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ARTICLE

Effects of Supercritical CO_2 Conditioning on Un-Cross-Linked Polyimide Membranes for Natural Gas Purification

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ABSTRACT: The effects of supercritical CO_2 ($scCO_2$) conditioning are examined through changes in gas permeability and solubility for 6FDA-based polyimide membranes. At pressures above the supercritical point, both CO_2 permeability and sorption unexpectedly decline, suggesting a structural rearrangement of the polymer facilitated by the presence of a highly soluble species. High-pressure permeability isotherms for He and N_2 do not exhibit a similar decline. Upon depressurization, a typical hysteresis is not observed; rather, CO_2 permeability remains at reduced levels compared to the original pressurization. Permeability isotherms of the conditioned polymer show a reduction in transport compared to unconditioned samples; however, sorption isotherms show an increase in penetrant solubility following $scCO_2$ conditioning. Pre- and post-CO_2/CH_4 mixed gas permeation testing at 35 °C shows a reduction in membrane permeability with a corresponding increase in the separation factor after $scCO_2$ conditioning.

1. Introduction

As the worldwide demand for natural gas continues to increase, the utilization of subquality and partially depleted natural gas reservoirs becomes more important. Typical carbon dioxide concentrations in subquality natural gas range from 5 to 25% with some reservoirs containing much higher concentrations.[1,2] In order to meet pipeline specifications for transport, the carbon dioxide concentration must be reduced to less than 2%.[2] Partially depleted natural gas reservoirs are currently being investigated as potential sources for supercritical carbon dioxide ($scCO_2$) sequestration for two purposes. The first purpose is to reduce the amount of carbon dioxide in the atmosphere that contributes to global warming. A second purpose is to gain utility from the injected carbon dioxide to pressurize such reservoirs through carbon dioxide injection to enhance methane recovery. Clearly, this reinjection process greatly increases the carbon dioxide content of the recovered natural gas.[3,4] For each of the above scenarios, membrane separation processes provide an attractive alternative to traditional absorption processes which are typically more expensive, much larger, and potentially harmful to the environment.

The use of $scCO_2$ as a tunable solvent also offers an environmentally safer and potentially cheaper option to typical organic solvents. Current studies using $scCO_2$ as a solvent include two- and three-phase catalytic reactions, polymerization reactions, and polymer processing.[5] In many of these processes the products (and/or byproducts) can only be removed through depressurization of the system, which ultimately leads to expensive CO_2 recompression costs. In these processes, membranes provide an economical method to purify the CO_2 solvent while maintaining the high pressures required to keep it supercritical.

It is well-known that subcritical CO_2 is a highly sorbing species and tends to plasticize glassy polymers, thus reducing the separating efficiency of the membrane.[6−8] However, there has been little work done to study the effects of $scCO_2$ on polymer membrane performance. Current research is being conducted using Sepa CF thin film, polyamide, and cellulose acetate membranes to purify $scCO_2$ after extraction of essential oils from vegetables.[9−11] In all of these studies, the working pressure for $scCO_2$ permeation is 12 MPa and the transmembrane pressure is varied from 0.5 to 4 MPa. Spricigo et al. and Sarmento et al. noted a short conditioning time resulting in a decrease in the CO_2 flux through the membrane which they attribute to membrane compaction. While these studies provide insight into oil retention and the conditioning effects of the oils on CO_2 permeation, they do not further explore the effects of $scCO_2$ on the membranes themselves. Semenova et al. studied the separating efficiency of Kapton for $scCO_2$/ethanol mixtures and found that the CO_2 flux increased linearly with pressure from 1 to 14 MPa.[12,13] Ohya et al. and Higashijima et al. confirmed the Kapton response to $scCO_2$ exposure for pressures up to 12 MPa. [14,15] Chen et al. probed the effects of $scCO_2$ conditioning on polycarbonate membranes through oxygen permeation and sorption and changes in the glass transition temperature. In this latter study, after conditioning the samples at various subcritical and supercritical CO_2 densities, the chamber was depressurized in less than 5 min. The rapid depressurization of such a highly soluble species traps additional free volume in the polymer matrix leaving the polymer in a "puffed up" state. This result was evident in the large increase in the Langmuir capacity constant of oxygen and nitrogen sorption as the CO_2 density increased.[16] Finally, Patil et al. studied $scCO_2$ conditioning effects on poly(vinyl alcohol) and a polyamide for pressures up to 20 MPa while maintaining a transmembrane pressure drop of between 0.05 and 0.3 MPa. The CO_2 permeances are modeled using Hagen−Poisseuille's relationship for viscous flow.[17]

