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Polymers of Intrinsic Microporosity (PIMs) substituted with Methyl Tetrazole[†]

Naiying Du^a, Gilles P. Robertson^a, Mauro M. Dal-Cin^a, Ludmila Scoles^a, Michael D.
Guiver^{a,b *}

^a National Research Council Canada, Ottawa, Ontario, K1A 0R6, Canada

^b WCU Department of Energy Engineering, Hanyang University, 17 Haengdang-dong,
Seongdong-gu, Seoul 133-791, South Korea

E-mail: naiying.du@nrc-cnrc.gc.ca; gilles.robertson@nrc-cnrc.gc.ca; mauro.dal-cin@nrc-cnrc.gc.ca; ludmila.scoles@nrc-cnrc.gc.ca; michael.guiver@nrc-cnrc.gc.ca

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* Corresponding author (M. D. Guiver, email: michael.guiver@nrc-cnrc.gc.ca)

Abstract

A polymer of intrinsic microporosity (PIM-1) containing nitrile groups was reacted by [2 + 3] cycloaddition reaction to give a polymer substituted with tetrazole groups (TZ-PIM), and then was further methylated to give a new PIM substituted with methyl tetrazole groups (MTZ-PIM). In contrast to TZ-PIMs, the MTZ-PIMs had distinctly improved solubility characteristics, enabling a more detailed investigation of the degree of conversion for the cycloaddition reaction and the structures of TZ-PIMs, which showed the presence of two kinds of tetrazole rings. Compared with PIM-1, the MTZ-PIM showed higher gas permselectivity with a corresponding decrease in gas permeability for pure gas pairs such as O₂/N₂ and CO₂/N₂, and for mixed gases, such as CO₂/N₂. Data for selectivity coupled with high gas permeability is close to the Robeson 2008 upper-bound performance limit for the O₂/N₂ and CO₂/N₂ pure gas pairs, and exceeds the upper-bound for the CO₂/N₂ mixed gas pair.

Keywords: microporosity; membrane; tetrazole

Introduction

During the last decade, polymeric microporous materials have been a topic of growing interest, because of their potential for applications in gas separation membranes, sorption resins, chromatographic materials and gas storage media. Among those materials, a new class of soluble rigid ladder-type polydibenzodioxanes having sites of contortion, referred to by the inventors Budd et al. and McKeown et al. as polymers of

intrinsic microporosity (PIMs), are recently attracting significant attention.^[1, 2, 3, 4, 5] The PIM materials have some significant advantages, such as good processibility, a broad range of physical properties, potential for introducing functionality onto the polymer chain and high gas permeability combined with a moderate selectivity, for membrane-based gas separations. Typically, PIMs are prepared by aromatic nucleophilic polycondensation of tetraphenol monomers having contorted centers with tetrahalogenated monomers, to generate ladder-type chain structures. However, relatively few of these monomers have been found suitable for providing high molecular weight homopolymers and copolymers, due to their unique structures or reactivities^[6, 7, 8, 9, 10, 11].

As a viable alternative to the design of new monomers, there are several approaches to access structurally new PIM materials yielding new properties, for example, (1) post-modifying PIMs,^[12, 13, 14, 15] (2) copolymerizing PIMs^[16] or (3) cross-linking PIMs.^[14] In our recent work, we reported a controlled [2 + 3] cycloaddition reaction (click reaction) between an inorganic azide and the nitrile groups on PIM-1, the most well-known and reported PIM-type material (Scheme 1). The reaction resulted in PIMs containing tetrazole groups (TZ-PIM), as well as unreacted nitrile groups, depending on the intended extent of conversion.^[13] In the present work, the data obtained from the MTZ-PIMs allows a more detailed investigation of the relationship between degree of conversion from nitrile to tetrazole groups for different reaction conditions, as well as new information about the structure of the substituted tetrazole group. In our previous work, dense films of TZ-PIM became too brittle to be handled for gas separation testing when the degree of conversion was above 70%, because of hydrogen bonding.

Methylation of the tetrazole rings in TZ-PIM reduces hydrogen bonding interactions, thereby improving the mechanical properties of the membrane. Here we report the synthesis of MTZ100-PIM, having 100% conversion to methyltetrazole from the nitrile-containing PIM-1, its structural characterization and gas transport properties.

