

# Effect of the Amide Bond Diamine Structure on the CO<sub>2</sub>, H<sub>2</sub>S, and CH<sub>4</sub> Transport Properties of a Series of Novel 6FDA-Based Polyamide– Imides for Natural Gas Purification

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**ABSTRACT:** A series of higher permeability polyamide– imides based on 2,2'-bis(3,4-dicarboxyphenyl) hexafluoropropane dianhydride with comparable plasticization resistance to Torlon were synthesized and formed into dense film membranes. Polymers possessing 2,4-diamino mesitylene (DAM) were stable up to 56 atm of pure CO<sub>2</sub>, which is due to enhanced charge transfer complex formation compared to polymers containing 4,4'-(hexafluoroisopropylidene) dianiline (6FpDA) and 2,3,5,6-tetramethyl-1,4-phenylenediamine (TmPDA). The new polymers containing DAM and TmPDA showed ideal CO<sub>2</sub>/CH<sub>4</sub> selectivities of near 50 with CO<sub>2</sub> and H<sub>2</sub>S permeabilities over an order of magnitude higher



than Torlon.  $CO_2$  and  $CH_4$  sorption in the DAM- and TmPDA-based materials was reduced, whereas  $H_2S$  sorption was enhanced relative to membranes containing fluorinated 6FpDA. Consequently, DAM- and TmPDA-based membranes showed increased stability toward high pressure  $CO_2$  but lower plasticization resistance toward pure  $H_2S$ . These results highlight the differences between  $CO_2$  and  $H_2S$  that challenge the rational design of materials targeting simultaneous separation of both contaminants.

# 1. INTRODUCTION

Polyamide-imides have gained attention for their use as gas separation materials due to their good mechanical and thermal properties. They also display high intrinsic efficiencies and resistance toward aggressive feeds containing condensable components due to their ability to form interchain hydrogen bonding as well as charge transfer complexes (CTC). An example of the robust nature of these materials was demonstrated by Kosuri and Koros, who measured single gas CO<sub>2</sub> permeability in Torlon 4000T, a commercially available polyamide-imide, and showed only  $\sim 4\%$  increase in permeability up to almost 800 psia.<sup>1,2</sup> Ideal CO<sub>2</sub>/CH<sub>4</sub> permselectivities of 52 were also reported. Despite these excellent properties, Torlon's use in natural gas purification is not practical because of very low fluxes resulting from a high degree of chain packing. Several researchers have shown that gas permeabilities can be increased in polyamide-imides by incorporation of bulky groups along the main chains which frustrate chain packing. The work by Nagel and Fritsch gives an excellent overview of a number of different polyamide-imides based on isomers of 2,2'-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA) and 4,4'-hexafluoroisopropylidene dianiline as the diamine, along with a detailed correlation of gas transport properties with free volume.<sup>3,4</sup> They showed CO<sub>2</sub> permeabilities as high as 56 barrer along with a CO<sub>2</sub>/CH<sub>4</sub> ideal selectivity of 36 for structures containing both fluorine moieties as well as pendent methyl groups ortho to the N-C imide bond, suggesting high permeabilities could be achieved in polyamide-imides possessing bulky groups that increase steric interactions along the polymer backbone. No information was given, however, regarding their performance toward H<sub>2</sub>S or elevated CO<sub>2</sub> feed pressures. Huang et al. measured O<sub>2</sub>/N<sub>2</sub> transport properties in 6FDA-based polyamide-imides possessing non fluorinated diamines.<sup>5</sup> They reported  $O_2$  permeabilities of 2.71 barrer and an  $O_2/N_2$  ideal selectivity of 5.27 for structures with 3,3',5,5'-tetramethylbis[4-(4-aminophenoxy)phenyl] sulfone as the diamine. However, neither CO<sub>2</sub> nor H<sub>2</sub>S transport was measured in their work. We recently reported on the effects of thermal annealing on a 6FDA-based polyamide-imide (6FDA-3-aminobenzoic acid-4,4'-hexafluoroisopropylidene dianiline, or 6F-PAI-1). The CO<sub>2/</sub>CH<sub>4</sub> separation performance was characterized using feed streams containing toluene as well as H<sub>2</sub>S and revealed a stable, mixed gas  $CO_2/CH_4$  selectivity of 30 at 69 atm total feed pressure.6 The amide-imide backbone functionality affords good plasticization resistance due to a combination of intermolecular hydrogen bonding and charge transfer complex (CTC) formation. In this work, the diamine forming a tail-tail connection (amide to amide) during polycondensation in 6F-PAI-1, namely 4-4'-hexafluoroisopropylidene dianiline, was

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Figure 1. Reaction sequence for 6FDA-polyamide-imide (6F-PAI-1,-2,-3) synthesis.



-H<sub>2</sub>O



replaced with nonfluorinated 2,4-diaminomesitylene (DAM) and 2,3,5,6-tetramethyl-1,4-phenylenediamine (TmPDA) with the goal to increase the  $CO_2$  and  $H_2S$  permeability and selectivity.

Work by Merkel et al. has shown interesting hydrocarbon and fluorocarbon solubility trends in various perfluorinated media.<sup>7,8</sup> They showed that H<sub>2</sub>S solubility is significantly reduced in both fluorinated glassy and rubbery polymers.<sup>9</sup> In the case of rubbery perfluoroelastomer TFE/PMVE49, which is based on tetrafluoroethylene, CO<sub>2</sub> solubility was higher than H<sub>2</sub>S. This was also shown for Cytop, a high free volume, highly fluorinated glassy polymer. They attributed this unusual behavior to "unfavorable" interactions between H2S and the polymer, however no attempt was made to describe the nature of these interactions. In this work, nonfluorinated DAM and TmPDA monomers were chosen to increase H<sub>2</sub>S/CH<sub>4</sub> selectivity through an increase in H<sub>2</sub>S sorption resulting from lower fluorine concentration in the polymer backbone. Additionally, pendant methyl groups on DAM and TmPDA located ortho to the rotatable N-C bond in polyimides have been shown to induce steric repulsions with neighboring carbonyl groups, causing the bond planes to configure in a highly nonplanar conformation, which significantly hinders chain packing. This is demonstrated in polyimides 6FDA-DAM and 6FDA-TmPDA,<sup>10</sup> which have CO<sub>2</sub> permeabilities as high as 350 and 450 barrer, respectively. These steric interactions were targeted in the 6F-PAI series in order to increase H<sub>2</sub>S and CO<sub>2</sub> diffusion coefficients. The overall H<sub>2</sub>S/CH<sub>4</sub> permselectivity was not expected to decrease as a result of the anticipated increase in diffusivities, as only a slight size difference between  $H_2S$  and  $CH_4$  (3.6 vs 3.8 Å) contributes to low diffusion selectivities that range between 1 and 2. Additionally, an expected increase in  $H_2S$  solubility relative to  $CH_4$  due to lower fluorine content was expected to offset any loss in size discrimination. In this paper, the physical properties of three different polyamide–imides based on diamines 6FpDA, DAM, and TmPDA are discussed along with the  $CO_2$ ,  $H_2S$ , and  $CH_4$ transport properties. Additionally, the stability of these materials toward pure gas  $H_2S$  and  $CO_2$  as well as mixtures of the two gases is reported and discussed in terms polymer chain packing, CTCs, and fluorine concentration in the polymer backbone.

# 2. MATERIALS/METHODS

2.1. Synthesis and Dense Film Formation. 6FDA was purchased from Alfar Aesar and dried at 120 °C under 30 mmHg vacuum prior to synthesis. All other chemicals were purchased from Sigma-Aldrich. DAM and TmPDA were dried at 90 °C and 15 mmHg reduced pressure before the synthesis.

All polyamide–imides were synthesized via two step reaction sequences originally described by Fritsch and Avella.<sup>4</sup> In the first reaction, the intermediate diacid containing the diimide functionality was formed by reaction between 6FDA and 2 equiv of 3-aminomethyl benzoic acid (3-ABA). Imidization was accomplished through thermal means, where temperatures between 160 and 200 °C were used to induce ring closure. The water formed was distilled off through azeotropy with xylene. Imidization was confirmed using FTIR-ATR spectroscopy and shown in Figure 2.

The diacid containing diimide, 6FDA–3ABA, was subsequently reacted with the various diamines through direct polycondensation as reported by Yamazaki et al.<sup>11</sup> With this method, a large batch of 6FDA–3ABA can be synthesized and reacted with different diamines to form a series of polyamide–imides differing only by the diamine forming the tail-to-tail connection. A schematic of the reaction is given in Figure 1, and the structures of 6F-PAI-1, -2, and -3 are shown in Table 1. The details of this reaction are given in our past work<sup>6</sup> as well as in the work by Fritsch et al.<sup>4,12</sup> With this reaction, molecular weights ranged from 50 to 60 kDa as measured by gel permeation chromatography.

