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Mixed-Penetrant Sorption in Ultra-Thin Films of Polymer of Intrinsic Microporosity PIM-1

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Abstract

Mixed penetrant sorption into ultra-thin films of a super-glassy polymer of intrinsic microporosity (PIM-1) was studied for the first time by using interference-enhanced in-situ spectroscopic ellipsometry. PIM-1 swelling and the concurrent changes in its refractive index were determined in ultra-thin (12 - 14 nm) films exposed to pure and mixed penetrants. The penetrants included water, *n*-hexane and ethanol and were chosen based on their significantly different penetrant-penetrant and penetrant-polymer affinities. This allowed studying microporous polymer responses at diverse ternary compositions and revealed effects such as competition for the sorption sites (for water / *n*-hexane or ethanol / *n*-hexane) or enhancement in sorption of typically weakly sorbing water in the presence of more highly sorbing ethanol. The results reveal details of the mutual sorption effects which often complicate comprehension of glassy polymers' behavior in applications such as high-performance membranes, adsorbents or catalysts. Mixed-penetrant effects are typically very challenging to study directly and their understanding is necessary owing to a broadly recognized inadequacy of simple extrapolations from measurements in pure component environment.

1. INTRODUCTION

It has long been a challenge to understand, predict and influence the long term performance of devices where glassy polymers are in contact with penetrants. Being non-equilibrium materials the physical properties of glassy polymers are inherently time-dependent and subject to processes of physical aging (structural densification¹⁻³) or swelling together with related plasticization phenomena.⁴⁻⁶ In particular, in membrane technology glassy polymers fre-

quently constitute semi-permeable interfaces that control molecular transport by utilizing the differences in affinity of various penetrants to the membrane material. According to the solution-diffusion model, transport occurs in three stages in dense polymeric membranes: first the penetrants dissolve in the membrane at high chemical potential, second they diffuse along a concentration gradient and third desorb on the low chemical potential side. All of these processes are strongly affected by the affinity of the penetrants to the membrane material, their effective molar volumes, concentrations and prior sample history. The combined outcomes are usually hard to predict and may be detrimental to the membrane performance. For instance in gas and vapor separations, membrane plasticization, defined as polymer dilation versus pressure, often occurs for highly interacting feed components and leads to deterioration of the ideal membrane selectivity based on pure-component measurements.

Currently, the mutual influence of: (i) multicomponent feed mixture effects on membrane performance, such as competitive sorption,⁷ (ii) matrix compression,⁸ (iii) membrane thickness⁹ or (iv) superimposed impact of components' sorption on chain dynamics,⁴ are difficult to predict or even access experimentally. In particular, the accessibility of the microporous structure of such novel and promising materials as polymers of intrinsic microporosity (PIMs) to mixtures of penetrants as well as the interplay between the matrix swelling and microporosity occupation in ternary (polymer, 2 penetrants) mixtures¹⁰ has yet to be fully explored.

In this work we studied for the first time the dilation (swelling) and change of refractive index (related with matrix expansion and microporosity occupation) of an ultra-thin, highly microporous polymer of intrinsic microporosity (PIM-1) in a presence of pure and mixed vapor penetrants. 12 nm PIM-1 films were prepared atop 500 nm SiO_2/Si wafers

to benefit from interference enhancement effect aiding highly sensitive optical spectroscopic ellipsometry analysis. Infrared spectroscopic ellipsometry was used to study the interaction between the PIM-1 matrix and the penetrants. The penetrants were chosen to reflect a large spectrum in different penetrant-penetrant and polymer-penetrant affinities. For pure components, by combining independent knowledge of PIM-1 thickness and its refractive index, it is possible to study the intricate balance between the micropores occupation and matrix swelling at various vapor activities. We answer the question whether it is possible to identify (a) competition for sorption sites, (b) sorption and dynamics enhancements, and (c) sequence dependence of polymer exposure to a pair of penetrants. All of these questions have great practical relevance in many technologically important processes, such as adsorption or membrane-based gas separation, nanofiltration, and pervaporation.