Scheme 1. Reaction scheme for the [2 + 3] cycloaddition reaction and complete conversion of PIM-1 to methylated tetrazole MTZ100-PIM.

Experimental Section

Materials

Dimethylacetamide (DMAc), toluene, methanol (CH_3OH), potassium carbonate (K_2CO_3), sodium azide (NaN_3), zinc chloride (ZnCl_2), methyl iodide (CH_3I), tetrahydrofuran (THF) and chloroform (CHCl_3) were purchased from Sigma-Aldrich and

used as received. 5,5',6,6'-Tetrahydroxy-3,3,3',3'-tetramethylspirobisindane (TTSBI, Sigma-Aldrich) was purified by crystallization from methanol. Tetrafluoroterephthalonitrile (TFTPN, Matrix Scientific) was purified by vacuum sublimation at 150°C under inert atmosphere.

Characterization Methods

The structures of the polymeric materials were fully characterized using nuclear magnetic resonance (NMR) spectroscopy. NMR analyses were recorded on a Varian Unity Inova spectrometer at a resonance frequency of 399.961 MHz for ^1H , 376.276 MHz for ^{19}F and 100.579 MHz for ^{13}C . ^1H and ^{19}F NMR spectra were obtained from samples dissolved in CDCl_3 using a 5 mm pulsed field gradient indirect detection probe. ^1H - ^{13}C heteronuclear 2D experiments (HSQC, HMBC) were also obtained from the same indirect detection probe. ^{13}C NMR spectra were collected using a 5 mm broadband probe. The solvent signals (CDCl_3 ^1H 7.25 ppm, ^{13}C 77.00 ppm; DMSO-d_6 ^1H 2.50 ppm, ^{13}C 39.43 ppm) were used as the internal references. An external reference was used for ^{19}F NMR: CFCl_3 0 ppm.

Elemental analysis was carried out by Galbraith laboratories, Inc.

Molecular weight and molecular weight distributions were measured by gel permeation chromatography (GPC) using Ultrastyrigel columns and THF as the eluent at a flow rate of 1 mL/min. The values obtained were determined by comparison with a series of polystyrene standards.

FTIR spectra with a single bounce diamond ATR accessory were recorded with film samples at 4 cm^{-1} resolution, 64 scans, over the $400\text{--}4000\text{ cm}^{-1}$ range (Thermo Scientific FTIR Nicolet 6700).

Polymer thermal degradation curves were obtained from thermogravimetric analysis (TGA) (TA Instruments, model Q-5000IR). The TGA furnace was equipped with an interface for mass spectrometry detection of the off-gasses released from the polymer decomposition. Polymer samples for TGA were initially heated to $120\text{ }^{\circ}\text{C}$ under nitrogen purge gas and maintained at that temperature for 1 h for moisture removal and then heated to $600\text{ }^{\circ}\text{C}$ at $5\text{ }^{\circ}\text{C}/\text{min}$ for degradation temperature measurement. A mass spectrometer (MS Thermostar, Pfeiffer Vacuum) was used to detect gases driven off from thermally degraded samples in the TGA instrument.

Glass transition temperatures (T_g) were observed from differential scanning calorimetry (DSC) (TA Instruments model 2920), and samples for DSC were heated at $10^{\circ}\text{ C}/\text{min}$ under a nitrogen flow of $50\text{ mL}/\text{min}$, then quenched with liquid nitrogen and reheated at $10\text{ }^{\circ}\text{C}/\text{min}$ for the T_g measurement.

Polymer dense-film membranes were tested for pure and mixed gas permeability using cross-flow cells with a permeation area of 9.62 cm^2 . Gases were obtained from BOC: air was dry and CO_2 free, O_2 and N_2 were UHP grade or equivalent, CO_2 was bone dry grade. Feed mixtures of CO_2/N_2 were prepared at 10, 20, 30 and 40 vol.% using mass flow controllers (1179 MKS), via a flow controller (MKS 247C) with the CO_2 flowrate set to a ratio of the N_2 flow. Feed and permeate concentrations for CO_2 were measured using a Quantek 906 CO_2 analyzer with a 0-100% range and a Varian 450 GC equipped with a thermal conductivity detector and on-line sampling. Oxygen concentrations for air

