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Thin Composite Carbon Molecular Sieve Membranes from a Polymer of Intrinsic Microporosity Precursor

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Abstract

Ultra-thin composite carbon molecular sieve (CMS) membranes were fabricated on well-defined inorganic alumina substrates using a polymer of intrinsic microporosity (PIM) polyimide as precursor. Details of the pyrolysis-related structural development were elucidated using focused-beam, interference-enhanced spectroscopic ellipsometry (both in the UV-VIS and IR range) which allowed accurate determination of the film thickness, optical properties as well as following the chemical transformations. The pyrolysis-induced collapse of thin and bulk PIM-derived CMS membranes was compared with CMS made from a well-known non-PIM precursor 6FDA-DABA. Significant differences between the PIM and non-PIM precursors were discovered and explained by a much larger possible volume contraction in the PIM. In spite of the differences, surprisingly, the gas separation properties did not fundamentally differ. The high temperature collapse of the initially amorphous and isotropic precursor structure was accompanied by a significant molecular orientation within the formed turbostratic carbon network guided by the laterally constraining presence of the substrate. This manifested itself in the development of uniaxial optical anisotropy, which was shown to correlate with increases in gas separation selectivity for multiple technologically important gas pairs. Reduction of CMS skin thickness significantly below ~1 micron induced large losses in permeability coefficients with only small to moderate effects on selectivity. Remarkably, skin thickness reduction and physical aging seemed to superimpose onto the same trend, which explains and strengthens some of the earlier fundamental insights.

1. Introduction

Carbon molecular sieve (CMS) membranes represent a special class of amorphous molecularly sieving materials that hold great promise in helping to reduce the industrial energy consumption, particularly in the fields of separation technology¹. CMS membranes belong to a very small group of amorphous materials that are able to consistently break the tradeoffs (*i.e.* upper bounds) between membrane permeability and selectivity². Existence of such tradeoffs in amorphous systems, first described for polymers by Robeson in 1991³ (later updated in 2008⁴), has its strong basis in the theory of molecular transport⁵. The tradeoffs present a considerable hurdle for the progress of membrane-based separation processes by hindering the development of simultaneously highly selective and highly permeable materials.

The key reason why CMS membranes are able to outperform materials defining the polymeric upper bounds, sometimes by a large margin, lies in their hierarchical micropores ($< 20 \text{ \AA}$) which are thought to be distributed in a bimodal way^{6–8}. The smaller micropores ($< 7 \text{ \AA}$), often subcategorized as ultramicropores to highlight their special role, possess just the right sizes to discriminate between small molecules, including permanent gases (He, H₂, CO₂, O₂, N₂, CH₄), condensable gases^{9,10} (olefins/paraffins), and even organic solvents^{11,12} (benzene, xylene isomers). These ultramicropores are formed by the slits between the consecutive graphite-like flakes or sheets. The larger micropores ($7 - 20 \text{ \AA}$), which exist as void spaces between the stacked sheets resulting from the packing frustration, are weakly or non-selective but provide efficient pathways enabling high permeabilities. In addition to the favorable microstructure, CMS membranes are very chemically stable and withstand high operational temperatures and pressures. The challenges for further progress of practicable CMS membranes mainly lie in their relative mechanical fragility, higher cost, and the tendency to a progressive loss of permeance with time as a result of slow densification (physical aging). These challenges are, unfortunately, amplified in ultra-thin ($< 1 \text{ }\mu\text{m}$) CMS membranes when aiming to benefit from the decreased transport resistance leading to high fluxes while preserving the strong molecular sieving properties (high selectivities).

With respect to their micro-morphology, in particular their bimodal pore size distribution, CMS materials resemble the recently discovered group of polymers of intrinsic microporosity, PIMs^{13–16}. PIMs are organic polymers possessing ultra-rigid, contorted backbones that prevent efficient molecular packing. They usually have undetectable glass transition temperatures, T_g , and high internal surface areas ($> 200 \text{ m}^2 \text{ g}^{-1}$). Thus PIMs themselves offer extremely attractive gas separation properties and redefined upper bounds for several important gas pairs (O₂/N₂, H₂/N₂ and H₂/CH₄^{17,18}, CO₂/N₂ and CO₂/CH₄^{19,20}).

CMS membranes are typically fabricated by a pyrolysis process of an organic polymer precursor under essentially inert atmosphere in a temperature range roughly from 400 to 1000 °C. A wide spectrum of

polymer precursors has been studied in the literature^{21,22} ranging from phenolic resins, polyphenylene oxide, polyacrylonitrile, and high performance polyimides such as Kapton, Matrimid or P84. Most of the studies have focused on the bulk CMS properties and less data exists on attempts to fabricate actual scalable membranes such as hollow fibers^{6,7}, or inorganic substrate-supported thin-film composites⁸. In particular, the reports dealing with defect-free, highly productive, thin (several μm) CMS membranes remain rare mainly due to challenges related with the defect control and the significant structural transformations during the pyrolysis of extremely high aspect ratio films. Some of the earlier studies by Centeno et al^{23–25} reported the pyrolysis of phenolic resin or polyetherimide precursors to obtain 0.8 - 3 μm thick and relatively defect-free CMS membranes supported by macroporous carbon substrates. Those membranes presented moderate to high performances in particular for O_2/N_2 and CO_2/CH_4 separations. Studies dealing with even more attractive, submicron CMS membranes are extremely rare^{26,27} and often challenged by the presence of non-selective defects which deem the resulting performance far from the apparent CMS potential. Some way of producing well defined ultra-thin CMS membranes has been recently reported by Hou et al²⁸ using carbon nanotubes as scaffolds positioned between the inorganic support and the CMS layer. However, the scalability of such an approach to industrial settings remains unlikely. The use of PIMs materials as a starting point for the preparation of carbons has remained largely unexplored with only a few studies focusing on bulk materials properties and directed mostly towards the olefin/paraffin separations^{9,10,29,30}. Studies on the ultra-thin ($< 1 \mu\text{m}$) PIMs-derived CMS membranes are not yet available.