Dense films membranes were fabricated using a draw casting technique. Polymer was dissolved in a given solvent at 18-20% wt. solids and spread over a clean glass surface using a stainless steel casting block with 254–500  $\mu$ m clearance. 6F-PAI-1 was dissolved in tetrahydrofuran (THF) within a THF-saturated glovebag. For 6F-PAI-2 and -3, the casting procedure was modified because of different glass surface wetting characteristics and solubility of the new polymers. For 6F-PAI-1, the surface was treated with Siliclad (Geleste Inc.) to increase hydrophobicity, thereby easing the removal of the vitirfied polymer film. 6F-PAI-2 and -3 exhibited a dewetting effect on this surface, whereby the polymer solution arranged itself in discontinuous "pools" in order to minimize surface contact. This is likely due to increased hydrophilicity of these materials resulting from lower fluorine content. Because of these issues, a nontreated, plain glass surface was used to cast 6F-PAI-2 and -3. Additionally, these materials were only soluble in high boiling, polar solvents such as N-methyl pyrrolidone (NMP) or N,N-dimethylformamide (DMF). Immediately after drawing the polymer solution, the glass plate was placed on a heating element at approximately 120 °C for 2-3 h in order to slowly evaporate enough solvent to vitrify the film. The solid films were then peeled off of the plate and soaked in methanol for 12 h at room temperature, followed by slow evaporation of methanol over 2 h. The films were then annealed in a vacuum oven at 30 mmHg absolute reduced pressure at 220 °C for 24 h, followed by slowly cooling over a period of 4 h. Without solvent exchanging, a significant amount of residual solvent remained in the membranes which greatly affected the resulting transport properties.

**2.2. Density and Fractional Free Volume.** The density of dense film membranes was measured using a density gradient column prepared from calcium nitrate. The average of at least three sections of a dense polymer film was added to the column to obtain the density of each sample. Fractional free volume was then calculated from the following equation:

$$FFV = \frac{\hat{V}_g - \hat{V}_o}{\hat{V}_g}$$

 $V_g$  is the specific volume of the glass at a certain temperature and is determined from the density measurements.  $V_{\rm o}$  is the specific occupied volume and is calculated from group contribution methods according to Bondi.  $^{13}$ 

**2.2. Thermal Analysis.** Residual solvent content in the films was checked with thermal gravimetric analysis (TGA) (STA 409 PC Luxx) using  $N_2$  at 30 cm<sup>3</sup>/min as the purge gas. Up to 5% residual solvent remained in the films not treated with MeOH. After solvent exchanging, films generally showed less than 0.5% residual solvent content.

Differential scanning calorimetry (TA Instruments, Q200 Series) was used to determine the glass transition temperature  $(T_g)$  of the dense films. N<sub>2</sub> at 50 cm<sup>3</sup>/min was used as the purge gas. The films were heated at 10 °C/min from 25 to 370 °C, followed by cooling to 25 °C, then repeating the cycle. The second heating run was used to calculate the tangent line at the step transition and was taken as the intrinsic  $T_g$ . The glass transitions temperatures are reported in Table 2.

**2.3. Spectroscopy.** FT-IR ATR Spectroscopy. Fourier transform infrared attenuated total reflectance spectroscopy (FT-IR ATR) was performed using a Bruker-Tensor 27 spectrometer equipped with a

Harrick MVP 2 Series ATR utilizing a N<sub>2</sub> purge at 30 cm<sup>3</sup>/min. An average of 128 scans with a resolution of 4 cm<sup>-1</sup> was taken. This was done to confirm imide and amide bond formation in 6FDA-3ABA and final polymer structures, respectively. Bulk powder was used for 6FDA-3ABA, and dense films with thicknesses ranging from 25 to 50  $\mu$ m were used for structure identification of the polymer membranes. Absorbance spectra are shown in Figure 2.

UV-Vis/Fluorescence Spectroscopy. Ultraviolet-visible spectroscopy was performed on a Beckman Coulter DU Series 700 general purpose spectrometer to compare differences in absorbance properties arising from *intramolecular* interactions of monomers and dilute polymer solutions. Concentrations of  $1 \times 10^{-6}$  mol/L in DMF were used to avoid saturation of the detector.

Solid state fluorescence spectroscopy (Horiba Scientific) was used to study differences in *intermolecular* charge transfer formation. A right angle configuration was used, and both excitation and emission profiles were collected. Excitation profiles were taken between 250 and 480 nm and monitored at 485 nm. Emission profiles were excited at 350 and 440 nm. The resulting spectra are shown in section 3.2.

**2.4. Gas Permeation and Sorption.** *Permeability.* Pure gas  $CO_2$ ,  $CH_4$  and  $H_2S$  permeability measurements were taken as a measure of the intrinsic separation capability of the dense polymer films. A constant volume, variable pressure apparatus was used.<sup>14</sup> The permeability coefficient is defined as the flux of the gas normalized by the transmembrane fugacity difference and film thickness (*l*) as defined in eq 1. The flux of a penetrant gas molecule, neglecting bulk flow, is described by diffusion jumps that depend on both the size of localized free volume fluctuations of the polymer chains as well as the frequency of these fluctuations. The steady state flux is given by eq 2.

$$P_A = \frac{J_A l}{\Delta f_A} \tag{1}$$

$$J_A = -D_A \frac{\partial CA}{\partial x} \tag{2}$$

For mixed gas measurements, the permeability was calculated by eq 3.  $J_T$  is the total flux of all components permeating through the membrane and  $y_A$  is the mole fraction of component A in the downstream. The compositions of the gases were determined using a gas chromatograph (Varian 450). The average of 3 injections was taken.

$$P_A = \frac{J_T l y_A}{\Delta f_A} \tag{3}$$

The ideal permselectivity given in eq 4 is described as the intrinsic separation capability of a polymer material, and is calculated from the ratios of the pure gas permeability coefficient of the fast gas relative to the slow gas. For mixed gas feeds, a separation factor is used as shown in eq 5. In the case of very low pressure in the downstream relative to the upstream side of the membrane, as was the case in this study, the ratio of the mixed gas permeability coefficients is equal to the separation factor.

$$\alpha^*{}_{A/B} = \frac{P_A}{P_B} \tag{4}$$

$$\alpha_{A/B} = \frac{[y_A/y_B]_{permeate}}{[y_A/y_B]_{feed}}$$
(5)

Gas transport through polymer membranes also depends on gas solubility. As such, the permeability coefficient can be described as the product of the diffusion and sorption coefficients via eq 6, where  $D_A$  and  $S_A$  are the diffusion and sorption coefficients, respectfully. Finally, from eq 4, the ideal permselectivity can be given as the product of the diffusion and solubility selectivities as shown in eq 7.

$$P_A = D_A \times S_A \tag{6}$$



Figure 2. (a-d) FT-IR ATR spectra in the 1900–1400 cm<sup>-1</sup> range.

$$\alpha^*{}_{A/B} = \left[\frac{D_A}{D_B}\right] \times \left[\frac{S_A}{S_B}\right] \tag{7}$$

Single gas permeability measurements were done at 4.5 atm upstream pressure while the downstream was maintained at less than 1% of 1 atm. In this situation, the transmembrane fugacity difference in eq 1 can be approximated as the upstream pressure without serious error. The gas was allowed to permeate through the membrane for a time period of 8–10 times the diffusion time lag in order to reach steady state, as discussed by Koros and Paul.<sup>15</sup> In accordance with their work, the single gas diffusion coefficients were calculated using eq 8, which relates gas diffusivity to the steady state permeation time lag.

$$D_{A} = \frac{l^{2}}{6\theta}$$
(8)

For the permeability vs pressure isotherms, the permeability was measured at a given pressure after 8-10 time-lags. The pressure was then increased by 2-3.5 atm and the membrane was allowed to reach steady state again before a measurement was taken. This process of incremental pressure increases was performed up to the point where the permeability coefficient began to increase, whereby the pressure was held constant for approximately 12 h until a measurement was taken. Because plasticization involves small and/or large scale chain relaxations, permeability beyond the plasticization pressure can be time dependent. This phenomena is discussed in detail in the work by Wind et al.<sup>16</sup> The 12 h permeation time was performed to provide a meaningful comparison of the magnitude of permeability increase between the different materials once membrane plasticization began.

