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Polymer of Intrinsic Microporosity Incorporating Thioamide Functionality: Preparation and Gas Transport Properties

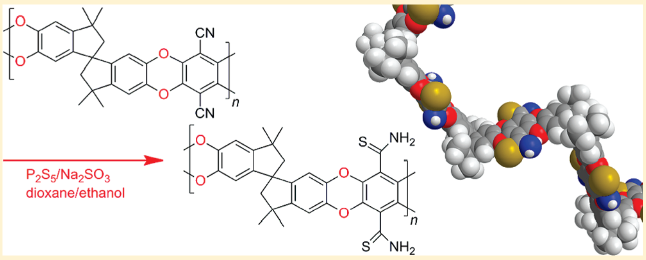
Christopher R. Mason,[†] Louise Maynard-Atem,[†] Nasser M. Al-Harbi,[†] Peter M. Budd,*[,†] Paola Bernardo,[‡] Fabio Bazzarelli,[‡] Gabriele Clarizia,[‡] and Johannes C. Jansen[‡]

[†]School of Chemistry, University of Manchester, Manchester, M13 9PL, United Kingdom

[‡]Institute on Membrane Technology (ITM-CNR), Via P. Bucci, cubo 17/C, c/o University of Calabria, 87030 Rende (CS), Italy

Supporting Information

ABSTRACT: A novel polymer of intrinsic microporosity, thioamide-PIM-1, has been prepared by postmodification of PIM-1, using phosphorus pentasulfide as a thionating agent in the presence of sodium sulfite. The chemistry was first tested on a low molecular weight model compound, 3,13-dicyanobenzo-1,2,4′,5′-bis(1,4-benzodioxane). For the polymer, up to 80% conversion of nitrile to thioamide was achieved. Modification leads to a reduction in the BET surface area of the polymer, from 770 $m^2\ g^{-1}$ for the parent PIM-1 to 263 $m^2\ g^{-1}$ on 80% conversion of nitrile to thioamide. After modification, the polymer is no longer soluble in chlorinated solvents such as $CHCl_3$, but is soluble in polar aprotic solvents such as THF, DMF, DMSO, and DMAc. Self-supported membranes of thioamide-PIM-1 were cast from THF. Single gas permeability measurements showed increased selectivities but reduced permeabilities compared to the parent polymer. Ethanol treatment, which removes occluded THF as well as enhancing free volume, has a pronounced effect on membrane permeability. For the as-prepared membrane, an ideal CO_2/N_2 selectivity of 38.5 was achieved with a CO_2 permeability of 150 barrer. Ethanol treatment increased the CO_2 permeability to 1120 barrer, with a decrease in CO_2/N_2 ideal selectivity to 30.3.



INTRODUCTION

Gas separation membranes are of interest for a variety of important applications, such as air separation, hydrogen recovery, carbon dioxide capture and the recovery of volatile organics from gas streams.[1] Membrane processes offer energy-efficient and low-cost solutions for many industrial problems. High free volume polymers have been investigated as gas separation membranes, due to their ease of processing, mechanical stability and promising gas transport properties.[2]

In recent years, a novel class of high free volume polymer has been developed, referred to as "polymers of intrinsic microporosity" (PIMs).[3−6] PIMs possess a fused-ring, ladder-type structure interrupted by sites of contortion. These structural features prevent the polymer from packing space efficiently in the solid state, leading to its high free volume and microporosity (effective pore size <2 nm as defined by IUPAC[7]). The contorted structure also means that high molecular weight non-network PIMs are soluble in common organic solvents and can be solution-processed into free-standing membranes. The high free volume and solution processability make them attractive candidates for gas and vapor separation processes. Membranes of the archetypal PIM, known as PIM-1 (Scheme 1), have demonstrated high permeability and good selectivity, surpassing Robeson's 1991 upper bound[8] and defining the 2008 upper bound[9] for several important gas pairs (e.g., O_2/N_2 and CO_2/CH_4).[5,10] PIM-1 is a glassy polymer which shows no evidence of a glass transition below the degradation temperature.

As a consequence of the particularly promising gas transport properties, coupled with the ease of processing, there have recently been a number of publications reporting the production of novel PIMs. Changes to the polymer structure have typically been introduced either by differing the monomer which introduces the site of contortion[11−15] or the monomer that makes up the rigid backbone within the polymer.[14−17] These modifications to the polymeric structure have been shown to alter the gas transport properties of the membrane, allowing for tuning of the properties by incorporation of different moieties and functionalities.

The postmodification of PIMs also presents a route to novel polymers. PIM-1 possesses nitrile groups upon which, in principle, chemistry can be performed. However, attempts to postmodify PIM-1 frequently lead to intractable products. The only reports of successful PIM-1 postmodification and its effect on the gas transport properties are the preparation of carboxylated PIM-1[18] and the incorporation of tetrazole groups.[19] For the carboxylated polymer, the nitriles in the polymer were converted to

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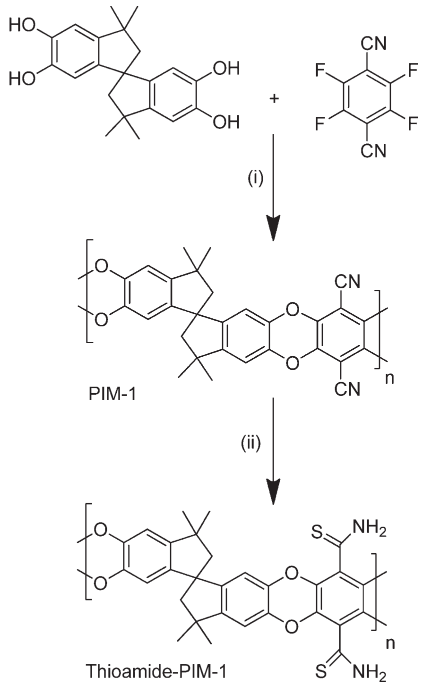
Scheme 1. Preparation of PIM-1 and Post-Modification To Give Thioamide-PIM-1[a]



[a] Reagents and conditions: (i) low-temperature method, K_2CO_3, DMF, 65 °C; high-temperature method, K_2CO_3, DMAc/toluene, 155 °C, high shear. (ii) P_2S_5/Na_2SO_3, dioxane/EtOH, reflux.

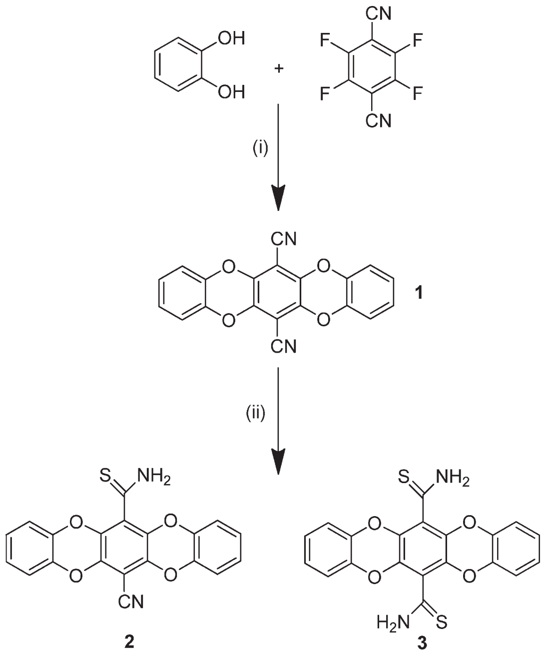
carboxylic acids via base hydrolysis.[18] The degree of hydrolysis was shown to vary the gas transport properties for the gas pair O_2/N_2 in line with the permeability/selectivity trade-off, highly permeable low carboxylated PIM-1 having low selectivity and vice versa, allowing for tuning of the transport properties. All of the polymers prepared surpassed Robeson's 1991 upper bound for the gas pair O_2/N_2.