2. EXPERIMENTAL PART

2.1. Sample Preparation

The PIM-1 polymer was synthesized in a polycondensation reaction as previously described.¹¹ PIM-1 films were made by spin coating the polymer solution in tetrahydrofuran onto 500 nm thermally-grown silicon oxide covered silicon wafers (Si-Mat, Germany) to obtain films of about 12 nm in thickness. All films were solvent-rejuvenated to reset their thermal history. This was done by immersing the films in liquid *n*-hexane for 5 minutes which was sufficient to reach equilibrium,^{6,11} followed by quenching them together with solvent evaporation on a hot plate at 160 °C which was approximately 100 °C above the boiling point of the solvent.

The procedure was found to produce freshly-quenched, essentially solvent-free films with very reproducible refractive index (density) as shown in Supporting Information.

2.2. UV-Vis Spectroscopic Ellipsometry (UVSE)

An RC2-D variable angle spectroscopic ellipsometer (J. A. Woollam Co., Inc.) operating in a wavelength range 193 - 1000 nm was used in all experiments. The optical modelling was done with the commercial software package CompleteEASE 5.21. All substrates were characterized prior to PIM-1 film deposition by performing 5-spot, multi angle of incidence (65, 70 and 70°) fits using known optical constants of thermally grown silicon oxide.¹² Separate characterization of all substrates was found necessary as each individual substrate differed slightly in the thickness of the nominally 500 nm silicon oxide (up to ~ 0.5 nm). All films were modelled as uniform Cauchy-type layers deposited on top of the thicker silicon oxide. The fitted properties of the PIM-1 films included their thickness, refractive index (always quoted at 632.8 nm) and the shape of the optical dispersion in the range from 450 - 1000 nm (B parameter of the Cauchy equation¹³). A small Urbach tail was taken into account by also fitting the extinction coefficient, k .

2.3. Infrared Spectroscopic Ellipsometry (IRSE)

In-situ infrared spectroscopic ellipsometry (IRSE) in liquid environments was performed at room temperature in backside illumination of the IR-transparent silicon wedges using a specially designed flow cell in a custom-built IR ellipsometer attached to a Bruker Vertex 70 spectrometer.¹⁴ All measurements were carried out on freshly rejuvenated, slightly thicker

(approx. 100 nm) films after film equilibration with liquid penetrants. To suppress systematic uncertainties and increase optical contrast and sensitivity, PIM-1 spectra were referenced to spectra of a clean substrate obtained under the same experimental conditions.

Measurements were performed in a non-ATR ellipsometric configuration that allows one to measure both amplitude ratio and phase difference between the out-of-plane and in-plane polarized components. Due to the better signal-to-noise ratio, only the in-plane component (R_s) is shown, which is sufficient to observe and interpret potential vibrational band shifts without the need for optical modeling of $\tan(\Psi)$ and Δ .

3. RESULTS AND DISCUSSION

3.1. Swelling and Refractive Index Changes in PIM-1 Exposed to Single Component Vapors

All films used for UV-Vis ellipsometry experiments were in the 12-14 nm range. This particular thickness range was chosen to assure relatively fast sample equilibration (usually within 1 h) while maintaining high accuracy of the data due to the use of interference-enhancement effect.⁶ Standard UV-Vis spectroscopic ellipsometry is typically used to analyze films deposited directly on native oxide silicon wafers. In such cases the technique is considered to accurately determine film refractive index for films with thicknesses down to about 80-100 nm where at least one full oscillation from thin-film interference falls within the visible range in the ψ and δ spectra. Below that range the accuracy for the refractive index drastically decreases as the ψ and δ spectra become increasingly featureless. The use of the

thick (500 nm) supporting silicon oxide can extend this range to about 5 nm by amplifying the sensitivity towards the properties of the ultra-thin PIM-1 while keeping the substrate surface chemistry equivalent to the native oxide wafer. The effectiveness of this approach was evaluated by performing fit parameter correlations and numerical sensitivity analysis as shown in the Supporting Information. In the absence of the oxide much thicker films (about 100 nm) would have to be used. Given the extremely slow relaxation behavior of PIM-1 this would greatly extend the time necessary for film equilibration with vapors (from 1 to over 24 h) and likely introduce undesired aging effects superimposed on the diffusion and relaxation induced by the penetrants.⁹

