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

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2 **Abstract**

3 A series of polybenzimidazoles containing sulfonyl groups were synthesized in
4 Eaton's reagent for high temperature H₂/CO₂ separation membranes. The key
5 monomer, 3,3',4,4'-tetraaminodiphenylsulfone, was prepared via a novel and
6 economical synthetic route starting from 4,4'-dichlorodiphenylsulfone. These
7 polybenzimidazoles with sulfonyl moieties had enhanced solubilities in dipolar
8 aprotic solvents relative to the commercial Celazole[®] that is prepared from
9 diaminobenzidine. Thermal gravimetric analysis showed that the materials were stable
10 at elevated temperatures with 5% weight loss values of at least 485 °C in either air or
11 N₂. Glass transition temperatures of three polybenzimidazoles in this series were
12 ascertained by dynamic mechanical analysis to be 438-480 °C. These sulfonyl-
13 containing polybenzimidazoles exhibited excellent gas separation properties for
14 H₂/CO₂. Polymers from tetraaminodiphenylsulfone and either terephthalic or
15 isophthalic acid crossed Robeson's upper bound for H₂/CO₂.

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2 **Introduction**

3 Polymeric membranes for gas separation have become an important
4 technology for various industrial refinery processes. In contrast to traditional
5 separation technologies such as cryogenic distillation, pressure swing adsorption and
6 chemical absorption, membrane separations offer several advantages, including lower
7 energy consumption, lower capital investment and ease of operation. [1] Due to a
8 significant growth in interest over the last ~30 years, numerous polymers have been
9 developed as membranes for a variety of gas separations. [2] An inherent trade-off
10 relationship between permeability and gas selectivity based on empirical observations
11 of available gas transport data has been reported by Robeson, [3,4] and the theory
12 behind this phenomenon was described by Freeman. [5] Most of the available gas
13 transport data on polymeric membranes from research laboratories have been
14 measured in the temperature range of 25-35 °C. However, for many industrial
15 applications, the ideal operating temperature may vary significantly from ambient
16 conditions. For example, a high operation temperature (150-300 °C) is required to
17 improve the thermal efficiency for H₂ separation from pre-combustion syngas in the
18 *Integrated Gasification Combustion Cycle* (IGCC) system for electricity production.
19 [6,7] These harsh conditions eliminate most polymer membranes from consideration
20 due to thermal instabilities that lead to degradation and loss of mechanical properties.
21 [8]

22 Polybenzimidazoles (PBIs), initially developed by Marvel, are well known for
23 their outstanding thermal stability, often exhibiting glass transition temperatures
24 greater than 400°C as well as flame retardance and chemical stability. [9,10] Due to
25 these characteristics, they are promising candidates for gas separation membranes that
26 can be used at high temperatures. Membranes prepared from a commercial
27 polybenzimidazole, Celazole[®], have been shown to have attractive gas transport
28 properties. [11,12] Celazole[®] (sometimes referred to as *m*-PBI in the literature) [7,12]
29 is prepared from 3,3'-diaminobenzidine and isophthalic acid. However,
30 polybenzimidazoles based on the 3,3'-diaminobenzidine monomer have very limited
31 solubilities in common solvents due to their rigid rod structures and intermolecular
32 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)

1 *Synthesis of 3,3'-dinitro-4,4'-dichlorodiphenylsulfone*

2 Excess 4,4'-dichlorodiphenylsulfone (100.5 mmol, 28.75 g) and 290 mL of
3 96% H₂SO₄ were added to a 500-mL three-necked flask equipped with a condenser,
4 mechanical stirrer and addition funnel. The reaction mixture was stirred at room
5 temperature until the 4,4'-dichlorodiphenylsulfone completely dissolved. Nitric acid
6 (69.3%) (201.0 mmol, 18.28 g) was added dropwise via the addition funnel. Upon
7 completion of addition, the solution was stirred for 6 h at room temperature. The final
8 heterogeneous solution containing a pale yellow precipitant was poured into 2 L of
9 deionized water, and NaHCO₃ was added until the solution reached a pH of 7. Then
10 the crude product was filtered and dried in *vacuo* at 100 °C. The product was
11 recrystallized from acetic acid to obtain a 92% yield. ¹H NMR (d₆-DMSO): δ 8.70 (d,
12 2H), δ 8.32 (d, 2H), δ 8.29 (dd, 2H), δ 8.05 (d, 2H).

