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J. Phys. Chem. B, **Just Accepted Manuscript** • DOI: 10.1021/acs.jpcb.7b03891 • Publication Date (Web): 22 Jun 2017

Downloaded from <http://pubs.acs.org> on July 9, 2017

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How Do Organic Vapors Swell Ultra-Thin Films of Polymer of Intrinsic Microporosity PIM-1?

Wojciech Ogieglo,[†] Khosorov Rahimi,[†] Sebastian Bernhard Rauer,[†] Bader

Ghanem,[‡] Xiaohua Ma,[‡] Ingo Pinnau,^{*,‡} and Matthias Wessling^{*,†}

[†]*DWI - Leibniz Institute for Interactive Materials, Forckenbeckstr. 50, 52074 Aachen,
Germany*

[‡]*King Abdullah University of Science and Technology (KAUST), Advanced Membranes and
Porous Materials Center (AMPMC), Al-Jazri Building 4, Thuwal, 23955-6900, Kingdom
of Saudi Arabia*

E-mail: ingo.pinnau@kaust.edu.sa; manuscripts.cvt@avt.rwth-aachen.de

Abstract

Dynamic sorption of ethanol and toluene vapor into ultra-thin supported films of polymer of intrinsic microporosity PIM-1 down to a thickness of 6 nm are studied with a combination of in-situ spectroscopic ellipsometry and in-situ X-ray reflectivity. Both ethanol and toluene significantly swell the PIM-1 matrix and, at the same time, induce persistent structural relaxations of the frozen-in glassy PIM-1 morphology. For ethanol below 20 nm three effects were identified. First, the swelling magnitude at high vapor pressures is reduced by about 30 % as compared to thicker films. Second, at low penetrant activities (below $0.3 p / p_0$) films below 20 nm are able to absorb slightly more penetrant as compared with thicker films despite similar swelling magnitude. Third, for the ultra-thin films the onset of the dynamic penetrant-induced glass transition P_g has been found to shift to higher values indicating higher resistance to plasticization. All of these effects are consistent with a view where immobilization of the super-glassy PIM-1 at the substrate surface leads to an arrested, even more rigid and plasticization-resistant, yet still very open, microporous structure. PIM-1 in contact with the larger and more condensable toluene shows very complex, heterogeneous swelling dynamics and two distinct penetrant-induced relaxation phenomena, probably associated with the film outer surface and the bulk, are detected. Following the direction of the penetrant's diffusion the surface seems to plasticize earlier than the bulk and the two relaxations remain well separated down to 6 nm film thickness, where they remarkably merge to form just a single relaxation.

Graphical TOC Entry

1. Introduction

Polymers of intrinsic microporosity (PIMs) are solution-processable glassy polymers with unusually high interconnected porosity and pore sizes on the order of 1-2 nm.¹ They are ascribed large potential in the next generation membrane gas separation processes due to their very high permeability while retaining good to excellent selectivities.² The possible application areas of PIMs are not limited to gas separations. Polymers of the PIMs class have been demonstrated promising also for homogeneous catalysis,³ removal of butanol from aqueous solutions by pervaporation in fermentation-based butanol production,⁴ sensors,⁵ and very recently even in redox flow batteries.⁶ In most cases the key enabling feature is the extreme rigidity of the PIMs matrix and its high interconnected microporosity.

As many other glassy polymers PIMs often suffer from penetrant-induced plasticization⁷⁻¹⁴ which hinders their application in strongly interacting mixtures. These mixtures usually include condensable vapors and gases, such as carbon dioxide, methane, ethane, ethylene and other higher molecular weight organic compounds. The plasticization processes are known to dramatically reduce mixed gas selectivities and to date render membrane technology inadequate for, for instance, ethylene/ethane separations.¹⁵ Dissolution of the highly condensable components in the polymer matrix has long been known to reduce the system's glass transition leading to softening or lubrication of the initially rigid size-sieving polymer structure.¹⁶ In extreme cases when sufficient penetrant fraction is reached it is possible to observe the penetrant induced glass transition, P_g , and the polymer isothermally transits from glassy to rubbery state.^{7,17-21}

In membrane processes often thin layers on the order of 100 nm and less are used to maximise productivity. This is achieved usually in a form of composite membranes where the thin dense selective layer is supported by a much more open, porous and mechanically stable substrate. Reducing the thickness of a glassy polymer to nano-scale dimensions is known

to often cause significant deviations particularly in its dynamic characteristics, for instance, impacting the glass transition temperature T_g . Both positive (increases) and negative (reductions) deviations in the polymer T_g versus thickness have been reported. Positive deviations are hypothesised to stem from a significant degree of film immobilization following strong interaction of the polymer with the substrate, while negative deviations are assigned to the growing influence of the more mobile free film surface as the thickness reduces. The topic is, however, extremely dynamic and these simplistic views on the origins of T_g deviations have been increasingly challenged.^{22,23}

The nano-confinement effects, defined as forcing formation of a film much below equilibrium polymer coil, have only rarely been systematically studied in conjunction with the interaction with penetrants and mostly in model systems, like polystyrene (PS) or polymethylmethacrylate (PMMA).^{19,20,24–28} Since both isobaric glass transition, T_g , and the isothermal penetrant-induced glass transition, P_g , are dynamic phenomena it is plausible to suspect that the nano-confinement effects will also influence the penetrant-related plasticization properties of super-glassy polymers, like PIMs.