It is clear that the use of $scCO_2$ is becoming more prevalent and that polymer membranes can play an important role in the purification and reuse of CO_2 in the supercritical state. However, few studies have been conducted to determine what effects $scCO_2$ conditioning has on the polymer. In fact, no studies exist that explore how $scCO_2$ affects high-performance polymer membranes used in natural gas purification. The objective of this study is to investigate the effects of $scCO_2$ conditioning on 6FDA-based polyimides. The membranes are conditioned using

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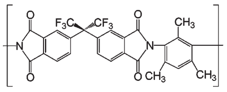
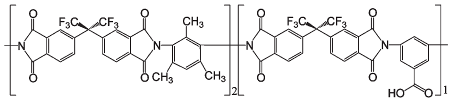
Table 1. Polymer Structures and Physical Properties[a]

Polymer Structure	T_G (°C)	Fractional Free Volume
 6FDA-DAM	373	0.190
 6FDA-DAM:DABA (2:1)	358	0.169

[a] Occupied volumes are determined using a group contribution method.[28]

$scCO_2$ and then probed with a 50/50 CO_2/CH_4 feed mixture to determine how conditioning affects the performance of the membrane.

2. Material and Methods

2.1. Polymer Preparation. Table 1 shows the structure of the 6FDA-DAM and 6FDA-DAM:DABA (2:1) polyimides used for this study. The DABA diamine was added to the polymer backbone to make use of the acid site for future cross-linking studies. These polymers were synthesized through a two-step polycondensation reaction in which the first step produces a high molecular weight polyamic acid and the second step serves to close the ring, producing a chemically stable polyimide. The 6FDA-DAM in this work was chemically imidized in the presence of triethylamine and acetic anhydride for 1 h at 100 °C, whereas the 6FDA-DAM:DABA (2:1) was thermally imidized for 24 h at 200 °C. The dense films were cast from a 3−5% weight solution in THF on a Teflon surface in an inert environment. The 6FDA-DAM films were dried at 100 °C for 12 h and then annealed at 120 °C for 24 h, whereas the 6FDA-DAM:DABA (2:1) films were annealed at 220 °C for 48 h prior to $scCO_2$ conditioning. The annealing temperature and time for the 6FDA-DAM:DABA (2:1) polymer are increased in order to obtain direct comparisons with future cross-linked films which require this protocol to achieve maximum cross-linking.

2.2. Gas Permeation and Sorption. Gas permeation measurements are taken using a constant volume-variable pressure system described by Damle and Koros.[18] Moore et al. describes the technique used to mask the membranes for permeation testing.[19] Devcon 14250 epoxy was used to mask the 6FDA-DAM films; however, under $scCO_2$ conditions, the films occasionally delaminated from the epoxy. Therefore, Duralco 4525 epoxy was used for all 6FDA-DAM:DABA (2:1) permeation experiments. The 6FDA-DAM permeation measurements were taken at 50 °C, and the 6FDA-DAM:DABA (2:1) measurements were taken at 35 °C. At high pressures, CO_2 plasticizes the polymer; therefore, the measured permeabilities are no longer constant and vary with conditioning time and pressure interval. As a result, true steady-state CO_2 permeabilities cannot be determined upon pressurization and depressurization of the system. For example, the largest drift for the 6FDA-DAM:DABA (2:1) occurred at 900 psia when the CO_2 permeability increased 14% and 26% over 6 and 12 h, respectively, before the pressure was increased to the next interval. To avoid such ambiguities, it is useful to define a set time following exposure to the feed after which a permeability measurement is taken and the pressure is raised (or lowered as for depressurization). For the 6FDA-DAM, the set time between measurements was 24 h. In an attempt to shorten the overall experiment time, the set time was lowered to 12 h for the 6FDA-DAM:DABA (2:1). Steady-state permeabilities were determined for He and N_2 feeds. For mixed gas experiments, a 50/50 CO_2/CH_4 feed was used, and both the feed and permeate were analyzed using an HP 5890 gas chromatograph with a thermal conductivity detector. The stage cut was maintained below 1% to prevent concentration polarization from occurring. Mixed gas permeabilities and samples analyzed by GC were collected after 10 time lags of the slow gas.

