CO₂/CH₄ Pure- and Mixed-Gas Dilution and Sorption in Thin (~500 nm) and Ultra-Thin (~50 nm) Polymers of Intrinsic Microporosity

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ABSTRACT

In this work, we present i) the dilation and refractive index variation associated with changes in film density and ii) gas uptake of pure CO₂ and CH₄, as well as their equimolar mixture in thin films of two polymers of intrinsic microporosity (PIMs), i.e. PIM-1 and poly(trimethylsilyl)propyne (PTMSP). A conventional low-free-volume glassy polymer, cellulose triacetate (CTA), was also investigated as reference material. All experiments were performed with ~50 and ~500 nm thick films up to partial pressures of 25 bar using in-situ interference-enhanced spectroscopic ellipsometry. In all cases, film thickness reduction promoted the collapse of the frozen-in free volume. Particularly for thin PIM-1 and PTMSP films, the CO₂ and CH₄ pure-gas uptakes were generally lower than in bulk samples. In the most extreme case of the ultra-thin ~50 nm PTMSP film, we could detect a strikingly similar qualitative behavior to the penetrant partial molar volume and dilation in rubbery polymers. Remarkably, in PIM-1 the collapse of the frozen-in free volume seemed to be opposed by its ultramicropores ($< 7 \text{ \AA}$), which was not the case in PTMSP with larger micropores ($> 10 \text{ \AA}$). In mixed-gas experiments, the refractive index response of all investigated films closely followed the trend observed during CO₂ pure-gas sorption. In both thickness ranges and throughout the entire pressure range, the samples dilated less in the multi-component environment than in the corresponding ideal pure-gas conditions. We found this phenomenon consistent with the pure- and mixed-gas uptake behavior of PIM-1 and PTMSP bulk films reported in the literature.

INTRODUCTION

Membrane-based gas separation processes play an increasingly important role in industrial applications because of their potentially lower energy requirements than conventional methods such as distillation, adsorption, or absorption.¹ Currently, only a limited number of polymers have been utilized as membrane materials in commercial gas- and vapor separation systems.^{2,3} These include low-free-volume glassy polymers such as cellulose triacetate (CTA), polysulfone (PSF), polyimides (P84, Matrimid), or poly(phenylene oxide) (PPO), as well as rubbery polymers, e.g., polydimethylsiloxane (PDMS) or polyether-polyamide block copolymers (PEBAX®). Despite their commercial availability, many membrane polymers possess suboptimal combinations of permeability and selectivity in comparison to some of the more recently developed materials, such as polymers of intrinsic microporosity (PIMs).

In PIMs, large internal microporosity results from severely hindered chain packing due to the presence of rigid, sterically hindered main chain contortion sites and/or bulky side-chain substitutions. These characteristics of glassy PIMs are responsible for their exceptionally high fractional free volumes (FFV), which result in high gas sorption uptakes and high gas permeabilities.^{4,5} Because PIMs exhibit one to three orders of magnitude higher permeabilities than conventional low-free-volume glassy polymers combined with moderate- to high gas pair selectivities, finely tuned PIMs redefined the state-of-the-art of several relevant gas pair separations, such as O₂/N₂, H₂/N₂, H₂/CH₄, and CO₂/CH₄.^{6,7} Even though glassy in nature, PIMs are often solubility-selective (e.g., reverse selective), and in gas (or vapor) mixtures the larger and more soluble molecule may permeate faster while simultaneously suppressing the permeation of the other components.^{8–10} Such mixed-gas sorption and especially the corresponding volume expansion (swelling) have so far remained largely unexplored experimentally.

The gas permeation properties of PIMs are generally analyzed employing bulk samples (*i.e.*, freestanding, isotropic dense films of thickness $> 10\ \mu\text{m}$). However, industrial separations require the fabrication of high-performance integrally-skinned asymmetric or thin-film composite flat-sheet or hollow fiber membranes that generally have selective layer thicknesses significantly less than $1\ \mu\text{m}$. The transformation of bulk films into thin films poses challenges such as large scale production of *defect-free* membranes. In addition, thin polymer films may behave differently than in bulk because of accelerated physical aging or nanoconfinement effects (*i.e.*, forcing the polymer to assume conformations far from equilibrium, for example, as an ultra-thin film with a thickness comparable to its radius of gyration). These phenomena are increasingly well-documented in the literature^{11–17} and alter the physical properties of bulk polymer materials (*e.g.*, density, glass transition temperature), as well as their molecular separation properties^{18–20}, particularly when their thickness is reduced to the submicron scale.

