hot-filtered to remove any insoluble particles. After cooling, the

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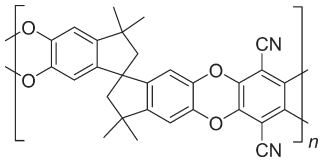
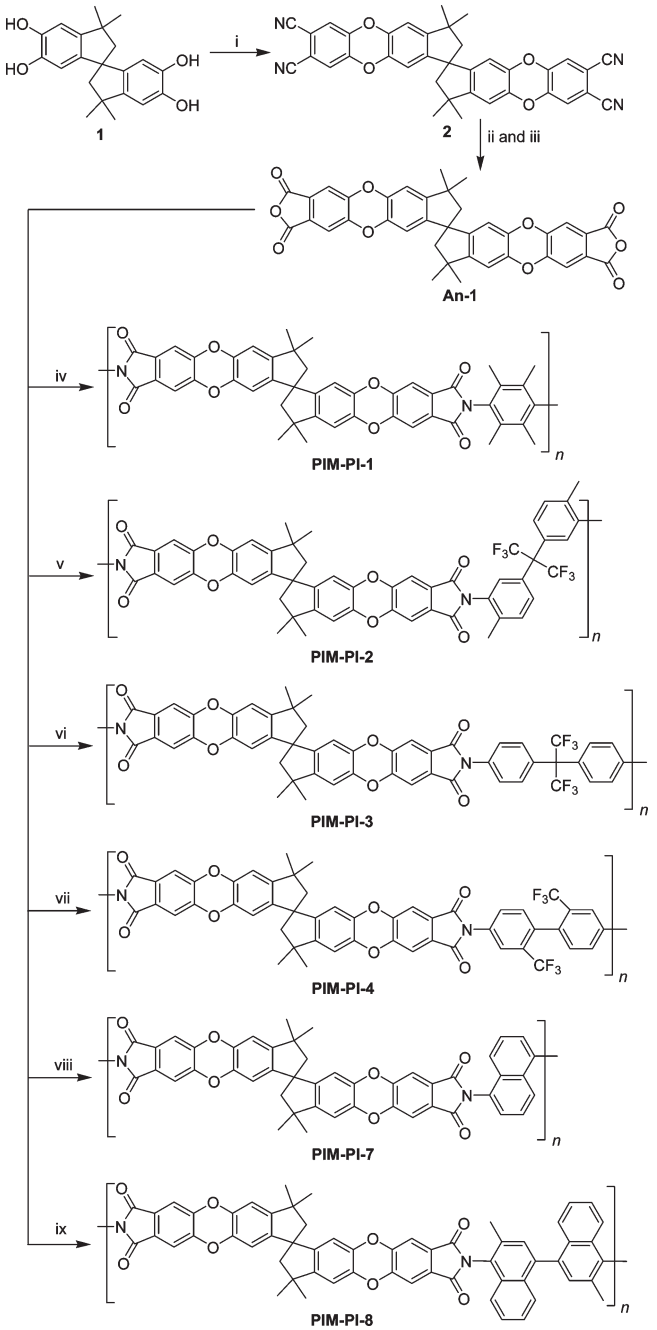
Scheme 1. Molecular Structure of PIM-1



Scheme 2. Preparation of PIM-Polyimides[a]



[a] Reagents and conditions: (i) 4,5-dichlorophthalonitrile, K_2CO_3, DMF, 80 °C; (ii) KOH, EtOH/H_2O, reflux, 24 h; (iii) acetic anhydride, reflux, 24 h; (iv) 2,3,5,6-tetramethyl-1,4-phenylenediamine, *m*-cresol, quinoline, toluene, reflux, 5 h; (v) 5,5′-(hexafluoroisopropylidene)di-*o*-toluidine, *m*-cresol, quinoline, toluene, reflux, 5 h; (vi) 4,4′-(hexafluoroisopropylidene)dianiline, *m*-cresol, quinoline, toluene, reflux, 5 h; (vii) 2,2′-bis(trifluoromethyl)-4,4′-diaminobiphenyl, *m*-cresol, quinoline, toluene, reflux, 5 h; (viii) 1,5-diaminonaphthalene, *m*-cresol, quinoline, toluene, reflux, 5 h; (ix) 3,3′-dimethylnaphthidine, *m*-cresol, quinoline, toluene, reflux, 5 h.

filtrate was acidified by concentrated hydrochloric acid. The resulting white precipitate was filtered off, washed with cold water (1000 mL), and dried to yield the tetracarboxylic acid (15.8 g, 95% yield) as a white solid which was used in the following reaction without further purification. ^{1}H NMR (DMSO-d_6, δ ppm): 1.3 (6H, s, CH_3), 1.33 (6H, s, CH_3), 2.11 (2H, d, J = 13 Hz, CH_2), 2.27 (2H, d, J = 13 Hz, CH_2), 6.34 (2H, s, Ar), 6.90 (2H, s, Ar), 7.34 (2H, s, Ar), 7.41(2H, s, Ar). FT-IR (thin film, cm^{-1}): 3373 (OH), 3017 (aromatic C−H), 2945 (aliphatic C−H), 1715 (C═O), 1216 (C−O−C str).