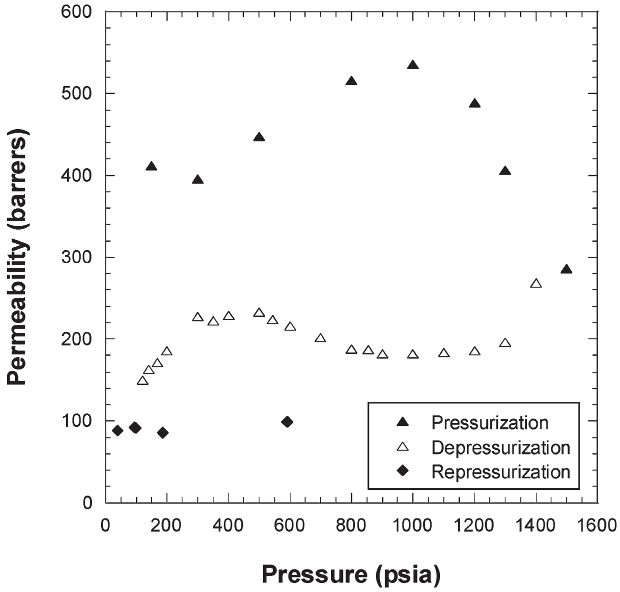


Figure 1. CO_2 permeability isotherm illustrating the effect of $scCO_2$ conditioning on 6FDA-DAM at 50 °C.

Sorption measurements were performed using the gravimetric sorption technique. The sorption chamber for the $scCO_2$ conditioning measurements was a high-pressure Jerguson transparent gauge (model 19-TCH-32) that was outfitted with a bolted flange on one end to allow access to the inner chamber. The stock gaskets between the chamber and borosilicate glass were replaced with Grafoil gaskets to provide a better seal in the $scCO_2$ environment. A Grafoil gasket was also used in the flange. An Isco syringe pump was used to pressurize the CO_2 into the supercritical state for conditioning measurements. Dilation measurements were taken in conjunction with sorption measurements in order to accurately describe the changing volume of the polymer as more CO_2 sorbed into the sample. The polymer volume was assumed to increase isotropically. The buoyancy of the sample, copper wire used to hold the sample, and the spring itself were determined and included in the sorption calculations.[20] All sorption experiments were conducted at 35 °C.

3. Results and Discussion

3.1. Gas Permeation Experiments. *3.1.1. Pure Gas.* In the presence of highly sorbing components, polymer chain mobility is enhanced, causing plasticization and an increase in gas permeation. Figure 1 shows permeability results for the 6FDA-DAM polymer exposed to increasing CO_2 pressures up to 1500 psi at 100−200 psi intervals. Upon pressurization, a typical increase in permeability with an increase in pressure is observed, until the pressure reaches 1000 psi. At that point, the permeability begins to decrease until the final pressure of 1500 psi is reached. While not shown, fugacity-based permeabilities exhibit the same response as shown in Figure 1; therefore, this decrease in permeability in the $scCO_2$ region suggests a structural reorganization of the polymer. Figure 2 displays He and N_2 permeability isotherms up to 1500 psi, and as shown, the permeabilities remain constant.

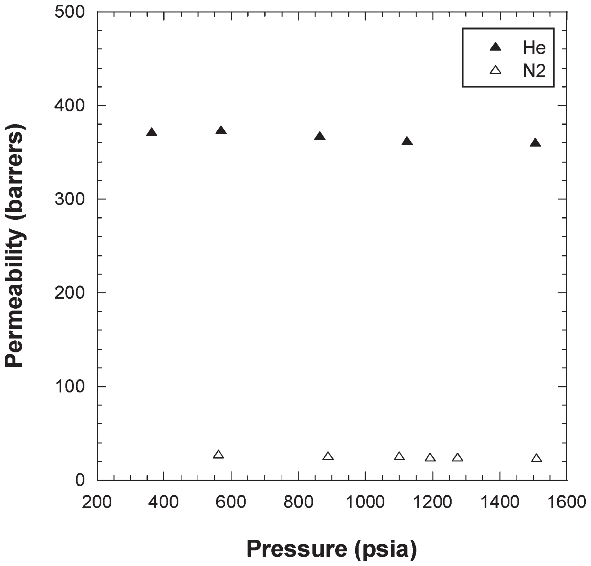


Figure 2. He and N_2 permeability isotherms for 6FDA-DAM up to 1500 psi at 50 °C.

