Gas Transport in a Polymer of Intrinsic Microporosity (PIM-1) Substituted with Pseudo-Ionic Liquid Tetrazole-Type Structures

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ABSTRACT: We report a side group modification strategy to tailor the structure of a polymer of intrinsic microporosity (PIM-1). PIM-1 with an average of ~50% of the repeat units converted to tetrazole is prepared, and a subsequent reaction then introduces three types of pseudo-ionic liquid tetrazole-like structures (PIM-1-ILx). The presence of pseudo-ionic liquid functional groups in the PIM-1 structure increases gas selectivities for O2/N2 and CO2/N2, while it decreases pure-gas permeabilities. The overall gas separation performance of PIM-1-ILx is close to the 2008 Robeson upper bound. Since the tetrazoles are versatile groups for building a wide variety of ionic liquids, the modification method can be expanded to explore a broad spectrum of functional groups.

1. INTRODUCTION

Polymeric materials development with a specific functionality for gas separation membranes has become a productive field of research. Several approaches have been developed that enable fine-tuning of microporosity to overcome the gas permeability/selectivity trade-off and permeability decline caused by physical aging.

One of the most effective approaches for engineering polymer structures is the use of rigid, contorted molecular backbones that are unable to pack efficiently. The first generation of polymers of intrinsic microporosity, PIM-1, was introduced in 2004,1−9 and the second generation, Tröger’s base polymer, was introduced in 2013.10−12 Using this method, a significant improvement in the performance of polyimides has been reported (PIM-PIs).13−16 Another approach to disrupt polymer chain packing and increase fractional free volume further (increased permeability) is by incorporating bulky or rigid structures in the polymer repeat unit. Extensive studies have been done to improve the gas transport performance of PIM membranes using this strategy.17 For instance, polymers with spirobifluorene units2,5,9 and triptycene-modified Tröger’s base PIMs have been reported.10,18−23 The rigidity of the backbone and the presence of pendant groups are crucial points in this strategy. Optimum microstructures resulting from this approach depend on how the building blocks (monomers) fit together.24 A third design approach for fine-tailoring of chain packing is by changing the linkage geometry in a similar polymer (i.e., ortho, para, or meta).25,26 A modification of this approach is based on the thermal rearrangement of polymer chains. Thermally rearranged (TR) polymers have gained much attention during the past years as a promising strategy for producing high-performance membranes.27−32 Details of the TR process are discussed in two reviews.32,33 A fourth strategy for synthesizing polymers with outstanding membrane gas transport performance is by two-dimensional, ribbon-like polymer structures.34−36 Rigidity and intrinsic free volume are crucial elements for successful design in this strategy.24

Another interesting alternative for tailoring microstructure is polymer side group modification. The presence of a bulky side group frustrates chain packing and increases fractional free volume (high permeability), while the nature of the side group may determine gas pair selectivity.24 This approach has often been used with rigid backbones and resulted in ultra-microporosity in the solid state.37,38 In particular, Smith et al. introduced an innovative rigid side group on a flexible backbone.39

Ionic liquids have been explored and utilized as alternative membrane materials for CO2 membrane separations due to their high CO2 sorption capacity.40−44 In previous work, promising CO2 separation performance of ionic liquids (ILs), with high permeabilities, solubilities, and diffusivities, was already demonstrated in supported ionic liquid membranes.
However, the main drawbacks of SILMs have become apparent. Since ionic liquids are held within the pores of the support structure via relatively weak capillary forces, they are easily susceptible to being pushed through the support and result in severely compromising the membrane selectivity, if the transmembrane pressure differential exceeds the capillary forces. Therefore, SILMs can usually only be operated at low pressure differentials of ~0.2 atm. The design and optimization of porous supports have partly overcome some of these limitations, and in some instances, ILs sorbed in these supports have been reported to be stable at pressures of up to 7 atm. Polymeric ionic liquids are alternative systems, which may provide improved stability and CO₂ transport. It has been observed that polymeric ILs have a higher and faster absorption capacity for CO₂ than room temperature ionic liquids. However, the polymer chains selected were inappropriate for high CO₂ permeability, resulting in poor gas transport. Beyond that mentioned above, many polymeric ILs reported previously were too brittle to be used as standalone membranes.