Very little is known about the details of organic penetrant induced plasticization phenomena in PIMs and even less in ultra-thin PIMs films.^{29,30} This is in part due to challenges in isolating the behavior of the thin dense selective skin of a composite membrane exposed to the plasticizing medium. In particular, it has remained elusive to decouple the film dilation from the penetrant uptake in films well below micron level where most standard gravimetric and dilatometric techniques are not applicable. However, as shown before this can be done for layers deposited on dense, inorganic substrates with the state of the art in-situ spectroscopic ellipsometry³¹ and in-situ X-ray reflectivity.³²

Here, we investigate the vapor-induced plasticization of thin, Si-wafer supported PIM-1

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3 films down to about 6 nm film thickness. We have used a combination of high temporal
4 resolution in-situ spectroscopic ellipsometry and in-situ X-ray reflectivity to study the dy-
5 namic and equilibrium swelling of the films as a function of the penetrant activity. The
6 results of this study are primarily anticipated to enhance the understanding of the PIM-1
7 behavior in streams involving condensable penetrants and thus facilitate its application in
8 emerging areas, for instance, in membrane-based molecular separations. The knowledge on
9 the plasticization induced by organic vapors in the PIMs class can also be helpful in the
10 areas requiring processing of the softened material especially in the ultra-thin film geometry.
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24 2. Experimental part

25 2.1. Sample preparation

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28 PIM-1 was synthesised as described earlier, by a polycondensation of 5,5',6,6'-tetrahydroxy-
29 3,3,3',3'-tetramethyl-1,1'-spirobisindane and 1,4-dicyanotetrafluorobenzene under high-intensity
30 mixing at 155 °C.³³ The product was cyclic-free with polydispersity of about 2 and average
31 molecular weight of about 50 kg/mol. Thin films were prepared by spin coating clean Si
32 wafer substrates from THF solutions under nitrogen flow to limit the undesired effects of
33 humidity. All films were made at 2000 rpm and the thicknesses were adjusted by changing
34 the polymer concentration. The freshly prepared samples were always rejuvenated in liquid
35 *n*-hexane prior to experiments. The rejuvenation procedure consisted of immersing the films
36 in a liquid for several minutes followed by a quick drying by air stream and annealing at 160
37 °C for 5 minutes to remove the solvent without a significant collapse of the PIM-1 microporosity.
38 All vapor experiments were performed within 3 minutes after the film rejuvenation.
39 This protocol led to very reproducible film properties ($n = 1.550 \pm 0.008$, Supporting Infor-
40 mation) and limited effects of physical aging.
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2.2. Ellipsometry analysis

RC2 dual rotating compensator variable angle spectroscopic ellipsometer (J.A. Woollam, Co.) was used for all experiments. The device was coupled to a commercial, temperature-controlled stainless steel in-situ cell. The vapor pressure was set by a fully automated system where a nitrogen stream saturated with organic vapors was mixed with a dry nitrogen at a desired ratio to set the relative vapor pressure for a predefined time intervals. All experiments were done at 25 °C.

Optical modeling to extract film thickness and refractive index was done using CompleteEASE 5.0 software package. The optical model consisted of a Cauchy-type layer (representing PIM-1) deposited on Si wafer / native Si oxide or Si wafer / 500 nm silicon oxide. As commonly done during ellipsometry measurements in the process of thickness and refractive index determination the measured spectra were iteratively fitted to the spectra generated by the optical model, containing parameters such as thickness and refractive index, until sufficient match was reached. The fit quality was assessed by minimization of the (root) mean squared error (MSE) parameter and the fit parameters were carefully checked for unwanted correlations. Spectroscopic ellipsometry measures polarized component (p and s) intensity ratios instead of absolute intensities and is, therefore, extremely precise and highly accurate. On well defined substrates, such as Si wafers used in this study, spectroscopic ellipsometry is able to determine film thickness with accuracy of ~ 0.1 nm and detect changes with precision ~ 0.01 nm. The high precision is particularly heavily exploited in the present study to observe dynamic changes in film properties.³⁴ The film properties, both in a dry and swollen state, were determined from exactly the same spot, approximately 2 mm in diameter in the center of the sample following its immobilization in the in-situ measurement chamber.

The optical dispersions for the substrates were taken from literature.³⁵ Optical dispersion of the ambient was assumed to be independent of the vapor pressure and was always kept at a value for vacuum ($n = 1$). The film properties were fitted in the wavelength range of 500-1000 nm where the film could be considered transparent with a slight Urbach absorption tail added to account for an absorption peak in PIM-1 at around 450 nm. For more details of ellipsometry the reader is referred elsewhere.^{31,36} Refractive index values are always given at 632.8 nm.