To aid the development of thin-film membrane systems, it is vital to study the sorption, diffusion, and permeation behavior of thin ($< 1\ \mu\text{m}$) films under high-pressure pure-^{21–23} and multicomponent²⁴ penetrants. For example, Tiwari et al.²³ recently investigated CO₂ sorption in $\sim 125\ \text{nm}$ PIM-1 films using in-situ spectroscopic ellipsometry and detected reductions in gas solubility with aging. Our earlier study on pure CO₂ sorption in several thin PIM films in the thickness range of $7 - 128\ \text{nm}$ revealed pronounced thickness dependence of the dilation/sorption behavior.²² The thinnest film of $\sim 7\ \text{nm}$ swelled significantly more than the thicker films. Films thicker than about $21\ \text{nm}$ displayed dilation quite similar to that of $128\ \text{nm}$ samples. However, significant reductions in microporosity in thinner films below $128\ \text{nm}$ were observed and resulted in a shift of the balance between free volume occupation and polymer matrix dilation. Thinner PIM films showed significantly higher partial CO₂ molar volumes.

In this work, we present the dilation and sorption behavior of relevant thin polymer films for the binary CO₂-CH₄ gas pair, motivated by recent studies that proposed the occurrence of mixture effects in bulk films. For example, the CO₂/CH₄ *solubility selectivity* of the low-free-volume (non-microporous) CTA²⁵ and 6FDA-mPDA polyimide²⁶ as well as PIM bulk film materials^{5,27,28} increased as a result of mixture effects as the pressure was raised. The enhanced solubility selectivity resulted from a larger reduction in the sorption uptake of CH₄ than CO₂ in the mixture environment relative to their values obtained from pure-gas measurements. Interestingly, mixed-gas CO₂/CH₄ sorption in rubbery PDMS rubber followed a qualitatively similar trend to glassy polymer films.²⁹ Using in-situ interference-enhanced spectroscopic ellipsometry, which allows simultaneous observation of thickness and refractive index changes, we investigated high-pressure dilation and sorption of three technologically important glassy polymers, *i.e.*, cellulose triacetate (the most utilized membrane material for natural gas separation), PIM-1 (the archetypal ladder PIM polymer), and PTMSP (the first synthesized PIM). Dilation and gas sorption were tested in thin films of ~50 and ~500 nm for pure CO₂ and CH₄ and a 50:50 molar gas mixture up to 25 bar partial pressure.

EXPERIMENTAL SECTION

Materials and Thin Film Preparation

Cellulose triacetate (CTA, degree of substitution ~ 2.9) and PTMSP were obtained from Eastman (CA-436-80S) and Gelest Inc. (lot number SSP-070-4C-22520), respectively. PIM-1 was prepared in-house as previously described.³⁰

PIM-1, PTMSP and cellulose triacetate thin films were spin-coated on top of 500 nm thermal silicon oxide covered silicon wafers (100) from chloroform, toluene, and dichloromethane,

respectively. Solution concentrations were adjusted in the range of 0.5 – 5 wt.% to obtain film thicknesses of approximately 40-50 nm (denoted as “Thin”) and 450-550 nm (denoted as “Thick”). Before high-pressure experiments, each sample was rejuvenated by swelling in methanol for 5-10 min and subsequently quenched on a hot plate set at 160 °C for up to 10 min. This procedure served to reset the sample history and produced a reliable starting point for the subsequent sorption experiments.

Characterization and Methods

A RC-2 dual compensator ellipsometer (J. A. Woollam Co., Inc.) was used throughout this study in conjunction with a home-built high-pressure cell identical to the one described previously.²² In brief, the high-pressure cell had one cm thick sapphire windows positioned perpendicularly to the probing polarized light beam at an angle of incidence of 70° versus the normal to the horizontal sample plane. The cell body was constructed from stainless steel and pressure tested up to 100 bar. Film thickness and refractive index were extracted using a layered optical model and modeled using a Cauchy-type parametrization ($n(\lambda) = A + B/\lambda^2$) in a wavelength range of 500 – 1000 nm where all polymer films could be considered transparent. The refractive index of the high-pressure gases was always included in the analysis, and the data for CO₂³¹ and CH₄³² were taken from the literature. For the equimolar CO₂-CH₄ (50:50 molar) gas mixture, the refractive index was calculated as an arithmetic average of the refractive index of pure components for a given total pressure. A slight pressure-induced birefringence effect of the windows in the form of delta-offset was fitted together with data. The thick ~500 nm silicon oxide substrates served to provide interference enhancement effect to improve the accuracy of data modeling, in particular for the “Thin”, sub-50 nm films. This effect has been thoroughly described earlier together with more details of the optical modeling.²²

All high-pressure ellipsometry experiments were performed at a temperature of 35 °C, which was controlled within 1-2 °C by a silicone-coated, high voltage resistive heating element coupled with a 5 kW PID-controlled heater. After stabilization under vacuum was completed (changes in the model-obtained film refractive index $< 10^{-4} \text{ h}^{-1}$), which took about 0.5 to 2 h, high-pressure gas was charged into the cell in a stepwise manner. The signal was recorded for 10-15 min at each pressure step before moving to another set point. Average data from the last 1-2 min of each step were used to plot sorption isotherms. For pure CO₂ and CH₄, the maximum pressure was 25 bar, whereas the total pressure was set up to 50 bar for the equimolar CO₂-CH₄ mixture.