In order to enhance the ability of the polymer to interact with penetrant species, we sought to introduce thioamide functionality. We report here the preparation of thioamide-PIM-1 via the thionation of the aromatic nitriles (Scheme 1). Phosphorus pentasulfide has recently been reported as a thionating agent for the preparation of thioamides from nitriles.[20−22] To investigate the chemistry and as a reference for the thionation of PIM-1, the reaction was first performed on a low molecular weight model compound, 3,13-dicyanobenzo-1,2,4′,5′-bis(1,4-benzodioxane) (Scheme 2). The gas permeation properties are reported and discussed for a thioamide-PIM-1 polymer with 80% conversion of nitriles to thioamide groups.

■ EXPERIMENTAL SECTION

Materials. Dimethylformamide (DMF, Sigma-Aldrich) was distilled under vacuum onto 4 Å molecular sieve. Tetrahydrofuran (THF, Sigma-Aldrich) was distilled under nitrogen from sodium metal using benzophenone as an indicator. Absolute ethanol (Sigma-Aldrich) was stored over 3 Å molecular sieve. Potassium carbonate (Fisher Scientific) was dried in an oven at 110 °C overnight prior to use. 5,5′,6,6′-Tetrahydroxy-3,3,3′,3′-tetramethyl-1,1′-spirobisindane (Avocado) was recrystallized from hot methanol by addition of dichloromethane. Tetrafluoroterephthalonitrile (Sigma-Aldrich) was recrystallized from methanol for PIM-1 preparation and used as received for model compound preparation. Anhydrous dimethylacetamide (DMAc, Sigma-Aldrich), 1,4-dioxane (Sigma-Aldrich), 1,2-dihydroxybenzene (Sigma-Aldrich), phosphorus pentasulfide (BDH or Sigma-Aldrich) and sodium sulfite (Fisher Scientific) were used as received.

Scheme 2. Preparation and Thionation of Model Compound[a]



[a] Reagents and conditions: (i) K_2CO_3, DMF, 65 °C. (ii) P_2S_5/Na_2SO_3, dioxane/EtOH, reflux.

Characterization Methods. ^{1}H NMR spectra were recorded on a Bruker Ultrashield 300 or 400 MHz spectrometer. Splitting patterns are abbreviated as follows: singlet (s) or multiplet (m). The solvent signals ($CDCl_3$, $\delta H = 7.27$ ppm; DMSO, $\delta H = 2.50$ ppm) were used as the internal references.

Chemical ionization (CI) mass spectra were recorded on a Micromass Trio 2000 spectrometer. Electrospray mass spectra were recorded on a Micromass Platform II spectrometer. MALDI mass spectra were recorded on a Micromass Tofspec 2E instrument using a trans-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene] malononitrile (DCTB) matrix.

Infrared spectra of solids were recorded on a Biorad FTS 6000 spectrometer with an Attenuated Total Reflectance (ATR) accessory. Each sample was scanned 16 times at a resolution of 4 cm^{-1}. The band that appears at approximately 2340 cm^{-1} is due to changes in atmospheric carbon dioxide between background and sample runs.

Elemental analysis was obtained on a Carlo Erba instruments EA1108 elemental analyzer.

Molar mass distributions were determined by gel permeation chromatography (GPC) with chloroform as the solvent. Measurements were performed using Polymer Laboratories PLgel columns (2 × Mixed-B), a Viscotek GPCmax VE2001 solvent/sample module, and a Viscotek TDA302 triple detector array (refractive index, light scattering and viscosity detectors).

Low-temperature (77 K) N_2 adsorption/desorption measurements of powders were carried out using a Beckman Coulter SA3100 instrument. Samples were degassed for 16 h at 120 °C under high vacuum prior to use.

Thermogravimetric analysis was carried out using a TA Instruments Q500 thermogravimetric analyzer with a heating rate of 10 °C min^{-1} under a flow of N_2.

Table 1. Number-Average Molar Mass, M_n, and Weight-Average Molar Mass, M_w, from Multidetector GPC and BET Surface Area, S_{BET}, from N_2 Adsorption at 77 K, for PIM-1 Samples

PIM-1 batch	M_n (g mol^{-1})	M_w (g mol^{-1})	S_{BET} (m^2 g^{-1})
LMA03	43 000	120 000	770
LMA06	52 900	189 500	650
NMH03	29 000	80 000	

Preparation of PIM-1. PIM-1 batches LMA03 and LMA06 were prepared by the low-temperature method reported by Budd et al.[4] PIM-1 batch NMH03 was prepared by a high-temperature, high-shear method similar to that reported by Du et al.[23] Characterization data are given in Table 1.

Preparation of Model Compound, 3,13-Dicyanobenzo-1,2,4′,5′-bis(1,4-benzodioxane). To a two-neck round-bottom flask, under an inert atmosphere of nitrogen, were added anhydrous DMF (120 mL), 1,2-dihydroxybenzene (4.49 g, 40.8 mmol), tetrafluoroterephthalonitrile (3.71 g, 18.5 mmol), and potassium carbonate (16.9 g, 122.4 mmol). The mixture was heated to 65 °C and left to stir at this temperature for 24 h. After cooling to room temperature the precipitate was collected by vacuum filtration. The solid was then stirred in water (200 mL) for approx 30 min followed by acetone (200 mL) for a further 30 min to remove any remaining starting materials. The product was dried in an oven at 110 °C overnight giving 3,13-dicyanobenzo-1,2,4′,5′-bis(1,4-benzodioxane) (**1**) as a luminous yellow solid (5.77 g, 91.6%): mp > 300 °C. ^{1}H NMR ($CDCl_3$; 300 MHz) δ (ppm): 6.94−6.98 (8H, m); LRMS, m/z (CI): 358 ($M^+ + NH_4$,), 340 (M^+). IR (ATR; cm^{-1}): 2239, 1449, 1307, 1245, 1100, 1030, 999, 751. Anal. Calcd for $C_{20}H_8N_2O_4$: C, 70.59; H, 2.37; N, 8.23. Found: C, 70.30; H, 2.26; N, 8.17.