*Gas Sorption.* Gas sorption in glassy polymers is envisioned to occur in two different idealized environments.<sup>17</sup> The Langmuir mode consists of molecular scale packing defects or "holes" that occur as a result of the polymer being below its glass transition temperature  $(T_g)$ . The concentration in this environment,  $C_{H}$ , is described by eq 9. The Henry's Law environment consists of polymer chains in packing equilibrium with one another and is analogous to gas dissolution in a rubbery polymer. The concentration in this mode,  $C_D$ , is described in eq 10.

$$C_H = \frac{C_H' bp}{1 + bp} \tag{9}$$

$$C_D = k_D p \tag{10}$$

p is the equilibrium pressure of the gas in contact with the membrane.  $C_{\rm H}'$  is the Langmuir capacity constant and represents the maximum amount of penetrant gas that can adsorb into these cavities. The Langmuir affinity constant, b, is the affinity of the gas for this region. The Henry's law coefficient,  $k_{\rm D}$ , characterizes the ease to which polymer chains can open up to accommodate a penetrant gas molecule, and is analogous to the sorption coefficient in rubbery polymers. Together, these regions sum to give the total concentration as shown in eq 11.

$$C = k_{D}p + \frac{C_{H}'bp}{1+bp}$$
(11)

The sorption coefficient in eq 6 is the pressure normalized concentration of the penetrant gas molecule inside the polymer membrane, and is given by eq 12.

$$S = k_D + \frac{C_H b}{1 + bp}$$
(12)

In this work, the concentration vs pressure isotherms were measured via a pressure decay technique, which is described in detail elsewhere.<sup>18</sup> The dual-mode parameters  $C_{H}'$ , *b*, and  $k_{\rm D}$  were obtained by fitting the concentration isotherms to eq 11 using a nonlinear least-squares method. The sorption coefficients were then calculated from eq 12. The data fit the equation well, and in most cases,  $R^2$  was above 0.98. Standard deviations of the fit are reported in Table 5. For H<sub>2</sub>S, membrane swelling occurred above ~5.5 atm for 6F-PAI-2 and -3, which was signified by an upswing in the isotherm that was concave to the *y*-axis. This caused difficulty in fitting the data due to nonlinearity in the isotherm at elevated pressures. In this case, only qualitative estimates can be made.

# 3. RESULTS AND DISCUSSION

**3.1. IR Spectroscopy.** ATR absorbance spectra for 6FDA-3ABA and the various 6F-PAI analogues is shown in Figures 2



Figure 3. FT-IR ATR spectra in the 3700–2600 cm<sup>-1</sup> range showing the N-H stretching mode centered around 3350 cm<sup>-1</sup>.

and 3. Symmetric and asymmetric imide stretches are shown between 1700 and 1800 cm<sup>-1</sup>, confirming imide bond formation in 6FDA-3ABA and preservation of this bond in the subsequent polymers. Additionally, the carbonyl stretch of the carboxylic acid in 6FDA-3ABA occurs near 1690 cm<sup>-1</sup>, which is depicted in Figure 2d. The carbonyl stretch in the amide bond occurs at lower wavelengths, and is shown near 1660 cm<sup>-1</sup> for the polyamide-imides. The amide bond also results in a broad, medium strength N-H stretching frequency centered around 3350 cm<sup>-1</sup>. This confirms the formation of the amide bond as well as highlights the nature of interchain hydrogen bonding. The broad peak results from varying degrees of hydrogen bonding between the randomly packed polymer chains. Thus, the shape and span of this peak qualitatively suggests the N-H groups exist in a hydrogen bonded state. It is difficult, however, to distinguish between bonded and nonbonded protons, and so the authors do not make any attempt to assess different degrees of hydrogen bonding between the three different structures.

**3.2. UV–Vis/Fluorescence Spectra.** Solution state UV– vis was performed in dilute conditions to wash out intermolecular interactions and thus examine differences in *intramolecular* charge transfer, such as  $\pi$  electron conjugation across the polymer backbone. Figure 4 compares the precursor diacid 6FDA-3ABA with polymers 6F-PAI-1, -2, and -3. Torlon was also measured as a reference for which to compare the 6F-PAI series.

The wavelengths of maximum absorption occur at 270 nm for all four polymers as well as 6FDA-3ABA. This absorption results from the conjugated  $\pi$  electrons of the aromatic rings, which exist in all five structures. The absolute intensities are not as significant, as small differences in concentration can affect this. Small variances in the scale can occur when measuring very low milligram quantities, and while attempts were made to keep the concentrations the same, it is likely that small differences in solid addition occurred, which may give rise to different



Figure 4. UV-vis spectra comparing (a) 6F-PAI-1, (b) Torlon, (c) 6FDA-3ABA, (d) 6F-PAI-2, and (e) 6F-PAI-3.

intensities. Therefore, only the qualitative aspects, such as peak position and shape are analyzed. As can be seen in Figure 4, the shape of the peaks as well as absorption cutoff wavelength are approximately equal for 6FDA-3ABA and 6F-PAI-2. This shows that very little difference in conjugation occurred by addition of DAM as the amide linker, which is the only difference between the two structures. The methyl group ortho to the N-C imide bond in 6FDA-3ABA inhibits planarity between the 6FDA and 3ABA moiety, thus it is unlikely for the lone pair electrons of the *imide* nitrogen to conjugate with the aromatic  $\pi$  electrons. Similarly, methyl groups on DAM that are located ortho to the amide nitrogen in 6F-PAI-2 inhibit planarity around the N-C amide bond. Thus, intrinsically, no significant difference in intramolecular charge transfer occurs across the backbones of the diacid monomer 6FDA-3ABA and 6F-PAI-2. 6F-PAI-3, however, shows an absorption cutoff around 280 nm, which is lower than all other materials measured. Para configurations

such as in TmPDA have greater rotational mobility compared to meta.<sup>3</sup> Thus, rotation around the amide N–C bond may be less restricted in 6F-PAI-3 compared to DAM in 6F-PAI-2, which further decreases planarity across this bond. This may reduce electron conjugation across the N–C bond, resulting in lower wavelengths of light absorption. This is also supported by the lower extent of intermolecular CTC formation in 6F-PAI-3 as will be discussed in the next section.

6F-PAI-1 and Torlon both show broader absorption peaks that are red-shifted toward longer absorption wavelength cutoffs. 6F-PAI-1 contains six aromatic rings per repeat unit, which is one higher than Torlon and 6F-PAI-2 and -3. The peak intensity and broadening may be due to increased concentration of aromatic  $\pi$  electrons, however, Torlon also shows peak broadening that is similar in shape to 6F-PAI-1 and higher in intensity than 6F-PAI-2 and -3. Therefore, the red shift in peak width and longer absorption cutoff wavelengths is due to increased electron conjugation across the polymer backbone. Because Torlon has no bulky pendent groups on the aromatic rings, it has a higher degree of backbone planarity than 6F-PAI-2 and -3. The lone pair electrons on the phenyl ether oxygen in Torlon can also conjugate with the aromatic rings, which results in a broader peak that is shifted toward longer absorption wavelengths. For 6F-PAI-1, the increase in intramolecular conjugation occurs over the amide bond since it contains the same imide functionality as 6F-PAI-2 and -3. Although the bulky CF<sub>3</sub> groups of the 6FpDA diamine inhibit close intermolecular chain packing in the solid state, this effect is not relevant in the dilute solution state, where interactions between adjacent polymer chains are unlikely. 6FpDA is also absent of pendent methyl groups which could induce rotation around the N-C bond and reduce planarity. Thus, the UV-vis spectra reveal the backbones of Torlon and 6F-PAI-1 have intrinsically higher extents of  $\pi$ -electron conjugation, which is believed to be due to a greater degree of planarity resulting from the absence bulky pendent groups along the polymer backbones.

Solid State Fluorescence Spectroscopy. Intermolecular charge transfer has been shown to increase membrane stability against swelling and plasticization by increasing dipole-dipole types of physical interactions in the solid state between electron-rich and -poor regions on adjacent chains.<sup>6,19</sup> Red shifts in wavelength of maximum absorption indicate greater electron conjugation, which can be either intra or intermolecular in nature. Because of the difficulty in obtaining films thin enough to avoid saturation of the UV-vis detector, fluorescence spectroscopy was used instead. Changes in position and shape of the fluorescence excitation profiles signify the formation of CTCs, thus it can be used to compare changes to the polymer microstructure in the solid state. Figure 5 shows the fluorescence excitation profiles for 6F-PAI-1,2 and 3, Torlon, and polyimides 6FDA-6FpDA and 6FDA-DAM. 6FDA-TmpDA polyimide was not measured, however, the authors expect a similar absorption spectra as 6FDA-DAM due to similar steric interactions resulting from pendent methyl groups ortho to the N-C imide bond.