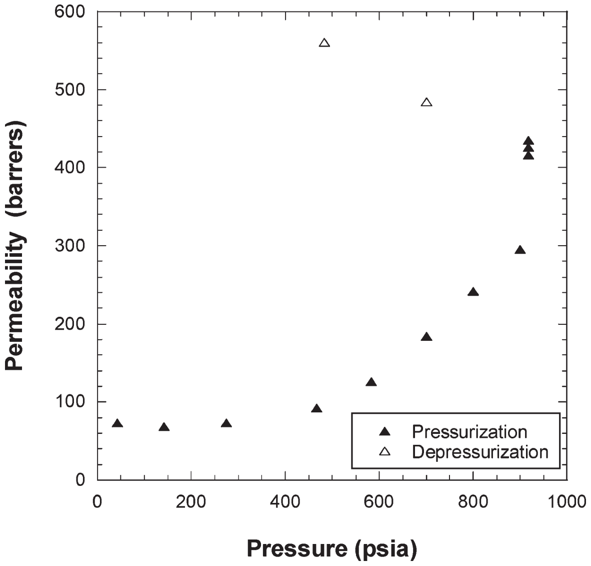


Figure 3. Typical depressurization response for a 6FDA-based polyimide.

Table 2. Polymer Chain *d*-Spacing Extracted from WAXD Data for Unconditioned and Conditioned Samples of 6FDA-DAM along with Corresponding CO_2 Permeabilities at 150 psi

sample	chain spacing (Å)	permeability (barrers)
unconditioned	5.9 ± 0.1	412
conditioned	5.4 ± 0.1	90

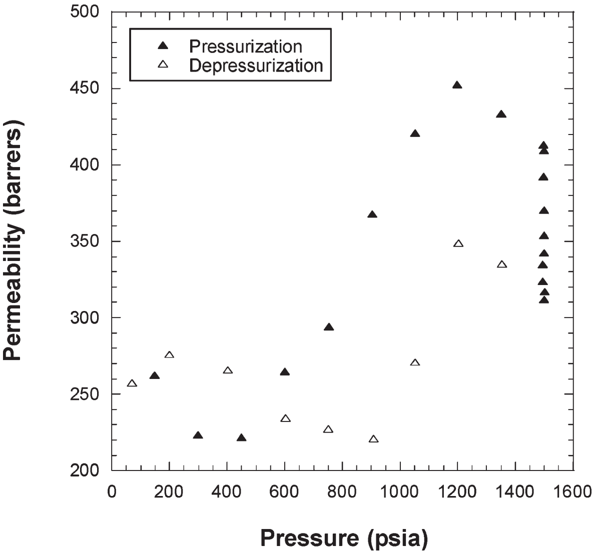


Figure 4. CO_2 permeability isotherm illustrating the effect of $scCO_2$ conditioning on 6FDA-DAM:DABA (2:1) at 35 °C.

Therefore, the observed decline in the CO_2 permeability isotherm is not solely a function of the high hydrostatic pressure but requires the presence of a swelling agent to increase the polymer chain mobility which works in conjunction with the high pressure to facilitate this reorganization. Once 1500 psi is reached, the pressure was then slowly decreased in 50−100 psi increments. Clearly, the permeabilities remain stable around 200 barrers down to 150 psi. The system was then evacuated for 3 days before it was repressurized and further permeability measurements were taken. As can be seen from Figure 1, the permeabilities upon repressurization are steady to 600 psi at around 95 barrers.

Figure 3 presents a typical hysteretic response that would be expected for a related 6FDA-based polymer that is depressurized from a high-pressure CO_2 environment. The increase in permeability upon depressurization is due to an increase in excess volume of the swollen polymer as a result of slow polymer relaxation times as CO_2 desorbs from the polymer, leaving it in a "puffed up" state. Similar nonequilibrium hysteretic responses have been shown to be completely stable for Lexan polycarbonate over 2 months if a depressurization system is halted at a specific pressure, say 500 psi.[21] In Figure 1, there is no hysteretic response, which seems to indicate that a stabilization of the sample has been induced by the exposure to high-pressure CO_2. Moreover, the permeability of the 6FDA-DAM polymer upon repressurization is about a quarter of the initial permeability, which is not typical of a repressurization response under normal conditions.

To more closely investigate the effects of this structural reorganization, wide-angle X-ray diffraction was performed on unconditioned and conditioned samples of 6FDA-DAM to determine the average *d*-spacing. The average *d*-spacing of an amorphous polymer can reflect the average interchain spacing, and this chain spacing can be correlated with the gas permeability in polyimides.[22] Table 2 shows the *d*-spacing for the unconditioned and conditioned 6FDA-DAM samples with the corresponding CO_2 permeabilities at 150 psi. These results demonstrate that a measurable decrease in the average chain spacing is observed between the unconditioned and conditioned samples, which correlate well with the decrease in polymer permeability. Density measurements were conducted to determine the corresponding fractional free volumes of unconditioned and conditioned 6FDA-DAM: DABA (2:1) samples; however, there was no measurable difference in the densities of the samples.