Thionation of Model Compound. To a one-neck round-bottom flask was added phosphorus pentasulfide (578 mg, 1.3 mmol), sodium sulfite (164 mg, 1.3 mmol), and ethanol (5 mL). The mixture was stirred at room temperature for 1 h before **1** (110 mg) and 1,4-dioxane (40 mL) were added. The reaction mixture was then set to reflux and stirred for 20 h. After cooling to room temperature, water (40 mL) was added and the mixture stirred for a further 4 h. The product was extracted with chloroform (40 mL) and the organic layer washed with brine (2 × 40 mL) and dried ($MgSO_4$). The solvents were removed by rotary evaporation and the solid dried in an oven at 110 °C overnight. This gave a mixture of mono (**2**) and di (**3**) thioamide-containing products as a yellow solid (103 mg). ^{1}H NMR (DMSO; 300 MHz) δ (ppm): 6.86−7.2 (m), 9.84 (s), 9.88 (s), 10.23 (s) 10.42 (s). LRMS, m/z (ES$^-$): 407 (**3**, M^-), 373 (**2**, M^-). IR (KBr; cm^{-1}): 3371, 3259, 3161, 2238, 1610, 1491, 1446, 1309, 1271, 1251, 1107, 1037, 991, 843, 743.

Thionation of PIM-1. Thioamide-PIM-1 batch PBCM34 was prepared from PIM-1 NMH03 using an old batch of phosphorus pentasulfide (BDH); batch DNM45 was prepared from PIM-1 LMA03 using a fresh batch of phosphorus pentasulfide (Sigma-Aldrich). To a one-neck round-bottom flask was added phosphorus pentasulfide (7.72 g, 17.4 mmol), sodium sulfite (2.19 g, 17.4 mmol) and ethanol (20 mL). The mixture was stirred at room temperature for 1 h before PIM-1 (2 g) and 1,4-dioxane (200 mL) were added. The reaction mixture was then set to reflux and stirred for 20 h. After cooling to room temperature, water (200 mL) was added and the mixture stirred for a further 4 h, causing the formation of a yellow precipitate. The precipitate was collected by filtration and then washed by stirring in chloroform followed by hot methanol to remove any side products and impurities. The solid was collected and precipitated from hot THF by pouring into methanol (300 mL). Drying of the precipitate in a vacuum oven at 90 °C overnight yielded the thioamide containing polymer as an orange solid (1.93 g PBCM34; 2.16 g DNM45).

A further batch of thioamide-PIM-1 (DNM128) was prepared under identical conditions to DNM45.

Membrane Preparation. Thioamide-PIM-1 (250 mg) was vigorously stirred in anhydrous THF (12 mL) overnight to ensure complete dissolution of the polymer. The solution was then filtered through glass wool, to remove any insolubles, into a leveled glass Petri dish inside a desiccator. The lid of the desiccator was put in place and the solvent allowed to evaporate slowly for 5 days through a small outlet at the top of the desiccator. The resulting membrane could then be easily removed from the glass surface.

For comparison purposes, a membrane of PIM-1 batch LMA06 was prepared by casting from $CHCl_3$.

Membrane Permeation Measurement. Single gas permeation rate measurements were carried out at 25 °C in a fixed-volume pressure-increase setup, equipped with computer-controlled pneumatic valves to allow response times of less than 0.5 s. The feed pressure was 1 bar. The gases (purity 99.998%) were tested in the following order: He, H_2, N_2, O_2, CH_4, and CO_2. Before each experiment the system was evacuated ($\leq 2 \times 10^{-2}$ mbar) on both the feed side and the permeate side for a sufficiently long time to remove previous gases.

The measurements were carried out in the time lag mode,[24] allowing for the determination of the diffusion coefficient of each gas through the membrane. For the fixed-volume pressure increase instrument used, the transient permeation curve can be described by the equation

$$p_t = p_0 + (\mathrm{d}p/\mathrm{d}t)_0 \cdot t + \frac{RT \cdot A \cdot l}{V_P \cdot V_m} \cdot p_f \cdot S \left(\frac{D \cdot t}{l^2} - \frac{1}{6} - \frac{2}{\pi^2} \sum_1^{\infty} \frac{(-1)^n}{n^2} \exp\left(-\frac{D \cdot n^2 \cdot \pi^2 \cdot t}{l^2} \right) \right) \tag{1}$$

in which p_t is the permeate pressure at time t and p_0 is the starting pressure, usually less than 0.05 mbar. The baseline slope $(\mathrm{d}p/\mathrm{d}t)_0$ is normally negligible if the membrane is defect-free. R is the universal gas constant, T is the absolute temperature, A is the exposed membrane area, V_P is the permeate volume, V_m is the molar volume of a gas at standard temperature and pressure (0 °C and 1 atm), p_f is the feed pressure, S is the solubility, D is the diffusion coefficient, and l is the membrane thickness.

Permeability coefficient, P, was calculated from the slope of the time-pressure curve in steady state condition:

$$p_t = p_0 + (\mathrm{d}p/\mathrm{d}t)_0 \cdot t + \frac{RT \cdot A}{V_P \cdot V_m} \cdot \frac{p_f \cdot P}{l} \left(t - \frac{l^2}{6D} \right) \tag{2}$$

The last term in eq 2 corrects for the so-called time lag in permeation, Θ,

$$\Theta = \frac{l^2}{6D} \tag{3}$$

This allows for the calculation of diffusion coefficient of the penetrant.

The solubility of the gas in the polymer matrix is determined indirectly, via the equation

$$S = P/D \tag{4}$$

The ideal selectivity between two different gases is defined as the ratio of the single gas permeabilities and it provides a useful measure of the intrinsic permselectivity of a given membrane for the components. It can be decoupled into solubility-selectivity and diffusivity-selectivity

$$\alpha_{A/B} = (S_A/S_B) \times (D_A/D_B) \tag{5}$$

The membranes were tested as prepared (fresh) and after soaking in ethanol (film immersed in ethanol overnight, then dried for 1 day at

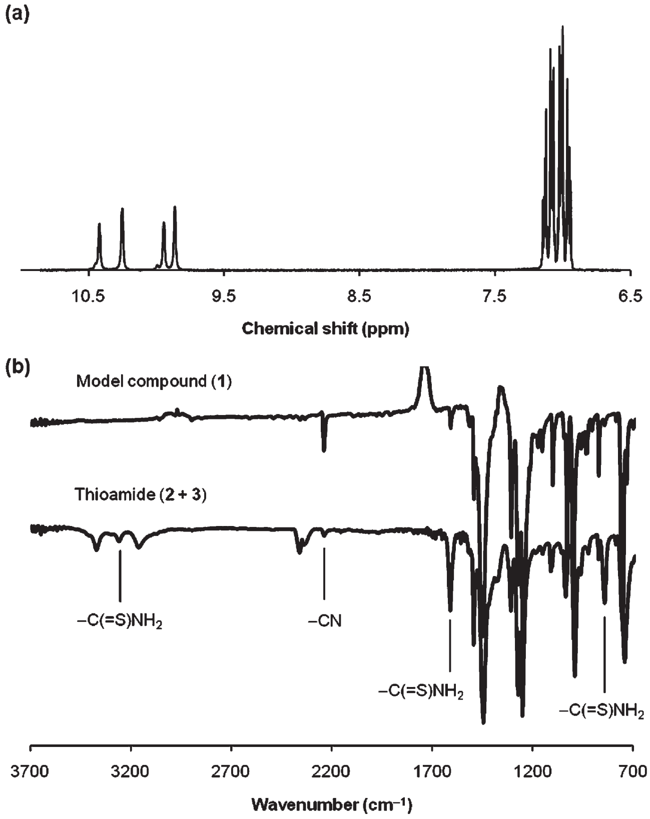


Figure 1. (a) ^{1}H NMR spectrum of thioamide-containing model compound in DMSO; (b) ATR-IR spectra of **1** before and after thionation.

ambient temperature and pressure). This treatment was reported to induce a dramatic increase in the permeability of PIM-1 membranes.[10] The thickness of the isotropic dense films was determined before and after this treatment, using a digital micrometer (Mitutoyo).