For pure components, the concentration of the dissolved penetrant was estimated using the well-known Clausius-Mossotti approach, as extensively described in the literature.^{22,23,33,34} This approach combines film thickness and refractive index changes to calculate dissolved penetrant concentration. Briefly, the refractive index of component 1 is related to its molar refraction (R_1), molecular weight ($M_{w,1}$), and mass density (ρ_1) through:

$$\frac{n_1^2-1}{n_1^2+2} = \frac{R_1}{M_{w,1}} \cdot \rho_1 = q_1 \cdot \rho_1 \quad \text{eq. 1}$$

The ratio of $R_1/M_{w,1}$ is constant for a given substance and is denoted q_1 . In a mixture, the resulting refractive index n_{mix} was calculated from additive $q \cdot C$ contributions of all components:

$$\frac{n_{\text{mix}}^2-1}{n_{\text{mix}}^2+2} = q_1 \cdot C_1 + q_2 \cdot C_2 \quad \text{eq.2}$$

where C (g cm^{-3}) is the concentration in a film of each of the mixture components. The concentration of the polymer in the film was calculated from its dilation (represented by h_{swollen}) versus thickness in vacuum (h_{vacuum}):

$$C_{\text{polym.}} = \rho_{\text{polym.}} \cdot \frac{h_{\text{vacuum}}}{h_{\text{swollen}}} \quad \text{eq. 3}$$

The densities of the polymers were taken from bulk sample values (**Table 1**), and for the gaseous components the following data were used (based on the NIST database): CO₂ density of 0.95 g cm⁻³ and corresponding $n_{\text{CO}_2} = 1.23$, CH₄ density of 0.01723 g cm⁻³ and corresponding n_{CH_4} of 1.0106. This resulted in constants $q_{\text{CO}_2} = 0.000153689$ and $q_{\text{CH}_4} = 0.000410286$. We note here that the q constant of CO₂ is approximately three times lower than for CH₄, mostly as a result of ~2.8 times higher CO₂ molecular weight. Refractive indices of high-pressure gaseous CO₂ and CH₄ are, in fact, quite similar; for example, at 10 bar $n_{\text{CO}_2} = 1.003994$, whereas $n_{\text{CH}_4} = 1.003734$ (as interpolated using literature data for CO₂³¹ and CH₄³²).

Dilation or swelling is defined as $100\% \cdot (h_{\text{swollen}} - h_{\text{vacuum}})/h_{\text{vacuum}}$. Relative refractive index change was calculated in an analogous way as dilation: $100\% \cdot (n_{\text{swollen}} - n_{\text{vacuum}})/n_{\text{vacuum}}$. Partial molar volumes for CO₂ and CH₄ dissolved in thin polymer films were calculated from the slope of dilation percentage versus C , as commonly practiced.^{22,33,34} Dissolved penetrant concentration was converted to units cm³ (STP)gas cm⁻³ polymer using the ideal gas law.

For the sake of clarity, error bars in figures containing sorption isotherms were omitted. Benefiting from the very high precision of ellipsometry, the numerical relative standard deviation for values used to calculate the sorption isotherms were below about 0.5% for thickness and 0.2% for the refractive index. Systematic errors related to experimental inaccuracies were minimized by a high reproducibility in: (a) sample position within the high-pressure cell, (b) high-pressure cell alignment, symmetry, and positioning on the ellipsometer stage, and (c) experimental sequence. **Table 1** contains some physical properties of the samples used in this study.

Table 1. Film Thicknesses, Refractive Indices, and Bulk Physical Properties of the Polymers Used in this Study

thin-film sample	polymer chemical name	film thickness range [nm]	film refractive index at vacuum [-]	bulk density [g cm ⁻³]	BET surface area [m ² g ⁻¹]
CA ^{Thick}	Cellulose triacetate ^a	507-519	1.471	1.21	-
CA ^{Thin}		38-43	1.463		
PIM-1 ^{Thick}	PIM-1 ^b	462	1.582	1.14	760-830
PIM-1 ^{Thin}		38	1.593		
PTMSP ^{Thick}	Poly(trimethylsilyl)propyne ^c	497	1.466	0.75	780-949
PTMSP ^{Thin}		50-52	1.542		

