Synthesis and Characterization of Polybenzimidazoles derived from Tetraaminodiphenylsulfone for High Temperature Gas Separation Membranes

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Abstract

A series of polybenzimidazoles containing sulfonic groups were synthesized in Eaton’s reagent for high temperature $\text{H}_2/\text{CO}_2$ separation membranes. The key monomer, 3,3’,4,4’-tetraaminodiphenylsulfone, was prepared via a novel and economical synthetic route starting from 4,4’-dichlorodiphenylsulfone. These polybenzimidazoles with sulfonic moieties had enhanced solubilities in dipolar aprotic solvents relative to the commercial Celazole® that is prepared from diaminobenzidine. Thermal gravimetric analysis showed that the materials were stable at elevated temperatures with 5% weight loss values of at least 485 °C in either air or $\text{N}_2$. Glass transition temperatures of three polybenzimidazoles in this series were ascertained by dynamic mechanical analysis to be 438-480 °C. These sulfonyl-containing polybenzimidazoles exhibited excellent gas separation properties for $\text{H}_2/\text{CO}_2$. Polymers from tetraaminodiphenylsulfone and either terephthalic or isophthalic acid crossed Robeson’s upper bound for $\text{H}_2/\text{CO}_2$. 
Introduction

Polymeric membranes for gas separation have become an important technology for various industrial refinery processes. In contrast to traditional separation technologies such as cryogenic distillation, pressure swing adsorption and chemical absorption, membrane separations offer several advantages, including lower energy consumption, lower capital investment and ease of operation. [1] Due to a significant growth in interest over the last ~30 years, numerous polymers have been developed as membranes for a variety of gas separations. [2] An inherent trade-off relationship between permeability and gas selectivity based on empirical observations of available gas transport data has been reported by Robeson, [3,4] and the theory behind this phenomenon was described by Freeman. [5] Most of the available gas transport data on polymeric membranes from research laboratories have been measured in the temperature range of 25-35 °C. However, for many industrial applications, the ideal operating temperature may vary significantly from ambient conditions. For example, a high operation temperature (150-300 °C) is required to improve the thermal efficiency for H₂ separation from pre-combustion syngas in the Integrated Gasification Combustion Cycle (IGCC) system for electricity production. [6,7] These harsh conditions eliminate most polymer membranes from consideration due to thermal instabilities that lead to degradation and loss of mechanical properties. [8]

Polybenzimidazoles (PBIs), initially developed by Marvel, are well known for their outstanding thermal stability, often exhibiting glass transition temperatures greater than 400°C as well as flame retardance and chemical stability. [9,10] Due to these characteristics, they are promising candidates for gas separation membranes that can be used at high temperatures. Membranes prepared from a commercial polybenzimidazole, Celazole®, have been shown to have attractive gas transport properties. [11,12] Celazole® (sometimes referred to as m-PBI in the literature) [7,12] is prepared from 3,3’-diaminobenzidine and isophthalic acid. However, polybenzimidazoles based on the 3,3’-diaminobenzidine monomer have very limited solubilities in common solvents due to their rigid rod structures and intermolecular hydrogen bonding. [13] For instance, m-PBI is only partially soluble in
dimethylacetamide and insoluble in other common solvents, and PBIs based on 3,3’-diaminobenzidine and terephthalic acid are insoluble in common organic solvents. [10] Structural modification of polymer backbones to include flexible linkages usually increase the solubility of PBIs. [14] However, a reduction in rigidity causes a decrease in the glass transition temperature, thus compromising the high temperature properties of these glassy polymers. [15]

This work describes the synthesis and characterization of the sulfonyl-containing tetraamine monomer, 3,3’,4,4’-tetraaminodiphenylsulfone (TADPS), and of a series of PBIs containing this monomer. This tetraamine monomer was prepared via a novel synthetic route from the economical reagent 4,4’-dichlorodiphenylsulfone. Due to the sulfonyl linkage between the two diaminophenyl groups, tetraaminodiphenylsulfone has a bent structure compared to diaminobenzidine with a linear structure. We hypothesized that the kinked structure introduced by the sulfonyl linkages in the PBI backbones would reduce the chain packing efficiency and therefore enhance the gas transport properties of the PBIs. Initial investigations of pure gas transport properties are also discussed herein.