RESULTS AND DISCUSSION

Thionation of model compound. Thionation was first performed on model compound (**1**), which has the structure of the PIM-1 rigid chromophore and therefore any modification should be applicable to PIM-1. **1** was prepared in 91% yield from tetrafluoroterephthalonitrile (TFTPN) and 1,2-dihydroxybenzene (catechol) in the presence of base, using a procedure similar to that used in the preparation of PIM-1 (Scheme 2).[4] Thionation of the model compound with phosphorus pentasulfide was carried out in the presence of sodium sulfite, which is reported to aid the reaction over phosphorus pentasulfide alone.[21] After 20 h refluxing in a solvent mixture of 1,4-dioxane/ethanol, with 4 equiv of phosphorus pentasulfide, the isolated solid contained a combination of both the mono (**2**) and di- (**3**) thioamide compounds, as evidenced by ^{1}H NMR, infrared and mass spectrometry.

The ^{1}H NMR of the mixture in DMSO-d_6 (Figure 1a) shows the presence of four peaks in the region of 9.8–10.5 ppm. These peaks represent the two differing thioamide protons for both the unsymmetrical (**2**) and symmetrical (**3**) molecules. It is thought the two thioamide protons for each species are not equivalent due to the resonance structure of the thioamide functional group, restricting rotation around the C–N bond.[21] The aromatic protons (Ar–H) of all possible species fall in the region of 6.9–7.2 ppm. Figure 1b shows the infrared spectra of the thionated product and the starting compound. The thionated product shows three new fairly broad peaks at 3371, 3259, and 3162 cm^{-1} and the emergence of two stronger sharp peaks at 1610 and 843 cm^{-1}. These five new peaks are characteristic vibrations for the thioamide functionality.[25] The nitrile stretching vibration is still visible at 2238 cm^{-1} in the product, confirming that not all the nitriles were converted in the reaction. This is further evidenced by the electrospray mass spectrometry of the material, which shows negative molecular ion peaks for both the mono- and di- thioamide products at $m/z =$ 373 and 407, respectively.

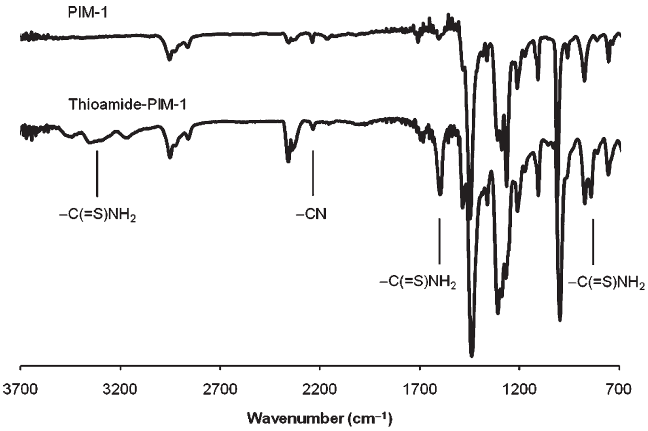


Figure 2. ATR-IR spectra of thioamide-PIM-1 (DNM45) and the starting PIM-1 (LMA03).

As complete conversion was not achieved, the percentage conversion of nitrile to thioamide was estimated both by integration of the ^{1}H NMR peaks and from the weight percent of sulfur determined by elemental analysis. Integration of the amide protons relative to the aromatic protons determines the conversion of nitrile to thioamide to be approximately 70% for this model reaction. This figure is in good agreement with elemental analysis, which showed a 10.3 wt % of sulfur, corresponding to 66% conversion of nitrile to thioamide.

Thionation of PIM-1. Thionations were carried out on two different batches of PIM-1, using the procedures established for the model compound. The products were characterized using infrared spectroscopy, MALDI mass spectrometry, ^{1}H NMR spectroscopy and thermogravimetric analysis.

Figure 2 compares the infrared spectrum of thioamide-PIM-1 (DNM45) with that of the starting polymer. With the exception of the C–H stretches from the additional aliphatic spirobisindane moieties, the peaks in the spectra for the new material coincide with the new bands in the thionated model compound. Five new peaks, with respect to the parent PIM-1, appear at 3448, 3354, 3169, 1600, and 843 cm^{-1}, showing the successful incorporation of thioamide functionality onto the PIM-1 backbone. The peak at 2238 cm^{-1} shows the presence of unconverted nitriles, as in the model reaction.

The MALDI mass spectrum for thioamide-PIM-1 (DNM45) is shown in Figure 3. It shows clusters of peaks, with the peaks within each cluster separated by 34, the mass of the sulfur and two hydrogens added to a nitrile upon conversion. These arise from various combinations of possible repeat units (no-, mono- and dithioamide).

Figure 4 compares the proton NMR spectrum from 5.5 to 11.5 ppm for thioamide-PIM-1 (DNM45) in DMSO with that