The tetracarboxylic acid (13.46 g; 0.02 mol) was added to acetic anhydride (105 mL). The resulting mixture was heated under reflux and a nitrogen atmosphere for 24 h. On cooling, the pale yellow powder was collected by filtration, washed with acetic acid and toluene, and dried at 80 °C under vacuum to give **An-1** (11 g, 86% yield), which was recrystallized from toluene and dried in a vacuum oven prior to use. Analysis calculated for $C_{37}H_{24}O_{10}$: C, 70.7; H, 3.85%. Found: C, 69.51; H, 3.43%. ^{1}H NMR (DMSO-d_6, δ ppm): 1.07 (s, 6H, CH_3), 1.22 (s, 6H, CH_3), 1.94 (d, 1H, J = 13 Hz, CH_2), 2.09 (d, 1H, J = 13 Hz, CH_2), 6.19 (s, 1H, Ar−H), 6.77 (s, 1H, Ar−H), 7.39 (s, 1H, Ar−H), 7.43 (s, 1H, Ar−H); m/z (EI) 628 (M+). FT-IR (thin film cm^{-1}): 3059 (aromatic C−H), 2952 (aliphatic C−H), 1843 (asymmetrical C═O, str), 1771 (symmetrical C═O, str), 1327 (C−O str).

Typical Procedure for the Synthesis of PIM-PIs. To a dried 50 mL reaction tube equipped with a Dean−Stark trap, nitrogen inlet, and reflux condenser were added **An-1** (1.15 g, 1.83 mmol), 2,3,5,6-tetramethyl-1,4-phenylenediamine (0.3 g, 1.83 mmol), *m*-cresol (10 mL), quinoline (0.1 mL), and anhydrous toluene (2 mL). After the reaction mixture had been stirred at room temperature for 0.5 h, the temperature was raised gradually to 200 °C and then held at that temperature for 5 h. During this time water was removed from the reaction mixture by azeotropic distillation. The resulting viscous solution was cooled and diluted with chloroform (20 mL) and then added dropwise to vigorously stirred methanol (600 mL). The resulting solid precipitate was collected by filtration. Purification was achieved by reprecipitation from chloroform (20 mL) into methanol (500 mL) to give **PIM-PI-1** (BD-100) as a pale-yellow powder, which was dried in a vacuum oven at 90 °C (1.3 g, 94% yield). Analysis calculated for $C_{47}H_{36}N_2O_8$ (repeat unit): C, 74.59; H, 4.79; N, 3.7%. Found: C, 72.77; H, 4.62; N, 3.46. ^{1}H NMR ($CDCl_3$, δ ppm): 1.27 (6H, br s, CH_3), 1.32 (6H, br s, CH_3), 2.0 (12H, br s, CH_3), 2.13 (2H, br d, J = 13 Hz, CH_2), 2.25 (2H, br d, J = 13 Hz, CH_2), 6.34 (2H, br s, Ar), 6.68 (2H, br s, Ar), 7.22 (2H, br s, Ar), 7.3 (2H, br s, Ar). FT-IR (thin film cm^{-1}): 1781 (asym C═O, str), 1726 (sym C═O, str), 1360 (C−N, str), 746 (imide ring deformation). GPC: M_n = 17 000, M_w = 38 000 g mol^{-1}, M_w/M_n = 2.2. BET surface area = 682 m^2 g^{-1}, total pore volume = 0.62 cm^3 g^{-1} (at p/p^o = 0.98, adsorption). TGA analysis: (nitrogen) initial weight loss due to thermal degradation commences at ∼465 °C; (air) initial weight loss due to thermal degradation commences at ∼400 °C. Another batch of **PIM-PI-1** (BD-99) was prepared in the same manner.

The following polymers were prepared using the same procedure.

PIM-PI-2 (BD-101) was prepared from **An-1** and 5,5′-(hexafluoroisopropylidene)-di-*o*-toluidine as an off-white powder in 85% yield. Analysis calculated for $C_{54}H_{36}F_6N_2O_8$ (repeat unit): C, 67.93; H, 3.80; N, 2.93%. Found: C, 65.54; H, 3.43; N, 2.63. ^{1}H NMR ($CDCl_3$, δ ppm): 1.25 (6H, br s, CH_3), 1.3 (6H, br s, CH_3), 2.12−2.15 (8H, br m, 2CH_3 and CH_2), 2.20 (2H, br d, J = 13 Hz, CH_2), 6.31 (2H, br s, Ar), 6.64 (2H, br s, Ar), 7.18−7.35 (10H, br m, Ar). FT-IR (thin film cm^{-1}): 1780 (asym C═O, str), 1725 (sym C═O, str), 1368 (C−N, str), 746 (imide ring deformation). GPC: M_n = 30 000, M_w = 49 000 g mol^{-1}, M_w/M_n = 1.6. BET surface area = 500 m^2 g^{-1}, total pore volume = 0.63 cm^3 g^{-1} (at p/p^o = 0.9, adsorption). TGA analysis: (nitrogen) initial weight loss due to thermal degradation commences at ∼485 °C; (air) initial weight loss due to thermal degradation commences at ∼427 °C.

PIM-PI-3 (BD-102) was prepared from **An-1** and 4,4′-(hexafluoroisopropylidene)dianiline as an off-white powder in 93% yield. Analysis calculated for $C_{52}H_{32}F_6N_2O_8$ (repeat unit): C, 67.39; H, 3.48; N, 3.02%). Found: C, 65.66; H, 3.26; N, 2.81. ^{1}H NMR ($CDCl_3$, δ ppm): 1.25 (6H, br s, CH_3), 1.31 (6H, br s, CH_3), 2.12 (2H, br d, $J = 13$ Hz, CH_2), 2.27 (2H, br d, $J = 13$ Hz, CH_2), 6.28 (2H, br s, Ar), 6.65 (2H, br s, Ar), 7.19 (2H, br s, Ar), 7.29 (2H, br s, Ar), 7.40−7.48 (8H, br m, Ar). FT-IR (thin film cm^{-1}): 1780 (asym C═O, str), 1725 (sym C═O, str), 1357 (C−N, str), 743 (imide ring deformation). GPC: M_n = 22 000, M_w = 45 000 g mol^{-1}, M_w/M_n = 2.0. BET surface area = 471 m^2 g^{-1}, total pore volume = 0.52 cm^3 g^{-1} at (p/p^o = 0.98, adsorption). TGA analysis: (nitrogen) initial weight loss due to thermal degradation commences at ∼480 °C; (air) initial weight loss due to thermal degradation commences at ∼420 °C.