Experimental

Materials

4,4’-Dichlorodiphenylsulfone (DCDPS) was kindly provided by Solvay and recrystallized from toluene before use. Isopropanol, acetic acid, ammonium hydroxide solution (29%), nitric acid (69.3%) and sulfuric acid were purchased from Spectrum Chemicals and used as received. Hydrazine hydrate, palladium on carbon, sodium bicarbonate and 4,4’-oxybis(benzoic acid) were purchased from Sigma-Aldrich and used as received. Dimethylsulfoxide (DMSO), dimethylacetamide (DMAc) and N-methyl-2-pyrrolidone (NMP) were purchased from Fisher and used as received. Eaton’s Reagent was purchased from Alfa Aesar. Celite was purchased from EMD Chemicals. Isophthalic acid was provided by Amoco and recrystallized from methanol before use. Terephthalic acid was provided by Eastman and recrystallized from methanol before use.

Synthesis of the 3,3’,4,4’-tetraaminodiphenylsulfone monomer (TADPS)
*Synthesis of 3,3’-dinitro-4,4’-dichlorodiphenylsulfone*

Excess 4,4’-dichlorodiphenylsulfone (100.5 mmol, 28.75 g) and 290 mL of 96% H$_2$SO$_4$ were added to a 500-mL three-necked flask equipped with a condenser, mechanical stirrer and addition funnel. The reaction mixture was stirred at room temperature until the 4,4’-dichlorodiphenylsulfone completely dissolved. Nitric acid (69.3%) (201.0 mmol, 18.28 g) was added dropwise via the addition funnel. Upon completion of addition, the solution was stirred for 6 h at room temperature. The final heterogeneous solution containing a pale yellow precipitant was poured into 2 L of deionized water, and NaHCO$_3$ was added until the solution reached a pH of 7. Then the crude product was filtered and dried in *vacuo* at 100 °C. The product was recrystallized from acetic acid to obtain a 92% yield. $^1$H NMR (d$_6$-DMSO): δ 8.70 (d, 2H), δ 8.32 (d, 2H), δ 8.29 (dd, 2H), δ 8.05 (d, 2H).

*Synthesis of 3,3’-dinitro-4,4’-diaminodiphenylsulfone*

3,3’-Dinitro-4,4’-dichlorodiphenylsulfone (125.1 mmol, 21.80 g), NH$_4$OH (312.7 mmol, 43.6 mL) and 300 mL of DMSO were added into a 500-mL pressure reactor equipped with heating coils and an overhead stirrer. The reactor was pressurized to 60 psi with nitrogen then heated to 140 °C. After 16 h, the reaction mixture was cooled and precipitated in deionized water. The yellow precipitant was filtered, washed with copious amounts of water and dried in *vacuo* at 80 °C. A 90% yield of product was obtained. $^1$H NMR (d$_6$-DMSO): δ 8.42 (d, 2H), δ 8.04 (bs, 4H), δ 7.75 (dd, 2H), δ 7.10 (d, 2H).

*Synthesis of 3,3’,4,4’-tetraaminodiphenylsulfone.*

3,3’-Dinitro-4,4’-diaminodiphenylsulfone (30.9 mmol, 10.46 g), 1.05 g Pd/C and 700 mL of isopropanol were added to a 1000-mL three-necked flask equipped with a condenser, mechanical stirrer and addition funnel. The reaction mixture was heated in a thermocouple-regulated oil bath set at 100 °C and stirred. Hydrazine hydrate (10.2 mL, 216.4 mmol) was added dropwise through the addition funnel. After complete addition, the solution was stirred and refluxed for 12 h in the 100 °C oil bath. The reaction mixture was hot-filtered through Celite. The product started to crystallize from the filtrate upon cooling. The light grey lustrous crystals were filtered.
and washed with water. The monomer product was dried in vacuo at 100 °C overnight to afford a 62% yield. Melting point: 176 °C.

