Ultraselective glassy polymer membranes with unprecedented performance for energy-efficient sour gas separation

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Membrane-based separation of combined acid gases carbon dioxide and hydrogen sulfide from natural gas streams has attracted increasing academic and commercial interest. These feeds are referred to as “sour,” and herein, we report an ultra $\text{H}_2\text{S}$-selective and exceptionally permeable glassy amidoxime-functionalized polymer of intrinsic microporosity for membrane-based separation. A ternary feed mixture (with 20% $\text{H}_2\text{S}$:20% $\text{CO}_2$:60% $\text{CH}_4$) was used to demonstrate that a glassy amidoxime-functionalized membrane provides unprecedented separation performance under challenging feed pressures up to 77 bar. These membranes show extraordinary $\text{H}_2\text{S}/\text{CH}_4$ selectivity up to 75 with ultrahigh $\text{H}_2\text{S}$ permeability $>$4000 Barrers, two to three orders of magnitude higher than commercially available glassy polymeric membranes. We demonstrate that the post-synthesis functionalization of hyper-rigid polymers with appropriate functional polar groups provides a unique design strategy for achieving ultraselective and highly permeable membrane materials for practical natural gas sweetening and additional challenging gas pair separations.

INTRODUCTION

Hydrogen sulfide ($\text{H}_2\text{S}$) is a flammable, highly toxic gas that causes nearly instant death when its concentrations are greater than 1000 parts per million (ppm) (1). Even as low as 5-ppm level causes eye, nose, and throat irritation. Hence, selective removal of $\text{H}_2\text{S}$ from large-scale industrial gas streams in natural gas processing, biogas upgrading, and geothermal energy production is a mandatory U.S. pipeline specification with a maximum concentration of 4 ppm (2−4). Raw natural gas contains many impurities, but $\text{H}_2\text{S}$ and carbon dioxide ($\text{CO}_2$) are arguably the two most important to remove after primary dehydration (5, 6). Over 40% of proven raw natural gas reserves in the United States are termed “sour” and require treatment to remove excess $\text{CO}_2$ and $\text{H}_2\text{S}$ (7); moreover, concentrations, in certain areas in the Middle East (e.g., Qatar and Saudi Arabia), of oil and gas reservoirs can contain $\text{H}_2\text{S}$ up to ~15 to 20 mole percent (mol %) (5, 8, 9). These factors cause large reserves of natural gas globally to remain untapped today due to the difficulties involved in processing such low-quality gas. Hence, $\text{H}_2\text{S}$, $\text{CO}_2$, and preferably combined $\text{CO}_2 + \text{H}_2\text{S}$ purification of these feeds is a globally important topic (3, 10). Chemical separations account for about 50% of U.S. industrial energy use and 10 to 15% of the nation’s total energy consumption (11). Developing alternative approaches for purifying mixtures without using heat would substantially lower global energy use, emissions, and pollution. While an absorption-based process currently dominates most sour gas treatment operations, it is highly energy intensive and brings environmental concerns and high capital and maintenance costs—especially when acid gas concentrations are high (7, 12, 13). The above factors have motivated our study of membranes to supplement or replace absorption units based on potential advantages, including higher energy efficiency, smaller footprints, and reduced environmental impact (10, 14–16). Despite these intrinsic advantages, to continue to expand the impact of this technology, higher separation efficiency (selectivity) and higher productivity (permeability) as well as stable performance of membranes under realistic conditions are needed (2, 7, 17).

While many polymers have been developed for $\text{CO}_2$ removal from natural gas streams, much less attention has been given to $\text{H}_2\text{S}$ removal due to the highly toxic and corrosive nature of these feeds (5, 7, 9, 18). Most prior studies of membrane-based $\text{H}_2\text{S}$ removal from sour gas have focused on rubbery polymers at fairly low $\text{H}_2\text{S}$ partial pressures (18), which is well below realistic aggressive wellhead pressures that can exceed 60 bar. To process feeds with combined high $\text{CO}_2$ and $\text{H}_2\text{S}$ total acid gas partial pressures, a new generation of more robust membrane materials is required, which is the topic of this work. Recently, Koros and co-workers (5, 7, 9, 18, 19, 20) developed several advanced glassy membrane materials including cross-linkable polyimides and fluorinated polyamide-imides (PAIs) to address these needs. These glassy polymers represent a promising platform of polymeric materials for membrane-based gas separations with good intrinsic stability and attractive selectivities under aggressive feed conditions. However, despite being stable under high-pressure feed conditions, $\text{H}_2\text{S}$ permeabilities were generally less than 100 Barrer [1 Barrer = $10^{-10}$ cm$^2$(STP) cm$^{-1}$ s$^{-1}$ cmHg$^{-1}$], and $\text{H}_2\text{S}/\text{CH}_4$ selectivity was less than ~30. Although useful, these materials will require large membrane areas, which lead to increased cost and space requirements for large-scale separation processes.

Materials research is of critical importance to enable advanced membranes for large-scale, energy-efficient molecular separations (17). Recently developed glassy ladder polymers of intrinsic microporosity (PIMs) are characterized by highly rigid and contorted backbone structures that frustrate efficient chain packing, leading to high free volume with interconnected micropores of less than 2 nm (21). PIMs can separate diverse mixtures of gas molecules with different sizes and shapes and show very high gas permeability typically combined with moderate selectivity for some gas pairs like $\text{O}_2/\text{N}_2$ and $\text{H}_2/\text{N}_2$ (15, 21). However, their practical use for natural gas separation has been severely restricted compared to commercial membrane materials.
such as cellulose triacetate, due to low mixed-gas CO$_2$/CH$_4$ selectivity. For example, the prototype ladder PIM-1 (Fig. 1A) showed a very high mixed-gas permeability of 4500 Barrer but with very low CO$_2$/CH$_4$ selectivity of only 8 when tested at a partial CO$_2$ pressure of 10 bar (22).