As shown in Figure 5, 6F-PAI-2 formed additional CTCs relative to 6F-PAI-1 and -3. Both the shape and bandwidth changed along with a red-shift in the wavelength of maximum absorption. Meta-connected DAM increases chain packing relative to para connected TmPDA. This facilitates electronic interactions between adjacent chains in the solid state. 6F-PAI-1 and -3 show similar shaped absorption bands as well as



Figure 5. Fluorescence excitation spectra comparing 6FDA polyimides and Torlon (solid lines) and 6FDA polyamide–imides (dashed lines).

wavelengths of maximum absorption. Although 6F-PAI-1 showed increased intramolecular charge transfer in the UVvis spectra, in the solid state, the bulky  $-(CF_3)$ - groups inhibit close, parallel chain packing. This can significantly interfere with parallel stacking of adjacent aromatic and imide groups required for intermolecular CTC formation. For 6F-PAI-3, the pendent methyl groups ortho to the amide bond induce rotation around the N-C bond as a result of TmPDA having greater rotational mobility. This can also hinder the close overlap of adjacent polymer chains as do the CF<sub>3</sub> groups in 6FpDA, thus limiting the formation of intermolecular CTCs. The low UV-vis absorption cutoff wavelength in 6F-PAI-3 shown in Figure 4 supports the idea that its backbone is highly nonplanar. A comparison with the analogue polyimides shows that CTC formation decreased with meta connected DAM in the polyimide series relative to para connected 6FpDA. This suggests that DAM may inhibit planarity and polymer chain packing when connected over an *imide* bond, however, the opposite effect occurs when DAM is incorporated over an amide bond as it is in 6F-PAI-2, where intermolecular CTC formation is enhanced. This leads to large permeability increases in the polyimide series whereas permeabilities are reduced in the polyamides-imides. The permeability trends will be further discussed in section 3.4.

The excitation spectra for Torlon shows two absorption bands, the first near 370 nm and the second near 450 nm. This longer wavelength absorption gives rise to the more deeply colored (yellow) appearance of Torlon, and suggests charge transfer is enhanced relative to the 6F-PAI-1 and -3, which are both much lighter in color. 6F-PAI-2, which also absorbs near 460 nm, also displays a much darker color than 6F-PAI-1 and -3. Because 6F-PAI-2 showed a lower UV—vis absorption cutoff wavelength compared to Torlon, the second absorption band near 460 nm for 6F-PAI-2 shown in the fluorescence excitation spectra reveal that CTC formation in this material most likely occurs *intermolecularly*, whereas in Torlon, the darker color resulting from increased charge transfer is likely both inter as well as intramolecular in nature.

Fluorescence emission profiles are given in Figure 6. All polymers show wavelengths of maximum intensity near 490 nm when excited at 350 nm. Additionally, 6F-PAI-2 excited at both 350 and 440 nm emits at the same wavelength. This indicates the formation of a ground state CTC, further suggesting the red

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Figure 6. Fluorescence emission profiles for 6F-PAI-1, -2 and -3. 6F-PAI-2 excited at both 350 and 440 nm is shown.

shifting of excitation wavelengths shown in Figure 5 is due to intermolecular  $\pi - \pi$  stacking. The fluorescence emission shape and bandwidth are similar for 6F-PAI-1 and -3, as it was for the excitation profiles. This indicates similar intermolecular interactions exist between polymer chains for both materials. Excitation of 6F-PAI-2 at 440 nm, corresponding to the maximum excitation wavelength in Figure 5, caused a second band to appear near 515 nm, which may be due to an additional CTC arising from the solid state packing promoting meta connection. The effect of charge transfer on the permeation properties and plasticization resistance will be further discussed in section 3.4 and 3.5.

**3.3.** Physical and Thermal Properties. The physical properties for the 6F-PAI series as well as the analogue *polyimides* are given in Table 2. An increase in  $T_g$  is observed in

Table 2. Physical Properties of 6F-PAI and Analogue Polyimides $^a$ 

	$ ho (g/cm^3)$	$\overset{T_{g}}{(^{\circ}C)}$	$     \nu_f \left( {\rm cm}^3 / {\rm mol} \right) $	FFV	d- spacing (Å)	$\varepsilon$ (dielectric constant)			
Polyamide-Imide									
6F-PAI-1	1.3867	324	135	0.18	4.5	3.6			
6F-PAI-2	1.3374	330	87	0.14	6.3	4.1			
6F-PAI-3	1.3281	350	84	0.13	6.3	4.0			
Torlon	1.3550	295	70	0.15	4.2	5.3			
Analogue Polyimides									
6FDA- 6FpDA	1.4660	320	80	0.16	5.9	3.3			
6FDA- DAM	1.3342	395	79	0.19	6.3	3.4			
6FDA- TmPDA	1.3247	420	80	0.19	6.3	3.4			

<sup>*a*</sup>Polyimide values for *d*-spacing,  $T_g$  and density were adapted from the following: 6FDA-6FpDA, Coleman and Koros;<sup>28</sup>6FDA-DAM, Kim et al.;<sup>29</sup> 6FDA-TmPDA, Powell<sup>30</sup> and Lui;<sup>31</sup> Torlon, Teoh et al.<sup>32</sup>

the structures bearing pendent methyl groups. This trend is shown in both the polyamide—imides as well as the polyimides, and results from steric interactions from the methyl groups which inhibit localized, rotational mobilities. Consequently, long-range, segmental scale rigidity is increased in 6F-PAI-2 and -3 as well as their corresponding analogue polyimides.

A comparison of the calculated fractional free volumes (FFV) reveals that the polyamide-imide FFV decreases with incorporation of DAM and TmPDA monomers, while the same substitutions in the polyimides results in an increase in the FFV. This unexpected trend is likely due to differences between amide and imide bond sterics, and correlates well with the differences in fluorescence behavior as shown in Figure 5. DAM and TmpDA are connected over an imide bond in the polyimides, where two carbonyl groups contribute to steric repulsions with pendent methyl groups. In contrast, only one carbonyl exists over the amide bond. Furthuremore, the imide nitrogen in the polyimides likely has less degrees of vibrational freedom due to it being bonded to two carbonyl carbons. This effectively secures the imide nitrogen in place, and allows only for rotation around the N-C diamine bond to minimize the steric repulsions between the methyl and carbonyl groups. On the other hand, the amide nitrogen may have more vibrational degrees of freedom to minimize the carbonyl methyl group interactions. These factors are believed to contribute to much lower planarity between the diimide and diamine moieties in DAM and TmPDA polyimides compared to their corresponding polyamide-imides, thus causing the opposite trends in FFV. Within the polyamide-imide series, chain packing is promoted by incorporation of DAM and TmPDA over the amide bond. The decrease in FFV for 6F-PAI-2 and -3 relative to 6F-PAI-1 is due to the packing inhibiting CF<sub>3</sub> groups attached to 6FpDA, as well as the more rigid, linear structures of DAM and TmPDA. Previous researchers have show that rigid, linear rod-like diamines increase chain packing in amide bonds as compared to diamines containing a flexible kink such as in the isopropyl carbon of 6FpDA in 6F-PAI-1, which can increase chain mobility and disrupt chain packing along the backbone.<sup>4</sup> These interesting trends will be further discussed in context with the transport data in section 3.4.