Figure 4 presents permeability results for the 6FDA-DAM:DABA (2:1) polymer which was tested using a similar protocol. As stated earlier, the time between pressurization and depressurization measurements is ~12 h, and the film was allowed to remain at 1500 psi for 10 days. Since the 6FDA-DAM:DABA (2:1) polymer was annealed at a higher temperature than the 6FDA-DAM polymer, a direct comparison of the CO_2 permeability isotherms is not possible; however, 6FDA-DAM:DABA (2:1) is a lower free volume polymer than 6FDA-DAM which results in a lower intrinsic

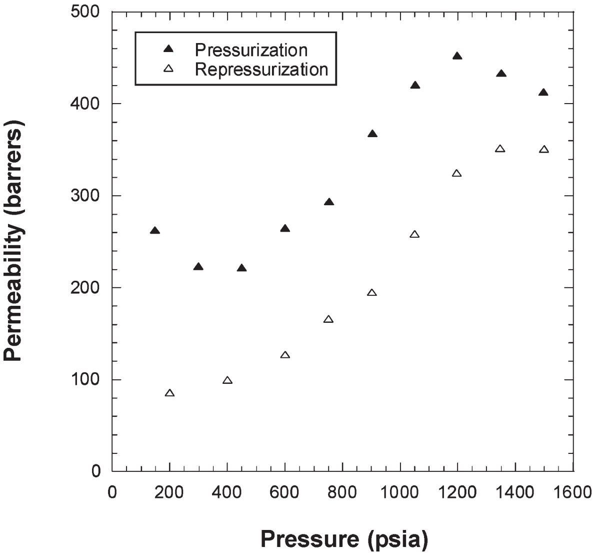


Figure 5. Comparison of pressurization responses prior to and after $scCO_2$ conditioning on 6FDA-DAM:DABA (2:1).

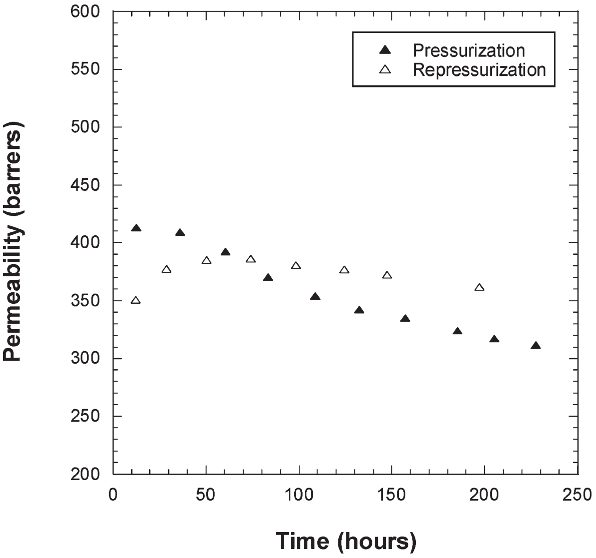


Figure 6. Time-based permeation response at 1500 psia for 6FDA-DAM:DABA (2:1).

CO_2 permeability (Table 1). As shown in Figure 4, the CO_2 permeability for 6FDA-DAM:DABA (2:1) also decreases in the supercritical region, thus confirming the response observed with the 6FDA-DAM polymer; however, this decline occurs at a higher pressure of 1200 psi. The 6FDA-DAM polymer has a higher CO_2 sorption capacity than 6FDA-DAM:DABA (2:1); therefore, the observed higher pressure before the permeability decline in 6FDA-DAM:DABA (2:1) suggests there is some threshold capacity for CO_2 for which this structural reorganization can occur.[23]

Once at 1500 psi, the permeability decreases 24% as it approaches a steady-state value between 250 and 300 barrers. As with the 6FDA-DAM polymer, the permeabilities upon initial depressurization remain lower than those during pressurization; however, there is a pressure range between about 150 and 550 psi where the depressurization permeabilities rise above those of the pressurization cycle. The first pressurization cycle exhibits a typical dual-mode response at low pressures and when extrapolated to 60 psi reveals the conditioned polymer to have a lower CO_2 permeability than the unconditioned polymer when completely depressurized. Therefore, the 6FDA-DAM:DABA (2:1) polymer exhibits the same response, just to a lesser degree, as the 6FDA-DAM polymer upon depressurization. This less drastic response is most likely a result of the 6FDA-DAM:DABA (2:1) polymer containing less intrinsic free volume than 6FDA-DAM and also undergoing more aggressive annealing conditions.

