High Pressure CO₂ Sorption in Polymers of Intrinsic Microporosity under Ultra-Thin Film Confinement

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High pressure sorption, polymers of intrinsic microporosity, in-situ ellipsometry, nano-confinement, gas sorption, gas separations

Abstract

Ultra-thin microporous polymer films are pertinent to the development and further spread of nanotechnology with very promising potential applications in molecular separations, sensors, catalysis or batteries. Here, we report high pressure CO₂ sorption in ultra-thin films of several chemically different polymers of intrinsic microporosity (PIMs), including the prototypical PIM-1. Films with thicknesses down to 7 nm were studied using interference-enhanced in-situ spectroscopic ellipsometry. It was found that all PIMs swell much more than non-microporous polystyrene and other high performance glassy polymers reported previously. Furthermore, chemical modifications of the parent PIM-1 strongly affected the

swelling magnitude. By investigating the behavior of the relative refractive index, n_{rel} , it was possible to study the interplay between micropores filling and matrix expansion. Remarkably, all studied PIMs showed a maximum in n_{rel} at swelling of 2 - 2.5% indicating a threshold point above which the dissolution in the dense matrix started to dominate over sorption in the micropores. At pressures above 25 bar all PIMs significantly plasticized in compressed CO₂ and for the ones with the highest affinity to the penetrant a liquid-like mixing typical for rubbery polymers was observed. Reduction of film thickness below 100 nm revealed pronounced nano-confinement effects and resulted in a large swelling enhancement and a quick loss of the ultra-rigid character. Based on the partial molar volumes of the dissolved CO₂ the effective reduction of the T_g was estimated to be ~ 200 °C going from 128 nm to 7 nm films.

1. Introduction

Polymers of intrinsic microporosity, PIMs (solution processable or network polymers) are high-performance polymers which, by their nature, pack inefficiently in the solid state and thus produce intrinsically high free volume amorphous structures.^{1,2} The combination of these two features, easy processability with microporosity, is crucial for their potential to revolutionize a variety of fields, including heterogeneous catalysis and industrial membrane technology. In particular for membrane technology, PIMs have shown some of the highest permeability/selectivity combinations among all glassy polymers³ in many relevant separation applications, like CO₂/CH₄⁴, CO₂/N₂^{4,5}, H₂/CH₄⁶, H₂/N₂⁶, O₂/N₂⁷ or, after conversion to carbon molecular sieves by controlled pyrolysis, for C₂H₄-C₂H₈⁸ separations. The outstanding performances of PIMs materials are directly related to their non-planar bulky contortion sites and the rigidity of the polymer chains, which limit thermal motions and provide molecular sieving effect. In addition to their potential for molecular separation and due to their large degree of chemical tunability, PIMs can be tailored to serve as H₂ adsorbents⁹ or proton conductors in batteries.¹⁰

Further advancement of PIMs will require fundamental understanding of their thin- and ultra-thin film-forming properties and response to high activity fluids. For instance, one common strategy to maximize membrane productivity, i.e. permeance, as well as reduction of material cost associated with polymer

synthesis is to form thin-film composites. These are composed of a non-selective, porous, cost effective, mechanically and chemically stable support material (porous polysulfone, polyacrylonitrile, alumina etc.) with a thin selective polymer layer. However, fabrication of highly selective *ultra-thin* films¹¹ may pose many challenges mainly related to avoiding non-selective pinholes or defects. A lesser known challenge arises from the existence of so called nano-confinement effects.^{12–19} These are related to modification of various physicochemical properties of glassy polymers, such as T_g ^{13,17,20,21}, viscosity¹⁹, swellability²² etc., by confining them to ultra-thin (~100 nm or less) films. In particular, very little is known about swelling behavior in response to high pressure, highly soluble gases, like the technologically important CO₂, of ultra-thin glassy films^{23–26} and even less for polymers from the PIMs class.²⁷ Noteworthy, in the prospects of realizing the PIMs full potential efforts have taken place to produce PIMs-based asymmetric hollow fibers with extremely thin skins (well below 100 nm^{28,29}) supported by a highly porous structure made from the same material. In this view of rapidly advancing applications of ultra-thin PIMs we believe that the present study holds high relevance.