Here, we report the incorporation of pseudo-ILs by side group modification of PIM-1. Compared with conventional polymers used in membranes, PIMs typically have high gas permeability combined with moderately good selectivity. Gas selectivity in PIMs is not mainly diffusivity dominated as in common polymeric membranes but has significant contributions from solubility, which is similar to ionic liquids. From the viewpoint of functional polymer design, the incorporation of pseudo-IL-type structures into PIMs may provide a conceptually new avenue of exploration for membrane gas separations.

Initially, PIM-1 was modified using a “click chemistry” [2 + 3] cycloaddition reaction with sodium azide and zinc chloride to yield ladder polymers containing 50% tetrazole units. Tetrazole groups are versatile groups for building a wide variety of ionic liquids through the incorporation of suitable functional groups, such as amines. Amines have already shown their utility in ILs for CO₂ capture. There are few reports of ILs derived from negatively charged tetrazole with amine, and their use has been confined to solvents, catalysts, or energetic materials. Here, we report the synthesis, characterization, and single gas transport properties of a new class of polymers with tetrazole-based pseudo-ionic liquids (PIM-1-ILs).

2. EXPERIMENTAL SECTION

2.1. Materials. The monomers (i.e., 5,5’,6,6’-tetrahydroxy-3,3’,3’-tetramethylspiribisindane (TTSBI) and tetrafluoroterephthalonitrile (TFTPN)) were purchased and purified according to a reported procedure. The solvents with a purity of >99%, salts with a purity of >99%, and amines: methylamine (40 wt % in H₂O), diisopropylamine, and N,N-diisopropylethylamine were purchased from Sigma-Aldrich and used as received. The solvent abbreviations are methanol (MeOH), tetrahydrofuran (THF), dimethyl sulfoxide (DMSO), dimethylacetamide (DMAc), dimethylformamide (DMF), and N-methylpyrrolidone (NMP). KBr was purchased from VWR International, infrared spectroscopy grade.

2.2. Preparation of PIM-1. PIM-1 (Mₙ, 86,000 Da; PDI, 2.0) was prepared as follows, using a reported procedure. The resulting PIM-1 was produced as a bright yellow spaghetti-like polymer, which was refluxed in deionized water for several hours to remove residual solvents and salts and then dried at 100 °C for 48 h in a vacuum oven.

2.3. Preparation of Tetrazole-Containing PIMs (TZPIM-50) from PIM-1 Solution. TZPIM-50 was prepared based on a previous report. The equivalence ratio of nitrile groups in PIM-1 NMP solution (1−3 g in 20 mL)/NaN₃/ZnCl₂ was 1:4:2. After the reaction proceeded for 2 days at 120 °C, the reaction mixture was cooled to 60 °C, and 15 mL of diluted HCl (1:10 by volume in water) was added. The mixture was kept stirring for 3−5 h, and then, the TZPIM (~50% degree of substitution) was precipitated and washed in the same dilute HCl. After being filtered and washed...
with water, the resulting polymer was dried in a vacuum oven at 120 °C overnight.

2.4. Preparation of PIM-1-ILs from TZPIM-50. PIM-1-ILs were synthesized from TZPIM-50. In TZPIM-50, 50% nitrile groups in PIM-1 were converted into tetrazole groups. TZPIM50 (5 mmol) with different amines in methanol solutions (15 mmol amines in 50 mL MeOH) was reacted at reflux temperature for 5-6 h, and then, the polymers were reprecipitated into water and washed with water (Scheme 1c). The polymers were dried at 80 °C in a vacuum oven for 2 days.

2.5. Characterization Methods. The structural characterization of polymers was accomplished using proton nuclear magnetic resonance (NMR) spectroscopy. Proton NMR spectra were obtained on a Varian Unity Inova spectrometer (400 MHz). The NMR solvents were CDCl₃ or DMSO-d₆. ¹H spectra were obtained by using a 5 mm pulsed field gradient indirect detection probe, and the internal references used the solvent signals CDCl₃ ¹H 7.25 ppm and DMSO-d₆ ¹H 2.50 ppm. Infrared spectra (FTIR) were obtained using a Bruker IFS 66V/S instrument under vacuum conditions of 4 mbar. The samples, which were in a powder form, were scanned in the 5–40° 2θ range, with an increment of 0.04° and at a scan speed of 8 s per point.