PIM-PI-4 (BD-103) was prepared from **An-1** and 2,2′-bis-(trifluoromethyl)-4,4′-diaminobiphenyl as an off-white powder in 92% yield. Analysis calculated for $C_{51}H_{30}F_6N_2O_8$ (repeat unit): C, 67.11; H, 3.31; N, 3.07. Found: C, 65.33; H; 3.06; N; 2.78. ^{1}H NMR ($CDCl_3$, δ ppm): 1.26 (6H, br s, CH_3), 1.32 (6H, br s, CH_3), 2.24 (2H, br d, $J = 13$ Hz, CH_2), 2.37 (2H, br d, $J = 13$ Hz, CH_2), 6.37 (2H, br s, Ar), 6.67 (2H, br s, Ar), 7.23 (2H, br s, Ar), 7.32 (2H, br s, Ar), 7.37 (2H, d, $J = 10$ Hz, Ar), 7.63 (2H, br d, $J = 13$ Hz, Ar), 7.84 (2H, s, Ar). FT-IR (thin film cm^{-1}): 1781 (asym C═O, str), 1730 (sym C═O, str), 1356 (C−N, str), 742 (imide ring deformation). GPC: M_n = 11 000, M_w = 31 000 g mol^{-1}, M_w/M_n = 2.8. BET surface area = 486 m^2 g^{-1}, total pore volume = 0.65 cm^3 g^{-1} at (p/p^o = 0.98, adsorption). TGA analysis: (nitrogen) initial weight loss due to thermal degradation commences at ∼485 °C; (air) initial weight loss due to thermal degradation commences at ∼445 °C.

PIM-PI-7 (BD-106) was prepared from **An-1** and 1,5-naphthalenediamine as off-white powder in 92% yield). Analysis calculated for $C_{47}H_{30}N_2O_8$ (repeat unit): C, 75.19; H, 5.36; N, 4.96%). Found: C, 72.55; H, 3.71; N, 3.74. ^{1}H NMR ($CDCl_3$, δ ppm): 1.27 (6H, br s, CH_3), 1.33 (6H, br s, CH_3), 2.12 (2H, br d, $J = 13$ Hz, CH_2), 2.29 (2H, br d, $J = 13$ Hz, CH_2), 6.35 (2H, br s, Ar), 6.69 (2H, br s, Ar), 7.27−7.67 (10H, br m, Ar). FT-IR (thin film cm^{-1}): 1779 (asym C═O, str), 1727 (sym C═O, str), 1359 (C−N, str), 746 (imide ring deformation). GPC: M_n = 11 000, M_w = 42 000 g mol^{-1}, M_w/M_n = 3.8. BET surface area = 485 m^2 g^{-1}, total pore volume = 0.48 cm^3 g^{-1} (at p/p^o = 0.98, adsorption). TGA analysis: (nitrogen) initial weight loss due to thermal degradation commences at ∼492 °C.

PIM-PI-8 (BD-123) was prepared from **An-1** and 3,3′-dimethylnaphthidine as off-white powder in 97% yield. Analysis calculated for $C_{59}H_{40}N_2O_8$ (repeat unit): C, 78.31; H, 4.46; N, 3.10%). Found: C, 76.45; H, 4.09; N, 2.83. ^{1}H NMR ($CDCl_3$, δ ppm): 1.29 (6H, br s, CH_3), 1.35 (6H, br s, CH_3), 2.17 (2H, d, CH_2), 2.33−2.35 (8H, br m CH_2, CH_3), 6.39 (2H, br s, Ar), 6.71 (2H, br s, Ar), 7.24−7.53 (14H, br m, Ar). FT-IR (thin film cm^{-1}): 1780 (asymmetric C═O, str), 1724 (symmetric C═O, str), 1359 (C−N, str), 747 (imide ring deformation). GPC: M_n = 54 000, M_w = 116 000 g mol^{-1}, M_w/M_n = 2.1. BET surface area = 683 m^2 g^{-1}, total pore volume = 0.85 cm^3 g^{-1} at (p/p^o = 0.98, adsorption). TGA analysis: (nitrogen) initial weight loss due to thermal degradation commences at ∼480 °C, (air) initial weight loss due to thermal degradation commences at ∼410 °C. A second batch (**PIM-PI-8ii**) was lower in molar mass by GPC: M_n = 18 000, M_w = 41 000 g mol^{-1}, M_w/M_n = 2.3, but nevertheless formed self-supported membranes suitable for permeability measurements.

Characterization of PIM-PIs. Molar mass distributions were determined by multidetector gel permeation chromatography (GPC) with chloroform as solvent. Measurements were carried out at GKSS Research Centre Geestacht GmbH using PSS (Polymer Standards Service GmbH) SDV columns (Guard 5 μm, 5 cm; 50 Å, 30 cm; 10^3 Å, 30 cm; 10^5 Å, 30 cm), Waters 717 plus autosampler, Shodex RI 101 refractive index detector, PSS SLD 7000 multiangle laser light scattering (MALLS) detector, and Viscotek Model 200 viscosity detector. Some measurements were also carried out at the University of Manchester using Polymer Laboratories PLgel columns (2 × MIXED-B), Vicotek GPCmax VE2001 solvent/sample module, and Viscotek TDA302 triple detector array. Nitrogen adsorption/desorption measurements at 77 K were carried out using a Beckman Coulter SA3100 instrument. Apparent surface areas were calculated by the multipoint Brunauer, Emmett, Teller (BET) method. Thermogravimetric analysis (TGA) measurements were made using a Seiko 220 instrument at a heating rate of 10 °C min^{-1} from room temperature to 600 °C.