Here, we report high-pressure CO₂-induced swelling and sorption in thin PIMs of various chemistries by using in-situ spectroscopic ellipsometry. The materials include the prototypical PIM-1, several other intrinsically microporous polymers as well as non-microporous polystyrene. For the first time, by using the interference enhancement effect provided by depositing the thin PIMs films on top of a thick (~500 nm) thermal oxide instead of directly on a silicon wafer we extend the applicability of the technique well below 100 nm.

2. Experimental Part

2.1. Sample preparation

For the full synthetic routes to obtain the investigated polymers of intrinsic microporosity the reader is referred to literature references.^{5,30–32} In brief, PIM-1 was synthesized by a polycondensation reaction of 5,5',6,6'-tetrahydroxy-3,3,3',3'-tetramethyl-1,1'-spirobisindane and 1,4-dicyanotetrafluorobenzene in basic medium under high-intensity mixing at 155 °C. PIM-6FDA-OH was synthesized by one-step high-

temperature polycondensation reaction of 4,4-(hexafluoroisopropylidene)diphtalic anhydride and 3,3,3',3'-tetramethyl-1,1'-spirobisindane-5,5'-diamino-6,6'-diol. Amidoxime-functionalized PIM-1 was synthesized by post-modification of PIM-1 with hydroxyl amine at 69 °C³². Tröger's base-derived PIM was synthesized in three steps as described in the literature by polymerization of 2,6(7)-diaminotriptycene with five equivalents of dimethoxymethane in trifluoroacetic acid (TFA).³³ The chemical structures and some relevant properties of the polymers are listed in Table 1.

Table 1 Structures and properties of the studied polymers, literature references are given next to polymer names.

Name	Chemical structure	Density (bulk) ρ , g/cm ³	M_w , kg/mol	Polydispersity, -	BET surface area, m ² /g
PIM-1 ^{2,31,34}		1.09	50	~2	830
PIM-6FDA-OH ³¹		1.26	165	1.94	225
Tröger's base PIM ³³		1.14	50	>2	899
Amidoxime PIM-1 ⁵		1.07	115	1.8	480
PS (polystyrene)		1.05	280	>2	-

Thin films were spin-coated on ~ 500 nm thermal oxide-covered silicon wafers at 2000 rpm from tetrahydrofuran (PIM-1 and PIM-6FDA-OH), dimethylacetamide (amidoxime PIM-1), chloroform (Tröger's base PIM) and toluene (PS). Thickness was adjusted by changing the solution concentration in a range of 0.5 - 3% (w/w). Prior to the high pressure experiments all films were rejuvenated by immersing in liquid *n*-hexane for 5 minutes followed by drying for another 5 minutes on a hot plate at 160 °C. As described previously^{34–36}, the rejuvenation procedure helped to re-set the thermal history and produce films with well-defined and reproducible starting properties. Even though the rejuvenation procedure was not necessary for PS, as its $T_g = 100$ °C is easily accessible, it was still performed to assure comparability of the results. For PS the exposure to *n*-hexane was extended to 30 min due to lower mutual affinity of the solvent and the polymer than for the PIMs.