Once depressurized, the 6FDA-DAM:DABA (2:1) polymer was probed with a 50/50 CO_2/CH_4 gas mixture to determine how $scCO_2$ conditioning affects the separating efficiency of the membrane. These results will be discussed in section 3.1.2. After the mixed gas testing, the membrane was placed back into the high-pressure permeation system for repressurization to 1500 psi CO_2. Figure 5 presents a comparison of CO_2 permeability upon pressurization and repressurization in the 6FDA-DAM:DABA (2:1) polymer. As with 6FDA-DAM, the permeability upon repressurization is greatly reduced when compared to the initial pressurization cycle. However, the repressurization curve reveals the plasticization pressure has been greatly reduced as seen by the upswing in permeability at the onset of the repressurization curve. The structural rearrangement is again observed upon repressurization, although to a lesser extent than the initial pressurization. Figure 6 illustrates this response by comparing the CO_2 permeability response versus conditioning time at 1500 psi during pressurization and repressurization. Because the polymer is in a higher free volume state during the initial pressurization, the CO_2 permeability decays substantially over 10 days. However, during repressurization, the film begins the conditioning period in a much lower free volume state; therefore, the film is swollen slightly before beginning to decay. It is expected that the initial pressurization and repressurization responses would asymptotically approach an identical permeability. A similar response was observed by Berens and Hopfenberg in a polystyrene/hexane system.[24] In this system, preswollen and "as-received" polystyrene powders asymptotically approached an identical sorption capacity over time under hexane conditioning. They attributed this phenomenon as a convergence toward true thermodynamic equilibrium for those specific conditions. Therefore, for both pressurization cycles, as the film is exposed to $scCO_2$ at 1500 psia over long periods of time, the CO_2 permeability appears to approach an ultimate thermodynamic equilibrium for transport regardless of the film history. All of the above responses further confirm the structural reorganization of the polymer to a new pseudoequilibrium state with reduced free volume following $scCO_2$ conditioning.

3.1.2. Mixed Gas. After the 6FDA-DAM:DABA (2:1) polymer was conditioned with $scCO_2$, yet before the repressurization, it was probed with a 50/50 CO_2/CH_4 gas mixture to determine how conditioning affects the separating efficiency of the membrane. Figures 7 and 8 present the mixed gas permeabilities and separation factor for the same membrane prior to and after $scCO_2$ conditioning. The unconditioned film exhibits a typical binary feed permeation response for both CO_2 and CH_4 when nonideal effects are taken into account, i.e., a decrease in the CO_2 permeability with little change in the CH_4 permeability. These effects which include bulk flow and nonideal thermodynamics affect mixed gas permeation and can be detrimental to the overall separation, especially in feeds with large concentrations of both components.[25,26] For this reason the CO_2/CH_4 separation factor decreases with increasing pressure. Consistent with the hypothesis that $scCO_2$ conditioning of the polymer yields a new equilibrium state of reduced capacity, the CO_2 permeability of the conditioned

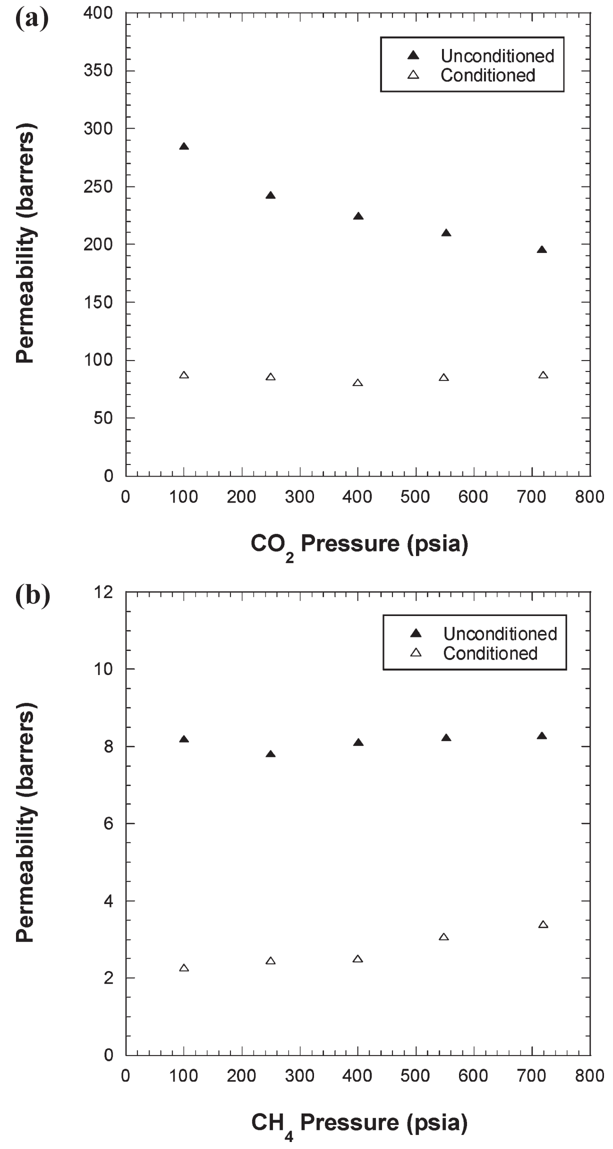


Figure 7. CO_2 and CH_4 permeation isotherms for 50/50 CO_2/CH_4 mixed gas feed testing.