Here, we report in detail the preparation of ultra-thin, supported CMS membranes made from an aromatic carbon-rich PIM-polyimide precursor. Particular focus was placed on the pyrolysis-related collapse of the precursor films into carbon structures. The behavior of the PIM-derived CMS membranes was compared with non-PIM-derived ones in both -and bulk (thick film) geometries. Preparation of the thin-film CMS on well-defined inorganic alumina Anodisc® substrates allowed for an isolation of the skin behavior from the usually difficult to elucidate effects of the substructure often encountered in all-polymeric asymmetric thin-skinned carbon hollow fibers⁶. An easily applied PDMS coating procedure was used to very effectively eliminate the influence of occasional non-selective defects and improve the membrane mechanical stability. Two types of spectroscopic ellipsometry (SE), UV-VIS SE and infrared (IRSE), were used for the analysis. UV-VIS ellipsometry allowed for a very accurate determination of the thickness of both precursor and carbon films in a submicron range, which was crucial for the extraction of accurate permeability values. IRSE enabled following the pyrolysis-induced gradual chemical changes in ultra-thin films. Combination of both UV-VIS SE and IRSE allowed, for the first time, for a determination of the pyrolysis-induced structural orientation producing optical anisotropy which was found to correlate with increased selectivities upon film thickness reduction significantly below the ~ 1

micron range. Remarkably, physical aging was found to be largely equivalent to the skin thickness reduction in terms of the gas separation performance, which presents a highly valuable fundamental insight explaining some of the behavior reported earlier.

2. Materials and methods

2.1. Polymer synthesis

SBFDA-DMN, later referred to as PIM polyimide, was synthesized by reaction of 9,9'-spirobifluorene-2,2',3,3'-tetracarboxylic dianhydride (456 mg, 1.00 mmol) and 3,3'-dimethylnaphthidine (312 mg, 1.00 mmol) in *m*-cresol (3 mL). The solution was heated to 70 °C for 2 h before isoquinoline (5 drops) was added. Thereafter, the system was heated up to 120, 150 and eventually to 180 °C and kept for 1 h at each temperature. Finally, the polymer was precipitated in methanol (100 mL), filtered, dried and re-precipitated twice in methanol. After filtration, the polymer was further dried in a vacuum oven at 120 °C overnight and an off-white filament (730 mg, yield: 95%) was obtained. ¹H NMR analysis yielded (400 MHz, CDCl₃): δ 8.56 (s, 2H), 8.09 (s, 2H), 7.42 - 7.62 (m, 16H), 6.97 (s, 2H), 2.42 (s, 6H); FT-IR analysis yielded (polymer film, ν, cm⁻¹): 3055 (m, str C-H), 1780 (s, str, imide), 1714 (s, str, imide), 1608 (m, str, Ph), 1389, 1373 (s, str, C-N), 747 (s, astr, imide). Molecular weight determined by GPC in chloroform: M_n = 6.5 × 10⁴ g mol⁻¹; M_w = 12.5 × 10⁴ g mol⁻¹; PDI = 1.92. T_d = 520 °C. Internal surface area determined by N₂ sorption at 77 K: S_{BET} = 686 m² g⁻¹.

6FDA-DABA, later referred to as non-PIM polyimide, was synthesized by reaction of 3,5-diaminobenzoic acid (152.0 mg, 1.00 mmol) and 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (444.4 mg, 1.00 mmol) in 2.3 mL *m*-cresol (25% solid content). The solution was heated at 60 °C for 30 min, and thereafter one drop of isoquinoline was added. The system was then gradually heated to 180 °C and kept for 2 h. A viscous solution was formed and the polymer was obtained by precipitation in methanol. The product was filtered and dried under vacuum. The solid was re-precipitated in methanol twice to obtain the desired polymer as an off-white filament (540 mg, yield: 96.4%). ¹H NMR analysis yielded (500 MHz, DMSO-*d*₆): 13.46 (s, 1H), 8.21 (d, 2H, J = 8.05 Hz), 8.16 (s, 2H), 7.96 (d, 2H, J = 8.10 Hz), 7.86 (m, 1H), 7.79 (s, 1H). Molecular weight determined by GPC using DMF as eluent: M_n = 3.26 × 10⁴ g mol⁻¹, PDI = 3.26.

2.2. Preparation of thin precursor and carbon films on silicon wafers

Thin films were spin-coated from chloroform (SBFDA-DMN) or tetrahydrofuran (6FDA-DABA) on top of 500 nm thermal silicon oxide-coated silicon wafers (obtained from Si-Mat, Germany) at 2000 rpm. The solution concentration was adjusted to obtain approximately 300 nm films, which was the optimal thickness for the subsequent ellipsometry analysis following the pyrolysis procedure. For infrared

spectroscopic ellipsometry analysis (IRSE) the films were prepared directly on native oxide wafers. After preparation, all films were annealed at 50 °C for 16 h to remove most of the solvent. The pyrolysis process was conducted following exactly the same protocol as for the thin-film composite membranes (see next section).

2.3. Preparation of thin-film composite membranes and membrane performance measurements

As schematically shown in Figure 1a, the precursor films were prepared on alpha alumina Anodisc® substrates (13 mm diameter with uniform surface pores of ~20 nm, Whatman®, Sigma Aldrich) by depositing 50-70 µL of ~0.5% w/w solution (resulting in ~ 1 micron carbon films after pyrolysis) or ~0.1% w/w solution (resulting in ~0.2 micron carbon films after pyrolysis) using an Eppendorf® pipette. The resulting uniformity of the precursor and CMS layer thickness was typically within 10% (as determined from 5 spots measured on the surface of the membrane with spectroscopic ellipsometry). The precursor films were pyrolyzed under nitrogen flow (1 L min⁻¹) in a horizontal quartz tube furnace while keeping the oxygen concentration below 7 ppm. The ramp rate was 3 °C min⁻¹ and the dwell time at the maximum set point temperature (varied between 500 and 1000 °C) was 1 h. Afterwards, the oven was left to passively cool down to room temperature overnight. Following the pyrolysis, all thin-film carbon membranes were coated with 0.5 - 1 micron of pre-polymerized polydimethylsiloxane (PDMS, solution in isooctane, Sylgard 184, using a precursor to crosslinker ratio 10:1 keeping the total concentration of 1% w/w and prepolymerized by reflux at 80 °C for 24 h) using the Eppendorf® pipette and subsequently fully cross-linked at 50 °C for 2 h. The PDMS coating served to plug the non-selective defects and protect from mechanical damage. A significant improvement of the overall mechanical stability of the composite membranes was noticed upon PDMS coating that aided handling. Because of the low substrate pore size and relatively high precursor solution viscosity no pore intrusion of the precursor solution was observed. The pyrolyzed films presented a sharp substrate/film interface with no evidence of delamination or macroscale defects, as shown in Figure 1b. The optical images of a systematic series of thin-film composite carbon membranes prepared at different temperatures are displayed in Figure 1c. No obvious defects or cracks were noticed following visual examination.