TGA was conducted using a Mettler Toledo TGA 3+ STAR System instrument. TGA samples were pretreated at 100 °C for 1 h under a N₂ atmosphere to remove adsorbed water. The degradation curves were obtained under a N₂ atmosphere with a heating rate of 10 °C/min to a maximum instrument temperature of 700 °C.

Gas permeability measurements were conducted on dense membranes. These were prepared from 1–2 wt % PIM solutions in CHCl₃ or NMP. Polymer solutions were prefiltered using 0.45 µm polypropylene syringe filters. The membranes were prepared by casting on glass or Teflon Petri dishes. The casting solvents were allowed to evaporate slowly in a glovebox at room temperature (for CHCl₃) or at 80 °C (for NMP) over a period of one day. The recovered membranes were immersed in boiling water for several hours. After drying under ambient conditions, they were further dried in a vacuum oven at 120 °C for one day. The thickness of the resulting membranes was in the range of 70–90 µm. The membranes PIM-1 (bright yellow) and PIM-1-ILs (brownish yellow) were flexible.

A Micromeritics TriStar 3000 porosimeter was used to measure N₂ physisorption. Adsorption–desorption isotherms were recorded at

The wide-angle X-ray diffraction spectroscopy (XRD) measurements were carried out on a Bruker AXS D8 Discover instrument equipped with a Cu Kα X-ray source and scintillator point point detector. The samples, which were in a powder form, were scanned in the 5–40° 2θ range, with an increment of 0.04° and at a scan speed of 8 s per point.

Figure 1. (a) Comparative FTIR spectra of TZPIM-50 and PIM-1-ILs. (b) TGA curves of PIM-1, TZPIM-50, PIM-1-IL1, PIM-1-IL2, and PIM-1-IL3. (c) Comparative ¹H NMR spectra of TZPIM-50 and PIM-1-ILs.
−196 °C after the samples, which were in a powder form, were outgassed. The specific surface areas of polymers were calculated based on the Brunauer–Emmett–Teller (BET) equation.

2.6. Gas Permeation Tests. Gas permeation tests were performed following procedures described in previous reports. In order to obtain the permeability ($P$) in barrer, the flow rate has to be calculated in cm$^3$/s and the pressure measured in cmHg using the following equation

$$P (\text{barrers}) = 10^{-10} \times \frac{273.15 \, (K)}{T \, (K)} \times \frac{l \, (cm)}{\Delta P \, (cmHg) \times A \, (cm^2)} \times \frac{dV \, (cm^3)}{dt \, (s)}$$

where $dV/dt$ is the permeate-side flow rate, and $T$ is the operating temperature (K). $A$ is the membrane effective area, which was 0.78 cm$^2$.

3. RESULTS AND DISCUSSION

An absorption band at 2240 cm$^{-1}$ in the FTIR spectrum (Figure 1a) of PIM-1 corresponds to nitrile groups. The absence of an N–H group is given by the lack of absorption bands in the range of 3000–3600 cm$^{-1}$. The absorption bands and their corresponding intensities in TZPIM-50, PIM-1-IL1, PIM-1-IL2, and PIM-1-IL3 exhibit similarities. In the tetrazole-substituted polymers, the nitrile absorption band intensities decreased to ~50% compared with PIM-1. Broad absorption bands in the range of 3250–3600 cm$^{-1}$, indicative of N–H stretching associated with N–H····N hydrogen bonding were observed. Absorption bands corresponding to quaternary nitrogen vibrations were in the range of 2300–2800 cm$^{-1}$. The stretching vibrations of the N==N and N–H groups were observed as an intense sharp absorption near 1650 cm$^{-1}$, which suggests that a portion of the nitrile groups were converted into tetrazole groups. Small new bands associated with the tetrazole ring appearing near 1550 cm$^{-1}$ are characteristic of C≡N stretching, while bending vibrations at 950 cm$^{-1}$ are characteristic of the tetrazole ring. Furthermore, the absorption band at 950 cm$^{-1}$ arises from –C==H bending vibration of aromatic alkenes. The absorption band around 1550–1660 cm$^{-1}$ is from the conjugated alkene (C==C) [phenyl–CN, electron withdrawing; –phenyl, electron donating]. The bands above 3000 cm$^{-1}$ are due to unsaturated –C==C–H stretch.