2.2. Optical modeling and high pressure experiments

For all experiments an RC-2 dual compensator spectroscopic ellipsometer (J. A. Woollam Co., Inc.) was used. In spectroscopic ellipsometry, experimentally generated data are fitted to an optical model representing the sample structure.³⁷ Here, the fitted properties included film thicknesses and optical dispersions (related with the refractive index) of the films. A Cauchy-type optical dispersion ($n(\lambda) = A + B / \lambda^2$) was used in a wavelength range 450 – 1000 nm. The Cauchy model was extended by an extinction parameter, k , to account for the onset of light absorption at the UV part of the spectrum. The reported refractive index refers to the value at 632.8 nm light wavelength. The thick, ~500 nm thermal oxide underlying the studied PIM films served to provide an interference enhancement effect which amplified the sensitivity of the technique and extended the range down to 5-7 nm thickness, **Figure 1a**. For a detailed description of this effect the reader is referred to the Supporting Information. In the absence of the thick thermal oxide accurate analysis of films below ~100 nm, especially in a high-pressure medium, would not have been possible. The optical properties of the underlying silicon wafer and the thermal oxide were taken from literature.³⁸ To maximize the accuracy of the analysis prior to the deposition of the thin PIM film each

individual substrate was characterized with respect to the thickness of the thermal oxide on 12 different locations. The typical standard deviation for all 12 spots was ~0.1 nm signifying extremely high uniformity of the used substrates.

For the compressed CO₂ experiments the rejuvenated samples were fixed in the center of a well optically aligned high pressure chamber, **Figure 1b**, thermally stabilized at 30 °C and evacuated for 30 min. Subsequently, the pressure was raised and lowered in steps up to 45 bar with 15-30 minutes dwell time at each pressure to produce sorption and desorption isotherms. The entire sorption-desorption run lasted approximately 8 hours. The optical dispersion of the high pressure CO₂ was taken into account together with a slight correction for the pressure induced birefringence³⁹. Unlike in typical high pressure ellipsometry analyses^{26,40,41}, we have found that the refractive index of the high pressure medium could directly be fitted and agreed very well with literature values.⁴² This surprising effect was related to the interference effect produced by the ~500 nm thermal oxide which apparently amplified the sensitivity of the technique to the properties of the medium as well. More detailed analysis can be found in the Supporting Information. For the PIM-1 film series in a thickness range 7 - 128 nm each experiment was repeated 3 times (including rejuvenation) to provide better statistics. Because the data for the 128 nm PIM-1 films showed very high reproducibility (relative standard deviation ~1.5%) the experiments for the thicker (>100 nm) films of the other PIMs (PIM-6FDA-OH, Tröger's base PIM and amidoxime PIM-1), as well as PS, were performed once.

Figure 1 a) Representation of the sample structure as well as the used ellipsometric optical model; b) schematic of the high-pressure chamber used for the compressed CO₂ experiments. The design of the high-pressure ellipsometry chamber is similar to the one described in the literature.^{26,40,43}

3. Results and Discussion

3.1. Thin PIM films of various chemistries in compressed CO₂

Film swelling data ($100\% \cdot (h_{\text{swollen}} - h_{\text{dry}}) / h_{\text{dry}}$) for >100 nm films at 30 °C in a range 0 - 45 bar CO₂ for all studied polymers are shown in **Figure 2**. We note here that film swelling and refractive index are determined *independently* which is a known advantage of ellipsometry. In all cases a pronounced hysteresis existed between the sorption and desorption runs which is a typical glassy polymer feature related with an inability of the pre-dilated structure to return to its starting physical state on experimental timescales upon desorption of the absorbed gas.^{26,37,39,44} As expected, the two PIMs with by design highest affinity to CO₂, Tröger's base and PIM-6FDA-OH, showed the largest swelling reaching around 15% at 45 bar. For the prototypical PIM-1 and amidoxime PIM-1 swelling is nearly identical. The lowest swelling of only 5% is found for the non-microporous polystyrene. Next to dilation, ellipsometry simultaneously provided valuable information on the changes in film refractive index. The data are plotted as a relative refractive index $n_{\text{rel}} = n_{\text{swollen}} / n_{\text{initial}}$ against swelling in **Figure 3a**. Initially, n_{rel} increased for all materials, even for PS which indicates sorption of the condensed penetrant ("liquid-like" CO₂ with $n \sim 1.23^{40}$, data for the supercritical state) into the micropores, or excess free volume elements with $n_{\text{VOID}} = 1.00$. As a result, a more optically dense structure is produced. Remarkably, all PIMs show maxima at similar swelling of about