permeation experiments were measured using an Advanced Micro Instruments O₂ meter, Model 65, calibrated to 20.9% oxygen for air with a range of 0-95%. Permeate flows were measured using bubble flow meters with a range of 0.1, 1.0 and 10 mL as appropriate. Permeance is corrected to standard temperature and pressure (STP) from a typical room temperature of 22 °C. Membranes were initially evaluated using air and allowed to stabilize overnight. Pure gas permeance was typically measured in the sequence N₂, O₂, CO₂, with a 0.34 MPa pressure difference (50 psi) with the permeate at atmospheric pressure. Mixtures were measured in increasing CO₂ feed concentrations and the pure gas sequence repeated in selected cases. Feed flows with mixed gases were maintained at 1,500 mL min⁻¹, thereby maintaining the permeate recovery below 2%.

Preparation of Methyltetrazole-Containing PIMs (MTZ-PIMs)

Synthesis of the PIM-1 starting material (M_n of 58,000 Da and PDI of 5.0) was as previously described ^[8], from which several samples of TZ-PIMs were prepared according to ^[13]. In two flasks, light yellow PIM-1 was dissolved in DMAc (10 mmol PIM-1 in 200 mL of solvent each) at 120 °C. NaN₃ (80 mmol) and anhydrous ZnCl₂ (20 mmol) were introduced into one of the flasks. In another flask, NaN₃ (80 mmol) and anhydrous ZnCl₂ (40 mmol) were introduced. The reaction mixtures were stirred at 120 °C for a total of 8 days. Samples were withdrawn from the flasks every 12 or 24 h and added to 200 mL of dilute HCl (1:50 by volume in water) to monitor the degree of conversion by the cycloaddition reaction. The withdrawn TZ-PIM samples were heated at 60 °C for 1 h in dil. HCl, filtered, washed on the filter with the dil. HCl followed by water, then acetone, and then dried in a vacuum at 120 °C for 24 h.

Methylation of TZ-PIM samples was conducted as follows: TZ-PIMs were dissolved in DMAc containing a molar excess of K_2CO_3 and CH_3I , and the reaction mixture was stirred at room temperature for 24 h. The resulting MTZ-PIMs were recovered by precipitation from the reaction mixtures by pouring into 50 mL deionized water containing several drops of HCl (the pH of the HCl-acidified water was 5.0). After boiling for 1 h, the brownish yellow MTZ-PIM polymers were filtered, washed on the filter with additional acidified water, followed by water and methanol and then dried in a vacuum at 120 °C for 24 h.

Dense Film fabrication

Dense polymer films for gas permeability measurements were prepared from 1-2 wt% solutions of PIM-1 or MTZ100-PIM in chloroform. Solutions of PIM-1 and MTZ-PIM were filtered through 0.45 μm polypropylene filters. PIM-1 solutions were poured into glass Petri dishes in a glove box at room temperature and allowed to evaporate slowly for 1 day at room temperature to provide films. MTZ-PIM solutions were poured into Teflon Petri dishes in a glove box and allowed to evaporate slowly for 1 day at 60 °C. The resulting dense-film membranes were subjected to the same post-treatment protocol. The membranes were first boiled in water (containing a few drops of HCl, pH = 5-6). After several washes in water, the membranes were soaked in methanol and dried at 100°C for 24 h, in a vacuum oven connected to a liquid nitrogen trap. The resulting flexible membranes had thickness in the range of 70-90 μm and were bright yellow (for PIM-1) or light brown yellow (for MTZ-PIM). Compared to its precursor (TZ-PIM),

MTZ100-PIM films could be readily cast and were more flexible, possibly due to a reduction in hydrogen bonding interactions.