For the reasons noted above, few studies have considered H$_2$S separations from natural gas feeds with PIMs. We recently developed a hydroxyl-functionalized polyimide of intrinsic microporosity (PIM-6FDA-OH) for simultaneous separation of CO$_2$ and H$_2$S from aggressive sour natural gas streams (7). Notwithstanding this attractive feature, H$_2$S permeability of PIM-6FDA-OH was still almost one order of magnitude lower than that of top performance rubbery materials with similar H$_2$S/CH$_4$ selectivity. Novel functionalized PIMs providing favorable interactions with H$_2$S to boost H$_2$S permeability and enhance solubility selectivity to further improve the PIMs-based membrane performance for H$_2$S selective separations are, therefore, appealing.

**RESULTS AND DISCUSSION**

**Pure-gas permeation**

Permeability and selectivity are intrinsic material properties used to characterize membrane material productivity and separation efficiency. The permeability ($P_i$) of penetrant $i$ can be defined as the steady-state flux ($n_i$) normalized by transmembrane pressure differential ($\Delta P_i$) and thickness of the membrane ($l$), viz.

$$P_i = \frac{n_i \times l}{\Delta P_i}$$ (1)

Permeability is usually given in the unit of Barrer, where 1 Barrer $= 1 \times 10^{-10}$ cm$^3$ (STP) cm cm$^{-2}$ s$^{-1}$ cmHg$^{-1}$. For nonideal gas feeds, the partial pressure difference in Eq. 1 is replaced by the penetrant fugacity difference ($\Delta f_i$). The fugacity-based permeability ($P_i^*$), thereby, is given by Eq. 2

$$P_i^* = \frac{n_i \times l}{\Delta f_i}$$ (2)

The transport of gas molecules through polymer materials is governed by the sorption-diffusion mechanism. Hence, the permeability of polymer membranes can be represented as the product of the diffusion coefficient ($D$) and sorption coefficient ($S$) of penetrant $i$ within the membrane

$$P_i = D_i \times S_i$$ (3)

The apparent diffusion coefficient $D$ (cm$^2$/s) can be estimated from the time-lag method: $D = \frac{l^2}{6\theta}$, where $l$ is the thickness of the membrane and $\theta$ is the time lag calculated through single gas permeation tests (7). Thus, the sorption coefficient $S$ [cm$^3$ (STP) cm$^{-2}$ cmHg$^{-1}$] can be deduced from the sorption-diffusion model using $S = P/S$.

For a given gas pair, the ideal selectivity ($\alpha_{ij}$) is defined as the ratio of gas permeabilities for the fast gas ($i$) and slow gas ($j$)

$$\alpha_{ij} = \frac{P_j}{P_i} \times \frac{D_i}{D_j} \times \frac{S_i}{S_j} = \alpha_D \cdot \alpha_S$$ (4)

Equation 4 allows the ideal selectivity of a membrane to be decoupled into the product of mobility selectivity ($\alpha_D$) and the solubility selectivity ($\alpha_S$).

We report here a high-performance glassy polymer membrane material for highly efficient and selective H$_2$S separation from sour natural gas streams. In our study, the prototype PIM-1 (Fig. 1A) has been used for postfunctionalization through a rapid reaction of the nitrile groups with hydroxylamine under reflux conditions in tetrahydrofuran (22, 23). Hence, an amidoxime-functionalized PIM-1 (AO-PIM-1; Fig. 1, A and B, and fig. S2) was prepared and characterized. In a preliminary study, low-pressure (1 to 2 bar) pure-gas permeation experiments were conducted on freshly cast and 6-month-old methanol-reconditioned AO-PIM-1 dense films using H$_2$S, CO$_2$, and CH$_4$ at 35°C with a constant-volume apparatus (fig. S3) (7). The pure-gas results of the AO-PIM-1 film and other materials (5, 7–9, 12, 19, 20, 24–28) are shown on productivity (permeability)–efficiency (selectivity) trade-off curves (29, 30) for CO$_2$/CH$_4$ in Fig. 1C and H$_2$S/CH$_4$ in Fig. 1D. As reported in an earlier study, AO-PIM-1 exhibits good performance for CO$_2$/CH$_4$ separation as the material demonstrated very high CO$_2$ permeability of ~1000 Barrer and moderate CO$_2$/CH$_4$ selectivity of ~30, thereby exceeding the 2008 Robeson upper bound (22). However, the results discussed below demonstrate that AO-PIM-1 displays extraordinary H$_2$S/CH$_4$ separation performance. No published H$_2$S/CH$_4$ performance permeability/selectivity upper bound plot exists, so we only show AO-PIM-1 separation performance relative to some other relevant polymer materials in Fig. 1D. The plot showing H$_2$S permeability and H$_2$S/CH$_4$ selectivity from literature data for the experimental H$_2$S/CH$_4$ upper bound line is drawn to aid the eye. A freshly prepared AO-PIM-1 membrane had an H$_2$S/CH$_4$ selectivity of ~30 at 1 bar equivalent to the industrial standard glassy polymer cellulose acetate, a selectivity value that is up to three times higher than most other glassy polymers including 4,4’-(hexafluoroisopropylidene)diphthalic anhydride (6FDA)-based polyimides and quite competitive to the best performing H$_2$S selective rubbery membranes (5, 9, 12, 19, 27). However, AO-PIM-1 demonstrated the H$_2$S permeability of ~1200 Barrers at 1 bar, which is up to two orders of magnitude higher than that of typical glassy polymer materials, such as cellulose acetate, 6FDA-durene-mPDA, 6F-PAIs, 6FDA-DAM-DABA (3:2), PIM-6FDA-OH, and poly(ethylene glycol) (PEG) cross-linked polymers (PEGMc), and even higher than most hydrophilic H$_2$S-selective rubbery materials (5, 7, 19, 24–27). These combined properties make the amidoxime-functionalized PIM (AO-PIM-1) a revolutionary candidate for membrane-based sour gas separations.