**Synthesis of tetraaminodiphenylsulfone-isophthalic acid polybenzimidazole (TADPS-IPA)**

The TADPS-IPA polymer was synthesized by direct polycondensation of the tetraamine and dicarboxylic acid in Eaton’s reagent (phosphorus pentoxide/methanesulfonic acid, PPMA) which served as both a condensing agent and solvent. This polymerization procedure was modified from previous literature. [9] TADPS (11.6 mmol, 3.2200 g), IPA (11.6 mmol, 1.9220 g) and Eaton’s reagent (22 mL) were added to a 100-mL three-necked flask equipped with a mechanical stirrer, nitrogen inlet, and a condenser. A stirred, thermocouple-regulated oil bath was used to heat the reaction to 145 °C. After refluxing for 24 h, the hot viscous solution was poured into 1 L of a stirring saturated NaHCO₃ solution to precipitate a highly fibrous solid. The solid was filtered again on an aspirator and then boiled in 500 mL of deionized water for 2 h (repeated 4 times with new DI water each time) to remove any residual salts. The solid polymer was finally dried at 150°C in vacuo for 24 h. Yield was 95%.

**Synthesis of tetraaminodiphenylsulfone-terephthalic acid polybenzimidazole (TADPS-TPA) and tetraaminodiphenylsulfone-oxybis(benzoic acid) polybenzimidazole (TADPS-OBA)**

The TADPS-TPA and TADPS-OBA polymers were synthesized in the exact manner as the TADPS-IPA polymer, except TPA (11.6 mmol, 3.2200 g) or OBA (11.6 mmol, 2.9854 g) were used instead of IPA. Yields were 96 and 95% respectively.

**Structural Characterization**

¹H NMR analysis was performed on a Varian Inova spectrometer operating at 400 MHz. All spectra were obtained from 15% (w/v) 1-mL solutions in DMSO-d₆.

Size exclusion chromatography (SEC) was conducted on the TADPS-IPA, TADPS-TPA and TADPS-OBA polybenzimidazoles to measure molecular weight distributions. The solvent was DMAc that was distilled from CaH₂ and that contained
dry LiCl (0.1 M). The column set consisted of 3 Agilent PLgel 10-μm Mixed B-LS columns 300x7.5 mm (polystyrene/divinylbenzene) connected in series with a guard column having the same stationary phase. The column set was maintained at 50 °C. An isocratic pump (Agilent 1260 infinity, Agilent Technologies) with an online degasser (Agilent 1260), autosampler and column oven was used for mobile phase delivery and sample injection. A system of multiple detectors connected in series was used for the analyses. A multi-angle laser light scattering (MALLS) detector (DAWN-HELEOS II, Wyatt Technology Corp.), operating at a wavelength of 658 nm, a viscometer detector (Viscostar, Wyatt Technology Corp.), and a refractive index detector operating at a wavelength of 658 nm (Optilab T-rEX, Wyatt Technology Corp.) provided online results. The system was corrected for interdetector delay and band broadening. Data acquisition and analysis were conducted using Astra 6 software from Wyatt Technology Corp. Validation of the system was performed by monitoring the molar mass of a known molecular weight polystyrene sample by light scattering. The accepted variance of the 21,000 g/mole polystyrene standard was defined as 2 standard deviations (11.5% for $M_n$ and 9% for $M_w$) derived from a set of 34 runs.

**Membrane preparation**

For each polymer, 0.5 g of polymer was weighed into a scintillation vial, 10 mL of DMAc was added, and the mixture was stirred until a homogeneous solution was obtained. The solution was syringe-filtered through a 0.45 μm PTFE filter into a new vial. Each vial was sonicated for 30 min to remove dissolved gases. A 10x10 cm² glass plate was cleaned with acetone and dried before use. The solution was cast on the glass plate on a leveled casting surface in the vacuum oven and allowed to dry under full vacuum at room temperature overnight. The temperature was then increased to 60°C under full vacuum for 4 h. The temperature was increased to 100 °C for another 1 h under full vacuum. The film was removed from the glass plate with the aid of water and treated in boiling water for 4 h to remove remaining solvent. The following day the film was dried in the oven at 140 °C under full vacuum.

**X-ray diffraction**

Powder X-ray diffraction (PXRD) was performed using a Scintag X-1 theta-theta diffractometer, with a Cu X-ray source and a Si(Li) solid state detector tuned to
Cu Kα radiation of 1.54 Å wavelength to characterize the amorphous nature of the PBI s in this study.