2 - 2.5% corresponding to pressures between 3-9 bar, while the non-microporous PS shows only a weak maximum around 0.5% swelling. As the polymers continued to swell in response to increasing CO₂ pressure the n_{rel} began to fall significantly below unity. This effect indicates, that once the micropores are mostly filled the subsequent dissolution proceeded within PIMs dense matrix with an overall reduction of the optical density accompanying the volume expansion. Apparently, the rigid PIMs matrix was able to withstand swelling on the order of 2 – 2.5% before the sorbing gas dissolved within the dense polymer matrix. For non-PIM materials this point occurred clearly at much lower swelling.²⁶

Figure 2 Film swelling as a function of CO₂ pressure for all analyzed polymers, a) PIM-1 compared with PS, b) all other PIMs; Film thicknesses: PIM-1: 128 nm, PS 112 nm, Tröger's base: 105 nm, PIM-6FDA-OH: 132 nm, amidoxime PIM-1: 135 nm. Closed and open symbols denote sorption and desorption runs, respectively.

It is noteworthy that, while n_{rel} maxima for all PIMs occurred at a similar swelling, the point where n_{rel} fell below unity is different for the different PIMs and did not correlate with the order of swelling, as shown in **Figure 2**. By using the Clausius-Mossotti equation it is possible to convert the dilation and refractive index changes into dissolved penetrant concentration.^{39,40,45} The equation relates the refractive index of a substance j , n_j , with the molar refraction, R_j , molecular weight, M_{wj} and mass density, ρ_j . The ratio R_j/M_{wj} is a constant for a given substance and is denoted q_j .

$$\frac{n_j^2 - 1}{n_j^2 + 2} = \frac{R_j}{M_{wj}} \cdot \rho_j = q_j \cdot \rho_j$$

For a mixture the resulting refractive index, n_{mix} , carries the contributions from all components. Specifically, for a mixture of a polymer and CO₂ the mass densities can be substituted with the respective concentrations, C :

$$\frac{n_{\text{mix}}^2 - 1}{n_{\text{mix}}^2 + 2} = q_{\text{CO}_2} \cdot C_{\text{CO}_2} + q_{\text{polym.}} \cdot C_{\text{polym.}}$$

The concentration of a polymer follows from mass conservation:

$$C_{\text{polym.}} = \rho_{\text{polym.}} \cdot \frac{h_{\text{dry}}}{h_{\text{swollen}}}$$

The densities of the polymers were taken from bulk, Table 1, and the density and refractive index of CO₂ were approximated by values 0.95 g/cm³ and 1.23, typical for its critical state (according to Sirard et al.⁴⁰ and Michels et al.⁴²). The mass concentrations of the dissolved CO₂ can be converted to the more commonly used units (cm³ CO₂ (STP) / cm³) by dividing by its molecular weight and using the ideal gas law (STP stands for standard temperature and pressure). The calculated concentrations are plotted in **Figure 3b**. For PS a good agreement with literature³⁹ was found considering the slightly lower sorption temperature in our study, 30 °C, and the resulting slightly larger equilibrium concentration as compared to the ellipsometric study of Horn et al.³⁹ performed at 35 °C. The sorption data for all PIMs, **Figure 3b**, follows the same order as swelling, **Figure 2**, and the concentrations were significantly higher (57 - 80 cm³ CO₂ (STP) / cm³ PIM at 25 bar) than for low excess free volume glassy polymers such as polysulfone (PSF), poly(p-phenylene oxide) (PPO), or Matrimid (22 - 38 cm³ CO₂ (STP) / cm³ polymer at 25 bar). Both Horn et al.³⁹ and Simons et al.⁴⁶ observed that when film swelling is plotted against concentration, **Figure 3c**, to find the apparent molar volume of the penetrant by fitting a straight line through the data an offset close to the graph origin is present. Horn et al.³⁹ suggested that this offset may be related with initially low swelling induced by dissolving CO₂. This argument agrees with our observation of n_{rel} maxima in **Figure 3a**, which indeed