PIM-1, TZPIM-50, and the PIM-1-ILs were further characterized by TGA, and the comparative results are shown in Figure 1b. No observed degradation of PIM-1 occurred before 450 °C at a heating rate of 10 °C/min in N$_2$. Usually, nitrile-containing polymers, such as PIM-1, have high thermal stability, which is likely due to strong dipolar interactions. It is observed that TZPIM-50 and PIM-1-ILs...
decompose thermally in three stages: the first two stages proceed with the degradation of the tetrazole ring (around 225−450 °C), while the final stage corresponds to the polymeric residue thermo-oxidative degradation at ~700 °C. As reported by Prokudin et al., decomposition between 225 and 450 °C can be attributed to the extrusion of N₂ from the decomposition of tetrazole groups.

As shown in Figure 1b, the initial stage weight losses (i.e., before 225 °C) for TZPIM-50, PIM-1-IL1, PIM-1-IL2, and PIM-1-IL3 are 8.90, 10.30, 11.07, and 13.43%, respectively, while the weight losses at the second stage (i.e., before 450 °C) are 13.54, 14.22, 15.9, and 17.98%, respectively. This indicates that the initial two-stage weight losses for PIM-1-ILs correspond to the complete decomposition of tetrazole, which provides further supporting evidence for the presence of tetrazole structures on the main chain.

The weight losses at the last stage of decomposition (before 700 °C) for TZPIM-50, PIM-1-IL1, PIM-1-IL2, and PIM-1-IL3 are 40.57, 44.61, 43.04, and 47.48%, respectively. The last-stage decomposition is close to 50% of the complete decomposition of PIM-1-ILs, which indicates that the residue of all polymer main chains had similar structures.

In summary, the PIM-1 is thermally more stable than TZPIM-50 and PIM-1-ILs. However, all PIM-1-ILs still show sufficiently high thermal stability for the gas separation membranes, even after the nitrile groups are converted to tetrazole groups by the [2 + 3] cycloaddition reaction and modification of tetrazole structures with different ionic liquids.

The 1H NMR spectra (Figure 1c) support the structures of these PIM-1-ILs. The 1H NMR signal intensities and signal shapes of these polymers were observed at 100 °C NMR probe temperatures. As expected from the molecular structure, the detected signal intensity ratio of the aromatic (6.2−6.8 ppm) and aliphatic (0.3−2.4 ppm, CH₂, and CH₃) regions in TZPIM-50 is exactly 4H:16H. For PIM-1-IL1, besides having similar aromatic and aliphatic regions with the same integration of 4H:16H, an additional signal arose at 3.3 ppm, which corresponds to N−CH₃ with an integration of 3H. The large polymer molecules, combined with hydrogen bonding and highly viscous DMSO-d₆ solvent, result in poor spectral quality and broad signals. Thus, the 1H NMR spectra were acquired at 100 °C to improve resolution and obtain more accurate signal integration. Labile −NH proton signals are particularly susceptible to temperature and may change shape and even chemical shift, while CH protons usually remain unchanged. The signals between 6.8 and 7.2 ppm were affected by temperature changes. Hence, to confirm the −NH proton signal, a drop of D₂O was added into the NMR tube. The tube was shaken vigorously, and the spectrum was re-acquired. Since deuterium atoms readily exchange with labile protons while remaining undetected by 1H NMR, the qualitative D₂O exchange resulted in the disappearance of the broad −NH proton signals results in the 6.8−7.2 ppm region, thus confirming the presence of −NH labile protons.

For PIM-1-IL2 and TZPIM-50, in comparing N−CH₃ (CH₃)₂ with −CH₂ and −CH₃ of the PIM main chain, the integration of aromatic (6.2−6.8 ppm) and aliphatic (0.3−2.4 ppm) regions is 4H:27H. Sharp signals are observed for N−CH (2H, d, 2.9 ppm) and N−CH (2H, m, 3.5 ppm). It is noteworthy that no observable signal appeared at around 6.8−7.2 ppm, which implies that hydrogen bonded −NH protons are absent.