Figure 1. Degree of nitrile conversion to tetrazole groups under different molar equiv ratios of PIM-1 nitrile groups to NaN₃ and ZnCl₂

Results and discussion

Although [2 + 3] cycloaddition chemistry has been known for many years, particularly between azide and ethynyl compounds, it underwent a renaissance with the discovery of the catalyzed reaction, becoming commonly referred to as ‘click chemistry’ on account of its rapid and quantitative nature. [2 + 3] Cycloaddition chemistry has been utilized for the construction and functionalization of polymeric materials.^[17] In the present work, two reaction conditions using different reagent ratios were investigated for the conversion of the nitrile group of PIM-1 to tetrazole, by reaction with an inorganic azide. The [2 + 3] cycloaddition reaction between an azide and a nitrile is far less

commonly reported than that between an azide and an ethynyl compound. The PIM-1 obtained using an optimized polycondensation process and used as the starting material was gel-free and had a high molecular weight ($M_n = 58,000$, PDI = 5.0).^[8] The polymer products of the reaction contain tetrazole groups, resulting in strong inter-chain hydrogen bonding interactions. These interactions led to solution gelation in polar solvents containing trace amounts of water, and consequently poor or imprecise ^1H and ^{13}C NMR spectra. Additionally, the degree of nitrile to tetrazole conversion using other methods, such as elemental analysis, was complicated by the strong adsorption of water by TZ-PIM. However, hydrogen bonding interactions can be suppressed by addition of a methyl group onto each tetrazole unit. The degree of conversion was more accurately obtained by calculating the amount of hydrogen on methyl tetrazole groups in the ^1H NMR spectrum. As shown in Figure 1, the reaction rate for the cycloaddition was increased by increasing the amount of ZnCl_2 catalyst. In the reaction system containing the lesser amount of catalyst, using a molar equiv. ratio of $-\text{CN} : \text{ZnCl}_2$ of 1 : 2 resulted in 74% of the $-\text{CN}$ being converted into tetrazole groups after eight days. With a higher a molar equiv. ratio of $-\text{CN} : \text{ZnCl}_2$ of 1 : 4, full conversion to tetrazole was achieved after 8 days, and the resulting fully methylated tetrazole derivative is denoted MTZ100-PIM. As shown in Table 1, the molecular weight of MTZ100-PIM was reduced from 58,000 for PIM-1 to 34,000 Da, which implied either that chain scission was minor during 8 days of the $[2 + 3]$ cycloaddition reaction, or that it was a consequence of solution behavior in the GPC measurements. However, the molecular weight of MTZ100-PIM was sufficient for casting robust and flexible membranes.

Table 1 Properties of PIM-1 and TZ-PIMs modified under different conditions

Polymer	M_n	M_n/M_w	Nitrogen
PIM-1	58,000	5.0	
MTZ100-PIM	34,000	3.0	17.98%

Elemental analysis for nitrogen in the resulting polymer was 17.98%, approaching the MTZ100-PIM calculated value of 19.49%, implying that the conversion of methyl tetrazole was close to complete.

Figure 2. Comparative FTIR spectra of PIM-1 and MTZ100-PIM

As seen from Fig. 2, PIM-1 shows the characteristic nitrile absorption band at 2238 cm^{-1} , which is completely absent in MTZ100-PIM. Instead, a narrow absorption band near 1580 cm^{-1} arises due to stretching vibration of the N=N and N-H groups, which implies that the nitrile groups were converted into tetrazole groups.^[18] It is notable

there are additional small bands near 1510 cm^{-1} , which are due to the C=N stretching vibrations^[19], characteristic of a tetrazole ring. A comparison of the FTIR absorption bands suggest that nitrile groups were completely converted into tetrazole groups in MTZ100-PIM.

The PIM-1 and MTZ100-PIM were fully characterized by ^1H , ^{13}C and ^{19}F NMR spectroscopy. Carbon NMR was particularly useful as there are many quaternary carbon atoms and few hydrogen atoms on the functionalized portion of these polymers. Comparative ^1H NMR spectra of PIM-1 and MTZ100-PIM are displayed in Fig. 3, while the ^{13}C NMR spectrum of MTZ100-PIM is displayed in Fig. 4. The aliphatic and aromatic hydrogen signals of PIM-1 were previously assigned^[13].