PIM-PI Membranes. Membranes were prepared by casting from chloroform solution. Values of film density, ρ, were determined by hydrostatic weighing. The measurements were performed with a Sartorius 6080 specific gravity determination kit and a Sartorius Research R200D electronic semimicrobalance (0.000 01 g accuracy) connected to a computer. According to the user's manual, the instrument allows density changes to be measured with an accuracy of 0.0001 g cm^{-3}. Fluorinert FC77 was used as the liquid for the density determination. The advantage of this liquid is its inertness (e.g., it does not swell the polymer), its low surface energy, and its high density (1.78 g cm^{-3}), which gives a large density difference relative to the polymer and consequently improves the precision of the result. Values of van der Waals volume, V_w, were calculated using HyperChem Professional version 7.5 software. This software allows for structural factors to be included in the van der Waals volume determination.[16] Typically, four repeating units were constructed, geometrically optimized, and the built-in functions of the QSAR Properties window applied to calculate the van der Waals volume for one repeat unit. Values of fractional free volume, f_V, were evaluated using $f_V = (V - 1.3V_w)/V$, where $V = 1/\rho$ is the specific volume.

Determination of Gas Permeability. Two experimental methods were used in the determination of the permeability of PIM-PIs. The barometric technique, employed at GKSS Research Centre Geestacht GmbH, was realized with a pressure increase time-lag apparatus operated at low feed pressure (typically 200−300 mbar), starting with an oil free vacuum ($< 10^{-4}$ mbar). Permeate pressure increase with time was recorded by two MKS Baratron pressure sensors (10 mbar max (permeate), 1 bar max (feed)) that were connected directly to a computer.[17] Software developed in the Labview environment enabled automated measurements. A standard set of gases (He, H_2, O_2, N_2, CO_2, CH_4) was used in the measurements at 30 °C. Typically, the steady-state flow across the membrane established after four time lags. Time lags from hours to 0.5 s can be measured precisely. More detailed description of the experimental procedure has been given elsewhere.[5] Another experimental method, employed at A.V. Topchiev Institute of Petrochemical Synthesis, was based on use of a gas chromatographic (GC) setup with differential thermostated cell with a penetrant pressure drop of 1 atm. The same set of gases as indicated above was tested at 22 °C. Pure penetrant gas with a pressure of 1 atm was passed through the upstream part of the cell, while the gas carrier (He in most cases and argon in the runs with He and H_2 as penetrants) was passed though the downstream part of the cell. After attaining steady-state conditions, as checked by a catharometer, a sample of the permeate was taken for GC analysis. Simultaneously, the flow of the permeate was measured using a soap bubble flowmeter.

Results and Discussion

Synthesis. Bis(carboxylic anhydride) **An-1** (Scheme 2) was obtained in good overall yield from the aromatic nucleophilic reaction between **1** and 4,5-dichlorophthalonitrile,[18] followed by hydrolysis of the four nitrile groups and, finally, dehydration of the resulting carboxylic acids. The PIM-PIs were prepared from the cycloimidization reaction between

Table 1. Molar Masses, Surface Areas, Film Densities, and Fractional Free Volumes of PIM-PIs

polymer	M_n [g mol^{-1}][a]	M_w [g mol^{-1}][a]	M_w/M_n[a]	S_{BET} [m^2 g^{-1}][b]	ρ [g cm^{-3}][c]	f_V[d]
PIM-PI-1	17 000	38 000	2.2	680	1.15	0.232
PIM-PI-2	30 000	49 000	1.6	500		
PIM-PI-3	22 000	45 000	2.0	471	1.26	0.226
PIM-PI-4	11 000	31 000	2.8	486	1.26	0.228
PIM-PI-7	11 000	42 000	3.8	485	1.19	0.223
PIM-PI-8i[e]	54 000	116 000	2.1	683		
PIM-PI-8ii[e]	18 000	41 000	2.3		1.14	0.231

[a] Number-average molar mass, M_n, weight-average molar mass, M_w, and polydispersity, M_w/M_n, determined by multidetector GPC (light scattering and refractive index detectors). [b] BET surface area, S_{BET}, determined from N_2 adsorption at 77 K. [c] Film density, ρ, determined by hydrostatic weighing in Fluorinert FC77. [d] Fractional free volume, f_V, derived from film density and van der Waals volume. [e] Two batches of **PIM-PI-8** were prepared: the first batch, designated **PIM-PI-8i**, was used for initial permeability measurements; the second batch, designated **PIM-PI-8ii**, was used for subsequent studies.

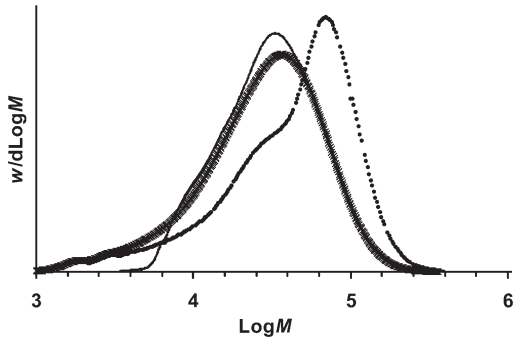


Figure 1. Weight distribution of log(molar mass) for **PIM-PI-1** determined by multidetector GPC in $CHCl_3$ (light scattering and refractive index detectors), using instruments in Geesthacht (×) and Manchester (—), and comparison with polystyrene equivalent distribution[12] (●) determined by conventional GPC in tetrahydrofuran.