The X-ray diffraction patterns in Figure 7 confirm the amorphous nature of all three structures. *d*-spacing, which was



Figure 7. XRD patterns depicting the amorphous nature of 6FDAbased polyamide—imides. For 6F-PAI-1, the average of the two peaks was used.

calculated using the Bragg equation, increases in structures based on DAM and TmPDA, which is shown across both series of polymers. Higher *d*-spacing in the *polyimide* series is consistent with higher FFV in 6FDA-DAM and 6FDA-TmPDA compared to 6FDA-6FpDA, however, they are not

р	olyamide—imide	$P_{\rm CO_2}$	$P_{\mathrm{CH}_4}$		$P_{\mathrm{H_2S}}$	$P_{\rm CO_2}/P_{\rm CH_4}$ (ideal selectivity)	$P_{\rm H_2S}/P_{\rm CH_4}$ (ideal selectivity)	
	6F-PAI-1	$32.8 \pm 0.05$	$0.79 \pm 0.01$		$6.2 \pm 7 \times 10^{-3}$	$42 \pm 0.6$	$8.1 \pm 0.04$	
	6F-PAI-2	$14.2 \pm 0.1$	$0.29 \pm 5 \times 10^{-3}$		$3 \pm 0.04$	$49 \pm 0.02$	$10.3 \pm 0.02$	
	6F-PAI-3	$21.6 \pm 0.03$	$0.46 \pm 0.01$		$5.0 \pm 0.04$	$47 \pm 0.02$	$10.9 \pm 0.02$	
	Torlon	$0.7 \pm 8 \times 10^{-3}$	$1.3 \times 10^{-2} \pm 1.0 \times 10^{-2}$	0 <sup>-3</sup>	$0.2 \pm 0.02$	$52.8 \pm 0.6$	$14.8 \pm 1.9$	
	polyimides	$P_{\rm CO_2}$	$P_{\mathrm{CH}_4}$	$P_{\rm H_2S}$	$P_{\rm CO_2}/P_{\rm CH_4}$	(ideal selectivity)	$P_{\rm H_2S}/P_{\rm CH_4}$ (ideal selectivity)	
	6FDA-6FpDA	46	1.5			30		
	6FDA-DAM <sup>b</sup>	350	17.6	nd		20	nd	
	6FDA-Durene <sup>b</sup>	456	28.4			16		
<sup>a</sup> Permeability is given in units of barrer:								
	$1 \text{ barrar} = 1 \times 10$	$-10 \text{ cm}^3(\text{STP}) \cdot \text{cm}^3$						

Table 3. Pure Gas Permeabilities and Permselectivities at 35 °C and 4.5 atm<sup>a</sup>

1 barrer =  $1 \times 10^{-10} \frac{\text{cm}^{\circ}(\text{STP}) \cdot \text{cm}}{\text{cm}^{2} \cdot \text{s} \cdot \text{cmHg}}$ 

<sup>b</sup>Sridhar et al.<sup>10</sup>

consistent with decreases in FFV as shown in the polyamideimides. These anomalous trends in *d*-spacing were also observed by Nagel et al., where materials with lower *d*-spacing displayed higher gas permeabilities.3 They measured the average hole size of the free volume elements using positron annihilation spectroscopy (PALS) and found that the materials with lower *d*-spacing had higher average hole sizes, which they attributed to the reason for higher permeability. Such phenomena would help to explain the trends in *d*-spacing, fractional free volume, and permeability in the materials in this work, however PALS was not available to the authors at the time of this work. Nevertheless, reduced fractional free volume as calculated in Table 2 is consistent with the permeability data which will presented in section 3.4 for the polyamide-imides, and supports the idea that DAM and TmPDA diamines increase chain packing over amide bonds but decrease it when incorporated over an imide bond.

The dieletric constant was also predicted from group contribution methods and shown in Table 2 to illustrate the effect of fluorine content in the polymer backbone. The predicted increase with lower fluorine concentration in both the polyamide–imide as well as the polyimide series can be attributed to increased polarizability due to lower fluorine content across the polymer backbone. The increased polarizability has significant implications on the sorption of  $H_2S$  and will be further discussed in section 3.4.

3.4. Permeation and Sorption Analysis. The overall goal of this work is to characterize robust, plasticization resistant membrane materials for aggressive natural gas separations. Industrially attractive materials need to have both high permeability and selectivity. An increase in selectivity from 15 to 30 can result in a 25% reduction in overall process cost,<sup>20</sup> thus selectivity is extremely important when considering materials for a given separation. Additionally, H<sub>2</sub>S is an important contaminant that has not been widely studied due to handling issues associated with its toxic nature. In our lab, state of the art facilities with the proper safety precautions were constructed to allow us to safely study pure H<sub>2</sub>S at elevated pressures. All permeation cells were located within a sealed plexiglass fume cabinet under lower total pressure relative to atmospheric pressure outside of the cabinet. Before accessing permeation cells that had been exposed to H<sub>2</sub>S, the gas was purged from the systems into a NaOH scrubber followed by rigorous purging of the cell with N<sub>2</sub> and pulling vacuum for at least 6-8 times the diffusion time lag in order to completely

evacuate residual  $H_2S$ . Additionally, respirators and  $H_2S$  monitoring badges were donned while working in the lab. The pure gas transport properties for the polyamide—imides are shown in Table 3. The  $CO_2$  and  $CH_4$  permeabilities for the polyimide series, which were gathered from the literature, are shown for comparison.  $H_2S$  was not measured in the polyimides due to their high susceptibility to plasticization at low feed pressures.

The selectivities of 6F-PAI-2 and -3 increased relative to 6F-PAI-1, and approach those shown by Torlon; however the  $CO_2$  and  $H_2S$  permeabilities are over an order of magnitude higher. These results show that polyamide—imides based on the packing inhibiting 6FDA and rigid, rod-like diamines containing pendent methyl groups combine to form materials with good gas permeability while still maintaining excellent selectivity.

A comparison of the permeabilities between the two types of analogous polymer series in Table 3 clearly shows the effect DAM and TmPDA being connected over different types of bonds. 6F-PAI-2 and -3 show lower permeabilities for all gases relative to 6F-PAI-1 in the *polyamide*—*imides*. In sharp contrast, the permeabilities are significantly increased in the *polyimide* series. As previously discussed with the fluorescence spectra and FFV values, chain packing is enhanced in the DAM and TmPDA connected polyamide—imides. Within the 6F-PAI series, the 6FpDA connected material tends to increase fractional free volume and chain mobilities, thus permeability is lowered in the more rigid, linear DAM- and TmPDA-based materials. This leads to higher selectivities for both the CO<sub>2</sub>/ CH<sub>4</sub> and H<sub>2</sub>S/CH<sub>4</sub> gas pairs for 6F-PAI-2 and -3.

The apparent diffusion coefficients were calculated from eq 8. Sorption coefficients were predicted from dual-mode fits to the experimentally determined concentration isotherms as described in section 2.4. In general, reasonable fits to the concentration isotherms were obtained as shown in Figures 8-10. Along with the difficulties in fitting H<sub>2</sub>S isotherms as already discussed, for 6F-PAI-3, very low sorption at higher pressures reduced the ability of the nonlinear least-squares fitting program to obtain accurate fits to the data. In this case, the dual-mode parameters were estimated manually, with the resulting values bringing reasonable fits to the data. These issues contributed to overall error in the predicted sorption values, and as such are associated with higher experimental uncertainty. Nevertheless, a couple of important trends can still be noted from the data shown in Tables 4-6.



Figure 8.  $CH_4$  concentration vs pressure at 35 °C. Solid lines represent dual-mode model fits to the experimental data.



Figure 9.  $CO_2$  concentration vs pressure at 35 °C. Solid lines represent dual-mode model fits to the experimental data. The dual-mode fit to 6F-PAI-3 was estimated manually.



Figure 10. H<sub>2</sub>S concentration vs pressure at 35 °C.

As can be seen in Tables 4 and 5 as well as Figures 8-10, reductions in CO<sub>2</sub> and CH<sub>4</sub> permeability for 6F-PAI-2 and -3 relative to 6F-PAI-1 were due to both lower sorption and diffusion coefficients. Reduced sorption in these materials is particularly pronounced in the high pressure, Henry's Law region, where rigid, rod-like DAM and TmpDA promote chain packing compared to kinked 6FpDA. This reduces the free

volume available for gas sorption. Additionally, for 6F-PAI-2, the diffusion coefficients for all gases decreased relative to 6F-PAI-1 and -3, which is an interesting trend considering it shows higher free volume, FFV, and increased sorption relative to 6F-PAI-3. Increased charge transfer interactions in 6F-PAI-2 cause higher cohesive forces between the polymer chains. This leads to lower diffusivities as more energy is required for a transient gap to open up for a diffusion step. Consequently, 6F-PAI-2 shows the highest  $CO_2/CH_4$  diffusion selectivity.

The sorption and diffusion coefficients of all gases in Torlon are lower than all three 6FDA-based polyamide-imides. The absence of packing inhibiting groups and greater backbone planarity, as supported by the UV-vis and fluorescence excitation spectra, contribute to a tighter packed microstructure, which reduces both the free volume available for gas sorption as well as the frequency of transient gap openings available for diffusion jumps. On the other hand, para connected TmPDA showed slightly increased diffusivities relative to 6F-PAI-2, while compared to 6F-PAI-1, only D<sub>CO2</sub> and  $D_{\rm CH_4}$  appear to decrease outside of the standard deviation. This caused a reduction in the  $CO_2/CH_4$  diffusion selectivity relative to 6F-PAI-2, whereas the H<sub>2</sub>S/CH<sub>4</sub> diffusion selectivity was not significantly affected. It is interesting to note that the H<sub>2</sub>S/CH<sub>4</sub> diffusion selectivity is between 0.8 and 1.6 for all materials, as diffusion should favor the molecule with lower kinetic diameter, which in this case is H<sub>2</sub>S. Such low diffusion selectivity may be due to more favorable sorption interactions between H<sub>2</sub>S and various polar substituents along the polymer backbone such as the amide N-H or carbonyl C=O. This would increase the energy barrier required to make a diffusion jump. In summary, it is evident that for H<sub>2</sub>S, the permselectivity is predominantly governed by sorption selectivity.