^aPolymer (CA-436-80S) obtained from Eastman, density measured measured geometrically.²⁵

^bPolymer derived from bis-catechol 5,5,6,6-tetrahydroxy-3,3,3,3-tetramethyl-1,1-spirobisindane using dibenzodioxane formation; density measured via Archimedes' technique,²⁷ BET surface area reported in refs.^{30,35}

^cPolymer obtained from Gelest Inc., density measured geometrically,^{36,37} and BET surface area reported elsewhere.⁷

RESULTS AND DISCUSSION

In this study, two thickness ranges were investigated, *i.e.*, ~50 nm (“Thin” films) and ~500 nm (“Thick” films). The thinnest samples were chosen to explore the nanoconfinement effects (*i.e.* deviations from bulk behavior) for which the typical onset is below ~100 nm. Nanoconfinement effects may manifest as deviations of glass transition temperature^{38,39} or dilation⁴⁰ in thin films *versus* bulk. The behavior of those ultra-thin films is particularly important for the development of high-permeance gas separation^{41,42} or organic solvent nanofiltration composite membranes.⁴³

The interaction with penetrants induces changes in the thickness and optical properties of polymer films. Sorption-induced expansion of the polymer matrix in the direction perpendicular to the substrate (swelling or dilation) can be observed experimentally with ellipsometry. Because of the confinement to the substrate, thickness increase is identical to volume increase.⁴⁴ Changes in the refractive index indicate changes in the film optical density — which in glassy amorphous materials directly reflects the balance between the frozen-in excess fractional free volume (EFFV) occupation or matrix dilation.^{21,22} Note that in PIM materials, the EFFV is interpreted as microporosity.

For polymers with large EFFV (or microporosity) that can be occupied by sorbing penetrants, the relative refractive index change associated with penetrant sorption is positive. This is a consequence of an increase of the film refractive index as a result of the occupation of the available EFFV by the sorbing penetrant whose refractive index is larger than that of vacuum (*i.e.*, 1.000). This mode of sorption is traditionally denoted as “hole-filling” adsorption process or *Langmuir’s type* sorption. Conversely, when the polymer matrix dilation is predominant (*i.e.*, *Henry’s type* sorption or mixing on a molecular level), the relative refractive index should decrease below 0 as a result of the “dilution” of the optical density of the polymer matrix with less optically dense (lower refractive index) penetrants. These phenomena were more thoroughly described earlier.^{21,22,45}

Pure-Gas Dilation and Refractive Index of Cellulose Triacetate

High-pressure dilation, refractive index change, and penetrant concentration data for pure CO₂ and CH₄ in both “Thick” (519 nm) and “Thin” (43 nm) CTA samples are shown in **Figure 1**. For both pure-gas penetrants, the “Thin” CTA sample dilated to a similar extent as the “Thick” one

(**Figure 1a**). For CTA, the changes in the refractive index, shown in **Figure 1b1** and **b2**, are subtle but carry important physical insights. The fact that for both “Thick” and “Thin” CTA films the changes in refractive index stay close to zero means that the hole-filling effect is roughly compensated for by dilation. For both CO₂ “Thick” and “Thin” and CH₄ “Thin” samples, the refractive index change was slightly positive at low pressures and turned negative at higher pressures.. In contrast, the refractive index change of the CTA “Thick” sample remained slightly positive at all pressures during CH₄ sorption. Hence, the EFFV of CTA is available (although very limited) at low pressures and becomes occupied as pressure is raised. The amount of this EFFV was found thickness dependent, and we quantified this effect using the isotherms reported in **Figure 1c** to retrieve the hole-filling related Langmuir’s sorption capacity (C_H') as a measure of the available EFFV (see details in the Supporting Information). Upon thickness reduction from 519 nm to 43 nm, the C_H' value of CO₂ reduced significantly from 6.0 to <4 cm³ (STP) cm⁻³. As a result of this nanoconfinement effect, the CO₂ uptake also decreased (*e.g.*, at 10 bar from 26.2 to 15.9 cm³(STP) cm⁻³). However, overall CO₂ gas uptakes of both “Thick” and “Thin” CTA samples were comparable to the values observed from bulk films^{25,46}. This observation suggests that for CTA it is roughly possible to extrapolate bulk solubility and permeability data to thin films, which in turn may have facilitated the development of commercial, industrial membranes based on CTA. Penetrant sorption data for CH₄ in CTA deviated from bulk data, however, in this case, we suspect experimental errors related with very small changes in both dilation (~1%) and refractive index (~0.25%) (**Figure 1a** and **1b2**) prevent drawing meaningful conclusions about the uptake.