indicates predominance of micropores filling rather than volume dilation in the initial stages of gas dissolution. Therefore, we suggest to differentiate between the initial apparent CO₂ molar volumes at low swelling related predominantly with microporosity filling, $v_{m,fill}$, and the apparent CO₂ molar volumes related with the dissolution and matrix dilation, $v_{m,diss}$. Both values for all polymers are given in **Table 2**. The values associated with microporosity filling are lower than the average for several standard high performance glassy polymers, $\sim 25 \text{ cm}^3/\text{mol}$ ^{39,46}, and are only slightly lower for PIMs than for PS. The dissolution-related apparent molar volumes are as high as $\sim 49 \text{ cm}^3/\text{mol}$ which is strikingly close to liquid molar volumes typical for dissolution of CO₂ in rubbery polymers.⁴⁶ This effect signifies a pronounced transition between the rigid glassy and the significantly plasticized rubbery-like state that occurs for the highest CO₂ sorbing Tröger's base PIM and PIM-6FDA-OH in the studied pressure range of 0 - 45 bar. PIM-1, amidoxime PIM-1 and PS do not approach the same level of plasticization at these pressures with $v_{m,diss}$ reaching only 30.6 - 36.0 cm^3/mol .

Finally, we examined the relationships between the maximum in the relative refractive index (Figure 3a, Y-axis), concentration at 45 bar (Figure 3b, Y-axis) or $v_{m,fill}$ (Table 2) versus the BET surface areas of the four PIMs (Table 1) and provided them in Supporting Information (Figure S6). No clear trends were identified which suggests that indeed, as hinted at the beginning of part 3.1, the affinity of the particular groups to CO₂ (e.g. 6FDA moieties in PIM-6FDA-OH) plays the most significant role in the occupation of the micropores, rather than simply their available amount. If the available amount of the micropores volume was dominant one would expect to find the largest maximum in relative refractive index or $v_{m,fill}$ for the polymers with the largest BET surface areas, which is not the case.

Figure 3 a) Relative refractive index ($n_{swollen}/n_{initial}$) as a function of film swelling; b) concentration of the dissolved CO_2 as a function of pressure; c) film swelling as function of the dissolved CO_2 concentration; Film thicknesses: PIM-1: 128 nm, PS: 112 nm, Tröger's base: 105 nm, PIM-6FDA-OH: 132 nm, amidoxime PIM-1: 135 nm. The $v_{m,fill}$ and $v_{m,diss}$ dashed lines are indications to illustrate the calculations. The actual values for each analyzed polymer are reported in Table 2.

Table 2 Molar volumes of CO_2 associated with microporosity filling, $v_{m,fill}$, and with dissolution in the matrix, $v_{m,diss}$, for all studied polymers of ~ 100 nm film thickness.

Polymer	$v_{m,fill}$ (cm³/mol)	$v_{m,diss}$ (cm³/mol)
PS	15.6	34.7
PIM-1	11.1	36.0
Amidoxime PIM-1	14.4	30.6
PIM-6FDA-OH	9.6	48.8
Tröger's base	13.7	47.8

In his seminal work, Wijmans⁴⁷, examined the relationship between the polymer T_g and the dissolved CO_2 partial molar volume. The relationship is linear, albeit with some scatter, and drops from a value of 53.6 cm³/mol for liquid CO_2 , which coincides with polymer T_g of roughly -170 °C, to approximately 5 cm³/mol for $T_g \sim 450$ °C. Placing our data of $v_{m,fill}$ and $v_{m,diss}$ on the master curve of Wijmans, **Figure 4**, seems to

suggest that the ~ 100 nm PIMs behavior at low pressures (0-6 bar, $v_{m,fill}$) would be typical for polymers with T_g in a range approximately 200 – 300 °C. Considering that for the bulk of the studied PIMs the T_{gs} are not measurable up to 450 °C this would already indicate significant effective plasticization going from bulk to thin films. Data for $v_{m,diss}$ comes close to the rubbery or liquid-like behavior as discussed above.