Table 1: Properties of the Used Penetrants; Data Taken from Literature¹⁵ (δ) and^{16,17} (d)

Parameter	Water	<i>N</i> -hexane	Ethanol
Dipole moment, D [C·cm]	1.85	0.08	1.69
Hildebrand parameter, δ [MPa ^{0.5}]	48	14.9	26.2
Kinetic diameter, d [Å]	2.7	4.3	4.5

Figure 1 shows the swelling (defined as $SW = 100 \% \cdot [h_{SW} - h_{DRY}]/h_{SW}$, where h is film thickness) and the relative refractive index (n_{SW}/n_{DRY}) for PIM-1 films exposed to vapors of pure water, *n*-hexane and ethanol at activities p/p_0 at 25 °C of 10, 25 and 45 %, respectively. Some relevant properties of the penetrants used in this study are shown in Table 1. In each case PIM-1 swells when exposed to penetrants and the swelling increases with increasing activity. In agreement with our previous work¹¹ *n*-hexane and ethanol swell PIM-1 to a similar extent, while water vapor induces only a small increase in film thickness. The kinetic diameter of water, Table 1, is much smaller than the typical size of the microporous cavity (on the order of 5 Å, as evidenced by positron annihilation lifetime spectroscopy¹⁸) while the

Figure 1: Swelling ($SW = 100 \% \cdot [h_{SW} - h_{DRY}]/h_{SW}$) and relative refractive index (n_{SW}/n_{DRY}) for 12 nm PIM-1 films exposed to pure vapors at various activities. PIM-1 polymer chemical structure is given.

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2
3 molecular sizes of *n*-hexane and ethanol are comparable to the excess free volume holes in
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5 the polymer. Counter-intuitively, however, it is the smallest water that takes the longest to
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7 equilibrate with PIM-1 (over 24 hours). The long timescales, however, are not related to the
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9 penetrant diffusion alone viewed as a simple Fickian process. The long equilibration reflects
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11 the capability of water to induce the slow sorptive relaxations within the rigid polymer
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13 matrix during which the material rearranges to accommodate the penetrant.^{4,19} Judging
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15 from their persistent character these rearrangements exist on multiple length scales and are
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17 not restricted to the nearest environment of the penetrant molecules. On the other hand,
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19 the much larger *n*-hexane and ethanol possess larger affinity to PIM-1 matrix and are able
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21 to swell the material much faster. While *n*-hexane reaches equilibrium within a few minutes,
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23 ethanol requires more time and at the highest vapor pressures the 1 h swelling interval
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25 seems still insufficient to approach equilibrium. The swelling kinetics indicates that the
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27 slightly larger ethanol always diffuses noticeably slower than *n*-hexane. While having similar
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29 affinities (similar final degree of swelling) the larger ethanol seems to induce more stress and
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31 rearrangement pressure onto the rigid PIM-1 network as it penetrates the structure.
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40 While swelling shows an anticipated increasing pattern with increasing activity the rel-
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42 ative refractive index shows a more complicated behavior. This complexity originates from
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44 an interplay between matrix dilation as a result of penetrant sorption and the occupation
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46 of the available micropores by the penetrant molecules.^{10,11} The first process, associated
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48 with matrix dilation, always leads to a decrease of the refractive index as the dense (high
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50 refractive index) polymer becomes optically diluted by the lower refractive index penetrants.
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52 On the other hand, the sorption into the micropores leads to an increase of the overall film
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54 refractive index due to the replacement of voids by the sorbing penetrant. The two processes
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are inseparable and their outcome in terms of the relative changes of the refractive index will depend on the balance between matrix dilation and occupation of microporosity. Dry PIM-1 with refractive index, $n_{DRY} \sim 1.55$, can be thought of as a mixture of dense polymer matrix ($n_M = 1.676^{11}$) with void ($n_V = 1.000$) representing microporosity. Application of the well-known Bruggeman effective medium approximation²⁰ to the dry sample allows calculating the amount of microporosity, expressed as volume fraction ϵ :