Pure-gas permeances, expressed in ‘gas permeation units’, with 1 GPU = 1 x 10⁻⁶ cm³(STP) cm⁻² s⁻¹ cmHg⁻¹ or 3.3 x 10⁻¹⁰ mol m⁻² s⁻¹ Pa⁻¹, were measured using a commercial 47 mm high pressure filter holder, Figure 1d, (Millipore Corporation) equipped with a custom made stainless steel mask (not shown) to seal the 13 mm diameter membrane with a 9.1 mm rubber O-ring in the filter holder center. Gas flow was measured with a soap bubble flow meter in the sequence: O₂, N₂, He, H₂, CH₄, CO₂. Vacuum and purge were applied sufficiently between the gas changes to prevent effects of any previous gas residues.

All measurements were carried out at 21 ± 1 °C. Each sample was duplicated with the exception of the thin carbon films pyrolyzed at the highest temperature in the series (800 °C). Despite several attempts, membranes pyrolyzed at 800 °C suffered from extreme mechanical fragility and only one sample could be characterized. Permeabilities, P_{gas} , expressed in barrer, with 1 barrer = 1×10^{-10} cm³(STP) cm cm⁻² s⁻¹ cmHg⁻¹ or 3.35×10^{-16} mol m m⁻² s⁻¹ Pa⁻¹ of the carbon films in the presence of the PDMS overcoat were extracted using the resistances-in-series model, as discussed later and detailed in the Supporting Information. Ideal selectivities, S , for gases A and B were calculated as $S_{A,B} = P_A/P_B$. Gas separation performance data for the bulk polymers was measured on thick films (> 70 μm) by using a constant volume/variable pressure system at 35 °C.

Figure 1. (a) Scheme of the fabrication of the PDMS-coated carbon (ultra)thin film membranes; (b) SEM cross-section micrograph of a typical carbon composite membrane before coating with PDMS; the image shows a very well defined smooth carbon film that is well attached to the supporting structure; no pore intrusion by the precursor solution is observed; (c) optical images of a series of thin-film composite carbon membranes pyrolyzed at different temperatures; (d) lower part of a high pressure cell used for the single gas separation performance measurements.

2.4. Spectroscopic ellipsometry measurement and analysis

UV-VIS and IR spectroscopic ellipsometry were used to extract the accurate thicknesses and optical properties (real and imaginary dielectric functions), to detect chemical changes following pyrolysis, and to evaluate molecular orientation (represented by development of optical anisotropy) of both precursor and carbon films, Figure 2a. Ellipsometry measures changes in light polarization upon specular reflection from the sample surface and expresses them in terms of the amplitude ratio (ψ , Ψ) and phase shift (δ , Δ) parameters which are related with the complex reflectance ratio (ρ) of the p - and s -polarized light by:

$$\tan (\Psi) \cdot e^{i \Delta} \equiv \frac{r_s}{r_p} = \rho$$

To extract useful sample properties, such as film thickness, an optical model representing the sample structure is constructed, Figure 2a. The model-generated Ψ and Δ are numerically fitted to the measured data allowing for the determination of the film thicknesses and the optical properties of the thin films by finding a global fit minimum.

Figure 2. (a) A general scheme of the spectroscopic ellipsometry measurement and data analysis; (b) examples of psi (red) and delta (green) spectra for a bare porous alumina Anodisc® support, support covered with precursor film, resulting carbon film after pyrolysis at 600 °C and a carbon film covered with the defect-plugging PDMS silicone protective layer; red and green lines are measured spectra, black dashed lines are data generated by the best fit optical models; (c) infrared ellipsometry spectra of initially

300 nm films revealing the changes in the vibrational bands related to the pyrolysis-induced chemical transformation.

For the UV-VIS range a spectroscopic ellipsometer M-2000 DI operating in a wavelength range of 193-1690 nm was used in conjunction with focusing probes, which focused the probing light to 300 μm (short axis). CompleteEASE software (v. 5.23) was used for data analysis. Each sample was measured at 3 angles of incidence (65, 70 and 75°) at 5 different spots and the average value for both thickness and refractive index was used later. The optical modeling was done assuming a layered optical model comprising the substrate (either a 500 nm silicon oxide-covered Si wafer or Anodisc®) and the thin film (either a precursor or carbon film). Prior to deposition of precursor films on the silicon wafers the precise thickness of the nominal 500 nm silicon oxide was determined by using an inbuilt optical model on at least 10 spots. The spot-to-spot variation was found to be lower than about 0.2 nm pointing to the extremely high uniformity of the oxide-covered wafers. The presence of the thick silicon oxide served to amplify the optical properties, in particular the optical anisotropy as described later, of the precursor and carbon films deposited subsequently. This amplification effect, usually not exploited in typical ellipsometry analysis, has been exhaustively studied earlier^{31,32} and deemed particularly useful for the absorbing films (*e.g.* pyrolysed carbons). The wavelength range for the optical modeling was 600 - 1690 nm where the films could be described with a Cauchy-type dispersion:

$$n(\lambda) = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4}$$

To account for the light absorption, particularly at higher pyrolysis temperatures where the films became strongly absorbing, the extinction coefficient (Urbach tail) as well as the exponent was fitted. The numerical correlations between the fit parameters were always carefully examined using the in-build cross-correlation matrix calculator to assure the uniqueness of the resulting values. Because of the wide wavelength range covering much of the near infrared region (up to 1690 nm) the spectral oscillations of the pyrolyzed carbon films were still relatively well resolvable allowing for high quality analysis. This was the case for films pyrolyzed up to 1000 °C on silicon wafers substrates, due to very low resulting film thickness of about 100 nm, and up to 650 °C on Anodisc® substrates for the thin-film composite membranes. Thin-film composite membranes pyrolyzed above 650 °C were found too strongly absorbing and for those samples the thickness shrinkage due to pyrolysis was assumed the same as for the thinner and better measurable samples pyrolyzed on silicon wafers.