The presence of new signals was noted in both ^1H and ^{13}C NMR spectra of MTZ100-PIM when compared with PIM-1 spectra. The proton spectrum had two new multiplets, both having intensities of 3H when compared with the 12H of the main chain four CH_3 groups; this ratio of exactly 6H : 12H indicated a full conversion of nitrile groups to methyltetrazole. However, the presence of two multiplets indicated the presence of more than one type of methyl tetrazole. The chemical shift displacements of the two new multiplets between 4.0 and 4.6 ppm (Fig. 3 B) is in concordance with methyl protons under the combined influence of an electron withdrawing heteroatom (N) and an anisotropic aromatic ring effect from the tetrazole moiety. The results from the carbon spectrum (Fig. 4) confirmed the presence of methyl groups attached onto two different nitrogen atoms of the tetrazole rings: 1-methyl or 2-methyl, as elucidated from the proton spectrum. When compared to the PIM-1 ^{13}C NMR spectrum, the MTZ100-PIM spectrum had two new signals in the aliphatic region (34 and 40 ppm). These two signals showed

clear $^1J_{\text{C-H}}$ correlations (2D HSQC NMR) with the proton signals at 4.0 - 4.6 ppm; hence the N-CH₃ groups. The spectrum also showed a series of four signals for the main chain C11 and C13, which could only occur when three tetrazole ring configurations were possible: one with both N-CH₃ at position C15, one with both N-CH₃ at position C17 and one with the N-CH₃ at positions C15 and C17. Furthermore, C14 shows a three-bond correlation ($^3J_{\text{C-N-C-H}}$) with H15 in the 2D HMBC spectrum. ^1H and ^{13}C NMR evidence support the chemical structures displayed in Fig. 3 and Fig. 4, where 1-methyl tetrazole and 2-methyl tetrazole groups are randomly distributed on the polymer chains. The signal intensities of the N-CH₃ groups obtained from ^1H NMR have a ratio of 1:1 for the two types of methyl tetrazole rings. NMR prediction software (ACD Labs v. 12.01, Nov 2008) was also used to correlate the experimental and theoretical ^1H and ^{13}C NMR spectra of the methyl tetrazole polymer, which provided a favorable match for the number of signals and their chemical shifts for both nuclei. Finally, the ^{19}F NMR spectra (not shown) were collected; no fluorine signals were evident.

Figure 3. Comparative ^1H NMR spectra of (A) PIM-1 and (B) MTZ100-PIM.

Figure 4. ^{13}C NMR spectrum of MTZ100-PIM.

Figure 5. TGA curves of PIM-1, TZ-PIM and MTZ100-PIM.

The MTZ100-PIM was further characterized by TGA and DSC, and the results compared to PIM-1 and its tetrazole precursor – TZ-PIM (Fig. 5). None of the polymers exhibited a discernable T_g in the measured range of 50°C to 350°C. The TGA curve of PIM-1 (Fig. 5) shows a high thermal stability, likely due to its nitrile-containing main chain having strong dipolar interactions. TZ-PIM and MTZ100-PIM are significantly less thermally stable compared with PIM-1, with MTZ100-PIM having a higher degradation temperature of 202°C when compared to 170°C for TZ-PIM. A possible explanation for the difference in thermal stability lies in the “heat shielding effect” of alkyl groups, providing fast relaxation of the energy of thermal excitation of heterocycles.^[20] Figure 5 shows that under nitrogen purge and with a heating rate of 10 °C/min, the decomposition of MTZ100-PIM was accompanied by three stages, whereas TZ-PIM only showed two stages of decomposition.

A TGA-MS experiment was conducted on MTZ100-PIM to investigate the polymer degradation process in greater detail. The test was done at a heating rate of 5 °C/min under a helium purge and showed the same three-step degradation curve as seen in the nitrogen atmosphere experiment. The gases released from the polymer decomposition were analyzed by MS (m/e 1-100) and correlated with the TGA curve. TGA-MS data of the MTZ100-PIM showed 2 degradation steps before 350 °C and ~7% weight losses during each step. Two MS signals of almost the same intensity for m/e 14 and 28 increased, peaked and then decreased during each step. Those specific signals detected by the MS are typical of nitrogen gas which originates from decomposition of the methyl tetrazole ring. The remaining decomposition observed during the 3rd degradation step was attributed to thermal degradation of the polymeric residue and fragments or remains of methyl tetrazole rings. TZ-PIM only has two decomposition stages due to the existence of a reversible reaction between 1H-form tetrazole and 2H-form tetrazole. Based on literature information and experimental observations, we propose a plausible degradation process to explain the three-step degradation curve for the MTZ groups. It is known that the 2-alkyl-form tetrazole is less thermostable than the 1-alkyl-form tetrazole, because N₂ readily splits off, resulting in nitrilimine formation during the initial stage of decomposition.^[20] It is also known that alkyl-form tetrazoles split off into alkyl azide during the thermolysis of 1-alkyl-form tetrazole, but rarely in the case of 2-alkyl-form.^[20] We observed a strong MS signal for m/e 57, which is present only during the 2nd degradation step and which could originate from methyl azide groups. We therefore suggest that the first stage of decomposition was mainly due to decomposition of the 2-methyl-form tetrazole of MTZ100-PIM into N₂ gas, and then the