**Physical aging and long-term stability**

Physical aging effects in microporous glassy polymers can lead to a decline in gas permeability due to undesirable polymer chain packing densification (31–33). It is typically done in a “static” mode, that is, after an initial permeation test the film/membrane is stored under ambient conditions and then retested. Physical aging is a potential drawback of using intrinsically microporous polymers for industrial membrane applications. However, previous studies demonstrated that this effect can be mitigated when the membrane is continuously operated (“dynamic” mode) with feeds containing highly sorbing feed components or rejuvenated when exposed to highly sorbing gases, such as H$_2$S/CO$_2$ in our study (32, 33). The dynamic aging process is much less pronounced as the free volume of the polymer is continuously occupied by a highly sorbing gas. Herein, we demonstrate the long-term stability of AO-PIM-1 for the first time by continuously operating a membrane with a feed mixture containing 20 mol % H$_2$S/20 mol %
Fig. 1. Polymer structure, void morphologies, and gas permeation properties of AO-PIM-1 films at 35°C. (A) Structures of PIM-1 and amidoxime-functionalized PIM-1 (AO-PIM-1). (B) Void morphology in AO-PIM-1. The Connolly surface of the AO-PIM-1 framework is shown in blue regions (outer pore surface) and gray regions (inner pore surface) as outlined geometrically by an N$_2$-sized probe (3.64 Å). (C) Pure-gas permeability/selectivity (CO$_2$/CH$_4$) trade-off curve comparison of PIM-1 and AO-PIM-1 to other polymeric materials [1 = cellulose acetate; 2 = 6FDA-PAT; 3 = 6FDA-mPDA6FDA-durene; 4 = polyethylene glycol (PEG) cross-linked polymer (PEGMC); 5 = 6FDA-DAM-DABA; 6 = PIM-6FDA-OH; 7 = PIM-PI-3]. The CO$_2$ and CH$_4$ permeabilities were measured at feed pressure of 2 bar at 35°C. (D) Pure-gas permeability/selectivity (H$_2$S/CH$_4$) trade-off curve comparison of PIM-1 and AO-PIM-1 to other polymeric. H$_2$S was measured under 1-bar feed pressure at 35°C to avoid plasticization effects. The dashed black line is a guide to the eye used only to indicate the general trade-off between H$_2$S permeability and H$_2$S/CH$_4$ selectivity in typical glassy polymers. (E) CO$_2$/CH$_4$ performance of AO-PIM-1 for long-term continuous active feed of 20 mol % H$_2$S/20 mol % CO$_2$ and 60 mol % CH$_4$ at feed pressure of 8.6 bar at 35°C. (F) H$_2$S/CH$_4$ performance of AO-PIM-1 for long-term continuous active feed of 20 mol % H$_2$S/20 mol % CO$_2$ and 60 mol % CH$_4$ at feed pressure of 8.6 bar at 35°C.
the separation efficiency (5, 12). As a more significant contribution occurs from higher sorption selectivity in AO-PIM-1, plasticization will lead to enhanced mixed-gas $\text{H}_2\text{S}/\text{CH}_4$ selectivity with increased feed pressure, as discussed below.

**Pure-gas sorption**

Below the onset of strong plasticization, the permeability coefficient, and permselectivity can be decoupled into diffusivity and solubility contributions (Eqs. 3 and 4) to obtain a better understanding of the role of amidoxime functionalization in $\text{H}_2\text{S}/\text{CH}_4$ and $\text{CO}_2/\text{CH}_4$ selectivity of the PIMs material. The apparent diffusion coefficient ($D$) was estimated using the time-lag method, and sorption coefficients ($S$) were deduced using $S = P/D$ for feed pressures below the onset of plasticization. This analysis is summarized for the AO-PIM-1 films with comparison to other glassy polymers in table S1. In comparison with the time-lag method, pure-gas sorption measurements for the sour gas components were performed on the parent PIM-1 and AO-PIM-1 films using the pressure-decay method (34, 35) at 35°C. The results of the $\text{H}_2\text{S}, \text{CO}_2,$ and $\text{CH}_4$ pure-gas sorption experiments are shown in figs. S5 to S7. The “dual-mode” sorption model with both Langmuir and Henry’s law is apparent in the concave sorption isotherms (9). The dual-mode sorption model was then fitted to the dual-mode sorption equations to each of the sorption isotherms to yield the dual-mode sorption parameters (figs. S8 to S10). A good agreement between the model and the sorption data was observed over the pressure range measured. Table S2 shows the best-fit dual-mode parameters for the PIM-1 and AO-PIM-1 materials and some other glassy polymers for $\text{H}_2\text{S}, \text{CO}_2,$ and $\text{CH}_4$ sorption. The sorption coefficients were obtained on the basis of the sorption data and the “dual-mode” sorption model. Sorption selectivity and diffusion selectivity values were then calculated using Eq. 3 and are provided in table S1. It can be seen that the diffusion coefficient ($D$) and sorption coefficient ($S$) values determined from the two methods are in good agreement. The diffusion coefficient of $\text{H}_2\text{S}$ was always smaller than that of $\text{CH}_4$ in the freshly made and methanol-treated aged AO-PIM-1 films. This trend may seem surprising, given the smaller kinetic diameter of $\text{H}_2\text{S}$ (3.6 Å) compared to $\text{CH}_4$ (3.8 Å). Such a reversed $\text{H}_2\text{S}/\text{CH}_4$ diffusion selectivity is not helpful to the overall $\text{H}_2\text{S}/\text{CH}_4$ perme selectivity. We hypothesize that this trend reflects strong hydrogen bonding of the highly polar $\text{H}_2\text{S}$ with amine and hydroxyl groups in the amidoxime moieties in AO-PIM-1.

Such a trend may lead to a lower diffusion coefficient resulting from the tendency of $\text{H}_2\text{S}$ molecules to “interact” with the sorption sites. This so-called stickiness of $\text{H}_2\text{S}$ within the polymer matrix can lead to higher activation energy of diffusion of $\text{H}_2\text{S}$ than expected. On the basis of these observations, the overall $\text{H}_2\text{S}/\text{CH}_4$ selectivity of AO-PIM-1 films is dominated by the sorption selectivity, whereas $\text{CO}_2/\text{CH}_4$ selectivity is controlled by both factors, although the contribution of the diffusion selectivity is more significant. The reversed $\text{H}_2\text{S}/\text{CH}_4$ diffusion selectivity reflects the strong polymer-penetrant interactions and is also found in other glassy polymers like hydroxyl-functionalized PIM-polymides and 6F-PAI materials in our previous research (7–9, 19). Future functionalization to the PIMs polymer backbone might further increase $\text{H}_2\text{S}$ perme selectivity by increasing $\text{H}_2\text{S}$ solubility and tightening the size discrimination in a narrow size range between 3.6 and 3.8 Å.