Figure 1. (a) Dilation, (b) refractive index change, and (c) estimated concentration of high-pressure CO₂ and CH₄ for “Thick” (519 nm) and “Thin” (43 nm) CTA films. CH₄ penetrant uptake data (open symbols in (c)) are probably strongly affected by calculation inaccuracy as a result of very small changes (at the limits of experimental sensitivity) both in dilation and refractive index. Previously reported data of pure-gas CO₂ and CH₄ sorption in bulk films are also shown.²⁵

Pure-Gas Dilation and Refractive Index of PIM-1

PIM-1 shows much larger deviations in its response to penetrants upon going from bulk to thin films than CTA. For both pure CO₂ and CH₄, PIM-1 “Thick” and “Thin” films dilated significantly less than PIM-1 bulk film, and the difference was particularly large for CH₄ (**Figure 2a**). Similarly to CTA, not much difference was found in the dilation of the “Thick” and “Thin” PIM-1 films. On the other hand, the discrepancy in the refractive index change (**Figure 2b**) was much larger for PIM-1 than CTA. For CO₂ (**Figure 2b1**), both “Thick” and “Thin” PIM-1 films showed clear maxima in the refractive index change indicating a balance between predominant EFFV filling at lower pressures (where the refractive index rises with pressure) and matrix dilation at higher pressures. On the right side of the local maxima, the film refractive index change decreased with increasing pressures and became smaller than the corresponding value in vacuum (*i.e.*, < 0). This can only occur if penetrant-induced dilation dominates, and the polymer matrix becomes “diluted” with the dissolved penetrant. In the “Thin” PIM-1 film, the maximum of the refractive index

change was almost two times lower than that of the “Thick” sample, thus indicating the existence of a much lower EFFV. The position of the maximum for the “Thin” PIM-1 shifted to lower pressures and peaked at ~4.5 bar as opposed to around ~6 bar for the “Thick” PIM-1. The significance of such a shift in thinner films was previously correlated with lower onsets of matrix dilation and the related enhanced swelling, which could promote plasticization.²¹

The behavior of the “Thick” and “Thin” film refractive indices during pure-gas CH₄ sorption (**Figure 2b2**) was strikingly dissimilar; methane progressively filled the available EFFV in the “Thick” film over the entire pressure range, and the refractive index continued to increase, whereas in the “Thin” film the refractive index immediately decreased below its value in vacuum. Thus, in comparison with the ~500 nm film, the thinner ~50 nm PIM-1 sample could accommodate less CH₄ in its EFFV and its dilation set in much earlier, which is consistent with the slightly enhanced dilation at low pressures (as seen in **Figure 2a**).

This pronounced EFFV reduction in the “Thin” PIM-1 sample diminished the available number of sorption sites for pure CO₂ and CH₄ (**Figure 2c**). A similar effect was previously reported by Tiwari et al.,²³ who observed a ~20% reduction in CO₂ uptake at ~25 bar in PIM-1 thin films resulting from a reduction of free volume due to physical aging. We note that the CO₂ data of Tiwari et al.²³ for a 125 nm PIM-1 film agree very well with our data for the ~500 nm film (**Figure 2c** in green). Consistent with the above discussion, upon going from bulk to “Thick” and then to “Thin” film, a continuous change in the concave shape of sorption isotherms was found for both CO₂ and CH₄. This is consistent with the gradual reduction of the Langmuir’s sorption capacity of PIM-1; in fact, for CO₂, the C_H' value gradually dropped with decreasing thickness in the order: 82.4 (bulk, ~150 μm^{47}) > 63.1 (462 nm) ~ 63.3 (125 nm²³) > 49.8 cm³(STP) cm⁻³ (38 nm) — these data are also reported in **Table S1** and graphically in **Figure S1**. Interestingly, PIM-

1 still preserved significant EFFV even at 38 nm, which is close to the practical fabrication limit of current thin-skinned membranes.

The solubility of methane was much more affected by the thickness reduction than that of CO₂, which suggests that the larger and less condensable CH₄ experienced the nanoconfinement-related changes in the available EFFV more than the smaller and more condensable CO₂. This analysis is also supported by the larger effect of thickness reduction on the CH₄ partial molar volume that is reported in **Table 2**. In fact, because of the significant loss of penetrant-accessible EFFV upon nanoconfinement, CH₄ partial molar volume in a “Thin” PIM-1 film reached very high values typical to the much more condensable CO₂.

Figure 2. (a) Dilation, (b) refractive index change, and (c) estimated concentration of CO₂ and CH₄ for “Thick” (462 nm) and “Thin” (38 nm) PIM-1 films up to 25 bar. Previously reported data^{23,47} of pure CO₂ and CH₄ dilation and uptake in bulk film samples are also shown.