An-1 and appropriate diamines, the choice of aromatic diamine being determined by their previous success as monomers for preparing relatively permeable polyimides. Hence, 2,3,5,6-tetramethyl-1,4-phenylenediamine,[19−22] 5,5′-(hexafluoroisopropylidene)-di-*o*-toluidine, 4,4′-(hexafluoroisopropylidene)-dianiline,[23] 2,2′-bis(trifluoromethyl)-4,4′-diaminobiphenyl,[24] 1,5-diaminonaphthalene,[25−27] and 3,3′-dimethylnaphthidine[19,28] were reacted with **An-1** under well-established conditions (*m*-cresol with a small amount of quinoline and toluene as solvent at 190 °C) to give PIM-polyimides **PIM-PI-1**, **PIM-PI-2**, **PIM-PI-3**, **PIM-PI-4**, **PIM-PI-7**, and **PIM-PI-8**, respectively. In addition, **PIM-PI-5** and **PIM-PI-6**, of only modest molecular masses, were prepared from the reaction of **An-1** with 1,3-diamino-2,4,6-trimethylbenzene and 1,1-bis(4-amino-3,5-di-iso-propylphenyl)fluorene, respectively, but proved not to form films of sufficient quality for gas permeability studies, possibly due to a high proportion of cyclic oligomers being formed during polymerization.

PIM-PI Characteristics. Average molar masses determined by multidetector GPC using light scattering and refractive index detectors are given in Table 1. Measurements on different instruments in Geesthacht and Manchester showed good agreement, as illustrated for **PIM-PI-1** in Figure 1, which also shows, for comparison, a previously reported[12] distribution obtained by conventional GPC with polystyrene calibration. All the PIM-PIs investigated had high apparent surface areas by nitrogen adsorption at 77 K and high fractional free volumes (Table 1). The polymers exhibited high thermal stability by TGA, with no degradation under N_2 up to a temperature in the range 465 °C (for **PIM-PI-1**) to 485 °C (for **PIM-PIs 2**, **4**, and **7**). They are glassy polymers, differential scanning calorimetry (DSC) showing no evidence of a glass transition below the degradation temperature. Solubility of the PIM-PIs in various solvents is indicated in Table 2.

Table 2. Solubility of PIM-PIs in Various Solvents[a]

polymer	$CHCl_3$	THF	*m*-cresol	acetone	DCM	NMP	DMAc
PIM-PI-1	++	++	++	−	−	++	+−
PIM-PI-2	++	++	++	−	++	++	+−
PIM-PI-3	++	++	++	−	+−	+−	+−
PIM-PI-4	++	++	++	−	+−	++	++
PIM-PI-7	++	++	++	−	++	++	++
PIM-PI-8	++	++	++	−	++	++	+−

[a] Qualitative solubility was determined with 10 mg of the solid polymer in 1 mL solvent at room temperature: ++, completely dissolved; −, insoluble; +−, partially soluble; THF: tetrahydrofuran; DCM: dichloromethane; NMP: *N*-methyl-2-pyrrolidone; DMAc: *N*,*N*-dimethylacetamide.

Table 3. Permeability Coefficients, P_i, at 30 °C Determined by the Barometric Method

	P_i [barrer][a]					
polymer	He	H_2	O_2	N_2	CO_2	CH_4
PIM-PI-1[b]	260	530	150	47	1100	77
PIM-PI-2	160	220	39	9	210	9
PIM-PI-3	190	360	85	23	520	27
PIM-PI-4	205	300	64	16	420	20
PIM-PI-7	190	350	77	19	510	27
PIM-PI-8i[c]	660	1600	545	160	3700	260
PIM-PI-8ii[c]	425	1020	320	100	2270	170

[a] 1 barrer = 10^{-10} cm^3[STP] cm cm^{-2} s^{-1} cmHg^{-1} = 3.35×10^{-16} mol m m^{-2} s^{-1} Pa^{-1}. [b] Initial measurements for a 126 μm thick membrane of **PIM-PI-1** batch BD-100 gave $P(O_2)$ = 250 barrer and $P(N_2)$ = 73 barrer; the data in the Table are for a 54 μm thick membrane prepared from the same material after reprecipitation;. [c] Data for batch **PIM-PI-8i** were reported previously;[12] batch **PIM-PI-8ii** is of lower molar mass (see Table 1).

Table 4. Ideal Separation Factors α_{ij} for Various Gas Pairs, Determined by the Barometric Method

polymer	O_2/N_2	H_2/N_2	H_2/CH_4	He/CH_4	CO_2/CH_4	CO_2/N_2	N_2/CH_4
PIM-PI-1	3.2	11.3	6.9	3.4	14.3	23.4	0.6
PIM-PI-2	4.3	24.4	24.4	17.8	23.3	23.3	1.0
PIM-PI-3	3.7	15.7	13.3	7.0	19.3	22.6	0.9
PIM-PI-4	4.0	18.8	15.0	10.3	21.0	26.3	0.8
PIM-PI-7	4.1	18.4	13.0	7.0	18.9	26.8	0.7
PIM-PI-8i	3.4	10.0	6.2	2.5	14.2	23.1	0.6
PIM-PI-8ii	3.2	10.2	6.0	2.5	13.4	22.7	0.6

Permeability Coefficients of PIM-PI Membranes. The permeability coefficients P_i of various PIM-PIs measured using the barometric technique are given in Table 3, and the ideal separation factors $\alpha_{ij} = P_i/P_j$ are presented in Table 4. It is seen that the structure of the diamine used exerts a strong effect on the observed permeability and that the usual trade-off behavior between permeability and permselectivity can be observed for PIM-PIs. An interesting feature of the PIM-PIs studied is the relative values of the permeability coefficients with respect to nitrogen and methane. It is well-known that polyimides are generally distinguished by separation factors $\alpha(N_2/CH_4) > 1$,[29] whereas these factors are less than 1 for most other polymers. For the highly permeable PIM-PIs the solubility separation, which favors CH_4 over N_2, dominates over the diffusion separation. Most polyimides reported in the literature have low gas permeabilities and the diffusion separation dominates.