The investigated PIM-1 films were deposited either directly on top of bare Si wafers (with native 1.5 nm of oxide in place) or on top of a 500 nm thick thermal silicon oxide. The first configuration was used in the dynamic studies to follow small changes induced in the films by the sorbing penetrant. The second configuration was used to determine accurate swelling factors and refractive indices of the films by the interference enhancement method, where the underlying thick oxide amplified accuracy towards determination of the thin PIM-1 film properties, in particular its refractive index. This approach was found to be applicable down to 5 nm polymer film thickness.

For films thinner than about 30 nm deposited directly on bare Si-wafer (with 1.5 nm native oxide left in place) the independent determination of film thickness and refractive index becomes almost impossible due to fundamental limitations of ellipsometry. However, the information about film swelling (relative thickness changes) and, in particular, swelling dynamics can still be extracted even for films of about 5 nm thickness. This was done by fixing the refractive index values for films below 30 nm to its respective value determined for thicker films and fitting only for thickness. For films thinner than 30 nm in liquid ethanol the refractive index was assumed to be equal to the refractive index determined for the thicker films. The sensitivity originates mostly from an almost linear relationship between the ellipsometric parameter delta with film thickness. A similar approach has been previously used

by Pham et. al.¹⁹ to detect slope changes in the experimental data corresponding to glass transition in ultra-thin polystyrene film in compressed CO_2 .

2.3. X-ray reflectivity

X-ray reflectivity of films was performed using an Empyrean setup from PANalytical. A Cu X-ray tube (line source of 120.04 mm^2) provided $CuK\alpha$ radiation with $\lambda = 0.1542\text{ nm}$. A parabolic graded multilayer system converted the divergent beam into an almost parallel beam (divergence $< 0.03^\circ$) and suppressed $CuK\beta$ radiation. After reflection from the sample the intensity was collected by a pixel detector (256 by 256 pixels of $55\text{ }\mu\text{m}$, all connected as a 0D detector) as a function of the scattering vector $q_z = (4/\lambda) \sin\theta$, 2θ being the scattering angle. The latter was fixed at twice the incident angle, which set q_z along the film normal. The detector was used in a scanning geometry that allowed all rows to be used simultaneously. To reduce the background, the divergent beam perpendicular to the scattering plane was controlled by a mask of 4 mm restricting the width of the beam at the sample position. The beam footprint on the sample was 20 mm which was smaller than the length of the sample.

Reflectivity studies in well-defined vapor atmospheres were made in an Anton Paar TTK-450 chamber with Kapton windows fixed perpendicular to the incident and detection directions. The film was allowed to equilibrate at each chosen solvent vapor pressure before each measurement. Fitted film thicknesses were highly reproducible for at least 2 swelling experiments. The same vapor generation system as used for in-situ ellipsometry was employed to control vapor saturation degree and flows. Due to larger inner volume of the chamber the flow was twice higher as compared with ellipsometry to assure approximately the same vapor residence time. The XRR data were fitted and analyzed with the Parratt formalism³⁷ and the

electron density profile, layer thickness and surface roughness are extracted.

3. Results and discussion

Prior to the experiments all films were solvent-rejuvenated in *n*-hexane to reset their thermal history. This procedure has been found necessary in freshly casted PIMs because their ultra-high free volume matrix tends to densify as a result of physical aging³⁸ in a hard to control manner. The usual history-resetting treatment of glassy polymers involving annealing above T_g is not possible in most PIMs, including PIM-1, due to risk of significant thermal decomposition. In the absence of rejuvenation the observation of polymer dynamics in response to the sorbing penetrant would be further complicated by the superimposed effects of sample history or aging state and solvent residues which are known issues in super-glassy polymers.³⁹

3.1. Properties of dry ultra-thin PIM-1 films

Figure 1a shows the refractive index of rejuvenated PIM-1 films (structure given in Figure 1b) deposited on top of a 500 nm silicon oxide-coated Si wafer. Down to about 20 nm the refractive index of the films stays constant and equal to its bulk value. However, below 20 nm the refractive index decreases very significantly to less than 1.45. Similar behavior has been reported for free standing polymer films (Superformvar and Vinylec E) by Hilfiker et al.⁴⁰ and it was ascribed to uniform reduction of the film density. For our data, we believe that such a significant reduction of the apparent refractive index of the film is rather related with the growing influence of the film free surface roughness (in the ~ 1 nm range) and not the change in the properties within the whole volume of the ultra-thin film. If the refractive index of the entire film uniformly dropped to values below 1.45 this would indicate a

Figure 1: (a) Refractive index (at 632.8 nm) of dry, rejuvenated PIM-1 films deposited on 500 nm silicon oxide-coated Si wafers as a function of thickness. The thick oxide served to enhance sensitivity toward thickness and refractive index of the ultra-thin films. The reduction of the refractive index below 20 nm is attributed to an increasing contribution of the free surface roughness with reducing film thickness. (b) Chemical structure of PIM-1

reduction in density of over 10 %. This seems unrealistic and does not find confirmation in the X-ray reflectivity-derived density profiles discussed later. Rather it seems that as the surface roughness becomes a significant fraction of the overall film thickness its reduced effective material density starts to influence the apparent value of the film refractive index which is measured by ellipsometry. Often roughness is approximated by a layer consisting of 50 % material and 50 % void which would correspond to refractive index of about 1.3. The value of 1.43 for the thinnest analyzed films seems, therefore, realistic if one considers that roughness layer comprises nearly a quarter of the overall film thickness.