Table 2. CO₂ and CH₄ Partial Molar Volumes (averaged over the 0 – 25 bar pressure range) in CTA, PIM-1, and PTMSP “Thick” and “Thin” films. PDMS Data were Calculated as Average from Literature and are Reported for Comparison^{48–50}.

thin-film sample	CO₂ partial molar volume [cm³ mol⁻¹]	CH₄ partial molar volume [cm³ mol⁻¹]
CA _{Thick}	28	(16)
CA _{Thin}	33	(20)
PIM-1 _{Thick}	22	12
PIM-1 _{Thin}	26	25
PTMSP _{Thick}	~6	-
PTMSP _{Thin}	42	27
PDMS	49	57

Note: values in brackets for CH₄ in CTA are estimates due to enhanced experimental error (at the detection limits of our technique). In PTMSP “Thick”, the progressive physical aging superimposed with CH₄ sorption thereby artificially lowering dilation – in this case, partial molar volume was not calculated.

Pure-Gas Dilation and Refractive Index of PTMSP

By far, the most dramatic nanoconfinement effects were observed in ultra-high free volume glassy PTMSP, which is one of the most permeable polymers ever reported.⁵¹ Note that the internal BET surface area of PTMSP is somewhat close to that reported for PIM-1 (**Table 1**). During our measurements, PTMSP was the only polymer for which the effects of rapid physical aging superimposed with sorptive dilation (resulting in the peculiar dilation isotherms of **Figure 3a**). In particular, up to about 10-15 bar for CO₂ and in the entire explored range for CH₄, each pressure increment induced an initial thickness increase that was immediately followed by continuous film densification as time progressed. An example of raw data for this phenomenon is reported in **Figure S2**. CO₂ uptake extensively accelerated the physical aging process by increasing the matrix

mobility (**Figure 3a**), whereas CH₄ was not able to dilate the “Thick” PTMSP and counteract the ongoing aging, which caused the observed apparent negative dilation.

The refractive index change data of **Figure 3b** clearly indicate that the “Thick” PTMSP indeed accommodated pure CO₂ and CH₄ mostly within its extremely large EFFV. The refractive index change reached an extraordinarily high value of 2.5% (the highest reported among similar studies^{21,22,24}). At the same time, the PTMSP matrix did not dilate nearly as much as PIM-1 (**Figure 3a**), and the resulting penetrant concentration was slightly lower in “Thick” PTMSP than in “Thick” PIM-1. While the CO₂ uptake in the “Thick” PTMSP was somewhat close to the literature values for bulk, CH₄ sorbed to a lower extent. This behavior is similar to that of “Thick” PIM-1 (seen **Figure 3c**) and again suggests that CH₄ could be more affected by the changes in the amount and possibly distribution of EFFV by transition from bulk to thin films.

For CO₂, the calculated C_H' value for our “Thick” 497 nm PTMSP film was 55.3 cm³ (STP) cm⁻³, which is slightly lower than the range of values estimated (see details in the Supporting Information) from digitalized data previously reported for fresh (unaged) bulk-films (*i.e.*, we obtained data of C_H' in the range 63-77 cm³ (STP) cm⁻³ from data reported elsewhere^{27,52,53}). For an aged PTMSP bulk-film,⁵⁴ we derived a much lower C_H' value of ~14 cm³ (STP) cm⁻³, reflecting the pronounced tendency of this material to quickly lose its EFFV during physical aging (estimation procedure and data are given in **Table S1**). For methane sorption in PTMSP, the C_H' showed a very similar trend, with 88.4 for fresh and 23.2 cm³ (STP) cm⁻³ for aged samples (as determined previously in the literature⁵⁴).

Figure 3. (a) Dilation, (b) refractive index change and (c) estimated concentration in high-pressure CO₂ and CH₄ for “thick” (497 nm) PTMSP film. Previously reported data of pure-gas CH₄ dilation⁵⁵ and CO₂-CH₄ sorption²⁷ are also shown.

The extraordinarily strong tendency of PTMSP to collapse its EFFV was further exemplified by the behavior of the “Thin” sample. In this case, in fact, the EFFV was effectively almost absent, and both CO₂ and CH₄ were forced to dissolve directly in its dense matrix (Henry’s type sorption). As a result, we observed an enhanced polymer matrix dilation (**Figure 4a**) and an immediate drop below zero of the refractive index change curve (**Figure 4b**). The estimated gas uptakes were also dramatically lower than those in bulk film samples as can be observed in **Figure 4c** (at 10 bar, for example, in comparison with the bulk film, the gas uptake in the “Thin” PTMSP was 4.7 and 1.5 times lower, respectively for CO₂ and CH₄).