**Mixed-gas sorption prediction**

To acquire the gas sorption insight under mixed-gas feed conditions corresponding to the ternary mixed-gas permeation tests conducted in this work, mixed-gas sorption values were predicted using the dual-mode sorption parameters for $\text{H}_2\text{S}, \text{CO}_2,$ and $\text{CH}_4$ in table S2. The estimated mixed-gas sorption model and parameter values for $\text{H}_2\text{S}, \text{CO}_2,$ and $\text{CH}_4$ at 35°C with a 20% $\text{H}_2\text{S},$ 20% $\text{CO}_2,$ and 60% $\text{CH}_4$ feed mixture in the parent PIM-1 and AO-PIM-1 materials are shown in figs. S11 to S16. The predicted gas sorption values for $\text{H}_2\text{S}, \text{CO}_2,$ and $\text{CH}_4$ showed a decrease in solubility in the mixture. Compared with other glassy polymers, $\text{CH}_4$ sorption in the PIM-1 and AO-PIM-1 materials experienced a significant reduction under mixed-gas feed conditions due to lower Langmuir affinity constant values. Although $\text{H}_2\text{S}$ sorption in both PIM-1 and AO-PIM-1 materials also experienced a notable reduction under mixed-gas feed conditions, the sorption values are still much higher than those of other glassy polymers due to the relatively higher $\text{H}_2\text{S}$ Henry’s law sorption coefficient and Langmuir capacity constant value in the PIM-1 and AO-PIM-1. On the basis of the mixed-gas sorption predictions, it is clear that strong competitive sorption effects should exist in these sour gas separation systems, which is consistent with our previous research in this area (5, 7, 9).

**Mixed-gas permeation**

The intrinsic pure-gas separation properties of dense isotropic films are useful starting points to ultimately create integrally skinned asymmetric or composite flat-sheet or hollow-fiber membranes for important large-scale applications. For permeation of mixed-gas feeds, a separation factor based on gas chromatographic measurement of upstream and downstream compositions indicate the membrane separation efficiency. When the permeate pressure is negligible, the separation factor equals to the ratio of the component mole fractions in the downstream $(y)$ and upstream $(x)$, viz.

$$
\alpha_{ij} = \frac{y_i}{x_i} = \frac{y_j}{x_j}
$$

Again, for nonideal mixtures, like these in this work, the separation factor equals to the ratio of the mixed-gas permeabilities of components $i$ and $j$, based on the fugacity-based driving force of permeability preferred, viz.

$$
\alpha_{ij}^* = \frac{P_i^*}{P_j^*}
$$
Notwithstanding the importance of the pure-gas permeation measurements, multicomponent, high-pressure mixture tests performed with isotropic films are necessary as the next step toward practical industrial separations. To take this step, the freshly cast and methanol-treated aged AO-PIM-1 films were further investigated using ternary mixed-gas permeation measurements with a 20 mol % H₂S, 20 mol % CO₂, and 60 mol % CH₄ feed up to 77 bar, as shown in Fig. 2. These highly aggressive conditions even greatly exceed a typical wellhead.

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**Fig. 2.** Mixed-gas permeation properties of AO-PIM-1 and PIM-1 membranes in a ternary mixture (20 mol % H₂S, 20 mol % CO₂, and 60 mol % CH₄) at 35°C under feed pressures up to 77 bar. (A) CO₂ permeability. (B) H₂S permeability. (C) CO₂/CH₄ selectivity. (D) H₂S/CH₄ selectivity. (E) Combined (H₂S + CO₂) permeability. (F) Combined (H₂S + CO₂)/CH₄ selectivity.
pressure threshold of ~68 bar in realistic field operations. CO\textsubscript{2} permeability was high but much lower than that of H\textsubscript{2}S under the same feed pressures (Fig. 2, A and B), suggesting that H\textsubscript{2}S in the mixed-gas feeds competes more effectively than CO\textsubscript{2} in the polymer matrix. Significant H\textsubscript{2}S-induced plasticization effects with enhanced H\textsubscript{2}S permeability in AO-PIM-1 were observed even under the lowest feed pressure tested due to the strong H\textsubscript{2}S interactions with the polymer backbone (5, 7, 9, 12), as shown in Fig. 2B. A similar effect was observed for the precursor PIM-1. The H\textsubscript{2}S/CH\textsubscript{4} selectivity in the freshly cast and methanol-treated AO-PIM-1 films did not decrease due to plasticization effects as observed for CO\textsubscript{2}/CH\textsubscript{4} selectivity (Fig. 2, C and D). Instead, the mixed-gas H\textsubscript{2}S/CH\textsubscript{4} selectivity of a fresh AO-PIM-1 film increased from 50 at 10-bar to ~70 at 77-bar feed pressure (Fig. 2D). For the parent PIM-1, the increase in H\textsubscript{2}S/CH\textsubscript{4} selectivity was less dramatic, with an increase from ~20 to 30 over the same feed pressure range.