An alternative explanation for the significant reduction of the refractive index with reducing film thickness could be formation of PIM-1 patches separated by void as a result of, for instance, dewetting. Dewetting of ultra thin films is known to occur, for instance, for block copolymer films.⁴¹ To evaluate this hypothesis we have performed atomic force microscopy (AFM) imaging of 7 and 50 nm films. The AFM topology maps revealed very high homogeneity and film continuity of both samples and no evidence of dewetting or patch formation

was detected (Supporting Information). The presence of PIM-1 patches for ultra thin films (6-7 nm) could also potentially be captured by optical modeling using an effective medium approximation (EMA) approach by mixing optical properties of dense, thick PIM-1 films with a certain volume percentage of empty space (void). We have found that the EMA approach has not improved the fit quality significantly (MSE of 7.6 as opposed to MSE of 5.1 for the direct Cauchy fit of the 7 nm film). The generated dielectric functions (shown in supporting information) suggest that the refractive index curvature is much steeper for the 7 nm film as compared with the 100 nm film. This effect, attributed to nanoconfinement to the substrate and the corresponding deviation of the film properties from bulk, probably prevents the use of the EMA approach. A detailed study of this particular phenomenon is currently underway but is considered outside of scope of this work.

3.2. Swelling of ultra-thin PIM-1 films in ethanol vapors

We have discovered that when instantly exposed to ethanol vapors PIM-1 films show thickness dependence in the swelling factor ($SF = h_{swollen} / h_{dry}$, where $h_{swollen}$ and h_{dry} stand for thickness of film swollen upon contact with vapors and initial dry thickness, respectively). Surprisingly, the relationship does not have a clear trend in any particular direction as can be seen from raw data for SF shown in Figure 2a. At low ethanol vapor pressure of $0.15 p / p_0$ the 6 nm film swells more than the 50 nm film. The opposite is true at a high ethanol vapor pressure of $0.9 p / p_0$ with the thinner film swelling very significantly less than the thicker film. Results for other thickness and vapor pressures are summarized in Figure 2b.

The chosen vapor pressures of the highly soluble ethanol cover a large range and thus allow observation of the polymer behavior at various plasticization stages. At the two lowest ones, 0.15 and 0.3, the polymer does not plasticize enough to traverse glass transition (SF of max.

Figure 2: Swelling factor of thin PIM-1 films deposited on 500 nm oxide wafers (a) kinetic data for 6 and 50 nm films (b) summarized as function of thickness for all analyzed films at all ethanol vapor pressure steps. Experimental noise increases for the 6 nm sample as compared with the 50 nm one.

1.07). Therefore, it remains a glassy, non-equilibrium material irrespective of thickness. At higher vapor pressures of 0.6 and, particularly, 0.9 the thicker films swell significantly more and approach a very plasticized viscoelastic state, while the swelling of the thinner films is evidently restricted by the confinement. Additionally, for the two thinnest films (6 and 12 nm) the thinner one (6 nm) swells more at each vapor pressure. This last observation is probably related to an increased contribution of excessively swollen, more mobile top interface, similar to the findings of Ogieglo et. al.²⁴ There has been a growing body of research suggesting the liquid-like properties of free interfaces of glassy films.^{42–44} Such a liquid-like region would possess a much higher conformational freedom and would be able to swell more and faster than the rest of the film. At 6 nm total film thickness the impact of the more mobile and swellable interface would also be larger than at 12 nm which is consistent with the data in Figure 2b. For films thicker than 50 nm the effect of the nm-scale mobile outer surface would not be detectable. At higher vapor pressures the restricted swelling of the 6 and 12 nm films seems to suggest, on the other hand, a significant restriction of the penetrant-induced dilation caused by a severe modification of the random polymer coil due to the confinement to the substrate. We note, that the approximate radius of gyration for the used PIM-1 is ~ 20 nm and thus both of the thinnest films would be subject to this

deviation from an equilibrium random coil. Thicker films with thickness of $\sim 3R_g$ would be much less restricted and thus, as seen in Figure 2 are able to swell more.

Figure 3: $\Delta n = n_{swollen} - n_{dry}$ (calculated using values at 632.8 nm) plotted as a function of swelling factor for all films and vapor pressures. Region above 0 indicates predominant effect of free volume filling ($n_{swollen}$ rises above n_{dry}) with limited swelling. Region below 0 indicates dominance of matrix expansion related with swelling ($n_{swollen}$ drops below n_{dry}) and the material becomes less optically dense than dry PIM-1.