$$\epsilon \cdot \frac{n_V^2 - n_{DRY}^2}{n_V^2 + 2n_{DRY}^2} + (1 - \epsilon) \cdot \frac{n_M^2 - n_{DRY}^2}{n_M^2 + 2n_{DRY}^2} = 0 \quad (1)$$

which for all samples varied slightly around the value of $\epsilon = 0.17$ due to slight variations of the dry refractive index after rejuvenation. This value is slightly lower than previously reported (0.25)¹¹ but still well within the expected range for polymers of intrinsic microporosity. The deviation could be related with the small thickness of the films used in this study (12-14 nm) and the related slightly enhanced chain packing of the nano-confined film.

As shown in Figure 1, the matrix dilation induced by water is very limited at each vapor activity and the increase of the refractive index indicates the dominance of the micropore filling, as reported before.²¹ For *n*-hexane at the two lowest vapor pressures, 10 and 25 %, the refractive index stays the same as for the dry film even though the film swells approx. 1.5 and 3.5%, respectively. This is a sign of an approximate balance between refractive index reduction related with the matrix dilation and refractive index increase related with microporosity occupation. At the highest activity of 45% the matrix expansion dominates and leads to a reduction of the swollen refractive index below that of the dry sample (indicated by relative refractive index values, n_{SW}/n_{DRY} , significantly lower than 1). In the case

of ethanol the clear effect of microporosity occupation is visible as an increase of the swollen refractive index at 10% vapor activity was observed. On the other hand, at higher ethanol vapor activities the compensation effect was evident, similar to *n*-hexane at 25 and 45% and the swollen refractive index stayed similar to the dry refractive index. Given also the similar extent of swelling for the two penetrants, one can conclude, that ethanol has a slight preference for sorption in the micropores, whereas *n*-hexane prefers to dissolve in the dense polymer matrix.

Considering the results shown in Figure 1 it can be concluded, that by a simultaneous measurement of film swelling and its refractive index by in-situ UV-Vis spectroscopic ellipsometry it is possible to gain qualitative indication on the interplay between sorption into the dense matrix and sorption into the micropores of the polymer.

3.2. Swelling of PIM-1 Films in Single Liquid Penetrants Studied with Infrared Spectroscopic Ellipsometry (IRSE)

IRSE is a sensitive analytical technique which allows studying chemical composition, hydration states or molecular interactions. For example it, has been used to investigate swelling-deswelling transitions in temperature-responsive brushes, protein adsorption onto such brushes, and the accompanying molecular interactions between solvent and polymer matrix.^{22–24} Particularly in the presence or absence of (specific) polymer-solvent interactions, one usually expects either distinct shifts of characteristic vibrational bands or little to no band shifts, respectively. Here, we have used the technique to study PIM-1-related bands in order to investigate the nature of interactions between pure liquid penetrants and

the swollen PIM-1 films.

Figure 2: IRSE data collected for PIM-1 films swollen with liquid water, ethanol and *n*-hexane, as well as for the dry PIM-1 film. Top graph shows a Kramers-Kronig transform (KKT) of the solution reference measurements and the ratio of swollen PIM-1 reflectance to the respective reference solvent reflectance. The three graphs at the bottom display magnifications of the nitrile vibration, ring mode 1 and ring mode 2 bands (see text).