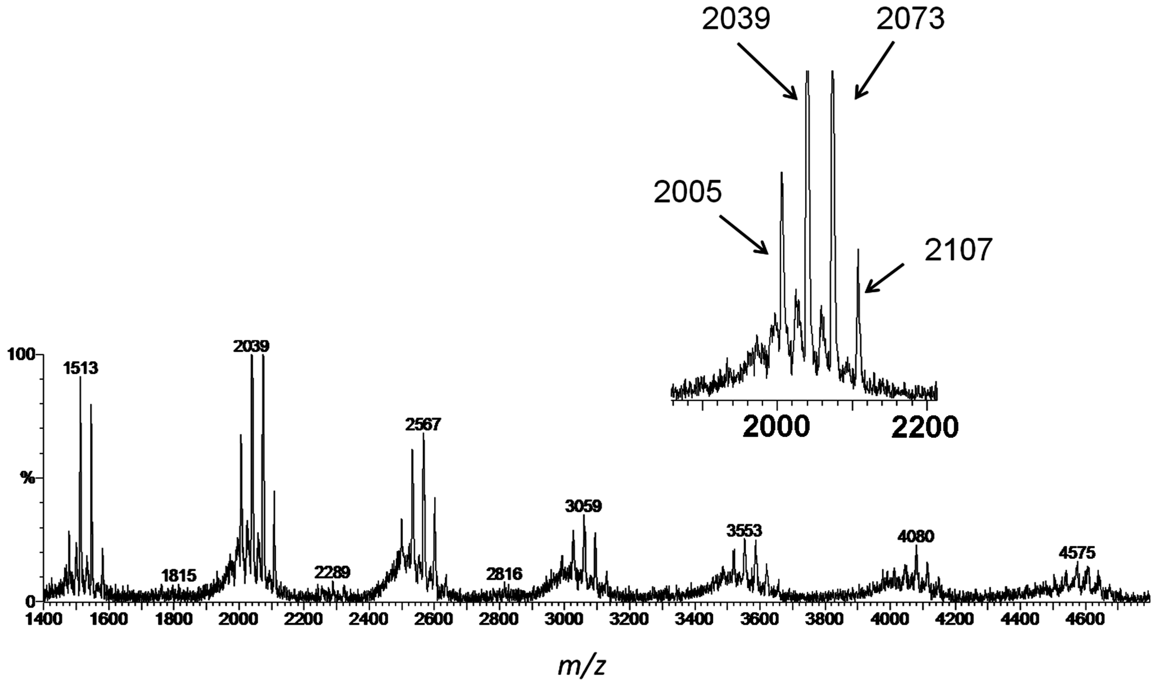


Figure 3. MALDI mass spectrum of thioamide-PIM-1 (DNM45).

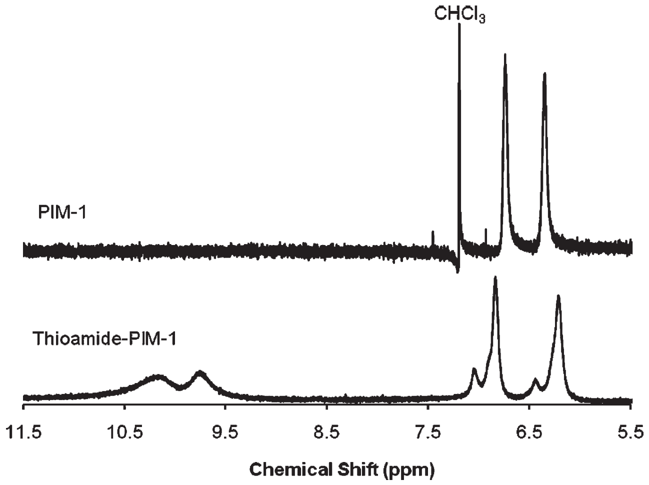


Figure 4. ^{1}H NMR spectra from 5.5 to 11.5 ppm of thioamide-PIM-1 (DNM45) in DMSO and its parent PIM-1 polymer (LMA03) in chloroform.

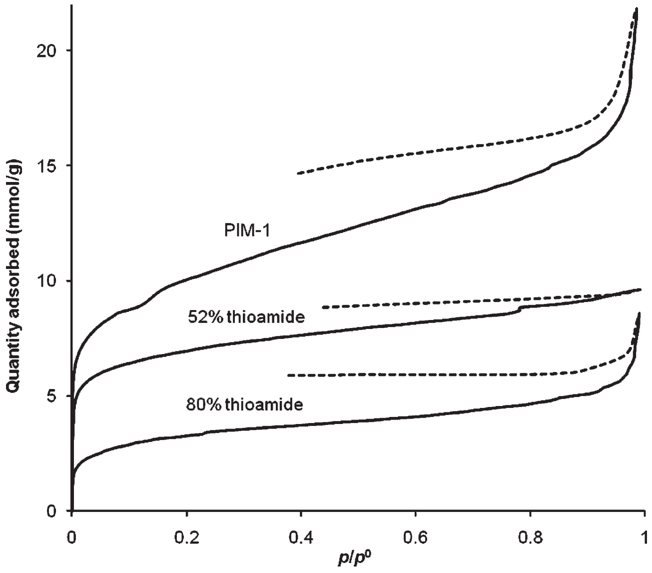


Figure 5. N_2 adsorption (solid lines) and desorption (dashed lines) isotherms at 77 K for powder samples of PIM-1 (LMA03), thioamide-PIM-1 with 52% conversion (PBCM34) and thioamide-PIM-1 with 80% conversion (DNM45).

for the parent PIM-1 in chloroform. As for the thioamide-containing model compound, new chemical shifts arise in the region of 9.5−10.5 ppm with respect to the parent molecule due to the thioamide protons. However, in the polymer the shifts for the symmetrical and unsymmetrical repeat units are fused into two broad peaks and are not distinguishable. The percentage conversion of nitrile to thioamide was determined both by integration of the thioamide NMR peaks and by elemental analysis. Batch DNM45 had 80% conversion by NMR, in good agreement with its elemental analysis which indicated 83% conversion. Batch PBCM34 had 52% conversion by NMR, while from elemental analysis it was slightly higher at 69%. The lower conversion for this batch probably reflects the use of an older sample of P_2S_5, rather than differences arising from the method of preparing the polymer. No phosphorus was found for any samples using elemental analysis, showing excess phosphorus pentasulfide was successfully removed via the work-up procedure.

To study the effect of thionation on the free volume of the polymer, surface area analysis of the materials was performed using N_2 gas sorption experiments (Figure 5). Although each sample showed some uptake at low relative pressure, indicative of microporosity, there was a decrease in the surface area with

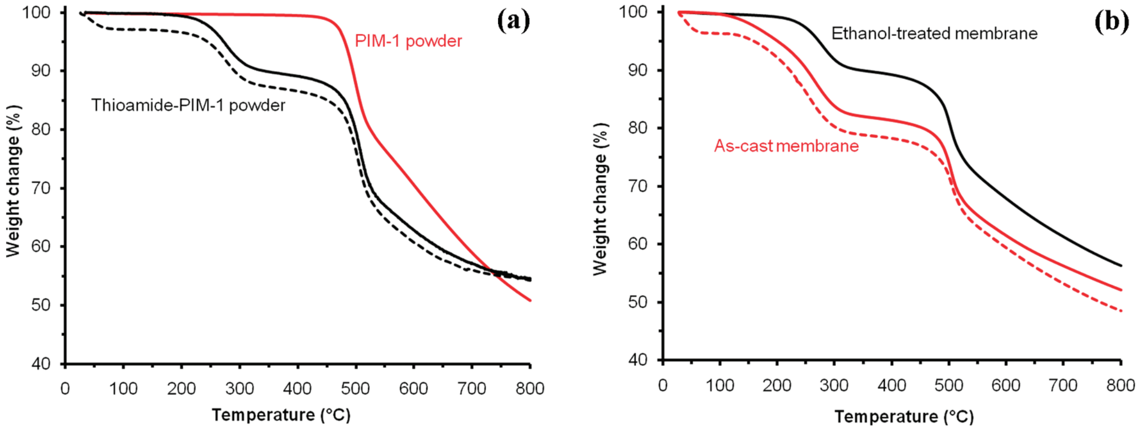


Figure 6. Thermogravimetric analysis of (a) powder samples of thioamide-PIM-1 batch DNM45 exposed to atmosphere (dashed black line) and preheated to 120 °C in the TGA to remove weakly adsorbed volatiles (solid black line) and, for comparison, PIM-1 batch LMA03 preheated to 160 °C in the TGA (solid red line), and (b) membrane samples of thioamide-PIM-1 batch DNM128 as cast from tetrahydrofuran (dashed red line), preheated to 80 °C in the TGA to remove weakly adsorbed volatiles (solid red line) and soaked in ethanol 72 h, then dried in air 20 h and preheated to 80 °C in the TGA (solid black line).