Figure 3 plots the change of the film refractive index ($\Delta n = n_{swollen} - n_{dry}$) upon swelling versus the swelling factor SF for all film thicknesses and vapor pressures. The Δn values above 0 indicate that free volume filling by the penetrant dominates, as the refractive index (and thus optical density) of the swollen polymer becomes larger than that of a dry film. In the case where Δn falls below 0 the matrix swelling dominates that is more and more of the penetrant dissolves in the matrix rather than sorbing into the rigid free volume pockets. In the thinner films, especially the thinnest 6 nm one, the hole filling mechanism is more pronounced at lower vapor pressures which may indicate a slightly more open structure. The more significant increase of the refractive index at 6 and 12 nm together with swelling similar to that of thicker films indicates that the overall penetrant concentration within the two thinnest films is slightly higher than in the thicker ones. The restricted swelling, as a result

of confinement to the substrate in comparison to thicker films, at higher vapor pressures is again visible.

Figure 4: (a) Dynamic thickness and ref. index (at 632.8 nm) changes of a 90 nm PIM-1 film upon stepwise increase in ethanol by $0.08 p / p_0$. Each step lasts 60 min and the exact position of the vapor pressure increase is indicated by a blue line on the upper horizontal axis. (b) swelling factor as a function of ethanol p / p_0 for a thick and thin film. Data for 5.7 nm has been offset by +0.15 for clarity. Extrapolation from linear regions allows approximating the onset of the P_g which seems to shift to higher values for thinner films (c) P_g values plotted against film thickness for PIM-1 plasticized with ethanol vapors.

Figure 4a shows a result of a dynamic vapor sorption experiment conducted with PIM-1 films deposited on native oxide wafers. A thin PIM-1 film is exposed to progressively increasing vapor pressure of a penetrant (ethanol) with each step equal to $0.08 p / p_{\text{sat}}$ and lasting

for 60 minutes. At low penetrant activities each increase in the vapor pressure results in a rapid initial increase in thickness followed by a period of a much slower relaxation. This behavior is typical for glassy polymers^{7,45–47} where the sorption of a penetrant can be viewed as occurring in two steps: the first fast one is related to Fickian diffusion and constitutes the, so called, primary (sorptive) polymer relaxation while the second slow one is the secondary (sorptive) relaxation (Figure 4a inset). The observation of the secondary relaxation is a clear indication of a glassy state where the non-equilibrium matrix slowly accommodates the sorbing penetrant. This often leads to inability to observe fully equilibrium properties at individual steps. As a compromise, all samples were measure with exactly the same experimental protocol involving 60 min steps to assure comparison between different samples. Such non-equilibrium behavior is absent in rubbery polymers which would only show the initial, primary relaxation followed by attaining a fully equilibrated state.¹⁷

The secondary relaxations are closely related with polymer plasticization, a phenomenon of a gradual "lubrication" of the polymer matrix induced by condensable species. Plasticization is usually undesired in, for instance, membrane technology where it leads to continuously changing properties of the separation layer over weeks to years. In other fields plasticization might be beneficial as it allows the ultra-rigid polymer networks to be processed or moulded into more or less complex shapes. In fact, one of the advantages of microporous PIMs is their ability to be solvent-plasticized which facilitates their processing making them much more flexible as compared with Metal Organic Frameworks or fully inorganic porous materials. As evident from Figure 4a PIM-1 is slowly plasticized with ethanol because the rate of secondary relaxation increases gradually with increasing penetrant vapor pressure. At a certain point a clear curve slope change is seen.

Similarly to the determination of T_g by dilatometric methods, the slope change can be viewed as an onset of penetrant induced glass transition, P_g , although the details are more

complex in thin supported films.^{7,48} In general, however, when the slope change occurs the polymer transits from glass to a significantly plasticized ("viscoelastic") state and eventually to a rubbery state at high enough penetrant activities. In contrast to polystyrene⁷ the process of plasticization in PIM-1 has been found to be dynamically heterogeneous in a sense of rather complex dynamical behavior after the slope change. This is clearly seen in Figure 4a at higher activities where the steps in thickness are difficult to clearly identify. Often multiple sub-steps seem to reveal themselves within the 60 min constant p / p_{sat} dwells. Such behavior seems absent in typical glassy polymers but we have consistently found it for all freshly rejuvenated, Si-wafer supported, PIM-1 films exposed to ethanol and toluene. The dynamic heterogeneities may reflect a very dramatic and multistep dynamic change while going from initially extremely rigid polymer network (T_g much above 400 °C) to a plasticized state where many different chain relaxational processes might be activated at different penetrant concentrations, lengthscales and timescales. Interestingly, researchers investigating PIM-1 free volume distributions using Xe sorption have found similar anomalous, sudden sorption effects⁴⁹ and it is well-known that Xe can swell glassy polymers significantly.¹³

Consistent with Figure 3 the refractive index shows initially an increase, associated with the occupation of the available microporosity by the liquid-like and optically denser void-filling ethanol. At p / p_{sat} of about 0.24 the refractive index starts to decrease quite steeply which is a direct consequence of film swelling induced by ethanol ($n_{ethanol} = 1.32$) as the optical density of the system reduces gradually below that of a dry PIM-1. These effects have also been previously discussed in detail¹⁸ and are especially prominent in polymers with large amounts of excess free volume or microporosity.