**Solubility**

Solubilities of the PBIs were determined by stirring 0.5 grams of polymer powder in 10 mL of solvent for 24 h at room temperature or 100 °C. The solvents were NMP, DMAc, DMSO and THF.

**Water uptake**

The membrane water uptake was determined by the weight difference between dry and wet membranes. Membranes (~0.2 grams) that had been vacuum-dried at 120 °C for 24 h were weighed (W_{dry}) and then immersed in deionized water at room temperature for 24 h. The wet membrane was blotted dry and immediately weighed again (W_{wet}). The water uptake of the membranes was calculated according to Equation 1. The water uptake measurements of the membranes were carried out in triplicate independently with different pieces of membranes to check the reproducibility of the results.

\[
(1) \text{Water Uptake (\%) } = \frac{W_{wet} - W_{dry}}{W_{wet}} \times 100
\]

**Thermal analysis**

The TADPS-based PBIs were characterized by thermogravimetric analysis (TGA) and dynamic mechanical analysis (DMA). TGA scans were conducted using a TA Instruments Q5000 thermogravimetric analyzer under nitrogen and air atmospheres. A heating rate of 10°C min^{-1} was employed from 25 to 700 °C. Dynamic mechanical analysis was performed using a TA Instruments Q800 configured in tensile geometry. Storage modulus (E’) and tan δ were measured in a temperature sweep mode (1 Hz, 2 °C min^{-1}) at temperatures ranging from 150 to 550 °C under a N₂ atmosphere.

**Gas transport**

Pure gas permeabilities of H₂, He, O₂ and CO₂ (UHP grade, Airgas, Radnor, Pennsylvania, USA) through the TADPS-based PBIs were measured via a constant-volume, variable-pressure method. [16] The upstream pressure was measured by a Honeywell Super TJE transducer (Honeywell Sensotec, Columbus, Ohio, USA) with
a 1500 psig range. The downstream pressure was maintained under vacuum and measured by an MKS Baratron 626B (MKS Instruments, Andover, Massachusetts, USA). Coupons of each film were masked to a metal disk with a pre-machined hole using Master Bond EP46HT-2 epoxy (Master Bond Inc., Hackensack, New Jersey, USA), and the exposed film area was measured. Prepared samples were stored in a desiccator prior to placement in the pressure cell to reduce exposure to moisture. Mounted membrane samples were placed in a 47-mm high-pressure filter holder (Millipore, Billerica, Massachusetts, USA) and degassed at 35 °C overnight. The downstream pressure rise was measured over a range of upstream pressures, and the calculated permeabilities are reported herein at 10 atm and 35 °C.

Results and Discussion

Synthesis and characterization of the 3,3’,4,4’-tetraaminodiphenylsulfone monomer (TADPS)

A synthesis procedure for the TADPS monomer has been previously reported as a four-step method starting from 4,4’-diaminodiphenylsulfone (DDS). [17] We developed a three-step synthetic route to make polymer-grade TADPS monomer starting with dichlorodiphenylsulfone (DCDPS), which is a widely used monomer for polysulfone synthesis (Figure 1).
Figure 1. Two possible routes for TADPS synthesis

TADPS is the key monomer in these PBIs. The SO₂ linkage was introduced to provide a bend in the structure to increase solubility of the PBIs (Figure 2). In the previously-reported synthetic route, protection and deprotection of the amino groups from DDS were required before and after nitration. [17] As a result, synthesis of TADPS via this method consisted of more synthetic steps, which contributed to inefficiency and increased cost. In this study, nitration of DCDPS was conducted first
to activate the sites with the chlorine substituents toward amination by nucleophilic substitution with ammonium hydroxide. Finally TADPS was achieved by reducing the nitro groups to amines. This method also produced an overall yield of 57% which is higher than the reported yield (34%) of TADPS derived from DDS. [17]

Figure 2. 3,3’-Diaminobenzidine (left) vs TADPS (right) molecules

The $^1$H NMR spectrum of TADPS is shown in Figure 3. All of the peaks integrate appropriately to confirm the molecular structure. The $^1$H NMR spectrum was also free of “extra” peaks that would correspond to organic side products or contaminants. The melting point of the recrystallized product was in good agreement with the reported value. [17]
Synthesis and characterization of polybenzimidazoles derived from TADPS