XRD measurements were performed to investigate chain packing (Figure 2a). The absence of a sharp diffraction peak in the XRD patterns indicates an amorphous structure for the synthesized polymers. The broad peak appearing at 3.8 Å is representative of aromatic systems, and the peak at 4.8 Å indicates the d-spacing of efficiently packed chains. The broad peaks at 6.6 and 11.7 Å for PIM-1 are attributed to loosely packed polymer chains due to their contorted ladder architecture and the creation of micropores. However, in comparison with TZPIM-50 and PIM-1-ILs, a peak at 6.6 Å did not have a sharp appearance owing to overlap between the 6.6 and 11.7 Å peaks.

The incorporation of the tetrazole groups into the PIM-1 structure caused a reduction in a broad peak at 2θ = 11.7°, suggesting that the d-spacing of TZPIM-50 membrane chains became smaller. This is in agreement with the results of the BET, presented in Figure 2b. The addition of the amines into the TZPIM-50 eliminated the broad peak at 2θ = 11.7° and slightly increased the peak at 6.6 Å. This can be attributed to the presence of the amine groups inside the micropore cavity.

The BET surface area of the PIM-1 membrane is higher than those of TZPIM-50 and PIM-1-ILs, which indicates that the overall PIM-1 porosity is higher than those of TZPIM-50 and PIM-1-ILs. This is because tetrazole and different pseudo-ionic liquid structures diminish the size of micropore cavities and interchain distance, by space filling and interchain interactions, which further rigidify the polymer chains. Although both tetrazole and ionic liquid groups partially occupy the micropores, these reductions are higher in PIM-1-ILs, and the surface area decreased as the IL size increased. It will be shown that the permselectivity improved for PIM-1-IL membranes, when compared with TZPIM-50 and PIM-1 membranes. The reductions of surface area were well-correlated with the permeability and selectivity for PIM-1, TZPIM-50, and PIM-IL membranes.

The adsorption capacity of CO₂ for PIM-1 is higher than those for TZPIM-50 and PIM-1-ILs, presented in Figure 2c. Based on these BET results, it appears that the increase in permselectivity of PIM-1-ILs can be attributed to the enhancement of diffusion selectivity rather than the affinity between the pseudo-ionic liquid and CO₂.

One of the crucial parameters for the processability of the synthesized PIMs is the solubility in organic solvents. Table 1

| solvent       | PIM-1 | TZPIM-50 | PIM-1-IL1 | PIM-1-IL2 | PIM-1-IL3 |
|---------------|-------|---------|-----------|-----------|-----------|
| THF           | ++    | -       | -         | -         | -         |
| CH₂Cl₂        | ++    | -       | -         | -         | -         |
| CHCl₃         | ++    | -       | -         | -         | -         |
| DMF           | -     | ++      | ++        | ++        | ++        |
| NMP           | +     | ++      | ++        | ++        | ++        |
| DMSO          | -     | +       | +         | +         | +         |
| methanol      | -     | -       | -         | -         | -         |

**Key:** ++, readily soluble; +, soluble with heating; −, partially soluble; −, insoluble.
lists the solubility data of the polymers. PIM-1 is readily soluble in THF, CH₂Cl₂, and CHCl₃, soluble by heating in NMP but insoluble in polar aprotic solvents such as DMF, DMAc, and DMSO. Different from PIM-1, TZPIM-50 is readily soluble in DMAc and NMP and soluble in DMF, DMSO and CHCl₃ with heating but insoluble in THF and CH₂Cl₂. The solubility of all the PIM-1-ILs is similar to that of TZPIM-50, but they are insoluble in CHCl₃, even with heating. When comparing TZPIM-50 and all three PIM-ILs, gels formed more readily for DMF solutions of TZPIM-50 and primary amine (PIM-1-IL1) due to strong hydrogen bonding, while PIM-1-IL3 exhibited the least gel formation. It was visually observed that the degree of swelling of the polymer membranes in chloroform increased in the order of PIM-1-IL1 < PIM-1-IL2 < PIM-1-IL3, while in methanol, they increased in the order of PIM-1-IL3 < PIM-1-IL2 < PIM-1-IL1. These interesting observations also indicate that the solubility of these polymers was affected by the different amine cations of the tetrazole pseudo-ionic liquids.