The position of the curvature change in thickness can be extracted by simple linear extrapolations to pin-point the onset of the P_g as done in Figure 4b. We have found, that with reducing film thickness the P_g initially stays at the same level and shifts to higher ethanol

vapor pressures below about 20 nm dry thickness, Figure 4c. This indicates, that with reducing thickness the entire film may become more resistant to plasticization or, alternatively, more dynamically arrested. The effect is opposite to what has been found for polystyrene in compressed CO_2 .¹⁹ The positive deviations, increases, in glass transition temperature with reducing thickness have been commonly ascribed to a certain degree of polymer chain immobilization stemming from adsorption to the substrate.⁵⁰ On the other hand, negative deviations or depressions of the T_g with reducing thickness, reported much more often, have been linked with an increasing contribution of the more mobile outer film interface with much weaker immobilization of the film at the substrate.^{24,51,52} Here for PIM-1, the effects of the hypothesized mobile outer film surface seem to be overcompensated by either adsorption to the substrate or possibly modification of the equilibrium polymer conformations by forcing it to form an ultra-thin, nanoconfined film close to or below its radius of gyration (R_g for PIM-1 with $M_w = 50$ kg/mol can be only roughly estimated to be about 10-20 nm in the melt assuming the chain rigidity factor $C_\infty = 100$, typical for a very rigid chain).

Considering the results presented in Figures 2, 3 and 4 for PIM-1 both the swelling magnitude and the chain dynamics seem to be reduced below 20 nm in effect making the ultra-rigid material even more resistant to plasticization while, in addition, its sorption capacity related with microporosity seems slightly increased.

Figure 5 and Table 1 (Supporting Information) show the XRR-derived electron density distribution along film thickness within the 5 nm and 50 nm films under dry nitrogen and ethanol vapors ($p / p_0 = 0.8$) equilibrated overnight. More information on the used models and fit qualities can be found in the Supporting Information. Two clear effects are observed. First, in agreement with ellipsometry, the films evidently become thicker in contact with vapors and the trend is the same as found in Figure 2. Based on the numerical fits of the

Figure 5: Electron density as a function of film thickness for a 50 nm (up left) and 5 nm (up right) PIM-1 films under dry nitrogen and exposed to ethanol activity of 0.8

data the nominal 5 nm film swells from 6.0 nm to 6.7 nm, corresponding to $SF = 1.12$. The nominal 50 nm film swells from 48.2 nm to 56.4 nm, $SF = 1.17$, which is more than for the 5 nm film. This swelling factor is also in a very good agreement with Figure 2a where for a slightly higher activity, 0.9, the SF was also proportionally higher and equal to 1.19. The second observation, also in agreement with ellipsometry, Figure 3, is an increase of the electron density, ED , going from dry nitrogen to ethanol vapors. This translates into the increases in the calculated mass densities by approximately 12.9 % and 13.5 % for the thick and thin films, respectively. Clearly, ethanol vapors are able to fill the available voids within the PIM-1 matrix in addition to swelling it. The reduced freedom for the thinner film to dilate as a result of penetrant sorption is consistent with its larger relative increase in density in an attempt to accommodate the penetrant despite restricted swelling. As discussed earlier, the X-ray reflectivity-derived data does not suggest a very significant reduction of the mass density for the thinner film. However, the much larger contribution of the roughness layer, extending over a quarter of the film thickness at 5 nm, is clearly seen.

To investigate the impact of the nano-confinement on the swelling of PIM-1 in liquid ethanol ($a = 1$), as opposed to vapors shown earlier, additional experiments using films supported

on a thick, 500 nm thermally-grown silicon oxide were performed. Here as well the oxide served to enhance the optical contrast for the ellipsometric analysis by the interference enhancement effect. This allowed extracting accurate values of SF for 60 nm and 5 nm PIM-1 films which would otherwise be extremely difficult. Ellipsometry imaging maps of the SF for the two films are shown in Supporting Information. While the 60 nm film shows the usual swelling found in bulk films, about 1.71,^{2,21} the 5 nm film swells to only 1.46. This again suggests a severe restriction in the ultra-thin film's ability to swell in a liquid ($a = 1$).

3.2. Sorption of toluene vapors into ultra-thin PIM-1 films

When PIM-1 films are subjected to sorption of a much more condensable and larger toluene ($T_c = 591.8$ K, kinetic diameter $d = 6.1$ Å for toluene; $T_c = 513.9$ K, kinetic diameter $d = 4.5$ Å for ethanol, respectively^{53,54}) the thickness and refractive index behavior becomes even more complex than in the case of ethanol. Figure 6 shows dynamics of thickness and refractive index for 100.4 nm and 51.6 nm films in toluene recorded with the stepwise protocol. For the 100.4 nm film while the thickness steadily increases almost no changes in the refractive index are seen in the first 450 minutes. Suddenly, at around 450 min the refractive index shows a significant jump accompanied by even faster increase in thickness and its dynamics. We hypothesise, that this anomalous behavior, found consistently for toluene sorption in all analyzed films, is related to a spacially heterogenous sorption of toluene in the direction perpendicular to the film surface.