From the concentration isotherms shown in Figures 8-10, the sorption of both CH<sub>4</sub> and CO<sub>2</sub> was reduced in 6F-PAI-2 and -3 relative to 6F-PAI-1, causing an increase in the  $CO_2/$ CH<sub>4</sub> and H<sub>2</sub>S/CH<sub>4</sub> sorption selectivity. These changes can be further analyzed through the dual-mode framework. As shown in Table 6, the Langmuir capacity constant, or  $C_{H'}$ , is not substantially affected by the diamine structures. This is also visually evident in the concentration isotherms, where  $C_{H}'$  can be found from the intersection of the back-extrapolated, high pressure linear region of the isotherm with the concentration axis. From this data, it appears that the diamine structure has a much greater impact on the equilibrium packing region, as sharp decreases in Henry's law sorption occurred. This is probably due to the more rigid and linear structure of DAM and TmPDA, which reduced free volume and increased the rigidness of the polymer matrix. The kink in the isopropyl carbon of 6FpDA increases flexibility in this region, which allows for better accommodation of gas molecules into the densely packed polymer chains. These factors are expressed by significantly reduced  $k_{\rm D}$  values for CO<sub>2</sub> and CH<sub>4</sub> in 6F-PAI-2 and -3.

For  $H_2S$ , total concentration in the membrane increased in the DAM and TmPDA analogues despite the fact that  $CO_2$  and  $CH_4$  sorption was lowered. Reduced fluorine content in these structures increases overall polarizability, which is expressed by an increase in the dielectric constants as shown in Table 2. The highly electronegative fluorine atoms, combined with a short atomic radius, reduce the ability of the valence electrons to be distorted by an external field. Dipole–induced dipole interactions between polar  $H_2S$  and the polymer backbone

polyamide—imide	$D_{\rm CO_2}$ (×10 <sup>8</sup> )	$D_{{ m CH}_4}~( imes 10^8)$	$D_{ m H_2S}~( imes 10^8)$	$D_{\mathrm{CO}_2}/D_{\mathrm{CH}_4}$	$D_{\mathrm{H_2S}}/D_{\mathrm{CH_4}}$			
6F-PAI-1	$1.9 \pm 0.1$	$0.2 \pm 0.01$	$0.1 \pm 0.04$	$10 \pm 0.8$	$0.8 \pm 0.2$			
6F-PAI-2	$1.1 \pm 0.2$	$0.1 \pm 6 \times 10^{-3}$	$0.1 \pm 7 \times 10^{-3}$	$12 \pm 0.2$	$1 \pm 0.08$			
6F-PAI-3	$1.4 \pm 0.3$	$0.2 \pm 3 \times 10^{-3}$	$0.3 \pm 0.1$	$9 \pm 0.2$	$1.6 \pm 0.6$			
Torlon	0.1	$9 \times 10^{-3} \pm 8 \times 10^{-4}$	$8 \times 10^{-3} \pm 2 \times 10^{-5}$	$10 \pm 8 \times 10^{-4}$	$0.8 \pm 0.07$			
<sup><math>^{2}Units of the diffusion coefficients are cm<math>^{2}</math>/s.</math></sup>								

## Table 4. Apparent Diffusivities and Diffusion Selectivities at 35 °C and 4.5 atm<sup>a</sup>

Table 5. Sorption Coefficients and Selectivities at 35 °C and 4.5 atm<sup>a</sup>

polyamide—imide	$S_{\rm CO_2}$	$S_{CH_4}$	$S_{ m H_2S}$	$S_{\rm CO_2}/S_{\rm CH_{4a}}$	$S_{\mathrm{H_2S}}/S_{\mathrm{CH_4}}$
6F-PAI-1	$7.2 \pm 0.7$	$2.4 \pm 1.2$	$12.2 \pm 2.4$	$3.0 \pm 0.02$	$5 \pm 0.03$
6F-PAI-2	$6.8 \pm 0.9$	$1.8 \pm 0.5$	$14.4 \pm 1.6$	$3.7 \pm 0.02$	$8 \pm 0.02$
6F-PAI-3	$4.5 \pm 2$	$0.7 \pm 0.05$	$13 \pm 2.4$	$6.4 \pm 0.03$	$18 \pm 0.04$
Torlon	2.4	0.4	$7.2 \pm 0.9$	6	18

<sup>a</sup>Sorption coefficients are given in units of  $(cm^3(STP)/cm^3 \times atm)$ . Values given are predicted from dual-mode parameters as estimated from the concentration isotherms.

Table 6. Dual-Mode Sorption Parameters at 35 °C

		CO <sub>2</sub>		$CH_4$			$H_2S^a$		
polyamide– imide	$k_{\rm D} \ ({\rm cm}^3({ m STP})/{ m cm}^3 \times { m atm})$	$\binom{C_{\rm H}{'}}{({ m cm}^3({ m STP})/{ m cm}^3)}$	b (atm <sup>-1</sup> )	$k_{\rm D} \ ({\rm cm}^3({ m STP})/{ m cm}^3 \times { m atm})$	$\binom{C_{\rm H}{'}}{({ m cm}^3({ m STP})/{ m cm}^3)}$	b (atm <sup>-1</sup> )	$k_{\rm D} \ ({\rm cm}^3({ m STP})/{ m cm}^3 \times { m atm})$	$\binom{C_{\mathrm{H}}'}{(\mathrm{cm}^3(\mathrm{STP})/\mathrm{cm}^3)}$	b (atm <sup>-1</sup> )
6F-PAI-1	0.1	31.2	0.05	0.04	15	0.02	0.4	32	0.2
6F-PAI-2	0.04	37.6	0.04	$3 \times 10^{-5}$	14.4	0.02	0.4	36.8	0.2
6F-PAI-3 <sup>b</sup>	$5 \times 10^{-6}$	33.5	0.02	$2 \times 10^{-3}$	3.5	0.1	_	_	_
Torlon	$5 \times 10^{-5}$	18	0.02	$3 \times 10^{-3}$	2.1	0.03	0.28	17	0.06

<sup>a</sup>H<sub>2</sub>S values for 6F-PAI-3 could not be calculated because of membrane swelling. <sup>b</sup>Values were estimated manually.



Figure 11. Pure gas  $CO_2$  permeability vs pressure at 35 °C. The Torlon permeability axis is depicted on the right.  $CO_2$  permeability vs pressure data for Torlon was adapted from Kosuri.<sup>1</sup>

are enhanced by more polarizable DAM and TmPDA relative to 6FpDA. This suggests  $H_2S$  sorption is more strongly dependent on intermolecular interactions than are the quadrapolar CO<sub>2</sub> and nonpolar CH<sub>4</sub>, where sorption is mostly governed by condensability and free volume. This increased the  $H_2S/CH_4$  solubility selectivities for both 6F-PAI-2 and -3, thus overall  $H_2S/CH_4$  permselectivity was increased slightly.

**3.5. Plasticization Analysis.** Natural gas wells can reach pressures above 70 atm, where elevated partial pressures of  $CO_2$  and  $H_2S$  can cause significant swelling and plasticiza-

tion,<sup>21,22</sup> resulting in large selectivity losses. Cellulose acetate and most un-cross-linked polyimides plasticize at CO<sub>2</sub> partial pressures near 14 atm,<sup>23,24</sup> and with the combined effect of highly condensable H<sub>2</sub>S, this pressure is expected to be much lower. Thus, the need for intrinsically stable materials that can extend high selectivities into these aggressive conditions underscores material development for natural gas separation materials. Figures 11 and 12 show pure gas permeability vs pressure isotherms for CO<sub>2</sub> and H<sub>2</sub>S, respectively.

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Figure 12. Pure gas H<sub>2</sub>S permeability vs pressure at 35 °C. The Torlon permeability axis is shown on the right.