The TADPS-based PBIs in this study were synthesized by direct polycondensation using Eaton’s reagent as both a solvent and condensing agent (Figure 4). [9] PBI synthesis in acid solution was originally carried out in poly(phosphoric acid) (PPA), which is a beneficial method for preparing acid-doped PBI fuel cell membranes. [18] However, using Eaton’s reagent as a reaction solvent has some obvious advantages for general PBI synthesis. First, Eaton’s reagent is much less viscous than PPA and thus it is easier to handle. Secondly, the method conducted in Eaton’s reagent can be accomplished at a lower temperature (135-145 °C) than that required in PPA (180-200 °C). Finally, Eaton’s reagent is easier to remove than PPA once the polymerization is completed. [19]
After polymer isolation and drying, the TADPS-based PBIs were characterized by NMR spectroscopy. The $^1$H NMR spectra shown in Figure 5 confirm the expected polymer structures and show that the solvent was effectively removed. The integral values were consistent with the expected chemical structures and no extraneous peaks were observed in the spectra.

The TADPS-based PBIs were sufficiently high molecular weight to form transparent and ductile films. SEC of the PBIs quantitatively substantiated the molecular weights (Figure 6 and Table 1). The chromatograms of the polymers showed a monomodal Gaussian distribution with reasonable polydispersities. It is noted that the polydispersities in Table 1 are somewhat lower than the value of two that is expected for polymers prepared by polycondensation. The reported molecular weights were measured by static light scattering in the SEC which directly measures weight average molecular weight. Thus, the $M_w$ values may be more accurate than the $M_n$ values that were calculated from the software.
**Figure 5.** $^1$H-NMR spectra of TADPS-based polybenzimidazoles

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**Table 1.** Molecular weights of TADPS-based polybenzimidazoles by SEC

<table>
<thead>
<tr>
<th></th>
<th>$M_n$ (kDa)</th>
<th>$M_w$ (kDa)</th>
<th>PDI</th>
<th>$d_n/d_c$ (mL/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TADPS-TPA</td>
<td>20</td>
<td>31</td>
<td>1.5</td>
<td>0.31</td>
</tr>
<tr>
<td>TADPS-IPA</td>
<td>18</td>
<td>29</td>
<td>1.6</td>
<td>0.28</td>
</tr>
<tr>
<td>TADPS-OBA</td>
<td>35</td>
<td>63</td>
<td>1.8</td>
<td>0.30</td>
</tr>
</tbody>
</table>
Figure 6. Light scattering SEC chromatograms of TADPS-based polybenzimidazoles

X-ray diffraction

XRD was used to probe whether any regions of crystallinity existed in these sulfonyl-containing PBI membranes. As shown in Figure 7, the broad amorphous halos observed for all three of the polymers confirmed that they were completely amorphous. This can be desirable for gas separation membranes since crystalline domains reduce both gas diffusivity and solubility resulting in a reduction in permeability. [20]
**Figure 7.** XRD of the TADPS-based polybenzimidazoles

Solubility and water uptake

The low solubility of PBIs often limits their processibility by solvent-casting to form thin membranes. The solubilities in various solvents and water uptake of these PBIs are listed in Table 2. With introduction of sulfonyl linkages into the PBI chains, their solubilities were significantly enhanced compared to poly-[2,2’-(m-phenylene)-5,5’-bisbenzimidazole], the commercial polybenzimidazole (Celazole®, m-PBI). All three of the TADPS-based PBIs were completely soluble in common dipolar aprotic solvents at a 5.0 wt% polymer concentration, which is in the range of concentrations for solution processing to form thin membranes. As expected, all of these polymers were still insoluble in common organic solvents such as THF and methanol.
PBIs, in general, have high water uptake due to the hydrophilicity of the imidazole ring. [21] All of these sulfonyl-containing PBIs exhibited high hydrophilicity, with TADPS-TPA showing a water uptake of 25 wt%.