Remarkably for both pure penetrants, the almost complete loss of EFFV observed for the ~50 nm PTMSP film followed *qualitatively* the sorption behavior normally observed in rubbers. In fact, the trend of the refractive index was very similar to data recorded during high-pressure CO₂ sorption²⁹ and refractive index in PDMS.³³ Furthermore, the penetrant molar volume of CO₂ for the “Thin” PTMSP reached values close to those typical of rubbery PDMS (**Table 2**). This

irregular behavior of ultra-thin PTMSP films corroborates previous findings that discussed its peculiar dilation behavior (atypical for a glassy polymer) in liquid organic solvents.⁵⁶

Figure 4. (a) Dilation, (b) refractive index change, and (c) estimated concentration in high-pressure CO₂ and CH₄ for “thin” (50 nm) PTMSP film. Previously reported data of pure CH₄ dilation⁵⁵ and sorption²⁷ are also shown. Estimated data for refractive index change and uptake in PDMS were taken from Sirard et al.³³

Microporosity Distribution and CO₂ Sorption Uptake

CTA is the only low EFFV polymer used in this study and its bulk- or “Thick” film Langmuir’s sorption capacities for CO₂ were quite limited (**Figure 1**), *i.e.*, lower than 8.5 cm³(STP) cm⁻³ (see details in Supporting Information). Even though upon confinement to a 43 nm film, the C_H ’ value appeared dropping significantly (see **Table S1**), the relative contribution of the Langmuir’s mode sorption to its overall gas solubility was not large. As a result, thickness reduction did not impact CTA overall gas uptake to a significant extent (**Figure 1**).

On the other hand, PIM-1 and PTMSP are *microporous* polymers (**Figure 5a**). The porosity of PTMSP is predominantly composed of large micropores (>10 Å), whereas PIM-1 contains both micropores and ultramicropores (*i.e.*, micropores <7 Å), **Figure 5a**).⁷ This difference in microporosity distribution seems to influence the sorption and dilation behavior of PIM-1 and PTMSP upon thickness reduction. **Figure 5a** suggests that the presence of ultramicropores in PIM-

1 (*i.e.*, $<7 \text{ \AA}$) to some extent *prevents* the negative effect of thickness reduction on solubility. In fact, despite these two glassy polymers having similar internal surface areas (as seen in **Table 1**), when sample thickness was reduced from ~ 500 to ~ 50 nm, CO₂ solubility reduced by 15% in PIM-1 and 80% and PTMSP, respectively at 10 bar (**Figure 5b**).

Our analysis is supported by previous works showing that CO₂ solubility in bulk-film PIM-1 appears somehow insensitive to aging⁵⁷ whereas the microporosity of PTMSP in bulk films collapses significantly during physical aging, *e.g.*, at 10 bar the CO₂ solubility in PTMSP fresh²⁷ and aged⁵⁴ bulk films was reduced by 48% (not shown in **Figure 5b**). Hence, in comparison with bulk- and “Thick” PTMSP films (**Figure 5b**), the ultra-thin PTMSP film adsorbed dramatically less gas and showed a qualitative trend normally observed in rubbery polymers (exhibiting almost exclusively Henry’s sorption, that is, molecular mixing behavior). A qualitative summary of our findings is shown in **Figure 6**.

Additional evidence that ultramicroporosity might help to reduce the negative effect of physical aging or thickness reduction on gas solubility can be found in our recent studies on ultramicroporous membranes made of a PIM-polyimide precursor and derived carbon molecular sieves. Upon thickness reduction (from $\sim 1 \text{ }\mu\text{m}$ to ~ 200 nm) or aging, these membranes preserved their gas pair permselectivity (mainly defined by the ultramicropores, $< 7 \text{ \AA}$) but lost a large proportion of their permeability (primarily defined by the larger micropores, $\sim 7 - 20 \text{ \AA}$).^{58,59}

Figure 5. (a) NLDFT-analyzed pore-size distributions assuming carbon slit-pore geometry for PIM-1 and PTMSP (data digitalized from literature⁶⁰). (b) Comparison of CO₂ solubility in CTA, PIM-1, and PTMPS at various film sample thicknesses and 35 °C — literature uptake data were digitalized from refs.^{25,27,47}

Figure 6. Summary of the effect of tenfold reduction of polymer film thicknesses on the collapse of the fractional free volume (FFV).