It is well-known, that sorption of organic molecules in glassy polymers might show deviations from Fickian diffusion when the interaction of the sorbing species influences the rate of the inherent polymer chain relaxations to a large extent.^{20,24,49,55–57} Toluene, being a large and condensable molecule is not able to penetrate PIM-1 matrix as fast as a smaller and less condensable ethanol. At the top film surface toluene seems to face a dynamic barrier

Figure 6: Film thickness and refractive index (at 632.8 nm) evolution for 100.4 nm (a) and 51.6 nm (b) PIM-1 films exposed to increasing vapor pressure of toluene. Sorption dynamics become increasingly complex both for thickness and refractive index.

for further diffusion through the initially extremely rigid PIM-1. The first several nm of the film top surface become rapidly swollen but the bulk of the film may remain essentially non-penetrated, similar to the often observed Case II diffusion.^{24,56} This is consistent with the behavior of the refractive index up to ~ 450 min where it stays essentially constant. Refractive index values extracted from ellipsometry data with the used uniform optical model are predominantly representative to the overall, total film refractive index rather than to the surface of the film. The thickness, however, does adequately capture the overall swelling even when the swelling is dominated by the top interface. These properties are typical for

ellipsometry which, for dielectric transparent materials with $n \approx 1.5$, is inherently more sensitive to changes in the film thickness rather than in its refractive index. The strong evidence for growing film heterogeneity is also the steadily increasing fit root mean square error (MSE) going from dry to swollen film indicating the inability of the uniform model to accurately describe the film properties (Supporting Information). The increase in the MSE for ethanol has been found much smaller, meaning that the film remained more uniform while swelling, which is consistent with easier penetration through the entire volume of the PIM-1 films (Supporting Information). Additionally, for toluene the data seemed to be fitted significantly better with an optical model which allowed for a gradual change in the refractive index in the direction perpendicular to the film plane (graded model³¹), although the actual resulting fit parameters were not robust enough and are not discussed here in detail. The sudden jump in the refractive index seen at higher activities in Figure 6 is probably an artifact related with the inadequacy of the used uniform optical model and is thus not discussed. Even though liquid toluene has a very high refractive index (1.495⁵⁸) such large increases of film index (from dry 1.53 up to almost 1.59) seem unrealistic given the overall significant film swelling which should decrease film index.

Figure 7 shows film thickness as a function of increasing vapor pressure of toluene for films in the range from 100.4 to 6.4 nm. The data shows highly anomalous, penetrant-induced accelerations of swelling as indicated with arrows. Because the vapors diffuse into the film from the top we attribute the first anomalous acceleration which occurs at lower activities (and thus lower swelling) to occur in the surface of the film. As the diffusion progresses deeper into the film a second acceleration is observed and attributed to the remaining part of the film, denoted as bulk. The surface relaxations are clearly visible in Figure 7 where the thickness data is combined for all toluene-exposed films. The surface relaxation starts to be visible in addition to the bulk relaxation from 51.6 nm down to 15.4 nm. Possibly, for the thickest 100.4 nm film, the surface effect is too small in relation to overall film thick-

ness to be clearly detected. Remarkably, at 6.4 nm both relaxation processes seem to blend together to form just a single relaxation event placed more or less in-between the surface and bulk relaxations seen for thicker films. This is a striking effect of polymer confinement to the substrate. Most probably due to the severe restriction of the polymer conformations related with formation of a film with only 6.4 nm thickness the dynamical heterogeneity of toluene sorption seen for thicker films seems to largely disappear. It is no longer possible to distinguish bulk and surface regions with respect to their dynamics.

Figure 7: PIM-1 film thickness as function of increasing vapor pressure of toluene in time for all initial, dry thicknesses analyzed. Reducing film thickness allows observation of both the bulk- and surface-related polymer relaxations down to the lowest analyzed thickness, 6.4 nm, where the bulk and surface relaxations seem to blend together to form just a single dynamic response as a result of nano-confinement to the substrate.

A magnification of the surface relaxation event for a 28.7 nm film is shown in Figure 8a. It remarkably resembles a curvature change associated with glass transition with the difference that it occurs when the film is subjected to a *constant*, not stepwise increasing vapor pressure of the penetrant. The surface relaxation is, therefore, a direct manifestation of the inherent polymer dynamics in the surface region. One may suggest, that the very surface region of the PIM-1 is much more dynamic and itself plasticizes at much lower vapor pressures than the bulk when subject to diffusion of a large, condensable species. This view would be con-

Figure 8: (a) a magnification of the " P_g -like" surface relaxation event strikingly resembling a glass transition curve slope change; (b) p / p_{sat} positions of the " P_g -like" relaxation events for the bulk and the surface plotted versus dry film thickness. The respective positions of the two relaxation types are essentially independent of the overall film thickness down to 6.4 nm.

sistent with the earlier findings for polystyrene in liquid n-hexane.²⁴ However, it may also be that the surface, which is penetrated by the toluene first simply reaches the plasticization threshold earlier than the rest of the film.