**Table 2.** Solubility in common solvents at 25 °C and water uptake of polybenzimidazoles

<table>
<thead>
<tr>
<th></th>
<th>NMP</th>
<th>DMAc</th>
<th>DMSO</th>
<th>THF</th>
<th>Water Uptake</th>
</tr>
</thead>
<tbody>
<tr>
<td>TADPS-IPA</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>-</td>
<td>18%</td>
</tr>
<tr>
<td>TADPS-TPA</td>
<td>+</td>
<td>++</td>
<td>++</td>
<td>-</td>
<td>25%</td>
</tr>
<tr>
<td>TADPS-OBA</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>-</td>
<td>12%</td>
</tr>
<tr>
<td><em>m-PBI</em></td>
<td>+</td>
<td>+</td>
<td>++</td>
<td>-</td>
<td>15%</td>
</tr>
</tbody>
</table>

Soluble at room temperature (++), partially soluble at room temperature and fully soluble at refluxing temperature (+), and insoluble (-).

*The data for *m*-PBI (Celazole®) is from previous literature. [22,21]

**Thermal gravimetric analysis**

PBIs are renowned for their excellent thermal stability. [10,11] Introduction of the SO₂ linkage into the polymer chain resulted in polymers that did not show any weight loss before 400°C in either air or N₂ (Figure 8a-b). The 5% weight loss
temperatures are listed in Table 3. It was observed that all of the TADPS-based PBIs exhibited lower decomposition temperatures than \textit{m}-PBI, and this was likely due to the introduction of the relatively less stable sulfonyl groups. Overall, the high thermal stabilities of all three TADPS-based PBIs make them potential candidates for high temperature membrane separations.

\textbf{Table 3.} Thermal properties of polybenzimidazoles

<table>
<thead>
<tr>
<th></th>
<th>( T_g )</th>
<th>5% weight loss in ( N_2 )</th>
<th>5% weight loss in ( \text{Air} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>TADPS-OBA</td>
<td>428 °C</td>
<td>485 °C</td>
<td>510 °C</td>
</tr>
<tr>
<td>TADPS-TPA</td>
<td>480 °C</td>
<td>499 °C</td>
<td>525 °C</td>
</tr>
<tr>
<td>TADPS-IPA</td>
<td>447 °C</td>
<td>503 °C</td>
<td>532 °C</td>
</tr>
<tr>
<td>\textit{m}-PBI *</td>
<td>417 °C</td>
<td>576 °C</td>
<td>-</td>
</tr>
</tbody>
</table>

* The reported data for \textit{m}-PBI (Celazole\textsuperscript{®}) is from previous literature [23]
Figure 8. Thermal gravimetric analysis of sulfone-containing polybenzimidazoles in (a) N₂ and (b) air
Dynamic mechanical analysis

DMA results for the series of TADPS-based PBIs under N₂ are shown in Figure 9a-b. These samples were treated with boiling water for 4 hours and then dried in vacuo at 180 °C for at least 24 hours before DMA testing. Two motional relaxation processes were observed with increasing temperature (designated β and α), consistent with results reported for other PBIs such as m-PBI. [23] Here, the β processes correspond to localized sub-glass transition motions of limited range, while the α process corresponds to the glass-rubber relaxation.

Storage moduli (Figure 9b) reveal that all three of these sulfonyl-containing PBIs maintain a stable plateau up to at least 230 °C. Up to this temperature, TADPS-TPA, TADPS-IPA and TADPS-OBA maintain a storage modulus of 3.5, 2.6 and 2.1 GPa, respectively. Above that temperature, the storage moduli of these PBIs started to decrease slowly as the temperature was increased up to 430, 397 and 371 °C respectively. The initial reductions in storage moduli corresponded to the beta relaxations of these polymers. [23] Afterwards, a large drop in storage modulus was observed for all three of the polymers which corresponds to the glass transition. The storage modulus curves indicated that the TADPS-based PBIs are high-temperature amorphous polymers that maintain their structural stiffness up to 430, 397 and 371 °C respectively. For all three of these materials, at temperatures beyond 496, 481 and 456 °C respectively (very close to the 5% weight loss values in N₂ from TGA), a stiffening occurs that is likely associated with degradation by in-situ crosslinking.