In a ternary mixture, condensable gases, H\textsubscript{2}S and CO\textsubscript{2}, compete for Langmuir sorption sites in the glassy polymer matrix (12). Because these sorption sites have higher H\textsubscript{2}S affinity in AO-PIM-1, the sorption capacity of CO\textsubscript{2} is greatly reduced. H\textsubscript{2}S, CO\textsubscript{2}, and CH\textsubscript{4} binding energies (BEs) on density functional theory (DFT)–optimized structures of the polymer-penetrant complex and the corresponding BEs on AO-PIM-1 polymer network are shown in figs. S14 to S17. A higher negative value of BE relates to a stronger adsorption. The results showed that BEs of H\textsubscript{2}S molecules in single AO-PIM-1 polymer chain and DFT-optimized structures of the polymer-penetrant complex are nearly one order of magnitude higher than those of CO\textsubscript{2} and CH\textsubscript{4}, which is consistent with pure-gas pressure-decay sorption experimental data (figs. S5 to S7). This result indicates that H\textsubscript{2}S molecules in AO-PIM-1 are nearly one order of magnitude more strongly adsorbed than those of CO\textsubscript{2} and CH\textsubscript{4}. Moreover, because H\textsubscript{2}S is more condensable than CO\textsubscript{2}, its solubility in AO-PIM-1 membranes is higher than that of CO\textsubscript{2}, which leads to penetrant-induced plasticization even at low feed pressures. Methane is not significantly affected due to its lower affinity for the Langmuir sorption sites (9, 12). The aforementioned effects lead to an increased H\textsubscript{2}S/CH\textsubscript{4} selectivity with increasing H\textsubscript{2}S partial pressure. This “plasticization-enhanced hydrogen sulfide separation” is a variation on the theme of removal of condensable gases from light gases, e.g., hydrocarbons from hydrogen (31), in which penetrant-induced plasticization of highly branched, cross-linked poly(ethylene oxide) rubbery polymers allowed good separation despite plasticization. Our mixed-gas permeation results indicate that this favorable plasticization-enhanced selectivity can be extended to the separation of H\textsubscript{2}S from sour natural gas feeds using the family of amidoxime-functionalized ladder PIMs (e.g., AO-PIM-1). Therefore, penetrant-induced plasticization, which tends to deteriorate the membrane performance of CO\textsubscript{2}/CH\textsubscript{4} separation using conventional glassy polymers, significantly enhances the separation efficiency of H\textsubscript{2}S from sour gas mixtures for the AO-PIM-1 membrane. At the high end of the mixed-gas feed pressure range (77 bar), the H\textsubscript{2}S/CH\textsubscript{4} selectivity reached nearly 75 in the freshly cast AO-PIM-1 film. This remarkable selectivity exceeds that of all glassy polymers and even the most selective rubbery polymers (5, 7–9, 12, 18, 19, 27). Moreover, the AO-PIM-1 ultrahigh H\textsubscript{2}S permeability of ~4300 Barrer under the extremely aggressive feed pressures up to 77 bar makes it a breakthrough material, with an extraordinary combination of ultrahigh selectivity and permeability. To further emphasize this point, table S2 summarizes most of the high-pressure studies of ternary mixed gases containing H\textsubscript{2}S using polymeric dense films for acid gas separations from natural gas, including the precursor polymer PIM-1. The unique separation performance at the exceedingly challenging feed conditions makes AO-PIM-1 materials extremely impressive, since most previous literature reports on mechanically weak hydrophilic rubbery polymers, which usually show high H\textsubscript{2}S/CH\textsubscript{4} selectivity, were investigated only at low feed pressures. As reported here, ternary mixed-gas permeation with up to 20% H\textsubscript{2}S at feed pressures up to 77 bar shows the AO-PIM-1 material to be an outstanding candidate for these challenging H\textsubscript{2}S separations.

The intrinsic difference and somewhat opposing mechanisms between glassy and rubbery materials in terms of CO\textsubscript{2}/CH\textsubscript{4} and H\textsubscript{2}S/CH\textsubscript{4} separation performance complicate comparisons of separation efficiency for overall sour natural gas separation. As in the past, we address this challenge using a “combined acid gas selectivity (\(\alpha_{\text{CAG}}\)).” The combined acid gas selectivity (\(\alpha_{\text{CAG}}\)) is defined as the ratio of combined acid gas permeability (\(P_{\text{H2S}} + P_{\text{CO2}}\)) and methane permeability (\(P_{\text{CH4}}\)) (7, 9). The combined mixed-gas (H\textsubscript{2}S + CO\textsubscript{2}) permeability and \(\alpha_{\text{CAG}}\) selectivity of AO-PIM-1 and PIM-1 as function of feed pressure are shown in Fig. 2 (C and D). As mentioned earlier, the selectivity increases significantly by increasing the feed pressure due to enhanced acid gas solubility effects.

The separation efficiency for specific gas pairs and the membrane productivity are trade-off parameters because selectivity generally decreases with an increase in the permeability of the more permeable gas component as reflected by the well-known Robeson upper bound (29, 30). This overall separation performance of the AO-PIM-1 membrane is compared with literature data listed in table S3 via such a combined acid gas productivity–efficiency trade-off plot in Fig. 3. The overall combined H\textsubscript{2}S + CO\textsubscript{2} acid gas performance of AO-PIM-1 is located at the far upper right quadrant and well above what we suggest as an upper

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**Fig. 3. Combined ternary acid gas (CO\textsubscript{2}+ H\textsubscript{2}S)/CH\textsubscript{4} performance demonstrated by productivity–efficiency trade-off for typical polymer membranes and AO-PIM-1 in sour gas separations.** Ternary mixed-gas permeabilities and selectivities are listed in table S3. Experimental upper bound lines are drawn to guide the eye: the solid black ones reveal the trade-off between H\textsubscript{2}S or combined acid gas (CO\textsubscript{2} + H\textsubscript{2}S) permeabilities and selectivities in typical glassy polymers; the dashed black ones show the case of hydrophilic rubbery membranes. AO-PIM-1 films (this work) were measured with ternary sour gas mixtures containing H\textsubscript{2}S as high as 20 mol % at exceedingly aggressive feed pressures higher than 55 bar and up to 77 bar; typical rubbery materials were tested at low feed pressures of ~10 bar; mixed-matrix membranes were measured at 6.9 bar (36, 37); typical glassy polymers including cellulose acetate, 6FDA-based polyimides, cross-linkable polyimides (PEGMC), fluorinated PAIs (6F-PAIs), and intrinsically microporous polyimides (PIM-6FDA-OH) were measured with ternary gas mixtures containing H\textsubscript{2}S ranging from 10 to 20 mol % at aggressive feed pressures of greater than 34.5 bar but generally less than 60 bar (5, 7–9, 12, 18, 19, 27).
bound for typical glassy and rubbery polymers based on the sparsely available data. Specifically, compared with very recently published metal-organic framework (MOF)-based mixed matrix membranes (MMMs) (36, 37), H2S permeability of AO-PIM-1 films was more than one order of magnitude higher than that of MMMs. Meanwhile, the H2S/CH4 selectivities of the AO-PIM films are more than three times higher than those of MOF-based MMMs. These results indicate that this unique material performs significantly better than other glassy polymers and MOF-based MMMs and the best performing hydrophilic rubbery materials based on either H2S or the combined acid gas metric. Furthermore, the extreme sour mixed-gas testing conditions considered here are significantly more realistic than have been examined in the past with rubbery materials.