Table 2. Gas Permeability (barrer[a]) and Ideal Selectivity against N_2 for Thioamide-PIM-1 with 80% Conversion (DNM45)

		N_2	CH_4	O_2	He	H_2	CO_2
before EtOH treatment (81 μm ± 13.5)	permeability	3.9	8.7	19	55	92	150
	α (i/N_2)	-	2.2	4.9	14.1	23.6	38.5
after EtOH treatment (90 μm ± 3.23)	permeability	37	56	140	270	610	1120
	α (i/N_2)	-	1.5	3.8	7.3	16.5	30.3

[a] 1 barrer $=10^{-10}$ cm^3 cm cm^{-2} s^{-1} $cmHg^{-1}$ = 3.35×10^{-16} mol m m^{-2} s^{-1} Pa^{-1}

increasing conversion of nitrile to thioamide. The apparent BET surface area fell from 770 m^2 g^{-1} for PIM-1 to 544 m^2 g^{-1} upon approximately 50% conversion to 263 m^2 g^{-1} for the 80% converted polymer. This is a trend that has recently been seen for a carboxylated version of PIM-1. Increased carboxylation of PIM-1 resulted in a decrease in apparent surface area and porosity.[26] There are various reasons why chemical modification may lead to a reduction in effective porosity. In the case of thioamide-PIM-1, the thioamide is bulkier than the nitrile, occupying some of the free volume available in the parent polymer. In addition, the presence of groups which are capable of hydrogen bonding promotes intermolecular interactions between neighboring chains, resulting in a reduction in the polymer's free volume.

Thermogravimetric analysis (Figure 6a) of thioamide-PIM-1 powder showed a weight loss of about 3% at low temperatures (below 60 °C) if exposed to air, even for just a couple of minutes, after 1.5 h under vacuum. This can be attributed to species adsorbed weakly from the atmosphere, presumably humidity. Preheating in the TGA under N_2 eliminates this low-temperature weight-loss and enables better comparison of other features. Thioamide-PIM-1 powder shows a weight-loss of about 10% in the temperature range 190−350 °C. This can be attributed to thermal decomposition of the thioamide group leading to loss of H_2S. Low-molar-mass thioamides are known to decompose, giving H_2S and nitrile, at temperatures around 200 °C.[27] Thus, above 300 °C the polymer reverts to PIM-1, although thermal cross-linking may also occur. There is further weight-loss above 430 °C, which may be attributed to degradation of the backbone.

Unlike PIM-1, thioamide-PIM-1 at 80% conversion is not soluble in solvents such as $CHCl_3$ and CH_2Cl_2. Thioamide-PIM-1 does however maintain good solubility in tetrahydrofuran, so solution processing and film formation is still possible. Also, with the incorporation of the thioamide functionality the polymer becomes soluble in polar aprotic solvents such as DMF, DMSO and DMAc. Free standing thioamide-PIM-1 membranes were prepared from batch DNM45 by casting from THF solution in order to perform single gas permeation experiments.

Thermogravimetric analysis of a membrane (Figure 6b) shows the features discussed above for a powder sample. In addition there is a weight-loss commencing at about 100 °C which runs into that associated with thermal decomposition of the thioamide group. This additional weight loss of about 8% may be attributed to occluded THF. Ethanol treatment removes this occluded solvent and the thermal behavior of an ethanol-treated membrane is very similar to that of a powder sample. The presence of THF in the as-cast membrane, and its removal from the ethanol-treated membrane, was verified by NMR (see Supporting Information).

Membrane Permeation. The results of single gas permeation experiments carried out on thioamide-PIM-1 (DNM45), before and after ethanol treatment, are reported in Table 2. The permeation rate order in thioamide-PIM-1 is the same as in PIM-1 ($CO_2 > H_2 > He > O_2 > CH_4 > N_2$). Double logarithmic "Robeson" plots of selectivity versus permeability are shown in Figure 7 for the gas pairs CO_2/N_2 and O_2/N_2. Thioamide-PIM-1 presents a considerably higher ideal selectivity than PIM-1, but the lower free volume in this polymer causes also a reduction of the permeability coefficient of over 1 order of magnitude. Similar

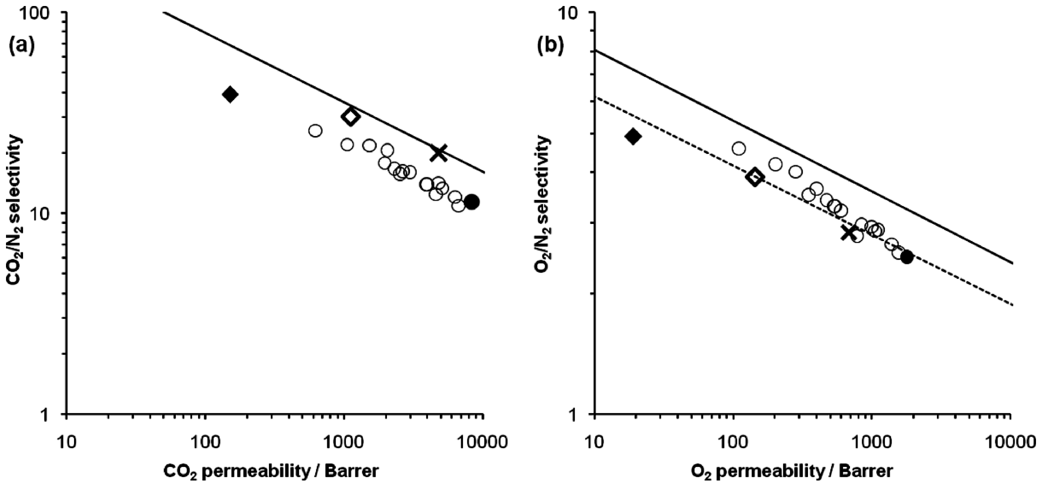


Figure 7. Double logarithmic plots of selectivity versus permeability for (a) CO_2/N_2 and (b) O_2/N_2 showing Robeson's 2008 (solid line)[9] and 1991 (dashed line)[8] upper bounds, with data from this work for PIM-1 batch LMA06 (×) and thioamide-PIM-1 batch DNM45 as-prepared (◆) and after ethanol treatment (◇), and data of Du et al.[18] for PIM-1 (●) and PIM-1 carboxylated to varying extents (○).

trends were observed by Du et al.[18] for carboxylated PIM-1, as is also shown in Figure 7. Considering the CO_2/N_2 separation, which is relevant for CO_2 capture from flue gas, the ideal selectivity in thioamide-PIM-1 is significantly higher than in PIM-1 ($CO_2/N_2 = 38.5$ for thioamide-PIM-1 batch DNM45 and 20 for PIM-1 batch LMA06). High selectivity can be more important than a high permeability, because membrane module design or process design can never improve a low selectivity, but a low permeability can be overcome, at least to some extent, by reducing the effective film thickness.