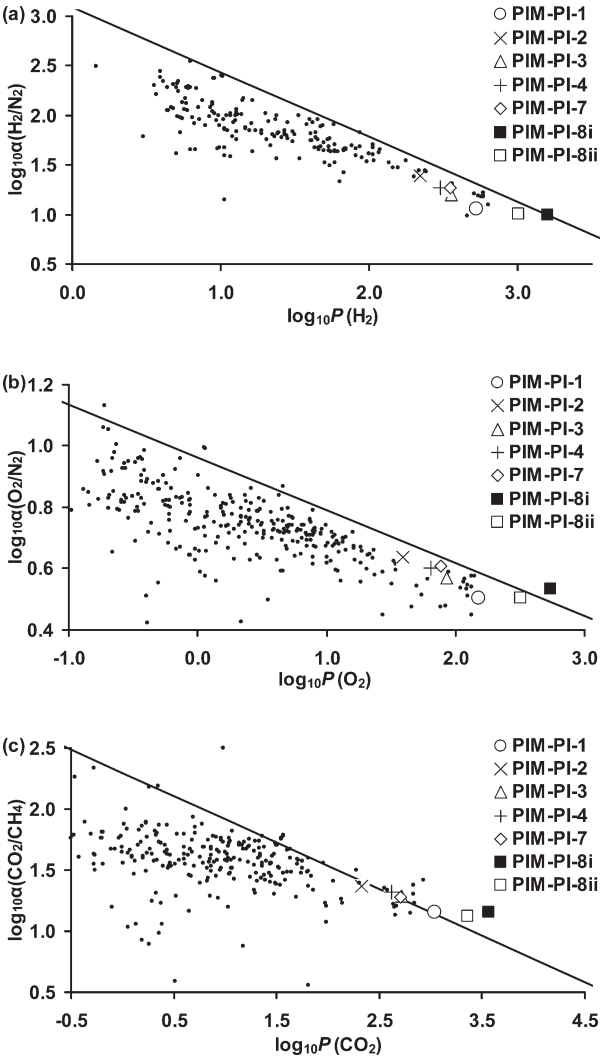


Figure 2. Robeson plots for polyimides (●) and PIM-PIs and the gas pairs (a) H_2/N_2, (b) O_2/N_2, and (c) CO_2/CH_4. The solid lines represent Robeson's 1991 upper bounds.[10]

Polyimides are the class of membrane gas separation materials that has been explored more than any other class of glassy polymer.[30] Hence, it is interesting to assess the novel group of polyimides, namely PIM-PIs, in comparison with other polyimides. For this purpose Robeson diagrams were plotted, showing data for PIM-PIs and other polyimides (Figure 2). The database held at the A.V. Topchiev Institute of Petrochemical Synthesis[30] served as the source of data for polyimides. The upper bounds drawn by Robeson[10] in 1991 are shown in Figure 2a−c. Since some data for polyimides were reported in more recent publications, some of the points for polyimides are located above the upper bounds. It is obvious that PIM-PIs are located among the most permeable polyimides. In the diagram for the CO_2/CH_4 pair, the points are located at the upper bound or slightly above. This is in agreement with the results of the study of **PIM-1**, which showed especially good results for the separation of the mixtures CO_2/CH_4 and CO_2/N_2.[5]

Two PIM-PIs, namely **PIM-PI-1** and **PIM-PI-8**, were selected for further studies using the gas chromatographic method. Permeability data are presented in Table 5 and selectivities in Table 6. Reasonable agreement between the barometric and gas chromatographic methods was achieved for comparable samples. Data for **PIM-1**[5] are

Table 5. Permeability Coefficients, P_i, Determined by the Gas Chromatographic Method

	P_i [barrer]					
polymer	He	H_2	O_2	N_2	CO_2	CH_4
PIM-PI-1	340	750	280	91	2000	175
PIM-PI-8ii	520	1360	490	140	3190	240
PIM-1[5]	760	1630	580	180	4390	310

Table 6. Ideal Separation Factors α_{ij} for Various Gas Pairs, Determined by the Gas Chromatographic Method

polymer	O_2/N_2	H_2/N_2	H_2/CH_4	He/CH_4	CO_2/CH_4	CO_2/N_2	N_2/CH_4
PIM-PI-1	3.1	8.2	4.3	1.9	11.4	22.0	0.5
PIM-PI-8ii	3.5	9.7	5.7	2.2	13.3	22.8	0.6
PIM-1[5]	3.2	9.1	5.3	2.5	14.2	24.4	0.6

included in Tables 5 and 6 for comparison. The main emphasis in these experiments was on further investigation of the unusual effects of film forming protocol on the observed gas permeability, as has been demonstrated for **PIM-1**.[5] A strong sensitivity of this kind was observed for both **PIM-PI-1** and **PIM-PI-8**. In these experiments, the effects of extended immersion of the film in methanol and ethanol were examined. This treatment is expected to remove any residual solvent and allow relaxation of the chains in the swollen state. For other glassy polymers it is common practice to heat to the glass transition, T_g, to allow relaxation and erase prior thermal history,[31] but this is not possible here, as the polymers do not exhibit a discernible T_g. It was shown that both methanol and ethanol exert similar effects on gas permeability. As is seen in Table 7, soaking of the film in methanol or ethanol leads to marked increases in gas permeability, as compared with the films cast from chloroform and subjected to removal of the solvent in vacuum at room temperature for several days until constant weight of the film is achieved. These effects are virtually identical to those observed in PIM-1,[5] though the permeability coefficients of the films of **PIM-1** are higher. These observations are consistent with an assumption of local interactions between some sites of the PIM structure and lower alcohols. It is worth noting that increases in permeability due to the variation of film treatment protocol are accompanied by very weak, if any, decreases in permselectivity due to classical trade-off behavior (see Table 7).