residue of 2-methyl-form tetrazole continued to decompose; while the 1-methyl-form tetrazole started to decompose during the second stage by releasing methyl-azide first, and then the residue of 1-methyl-form tetrazole decomposed to release N₂. The experimental total weight loss value (~14.2 %) for MTZ100-PIM during the first two decomposition steps was in good agreement with the ~14.8% calculated weight loss expected from methyl tetrazole decomposition. The first two MTZ decomposition steps in the TGA-MS showed 1-methyl tetrazole and 2-methyl tetrazole is a 1:1 ratio in MTZ100-PIM. The weight loss from these two different tetrazole rings was consistent with the ¹H-NMR result showing a ratio of 1:1 for the tetrazole rings. Although MTZ100-PIM is less thermally stable when compared with PIM-1, it shows sufficiently high thermal stability for application as a polymeric material in membrane gas separation.

The solubility of the MTZ100-PIM is distinctly different from its tetrazole precursor. PIM-1 is readily soluble in THF, CH₂Cl₂ and CHCl₃, but insoluble in polar aprotic solvents such as dimethylformamide (DMF) and DMAc. After complete conversion to tetrazole (TZ100-PIM) by [2 + 3] cycloaddition reaction at 120 °C for 8 days, the resulting polymer was no longer soluble in CH₂Cl₂ and CHCl₃, but became soluble in polar aprotic solvents such as DMF and DMAc. After methylation, MTZ100-PIM was readily soluble in non-polar and polar aprotic solvents, indicating that the MTZ100-PIM has excellent solvent processability.

Gas permeabilities and selectivities of MTZ100-PIM, PIM-1 and TZPIM2 ^[13] are similar to those observed for many glassy or rubbery polymers: higher permeability is gained at the cost of lower selectivity and vice versa, as expected from the experimental and theoretical upper bounds for permanent gases^[21]. Mixed-gas for CO₂/N₂ and pure-gas

permeability coefficients (P) for O₂, N₂, and CO₂ were measured on dense films of PIM-1 and MTZ100-PIM. A summary of the P values and ideal selectivities for various gas pairs is shown in Table 2. Gas permeability and selectivity of PIM-1 are known to be very sensitive to film preparation conditions and post-treatment protocols ^[22]. Since PIM-1 was treated by the same post-treatment protocol as MTZ100-PIM, there is variation between previously reported permeability data and the present data for PIM-1, as shown in Table 2.

Table 2. Pure and mixed gas permeabilities and selectivities of MTZ100-PIM and PIM-1

Polymers	P (Barrer ^a)			α ^b	
	O ₂	N ₂	CO ₂ ($v_{CO_2} : v_{(CO_2 + N_2)}$)	O ₂ /N ₂	CO ₂ /N ₂
PIM-1	1521	687	8461 (pure)	2.2 (pure)	12.3 (pure)
		324	9810 (40% mixed)		30.2 (mixed)
		388	11095(30% mixed)		28.6 (mixed)
		393	10247(20% mixed)		26.0 (mixed)
MTZ100-PIM	269.6	62.7	1391(pure)	4.3 (pure)	22.2 (pure)
		42.0	1674 (40% mixed)		39.9 (mixed)
		45.7	1780 (30% mixed)		39.0 (mixed)
		49.5	2057 (20% mixed)		41.6 (mixed)

^a Permeability coefficients measured at 25°C and 50 psig feed pressure.