13 *Synthesis of 3,3'-dinitro-4,4'-diaminodiphenylsulfone*

14 3,3'-Dinitro-4,4'-dichlorodiphenylsulfone (125.1 mmol, 21.80 g), NH₄OH
15 (312.7 mmol, 43.6 mL) and 300 mL of DMSO were added into a 500-mL pressure
16 reactor equipped with heating coils and an overhead stirrer. The reactor was
17 pressurized to 60 psi with nitrogen then heated to 140 °C. After 16 h, the reaction
18 mixture was cooled and precipitated in deionized water. The yellow precipitant was
19 filtered, washed with copious amounts of water and dried in *vacuo* at 80 °C. A 90%
20 yield of product was obtained. ¹H NMR (d₆-DMSO): δ 8.42 (d, 2H), δ 8.04 (bs, 4H), δ
21 7.75 (dd, 2H), δ 7.10 (d, 2H).

22 *Synthesis of 3,3',4,4'-tetraaminodiphenylsulfone.*

23 3,3'-Dinitro-4,4'-diaminodiphenylsulfone (30.9 mmol, 10.46 g), 1.05 g Pd/C
24 and 700 mL of isopropanol were added to a 1000-mL three-necked flask equipped
25 with a condenser, mechanical stirrer and addition funnel. The reaction mixture was
26 heated in a thermocouple-regulated oil bath set at 100 °C and stirred. Hydrazine
27 hydrate (10.2 mL, 216.4 mmol) was added dropwise through the addition funnel.
28 After complete addition, the solution was stirred and refluxed for 12 h in the 100 °C
29 oil bath. The reaction mixture was hot-filtered through Celite. The product started to
30 crystallize from the filtrate upon cooling. The light grey lustrous crystals were filtered

1 and washed with water. The monomer product was dried in *vacuo* at 100 °C overnight
2 to afford a 62% yield. Melting point: 176 °C.

3 **Synthesis of tetraaminodiphenylsulfone-isophthalic acid polybenzimidazole** 4 **(TADPS-IPA)**

5 The TADPS-IPA polymer was synthesized by direct polycondensation of the
6 tetraamine and dicarboxylic acid in Eaton's reagent (phosphorus pentoxide/
7 methanesulfonic acid, PPMA) which served as both a condensing agent and solvent.
8 This polymerization procedure was modified from previous literature. [9] TADPS
9 (11.6 mmol, 3.2200 g), IPA (11.6 mmol, 1.9220 g) and Eaton's reagent (22 mL) were
10 added to a 100-mL three-necked flask equipped with a mechanical stirrer, nitrogen
11 inlet, and a condenser. A stirred, thermocouple-regulated oil bath was used to heat
12 the reaction to 145 °C. After refluxing for 24 h, the hot viscous solution was poured
13 into 1 L of a stirring saturated NaHCO₃ solution to precipitate a highly fibrous solid.
14 The solid was filtered again on an aspirator and then boiled in 500 mL of deionized
15 water for 2 h (repeated 4 times with new DI water each time) to remove any residual
16 salts. The solid polymer was finally dried at 150°C in *vacuo* for 24 h. Yield was
17 95%.

18 **Synthesis of tetraaminodiphenylsulfone-terephthalic acid polybenzimidazole** 19 **(TADPS-TPA) and tetraaminodiphenylsulfone-oxybis(benzoic acid)** 20 **polybenzimidazole (TADPS-OBA)**

21 The TADPS-TPA and TADPS-OBA polymers were synthesized in the exact
22 manner as the TADPS-IPA polymer, except TPA (11.6 mmol, 3.2200 g) or OBA
23 (11.6 mmol, 2.9854 g) were used instead of IPA. Yields were 96 and 95%
24 respectively.