Torlon, widely recognized for its outstanding plasticization resistance, is shown again as a baseline for which to compare the performance of the 6F-PAI series. From Figure 11, CO<sub>2</sub> plasticization resistance increases in the order 6F-PAI-3 ~ 6F-PAI-1 < 6F-PAI-2 < Torlon. This is inferred from the plasticization pressure, which is the pressure at which the permeability coefficient begins to increase from its minimum value. The plasticization pressure for 6F-PAI-3 of 24 atm is slightly lower than 6F-PAI-1, which begins to increase around 28 atm. The overall extent of permeability increase, however, is  $\sim$ 10% for both materials, suggesting similar resistance to chain swelling once a threshold CO<sub>2</sub> concentration in the membrane was reached. This similar resistance occurs despite the fact that  $k_{\rm D}$  for 6F-PAI-3 was orders of magnitude lower than  $k_{\rm D}$  in 6F-PAI-1. The fluorescence excitation spectra in Figure 5 suggest that similar intermolecular interactions exist between the polymer chains in 6F-PAI-1 and -3, and that no additional CTCs formed, which would certainly alter the excitation spectra. Thus, the similar magnitudes in permeability increase are likely the result of similar intermolecular interactions throughout the entire polymer network in both materials, not just chain mobility in the Henry's environment as inferred from  $k_{\rm D}$  and previously suggested by Wind et al.<sup>23</sup> Instead, for structures with similar charge transfer interactions, the absolute plasticization pressure appears to depend on the pressure at which the Langmuir sorption sites become saturated. As can be seen in Figure 11, both 6F-PAI-1 and -3 show initial upswing in permeability once the permeability stops decreasing with pressure. In other words, the permeability continues to decrease as long as the microcavities have not been saturated by penetrant gas molecules. As sorption begins to occur predominantly in the Henry's environment with higher pressure, the permeability begins to increase, which suggests polymer chain swelling occurs when gas sorption occurs primarily in the densely packed region. Therefore, the higher plasticization pressure in 6F-PAI-1 may be due to higher pressures being required to saturate the Langmuir sorption sites. 6F-PAI-2 shows the highest plasticization pressure out of the fluorinated polyamide-imides, which occurs near 30 atm. Additionally, beyond the plasticization pressure, the CO<sub>2</sub> permeability increases by less than 5%. Similar to 6F-PAI-1 and -3, the permeability in 6F-PAI-2 continues to decrease

slightly until the point at which the permeability begins to increase, again suggesting that the polymer chains begin to swell once additional sorption occurs primarily in the Henry's environment. For 6F-PAI-2, however, lower increases in permeability correlates with significantly greater CTC formation relative to 6F-PAI-1 and -3 as discussed in section 3.2. Such charge transfer interactions strengthen the physical interactions between neighboring chains in a manner similar to covalent cross-linking, allowing 6F-PAI-2 to operate up to almost 55 atm of pure  $CO_2$  with only minor increases in  $CO_2$ permeability. In general, the plasticization pressures of all three materials represent substantial improvements from conventional un-cross-linked materials such as cellulose acetate, and even compared to cross-linked materials, they hold a potential key advantage in the fact that this high plasticization resistance is intrinsic to these materials, so an additional cross-linking step is not required.

Despite improved stability against high pressure CO2, the H<sub>2</sub>S plasticization resistance is lower in both 6F-PAI-2 and -3 relative to 6F-PAI-1. This is suggested by lower plasticization pressure as well as a greater extent of permeability increase beyond the initial permeability upswing. For 6F-PAI-2 and -3, the plasticization pressure is around 5.8, whereas for 6F-PAI-1, it occurs closer to 7 atm. The upswing in the concentration isotherms in 6F-PAI-2 and -3 does not occur until approximately 7 atm, while the permeability isotherms increase near 5.8 atm. This means the initial upswing in permeability is due to an increase in the H<sub>2</sub>S diffusion coefficient. Because CH<sub>4</sub> is nonpolar, its sorption in this region is governed by its kinetic diameter and the energy required for the densely packed polymer chains to open up to sufficient size for accommodation of a  $CH_4$  molecule. The fact that  $k_D$  for  $CH_4$  was reduced from 0.04 (cm<sup>3</sup>(STP)/cm<sup>3</sup>·atm) in 6F-PAI-1 to  $3 \times 10^{-5}$  $(cm^{3}(STP)/cm^{3} \cdot atm)$  and  $2 \times 10^{-3} (cm^{3}(STP)/cm^{3} \cdot atm)$  in 6F-PAI-2 and -3 respectively suggests that additional energy is required to open up the chains in this region. Lower  $k_{\rm D}$  for  $\rm CO_2$ is also visually evident in Figure 9. Although  $k_{\rm D}$  for  $\rm H_2S$  could not be accurately determined in 6F-PAI-2 and -3, it appears that the increased H<sub>2</sub>S sorption in 6F-PAI-2 and -3 relative to 6F-PAI-1 is more pronounced in the Henry region, where nonfluorinated DAM and TmPDA were shown to have the greatest impact on gas sorption. Thus, this increase is due to

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increased thermodynamic affinity toward the polymer chains as gas sorption transitions into a Henry's law dominated mechanism. As a result of the higher sorption levels, chain swelling in these materials occurs at lower H<sub>2</sub>S pressures, causing increased permeability. Perhaps even more surprising is the H<sub>2</sub>S plasticization pressure for Torlon, which is clearly more stable against CO<sub>2</sub> than 6F-PAI-1; however, as can be seen in Figure 12, Torlon's H<sub>2</sub>S plasticization pressure occurs near 5.8 atm, which is slightly lower than 6F-PAI-1. Because Torlon is nonfluorinated, H<sub>2</sub>S sorption may be even more thermodynamically favorable. As such, Torlon is less stable toward H<sub>2</sub>S despite its remarkable stability against CO<sub>2</sub>. These results highlight the inherent difficulties in designing high selectivity materials targeting simultaneous removal of CO2 and  $H_2S$ . As shown in Table 4,  $D_{H_2S}/D_{CH_4}$  is generally between 1 and 2. Smaller kinetic diameter differences between the gases relative to CO<sub>2</sub> and CH<sub>4</sub> limit the size discrimination capabilities for H<sub>2</sub>S relative to CH<sub>4</sub> in pure polymer membranes. On the other hand, differences in H<sub>2</sub>S and CH<sub>4</sub> solubility, as inferred from critical temperatures, are higher for H<sub>2</sub>S than CO<sub>2</sub>. It is therefore more advantageous to target solubility selectivity for H<sub>2</sub>S/CH<sub>4</sub>. However, as the sorption and permeability data in this work show, this can compromise plasticization resistance even when CTC formation, which generally stabilizes materials against plasticization, is enhanced as it is in Torlon and 6F-PAI-2.

3.6. Mixed Gas Permeation Analysis. The previous analysis on membrane stability toward CO<sub>2</sub> and H<sub>2</sub>S was based only on single gas feed streams. Although these results were promising in that high ideal permselectivities and pure gas plasticization resistances were shown, the true separation performance of a material must be assessed using mixed gas feeds. Factors such as competitive sorption and bulk flow effects can reduce permselectivities relative to their corresponding ideal, pure gas values.<sup>25,26</sup> Also, increases in  $CO_2$  and  $H_2S$ partial pressure can cause localized increases in polymer chain mobility as their concentration inside the membrane increases. This can increase the diffusion coefficients of the larger, slower gases while the fast gas is unaffected,<sup>27</sup> thus by only using single gas analysis, even the plasticization resistance can be overestimated. The mixed gas separation performance of 6F-PAI-1 was addressed in our previous paper. In this paper, we wish to show the effects of the apparent greater sorption affinity of H<sub>2</sub>S for 6F-PAI-2, which does not plasticize in mixtures containing only CO<sub>2</sub> and CH<sub>4</sub>, but does so in the presence of H<sub>2</sub>S at low total feed pressures. Figures 13-15 compare 6F-PAI-2 using a ternary feed stream containing CO2, H2S, and CH4. Higher fluorinated 6F-PAI-1 is shown for comparison. It should be noted that absolute values of the permselectivities cannot be accurately compared due to different H<sub>2</sub>S feed concentrations that were used for the two different materials. In this situation, only a comparison of the plasticization resistance at similar H<sub>2</sub>S partial pressures in the feed is meaningful.

As can be observed in Figures 13–15,  $H_2S$  causes significant performance reductions in lower fluorinated 6F-PAI-2. On the other hand, more fluorinated 6F-PAI-1 does not show any permeability increases up to 60 atm total feed pressure. 6F-PAI-2 showed permeability upswings near 10 atm total feed pressure, corresponding to approximately 1 atm of  $H_2S$  partial pressure. At 60 atm,  $H_2S$  partial pressure is 6 atm. It is clear that 6F-PAI-1 does not plasticize even at higher  $H_2S$  partial pressures than 6F-PAI-2. This suggests that the material with



**Figure 13.**  $CO_2/CH_4$  selectivity vs pressure at 35 °C. The feed gas for 6F-PAI-1 was composed of 10% H<sub>2</sub>S, 20% CO<sub>2</sub>, and 70% CH<sub>4</sub>. For 6F-PAI-2, the feed gas was composed of 20% H<sub>2</sub>S, 20% CO<sub>2</sub>, and 60% CH<sub>4</sub>.