To determine the degree of optical anisotropy for the films prepared on silicon wafers a separate analysis with a uniaxial anisotropic optical model was performed. The model allowed the two components of the optical dispersion: in-plane of the sample, n_{xy} ($n_x = n_y$, uniaxial anisotropy by definition), and out-of-plane

of the sample, n_z , to be independently described by two separate Cauchy formulas. To limit the number of fit parameters and improve fit uniqueness, the shape parameters of both dispersions were coupled ($B_{xy} = B_z$) in a similar way to the analysis performed previously in study of anisotropically swollen zwitterionic, silicon wafer supported films³³. For the determination of surface porosity of the Anodisc® substrates an effective medium approximation (EMA) model mixing the optical properties of the dense alumina ($n = 1.755$ at 1000 nm) with void ($n = 1.000$) was used as previously described³⁴. Surface roughness of the porous support was found below ~ 15 nm (as determined by AFM) and was neglected in the analysis. The justification is given elsewhere³⁵. For the extraction of the broad range extinction coefficient of the pyrolyzed carbon film series a B-Spline optical model³⁶ was used and the details are given in the Supporting Information. More details on the technique itself as well as its application to thin film membranes can be found in the literature^{34,35,37,38}.

For IRSE a novel custom built spectroscopic ellipsometer coupled with a Bruker Tensor 37 spectrometer was used³⁹. Samples were measured at seven angles of incidence (45, 50, 55, 60, 65, 70 and 75°) to optimally decorrelate film thickness and anisotropy. Thickness variations, as well as the opening angle of the set-up ($\pm 2.1^\circ$), were accounted for by fitting the measured polarization degree in an averaging scheme according to Jellison et al⁴⁰. Film anisotropy was modeled based on a uniaxially anisotropic dielectric function consisting of anisotropic high-frequency constants ($\epsilon_{\infty,xy}$, $\epsilon_{\infty,z}$) and sums of vibrational oscillators associated with the PIM's molecular vibrational modes.

3. Results and Discussion

3.1. Spectroscopic ellipsometry analysis of thin precursor and carbon films deposited on silicon wafers and porous inorganic supports

Spectroscopic ellipsometry is a powerful optical technique that has its roots in solid-state physics and has mostly been applied to the analysis of dielectric functions of semiconductor, metal and organic films deposited on dense substrates (silicon wafers, glass slides, metal-covered glass etc.). To study the pyrolysis-related changes of the thin PIM and non-PIM structures with UV-VIS ellipsometry the ~ 300 nm thick precursor films were deposited on top of a 500 nm thermally-grown silicon oxide/silicon wafer system. The presence of the relatively thick oxide allowed for a significant enhancement of measurement and modeling accuracy^{31,32}. In particular, the determination of the optical anisotropy related with structural orientation of the carbon films pyrolyzed at higher temperatures became more reliable, as discussed later. For measurements in the infrared region, the thick thermal oxide was not necessary; in fact, its presence would complicate the analysis because of the intrinsic infrared light absorption of SiO₂. Thus, the samples for IRSE were prepared directly on native oxide wafers.

Recently, spectroscopic ellipsometry has found useful applications in the structural analysis of thin membranes where it was shown to be able to accurately determine thicknesses, refractive indices, lateral homogeneity, as well as in-situ behavior of the thin separating layers deposited directly on top of various porous supports (polymeric and inorganic)^{34,35,37}. Here, for the first time, we have extended the applicability of the technique to the analysis of thin-film composite carbon membranes. As seen in Figure 2b, the UV-VIS ellipsometry spectra (red and green lines in the graphs) show a high sensitivity toward the structure of the composite membranes. For a bare support, the spectra show the so called optical envelopes, almost horizontal lines, and their positions allow for a precise determination of a useful membrane structural parameter: surface porosity (void volume fraction within the dense aluminum oxide matrix). In the presence of the precursor film the spectral oscillations emerge as a result of the polarized light interference. The amplitude and wavelength of the spectral oscillations are directly related with the film thickness and its refractive index. Detailed ellipsometry modeling showed that the substrate porosity was not affected by the deposition of the thin precursor skin, which strengthened the evidence provided by the SEM for virtually non-intruded substrate pores, Figure 1b. Upon polyimide pyrolysis, various chemical reactions take place such as removal of CO, CO₂, H₂ or N₂⁴¹. This leads to a progressive collapse of the structure, enrichment in carbon element, and increasing degree of conjugation yielding an amorphous turbostratic molecularly sieving structure^{7,42,43}. The increased degree of conjugation (partial graphitization) is accompanied by a dramatic change in the optical properties. In particular, the films became strongly absorbing in the visible and near infrared regions (370 nm up to ~1000 nm), Figure 1c, and the spectral oscillations necessary to determine the film thickness start disappearing. However, at least up to 650 °C on Anodisc® substrates, and due to much lower (< 100 nm) film thickness up to 1000 °C on silicon wafers, the films still remain transparent enough to observe oscillations in the spectral range of 1000 – 1690 nm. The increasing conjugation also leads to a sharp increase in the electrical conductivity reflected in the development of the strong near infrared optical absorption, as shown in Figure S1 (Supporting Information) where the data were extracted in a separate analysis using a B-Spline optical model³⁶.

Upon the deposition of the defect-plugging PDMS (which is optically transparent over the entire used wavelength range) the superposition of PDMS-related oscillations with the residual carbon film oscillations occurs. This superposition presents the possibility to determine the thickness of the PDMS layer covering the underlying carbon selective membrane skin. The knowledge of the respective layer thicknesses in the composite is crucial for the accurate determination of the permeability of the pyrolyzed carbon films using the resistance-in-series model, as discussed later.