Last, the performance of the AO-PIM-1 membrane that was exposed to long-term testing at 8.6-bar feed pressure (Fig. 1, E and F) was reevaluated with the same ternary 20% H2S/20% CO2/60% CH4 mixture as function of feed pressure up to 77 bar. The membrane maintained its integrity as demonstrated by mixed-gas H2S permeability of >4000 Barrer and combined acid gas selectivity of ~80 at 77 bar (Fig. 4).

**CONCLUSION**

In summary, a solution-processable ultra H2S/CH4 selective and highly H2S permeable AO-PIM (AO-PIM-1) was prepared and characterized. A ternary feed mixture containing 20% H2S/20% CO2/60% CH4 showed that the AO-PIM-1 membrane provided outstanding separation performance for purification of sour gas streams under challenging feed pressures up to 77 bar. Such membrane exhibited ultrahigh H2S permeability of >4000 Barrers, two to three orders of magnitude higher than commercially available glassy polymeric membranes. Most interestingly, H2S-induced plasticization significantly enhanced hydrogen sulfide separation using AO-PIM-1 films, in contrast to the negative effects caused by plasticizing for CO2/CH4 separation in traditional polymeric membrane materials. Moreover, the unique family of AO-PIMs materials can be scaled up to produce an integrally skinned asymmetric or composite structure in flat-sheet or hollow-fiber geometry. Given the global quest for clean energy and sustainable development, the synthesis of such novel gas separation membranes with superior performance opens the door to enormous opportunities for natural gas purification, biogas upgrading, and reducing greenhouse gas emissions. Future developments toward commercialization and integration in...
natural gas processing require fabrication of amidoxime-functionalized PIMs as integral asymmetric or thin-film composite hollow-fiber membranes.

**MATERIALS AND METHODS**

**Materials**

The monomers 1,4-dicyanotetrafluoroazobenzene (DCTB) was purchased from Matrix Scientific, and 5,5′,6,6′-tetrahydroxy-3,3′,3,3′-tetramethyl-1,1′-spirobisindane (TTSTBI, 98%) was supplied by Alfa Aesar (USA). N, N-dimethylacetamide (DMAc) (99%), toluene (anhydrous, 99.8%), potassium carbonate (anhydrous, 99.5%), chloroform (99.5%), n-hexane (anhydrous, ≥99%), methanol (99.5%), tetrahydrofuran (99.8%), and hydroxyamine (50 weight % solution in water, 99.99%) were purchased from Sigma-Aldrich (USA). CO2 and CH4 with 99.999% purity were obtained from Airgas Inc. (USA), whereas H2S (99.6% purity) and ternary gas mixture with a composition of 20 mol % H2S, 20 mol % CO2, and 60 mol % CH4 were supplied by Praxair Inc. (USA).

**Methods**

**Polymer synthesis**

The parent polymer PIM-1 (fig, S1) was synthesized according to a high-temperature, high-concentration approach reported by Du et al. (38) and Swaidan et al. (22). A typical procedure was conducted as follows: A flask was charged with 5.1 g (15 mmol) of TTSTBI, 3.0 g (15 mmol) of DCTB, 6.2 g (45 mmol) of K2CO3, and 25 ml of DMAc. The mixture was vigorously stirred for 6 min under a flow of inert atmosphere of argon at 155°C, and then 20 ml of toluene was added into the mixture under stirring. Afterward, 0.2 ml of deionized (DI) water and 2 ml of toluene were added to the mixture. The resultant polymer was poured into methanol and filtered. The product was then precipitated from a chloroform/methanol mixture, refluxed in boiled DI water, and then filtered and dried at 120°C under vacuum to give PIM-1 as a bright yellow powder.

The AO-PIM-1 (figs, S1 and S2) was prepared, as reported (22, 23), by dissolving 0.6 g of PIM-1 powder in 40 ml of tetrahydrofuran (THF) and heating to 65°C under N2. Then, 6.0 ml of hydroxyamine was added dropwise. Thereafter, the mixture was refluxed at 69°C for 20 hours under stirring. The resultant polymer was then cooled to room temperature and purified by the addition of ethanol, filtered and thoroughly washed with ethanol, and dried at 110°C for 3 hours to yield AO-PIM-1 as an off-white solid.

**Membrane fabrication**

The vacuum-dried AO-PIM-1 polymer was dissolved in DMAc to form a 2 to 3% (w/v) concentration. Then, the polymer dope was filtered and poured onto a leveled glass plate with a stainless steel ring. After slowly evaporating the solvent at 45°C for 2 days, the vitrified films were soaked in methanol, air-dried, and then annealed at 120°C under high vacuum to remove the residual solvent trapped in the micropores. The thicknesses of the dense films were approximately 50 to 60 μm, as measured by a digital micrometer.