Since **PIM-PI-8** was found to be the most permeable among the PIM-PIs studied, the temperature dependence of the permeability coefficients in this material was measured for several gases in the range 21−55 °C. The Arrhenius plots are linear, and this indicates that no changes due to removal of the solvents took place during heating (Figure 3). The activation energies of permeation in **PIM-PI-8** are compared with those of **PIM-1** in Table 8. It is seen that the two series of values are very similar. In both cases, negative activation energy E_P is observed for carbon dioxide.

Application of the Group Contribution Method for Analysis and Prediction of the Transport Parameters of PIM-PIs. The PIM-PIs form a group of polyimides prepared with a common dianhydride, **An-1**. Polyimides are the most explored membrane materials. Thus, the database created and sustained at the A.V. Topchiev Institute of Petrochemical Synthesis (TIPS)[30] includes the gas permeation parameters for about 300 different structures of homopolymers of this class. A group contribution method has previously been proposed[32] for the analysis and prediction of gas

Table 7. Gas Permeation Parameters (Determined by the Gas Chromatographic Method) of PIM-PI Films after Different Pretreatments[a]

polymer	type of pretreatment	$P(O_2)$ [barrer]	$P(N_2)$ [barrer]	$\alpha(O_2/N_2)$
PIM-PI-1	cast from $CHCl_3$	276	90.7	3.0
	cast from $CHCl_3$, immersed in MeOH for 1 day	733	216	3.4
PIM-PI-8ii	cast from $CHCl_3$	488/290[b]	142/89[b]	3.4/3.3[b]
	cast from $CHCl_3$, immersed in MeOH for 5 days	1150	416	2.8
	cast from $CHCl_3$, immersed in EtOH for 5 days	1071	377	2.8
PIM-1[5]	cast from $CHCl_3$	580	180	3.2
	cast from $CHCl_3$, immersed in MeOH for 5 days	1610	500	3.2

[a] The films after primary removal of the solvent ($CHCl_3$) were kept in vacuum at room temperature until constant weight is achieved (3−5 days). The films after contact with alcohols were kept in ambient atmosphere for 1 day. No traces of alcohols were present as indicated by gas chromatography analysis. [b] The first value is after heating in He at 75 °C; the second value after vacuum treatment at room temperature.

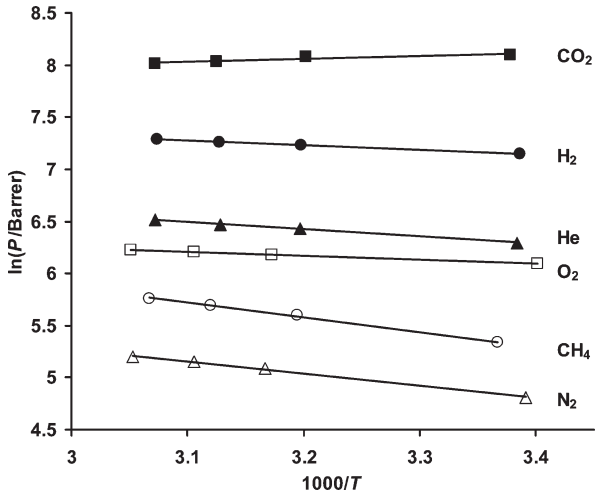


Figure 3. Temperature dependence of permeability coefficients P for **PIM-PI-8**.

Table 8. Activation Energies of Permeation E_P (kJ mol^{-1}) for Various Gases in PIM-PI-8 and PIM-1

polymer	He	H_2	O_2	N_2	CO_2	CH_4
PIM-PI-8	6.0	3.6	2.9	10.0	−2.2	12.1
PIM-1[5]	5.0	3.6	1.1	7.5	−1.5	10.9

permeability of polyimides, which were considered as alternating copolymers of the type $-[DAn-DAm]_n-$, where DAn is a dianhydride and DAm is a diamine that form the structure of the specific polyimide. Numerous polyimides are formed by the combination of about 11 dianhydrides and 70 diamines. The task of predicting the permeability coefficients is based on the search for the best increments or group contributions, x_j and y_k, using experimentally known values of the permeability coefficients P_i obtained for a number of polyimides. Therefore, one has an overestimated system of linear equations for a certain parameter A (e.g., permeability coefficient) and a specific gas:

$$\begin{aligned} x_1+y_1+C &= \log A_1 \\ x_1+y_2+C &= \log A_2 \\ x_2+y_1+C &= \log A_3 \\ &\cdots \\ x_j+y_k+C &= \log A_i \end{aligned} \qquad (1)$$

where j is the number of a dianhydride, k is the number of a diamine, i is the number of the polyimide, and C is a constant

Table 9. Increments Found Using the Group Contribution Approach[a]

structure	He	O_2	N_2	CO_2	CH_4
dianhydride **An-1**	0.109	0.499	0.567	0.715	0.945
diamine (**PIM-PI-1**)	0.262	*0.051*	*0.013*	*0.115*	*0.332*
diamine (**PIM-PI-2**)	−0.059	−0.943	−1.137	−0.920	−1.104
diamine (**PIM-PI-3**)		*-0.749*	*-0.923*	*-0.583*	*-0.777*
diamine (**PIM-PI-4**)	0.038	−0.728	−0.901	−0.619	−0.762
diamine (**PIM-PI-8**)		0.202	0.099	0.326	0.359

[a] The increments taken from ref 32 are given in italics.