Figure 4 Relationship between the CO₂ partial molar volume and glass transition temperature (from Wijmans⁴⁷ based on data by Wessling et al.⁴⁸) with the superimposed data measured for ~ 100 nm PIMs. Adapted from Wijmans, J. G. The Role of Permeant Molar Volume in the Solution-Diffusion Model Transport Equations. *J. Memb. Sci.* **2004**, 237 (1–2), 39–50. Copyright 2018 American Chemical Society.

3.2. Ultra-thin (<100 nm) PIM-1 films in compressed CO₂

Using interference enhancement *in-situ* spectroscopic ellipsometry we were able to significantly extend the applicability of the technique for films below 100 nm. Ultra-thin films in this range are particularly important in many emerging nanotechnology areas, with PIMs in particular, owing to their intrinsic microporosity combined with relatively easy solution processability. Approaching thicknesses similar or below the characteristic equilibrium coil length-scale (from several to tens of nm) has long been known to affect the properties of glassy materials by inducing, so called, nano-confinement effects.^{19,49–53} These nano-confinement effects manifest themselves in variations of the glass transition temperature, permeability of small molecules and mechanical properties. Indeed, we observed that much variation exists in the swelling behavior of PIM-1 films in a range 7 - 128 nm, **Figure 5**. We note here, that the estimated radius of gyration

of the used PIM-1 is on the order of 20 nm, meaning that the 21 nm and, particularly, 7 nm films represented a severe confinement likely with a large modification of the equilibrium coil conformation. While the swelling magnitude for the 128 and 57 nm films is similar the shape of the sorption-desorption isotherms indicates that already the 57 nm film shows somewhat less glassy character and the hysteresis is smaller. Reducing the film thickness further leads to a large increase in maximum swelling up to almost 18% for the 7 nm film, which is close to three times higher than for the 128 nm film. We have attempted to study even thinner, ~ 3.5 nm, films for which the interference enhancement still produced acceptable signal. However, partial film dewetting driven by the minimization of the surface energy, as illustrated by atomic force microscopy images in the Supporting Information, prevented such analysis.

Figure 5 Film swelling as a function of CO₂ pressure for PIM-1 films of various thicknesses.

To study the effect of nano-confinement on the solubility within the micropores we have plotted the n_{rel} for all PIM-1 films in **Figure 6a**. Only the thickest 128 nm film showed a typical, distinct maximum around 2.5% swelling. By reducing film thickness the maxima progressively reduce strikingly linearly with film thickness (Supporting Information, Figure S5) and shift to lower swelling. This may be interpreted as a loss of the rigid polymer character and an increased tendency to expand in volume as triggered by sorbing high pressure CO₂ with reducing thickness. Such tendency may be understood by considering that the highly

non-equilibrium ultra-thin film may relax the stress by swelling. Clearly, the structure of the thinner films is not at equilibrium state and apparently has a larger tendency to swell, as shown in **Figure 5**. Concurrently, as observed before^{34,54}, the excessively swelling free surface, whose effect is amplified for the thinnest films may additionally contribute to the significantly larger overall swelling.⁵⁵ This, however, seems true only for the ultra-thin range below 100 nm. Going from bulk to about 100 nm a general trend of reducing CO₂-induced swelling and uptake is observed^{27,56}, **Figure 6b**. This trend was already noticed for Matrimid polyimide by Horn et al.³⁹ A possible explanation is accelerated physical aging for thinner films,⁵⁷ which leads to denser structures able to adsorb less gas. Extracting the initial and final apparent CO₂ molar volumes, **Figure 6c** and **Table 3**, confirms the large differences in the initial response to compressed CO₂ for the ultra-thin PIM-1 films with $v_{m,fill}$ increasing by a factor 2 going from 128 to 7 nm film suggesting more rubbery-like, enhanced swelling behavior under severe confinement. For $v_{m,diss}$ a less apparent trend is seen with only the value for the 7 nm film clearly larger than for thicker films, however, with less certainty due to increased error margins.