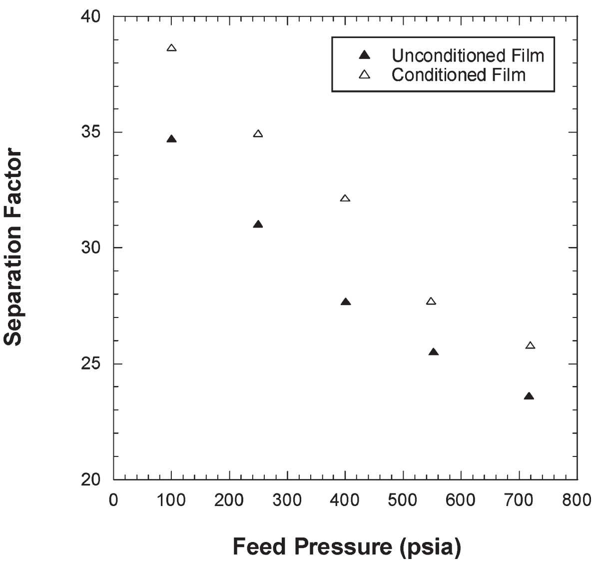


Figure 8. Separation factor for 50/50 CO_2/CH_4 mixed gas feed testing.

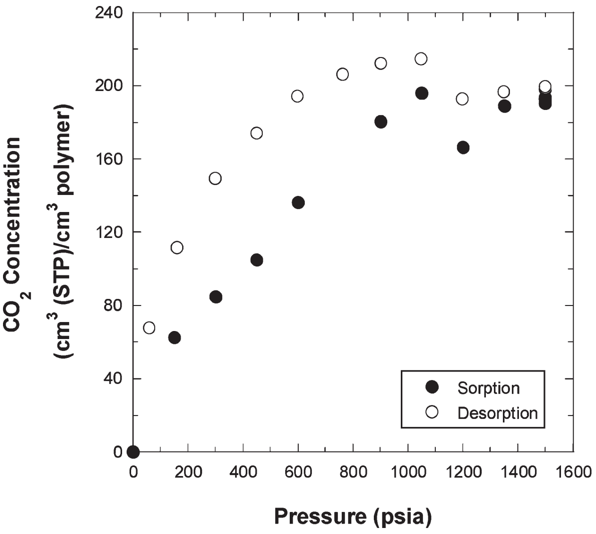


Figure 9. CO_2 sorption isotherm for 6FDA-DAM:DABA (2:1) at 35 °C.

film is greatly reduced and does not exhibit the typical downswing in permeability associated with Langmuir site filling.

For the purposes of natural gas purification, $scCO_2$ conditioning greatly diminishes the productivity of the 6FDA-DAM:DABA (2:1) membrane as observed by the 55% decrease in CO_2 permeability at 720 psia of the 50/50 CO_2/CH_4 mixed gas feed. More significantly, perhaps, is the corresponding 9% increase in the separation factor, which is important for practical applications.

3.2. Gas Sorption Experiments. Gravimetric sorption measurements in $scCO_2$ were measured following the exact protocol used for the CO_2 permeation isotherm in Figure 4 (i.e., 12 h conditioning at each data point, 10 days of conditioning at 1500 psia), and the results are shown in Figure 9. The typical dual mode curvature is not observable in this sorption isotherm because the concave curvature from the pressure axis associated with Langmuir site filling occurs at CO_2 pressures lower than 200 psia. At pressures above 200 psia, the sorption of CO_2 remains fairly linear up to 1050 psia as would be expected with the linear response of Henry's law sorption. Interestingly, at 1200 psia, there is a sharp decrease in the CO_2 concentration before rising to stable levels at 1350 and 1500 psia. This response at 1200 psia was also observed in CO_2 sorption in polystyrene samples at 35 °C.[27] In this case, the authors confirmed the repeatability of the data point and provided a few possible explanations which revolved around the uncertainty of the measurement due to sensitivity of the CO_2 density in this region.