Because of the lack of a thick silicon oxide layer for interference enhancement thicker ~ 100 nm films deposited on Si wedges were used. IRSE data collected for PIM-1 films swollen with liquid water, ethanol and *n*-hexane, respectively, as well as for the dry PIM-1 film are shown in Figure 2. The R_s graph shows the ratio of swollen PIM-1 *s*-polarized reflectance to the respective reference solvent reflectance. Kramers-Kronig transforms (KKT) of the

latter allow the identification of solvent related bands. The solvent bands point upwards in Rs (e.g., OH stretching of water and ethanol between 3700–3300 cm⁻¹, CH_x stretching for *n*-hexane between 3000–2800 cm⁻¹) and partially overlap with downward-pointing bands associated with PIM-1. Film swelling is related to changes in thin-film interference, which is clearly identified by shifts in the baselines at higher wavenumbers with respect to the dry state. From optical modeling of the swollen polymer films,²³ PIM-1 swelling was estimated to be a few percent. The observed changes agree very well with UV-Vis ellipsometry: PIM-1 hardly swells in water while it swells significantly, and to a similar extent, in ethanol and *n*-hexane. The three separate graphs in Figure 2 are magnifications of characteristic regions associated with PIM-1 nitrile-group vibrations and with two ring modes. The nitrile band is known to be sensitive to, e.g., solvatochromic effects and is frequently used as a reporter mode to indicate strength of solvent–matrix interactions.^{25,26} The two ring modes are complex combination modes that involve in-plane movements (breathing or bending) of PIM-1 cores with COC ether rings. These could be sensitive to effects of matrix dilation as well as to changes in the local dielectric environment when different solvents are present. In all solvent cases, shifts of the three vibrational bands induced by the solvents are very minor suggesting very limited short-distance specific interactions with PIM-1 matrix. The slightly more pronounced shifts in the ring modes for ethanol and *n*-hexane may suggest some longer range interactions related with matrix swelling. However, overall the IRSE results suggest very limited strength of penetrant interactions with the PIM-1 matrix. Thus, the mixing seems to have close to ideal thermodynamic character and is mainly driven by entropic and not energetic effects. The close to ideal character may facilitate theoretical handling of such mixed penetrant systems which is, however, outside of the scope of this work.

3.3. Swelling and Refractive Index Changes in PIM-1 Exposed to Mixed Vapors

To investigate the effects of mixed penetrants, we conducted experiments illustrated in Figures 3, 4 and 5 which show swelling and changes of the refractive indices of ~ 12 nm PIM-1 films exposed at 25 °C first to one vapor type to which subsequently the second vapor type was added with the same activity. For example, in Figure 3a the PIM-1 film was first exposed to 10% p/p_0 of *n*-hexane and, subsequently, 10% p/p_0 of water vapor was added while maintaining 10% p/p_0 of *n*-hexane partial pressure. To analyze the results it is helpful to consider the affinities of all the penetrants to PIM-1 polymer and to each other. The values of dipole moments and Hildebrand solubility parameters listed in Table 1 suggest that even though *n*-hexane forms a homogeneous liquid mixture with ethanol their properties are quite different and the molecules do not interact strongly. Both *n*-hexane and ethanol, however, swell PIM-1 to a similar extent.¹¹ The solubility of water in liquid *n*-hexane is very small (10^{-6} mole fraction²⁷). Water mixes with ethanol in every proportion. Thus, the choice of the penetrants allows comparing ternary mixtures (2 penetrants and PIM-1) with highly dissimilar penetrant-penetrant and penetrant-polymer affinities. The approximate degree of polymer-penetrant and penetrant-penetrant affinities is given in Table 2.