A summary of single gas permeability and ideal selectivity values for various gas pairs is shown in Table 2. It is known that the gas permeability and selectivity of PIM-1 are largely affected by pretreatment and membrane fabrication conditions and are especially sensitive to moisture. Variations in the permeability of PIM-1 between previously reported data and the present data are shown in Figures 3 and 4.

Table 2. Gas Permeabilities and Ideal Selectivities of PIM-1, TZPIM-50, PIM-1-IL1, PIM-1-IL2, and PIM-1-IL3

| Polymers       | P (barrer) | α   |
|----------------|------------|-----|
| PIM-1-H₂O      | 1113       | 0.29|
| PIM-1-MeOH     | 1545       | 3.2 |
| TZPIM-50-H₂O   | 276        | 2.1 |
| TZPIM-50-MeOH  | 752        | 3.9 |
| PIM-1-IL1      | 169        | 4.7 |
| PIM-1-IL2      | 151        | 4.3 |
| PIM-1-IL3      | 102        | 4.5 |

“Permeability coefficients measured at 25 °C and 100 psig (6.89 bar) feed pressure. 1 barrer = 10⁻¹² cm³ (STP)·cm/(cm²·s·cmHg).

αIdeal selectivity α = (P₂)/P₁.

The post-treatment protocol for PIM membranes is normally methanol, which is conducted to remove film forming history and residual solvents. However, methanol is unsuitable for PIM-1-IL pretreatment because of a propensity for swelling. In place of methanol, PIM-1-IL membranes were treated solely in boiling water, which was slightly acidified with HCl to pH 5, to remove residual polar aprotic casting solvent and salts. After being dried under ambient conditions, the membranes were dehydrated in a vacuum oven for at least 24 h by gradually increasing the temperature from room temperature to 120 °C. For comparison, the PIM-1 membrane was treated in a similar manner. Consequently, it is important to note that the gas transport properties of PIM-1 differ substantially from commonly reported literature values, which relate to differences in the water versus methanol post-treatment. Figure 3 shows that the O₂/N₂ selectivities for PIM-1 and PIM-ILs lie between the 1991 and 2008 Robeson upper bounds. The substitution of pseudo-ionic liquid pendant groups in the PIM-1 structure increases the selectivity of PIM-1-IL1, PIM-1-IL2, and PIM-1-IL3 up to 65, 50, and 58%, respectively, relative to PIM-1, with concomitant decreases in O₂ permeability approximately following the trade-off limits. The substituent resides in the PIM-1 cavities and decreases the overall microporosity, particularly for the sterically largest substituent. Compared with PIM-1, PIM-1-ILs generally exhibit lower oxygen permeabilities but higher O₂/N₂ selectivities, with performance trending closer to the 2008 Robeson upper bound.

PIM-1-ILs show good CO₂/N₂ transport performance, as shown in Figure 4, placing them close to the 2008 Robeson upper bound. The interchain distance of the PIM-1-ILs does not appear to be significantly changed with respect to PIM-1 by introducing pseudo-IL groups since they appear to occupy the interchain space. The sterically larger amine counterions have lower gas permeabilities (see Table 1), suggesting that the pseudo-ILs act more as interchain filling materials within the PIM structures. Thus, modifying the cations or anions in the
PIMs is a conceptually simple approach to tune gas selectivity and permeability.

4. CONCLUSION

A conceptually new approach to novel-structured polymers of intrinsic microporosity containing pseudo-ionic liquids (PIM-1-ILs) is presented, whereby tetrazole-modified PIM-1 with a degree of tetrazole substitution of ~50% was reacted with various amines to form ionic sites. Compared with PIM-1, the PIM-1-ILs exhibit overall attractive gas transport properties. Higher gas selectivity that of PIM-1 is achieved, while the overall performance is close to the 2008 Robeson upper bound for the $O_2/N_2$ and $CO_2/N_2$ gas pairs. Tetrazole groups are versatile groups for building a wide variety of ionic liquids through the incorporation of suitable functional groups, such as amines. We envisage that the gas transport properties of these PIM-1-ILs can be readily tuned by selecting different cations for TZPIMs, or the concept can be extended to other ionic structures, beyond using tetrazole.

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Notes

The authors declare no competing financial interest.

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