Depending on the gas species, the treatment of thioamide-PIM-1 with ethanol gives a five to 10-fold increase of the permeability, combined with a modest decrease of the ideal selectivity. As a consequence, referring to the CO_2/N_2 gas pair separation, after ethanol treatment the thioamide-PIM-1 is located very close to Robeson's 2008 upper bound (Figure 7).[9] Similar behavior was reported for PIM-1 films after treatment with lower alcohols (methanol, ethanol),[10] but the permeability enhancement is more pronounced for thioamide-PIM-1. Ethanol treatment serves both to remove occluded casting solvent (see discussion above and Supporting Information) and to enhance the free volume. Loss of the excess free volume, and hence a reduction in permeability, is expected over time. Aging effects will be the focus of further studies.

An interesting side effect of soaking of the membrane in ethanol is that on drying there is a notable contraction of the sample, accompanied by an increase of about 10% in the thickness, compared to the as-prepared membrane. This suggests that the as-prepared membrane contains some stresses which relax when the membrane is sufficiently plasticized by soaking in ethanol. Similar effects have been observed for solvent-cast perfluoropolymer membranes upon heating near the glass transition.[28] Such anisotropy in the as-cast membrane is likely to increase the selectivity and to reduce the permeability of the membrane. Nevertheless, it will not explain the entire difference in permeability before and after soaking, which depends also on changes in the free volume and loss of occluded solvent.

A more detailed analysis of the permeation data reveals that the increase in permeability on ethanol treatment is mainly caused by enhancement of the solubility coefficient and to a lesser extent by an increase in diffusivity (Figure 8a,c). The diffusion coefficient depends on the resistance the molecules experience when moving through the polymer matrix and, besides the properties of the polymer, e.g., its free volume, this is related to the size of the penetrant. Indeed, the diffusion coefficient of the six gases investigated correlates quite well with the squared effective molecular diameter, d_{eff}^2, introduced by Teplyakov and Meares,[29] showing a steep decrease of the diffusion coefficient with increasing molecular size. The correlation between the diffusion coefficient and the molecular dimensions is related to the transport mechanism, which is generally an activated mechanism in dense films, with distinct "jumps" of the penetrant from one free volume element to the next. For small molecules in polymers with a high free volume, this mechanism gradually changes into Knudsen-type diffusion if the penetrant molecules have a similar size to the narrowest "bottleneck" between two free volume elements. Indeed, this seems to be the case for He and H_2 in PIM-1, and to a lesser extent in thioamide-PIM-1 after ethanol treatment, whereas the fresh films of thioamide-PIM-1 behave more like a classical glassy polymer. As suggested by Meares,[30] the dependence of $\log(D)$ on d^2 is due to the fact that the activation energy of diffusion is believed to be proportional to the cross sectional area of the penetrant molecule and for more or less spherical molecules such as permanent gases the cross sectional area is proportional to d^2. Later, Teplyakov and Meares[29] further improved the correlation by defining an *effective* molecular diameter, but the physical meaning of the correlation is the same.

With exception of the smaller molecules He and H_2, the diffusion coefficient of all gases is approximately 1 order of magnitude lower than in untreated PIM-1, while the difference between the ethanol-treated and the fresh thioamide-PIM-1 is much smaller (Figure 8a). On the other hand, the ethanol treated sample of thiamide-PIM-1 has a much higher gas solubility than the as-cast sample, comparable to that of untreated PIM-1 (Figure 8c). The solubility depends on the physical-chemical interactions between the polymer matrix and the penetrant, and on the condensability of the latter. Gas critical temperature, T_c is a common index of the condensability

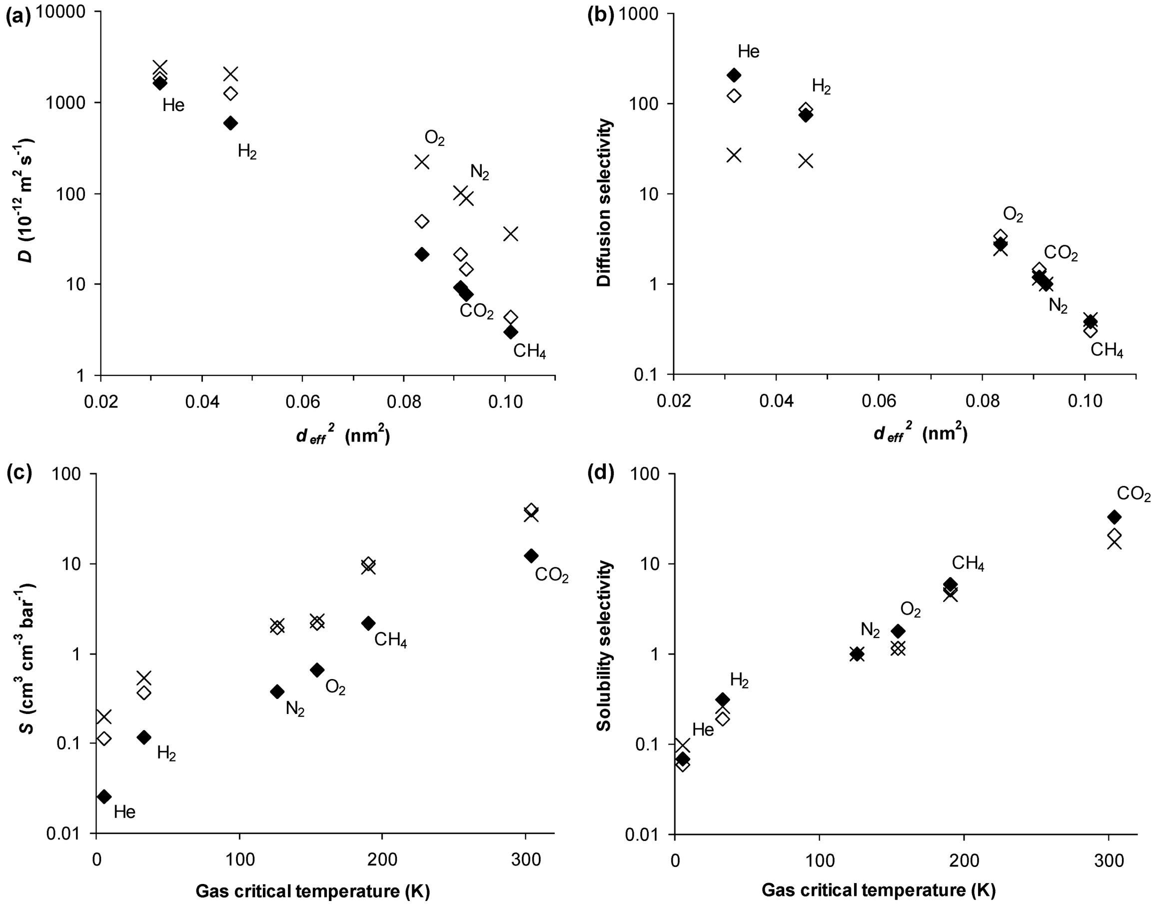


Figure 8. Diffusion and solubility coefficients and corresponding selectivities vs nitrogen as a function of the squared effective diameter of the gas and its critical temperature, respectively. PIM-1 batch LMA06 (×) and thioamide-PIM-1 batch DNM45 as-prepared (◆) and after ethanol treatment (◇).

of gas species, while also the normal boiling point or the Lennard-Jones energy parameter ε/k are often used successfully. For the three membrane samples investigated, the gas solubility increases unambiguously with T_c in an exponential fashion (Figure 8c). The absolute values also depend on the available free volume, which is the reason why this type of high free volume polymer often has a high solubility selectivity. Concerning the ideal selectivity (i/N_2) of thioamide-PIM-1, the diffusion selectivity is arguably less affected by the ethanol treatment than the solubility selectivity (Figure 8b,d).