Table 2: Approximate Polymer-Penetrant and Penetrant-Penetrant Affinities

	PIM-1	Water	<i>N</i> -hexane	Ethanol
PIM-1	-	low	high	high
Water	low	-	very low	high
<i>N</i> -hexane	high	very low	-	low
Ethanol	high	high	low	-

For *n*-hexane at the two lowest vapor pressures the compensation effect is visible, as

Figure 3: Swelling and refractive index changes for experiments where PIM-1 was exposed to first *n*-hexane and then water (a, b, c) and first water and then *n*-hexane (d, e, f). While swelling shows a more or less continuous increase with increasing vapor pressures the refractive index does not show this trend. This reflects competition between matrix dilation and occupation of micropores.

discussed earlier, where the refractive index of the swollen matrix stays approximately the same as the index of the dry polymer, Figure 3a and b. Only at the highest vapor pressure, Figure 3c, the matrix expansion effect dominates and the refractive index is reduced. It has to be noted that the swelling in *n*-hexane shown in Figure 3c is slightly higher than previously shown in Figure 1 which we attribute to the extremely non-equilibrium character of PIM-1. The subsequent exposure to water vapor leads to a slight increase of the refractive index, lower however as compared to PIM-1 directly exposed to water, Figure 1d, e and f. This would suggest, that when *n*-hexane comes in contact with PIM-1 it is able to occupy a significant proportion of the micropores and that, in turn, reduces the further water vapor uptake. This is conceivable considering the low mutual affinity of the very hydrophobic *n*-hexane, which now is present inside PIM-1 film, and water. If water first enters PIM-1, Figure 3d, e and f, mostly by filling the available microporosity (large increases in the refractive indices), the subsequent *n*-hexane sorption is now forced to occur predominantly within the dense PIM-1 matrix and not in the water-occupied micropores. This results in the significant swelling of the films together with large reductions of the refractive indices. The reductions in the swollen refractive indices are greater than when only *n*-hexane sorbs into PIM-1 (with the exception of Figure 3d where the compensation effect dominates). This clearly exemplifies the competition for the available sorption sites when the two penetrants have low mutual affinity.

Figure 4 shows similar experiments done with first ethanol and then water vapor. This system is different from the previous one (*n*-hexane / water) where now the penetrants have high mutual affinities but very different affinities to the dense PIM-1 matrix and thus very different matrix solubility characteristics. At the lowest vapor pressure the microporosity

Figure 4: Swelling and refractive index changes for experiments where PIM-1 was exposed to first ethanol and then water (a, b, c) and first water and then ethanol (d, e, f). While swelling shows a more or less continuous increase with increasing vapor pressures the refractive index does not show this trend. This reflects competition between matrix dilation and occupation of micropores.

filling for ethanol is quite significant, Figure 4a, more pronounced than in the case of *n*-hexane, Figure 3a, as discussed before. At higher vapor pressures the dense matrix sorption starts to become more and more visible and first a similar compensation effect is seen as for *n*-hexane (Figure 4b) followed then by a reduction of the swollen index (Figure 4c). However, when water now enters the system the swelling is larger than when water entered the *n*-hexane-preswollen PIM-1. The polymer dynamics also accelerate as seen from an increase in slope of swelling versus time. The extreme case is seen in Figure 4c with a very pronounced acceleration of swelling after water exposure. This behavior, being in stark contrast to Figure 3c, can be understood by considering that the water uptake is facilitated by the presence of a significant amount of ethanol in the polymer. This effect has previously been observed in study of Yushkin et al using the extended hydrostatic weighing.¹⁰ The favorable mutual interaction between the penetrants seems to play a decisive role and drastically alters the sorption behavior. A strong sorption enhancement effect like this could potentially lead to a very significant deterioration of the membrane separation performance. A similar effect is also seen in Figure 4f where ethanol sorbed after water leading also to a significant increase in swelling as a result of favorable interaction with water already present predominantly in PIM-1 micropores. These effects are absent in the low mutual affinity *n*-hexane / water pair.