Mixture effects on pure- and mixed-gas CO₂ and CH₄ refractive index and dilation

In this part, we compare the refractive index changes and dilation recorded during pure- and mixed- CO₂ and CH₄ gas sorption experiments in “Thick” and “Thin” films of CTA, PIM-1, and PTMSP. Unfortunately, individual penetrant uptakes for mixed-gas experiments could not be calculated because of the fundamental limitations of the employed technique.²⁴ **Figure 7** shows mixed-gas refractive index changes of “Thick” and “Thin” films of CTA, PIM-1, and PTMSP exposed to 50:50 CO₂-CH₄ molar mixtures. Upon comparison with the corresponding pure-gas data (**Figure 1b, 2b, 3b, and 4b**), we found that the mixed-gas refractive index behavior was heavily dominated by CO₂. In virtually all cases, the mixed-gas refractive index response strongly resembled that seen during pure CO₂ experiments; this result agrees with our recent mixed-gas sorption studies^{25,26,61} where the solubility of CO₂ appeared essentially unaffected by the co-sorption of CH₄. In **Figure 7**, some small differences could be identified: for example, the refractive index change during mixed-gas uptake in the “Thin” PIM-1 (**Figure 7b**) showed a weaker maximum and dropped below zero faster than in the case of pure CO₂ (**Figure 2b1**). This effect could probably be a result of additional CH₄ sorption, which induced stronger polymer matrix dilation, thereby reducing the refractive index faster than in the pure-gas case.

Figure 7. Refractive index change vs. CO₂ partial pressure in mixed-gas conditions (50:50 molar concentration) for (a) CTA, (b) PIM-1 and (c) PTMSP. Blue and red symbols and lines represent “Thick” and “Thin” samples, respectively.

Figure 8. Comparison between PIM-1 and PTMSP thin films dilation (upper panel) and bulk films uptake (lower panel) of 50:50 (molar) CO₂/CH₄ mixtures; data for bulk from refs.^{27,62}

Finally, **Figure 8** compares mixed-gas (Real mix.) and summed contributions of individual pure CO₂ and pure CH₄ data (Ideal mix.) from our ellipsometry measurements (upper panel) with available literature data for bulk film uptakes (lower panel). The remaining data for CTA (“Thick” and “Thin”) as well as “Thick” for both PIM-1 and PTMSP were qualitatively similar and are shown in **Figure S3**. The ellipsometry-derived mixed-gas dilation for thin films was, in all cases, consistently lower than the combined pure-gas contributions, which qualitatively resembles the results reported earlier for bulk.^{27,62} Thus, the non-idealities governing the mixed-gas uptake in bulk, which possibly originate from competitive sorption or attractive interactions involving the penetrants, are also manifested in films as thin as ~50 nm.

CONCLUSIONS

In this work, dilation and refractive index data of CO₂-CH₄ pure- and mixed-gas (50:50 molar) sorption in ~500 and ~50 nm thin CTA, PIM-1, and PTMSP films were discussed. Gas uptake and molar volumes were estimated using the well-known Clausius-Mossotti formula by combining the film dilation with the change of its refractive index data.

In the conventional low-free-volume cellulose triacetate (CTA), we found that film thickness reduction (down to ~50 nm) did not result in significant changes in the pure CO₂ and CH₄ dilation or uptake in comparison to the corresponding bulk film. However, for the high-free-volume, microporous PIM-1, a clear effect of film thickness reduction on the contraction of its excess fractional free volume (EFFV) was detected. As a result, the gas solubility was strongly affected by film thickness with thinner films sorbing much less gas than the bulk PIM-1 film. This effect was particularly strong for CH₄ in comparison to CO₂. A clear and continuous reduction in the hole-filling related Langmuir’s sorption capacity of PIM-1 (40% using CO₂ as a probe) was detected going from bulk to ultra-thin (~50 nm) film thickness.

For PTMSP, nanoconfinement led to a virtually complete collapse of its EFFV, and the thinnest ~50 nm film showed a similar qualitative trend with rubbery polymers like PDMS in terms of swelling and molar volume during both pure CO₂ and CH₄ sorption. This peculiar behavior of PTMSP was related to the absence of *harder to collapse* ultramicropores (<7 Å), which were instead widely available in PIM-1.

The pronounced collapse of the available EFFV observed in our thin films may explain the much earlier than in bulk films onset of penetrant-induced swelling, rapid increase in permeability with pressure, and much larger sorption-desorption hysteresis, which have all been observed in earlier studies in glassy thin films^{17,21,63}.

In mixed-gas experiments, for all studied materials, gas sorption was strongly influenced by the presence of carbon dioxide (in agreement with our previous studies^{26,29,61}). Previously reported CO₂-CH₄ mixed-gas total uptakes in PTMSP and PIM-1 bulk-film polymers^{27,62} were found consistently lower than in the corresponding ideal cases. Our sorptive dilation data in films as thin as ~50 nm reflected this behavior as well.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information contains dual-mode sorption model data fitting procedure, thickness and refractive index in PTMSP “Thick” vs. time, pure- and mixed-gas total dilation data of all tested thin-films, description of the optical models used for ellipsometry data fitting, and experimental data listed in a table format.

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Notes

The authors declare no competing financial interest.

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