■ CONCLUSIONS

Postmodification of the polymer of intrinsic microporosity PIM-1, using phosphorus pentasulfide as a thionating agent in the presence of sodium sulfite, yields thioamide-PIM-1 with up to 80% conversion of nitrile to thioamide. The product is soluble in a number of polar aprotic solvents and can be cast from solution to form free-standing membranes. In gas permeation, a thioamide-PIM-1 membrane exhibits increased ideal selectivity, at the expense of a reduction in permeability, compared to the parent polymer. Soaking the membrane in ethanol, which both removes occluded casting solvent and enhances polymer free volume, strongly enhances the permeability and slightly reduces the ideal selectivity. This makes thioamide-PIM-1 an interesting new member of the PIM family, which combines a high CO_2/N_2 selectivity with a more than average permeability, locating it very near Robeson's upper bound.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Experimental details for preparation of PIM-1, ^{1}H NMR spectra of as-cast and ethanol-treated thioamide-PIM-1 membrane, discussion of accuracy in permeability and diffusion measurements, and tables of permeability, diffusion, and solubility coefficients. This material is available free of charge via the Internet at http://pubs.acs.org/.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: Peter.Budd@manchester.ac.uk. Telephone: +44(0)161-275-4711.

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REFERENCES

(1) Bernardo, P.; Drioli, E.; Golemme, G. *Ind. Eng. Chem. Res.* **2009**, *48*, 4638–4663.

(2) Budd, P. M.; McKeown, N. B. *Polym. Chem.* **2010**, *1*, 63–68.

(3) Budd, P. M.; Ghanem, B. S.; Makhseed, S.; McKeown, N. B.; Msayib, K. J.; Tattershall, C. E. *Chem. Commun.* **2004**, 230–231.

(4) Budd, P. M.; Elabas, E. S.; Ghanem, B. S.; Makhseed, S.; McKeown, N. B.; Msayib, K. J.; Tattershall, C. E.; Wang, D. *Adv. Mater.* **2004**, *16*, 456–459.

(5) Budd, P. M.; Msayib, K. J.; Tattershall, C. E.; Ghanem, B. S.; Reynolds, K. J.; McKeown, N. B.; Fritsch, D. *J. Membr. Sci.* **2005**, *251*, 263–269.

(6) McKeown, N. B.; Budd, P. M. *Macromolecules* **2010**, *43*, 5163–5176.

(7) Everett, D. H. *Pure Appl. Chem.* **1972**, 577–638.

(8) Robeson, L. M. *J. Membr. Sci.* **1991**, *62*, 165–85.

(9) Robeson, L. M. *J. Membr. Sci.* **2008**, *320*, 390–400.

(10) Budd, P. M.; McKeown, N. B.; Ghanem, B. S.; Msayib, K. J.; Fritsch, D.; Starannikova, L.; Belov, N.; Sanfirova, O.; Yampolskii, Y.; Shantarovich, V. *J. Membr. Sci.* **2008**, *325*, 851–860.

(11) Du, N.; Robertson, G. P.; Pinnau, I.; Thomas, S.; Guiver, M. D. *Macromol. Rapid Commun.* **2009**, *30*, 584–588.

(12) Carta, M.; Msayib, K. J.; McKeown, N. B. *Tetrahedron Lett.* **2009**, *50*, 5954–5957.

(13) Carta, M.; Msayib, K. J.; Budd, P. M.; McKeown, N. B. *Org. Lett.* **2008**, *10*, 2641–2643.

(14) Ghanem, B. S.; McKeown, N. B.; Budd, P. M.; Fritsch, D. *Macromolecules* **2008**, *41*, 1640–1646.

(15) Du, N.; Robertson, G. P.; Pinnau, I.; Guiver, M. D. *Macromolecules* **2010**, *43*, 8580–8587.

(16) Du, N.; Robertson, G. P.; Pinnau, I.; Guiver, M. D. *Macromolecules* **2009**, *42*, 6023–6030.

(17) Du, N.; Robertson, G. P.; Song, J.; Pinnau, I.; Thomas, S.; Guiver, M. D. *Macromolecules* **2008**, *41*, 9656–9662.

(18) Du, N.; Robertson, G. P.; Song, J.; Pinnau, I.; Guiver, M. D. *Macromolecules* **2009**, *42*, 6038–6043.

(19) Du, N.; Park, H. B.; Robertson, G. P.; Dal-Cin, M. M.; Visser, T.; Scoles, L.; Guiver, M. D. *Nat. Mater.* **2011**, *10*, 372–375.

(20) Kaboudin, B.; Elhamifar, D. *Synthesis* **2006**, 224–226.

(21) Goswami, S.; Maity, A. C.; Das, N. K. *J. Sulfur Chem.* **2007**, *28*, 233–237.

(22) Ozturk, T.; Ertas, E.; Mert, O. *Chem. Rev.* **2010**, *110*, 3419–3478.

(23) Du, N.; Song, J.; Robertson, G. P.; Pinnau, I.; Guiver, M. D. *Macromol. Rapid Commun.* **2008**, *29*, 783–788.

(24) Crank, J. *The Mathematics of Diffusion*, 2nd ed.; Clarendon Press: Oxford, 1975.

(25) Lin-Vien, D.; Colthup, N. B.; Fateley, W. G.; Grassell, J. G. *The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules*; Academic Press: London, 1991.

(26) Weber, J.; Du, N.; Guiver, M. D. *Macromolecules* **2011**, *44*, 1763–1767.

(27) Clou, K.; Janssens, J. F.; Blaton, N.; Lenstra, A. T. H.; Desseyn, H. O. *Thermochim. Acta* **2003**, *398*, 47–58.

(28) Macchione, M.; Jansen, J. C.; De Luca, G.; Tocci, E.; Longeri, M.; Drioli, E. *Polymer* **2007**, *48*, 2619–2635.

(29) Teplyakov, V.; Meares, P. *Gas Sep. Purif.* **1990**, *4*, 66–74.

(30) Meares, P. *J. Am. Chem. Soc.* **1954**, *76*, 3415–22.