The positions of the bulk and surface relaxation events are summarized and plotted against the initial film thickness in Figure 8b. Both the surface and the bulk relaxations are relatively independent from the overall film thickness, which suggests, that the surface and the bulk are dynamically well separated and not significantly affected by the nanoconfinement down to a very low overall film thickness of 6.4 nm. This observation is quite similar to the behavior of thin PMMA films in methanol studied by Hori et. al.,²⁸ although in their study the polymer dynamics started to be affected by the substrate at much larger film thicknesses (~ 300 nm). Thus PIM-1, while showing a heterogenous, anomalous diffusion remains dynamically similar with reducing thickness when exposed to large, condensable penetrant molecules down to less than 10 nm film thickness.

Figure 9: Electron density as a function of film thickness for a 50 nm (up left) and 5 nm (up right) PIM-1 films under dry nitrogen and exposed to toluene activity of 0.8

Because the X-ray reflectivity data took much longer to record (approximately 2 hours per single spectrum) the technique was insensitive to the dynamics of swelling and could not detect the relaxations within the surface or the bulk. However, the equilibrium properties of the thick, 50 nm, and thin, 5 nm, films could be resolved, Figure 9 and Table 2 (Supporting Information). In contrast to ethanol, swelling of PIM-1 in toluene vapor shows an opposite effect, with the thin film swelling more than the thick one, $SF = 1.20$ and 1.17 , respectively. The relative increases in the mass densities were 13.7 % and 8.2 %, respectively. This behavior seems consistent with an increasing influence of the excessively swollen interface of the film with the reduction of overall thickness and thus with results presented in Figures 7 and 8.

Unfortunately, no ellipsometry imaging data (similar to Figure 4 for ethanol) could be generated for toluene due its unfavorably high refractive index ($n = 1.495$), which resulted in almost no optical contrast between the swollen PIM-1 layer and the liquid ambient. Thus the conclusions related to variations in the swelling magnitude of PIM-1 in toluene as a function of film thickness are less robust as compared to ethanol. Overall it seems, that the variations in the total swelling between the thick and thin films were somewhat smaller in toluene than in ethanol.

4. Conclusions

We have investigated the magnitude and the dynamics of swelling in ultra-thin PIM-1 films supported on Si wafers when exposed to ethanol and toluene vapors. The organic compounds have led to significant plasticization of the initially ultra-rigid PIM-1 structure and a clear effect of nano-confinement (film thickness dependence) has been observed. Both used techniques, in-situ ellipsometry and in-situ X-ray reflectivity gave consistent results.

For ethanol a relatively complex trend has been found. In the ultra-thin region, below roughly 20 nm, the thinnest 6 nm film has always swelled more than the thicker 12 nm film irrespective of the vapor pressure of the penetrant (in the range from 0.15 to 0.9 p / p_0). This effect could be attributed to the influence of the highly mobile and swellable free film surface whose contribution is larger for the thinner 6 nm as compared with the thicker 12 nm film. At higher ethanol vapor pressures (above 0.6 p / p_0) both ultra-thin films (6 and 12 nm) showed significantly lower swelling than the thicker, bulk-like (> 50 nm) films suggesting a large degree of polymer matrix arrest upon confinement to the substrate in a form of a film with thickness below polymer radius of gyration (about 20 nm). The same effects have been found in liquid ethanol (activity = 1). Reduction of film thickness below 20 nm has also impacted the dynamic response to plasticizing vapors and the onset of the penetrant-induced glass transition, P_g , has been found to shift to higher values for ultra-thin films. Thus below 20 nm PIM-1 has been found slightly more resistant to plasticization by condensable vapors.

Swelling in toluene vapors has been found even more complex than in ethanol. The larger and more condensable toluene faced a dynamic barrier at PIM-1 surface. The penetration of

the PIM-1 film has been found heterogeneous with the surface of the film behaving different than the bulk. Two types of structural relaxations, occurring at lower and higher vapor pressures have been found and could be associated with the sorption-induced relaxation in the surface and the bulk, respectively. The relaxations in the surface and in the bulk have remained well-separated down to the lowest analyzed thickness of 6.4 nm where they remarkably combined to form just a single relaxation event at an intermediate vapor activity. This indicated a strong nano-confinement effect, similar to what has been found for ethanol.

The results presented in this work are anticipated to shed light on the combined effects of penetrant and nanoconfinement in ultra-rigid polymers and thus to facilitate broadening of their application scope as highly efficient membranes or adsorbers.

Acknowledgement

This publication is based upon work supported by the King Abdullah University of Science and Technology (KAUST) Office of Sponsored Research (OSR) under Award No. SEED Fund OSR-2015-SEED-2445-01.

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