In comparison with m-PBI, the three TADPS-based PBIs had higher glass transition temperatures, which is likely due to the enhanced rigidity imparted by the
double bond feature of the C-S linkage. [24] Similar glass transition temperature enhancements in polymers have been observed with comparisons between poly(arylene ether) and poly(arylene ether sulfone). [8] The TADPS-OBA PBI had a lower glass transition temperature than the other two polymers. This can be attributed to the flexible ether linkages in the TADPS-OBA PBI that reduces the rigidity of the polymer chain.
Figure 9. (a) Dynamic mechanical analysis (tan δ vs temperature) of TADPS-based polybenzimidazoles under N₂, and (b) dynamic mechanical analysis (storage modulus vs temperature) under N₂.

Gas transport properties

Gas permeation properties of four gases (H₂, He, O₂ and CO₂) through the three sulfonyl-containing PBIs were measured at 35 °C by single gas permeation experiments. Tables 4-5 show the permeabilities and ideal selectivities of these materials. The permeability coefficients for TADPS-OBA were higher than those of TADPS-IPA and TADPS-TPA and increased from TADPS-IPA to TADPS-TPA to TADPS-OBA. For example, permeability of CO₂ was 0.11 Barrer for TADPS-IPA, 0.28 Barrer for TADPS-IPA, and 0.56 Barrer for TADPS-OBA. The ether linkages in
TADPS-OBA introduce additional kinks in the polymer backbone that disrupt chain packing, leading to higher gas permeability coefficients relative to those for the TADPS-TPA and TADPS-IPA polymers. This same phenomenon has also been observed for aromatic polyimides. [25,26] Permeability measurements of slower gases (N₂, CH₄) were attempted, but the estimated permeabilities were below the detection limit of the instrument. Further work with thinner films will be necessary to measure accurate permeabilities of these species at 35 °C and will be pursued as part of a future study.

Table 4. Permeabilities for TADPS-based polybenzimidazoles tested at 35 °C and 10 atm

<table>
<thead>
<tr>
<th>Samples</th>
<th>Thickness (μm)</th>
<th>H₂</th>
<th>He</th>
<th>O₂</th>
<th>CO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>TADPS-OBA</td>
<td>19.4 ± 0.7</td>
<td>5.7 ± 0.2</td>
<td>6.7 ± 0.2</td>
<td>0.17 ± 0.01</td>
<td>0.56 ± 0.02</td>
</tr>
<tr>
<td>TADPS-TPA</td>
<td>19.5 ± 1.1</td>
<td>5.5 ± 0.3</td>
<td>6.7 ± 0.4</td>
<td>0.09 ± 0.01</td>
<td>0.28 ± 0.02</td>
</tr>
<tr>
<td>TADPS-IPA</td>
<td>21.5 ± 1.7</td>
<td>3.6 ± 0.3</td>
<td>5.1 ± 0.4</td>
<td>0.05 ± 0.04</td>
<td>0.11 ± 0.01</td>
</tr>
</tbody>
</table>

The TADPS-IPA and TADPS-TPA PBIs are meta- and para-linked isomers. Generally, para-linked linear aromatic polymers pack less efficiently and have more segmental mobility than meta-oriented aromatic polymers. [27] Thus, higher fractional free volumes and higher permeabilities for para-oriented aromatic polymers are often observed. [28,29] TADPS-based PBIs follow this meta/para isomer effect. [27,28] Furthermore, whereas the permeabilities increase from TADPS-IPA to
TADPS-TPA to TADPS-OBA, the selectivities decrease as expected. For TADPS-OBA, the H$_2$/CO$_2$ selectivity was 10.1, which increased to 19.5 for TADPS-TPA and 32.2 for TADPS-IPA. A high H$_3$/CO$_2$ selectivity coupled with a H$_2$ permeability only moderately lower than those of TADPS-TPA and TADPS-OBA causes TADPS-IPA to cross both the prior H$_2$/CO$_2$ upper bound (initially reported in 1994) [4] and the present upper bound (revised in 2008). [30]

Table 5. Ideal selectivities for TADPS-based polybenzimidazoles tested at 35 °C and 10 atm

<table>
<thead>
<tr>
<th>Samples</th>
<th>Ideal Gas Selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>He/H$_2$</td>
</tr>
<tr>
<td>TADPS-OBA</td>
<td>1.2</td>
</tr>
<tr>
<td>TADPS-TPA</td>
<td>1.2</td>
</tr>
<tr>
<td>TADPS-IPA</td>
<td>1.4</td>
</tr>
</tbody>
</table>