**Membrane aging and rejuvenation**

Highly permeable glassy polymers tend to show decreasing gas permeability over time, which is known as physical aging. The aging effects are known to be substantial in PIMs materials and influence the physical properties (e.g., membrane thickness, density, free volume) with significant loss in permeability (39, 40). In previous research on physical aging in PIMs, the aging clock is usually "reset" via soaking an aged film in alcohols (e.g., methanol or ethanol) or n-hexane, which causes PIMs film to visibly swell and restore most of its original permeability. This process is considered a "rejuvenation" technique (39–41), allowing an aged glassy membrane to be easily rejuvenated. Further aging after this step is also typically slower than that in the original sample (41). This rejuvenation technique also counteracts the effects of aging in thin films or hollow fibers, where the aging is normally much faster. In this work, the aged films (aging under ambient conditions for 6 months) were solvent rejuvenated (methanol) to reset the aging. Briefly, the aged AO-PIM-1 film was dried at 120°C for 12 hours, soaked in pure methanol for 24 hours and n-hexane for another 24 hours to reset their thermal histories, air-dried, and then postdried at 120°C under vacuum for 24 hours to remove the residual solvents. In this work, two different AO-PIM-1 films, named freshly made and rejuvenated, were measured using both pure- and mixed-gas feeds.

**Gas permeation measurements**

Pure and ternary mixture permeation experiments were performed at 35°C using H2S, CO2, and CH4 as well as a mixture of these three components (20 mol % H2S, 20 mol % CO2, and 60 mol % CH4). For the challenging feeds considered in this work, additional safety measures were needed. Our group has constructed a state-of-the-art research facility for the safe handling of H2S. The film sample, dried at 120°C under high vacuum for 24 hours, was immediately installed in the membrane cell. Prior to the permeation test, the aluminum foil masked film was degassed for at least 24 hours on both sides under vacuum to ensure complete degassing of the membrane and system. Dense film permeation was conducted using a previously reported constant volume-variable pressure permeation apparatus (7, 12) described in the fig. S3 to ensure safety when handling H2S gas or mixtures. Several critical alterations were made to our regular permeation system design as provided in the paper by Yi et al. (7). Pure gases were introduced to the upstream side at 35°C and 2 bar (1 bar for H2S to minimize the plasticization effect). In addition, the CO2 and CH4 pure-gas permeation isotherms were measured at pressures from 2 to 20 bar and the H2S isotherm from 1 to 8 bar for the two different membrane samples (freshly made and rejuvenated). As the gas molecules diffused through the membrane, the increase in permeate pressure was measured by a downstream pressure transducer (MKS Instruments, Dallas, TX, USA) and recorded using LabVIEW software (National Instruments, Austin, TX, USA) until the "steady state" was reached (after at least 10 times the diffusion time lag). After the apparent steady state was achieved, the permeate receiver was again evacuated, and a second pressure increase test was done to verify that the steady-state permeation rate was truly achieved. The slope of the plot of the permeate pressure versus time (dp/dt) was then calculated and used to calculate the permeability coefficient.

In the case of the ternary mixed-gas permeation experiments, the retentate flow rate and upstream pressure were well maintained with the stage cut at 1% or below using 1000D syringe pumps (Teledyne Isco Inc., Lincoln, NE, USA) and a metering valve. The stage cut represents the ratio of permeate to retentate flow. The downstream composition was measured using a gas chromatograph (GC) (Varian 450 GC, Agilent Technologies, USA). The permeate gas composition was tested at least three times or until the steady-state operation was confirmed. Mixed-gas permeation values are based on the average of at least three GC permeate composition measurements at each pressure point up to approximately 77 bar. Because CO2 and H2S are highly condensable gases, all permeation measurements in this work were calculated using the fugacity-based driving force definition of dense film permeability for highly challenging feeds (5, 7).
Gas sorption measurements

The sorption coefficient reflects the thermodynamic contribution to transport. It can also be measured independently by the so-called pressure-decay sorption (fig. S18) (42); therefore, $D$ can be calculated from $D = P/S$. As shown in Eq. 7, for cases with negligible downstream pressure, the sorption coefficient can be expressed as

$$S_i = \frac{c_i}{f_i}$$

where $c_i$ is the concentration of a gas sorbed in the film and $f_i$ is the corresponding upstream fugacity driving force of component $i$. For glassy polymers, this relationship is usually described by the dual-mode sorption model (43, 44), which is given as

$$c_i = c_{D,i} + c_{H,i} = k_{D,i} \cdot f_i + \frac{C_{H,i} \cdot b_i \cdot f_i}{1 + b_i \cdot f_i}$$

where $c_{D,i}$ is the Henry’s law or dissolved mode penetrant concentration and $c_{H,i}$ is the penetrant concentration in the Langmuir mode or hole-filling sorption mode. In Eq. 8, $k_{D,i}$ is the Henry’s law sorption coefficient, $C_{H,i}$ is the Langmuir capacity constant, and $b_i$ is the Langmuir affinity constant. As with the permeability coefficient, fugacity ($f_i$) values are usually substituted in place of pressure values to connect more directly to the real thermodynamic properties of the penetrants.

Koros et al. (45, 46) extended the dual-mode sorption model represented by Eq. 8 to account for competition in binary gas mixtures at concentrations below which swelling-induced complications occur. Recently, this dual-mode sorption model was used for ternary mixed-gas feed cases (5, 7). The ternary mixed-gas dual-mode sorption model for components $A$, $B$, and $C$ can be given in Eqs. 9 to 11.

$$c_A = k_{D,A} \cdot f_A + \frac{C_{H,A} \cdot b_A \cdot f_A}{1 + b_A \cdot f_A + b_B \cdot f_B + b_C \cdot f_C}$$

$$c_B = k_{D,B} \cdot f_B + \frac{C_{H,B} \cdot b_B \cdot f_B}{1 + b_A \cdot f_A + b_B \cdot f_B + b_C \cdot f_C}$$

$$c_C = k_{D,C} \cdot f_C + \frac{C_{H,C} \cdot b_C \cdot f_C}{1 + b_A \cdot f_A + b_B \cdot f_B + b_C \cdot f_C}$$

Molecular simulations

Construction of AO-PIM-1 model. Two AO-PIM-1 models were constructed for a different purpose, as shown in fig. S14A. A model with 16 repeated polymer units (fig. S14A) was constructed to generate AO-PIM-1 periodic cell; a simplified model (fig. S14C) was constructed to save computational resource for DFT calculations. The terminations of the polymer chains were saturated by hydrogen atoms. After comparison with the DFT results between the simplified model and a model with five polymer units (fig. S14B), the simplified model can well represent a single AO-PIM-1 polymer chain and thus was used for all the following DFT calculations.