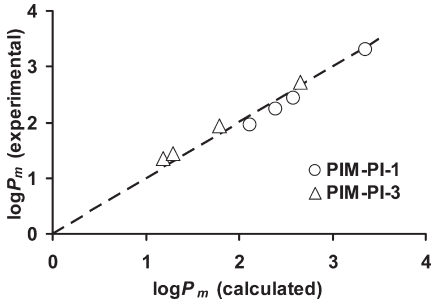


Figure 4. Correlation between predicted and experimental permeability coefficients (barrer) for **PIM-PI-1** and **PIM-PI-3**.

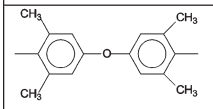
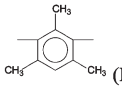
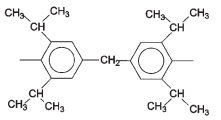
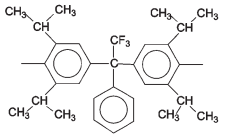
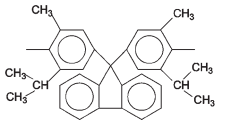
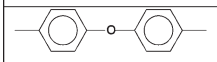
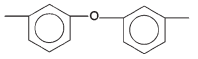
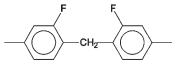
for a particular gas. The solution of this system of linear equation leads to the values of increments characteristic for the dianhydrides and diamines. Values of C and increments have been tabulated in the ref 32. The permeability coefficients can then be found as

$$\log P_m = \log M_{jm} + \log N_{km} + C_m \qquad (2)$$

where P_m is the predicted value of the permeability coefficient in respect of mth gas.

The PIM-PIs considered in the present paper have a common element, the PIM-type dianhydride **An-1**, that has not previously been studied. Some of the diamines that were employed in the preparation of PIM-PIs have increments for some gases tabulated in ref 32, whereas others do not. Thus, a corresponding system of linear equations was prepared, and the increments were found for **An-1** and for the diamines used in the preparation of **PIM−PI-1**, **-2**, **-3**, **-4**, **-7**, and **-8**. The values of P_m obtained using the barometric method were used in the calculations. Two sets of calculations were made for the permeability coefficients in respect of the following gases: He, O_2, N_2, CO_2, CH_4. First, the increments for all the mentioned PIM-PIs were determined. However, the value of the increment for **PIM-PI-7** differed significantly from those found for other PIM-PIs. On the assumption that there was a specific error in this case (e.g., greater errors in the determination of the experimental P_m, some deviations from the additivity rule used), the data for **PIM-PI-7** were excluded,

Table 10. Predicted Permeability Coefficients and Ideal Separation Factors for Several Polyimides Derived from Dianhydride An-1

Diamine	P_m [Barrer]				$\alpha = P_i/P_j$		
	O_2	N_2	CO_2	CH_4	O_2/N_2	CO_2/CH_4	CO_2/N_2
	149	40	1088	57	3.7	19	27
 (**PIM-PI-5**)	321	101	2366	204	3.2	11.6	23
	158	53	-	-	3.0	-	-
	263	102	-	-	2.6	-	-
	282	85	-	-	3.3	-	-
	7.0	1.4	37	1.5	5.0	25	26
	1.7	0.25	10	0.25	6.8	40	40
	2.7	0.48	15	0.89	5.6	17	31
	20.3	4.3	133	5.3	4.7	25	31

and the increments based on the data for all other PIM-PIs were computed. The results are presented in Table 9.

It is seen in Table 9 that the increments for **An-1** for all the gases are positive. This is in stark contrast with other dianhydrides tabulated in ref 32, for which all of the increments are negative. This is consistent with the higher gas permeability of the PIM-PIs considered. One can also note some correlation between the values of increments of diamines tabulated in ref 32 and found in the present paper. For example, the largest and positive values were obtained for the diamine of **PIM-PI-8**, which reveals higher permeability than other PIM-PIs studied.

Figure 4 shows the correlation between the experimental and calculated values of the permeability coefficients for **PIM-PI-1** and **PIM-PI-3**, for which increments for the diamines were obtained from the literature (Table 9). For the other PIM-PIs, increments were derived from the experimental data and so the experimental and calculated values are equal. A good agreement is seen between the two sets of values for **PIM-PI-1** and **PIM-PI-3**, which justifies the application of the group contribution approach.

Using the calculated increments, it is possible to predict the permeability coefficients of PIM-PIs that could be prepared from **An-1** and other diamines, whose increments can be found in ref 32. Calculations were carried out for two groups of polymers. The first group included diamines expected to give polymers with relatively high gas permeability and lower permselectivity, including 1,3-diamino-2,4,6-trimethylbenzene that gave low molecular mass polymer **PIM-PI-5**. For the second group of polymers, the opposite assumption was made. The values of the permeability coefficients and ideal separation factors found in this manner are given in Table 10. It is seen that relatively high values of P_m were calculated for some of the imaginable structures shown: for instance, permeability coefficient $P(CO_2)$ can be as large as about 2400 barrer. An analysis indicates that for some polymers of the first group the data points on Robeson plots are very close to the upper bounds. All this justifies further effort to prepare other polymers of the PIM family.

Conclusions

By applying the design principle of polymers of intrinsic microporosity (PIMs) to polyimides, new polymers (PIM-PIs) were obtained with gas separation properties exceeding the most permeable conventional polyimides, depending on the structure of the diamine unit. Utilizing a well-accepted group contribution method and varying the diamines, plausible gas permeation parameters are predicted for other PIM-PI structures, indicating the potential for synthesis of further PIM-PIs.

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