Figure 6 a) relative refractive index ($n_{rel} = n_{swollen} / n_{initial}$) as a function of film swelling; b) concentration of the dissolved CO₂ as a function of pressure; data from literature are given for comparison^{27,56}; c) film swelling as function of the dissolved CO₂ concentration.

Table 3 Molar volumes of CO₂ associated with microporosity filling, $v_{m,fill}$, and with dissolution in the matrix, $v_{m,diss}$, for PIM-1 films.

PIM-1 film thickness (nm)	$v_{m,fill}$ (cm ³ /mol)	$v_{m,diss}$ (cm ³ /mol)
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7	22.6	~ 42
21	18.1	35.9
57	15.2	31.4
128	11.1	36.0

The magnitude of the apparent plasticization of the ultra-thin PIM-1 films can be put into context by examining the positions of $v_{m,fill}$ for the ultra-thin PIM-1 films on the master curve of Wijmans (**Figure 7**). Clearly, a shift of approximately 200 °C results from the reduction of film thickness from 128 nm to 7 nm.

Figure 7 Relationship between the CO₂ partial molar volume and glass transition temperature (from Wijmans⁴⁷ based on Wessling et al.⁴⁸) with the superimposed $v_{m,fill}$ data measured for the ultra-thin PIM-1 films. Adapted from Wijmans, J. G. The Role of Permeant Molar Volume in the Solution-Diffusion Model Transport Equations. *J. Memb. Sci.* **2004**, 237 (1–2), 39–50. Copyright 2018 American Chemical Society.

4. Conclusions

High pressure CO₂ swelling and sorption in thin and ultra-thin films of several polymers of intrinsic microporosity (PIMs) and polystyrene (PS) were examined using in-situ high-pressure spectroscopic ellipsometry. An interference enhancement effect provided by a relatively thick (~500 nm) silicon oxide allowed for an unprecedented possibility to study films down to 7 nm. It was found that all PIMs swell much more as compared to a non-microporous PS or other high performance polymers and that the chemical

modifications of the prototypical PIM-1 strongly affect the total gas uptake. PIMs containing high affinity groups, PIM-6FDA-OH and Tröger's base PIM, showed the largest degree of swelling up to 15% at 45 bar and corresponding concentrations of well over 100 cm³ CO₂ (STP) / cm³ PIM. Determination of the relative refractive index, $n_{\text{rel}} = n_{\text{swollen}} / n_{\text{initial}}$, enabled studying an interplay between micropores filling and matrix expansion. All PIMs showed a maximum of n_{rel} at approximately 2 - 2.5% swelling, corresponding to a pressure range 3-9 bar, indicating a transition point where upon further pressure increase the gas is forced to dissolve within the polymer matrix rather than further filling the micropores. The corresponding volume dilation leads to significant plasticization of all PIMs at pressures above 25 bar with the apparent molar volumes of dissolved CO₂ reaching values typical for liquid mixing or sorption in rubbery polymers.

We discovered that reduction of film thickness down to 7 nm for PIM-1 resulted in significant changes of both swelling/sorption behavior, as well as loss in the rigid character of the polymer. Ultra-thin films (< 21 nm) swelled up to three times more than thicker ones (> 57 nm) and displayed up to two times larger initial, microporosity filling associated, apparent CO₂ molar volumes corresponding to an apparent reduction of T_g by about 200 °C. These nanoconfinement effects are suggested to be related to (a) severe modification of the quasi equilibrium coil conformation which when triggered with compressed CO₂ could relax the initial stress by swelling and (b) amplified effect of the excessively swollen free surface for thinner films.

5. Supporting Information

Explanation of sensitivity of the used technique to detect in-situ properties of ultra-thin films, refractive index and atomic force microscopy analysis of the ultra-thin PIM-1 films, dependence of maximum relative refractive index, concentration at 45 bar and $v_{\text{m,fill}}$ on BET surface areas for all PIMs

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