Construction of AO-PIM-1 periodic cell. Three-dimensional view of AO-PIM-1 in an amorphous periodic cell with 16 repeated polymer units is shown in fig. S2. Void morphologies of AO-PIM-1 were constructed by the Amorphous Cell with Materials Studio 8.0 using 10 polymer chains with the target density of 1.18 g cm$^{-3}$, as shown in Fig. 1B.

DFT calculations

The binding strength between two AO-PIM-1 polymer chains, representing annealed polymers, was investigated by combining two single polymer chains with various interacting configurations. The interaction energy of gas molecules (H$_2$S, CO$_2$, and CH$_4$) on a single polymer chain or polymer network was also investigated to indicate the preference of AO-PIM-1 to adsorb the molecules.

All the DFT calculations were performed using DMol$^3$ code in Materials Studio 8.0. The Becke exchange plus Lee-Yang-Parr correction exchange-correlation functional (47) with double numeric polarization basis set (48) was used. DFT semicore pseudopotential calculations were used to set the core treatment type. A real-space orbital global cutoff of 4.0 Å was applied. The convergence threshold parameters for the optimization were 2 x 10$^{-5}$ (energy), 4 x 10$^{-3}$ (gradient), and 5 x 10$^{-3}$ (displacement), respectively. To further improve the accuracy of the calculation results, the Grimme method for dispersion-corrected density functional theory (DFT-D) approach was used in the calculations. On the basis of the ordering of polymorphs by their energies and structure description, this method can provide a significant improvement relative to pure force field or pure DFT methods (49).

The DFT calculation procedure is described as follows: The generated polymer model and gas molecular models were geometrically optimized using the DFT method described above; following the total energy computation separately using the same method. The complexes with two polymer chains or one polymer chain and one gas molecule were generated by considering various configurations and geometrically optimized, followed by energy computations.

The BE between two polymer chains was calculated using the following equation

$$BE = E_{\text{complex}} - 2E_{\text{SP}}$$

where BE is the binding energy, $E_{\text{complex}}$ is the total energy of polymer complex, and $E_{\text{SP}}$ is the energy of a single polymer chain.

The BE between a gas molecule and one polymer chain (or two polymer chains) was calculated using the following equation

$$BE = E_{P+M} - E_{P} - E_{M}$$

where $E_{P+M}$ is the total energy of polymer and molecule, $E_{P}$ is the energy of polymer, and $E_{M}$ is the energy of molecule.

SUPPLEMENTARY MATERIALS

Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/5/eaaw5459/DC1

Fig. S1. Synthetic scheme for AO-PIM-1.
Fig. S2. Three-dimensional view of AO-PIM-1 (16 repeat units) in an amorphous periodic cell.
Fig. S3. Constant volume/variable pressure permeation apparatus for pure and mixed gases.
Fig. S4. Pure-gas H$_2$S permeability of AO-PIM-1 and PIM-1 as a function of upstream pressure.
Fig. S5. Pure H$_2$S permeability of AO-PIM-1 and PIM-1 as a function of upstream pressure at 35°C.
Fig. S6. Pure H$_2$S permeability of AO-PIM-1 and PIM-1 as a function of upstream pressure at 35°C.
Fig. S7. Pure H$_2$S dual-mode sorption model at 35°C for AO-PIM-1 and PIM-1 dense films.
Fig. S8. Pure CH$_4$ dual-mode sorption model at 35°C for AO-PIM-1 and PIM-1 dense films.
Fig. S9. CO$_2$ sorption isotherm at 35°C for AO-PIM-1 dense films.
Fig. S10. CH$_4$ sorption isotherm at 35°C for AO-PIM-1 dense films.
Fig. S11. H$_2$S sorption isotherm at 35°C for PIM-1 dense films.
Fig. S12. CO₂ sorption isotherm at 35°C for PIM-1 dense films.

Fig. S13. CH₄ sorption isotherm at 35°C for PIM-1 dense films.

Fig. S14. DFT optimized structure of a single chain of AO-PIM-1.

Fig. S15. Electrostatic potential in the AO-PIM-1 network.

Fig. S16. Electrostatic potential of gas molecules.

Fig. S17. DFT optimized structures of the polymer-penetrant complex and the corresponding BEs on the AO-PIM-1 network (parallel 1).

Fig. S18. Pressure-decay sorption apparatus for gas sorption experiments.

Table S1. Diffusion coefficients (D), sorption coefficients (I), diffusion selectivities (α), and sorption selectivities (β) of AO-PIM-1 and other glassy polymers at 35°C.

Table S2. Dual-mode sorption parameters for pure H₂S, CO₂, and CH₄ transport properties and separation performance of polymeric membranes for natural gas purification.

Table S3. Comparison of AO-PIM-1 with other polymers in mixed-gas feed streams at 35°C.

Fig. S20. Metal-organic framework adsorbents and membranes.

Fig. S21. Model for sorption of mixed gases in glassy polymers.

Fig. S22. Comparison of AO-PIM-1 with other polymers in mixed-gas feed streams at 35°C.

Table S3. Comparison of AO-PIM-1 with other polymers in mixed-gas feed streams at 35°C.

Fig. 1. Aromatic block co-polyimide membranes for sour gas feed separations.

Fig. 2. Metal-organic framework adsorbents and membranes.

Fig. 3. Model for sorption of mixed gases in glassy polymers.

Fig. 4. Comparison of AO-PIM-1 with other polymers in mixed-gas feed streams at 35°C.

Table 1. Diffusion coefficients (D), sorption coefficients (I), diffusion selectivities (α), and sorption selectivities (β) of AO-PIM-1 and other glassy polymers at 35°C.

Table 2. Dual-mode sorption parameters for pure H₂S, CO₂, and CH₄ transfer properties of a series of novel 6FDA-based polyimide-imides for natural gas purification.


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