Extending the ellipsometry analysis to the infrared region (IRSE), Figure 2c, reveals a dramatic change in the vibrational spectra as a result of pyrolysis. Remarkably, already at 550 °C the imide-associated carbonyl stretching feature around 1750-1675 cm⁻¹ reduces very significantly and at 600 °C it disappears completely yielding a relatively featureless spectrum typical to a turbostratic, highly conjugated carbon matrix. Similar findings were reported previously in bulk carbon molecular sieves derived from Matrimid⁴⁴. Above about 650 °C an additional vibrational band around 1265 cm⁻¹ appears. This vibration is attributed to a gradual growth of silicon oxide (up to about 25 nm at 1000 °C) on the surface of the silicon wafer. This growth is most probably fed by the small presence of oxygen in the pyrolysis furnace and facilitated by a partial exposure of the wafer surface by the degrading film (as discussed later and seen in Figure 4d).

3.2. Pyrolysis-induced volume or thickness collapse in PIM and non-PIM thin (~300 nm) and bulk (> 70 μm) films

The focus of this section is to elucidate the differences in the pyrolysis-related collapse of thin (~300 nm) and thick (> 70 μm) carbon films made from two different polyimide precursors, Figure 3a. The PIM-polyimide, SBFDA-DMN (Figure 1a, top), is characterized by a highly contorted, rigid aromatic structure, undetectable glass transition temperature, T_g , apparent BET surface area of 686 m² g⁻¹, and a high carbon element content (84% w/w). In particular, the high carbon content suggests a good starting point for a carbon molecular sieve as the amount of heteroatoms removed during the pyrolysis is comparatively low, leading potentially to a limited structural collapse and better mechanical properties. In contrast, the non-PIM polyimide, 6FDA-DABA (Figure 1a, bottom), is a standard, high performance glassy polymer with a T_g of about 375 °C (based on ref⁴⁵), absent microporosity, and a lower carbon element content (56% w/w). 6FDA-DABA and/or co-polymers containing its repeating units have also been used as CMS precursors before^{46,47}.

Figure 3. (a) Chemical structures of the polymer precursors (top PIM – SBFDA-DMN, bottom non-PIM – 6FDA-DABA) together with their corresponding molecular dynamics-derived random coil configurations; (b) volume shrinkage of the bulk and thin film (~300 nm) precursors as a result of pyrolysis; error bars for thin films were estimated from an analysis of the fit uniqueness by considering the 25% improvement of the fit quality by varying the respective thickness parameters while keeping the other parameters fixed; for the bulk an uncertainty of 5% was assumed (c) pyrolysis-induced structural collapse of the PIM (top) and non-PIM (bottom) thin film precursors; (d) top view optical images of the PIM thin films deposited on a Si wafer after pyrolysis at several different temperatures. The illumination conditions kept exactly the same.

As expected, the TGA-derived weight loss of the non-PIM powder sample was much larger as compared to the PIM with residual masses of 47 and 73% at 800 °C, respectively (Figure S2 in the Supporting Information). The same trend was observed for thick film samples with the respective weight losses of 61 and 78%, respectively. The slight discrepancy, particularly for the non-PIM, between the powder TGA and thick film samples could be related to a different surface to volume ratio in the powder and the thick films which might influence the outward diffusion of the gaseous pyrolysis products leading to different residual masses.

Figure 3b shows a comparison between the volume collapse of the thin and bulk, PIM and non-PIM films. The relative volume for the thin films was calculated directly from the ellipsometry-derived film thicknesses, as $L_{\text{pyrolyzed}}/L_{\text{pristine}}$. This is justified because the lateral confinement to the substrate forces the entire volumetric shrinkage to occur only in the direction perpendicular to the substrate³⁸. For the bulk films the volumes are calculated directly from the sample geometry by multiplying the film thickness

(measured at several locations with a micrometer screw) and its area (interpolated using an optical scanner and image processing software). A striking difference between the PIM and non-PIM polyimides can be observed. While almost no difference between the thin and bulk for the non-PIM is seen, the discrepancy between the thin and bulk PIM is very large. The thin PIM seems to collapse to a larger extent as compared with the bulk PIM with the residual film volumes of 53 and 74% at 800 °C, respectively. We believe, that this large difference is a direct consequence of the intrinsic microporous nature of the PIM. The presence of the micropores, especially in the larger range between ~ 7 and 20 Å allows for a much greater collapse in the thin PIM films. This effect is similar to dramatically accelerated physical aging which is known to proceed at much higher rates in thinner, supported films^{45,48}, and is also typically enhanced for polymers containing larger excess fractional free volumes (PIMs vs. non-PIMs). The non-PIM polyimide does not show this effect mainly due to the absence of the micropores, which inhibits the dramatic structural collapse, Figure 3c. In this context it is, therefore, possible to view the pyrolysis process as intimately related or coinciding with the structural changes typical to physical aging. This hypothesis will become relevant later where the performance of the thin-film carbon composite membranes with different thicknesses is presented.

As discussed in the previous section, the pyrolysis process leads to pronounced, progressive changes in the optical properties of the obtained carbon films. This is displayed in the top-view optical microscope images shown in Figure 3d. With increasing pyrolysis temperature the films become paler. This is a result of both increasing light absorption in the visible range and reducing film thickness due to the structural collapse (from the initial ~ 300 nm for the pristine material down to less than 100 nm for the film pyrolyzed at 1000 °C). X-ray photoelectron spectroscopy analysis (Supporting Information) showed that at the pyrolysis temperature of 500 °C very little chemical changes occurred as compared with the pristine material. However, starting from 600 °C and going toward higher pyrolysis temperatures, very dramatic transformation of the material took place. First, a new shoulder appeared in the C 1s peak at around 286.2 eV whose intensity increased with temperature. Second, the C 1s component measured at 288.2 corresponding to the N-C=O group reduced with temperature accompanied with a slight shift and broadening toward higher binding energies. These observations suggest the occurrence of decarboxylation reactions near the imide groups which may result in the creation of new C-O bonds (typically C-O, C=O, O-C=O) and overall an increased structural conjugation. In particular, this last effect was anticipated in CMS materials together with the observed increase in the C element content. Also starting from the pyrolysis temperature of 600 °C, nitrogen element content markedly reduced and an additional peak at a slightly lower binding energy of 398.7 eV appeared next to the imide-associated one at 400.0 eV. The additional, weaker peak likely indicated some degree of incorporation of N element into the aromatic

conjugated carbon structure. This has been previously reported in similar pyrolyzed N-containing materials based on polyacrylonitrile^{49,50}.