For the ethanol / *n*-hexane mixture the behavior is slightly more complex. Both penetrants have similar affinity to the polymer but low affinity to each other. From Figure 1 one can deduce, that *n*-hexane will have a slight preference for the hydrophobic dense polymer matrix over sorption into the microporosity. Ethanol shows the opposite behavior with a slight preference to sorb into the micropores. When Figures 5a (first ethanol, then *n*-hexane) and 5d (first *n*-hexane, then ethanol) are compared one can clearly see an asymmetry in the

Figure 5: Swelling and refractive index changes for experiments where PIM-1 was exposed to first ethanol and then *n*-hexane (a, b, c) and first *n*-hexane and then ethanol (d, e, f). While swelling shows a more or less continuous increase with increasing vapor pressures the refractive index does not show this trend. This reflects competition between matrix dilation and occupation of micropores.

final state. When ethanol sorbed first it occupies the micropores to a large extent and the refractive index first rises, Figure 5a. Subsequently *n*-hexane prefers to sorb into the dense matrix to avoid ethanol in the micropores which leads to a decrease of the refractive index and further significant increase in swelling. When *n*-hexane enters PIM-1 first it swells the material and also occupies the microporosity, however, apparently to a slightly lesser extent than ethanol does (evidenced by a less pronounced increase in the refractive index). Evidently some micropores still remain unoccupied because the subsequent ethanol sorption leads to an increase of the refractive index and thus preferential sorption into the voids within PIM-1. At still higher vapor pressures one can see similar effects, where sorption of *n*-hexane always leads to a significant decrease of the refractive index (preferential dense matrix sorption) while ethanol reduces the refractive index of the film to a lesser extent thus showing slight preference to occupy the remaining microporosity if it is available.

4. CONCLUSIONS

We directly studied the mixed penetrant sorption into a super-glassy polymer of intrinsic microporosity (PIM-1). By using interference-enhanced in-situ spectroscopic ellipsometry film swelling and the concurrent changes in its refractive index were studied in ultra-thin (12 - 14 nm) films exposed to pure- and mixed-vapor penetrants. The penetrants included water, *n*-hexane and ethanol and were selected based on their highly dissimilar penetrant-penetrant and penetrant-polymer affinities. This allowed studying the polymer response to binary mixtures with a large variability in strength of the mutual interactions. It was found, that for penetrants with a low mutual affinity (water / *n*-hexane or ethanol / *n*-hexane) there was

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3 a clear competition for sorption in the micropores. For instance, if water first occupies the
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5 PIM-1 micropores the subsequent sorption of *n*-hexane is forced to proceed predominantly
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7 within the dense matrix as if the *n*-hexane avoided water present in the micropores. On
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9 the other hand, for water and ethanol a pronounced sorption enhancement of the typically
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11 weakly sorbing water was found in the presence of the higher sorbing ethanol. Concur-
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13 rently, a substantial acceleration of the slow polymer sorption dynamics occurred. Such a
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15 mutually-enhanced plasticization effect, absent for pure water sorption, could translate into
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17 rapid deterioration of the material's performance when used as a membrane for separation
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19 applications.
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26 Infrared spectroscopic ellipsometry suggested that for sorption of pure penetrants the
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28 strength of specific interactions between the polymer matrix and sorbing penetrants was in
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30 all cases relatively weak and the dissolution has predominantly entropic character suggesting
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32 close to ideal thermodynamic behavior.
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36 While the mixed-penetrant effects are typically very challenging to study directly their
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38 understanding is often necessary due to a broadly found inadequacy of extrapolations from
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40 measurements in pure components. In this study this has been particularly exemplified by
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42 the very significant sequence-dependence of the final state in the penetrant-exposed PIM-
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44 1 films. The sequence-dependence could be traced back to the interplay between various
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46 degrees of preference to occupy sorption sites within micropores or to dissolve within the
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48 dense matrix, as well as to the mutual penetrant affinities.
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Supporting Information Available

Supporting Information contains data on the reproducibility of the film properties following rejuvenation steps and on the sensitivity of the ellipsometry technique to ultra-thin film properties. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Graphical TOC Entry