1 Barrer = 10⁻¹⁰ [cm³(STP)·cm]/(cm²·s·cmHg). ^b Ideal selectivity $\alpha = (P_a)/(P_b)$.

Figure 6 Pure gas permeabilities and selectivities of MTZ100-PIM and PIM-1 for the CO₂/N₂ gas pair (PIM-1—○ hollow circles and MTZ100-PIM—● solid circles).

Mixed-gas data are shown for illustrative and comparative purposes only, since mixed-gas data are not strictly applicable to the Robeson plot.

MTZ100-PIM exhibited pure gas pair selectivity for O₂/N₂ and CO₂/N₂ higher than PIM-1, with lower permeability observed (Table 2). The O₂/N₂ selectivities combined with permeabilities for both PIM-1 and MTZ100-PIM are close to the Robeson upper bound (2008),²¹ with the expected “trade-off” behavior as shown in Table 2. The CO₂/N₂ Robeson upper bound in Figure 6 shows selected literature data compared with this work. The upper bound may be considered to represent the “best” materials where the trade-off between selectivity and permeability is ideal, That is to say, if the permeability of a material decreases then the best expected increase in selectivity would be predicted by the slope of the upper bound. Materials along the upper bound, while

having different permeability and selectivity may be considered to have similar overall performance. The trade-off between selectivity and permeability for CO₂/N₂ for the PIM-1 and MTZ100-PIM membranes, nearly matches the upper bound slope; a line between the two data points is parallel to the upper bound. Hence, MTZ100-PIM membrane material has the same permeability-selectivity performance as PIM-1, but has significantly higher CO₂/N₂ selectivity.

The pure and mixed gas behavior with CO₂ and N₂ were strikingly different. For example, the ideal (pure gas) CO₂/N₂ selectivity for PIM-1 was 12.3, while the average mixed gas selectivity was 28.3, with a standard deviation of 2.1. The corresponding ideal gas selectivity of MTZ100-PIM was 22.2, higher than PIM-1, while the averaged mixed gas selectivity (40.1 ± 1.3) was significantly higher compared to the pure gas selectivity. This “enhanced selectivity” for mixed gas is the result of a slightly higher CO₂ mixed gas permeability, but primarily due to a suppression of the N₂ permeability. The mixed gas permeance of N₂ (averaged for the three different feed concentrations) was only 54% and 73% of the pure gas values for PIM-1 and MTZ100-PIM respectively. This behavior, previously observed for hydrocarbon/light gas separations ^[23,24] and for the TZ-PIM precursor ^[13], has been attributed to the condensable gas (hydrocarbon or CO₂) strongly occupying CO₂ sorption sites and excluding the sorption and/or passage of the non-condensable light gas, N₂.

Conclusions

A polymer of intrinsic microporosity containing nitrile groups (PIM-1) was sequentially modified by [2 + 3] cycloaddition with azide to provide a tetrazole-containing polymer,

and then converted to a methyl tetrazole polymer (MTZ-PIM). The MTZ100-PIM had markedly better solubility in non-protic and protic solvents than its tetrazole precursor, and maintained good processibility. The preparation of the highly soluble MTZ-PIM derivative allowed a detailed investigation of the cycloaddition reaction. The degree of conversion of nitrile group to tetrazole on PIM-1 was correlated with the reaction conditions; a polymer fully-substituted with methyl tetrazole rings could be obtained after an 8 day reaction time and an appropriate catalyst. Detailed structural analysis by FTIR and NMR confirmed the formation of methyl tetrazole from nitrile on PIM-1, and showed the presence of two methyl tetrazole forms: 1-methyl tetrazole and 2-methyl tetrazole. MTZ100-PIM exhibited lower thermal stability compared with PIM-1. A TGA-MS analysis showed that two mass losses on the TGA curves of MTZ100-PIM result from methyl and nitrogen extrusion from the degradation of methyl tetrazole rings. Compared with PIM-1, O₂, N₂ and CO₂ permeabilities of MTZ-PIM are lower, with corresponding moderate increases in pure-gas selectivities against N₂. Mixed-gas experiments with CO₂ and N₂ showed that MTZ100-PIM had performance significantly exceeding the 2008 Robeson upper-bound limit, suggesting it may provide a material useful for the fabrication of asymmetric or thin film composite membranes for gas separation.

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