At pressures above 1200 psi, the CO_2 concentration deviates from the linear trend between 150 and 1050 psi, indicating that some structural rearrangement is occurring. However, unlike the CO_2 permeation isotherm which shows a dramatic decrease in CO_2 permeability over the 10 day conditioning period at 1500 psia, the CO_2 sorption isotherm indicates a slight increase in CO_2 concentration over the same time period. Furthermore, upon desorption, a typical hysteresis is observed as the desorption curve lies above the sorption curve. Again, there is a significant deviation that occurs at 1200 psia during desorption. Although a slight rearrangement occurs in the $scCO_2$ region, it appears to occur to a lesser extent than during gas permeation experiments.

Low-pressure CO_2 sorption isotherms were measured before and after the sorption conditioning in $scCO_2$, shown in Figure 9, to determine if the conditioning process reduces

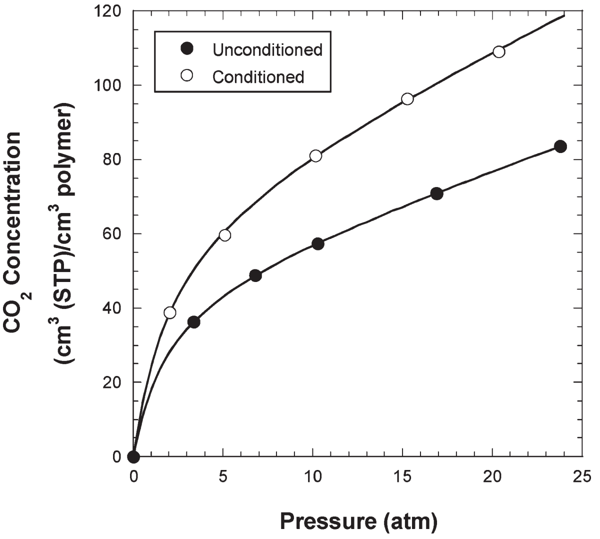


Figure 10. CO_2 sorption isotherms for 6FDA-DAM:DABA (2:1) prior to and after $scCO_2$ conditioning. Lines are the dual mode model fit for each data set.

Table 3. Dual Mode Model Parameters for 6FDA-DAM:DABA (2:1) Prior to and after $scCO_2$ Conditioning at 35 °C

polymer state	k_D (cm^3 STP/(cm^3 atm))	C_H' (cm^3 STP/cm^3)	b (1/atm)
prior to $scCO_2$ conditioning	1.64 ± 0.01	48.1 ± 0.4	0.52 ± 0.01
post $scCO_2$ conditioning	2.28 ± 0.15	69.9 ± 3.6	0.46 ± 0.05

the overall sorption capacity of the polymer. Figure 10 displays these results, and Table 3 displays the dual mode model parameters. The dual mode model parameters were fit using Microcal Origin software. The $scCO_2$ conditioned 6FDA-DAM:DABA (2:1) sorption isotherm clearly has a higher sorption capacity than the unconditioned film. This response is also evident in the dual mode sorption parameters which show a large increase in both k_D and C_H' for the conditioned film. These data confirm that $scCO_2$ conditioning in the sorption chamber does not lead to the structural reorganization of the polymer observed in the permeation isotherm in Figure 4, which leads to a lower free volume polymer structure.

The different structural responses observed through permeation and sorption measurements may therefore be a result of the penetrant concentration gradient present in the polymer. In permeation experiments, the CO_2 concentration decreases through the membrane from the upstream side to the downstream side which is under vacuum, whereas the CO_2 concentration in sorption experiments remains constant through the membrane. This concentration gradient may allow specific polymer configurations of lower energy to be formed and immobilized that might not be possible in a constant concentration CO_2/polymer mixture.

4. Conclusions

The conditioning effects of $scCO_2$ on two 6FDA-based polyimide membranes are examined through gas permeation and gravimetric sorption. At pressures above the supercritical point, the membranes experience a decline in gas permeation, suggesting a structural reorganization of the polymer matrix to a thermodynamically more stable state. Repressurization of the membrane with CO_2 confirms the new pseudoequilibrium state as the CO_2 permeability remains depressed compared to the initial pressurization. After $scCO_2$ conditioning, one of the membranes is probed with a 50/50 CH_4/CO_2 mixed gas feed. The overall productivity of the conditioned membrane decreases with a corresponding increase in the efficiency of the separation as compared to the unconditioned membrane. Corresponding $scCO_2$ sorption experiments indicate a more subdued structural rearrangement of the polymer; however, there is a gradient of the penetrant through the polymer during permeation which is not present during sorption.

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