As discussed previously, H$_2$/CO$_2$ separation was the focus for these PBIs. In Figure 10, the TADPS-based PBIs are plotted with the H$_2$/CO$_2$ upper bound to compare with m-PBI and other PBI derivatives reported by the Benicewicz group at near-ambient temperature (30-43 °C). [31] By introduction of fluorinated bulky linkages from the diacid monomers into the PBI backbone, the PBI derivatives had much higher H$_2$ permeabilities than m-PBI. [31] However, the H$_2$/CO$_2$ selectivities of these PBI derivatives were substantially lower than the m-PBI. As a result, the PBI derivatives still fell below the prior upper bound. Adding sulfonyl rather than
fluorinated linkages in the tetraamine monomer did not significantly improve $H_2$ permeabilities compared with $m$-PBI. The TADPS-OBA polymer also shows a lower $H_2$/$CO_2$ selectivity, but the selectivities of TADPS-TPA and TADPS-IPA were enhanced.

The upper bounds reported by Robeson were based on experimental results of gas transport properties of existing polymers measured at ambient temperature (25-35 °C). Freeman later provided the fundamental theory of the upper bound which agreed well with empirical observations. [5] Both Freeman et al. [5] and Robeson [3,32] showed that the slope of the upper bound is related to the ratio of the penetrant diameters and is unlikely to change as the state of the art develops. [5] As mentioned by Robeson, [30] limited data are available at the low-permeability limit of the $H_2$/$CO_2$ upper bound. A more complete structure-property study of PBIs could contribute to this region of the upper bound plot.

**Figure 10.** $H_2$/$CO_2$ upper bound plot comparison of TADPS-based
polybenzimidazoles with other PBIs. The gas transport data is reported by Li et al. [31] for m-PBI measured at 43 °C and other PBI derivatives were measured at different temperatures in the range of 30-41 °C.

It would be desirable to operate H₂/CO₂ separations at elevated temperatures for H₂ production from pre-combustion syngas. [6,12] TADPS-based PBIs are potential candidates for high temperature gas separation in part due to their thermal stabilities. Permeability obeys an Arrhenius-van't Hoff relation with temperature. [20] For H₂/CO₂ separation, Li et al. demonstrated that PBIs and their derivatives move toward the upper right and cross the upper bound as temperature increases. [31] TADPS-based PBIs show a similar behavior with temperature. The H₂ permeability and H₂/CO₂ selectivity of TADPS-IPA at 190 °C are shown in Figure 10. As temperature increases, the permeabilities of both H₂ and CO₂ increase while selectivity stays relatively constant. A full study and analysis of temperature-dependent gas separation properties of TADPS-based PBIs will be the focus of a subsequent publication.

Conclusions

3,3’,4,4’-Tetraaminodiphenylsulfone was synthesized via a novel route with fewer overall steps and improved yield relative to previously-reported methods, starting from an economical commercial monomer (dichlorodiphenylsulfone). A series of high molecular weight PBIs based on the 3,3’,4,4’-tetraaminodiphenylsulfone monomer were synthesized by solution polymerization in Eaton’s Reagent and their properties were compared to the commercial m-PBI (Celazole®) and other PBI derivatives for H₂/CO₂ gas separation. The TADPS-based
PBIs had increased glass transition temperatures and better organo-solubilities compared to \( m \)-PBI. Better solubility in organic solvents may likely be a major advantage since this may aid in solvent-casting thin, defect-free membranes. These TADPS-based PBIs were fabricated into films by solution casting for gas transport measurements at 35 °C. These TADPS-based PBIs exhibited good gas separation properties for \( \text{H}_2/\text{CO}_2 \) separation. TADPS-IPA and TADPS-TPA demonstrated a significant enhancement on the upper bound graph compared with \( m \)-PBI, and TADPS-IPA crossed both the prior and present upper bounds. Based on their attractive \( \text{H}_2/\text{CO}_2 \) transport properties, TADPS-based PBIs are promising candidates for further study.

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**References**


Graphical Abstract (for review)