25 **Structural Characterization**

26 ¹H NMR analysis was performed on a Varian Inova spectrometer operating at
27 400 MHz. All spectra were obtained from 15% (w/v) 1-mL solutions in DMSO-d₆.

28 Size exclusion chromatography (SEC) was conducted on the TADPS-IPA,
29 TADPS-TPA and TADPS-OBA polybenzimidazoles to measure molecular weight
30 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- μ m 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 μ m 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 K α radiation of 1.54 Å wavelength to characterize the amorphous nature of the PBIs 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 $\tan \delta$ 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

1 a 1500 psig range. The downstream pressure was maintained under vacuum and
2 measured by an MKS Baratron 626B (MKS Instruments, Andover, Massachusetts,
3 USA). Coupons of each film were masked to a metal disk with a pre-machined hole
4 using Master Bond EP46HT-2 epoxy (Master Bond Inc., Hackensack, New Jersey,
5 USA), and the exposed film area was measured. Prepared samples were stored in a
6 desiccator prior to placement in the pressure cell to reduce exposure to moisture.
7 Mounted membrane samples were placed in a 47-mm high-pressure filter holder
8 (Millipore, Billerica, Massachusetts, USA) and degassed at 35 °C overnight. The
9 downstream pressure rise was measured over a range of upstream pressures, and the
10 calculated permeabilities are reported herein at 10 atm and 35 °C.

11 12 **Results and Discussion**

13 **Synthesis and characterization of the 3,3',4,4'-tetraaminodiphenylsulfone** 14 **monomer (TADPS)**

15 A synthesis procedure for the TADPS monomer has been previously reported
16 as a four-step method starting from 4,4'-diaminodiphenylsulfone (DDS). [17] We
17 developed a three-step synthetic route to make polymer-grade TADPS monomer
18 starting with dichlorodiphenylsulfone (DCDPS), which is a widely used monomer for
19 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 ^1H NMR spectrum of TADPS is shown in Figure 3. All of the peaks integrate appropriately to confirm the molecular structure. The ^1H 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]

Figure 3. $^1\text{H-NMR}$ spectrum of the TADPS monomer

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]

Figure 4. Synthesis of polybenzimidazole using Eaton's reagent as a solvent

After polymer isolation and drying, the TADPS-based PBIs were characterized by NMR spectroscopy. The ^1H 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. ^1H -NMR spectra of TADPS-based polybenzimidazoles

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

	M_n (kDa)	M_w (kDa)	PDI	dn/dc (mL/g)
TADPS-TPA	20	31	1.5	0.31
TADPS-IPA	18	29	1.6	0.28
TADPS-OBA	35	63	1.8	0.30

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2 **Figure 6.** Light scattering SEC chromatograms of TADPS-based polybenzimidazoles

3 **X-ray diffraction**

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

Figure 7. XRD of the TADPS-based polybenzimidazoles

Solubility and water uptake

The low solubility of PBIs often limits their processability 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

	NMP	DMAc	DMSO	THF	Water Uptake
TADPS-IPA	++	++	++	-	18%
TADPS-TPA	+	++	++	-	25%
TADPS-OBA	++	++	++	-	12%
<i>m</i>-PBI*	+	+	++	-	15%

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 *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.

Table 3. Thermal properties of polybenzimidazoles

	T_g	5% weight loss in N₂	5% weight loss in Air
TADPS-OBA	428 °C	485 °C	510 °C
TADPS-TPA	480 °C	499 °C	525 °C
TADPS-IPA	447 °C	503 °C	532 °C
<i>m</i>-PBI *	417 °C	576 °C	-

* The reported data for *m*-PBI (Celazole[®]) is from previous literature [23]

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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

1 double bond feature of the C-S linkage. [24] Similar glass transition temperature
 2 enhancements in polymers have been observed with comparisons between
 3 poly(arylene ether) and poly(arylene ether sulfone). [8] The TADPS-OBA PBI had a
 4 lower glass transition temperature than the other two polymers. This can be attributed
 5 to the flexible ether linkages in the TADPS-OBA PBI that reduces the rigidity of the
 6 polymer chain.