For all pyrolysis temperatures, as well as for the pristine films, occasional defects on a scale of tens of microns were observed. We found these defects unavoidable despite careful solution filtration, which further signified the necessity of the PDMS-overcoat for the films deposited on the porous Anodics®. In addition, at the highest pyrolysis temperatures of 900 and 1000 °C (shaded region in Figure 3b) thin PIM films produced highly rough and defective films (see also Figure S8 in the Supporting Information). We attribute these morphological changes to partial film dewetting driven by the difference between the surface energies of the film and substrate⁵¹. The dewetting is known to occur in amorphous films at conditions allowing for a viscous flow of the material and is facilitated by the stress exerted upon the film⁵². Such conditions may occur as a result of the high thermal stress during pyrolysis. No similar surface features were found in the thick films which points to yet another important difference between thin and bulk carbon membranes that needs to be considered for their practical applicability.

In one of the earlier studies on graphitizing of polyimide carbon precursors Hatori et al⁵³ reported the development of uniaxial anisotropy in thicker ($< 10\ \mu\text{m}$) precursor films by means of analyzing the optical birefringence, Figure 4a. The authors observed both a very strong influence of the substrate, with supported films showing an order of magnitude larger birefringence, and a relatively strong effect of film thickness with thinner films displaying larger degrees of polymer chain orientations. Owing to its measuring principle spectroscopic ellipsometry has previously been used to determine the optical birefringence or anisotropy^{33,54–57}. Here, the capabilities of the technique have been further amplified by the use of the 500 nm silicon oxide present directly underneath the precursor/carbon films. An uniaxial anisotropic optical model assuming $n_x = n_y = n_{xy} \neq n_z$ was used as justified by a typical tendency of supported films of rigid polymers to be optically uniform in the x-y direction (substrate plane) possessing, however, a different refractive index, usually lower, in the perpendicular direction. Such properties are a result of the natural orientation of the rigid polymer chains guided by the substrate presence. Figure 4b shows the results of the uniaxial optical modeling of the PIM thin films with the more sensitive UV-VIS ellipsometry over the entire pyrolysis temperature range. Almost exactly the same trend could be reproduced with IRSE optical modeling (Supporting Information, Table S1). Above 700 °C due to the severe changes in the optical properties (particularly development of the broad absorption peaks in the NIR) IRSE modeling proved challenging. A quick increase in the degree of anisotropy ($n_{xy} - n_z$, right Y-axis) is seen starting from essentially isotropic, non-oriented precursor up to a sharp maximum at 700 °C. Increasing the pyrolysis temperature beyond 700 °C leads to a reduction of the respective n_{xy} and n_z values as well as a slight reduction in $(n_{xy} - n_z)$. This is attributed to the development of defects and film

dewetting, as discussed earlier. Apparently, at around 700 °C the development of internal film orientation along the substrate seems to be maximized and balanced against the subsequent film deterioration. The emergence of the carbon film orientation is a result of the microscopic molecular structure of the carbon molecular sieve, which comprises graphite-like sheets able to form stacks, Figure 4c. The development of such stacks occurs with a simultaneous pyrolysis-induced collapse, which is guided by the presence of the substrate to occur in the perpendicular direction, Figure 4d. This leads to a preferential orientation of the stacked structure in the plane of the substrate and explains the development of the optical anisotropy with $n_{xy} > n_z$ as the electron polarizability (related to delocalized electron clouds of the graphite-like sheets) along the x-y plane oriented stacks is much higher than in the z direction. The developing oriented stacking as a result of volumetric contraction has recently been studied in detail in slightly similar rigid polyimide systems⁵⁸. The oriented structural arrangement may have potential implications on the membrane performance, especially in terms of the physical aging process. Previously, it has been hypothesized that a similar structure may form at the interface of thin skin carbon hollow fibers as a result of a “house of cards” collapse leading to unusually low permeances of the obtained membranes⁶. This hypothesis is examined further in the context of the gas separation performance.

Figure 4. (a) Optical birefringence in thick Kapton-type polyimide-derived carbon films as well as a SEM micrograph of the cross-section of the supported film (PI-ON); reproduced with permission from Hatori et al⁵³; (b) refractive index in (n_{xy}) and out of plane (n_z) of the substrate as well as the difference ($n_{xy} - n_z$) plotted as function of pyrolysis temperature for the PIM-based carbon thin films (~300 nm pristine film

thickness) deposited on silicon wafer; error bars were estimated from an analysis of the fit uniqueness by considering the 25% improvement of the fit quality by varying the respective refractive index parameters while keeping the other parameters fixed; (c) molecular dynamics-derived microstructure of an exemplary turbostratic carbon morphology with highlighted stacking of the graphite-like flakes; (d) change in the thin carbon film morphology as a result of a unidirectional collapse guided by the presence of the substrate leading to the development of optical anisotropy.

3.3. Gas separation performance of the thin-film carbon molecular sieve membranes

Figure 5a and b show the permeabilities and ideal selectivities of the unaged (< 1 day old) ~1 micron thick PDMS-covered thin-film composite carbon membranes prepared from the PIM polyimide. The permeabilities of the carbon films were calculated using the resistances-in-series model utilizing the thicknesses of the respective layers determined with ellipsometry (expressed in microns), measured permeance of the whole membrane (in GPU) and permeability of the same thickness PDMS film determined separately on PDMS-coated Anodisc® membranes. The more detailed calculation scheme is shown in Figure S3 in the Supporting Information. Figure 5c and d show the bulk and ~1 micron permeability/selectivity data for the PIM polyimide carbons plotted on trade-off diagrams for two most relevant gas pairs, CO₂/CH₄ and O₂/N₂. Here, only the trajectories are shown which connect all points, from the pristine to the highest pyrolysis temperatures, 800 °C for the ~1 micron and 900 °C for the bulk, respectively. Full data sets for those and additional gas pairs are shown in Figure S5 in the Supporting Information.