**Figure 14.**  $H_2S/CH_4$  permselectivity vs pressure isotherm at 35 °C. The feed gas for 6F-PAI-1 was composed of 10%  $H_2S$ , 20% CO<sub>2</sub>, and 70% CH<sub>4</sub>. For 6F-PAI-2, the feed gas was composed of 20%  $H_2S$ , 20% CO<sub>2</sub>, and 60% CH<sub>4</sub>.



**Figure 15.**  $CO_2$  permeability vs pressure isotherm at 35 °C. The feed gas for 6F-PAI-1 was composed of 10% H<sub>2</sub>S, 20% CO<sub>2</sub>, and 70% CH<sub>4</sub>. For 6F-PAI-2, the feed gas was composed of 20% H<sub>2</sub>S, 20% CO<sub>2</sub>, and 60% CH<sub>4</sub>.

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Figure 16. CO2 and CH4 permeability vs pressure for 6F-PAI-2 at 35 °C. The feed gas was composed of 50% CO2 and 50% CH4.

higher fluorine content can support higher H<sub>2</sub>S concentrations without plasticizing. The decrease in the H<sub>2</sub>S/CH<sub>4</sub> selectivity in 6F-PAI-2 is not as high as the CO2/CH4 selectivity drop because  $P_{\text{H-S}}$  also increases with feed pressure. Also,  $P_{\text{CO}_2}$  for 6F-PAI-2 does not appear to increase until 40 atm total pressure, while H<sub>2</sub>S permeability began increasing at much lower feed pressure. This is believed to be due to the fact that CO<sub>2</sub> has a smaller kinetic diameter. Small scale increases in local chain mobilities are believed to affect the diffusion coefficient of the larger gases to a greater extent, and as such,  $P_{\rm CO_2}$  does not appear to show any plasticization effects until 40 atm total feed pressure. This idea of different gases being affected differently by changes in free volume is the basis of Park and Paul's modified method for calculating free volume from group contributions.<sup>13</sup> It also demonstrates the importance of mixed gas permeation for the assessment of plasticization resistance, as the permeability of the larger kinetic diameter gases more accurately reveal swelling and plasticization behavior with increases in acid gas concentration.

To test whether H<sub>2</sub>S was the cause of the low plasticization resistance, 6F-PAI-2 was degassed for greater than 1 week followed by subjecting it to a clean 50% CO<sub>2</sub> 50% CH<sub>4</sub> feed stream. Figures 16 and 17 show the  $P_{\rm CO_2}$ ,  $P_{\rm CH_4}$  and  $P_{\rm CO_2}/P_{\rm CH_4}$ isotherms up to 55 atm of total feed pressure. As can be observed, the CO<sub>2</sub> permeability is restored to its original, pure gas value of ~14 barrer.  $P_{CH_1}$  is slightly higher than its pure gas value of 0.29 barrer. This is due to swelling from the presence of H<sub>2</sub>S in the original applied feed stream. Localized chain dilations can become locked into the glassy chain conformation as the membrane is degassed. This resulted in reduced permselectivity at low pressure. With increasing total feed pressures, however,  $P_{CH}$  decreases, which causes the permselectivity to increase with feed pressure. This increase is believed to be the result of CO<sub>2</sub> out competing CH<sub>4</sub> for the limited number of Langmuir sorption sites. These results confirm that H<sub>2</sub>S has a significantly deleterious impact on the separation performance of 6F-PAI-2. However, Figures 16 and 17 suggest that the permeabilities can be restored after removal of H<sub>2</sub>S, and that large scale, glassy relaxations did not occur. This suggests that 6F-PAI-2 may be able to tolerate disruptions in process streams that may potentially expose the membrane



Figure 17.  $P_{CO_2}/P_{CH_4}$  vs pressure isotherm for 6F-PAI-2 at 35 °C. The feed gas was composed of 50% CO<sub>2</sub> and 50% CH<sub>4</sub>.

to  $H_2S$ , as the separation performance was still quite promising upon removal of the gas. Additionally, 6F-PAI-2 shows a  $CO_2/CH_4$  permselectivity near 40 above 55 atm of total feed pressure. On the basis of these results, 6F-PAI-2 has strong potential for  $CO_2/CH_4$  separations, which is suggested by its intrinsically high plasticization resistance and ability to maintain good selectivities at high feed pressures.

3.7. Conclusion. A new series of polyamide-imides based on bulky 2,2-dicarboxyphenyl hexafluoropropane dianhydride were synthesized and characterized toward high pressure CO2 and H<sub>2</sub>S for natural gas separations. 2,4-Diaminomesistylene (DAM) and 2,3,5,6-tetramethyl phenylenediamine (TmPDA) were used as the amide-amide bond diamine in attempts to reduce chain packing in the solid state through steric interactions. To our surprise, diffusivities and sorption coefficients for both CO2 and CH4 decreased in the DAMand TmPDA-based polymers relative to structures containing 6FpDA (4,4'-(hexafluoroisopropylidene) dianiline). This decrease was not expected as 6FDA-based polyimides containing DAM and TmPDA show significant permeability increases relative to 6FpDA analogues. These results suggest that steric interactions with ortho pendent groups around the amide bond are not as strong as they are in imide bonds, and that incorporating rigid, rod-like DAM and TmPDA diamines into amide bonds results in lower free volume and polymer chain mobility. Interestingly, the opposite trend was shown for H<sub>2</sub>S, where H<sub>2</sub>S had higher sorption in DAM- and TmPDA-based structures, which enhanced the H<sub>2</sub>S/CH<sub>4</sub> ideal permselectivity. These results suggest that the sorption of polar H<sub>2</sub>S is more dependent on intermolecular interactions with the membrane material than nonpolar CO<sub>2</sub> and CH<sub>4</sub>.

The plasticization resistance of the polyamide-imides was determined using both pure  $CO_2$  and  $H_2S_1$  as well as mixed gas feed streams. The DAM-based analogue showed almost no upswing through 55 atm of pure CO<sub>2</sub>. Furthermore, mixed gas permeation up to 55 atm total feed pressure showed a  $CO_2/$  $CH_4$  mixed gas permselectivity of ~40, which is much higher than typical un-cross-linked polymer materials at similar feed condtions. On the other hand, pure gas H<sub>2</sub>S plasticization resistance was actually reduced in DAM- and TmPDA-based polyamide-imides, which is likely due to lower fluorine in these materials. Mixed gas testing using a ternary feed stream showed plasticization in 6F-PAI-2 at low total feed pressures, whereas 6F-PAI-1 showed no permeability upswings up to 60 atm total feed pressure. Upon removal of the H<sub>2</sub>S containing feed stream, permeabilities in 6F-PAI-2 showed only minor hysteresis, and in fact the membrane maintained a CO<sub>2</sub>/CH<sub>4</sub> binary feed stream selectivity of ~40 at 55 a.m. total feed pressure. On the basis of these results, it is unlikely that H<sub>2</sub>S caused large scale, glassy relaxations. Rather, localized disruptions to the polymer microstructure occurred. These results suggest increased CTC formation, as was the case in 6F-PAI-2, may not be sufficient in stabilizing polymers against H<sub>2</sub>S plasticization and that intermolecular interactions should be taken into account. In particular, fluorine content in the polymer backbone may be used to reduce H<sub>2</sub>S affinity for the polymer, which can stabilize the membrane toward elevated concentrations of this highly condensable gas. Finally,  $D_{H_1S}/$ D<sub>CH</sub>, was between 0.8 and 1.6 for all three polyamide-imides

as well as Torlon. Thus, overall  $H_2S/CH_4$  permselectivity is governed mostly by solubility, whereas diffusion selectivity governs  $CO_2/CH_4$  separations. This work highlights the difficulty in designing materials that are highly selective for both  $CO_2$  and  $H_2S$ , a separation that would require materials with high mobility as well as solubility selectivity. Introduction of polar groups such as Cl or Br, which can increase the cohesive energy density, is one potential strategy. This total sour gas separation has not been actively targeted in the literature but nevertheless remains a relevant challenge in natural gas separations.

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#### Notes

The authors declare no competing financial interest.

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