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Figure 9. (a) Dynamic mechanical analysis ($\tan \delta$ vs temperature) of TADPS-based polybenzimidazoles under N_2 , and (b) dynamic mechanical analysis (storage modulus vs temperature) under N_2

Gas transport properties

Gas permeation properties of four gases (H_2 , He, O_2 and CO_2) 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 CO_2 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

Samples	Thickness (μm)	Pure Gas Permeabilities (Barrer)			
		H ₂	He	O ₂	CO ₂
TADPS-OBA	19.4 ± 0.7	5.7 ± 0.2	6.7 ± 0.2	0.17 ± 0.01	0.56 ± 0.02
TADPS-TPA	19.5 ± 1.1	5.5 ± 0.3	6.7 ± 0.4	0.09 ± 0.01	0.28 ± 0.02
TADPS-IPA	21.5 ± 1.7	3.6 ± 0.3	5.1 ± 0.4	0.05 ± 0.04	0.11 ± 0.01

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 H₂/CO₂ selectivity was 10.1, which increased to 19.5 for TADPS-TPA and 32.2 for TADPS-IPA. A high H₂/CO₂ selectivity coupled with a H₂ permeability only moderately lower than those of TADPS-TPA and TADPS-OBA causes TADPS-IPA to cross both the prior H₂/CO₂ 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

Samples	Ideal Gas Selectivity				
	He/H ₂	H ₂ /O ₂	He/O ₂	H ₂ /CO ₂	CO ₂ /O ₂
TADPS-OBA	1.2	33	38	10	3.2
TADPS-TPA	1.2	65	79	20	3.3
TADPS-IPA	1.4	67	94	32	2.1

As discussed previously, H₂/CO₂ separation was the focus for these PBIs. In Figure 10, the TADPS-based PBIs are plotted with the H₂/CO₂ 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 H₂ permeabilities than *m*-PBI. [31] However, the H₂/CO₂ 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

1 fluorinated linkages in the tetraamine monomer did not significantly improve H₂
 2 permeabilities compared with *m*-PBI. The TADPS-OBA polymer also shows a lower
 3 H₂/CO₂ selectivity, but the selectivities of TADPS-TPA and TADPS-IPA were
 4 enhanced.

5 The upper bounds reported by Robeson were based on experimental results of
 6 gas transport properties of existing polymers measured at ambient temperature (25-35
 7 °C). Freeman later provided the fundamental theory of the upper bound which agreed
 8 well with empirical observations. [5] Both Freeman et al. [5] and Robeson [3,32]
 9 showed that the slope of the upper bound is related to the ratio of the penetrant
 10 diameters and is unlikely to change as the state of the art develops. [5] As mentioned
 11 by Robeson, [30] limited data are available at the low-permeability limit of the
 12 H₂/CO₂ upper bound. A more complete structure-property study of PBIs could
 13 contribute to this region of the upper bound plot.

14 **Figure 10.** H₂/CO₂ upper bound plot comparison of TADPS-based
 15
 16

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

1 PBI had increased glass transition temperatures and better organo-solubilities
2 compared to *m*-PBI. Better solubility in organic solvents may likely be a major
3 advantage since this may aid in solvent-casting thin, defect-free membranes. These
4 TADPS-based PBIs were fabricated into films by solution casting for gas transport
5 measurements at 35 °C. These TADPS-based PBIs exhibited good gas separation
6 properties for H₂/CO₂ separation. TADPS-IPA and TADPS-TPA demonstrated a
7 significant enhancement on the upper bound graph compared with *m*-PBI, and
8 TADPS-IPA crossed both the prior and present upper bounds. Based on their
9 attractive H₂/CO₂ transport properties, TADPS-based PBIs are promising candidates
10 for further study.

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16 **References**

- 17 [1] Stern SA. Polymers for gas separations: the next decade. J Memb Sci
18 1994;94:1–64. doi:10.1016/0376-7388(94)00141-3.
- 19 [2] Baker RW. Future Directions of Membrane Gas Separation Technology. Ind
20 Eng Chem Res 2002;41:1393–411. doi:10.1021/ie0108088.
- 21 [3] Robeson LM. Correlation of separation factor versus permeability for
22 polymeric membranes. J Memb Sci 1991;62:165–85. doi:10.1016/0376-
23 7388(91)80060-J.
- 24 [4] Robeson LM, Burgoyne WF, Langsam M, Savoca AC, Tien CF. High
25 performance polymers for membrane separation. Polymer 1994;35:4970–8.
26 doi:10.1016/0032-3861(94)90651-3.

- 1 [5] Freeman BD. Basis of Permeability/Selectivity Tradeoff Relations in
2 Polymeric Gas Separation Membranes. *Macromolecules* 1999;32:375–80.
3 doi:10.1021/ma9814548.
- 4 [6] Merkel TC, Zhou M, Baker RW. Carbon dioxide capture with membranes at an
5 IGCC power plant. *J Memb Sci* 2012;389:441–50.
6 doi:10.1016/j.memsci.2011.11.012.
- 7 [7] O'Brien KC, Krishnan G, Berchtold KA, Blum S, Callahan R, Johnson W, et al.
8 Towards a pilot-scale membrane system for pre-combustion CO₂ separation.
9 *Energy Procedia* 2009;1:287–94. doi:10.1016/j.egypro.2009.01.040.
- 10 [8] Robeson LM, Farnham AG, McGrath JE. Synthesis and Dynamic Mechanical
11 Characteristics of Poly(Aryl Ethers). *Appl Polym Symp* 1975;26:375–85.
- 12 [9] Ueda M, Sugita H. Poly(benzimidazole) synthesis by direct reaction of diacids
13 and diamines. *Macromolecules* 1985;18:2723–6. doi:10.1021/ma00154a060.
- 14 [10] Vogel H, Marvel CS. Polybenzimidazoles, new thermally stable polymers. *J*
15 *Polym Sci* 1961;50:511–39. doi:10.1002/pol.1961.1205015419.
- 16 [11] Berchtold KA, Singh RP, Young JS, Dudeck KW. Polybenzimidazole
17 composite membranes for high temperature synthesis gas separations. *J Memb*
18 *Sci* 2012;415-416:265–70. doi:10.1016/j.memsci.2012.05.005.
- 19 [12] Pesiri DR, Jorgensen B, Dye RC. Thermal optimization of polybenzimidazole
20 meniscus membranes for the separation of hydrogen, methane, and carbon
21 dioxide. *J Memb Sci* 2003;218:11–8. doi:10.1016/S0376-7388(03)00129-7.
- 22 [13] Li X, Qian G, Chen X, Benicewicz BC. Synthesis and Characterization of a
23 New Fluorine-Containing Polybenzimidazole (PBI) for Proton-Conducting
24 Membranes in Fuel Cells. *Fuel Cells* 2013;13:832–42.
25 doi:10.1002/fuce.201300054.
- 26 [14] Kumbharkar SC, Liu Y, Li K. High performance polybenzimidazole based
27 asymmetric hollow fibre membranes for H₂/CO₂ separation. *J Memb Sci*
28 2011;375:231–40. doi:10.1016/j.memsci.2011.03.049.
- 29 [15] Kumbharkar SC, Karadkar PB, Kharul UK. Enhancement of gas permeation
30 properties of polybenzimidazoles by systematic structure architecture. *J Memb*
31 *Sci* 2006;286:161–9. doi:10.1016/j.memsci.2006.09.030.
- 32 [16] Lin H, Freeman BD. Permeation and Diffusion. In: Czichos H, Smith L, Saito
33 T, editors. *Springer-handb. Mater. Meas. Methods*, Springer; 2006, p. 371–87.
34 doi:10.1007/978-3-540-30300-8_7.
- 35 [17] Lakshmi Narayan T V., Marvel CS. Polybenzimidazoles. VI.
36 Polybenzimidazoles Containing Aryl Sulfone Linkages. *J Polym Sci Part A-1*
37 *Polym Chem* 1967;5:1113–8. doi:10.1002/pol.1967.150050516.

- 1 [18] Mader JA, Benicewicz BC. Sulfonated Polybenzimidazoles for High
2 Temperature PEM Fuel Cells. *Macromolecules* 2010;43:6706–15.
3 doi:10.1021/ma1009098.
- 4 [19] Jouanneau J, Mercier R, Gonon L, Cedex G. Synthesis of Sulfonated
5 Polybenzimidazoles from Functionalized Monomers : Preparation of Ionic
6 Conducting Membranes. *Macromolecules* 2007;40:983–90.
7 doi:10.1021/ma0614139.
- 8 [20] Ghosal K, Freeman BD. Gas Separation Using Polymer Membranes : An
9 Overview. *Polym Adv Technologies* 1994;5:673–97.
10 doi:10.1002/pat.1994.220051102.
- 11 [21] Brooks NW, Duckett RA, Rose J, Ward IM, Clements J. An NMR study of
12 absorbed water in polybenzimidazole. *Polymer* 1993;34:4038–42.
13 doi:10.1016/0032-3861(93)90664-V.
- 14 [22] Klaehn JR, Luther TA, Orme CJ, Jones MG, Wertsching AK, Peterson ES.
15 New Soluble N-Substituted Polybenzimidazoles by Post-Polymerization
16 Modification. *Polym Prepr* 2005;46:708–9.
- 17 [23] Menczel J. Thermal Measurements on Poly[2,2'-(m-phenylene)-5,5'-
18 bibenzimidazole] Fibers. *J Therm Anal Calorim* 2000;59:1023–7.
19 doi:10.1023/A:1010155215759.
- 20 [24] Guo R, Mcgrath JE. Aromatic Polyethers, Polyetherketones, Polysulfides, and
21 Polysulfones. In: Matyjaszewski K, Möller M, editors. *Polym. Sci. Compr.*
22 *Ref.*, vol. 5, Elsevier B.V.; 2012, p. 377–430. doi:10.1016/B978-0-444-53349-
23 4.00153-9.
- 24 [25] Tanaka K, Kita H, Okamoto K. Permeability and permselectivity of gases in
25 fluorinated polyimides. *Polymer* 1992;33:585–92. doi:10.2115/fiber.46.12_541.
- 26 [26] Tanaka K, Masaki O, Toshino H, Kita H, Okamoto K. Effect of Methyl
27 Substituents on Permeability and Permselectivity of Gases in Polyimides
28 Prepared from Methyl-Substituted Phnylenediamines. *J Polym Sci Part B*
29 *Polym Phys* 1992;30:907–14. doi:10.1002/polb.1992.090300813.
- 30 [27] Mi Y, Stern SA, Trohalaki S. Dependence of the gas permeability of some
31 polyimide isomers on their intrasegmental mobility. *J Memb Sci* 1993;77:41–8.
32 doi:10.1016/0376-7388(93)85233-M.
- 33 [28] Coleman MR, Koros WJ. Isomeric polyimides based on fluorinated
34 dianhydrides and diamines for gas separation applications. *J Memb Sci*
35 1990;50:285–97. doi:10.1016/S0376-7388(00)80626-2.
- 36 [29] Borjigin H, Liu Q, Zhang W, Gaines K, Riffle JS, Paul DR, et al. Synthesis and
37 Characterization of Thermally Rearranged (TR) Polybenzoxazoles: Influence
38 of isomeric structure on gas transport properties. Submitted to *Polymer* 2015.

- 1 [30] Robeson LM. The upper bound revisited. J Memb Sci 2008;320:390–400.
2 doi:10.1016/j.memsci.2008.04.030.
- 3 [31] Li X, Singh RP, Dudeck KW, Berchtold KA, Benicewicz BC. Influence of
4 polybenzimidazole main chain structure on H₂/CO₂ separation at elevated
5 temperatures. J Memb Sci 2014;461:59–68. doi:10.1016/j.memsci.2014.03.008.
- 6 [32] Robeson LM, Freeman BD, Paul DR, Rowe BW. An empirical correlation of
7 gas permeability and permselectivity in polymers and its theoretical basis. J
8 Memb Sci 2009;341:178–85. doi:10.1016/j.memsci.2009.06.005.

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★ TADPS-OBA

△ TADPS-TPA

▽ TADPS-IPA

□ m-PBI