It is important to note that the discrepancy in the selectivities calculated directly from the membrane permeance (expressed in GPU) and from the back-calculated CMS permeabilities (using resistances-in-series model, expressed in barrer) was relatively small, at most ~15% (in most cases much less), which follows directly from the mathematical formulation of the resistances-in-series model. The reason is the much higher permeability of PDMS for all analyzed gases as compared to the CMS layer, and the comparable PDMS and CMS thicknesses. For example, for one membrane sample pyrolyzed at 700 °C the selectivities were O₂/N₂ 6.2, CO₂/CH₄ 49.2, CO₂/N₂ 36.7, H₂/CO₂ 0.82, N₂/CH₄ 1.34, H₂/N₂ 30.0, H₂/CH₄ 40.3 when calculated from permeabilities (He 68.7, H₂ 186.3, N₂ 6.2, O₂ 38.6, CH₄ 4.6, CO₂ 227.7, all barrer). In turn, the selectivities were O₂/N₂ 6.1, CO₂/CH₄ 47.3, CO₂/N₂ 35.7, H₂/CO₂ 0.7, N₂/CH₄ 1.3, H₂/N₂ 25.8, H₂/CH₄ 34.2 when calculated from permeances (He 59.4, H₂ 152.3, N₂ 5.9, O₂ 35.8, CH₄ 4.45, CO₂ 210.7, all GPU). Table 1 lists the ellipsometry-derived (5 spots averages on 13 mm diameter membranes) thicknesses of all studied CMS layers as well as the PDMS overcoats.

Table 1. CMS and PDMS Membrane Layer Thicknesses for All Samples Used in This Study (the standard deviation from five spots on the membrane surface (13 mm diameter disc) was always <17 %

both in the case of the CMS layer and PDMS layer. In some cases, PDMS layer thickness is given as an estimate assuming that it would be similar because of following the same deposition protocol as for other samples where it was measured accurately).

Membrane	Thickness CMS layer [nm]	Thickness PDMS layer [nm]
Pristine Thick	1450	~600
Pristine Thick	1500	~600
500 °C Thick	1292	~600
500 °C Thick	1455	~600
550 °C Thick	1257	~600
550 °C Thick	1080	~600
600 °C Thick	1313	580
600 °C Thick	1458	602
650 °C Thick	936	691
650 °C Thick	1326	824
700 °C Thick	1035	472
700 °C Thick	1155	952
750 °C Thick	1109	448
750 °C Thick	986	821
800 °C Thick	927	705
Pristine Thin	296	~900
Pristine Thin	300	~900
500 °C Thin	352	~600
500 °C Thin	290	~600
600 °C Thin	200	735
600 °C Thin	199	~600
700 °C Thin	215	1100
700 °C Thin	205	615
800 °C Thin	135	~900
800 °C Thin	140	~900

The pristine PIM showed a typical reverse selective behavior with the $P_{CO_2} > P_{He}$ and $P_{CH_4} > P_{N_2}$ which is a consequence of the higher condensability of CO₂ over He and CH₄ over N₂ causing the transport to be dominated by solubility effects rather than the diffusivity. With increasing pyrolysis temperature the

permeabilities start to reduce which is a consequence of the developing progressively tighter carbon molecular sieve structure. At the same time, the molecular sieving character develops and at 800 °C the membranes become strongly size discriminating with the permeabilities following the kinetic diameters, d , of the gas molecules. An exception to that trend is observed for H_2 and He, with $P_{H_2} > P_{He}$ despite $d_{H_2} > d_{He}$ which is probably a consequence of some solubility contribution of the more condensable H_2 ($T_{k,H_2} = 33.2$ K, $T_{k,He} = 5.2$ K). A weak maximum for H_2 and He at 750 °C resembles the behavior reported earlier for $\sim 0.8 - 2$ μm CMS membranes^{23,25} and suggests a slight opening up of the structure at around 700 - 750 °C albeit, remarkably, only with respect to the smallest gases. The trend for the larger gases remains virtually unaffected and as a result the H_2/N_2 and H_2/CH_4 selectivities start sharply increasing. Interestingly, in the intermediate pyrolysis temperature region between 500 and 600 °C both permeabilities and selectivities seem to plateau despite the relatively large volume collapse accompanying those early stages of pyrolysis (Figure 3b, relative volumes of 94 and 70% for 500 and 600 °C, respectively). While in the bulk an opening up of the structure around 600 °C is clearly observed both from the gas permeation data (increase in permeabilities) and from the BET analysis (Supporting Information), this trend was not visible in thin films. It seems that for the thin PIM polyimide carbons in this temperature region the structural collapse and the free volume opening concurrent with the expulsion of CO and CO₂ balance each other to some extent and the permeabilities/selectivities for all gases remained largely unaffected. On the contrary in the bulk, where the collapse is significantly smaller, Figure 3b, but the expulsion of the volatiles still occurs to a similar extent (the same pyrolysis temperatures), the permeabilities and selectivities recorded a significant boost and shift past the upper bounds toward the attractive top-right region. This exemplifies a *strikingly* distinct behavior of the thin and bulk PIM polyimide-derived carbon membranes directly related to the different magnitude of the relative micropores collapse in the thin and bulk samples.

Surprisingly, comparing the behavior of bulk PIM- and non-PIM-derived carbon membranes it can be noticed that the performances do not show clear systematic trends, Figure S6a and b in the Supporting Information. The same seems valid upon comparison of the ~ 1 micron PIM- and non-PIM-derived thin-film composites, Figure S6c and d in the Supporting Information. All performance data seem to be positioned in a similar region of the tradeoff diagrams, which suggests approximately the same microscopic carbon molecular sieve structure regardless of the precursor chemistry.

Figure 5. Permeabilities (a) and ideal gas-pair selectivities (b) of ~1 micron thick carbon thin film composite membranes prepared from the PIM-polyimide as a function of the pyrolysis temperature; the development of a strongly size sieving structure is demonstrated by the gas permeability sequence at the highest pyrolysis temperature (800 °C) which follows the gas molecular size; in contrast, the pristine PIM is reverse selective ($P_{CO_2} > P_{H_2}$, $P_{CH_4} > P_{N_2}$). Each point represents an average of two membrane samples measured separately. Error bars are omitted for clarity of presentation. The difference in the performance between the two separate samples was always below 15-20%. Subfigures (c) and (d) show a comparison of the trade-off trajectories for bulk and thin film PIM-derived carbon membranes (maximum pyrolysis temperature of 900 °C for the bulk and 800 °C for the thin film). Bulk data are from ref. 58.

Reducing the selective layer thickness is broadly viewed as one of the most important and viable strategies to enhance the membrane permeance enough to assure sufficiently high mass transport for an industrial setting. Figure 6 shows the effect of a 5-fold reduction of the PIM polyimide carbon film thickness from ~1 micron to ~0.2 micron at pyrolysis temperatures in the range of 500 to 700 °C. In all cases the thickness reduction is accompanied by a significant reduction in permeability indicating the creation of tighter carbon molecular sieve structures. The permeability decrease is roughly similar to the thickness reduction effectively producing membranes with a similar or slightly lower permeance yet with a similar selectivity. This effectively eradicates the potential benefit of the thickness reduction on the

membrane productivity. Our findings are in remarkable support of the work of Sanyal et al.⁶ who suggested the development of highly compacted low selectivity carbon hollow fiber skin extending for several hundreds of nm leading to severe losses of permeability while maintaining similar selectivities. At the highest pyrolysis temperature of 700 °C, however, the decrease in permeability was also accompanied with an increase in selectivity which in some cases was quite significant *e.g.* H₂/N₂ or CO₂/N₂. We note here that at this particular pyrolysis temperature a maximum in the degree of in-plane orientation was observed, Figure 4b. It is suggested that the development of the in-plane orientation within the supported carbon structure may somehow be conducive to an increase in selectivity although the exact mechanism would require a further dedicated study possibly with the utilization of even more molecular ordering-sensitive experimental techniques (*e.g.* XRD). Remarkably, for the non-oriented carbons developed at 500 and 600 °C such a beneficial effect on the selectivity was not observed.

It is worth noting, that attempts were made to prepare thin-film composite carbon membranes with thickness even thinner than ~0.2 micron. However, in this range the membranes could not be repaired by the PDMS overcoat. The possible reason is shown in Figure S7 in the Supporting Information where the AFM tapping-mode topology surface maps indicate the formation of comparatively large scale (relative to the film thickness) defects for films below about 150 nm. We hypothesize that the structural instability of the extremely high aspect ratio films subjected to the pyrolysis-related stresses prevented the preservation of film consistency below about 0.2 μm film thickness. Efforts are underway to circumvent this problem and develop a method to study even thinner carbon molecular sieves that would potentially allow for attractive gas permeances.

Figure 6. The influence of a 5-fold film thickness reduction from ~ 1 micron to ~ 0.2 micron on the permeability/selectivity behavior of PIM-derived thin film carbon membranes presented on two trade-off diagrams; the arrows point from thicker to thinner films and the colors indicate the pyrolysis temperatures. Additional data are shown in the Supporting Information. In each case, two separate membrane samples are shown to better represent the data reproducibility and measurement uncertainties.

Finally, the effect of the physical aging on the behavior of the PIM polyimide-derived thin films of both ~ 1 and ~ 0.2 micron thickness is discussed, Figure 7. Upon aging for 30 days at 50°C an expected decrease in permeability is observed. Remarkably, the aging effect and the thickness effect seem to superimpose very well on a single trend line, Figure 7a. This essentially implies an equivalency between the physical aging and thickness reduction. Alternatively, the observation suggests that the thinner carbon films were already significantly pre-aged as compared with the thicker ones in the pyrolysis process itself. Given the observed behavior, where the permeability dropped significantly while the selectivity changed little or not at all (Figure 7a), we propose that the structural changes most likely affected the larger micropores in the range of $7 - 20 \text{ \AA}$, Figure 7b. This is related to the progressive collapse of the voids separating the stacked graphite-like sheets. On the other hand, the size-sieving ultramicropores formed by the stacked sheets themselves were little affected which translates into the largely preserved selectivity.

Figure 7. (a) Impact of the reduction of film thickness and physical aging on the performance of the thin-film composite carbon membranes derived from the PIM precursor together with possible changes in the pore size distribution, schematically suggested in (b) with indicated aging and thickness reduction impact. Similar to Figure 6, we show data for both analyzed membrane samples in each pair.

4. Conclusions

Ultra-thin composite carbon membranes (CMS) were fabricated on well-defined porous inorganic substrates using a novel polyimide polymer of intrinsic microporosity (PIM) as precursor. Comprehensive characterization of the obtained films was enabled by a combined use of UV-VIS and IR spectroscopic ellipsometry. The pyrolytic collapse in a thin film PIM precursor was found to lead to a much larger volume contraction than in a non-PIM thin film, which is consistent with the larger excess free volume fraction in the PIM. The combination of the pyrolytic stress and dewetting led to a breakdown of the film integrity above about 900 °C pyrolysis temperature which was not observed in the bulk CMS membranes. The developing turbostratic structure of a carbon membrane was shown to be significantly oriented by the proximity of a substrate. The degree of orientation increased with increasing pyrolysis temperature and correlated with slight increases in membrane selectivities.

The gas separation properties of the CMS membranes were positioned at or above the polymeric trade-off lines for a majority of technologically important gas pairs with notable but subtle dissimilarities between the thin and bulk, which were traced back to the relative differences in the pyrolysis-induced collapse. Reducing the skin thickness significantly below ~ 1 micron was found to quickly lead to large permeability losses without or only with very modest gains in selectivity. Remarkably, the effects of skin thickness reduction and physical aging on the gas separation performance could be superimposed onto the same trends which explains and corroborates some of the data measured before on carbon hollow fiber

CMS membranes. Unless this hurdle is overcome by some additional structural modifications or post-treatments we currently see little benefit in reducing the CMS membrane skin thickness much below ~ 1 micron as the challenges (physical aging, defect control) seem not to be balanced well against gains in productivity.

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6. Supporting Information

Supporting information is available.

7. References

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TOC graphic: