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جامعة الملك عبدالله
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King Abdullah University of
Science and Technology

Advanced Membranes and Porous Materials Center

Ultra-Thin Microporous Membranes Studied with In-Situ Spectroscopic Ellipsometry

Autoreferat

Wojciech Ogieglo, PhD

Field: exact and natural sciences

Discipline: chemical sciences

Thuwal 2022

1. Personal data

Name and surname: **Wojciech Ogieglo**

Current employer: Functional Polymer Membranes Group
Advanced Membranes and Porous Materials Center (AMPMC)
King Abdullah University of Science and Technology (KAUST)
23-955, Thuwal, Kingdom of Saudi Arabia

2. Information about obtained diplomas and degrees

03.2014	**Ph.D. in chemical engineering** The University of Twente, Faculty of Science and Technology Enschede, The Netherlands Ph.D. Thesis title: “In-situ spectroscopic ellipsometry for studies of thin films and membranes” Promotor: Prof. Dr.-Ing. Matthias Wessling Co-Promotor. Prof.dr.ir. N.E. Benes **Ph.D. with honors** (*cum laude*, top 5%), defense 21.03.2014
09.2009	**M.Sc. Double Degree** in a) Technology of polymers Cracow University of Technology, Department of Chemical Engineering and Technology Cracow, Poland **M.Sc. with distinction** b) Applied Chemistry Münster University of Applied Sciences, Department of Chemical Engineering Steinfurt, Germany **M.Sc. with distinction**

	M.Sc. Thesis title: “Investigation of interactions between ultraviolet laser beam and polymer matrices with a use of Total Organic Carbon and Laser Ablation ICP-MS” Promotor: Prof. dr. hab. inż. Jan Pielichowski Promotor: Prof. Dr. rer. nat. Martin Kreyenschmidt

3. Information on previous employment in scientific institutions

07.2022 – present	**Research Scientist (R4*)** Functional Polymer Membranes Group, Advanced Membranes and Porous Materials Center (AMPMC), King Abdullah University of Science and Technology (KAUST), Kingdom of Saudi Arabia
09.2017 – 06.2022	**Research Scientist (R3*)** Functional Polymer Membranes Group, Advanced Membranes and Porous Materials Center (AMPMC), King Abdullah University of Science and Technology (KAUST), Kingdom of Saudi Arabia
03.2015 – 06.2017	**Postdoctoral Researcher** DWI Leibniz Institute for Interactive Materials, Aachen, Germany
01.2014 – 02.2015	**Postdoctoral Researcher** University of Twente / Institute for Sustainable Process Technology (ISPT), the Netherlands

*According to the European Commission**, R3 designation refers to an “Established Researcher” status, characterized by an established reputation based on excellence in her/his field, conduction of independent research, publishing of papers as lead author etc. R4 designation refers to a “Leading Researcher” status, characterized by international reputation in the field, substantial contributions to the research field, recognition of the broader implications and applications of their research, serving on workshop/conferences/committees etc.

It has to be noted, however, that at my institution (KAUST) neither R3 and R4 Research Scientists lead their own research groups but work within a larger group with a full professor as head.

**Source: “Towards a European Framework for Research Careers” European Commission, Directorate General for Research and Innovation (July 2021).

4. Indication of achievements resulting from art. 16 sec. 2 of the Act of 14th of March 2003 on academic degrees and titles as well as degrees and titles in the field of art (Journal of Laws of 2016, item 882, as amended in Journal of Laws of 2016, item 1311) constituting the basis for habilitation

a) Title of scientific/~~artistic~~ achievement

Ultra-Thin Microporous Membranes Studied with In-Situ Spectroscopic Ellipsometry

b) A list of scientific publications constituting the basis for habilitation proceedings

The list includes 14 publications from the Journal Citation Report (JRC)

[H1] Raaijmakers, M.J., ***Ogieglo, W.,*** Wiese, M., Wessling, M., Nijmeijer, A. and Benes, N.E., 2015. *Sorption behavior of compressed CO_2 and CH_4 on ultrathin hybrid poly (POSS-imide) layers*. ACS applied materials & interfaces, 7(48), pp.26977-26988.

My contribution: development of the experimental procedure, development and validation of optical models for complex, multilayer porous layers, data analysis, writing of the original draft. **Contribution to authorship: 50 %**

IF_{2020} = 10.38, MSHE = 200, Cited (Oct. 2022) 15 times (WoS), 13 times (Scopus)

[H2] Chae, I.S., Luo, T., Moon, G.H., ***Ogieglo, W.,*** Kang, Y.S. and Wessling, M., 2016. *Ultra-high proton/vanadium selectivity for hydrophobic polymer membranes with intrinsic nanopores for redox flow battery*. Advanced Energy Materials, 6(16), p.1600517.

My contribution: development of the experimental procedure for the in-situ determination of thin selective layer properties without the need for its isolation form the porous substructure, data analysis and interpretation. **Contribution to authorship: 30 %**

IF_{20201} = 29.7, MSHE = 200, Cited (Oct. 2022) 99 times (WoS), 98 times (Scopus)

[H3] ***Ogieglo, W.,*** Ghanem, B., Ma, X., Pinnau, I. and Wessling, M., 2016. *How much do ultrathin polymers with intrinsic microporosity swell in liquids?* The Journal of Physical Chemistry B, 120(39), pp.10403-10410.

My contribution: sample preparation, development of the experimental procedure and custom instrumentation, data analysis and theoretical interpretation, data processing, writing of the original draft, final editing, response to reviewers' comments. **Contribution to authorship: 80 %**

IF_{2020} = 3.466, MSHE = 140, Cited (Oct. 2022) 18 times (WoS), 15 times (Scopus)

[H4] ***Ogieglo, W.,*** Furchner, A., Ghanem, B., Ma, X., Pinnau, I. and Wessling, M., 2017. *Mixed-penetrant sorption in ultrathin films of polymer of intrinsic microporosity PIM-1.* The Journal of Physical Chemistry B, 121(43), pp.10190-10197.

My contribution: conceptualization, methodology development and validation, sample preparation, development of custom instrumentation, data collection and data analysis, theoretical interpretation, writing of the original draft, final editing, response to reviewers' comments. **Contribution to authorship: 75 %**

IF_{2020} = 3.466, MSHE = 140, Cited (Oct. 2022) 9 times (WoS), 5 times (Scopus)

[H5] ***Ogieglo, W.,*** Rahimi, K., Rauer, S.B., Ghanem, B., Ma, X., Pinnau, I. and Wessling, M., 2017. *How do organic vapors swell ultrathin films of polymer of intrinsic microporosity PIM-1?* The Journal of Physical Chemistry B, 121(29), pp.7210-7220.

My contribution: methodology development and validation, sample preparation, data collection and data analysis, theoretical interpretation, writing of the original draft, final editing, response to reviewers' comments. **Contribution to authorship: 75 %**

IF_{2020} = 3.466, MSHE = 140, Cited (Oct. 2022) 20 times (WoS), 16 times (Scopus)

[H6] ***Ogieglo, W.,*** Ghanem, B., Ma, X., Wessling, M. and Pinnau, I., 2018. *High-pressure CO_2 sorption in polymers of intrinsic microporosity under ultrathin film confinement*. ACS applied materials & interfaces, 10(13), pp.11369-11376.

My contribution: methodology development and validation, sample preparation, data collection and data analysis, theoretical interpretation, writing of the original draft, final editing, response to reviewers' comments. **Contribution to authorship: 75 %**

IF_{2020} = 10.38, MSHE = 200, Cited (Oct. 2022) 16 times (WoS), 13 times (Scopus)

[H7] ***Ogieglo, W.,*** Pinnau, I. and Wessling, M., 2018. *In-situ non-invasive imaging of liquid-immersed thin film composite membranes*. Journal of Membrane Science, 546, pp.206-214.

My contribution: conceptualization, setup adaptation, customization of the apparatus, data analysis development and validation, data processing, data analysis, writing of the original draft, final editing, response to reviewers' comments. **Contribution to authorship: 90 %**

IF_{2020} = 8.742, MSHE = 140, Cited (Oct. 2022) 11 times (WoS), 3 times (Scopus)

[H8] ***Ogieglo, W.,*** Furchner, A., Ma, X., Hazazi, K., Alhazmi, A.T. and Pinnau, I., 2019. *Thin composite carbon molecular sieve membranes from a polymer of intrinsic microporosity precursor*. ACS applied materials & interfaces, 11(20), pp.18770-18781.

My contribution: development of sample preparation and characterization procedure, conduction of gas separation experiments, data processing, non-destructive determination of selective layer thicknesses, data analysis and interpretation, writing of the original draft, final editing, response to reviewers' comments. **Contribution to authorship: 75 %**

IF_{2020} = 10.38, MSHE = 200, Cited (Oct. 2022) 25 times (WoS), 20 times (Scopus)

[H9] Ali, Z., Ghanem, B.S., Wang, Y., Pacheco, F., ***Ogieglo, W.,*** Vovusha, H., Genduso, G., Schwingenschlögl, U., Han, Y. and Pinnau, I., 2020. *Finely Tuned Submicroporous Thin-Film Molecular Sieve Membranes for Highly Efficient Fluid Separations.* Advanced Materials, 32(22), p.2001132.

My contribution: development of novel sample characterization technique including topological mapping, data analysis and processing, data interpretation, draft editing. **Contribution to authorship: 30 %**

IF_{20201} = 30.85, MSHE = 200, Cited (Oct. 2022) 37 times (WoS), 34 times (Scopus)

[H10] ***Ogieglo, W.,*** Genduso, G., Rubner, J., Hofmann-Préveraud de Vaumas, J., Wessling, M. and Pinnau, I., 2020. *CO_2/CH_4 pure-and mixed-gas dilation and sorption in thin (～500 nm) and ultrathin (～50 nm) polymers of intrinsic microporosity*. Macromolecules, 53(20), pp.8765-8774.

My contribution: conceptualization, methodology development and validation, sample preparation, data collection and data analysis, theoretical interpretation, writing of the original draft, final editing, response to reviewers' comments. **Contribution to authorship: 70 %**

IF_{2020} = 5.985, MSHE = 140, Cited (Oct. 2022) 9 times (WoS), 9 times (Scopus)

[H11] ***Ogieglo, W.,*** Idarraga-Mora, J.A., Husson, S.M. and Pinnau, I., 2020. *Direct ellipsometry for non-destructive characterization of interfacially-polymerized thin-film composite membranes.* Journal of Membrane Science, 608, p.118174.

My contribution: conceptualization, setup adaptation, data analysis development and validation, data processing, data analysis, writing of the original draft, final editing, response to reviewers' comments. **Contribution to authorship: 60 %**

IF_{2020} = 8.742, MSHE = 140, Cited (Oct. 2022) 8 times (WoS), 7 times (Scopus)

[H12] ***Ogieglo, W.,*** Puspasari, T., Hota, M.K., Wehbe, N., Alshareef, H.N. and Pinnau, I., 2020. *Nanohybrid thin-film composite carbon molecular sieve membranes.* Materials Today Nano, 9, p.100065.

My contribution: conceptualization of the vapor phase infiltration/pyrolysis process in PIMs, methodology development and validation, sample preparation, data collection and data analysis, theoretical interpretation, writing of the original draft, final editing, response to reviewers' comments. **Contribution to authorship: 75 %**

IF_{2020} = 9.6, MSHE = 200, Cited (Oct. 2022) 20 times (WoS), 19 times (Scopus)

[H13] __***Ogieglo, W.,***__ Puspasari, T., Ma, X. and Pinnau, I., 2020. *Sub-100 nm carbon molecular sieve membranes from a polymer of intrinsic microporosity precursor: Physical aging and near-equilibrium gas separation properties.* Journal of Membrane Science, 597, p.117752.

My contribution: methodology development and validation, sample preparation, data collection and data analysis, theoretical interpretation, writing of the original draft, final editing, response to reviewers' comments. **Contribution to authorship: 80 %**

IF_{2020} = 8.742, MSHE = 140, Cited (Oct. 2022) 20 times (WoS), 17 times (Scopus)

[H14] __***Ogieglo, W.,***__ Song, K., Chen, C., Lei, Q., Han, Y. and Pinnau, I., 2021. *Nano-Confinement Effects on Structural Development and Organic Solvent-Induced Swelling of Ultrathin Carbon Molecular Sieve Films.* ACS Applied Materials & Interfaces, 13(18), pp.21765-21774.

My contribution: methodology development and validation, sample preparation, instrument modification, data collection and data analysis, theoretical interpretation, writing of the original draft, final editing, response to reviewers' comments. **Contribution to authorship: 80 %**

IF_{2020} = 10.38, MSHE = 200, Cited (Oct. 2022) 3 times (WoS), 2 times (Scopus)

WoS – Web of Science

MSHE – The Ministry of Science and Higher Education

Summary

Publications constituting the ***habilitation achievement*** are characterized by the following bibliometric parameters (Oct. 2022):

- Total impact factor IF: **154.3** (14 publications)
- Average IF: **11.02 (min. 3.466 – max. 30.85)**
- Total score of MSHE: **2380**
- Average score of MSHE: **170**
- Total citation number (Web of Science/Scopus): **311/321**
- Total citation without self-citations (Web of Science/Scopus): **280/271**
- Range of applicant participation: **min. 30 – max. 90 %**

Overall bibliographic parameters of the author (2012 – Oct 2022):

- H-index: **25** (Google Scholar), **22** (Web of Science), **22** (Scopus)
- H-index (excl. self-citations): **20** (Web of Science), **20** (Scopus)
- Total citation number (Web of Science/Scopus): **1259/1320**
- Total citation number excl. self-citations (Web of Science/Scopus): **1109/1152**

c) Discussion of the scientific/artistic aims of the presented work and achieved results, discussion of their possible application areas

The aim of research carried out as part of habilitation

Our civilization is facing unprecedented climate change challenges related to exponentially increasing anthropogenic greenhouse gas emissions since the industrial revolution. Fossil fuels, which contribute to those emissions, still comprise a very significant part of the energy generation mix, especially in developing countries. Increasing industrialization leading to improved standards of living will inevitably contribute to increasing global energy demands. To reduce the burden on the natural environment new energy-efficient technologies are required as part of the long-term solution. An area with a large potential for improvement is industrial separation processes which, in developed countries (*e.g.* USA), make up ~half of the energy consumed by the industry. Membrane separation technology is an emerging alternative to the extremely energy-hungry currently employed distillation, absorption, or evaporation techniques and in some cases would enable up to 90% energy savings[1].

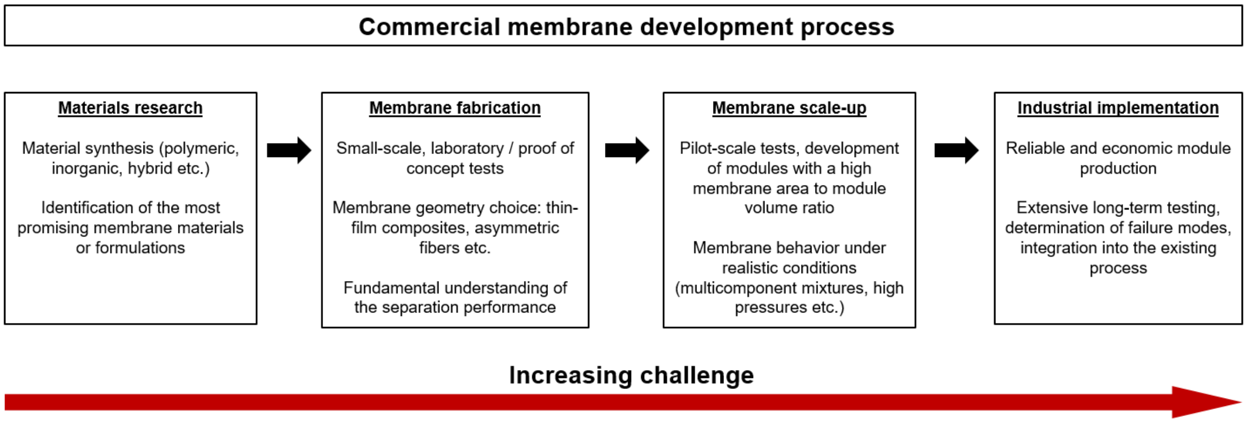

Figure 1 Simplified scheme of a full membrane development process

To compete with the established highly energy-intensive separation techniques, such as those used in carbon capture/natural gas processing, olefin/paraffin separation, or solvent purification, new high-performance membranes are required. These membranes need to possess highly favorable separation performance at the molecular level. To develop those breakthrough membranes, scientific and industrial research usually starts with materials development in the areas of organic or inorganic microporous materials, Figure 1. These include microporous polymers, carbon molecular sieves (CMS), metal organic frameworks (MOFs), hybrid and mixed-matrix materials, and many others. However, finding a suitable membrane material is only the first step in membrane development. A significant technical challenge lies in the translation of the materials' separation properties from thick self-standing films tested in the laboratory into economically viable membranes. This often involves the fabrication of very thin films supported on mechanically and chemically stable substrates that minimize transport resistance to the separated mixture. Unexpectedly, recent research has indicated that materials properties of thick self-standing films often cannot be used to simply extrapolate their behavior down to 2-3 orders of magnitude smaller size scales (~several μm) to reflect properties of practical membranes. This holds true, particularly for the highly promising membrane materials classes such as polymers of intrinsic microporosity (PIMs) or carbon molecular sieves (CMS). This habilitation centers around my efforts to translate the fundamental knowledge of how those promising microporous materials behave upon transformation into thin and ultra-thin membranes that could be applied to real-life, high-impact molecular separation solutions.

My research before obtaining a PhD degree (2010 – 2014)

During my PhD studies, I have extensively studied the combined effects of confining predominantly model macromolecular systems (polystyrene, PS, or polydimethylsiloxane, PDMS) as thin films with the effect of exposure to various fluids. The thicknesses of those model systems were well-positioned within the interest of the membrane community and spanned from as thin as 5 nm up to several micrometers. The research required the development of an entirely new methodology which focused on spectroscopic ellipsometry applied in-situ and in-operando on thin films supported by non-porous and porous supports. The **first breakthrough** was the development and validation of advanced optical models that would allow handling swelling and relaxation phenomena in complex membrane-related systems using spectroscopic ellipsometry. The examples include an optical model of a multilayer thin-film composite membrane structure[2], an anisotropic model allowing morphological studies of zwitterionic layers with strong potential in antifouling applications[3, 4], as well as a two-layer model to track a propagating penetrant front in submicrometer swollen films[5]. Building on top of those innovations, the **second breakthrough** constituted a unique possibility to study a model organic solvent nanofiltration membrane based on PDMS under *n*-hexane permeation at high pressures[6]. This study allowed the unprecedented possibility to quantify the solution-diffusion model contribution to the thickness response of a swollen selective membrane layer under permeation. The **third breakthrough** was the elucidation of penetrant-induced dynamics in PS thin films as a result of compressed CO_2 sorption[7] which resembles dilation relaxation in the vicinity of thermally induced glass transition, T_g. Such penetrant-induced relaxations related to penetrant-induced glass transition, P_g, are to some extent similar to those accompanying the classical thermally-induced T_g, yet different in some subtle aspects. This fundamental study had important consequences on our understanding of membrane swelling dynamics, plasticization, and long-term stability in CO_2-related challenging separations such as carbon capture or natural gas processing.

Discussion of research constituting this habilitation (2015 - 2021)

After my PhD, and building upon the developed expertise, I moved from studying predominantly model polymer systems to much more application-oriented microporous materials classes such as Metal Organic Frameworks (MOFs), hybrid materials based on polyhedral oligomeric silsesquioxane (POSS), polymers of intrinsic microporosity (PIMs), and carbon molecular sieve (CMS) membranes. Simultaneously, I have devoted significant effort to further extend the applicability of in-situ spectroscopic ellipsometry to more complex membrane structures. In the following sections, I will give a more detailed overview of the most important research directions that I have contributed to. This part is divided into three sections:

I. **Advanced in-situ ellipsometry for complex membrane systems**
II. **Polymers of intrinsic microporosity interacting with pure and mixed fluids**
III. **Development of robust and scalable carbon molecular sieve membranes based on polyimides of intrinsic microporosity precursors**

I. Advanced in-situ ellipsometry for complex membrane systems

a) A brief historical background and state of the art of spectroscopic ellipsometry

The introduction of ellipsometric measurement principles is ascribed to Paul Karl Ludwig Drude, Figure 2, who was a German physicist also known for his extraordinary contributions to bringing together electricity and optics at the turn of the 19th and 20th centuries. In particular, the Drude model of electrical conduction has been used to explain the transport properties of electrons in materials (with best-known applications in metallic substances).

Since its inception, ellipsometric systems have developed substantially over the past century with particular acceleration in the last ~20 years due to rapid progress in advanced optical elements (rotating compensators, CCD detectors, light sources, etc.), Figure 2. Currently, available ellipsometry systems cover a probing spectral range from deep, vacuum UV, through near UV-visible-near IR, far IR, and (in non-commercial setups) even micron-mm waves (THz ellipsometry). This allows studies of electronic transitions, band gaps, dielectric constants, metamaterials, as well as chemical characterization of surfaces. More recently, also in-situ (fluids, vacuum, active vapors etc.) as well as mapping capabilities (down to several micrometer special resolution) emerged on the market. Notable further research and development efforts are led by scientists working in the USA, Germany, France, Hungary, Sweden or the Netherlands. Several large companies offer wide portfolios of instruments and expert support (J.A. Woollam, Accurion, SENTECH, Horiba).

Figure 2 (left) A photograph of Paul Drude together with his original ellipsometer used at the University of Leipzig (right) examples of ellipsometers currently used to study optical properties of matter at a variety of wavelength ranges

b) Principles of in-situ spectroscopic ellipsometry – data acquisition and optical modeling

Ellipsometry is a very sensitive optical technique that utilizes a change in the polarization state of light reflected from a surface or a thin film on a substrate. Typically, the probing light is linearly polarized with equal contributions from *p* (in-plane) and *s* (out-of-plane) electrical field components. Upon reflection from a sample, the *p* and *s* components are affected differently and produce, in general, an elliptic polarization, Figure 3a. This particular shape of the reflected polarization representation is the origin of the name of the technique and the parameters describing ellipticity are measured by the detector system. Either monochromatic or spectroscopic light can be used, however, virtually all modern systems utilize the latter due to much larger measured data space which greatly increases accuracy. This habilitation is exclusively concerned with spectroscopic ellipsometry.

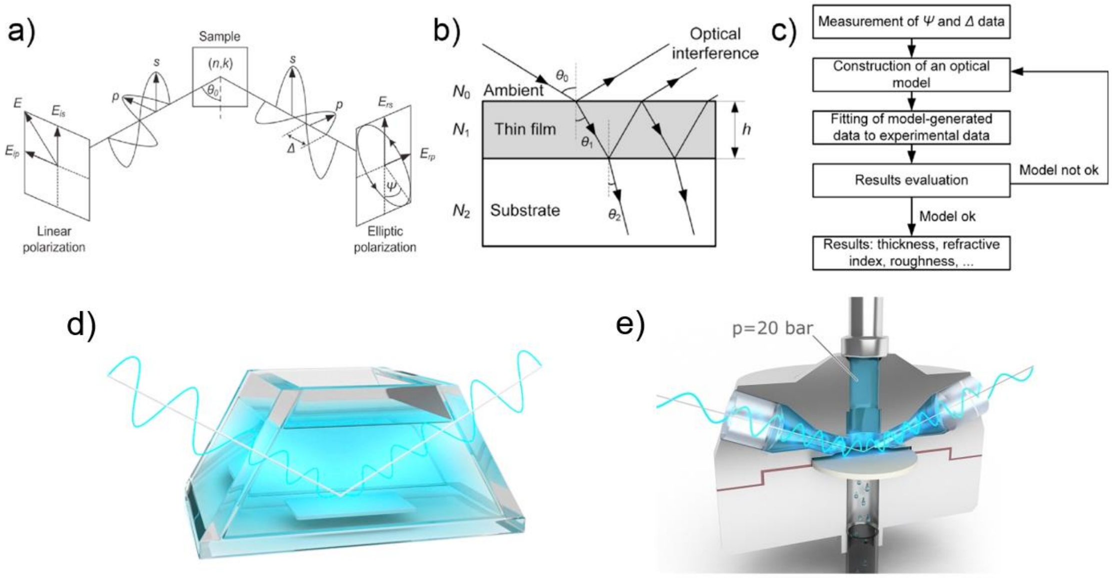

Figure 3 a) basic principles of ellipsometric measurement b) model of light reflection and refraction at each of the sample interfaces c) typical scheme of optical modeling and fit evaluation d) principle of in-situ ellipsometry e) advanced, high pressure in-situ ellipsometric cell developed as part of this habilitation work

The extraction of useful sample properties, like film thickness or refractive index, requires development and evaluation of an optical model which to a sufficient detail captures the system complexity, Figure 3b. The spectroscopic data, usually expressed as ellipsometric angles psi and delta, are then used as a basis for the fit of the model parameters. If a sufficient agreement is found, the model is considered valid and can, in turn, be used to compute a range of sample properties.

These include film thickness, refractive index, surface homogeneity, (micro)porosity, fractional free volume, optical anisotropy, roughness, or even out-of-plane density gradients, Figure 3c. Because of its non-invasive character, spectroscopic ellipsometry can be applied in-situ or in-operando (e.g. in the presence of fluids permeating through a membrane) with the utilization of relatively simple trapezoidal measurement cells, Figure 3d, or much more complex, high-pressure fluid stainless steel membrane permeation cells like the ones used in the work comprising this habilitation, Figure 3e.

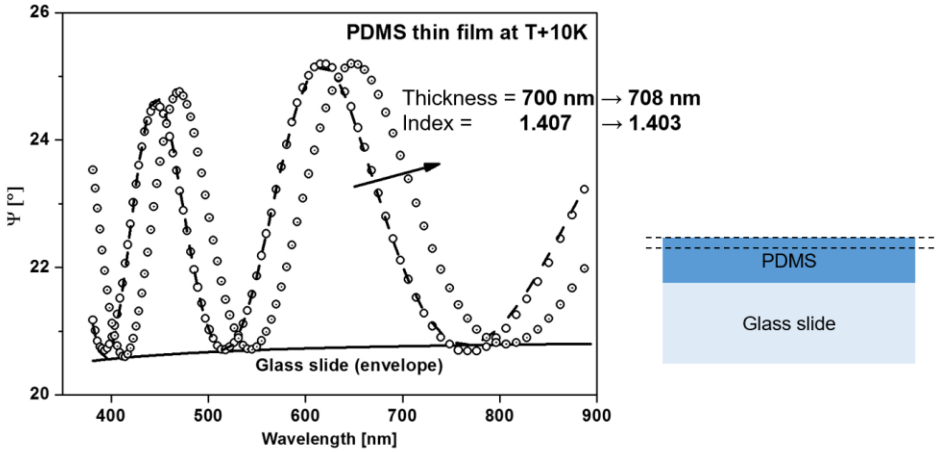

Figure 4 An example of an optical spectrum for a polydimethysiloxane (PDMS) thin film on a glass slide substrate which was heated by 10 K

Figure 4 shows an example of a psi parameter spectrum over a typical wavelength range of 370 – 900 nm that is produced by a 700 nm thick polydimethylsiloxane (PDMS) polymer film spin-coated on a glass slide. By fitting the measured data to an appropriate optical model the thickness and refractive index of the film can be extracted. Upon heating, the film thermally expands which results in a shift in the interference oscillations to the right. The shift corresponds to an increase of film thickness and a reduction of refractive index. These changes in film properties can be typically resolved with sub-nm (thickness) and 10^{-4} (ref. index) accuracy under optimal conditions.

Currently, the vast majority of ellipsometry characterization in the literature and industry is focused on thin films deposited on non-porous substrates of which Si wafers, glass slides, or metals (Au, Ti) are most ubiquitous. These systems are, however, of limited suitability for membrane research because a porous substrate is usually required. Porous substrates may pose significant difficulties to the interpretation of the reflected light polarization as a result of such effects as scattering, depolarization, or inhomogeneity (in-plane, out-of-plane).

c) In-situ spectroscopic ellipsometry for advanced membrane structures – thin-film composite membranes based on solution-processed films on porous supports

A major breakthrough resulting from my and my collaborators' work was the development of complex, multilayer optical models that would be suited to handle the analysis of realistic membrane structures, Figure 5a. This required complementation of ellipsometry with other techniques, like scanning electron microscopy (SEM) and atomic force microscopy (AFM)[2], as well as proper choice and combination of variable and constant parameters influencing light reflection and refraction at each of the sample interfaces. In particular, the use of an effective medium approximation theory[8] to handle substrate porosity yielded very good results [H1].

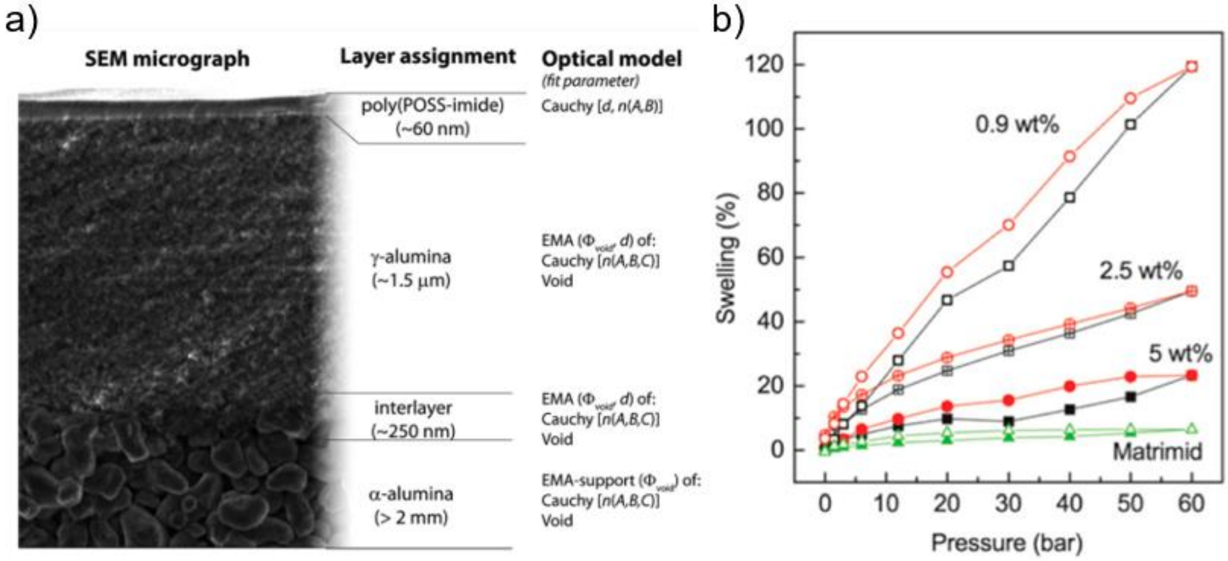

Figure 5 An example of a complex membrane structure comprising an ultra-thin poly(POSS-imide) selective layer deposited on a mesoporous gamma/alpha alumina composite substrate. On the right hand side the optical fit parameters corresponding to the distinct sample layers are listed. Reproduced with permission from ref. [9]

The developed optical models were validated by comparing the response of a well-known membrane polyimide, Matrimid, to high pressure CO_2 sorption when deposited as a thin film on standard Si wafer substrate versus on an alumina-based complex porous supports [H1]. The gained confidence allowed, in turn, studies of novel poly(POSS-imide) thermally imidized type of membrane systems under realistic high pressure conditions. Such properties as penetrant-induced dilation (swelling, Figure 5b), refractive index changes, or penetrant molar volumes of absorbed CO_2 and CH_4 could be determined which are important to estimate the suitability of this novel and robust material for gas separation applications [H1].

Advanced ellipsometry modeling was also very helpful in understanding swelling and penetrant sorption into the microporosity or excess free volume of polymers of intrinsic microporosity (PIMs) [H2][10]. The high microporosity (as high as 25%) which is accessible to water combined with limited swelling was shown to result in *excellent proton transfer* through a PIM-1-based membrane when used in a redox flow battery. At the same time, ion crossover was drastically limited and resulted in unprecedented coulombic, voltage, and, consequently, energy efficiencies of the fabricated batteries. Generation of such knowledge directly in thin films of PIM-1 would have been very difficult without the utilization of in-situ ellipsometry.

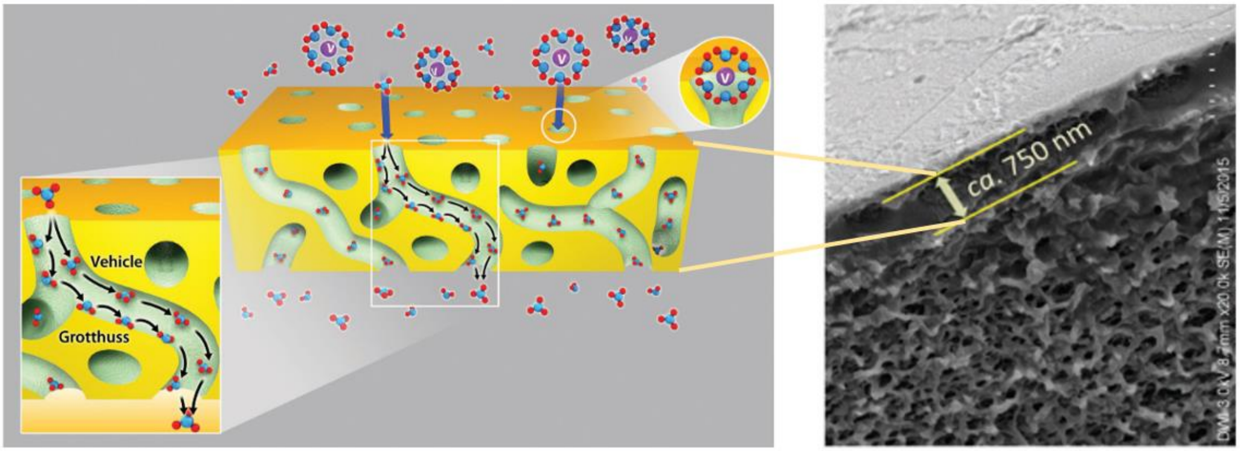

Figure 6 Representation of water channels within PIM-1 selective layer matrix that allow for efficient proton transfer in redox flow batteries. Reproduced with permission from ref. [10]

Another breakthrough was the development of an in-situ, non-invasive imaging technique that could be used to learn about the morphology of membranes when immersed in liquid mixtures [H7][11]. Such information is typically very difficult to obtain with other techniques, yet it is crucial to fully understand the response of both selective layer and support in the presence of a separated medium. By combining in-situ trapezoidal cell, focusing optics (light spot 300 μm short axis), and automated translation stage it was possible to provide non-intrusive mapping capabilities for various types of composite membranes, for example, to study their morphology depending on their fabrication method, Figure 7. Uniquely, thanks to the ability of ellipsometry to probe deep beyond the selective layer, the substrate porosity changes could be studied *in the presence of the selective layer*. For example, the extent of PAN[12] pore-filling with the liquid underneath the selective layer could be determined.

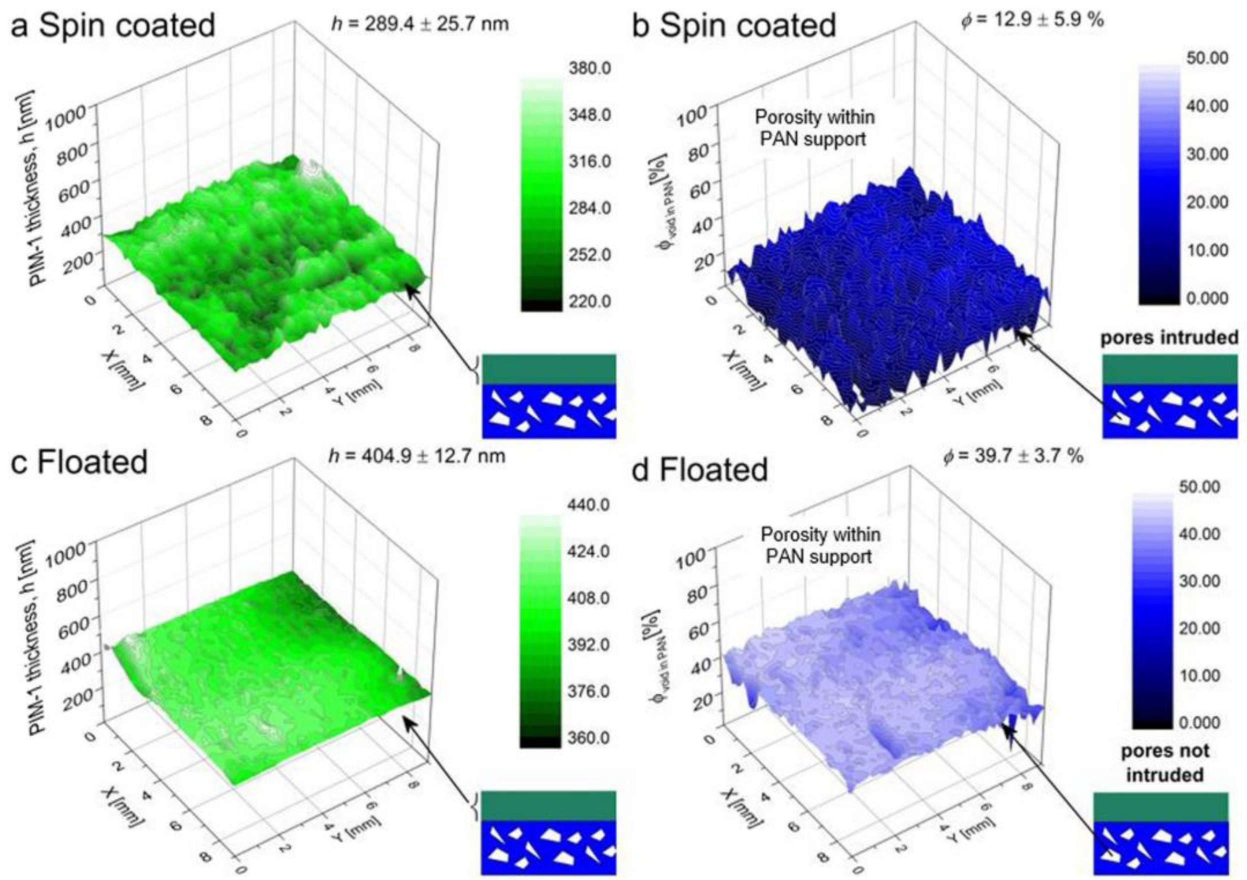

Figure 7 An example of morphological differences of the PIM-1/PAN membranes where the selective layer was deposited by direct spin-coating on a support (a and b) or floated onto the porous support following solidification on a non-rough support (c and d). Reproduced with permission from ref. [11]

d) In-situ spectroscopic ellipsometry for advanced membrane structures – interfacially-polymerized, high-roughness selective layers

An introduction of interfacially-polymerized (IP), thin-film composite membranes is a key historical development in membrane engineering that allowed arguably the largest commercial success of membranes in potable water production by reverse osmosis and nanofiltration[13-15]. IP membranes are made by a very rapid reaction of trimesoyl chloride (TMC) dissolved in the organic phase with aromatic or aliphatic diamines dissolved in the aqueous phase. This creates a very thin polyamide layer which in the presence of sufficient pressure driving force (10 – 70 bar, typically) can permeate pure water while rejecting salt. More recently, non-standard techniques have been developed to tighten the IP layer and expand the applicability of this type of thin-film composite membranes to gas separations [H9][16, 17].

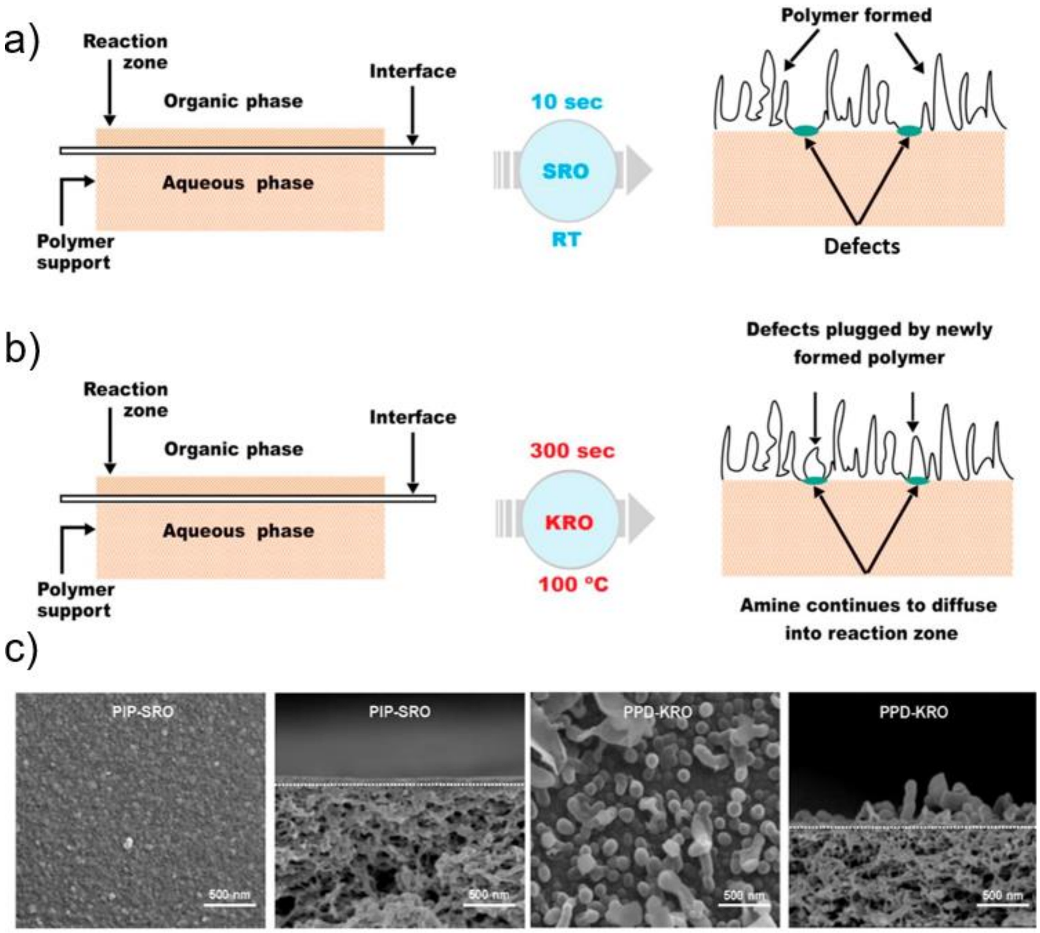

Figure 8 Standard (a) and modified (b) methods of creating ultra-thin interfacially polymerized (IP) polyamide layers on top of porous supports as well as a schematic representation of their rough morphology. Lower panel (c) represents top- and cross-sectional SEM images of standard and modified IP membrane selective layers. Reproduced with permission from ref. [16]

The morphologies of IP layers can range very widely from essentially smooth ultra-thin films (50 – 70 nm thick) to very rough, crumpled, or blob-like films extending several hundred nm from the support surface, Figure 8. Imaging, especially in a non-destructive or non-intrusive way, of those very important types of membranes has been very difficult and often requires the use of sophisticated tomography techniques[18]. The challenges are amplified by the lack of large chemical contrast between the IP layer and the support (both are organic polymers) and its delicate nature.

In collaboration with researchers from KAUST, Saudi Arabia, and Clemson University, the USA, [H11][19] I was able to develop optical models that allow determination of thickness, refractive index, and roughness of IP-layers *without the need for selective layer isolation or destruction of the membrane*, Figure 9. The development of those models required appropriate handling of the depolarization and light scattering of the reflected light as well as treatment of layer roughness as a separate optical layer with 50:50 volumetric ratio (effective medium approximation[8]) of void to dense polyamide.

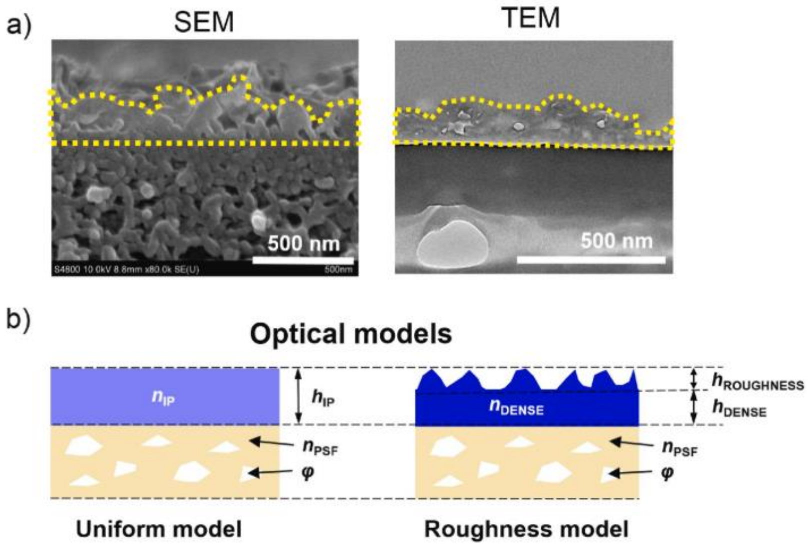

Figure 9 (a) SEM and TEM cross-sectional images of typical IP layers together with optical models that handle both smooth and rough IP structures. Reproduced with permission from ref. [19]

Extensive characterization of five different commercially available membranes with SEM, TEM and AFM confirmed a very good agreement of focused-beam variable angle spectroscopic ellipsometry (FB-VASE) with those more direct techniques [H11], Figure 10. Similar optical models were developed for non-commercial, highly promising state of the art IP membranes synthesized in our group at KAUST [H9][16, 17].

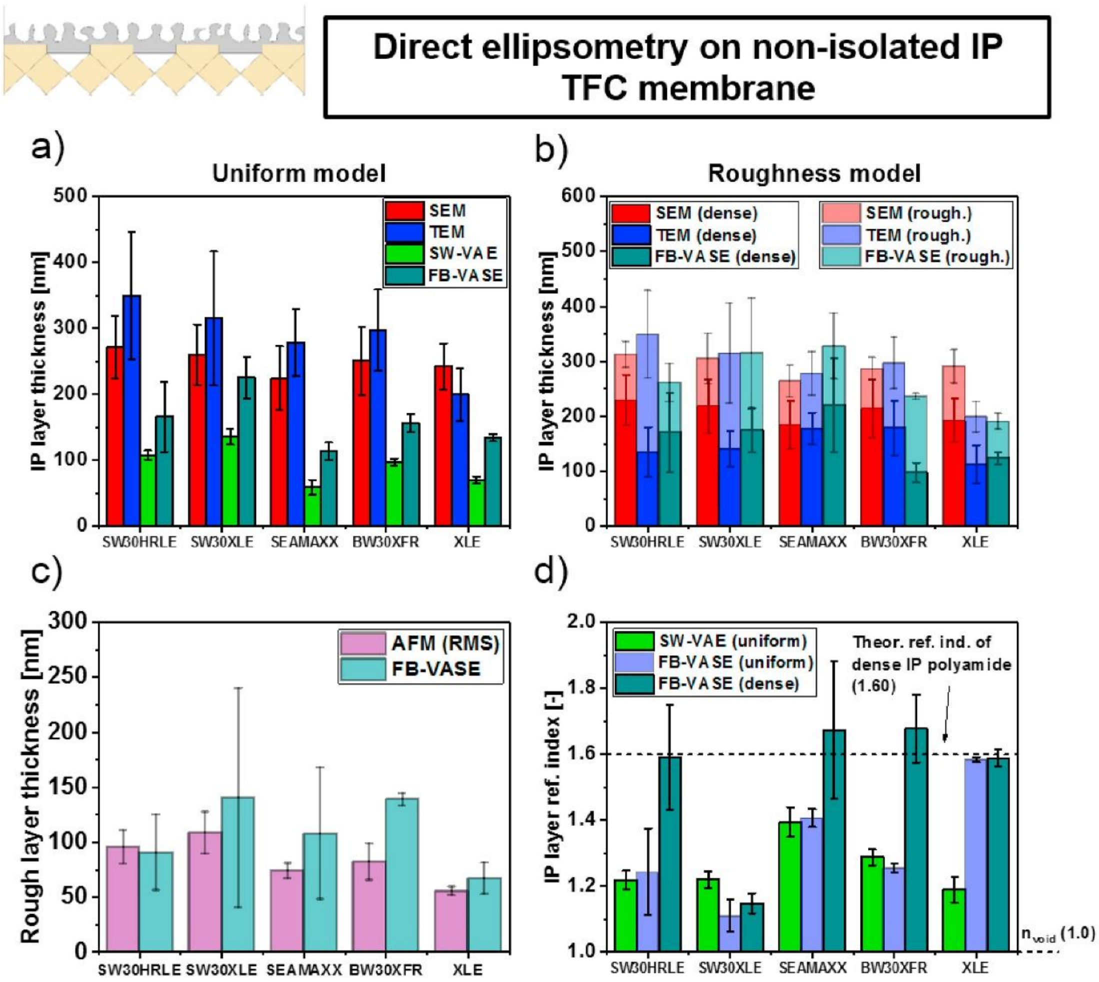

Figure 10 Validation of the developed ellipsometry modeling applied to five different commercially available IP thin-film composite membranes against SEM, TEM, and AFM. Reproduced with permission from ref. [19]

The importance of the developed spectroscopic ellipsometry models in the future research is signified by the fact that in-situ dynamic studies directly on non-modified, as received IP thin-film composite membranes are now enabled. For example, Figure 11 shows that an in-situ observation of thickness, roughness, and refractive index changes of several commercial IP membranes is possible under water and organic vapor cycling. Such studies will provide unprecedented wealth of information to allow tuning of novel membranes to the target separation tasks while benefiting from a relatively easy up-scalability of the IP technique into industrial settings.

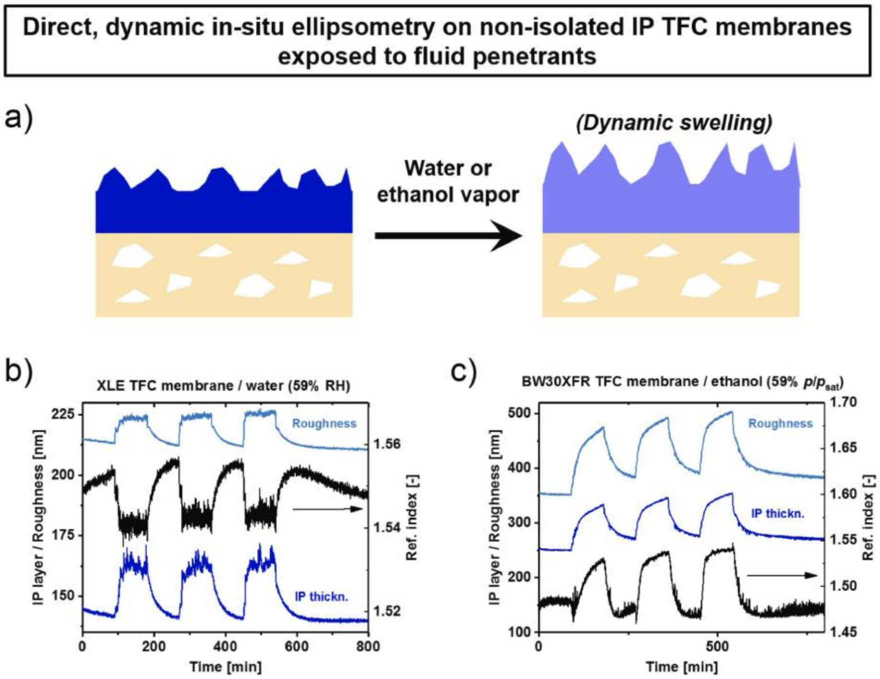

Figure 11 a) Scheme of swelling induced by the exposure of an IP thin-film composite membranes to interacting penetrants, b) and c) changes in roughness, thickness and refractive index of the IP selective layer as a result of water and ethanol cycling. Reproduced with permission from ref. [19]

Section I: Summary of achievements

- *Development and validation of optical models suitable to studies of smooth model and state-of-the art complex membrane structures based on thermoplastic, solution-processable and thermally treated polymers*
- *Development and validation of optical models for smooth and rough interfacially-polymerized thin-film composite membranes that can be used to treat liquid and gas streams*
- *Development of a non-destructive, non-intrusive imaging technique based on spectroscopic ellipsometry to study morphology of realistic membrane systems including the behavior of the selective layer and the porous underlying support*
- *Introduction of entirely new possibilities to study the behavior of existing and future membrane systems under realistic conditions*

II. Polymers of Intrinsic Microporosity interacting with pure and mixed fluids

Polymers of intrinsic microporosity, PIMs, are thermoplastic glassy polymers with rigid and contorted backbones that trap large fractional free volume or microporosity[20, 21]. PIMs combine their high microporosity (up to 25% v/v) with solution processability which makes them important candidates for next-generation membranes, catalysts, or adsorbents[22-25]. In many practical applications, but in membrane separations in particular, the usefulness of PIMs is constrained by the feasibility of reliably translating their excellent properties into thin-film composite or integral-skin membranes. This necessitates the studies of PIMs in a form of thin or ultra-thin films with thicknesses well below ~1 micrometer, Figure 12. In this section, I summarize the most important work that I, together with my collaborators, contributed to improving our understanding of the interactions of thin and ultra-thin PIMs films with pure and mixed penetrants.

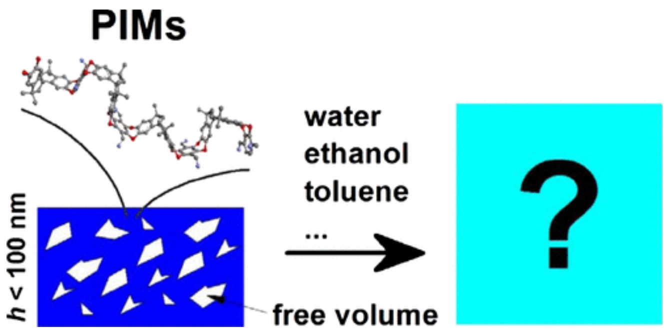

Figure 12 General representation of the problem of swelling of polymers of intrinsic microporosity (PIMs) with penetrnats. Reproduced with permission from ref. [26]

a) Thin and ultra-thin PIMs exposed to single component penetrants

To understand the nature of interaction between various organic solvents and water with two PIMs we have devised an experimental setup based on in-situ spectroscopic ellipsometry [H3][26]. PIM-1 as well as PIM-6FDA-OH (polyimide-type PIM, synthesized at KAUST) were dissolved in suitable solvents and spin-coated on top of silicon wafer substrates. After resetting their thermal history via solvent rejuvenation followed by rapid heating the thin films were exposed to various solvents until equilibration was achieved. With in-situ spectroscopic ellipsometry it was possible to observe the thickness changes (associated with film swelling) as well as refractive index changes (associated with both swelling and free volume occupation) in 53-72 nm thick PIMs films at room temperature, Figure 13.

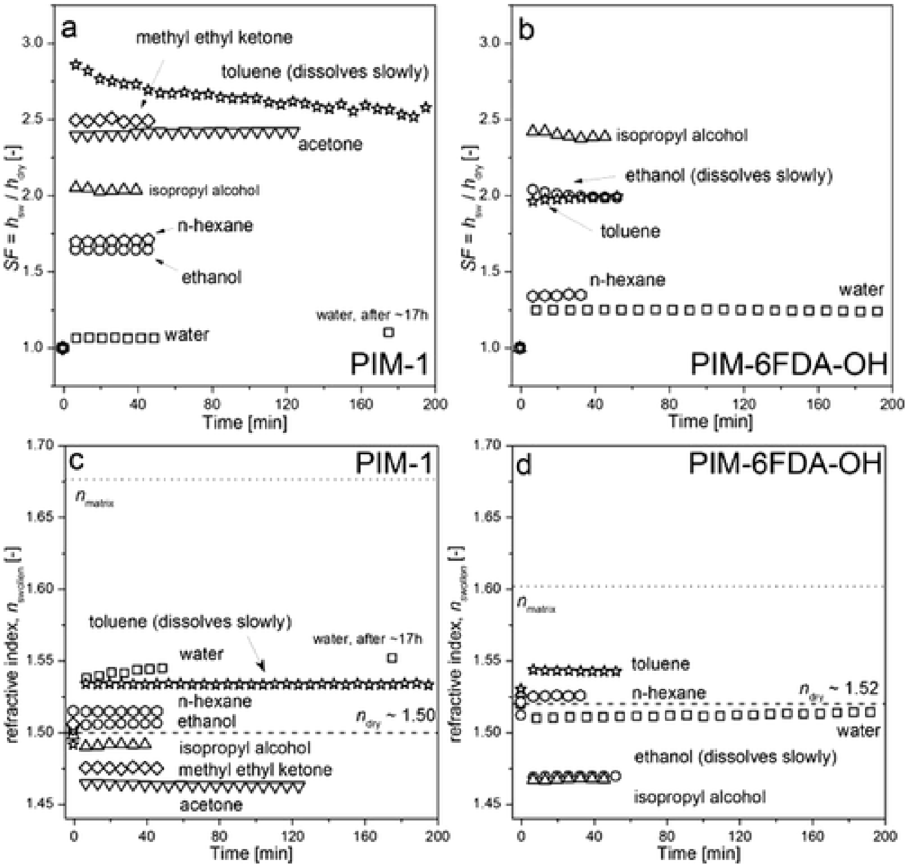

Figure 13 Swelling factor (SF) and refractive index of PIM-1 and PIM-6FDA-OH 53 – 72 nm thick PIMs films when exposed to various liquid penetrants. Data reproduced with permission from ref. [26]

The results indicated that PIMs swell significantly in organic solvents and often reach equilibrium within several minutes, Figure 13a and b. As a result of solvent absorption, both initially super-glassy PIMs plasticize completely and reach a rubbery state. In other words, the extremely high glass transition temperatures reduce well below room temperature in the presence of solvents. The refractive index information, Figure 13 c and d, could be used to perform unique calculations of the solvent volume fraction in a swollen film, Figure 14. The unprecedented possibility to independently observe refractive index of swollen films with in-situ spectroscopic ellipsometry enabled the development of a calculation scheme to accurately obtain penetrant volume fractions in initially high free volume polymers. We have shown that for accurate penetrant volume fraction calculation it is necessary to account for the presence of the initial free volume in the dry polymer matrix. If a simple volume additivity is assumed, as often done for swelling of rubbery polymers, the penetrant volume fraction will be significantly underestimated. For instance, PIM-1 dilated (swelled) in water only 6%, however, the volume fraction of water in the swollen PIM-1 matrix was calculated to be ~30%, which is much larger than what would be derived from simple volume additivity. This finding had major implications for the explanation of the proton transport through water-swollen PIM-1 when applied as redox flow battery separator in our subsequent work [H2][10].

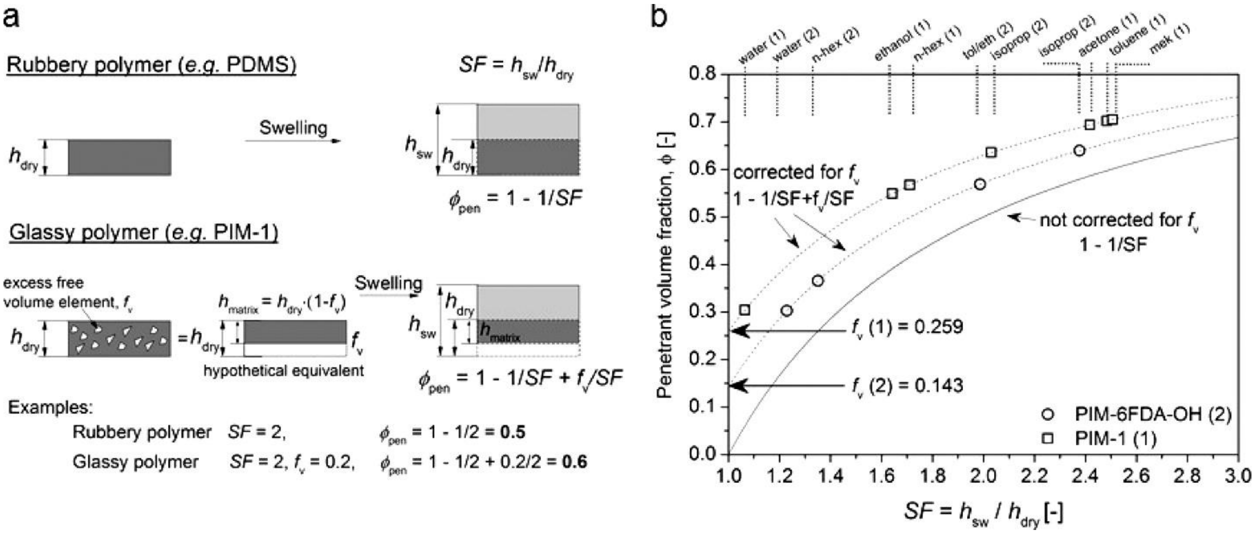

Figure 14 Calculation scheme to obtain penetrant volume fraction in a swollen high free volume polymer films accounting for the presence of the excess fractional free volume. Reproduced with permission from ref. [26]

Overall, the work on swollen PIMs thin films allowed an important experimental deconvolution of the effects of matrix dilation from occupation of available microporosity which has pronounced consequences in understanding transport in such uniquely rigid amorphous polymers.

To study the effects of penetrants before full PIMs matrix plasticization, we utilized thermodynamic activities < 1 and studied PIM thin films exposed to vapor penetrants [H5][27]. It was detected that the ultra-rigid PIMs can be significantly plasticized in the presence of organic vapors (ethanol, toluene) and that the PIM-penetrant mixture can traverse its glass transition at thermodynamic vapor activities <1. In addition, several practically important consequences of nano-confinement were found in PIM-1 exposed to ethanol vapors. For instance, it was found that below 20 nm thickness the swelling of PIM-1 is significantly suppressed or enhanced depending on the vapor activity. Moreover, the free film interface as well as the region of the film in contact with the substrate seem to play a role in the modifications of swelling behavior and chain dynamics in ultra-thin PIMs.

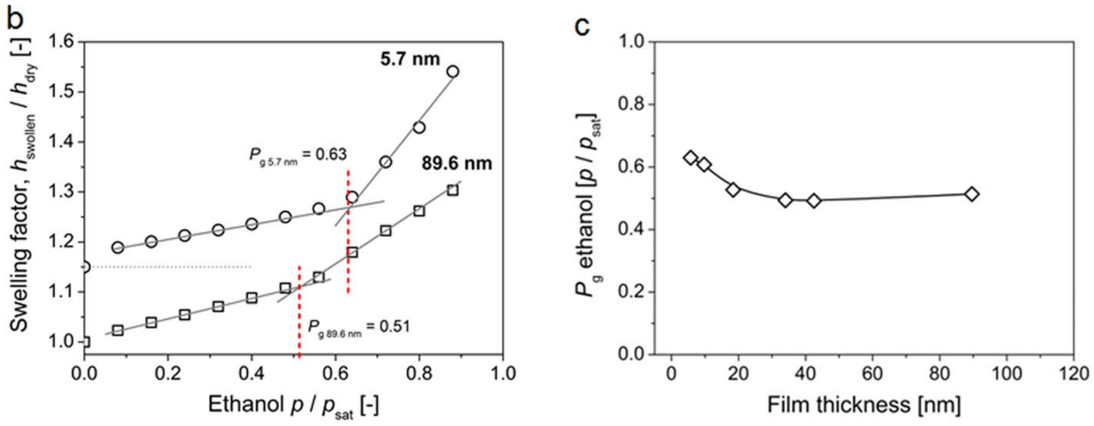

Figure 15 a) swelling factor as a function of ethanol vapor activity indicating a penetrant induced transition between the glassy and rubbery regimes of the polymer-solvent mixture b) thickness dependence of the penetrant-induced glass transition indicating a slight increase for films thinner than about 40 nm. Reproduced with permission from ref. [27]

To further study the potential applicability of PIMs-based membranes in gas separations we have studied the behavior of several promising PIMs (PIM-1, PIM-6FDA-OH, Tröger;s base PIM, and Amidoxime PIM-1 [H6][28]) in compressed CO_2 up to 45 bar, Figure 16. The limits of our experimental technique were pushed to the lowest thickness range ever reported in similar experiments, ~7 nm, thanks to the utilization of an interference-enhancement provided by thick SiO_2/Si substrates.

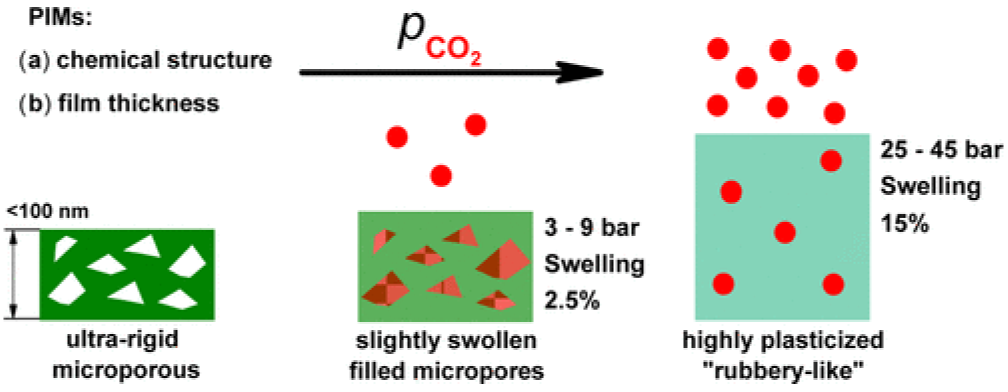

Figure 16 Schematic representation of the swelling and free volume (or microporosity) occupation in thin PIMs esposed to compressed CO_2. Reproduced with permission from ref. [28]

In that study [H6][28], we were able to determine CO_2-induced swelling, changes in refractive index, as well as concentration in films in the range of 7 – 135 nm, Figure 17. Determination of the relative refractive index, n_{rel}, enabled studying the interplay between matrix dilation and microporosity filling. Interestingly, all PIMs exhibited a maximum in n_{rel} at approximately 2-2.5% swelling which corresponded to a pressure range of 3 – 9 bar. Beyond this pressure range the matrix dilation started dominating which marked a potential onset of undesired penetrant-induced plasticization. These findings thus had important practical implications. Moreover, we discovered that reduction of film thickness down to 7 nm resulted in significant changes in swelling/sorption behavior. The effective reduction of T_g in ultra-thin PIM-1 was found to be as large as ~ 200 °C, Figure 18.

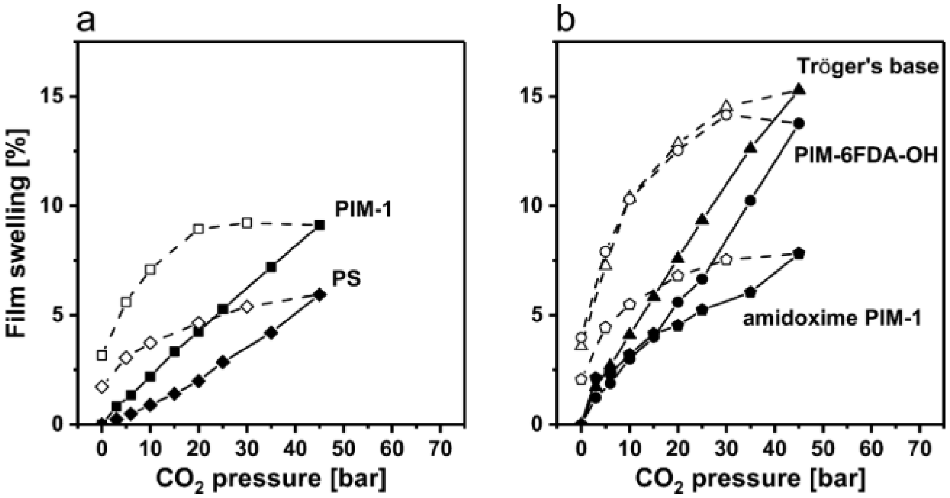

Figure 17 Sorption-desorption swelling isotherms of polystyrene (PS) as well as several PIMs showing the typical path dependence of swelling and, in turn, penetrant concentration. Reproduced with permission from ref. [28]

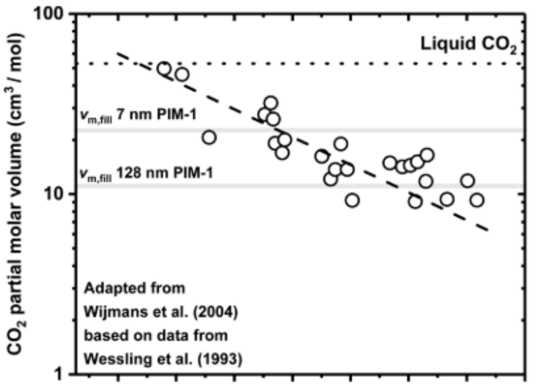

Figure 18 CO$_2$ partial molar volume as a function of polymer glass transition. Circles represent well-known, "traditional" glassy polymers, while the shaded lines correspond to PIM-1 with 128 and 7 nm thicknesses. Reproduced with permission from ref. [28]

b) Thin and ultra-thin PIMs exposed to mixed penetrants

For practical applications in membrane-based separations it is necessary to understand the behavior of the active material under conditions that approximate realistic process mixtures. While a great majority of studies is focused on single gas transport or sorption properties, the highly desired studies in mixtures are very rare. To address this issue, we have designed and conducted studies of PIMs exposed to vapor [H4][29] and gas [H10][30] mixtures.

Figure 19 shows PIM-1 film swelling and refractive index as a function of time in the presence of pure and later mixed vapors containing n-hexane and water[29]. The penetrants in that study included water, ethanol and *n*-hexane to reflect varying degrees of affinity towards the polymer matrix or towards the other penetrant. As a result, we could reveal directly such effects as competition for the sorption sites (for water/*n*-hexane or ethanol/*n*-hexane) or enhancement of sorption of typically weakly sorbing water in the presence of more highly sorbing ethanol. These important effects often complicate the comprehension of glassy polymer's behavior in various separation applications.

For natural gas separations, which is one of the most important membrane technology applications, it is essential to understand the behavior of membrane polymers in CO_2/CH_4 mixtures under high pressure. Cellulose triacetate (CTA), PIM-1 and poly(1-trimethylsilyl-1-propyne) (PTMSP) thin films were exposed to pure and mixed (50:50 molar) CO_2 and CH_4 in our study, Figure 20 [H10][30]. In the conventional low free volume CTA film thickness reduction from 500 to 50 nm did not result in significant changes in pure dilation or uptake in comparison to thick films. However, for the microporous PIM-1 a clear effect of thickness reduction was found. The gas solubility was significantly lower in the 50 nm films and the effect was particularly strong for CH_4. For PTMSP the nanoconfinement led to virtually complete collapse of the microporosity and the thinnest films showed a behavior which was strikingly similar to the rubbery PDMS. The peculiar differences between PIM-1 and PTMSP were explained by the different micropore distributions with PIM-1 possessing more of the harder to collapse ultramicropores (< 7 Å). In mixed-gas experiments, gas sorption was dominated by CO_2. Previously reported CO_2/CH_4 mixed-gas total uptakes in PTMSP and PIM-1 were found to correspond very well with our swelling data in thin films, Figure 21.

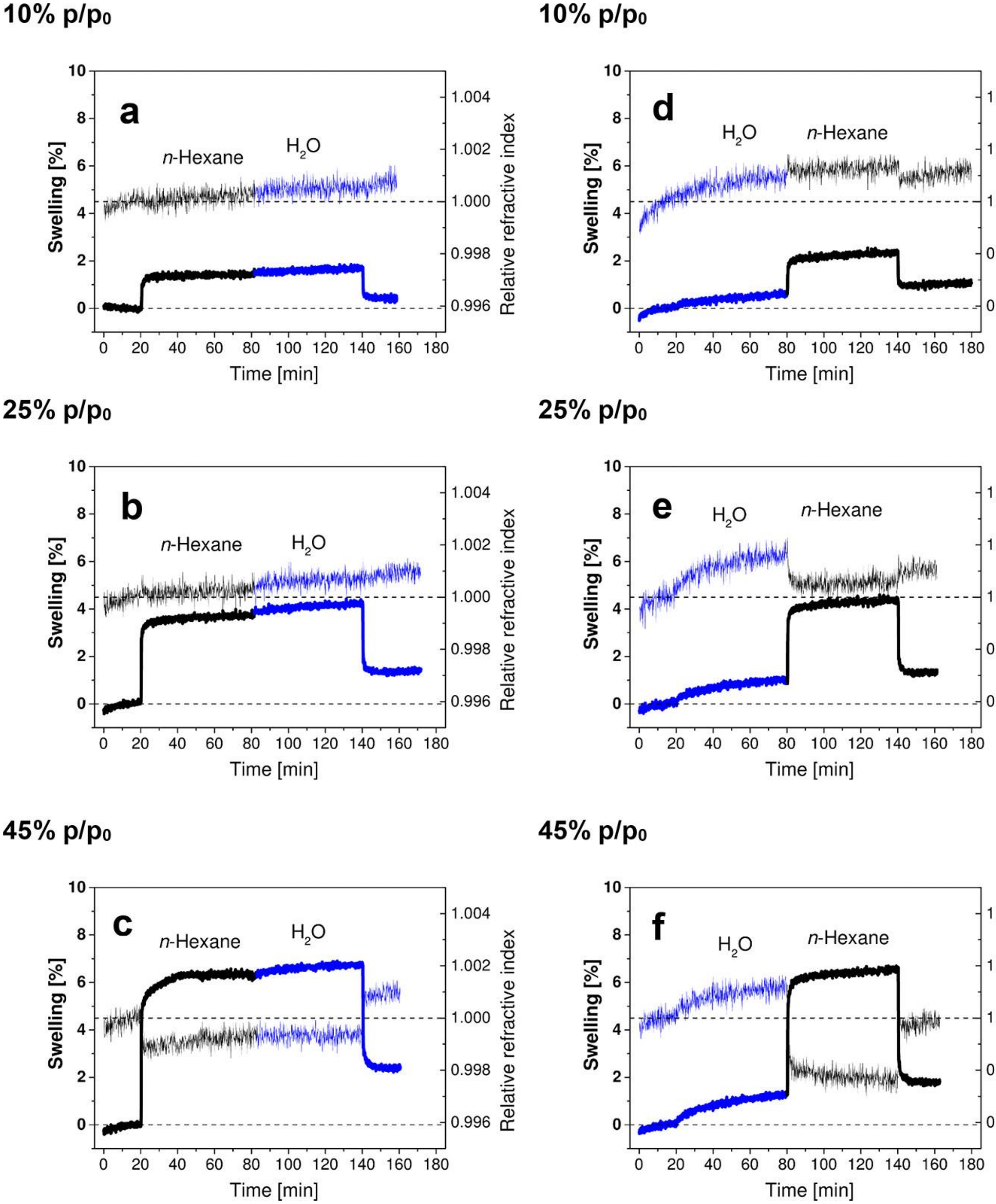

Figure 19 Swelling and refractive index changes of thin PIM-1 films exposed to n-hexane and water vapors at different sequences (either first n-hexane, with added water vapor or first water vapor with added n-hexane). The results indicate a striking asymmetry in the film's response depending on the sequence of exposure. Reproduced with permission from ref.[29]

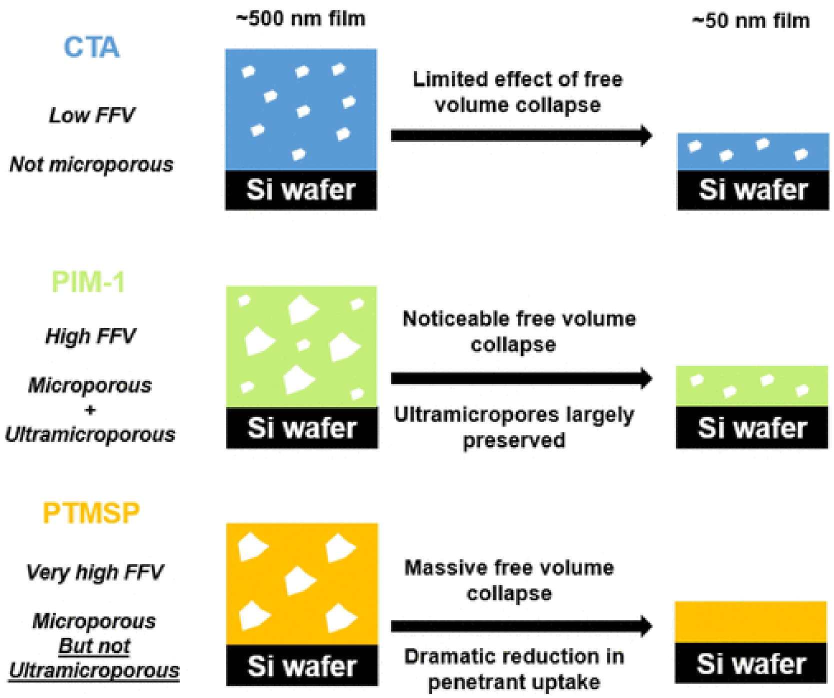

Figure 20 Schematic representation of the effect of film thickness reduction from 500 to 50 nm on the free volume or microporosity of several important membrane polymers. Reproduced with permission from ref. [30]

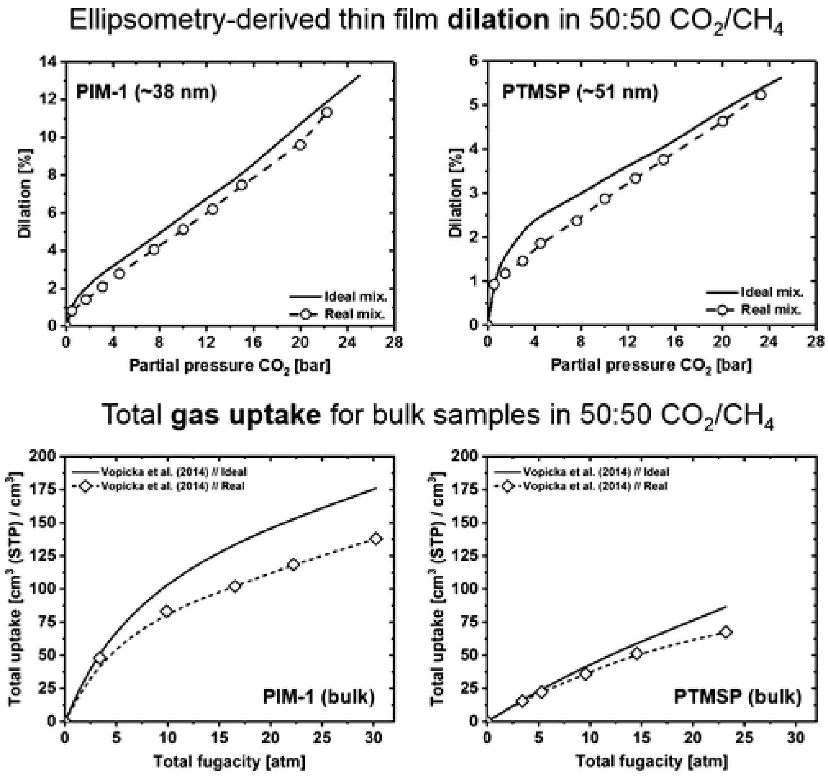

Figure 21 (upper panel) ellipsometry-derived swelling of PIM-1 films in 50:50 CO2/CH4 mixtures (lower panel) corresponding total uptake in thick PIM-1 films measured gravimetrically. Reproduced with permission from ref.[30]

Section II: Summary of achievements

- *Development of an accurate and robust in-situ experimental procedure to study thin and ultra-thin PIMs films exposed to various types of fluids, including pure liquids, pure compressed gases, as well as mixed vapors and mixed compressed gases.*
- *Development of a method to accurately calculate the penetrant volume fractions in swollen glassy polymers which takes into account the free volume fraction present in the non-exposed polymer. This method has direct implications for the understanding of proton transport in water-filled micropores of PIMs with potential uses in redox flow batteries.*
- *Providing an unprecedented possibility of direct dynamic observation of mixed-penetrant effects such as competition for sorption sites or enhancement of swelling by the presence of a second penetrant in microporous polymers. Such effects have important implications in membrane-based separations of strongly interacting mixtures.*
- *Shedding light on the role of the harder to collapse, ultramicropores (< 7 Å) in the deviations of the sorption behavior of microporous polymers as a result of nanoconfinement.*

III. Development of robust and scalable carbon molecular sieve membranes based on polyimides of intrinsic microporosity precursors

a) Carbon molecular sieve membranes with thin and ultra-thin selective layers

Carbon molecular sieve (CMS) membranes are a class of amorphous, microporous membrane materials that are promising for several important energy-intensive separations, such as natural gas/biogas purification or olefin/paraffin separations[31, 32]. In the literature, most CMS membranes were prepared by pyrolysis of well-known polymeric materials such as polyimides, phenolic resins, cellulose derivatives, etc. During my work at KAUST, I have, however, focused on the development of CMS membranes based on PIMs. Prior work at KAUST indicated that the use of already microporous and rigid PIMs, in particular PIM-polyimides (PIM-PIs), can result in carbon membranes with excellent properties in certain challenging separations. Transformation of the thick-film or bulk data into thin CMS membranes has remained largely unexplored yet critical to progress this technology.

In a recent article [H8][33], we have conducted a detailed study on how the properties of thin and ultra-thin CMS membranes derived from PIM-PI precursor deviate from the bulk. The used precursor polymer, SBFDA-DMN, has recently been developed in our group and presented high microporosity (BET, ~700 m^2/g) and excellent carbon-forming properties. The CMS membranes were made by drop casting the precursor polymer on top of anodisc inorganic (alumina) porous substrates with high porosity (~60%), small, uniform pore size (20 nm), and smooth surface, Figure 22. This allowed isolation of the properties of the selective layer from the often obstructing influences of the support (pore intrusion, wide pore size distribution, substrate gas transport resistance etc.).

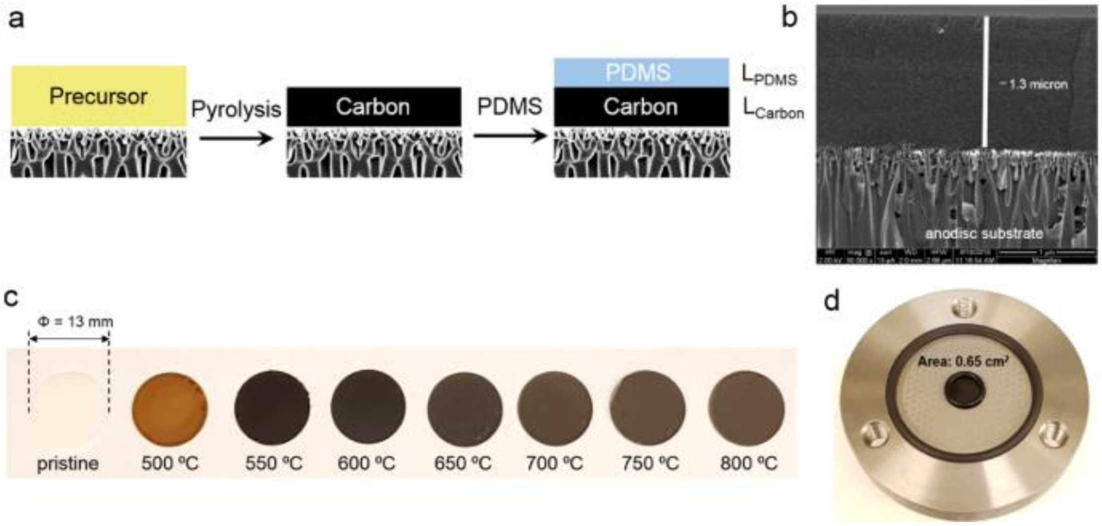

Figure 22 Fabrication scheme of the thin and ultra-thin CMS membranes based on a polyimide of intrinsic microporosity SBFDA-DMN. Reproduced with permission from ref.[33]

We have discovered that there are significant differences in the extent of the pyrolysis-induced collapse of the microporous PIM-PI precursor and the more standard, non-microporous polyimides. Specifically, the PIM-PI precursor collapses more (volumetrically) and results in thinner CMS selective layers. In addition, constraining the forming CMS layer onto a substrate resulted in a forced orientation of the developing turbostratic carbon structure and the emergence of optical anisotropy, Figure 23.

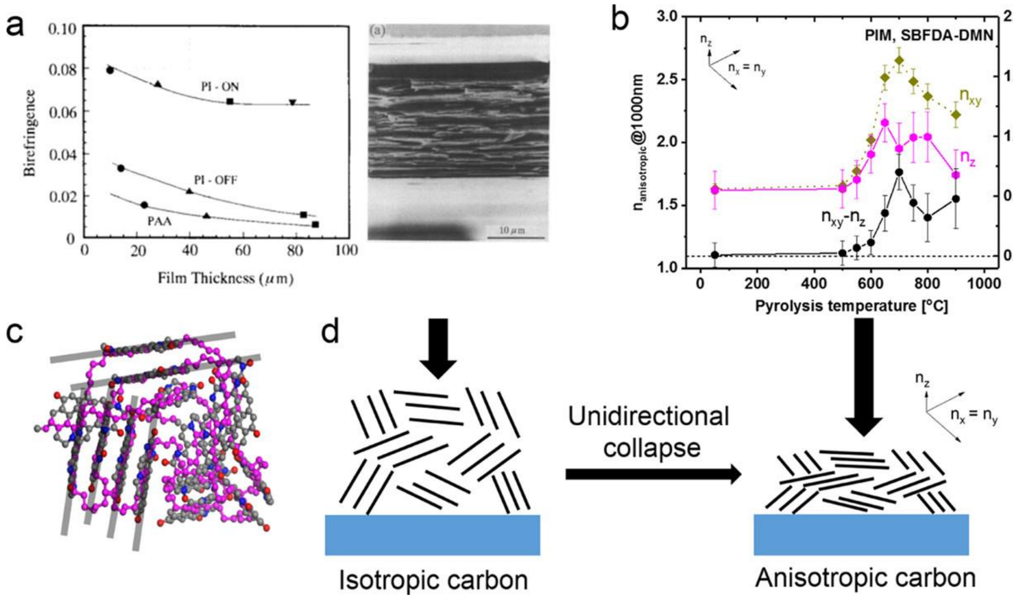

Figure 23 Development of constraint-induced anisotropy in ultra-thin CMS selective layers. Such anisotropy is nearly absent in thick, unsupported CMS films which are often the basis for the membrane material characterization. Reproduced with permission from ref.[33]

The developing anisotropy had pronounced consequences for the molecular transport through those ultra-thin CMS layers. The supported CMS selective layer was found to show significantly lower gas permeances than what could be anticipated based on thick film data. The reduction of the selective layer thickness followed the same trend lines as physical aging which pointed to an intimate link between the two phenomena with important consequences for the design of efficient membranes, Figure 24.

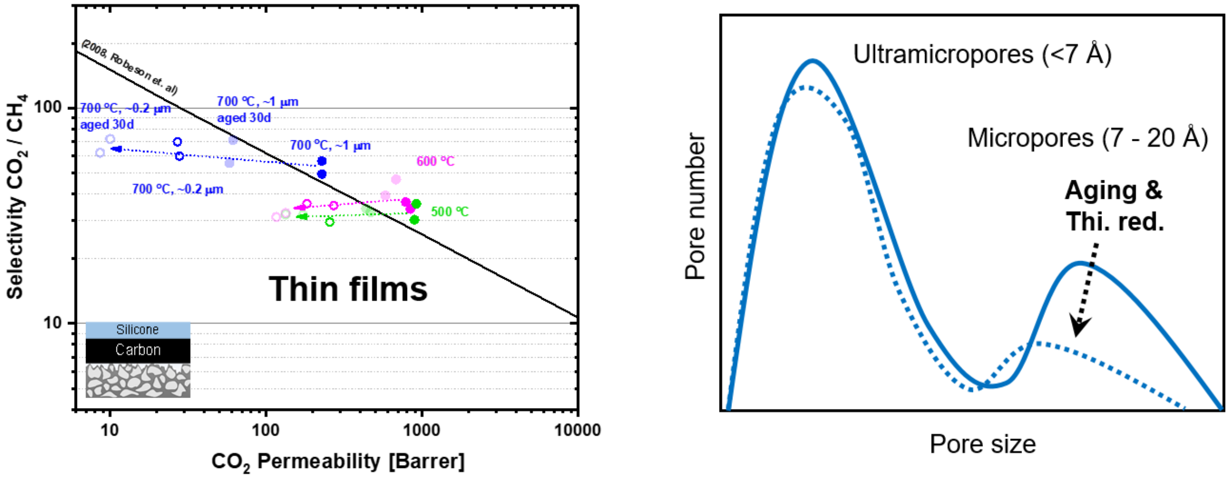

Figure 24 (a) Thickness and physical aging impact on the gas separation properties of the developed ultra-thin CMS membranes (b) scheme of the resulting micropore size distribution. Reproduced with permission from ref. [33]

The unexpected collapse of ultra-thin CMS selective layers was further studied for even thinner, sub-100 nm CMS layer in [H13][34]. For this study, a more complex substrate structure was employed with an intermediate γ-alumina layer (with 2 – 5 nm pores) to ensure a creation of well-defined sub-100 nm CMS layer, Figure 25. We have discovered, that the structural collapse discovered in [H8][33] continues and magnifies in even thinner selective CMS layers. Moreover, the ultra-thin CMS PIM-PI-based membranes showed severely accelerated physical aging and reached near-equilibrium properties at remarkably short aging times of several days, Figure 26. This led to an important and somewhat counterintuitive conclusion that the reduction of the selective layer thickness does not necessarily lead to improvement of gas permeance in gas separations.

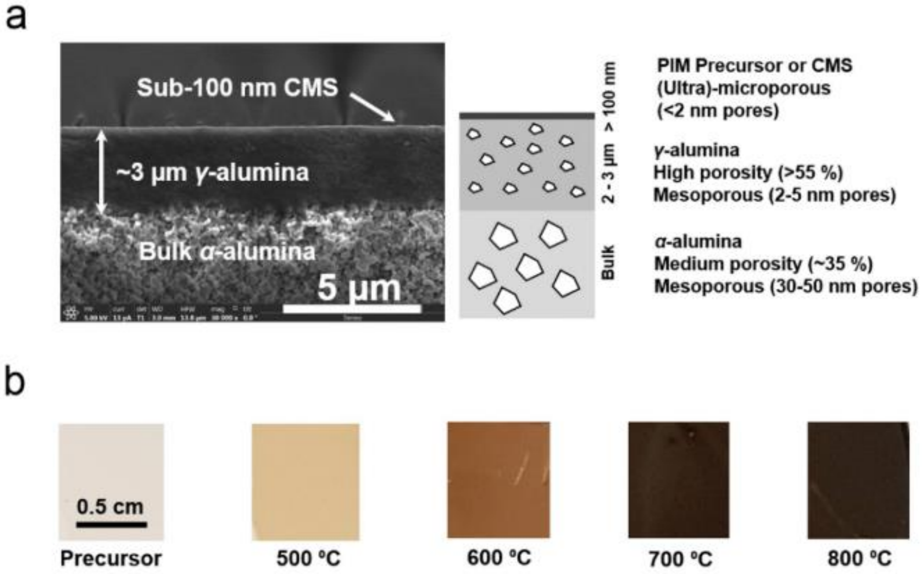

Figure 25 (a) scheme of a sub-100 nm CMS membrane on top of a complex multilayer porous substrate (b) photographs of the sub-100 nm selective layer membranes as a function of pyrolysis temperature. Reproduced with permission from ref. [34]

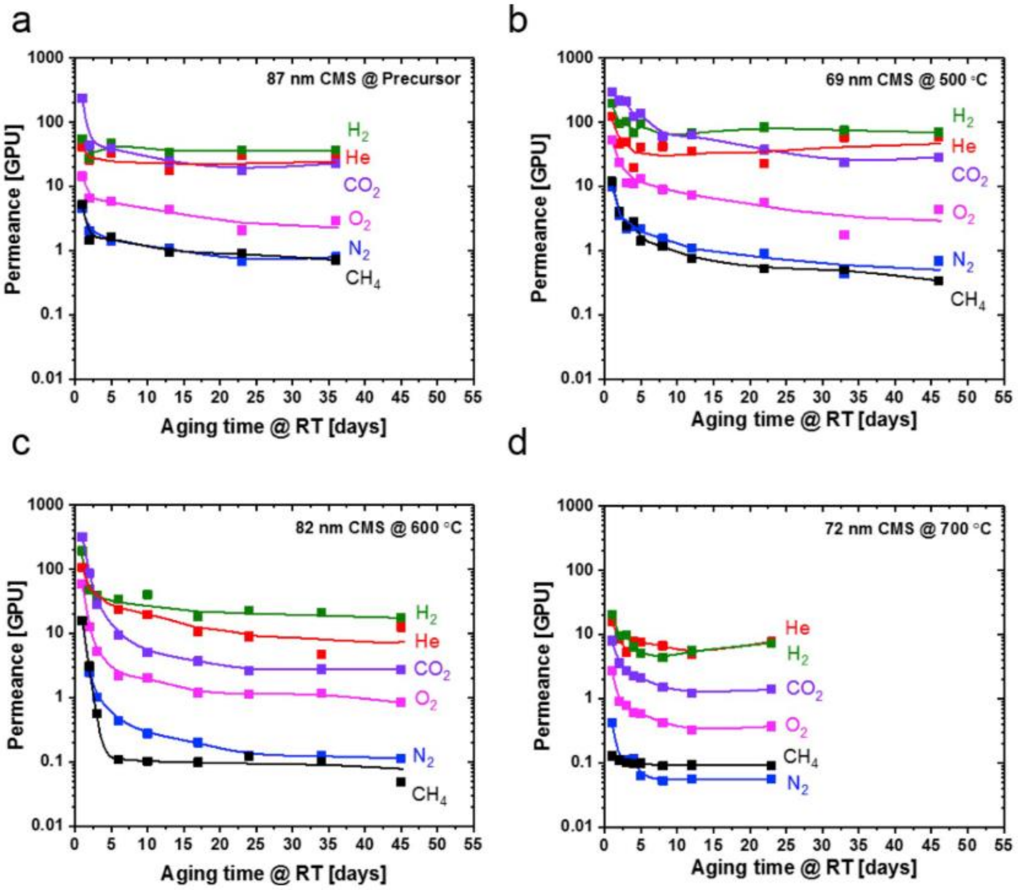

Figure 26 Permeances of multiple permanent gases through the sub-100 nm CMS (and precursor) membranes as a function of time (physical aging) and pyrolysis temperature. Reproduced with permission from ref. [34]

In a follow-up study [H14], we focused in much more detail on the peculiarities of the thin and ultra-thin CMS layers with respect to their structure as well as response to organic vapor (ethanol) exposure. Such knowledge would be crucial not only for a better understanding of their gas separation properties but also would form a more solid foundation for the application of thin CMS membranes in organic-organic separations.

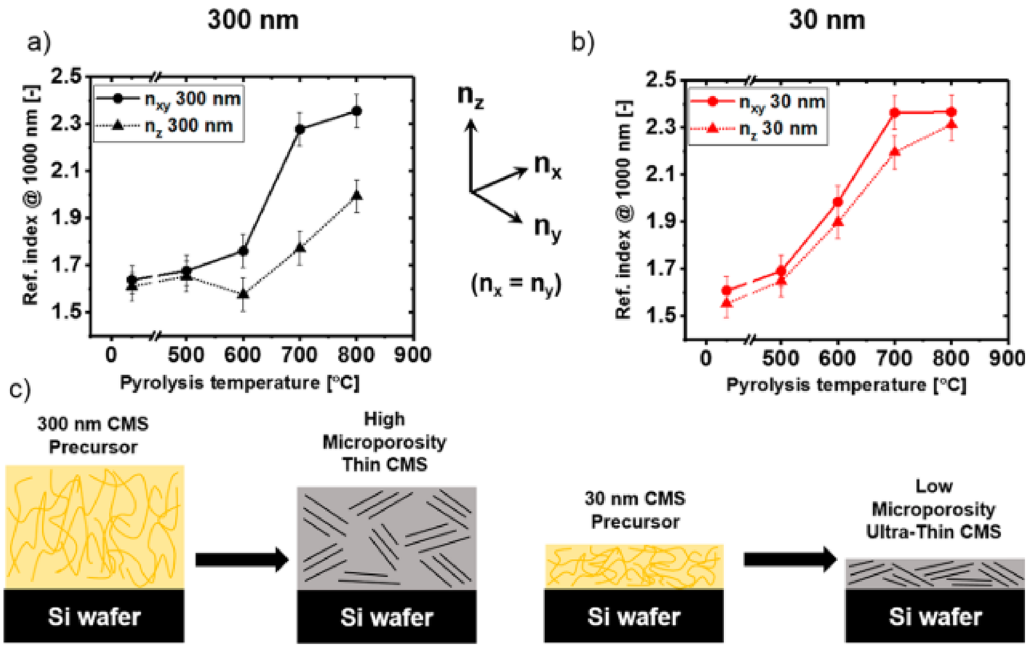

Figure 27 Refractive index as a function of treatment temperature for (a) thin (~300 nm) and (b) ultra-thin (~30 nm) CMS layers based on a PIM-PI precursor; (c) proposed structural differences between the thin and ultra-thin CMS film collapse. Reproduced with permission

Evidence from ellipsometry (anisotropy in the refractive index) as well as transmission electron microscopy (TEM) strongly suggested anisotropic nature of the thin CMS layers with refractive index in-plane of the substrate (n_{xy}) generally larger than the out-of-plane component (n_z). We discovered a very strong dependence of the pyrolysis-induced collapse on the thickness of the CMS films particularly in the ultra-thin range (< 100 nm). These results are consistent with the observed dramatic deterioration of the gas permeance of such ultra-thin membrane skins [H13][34].

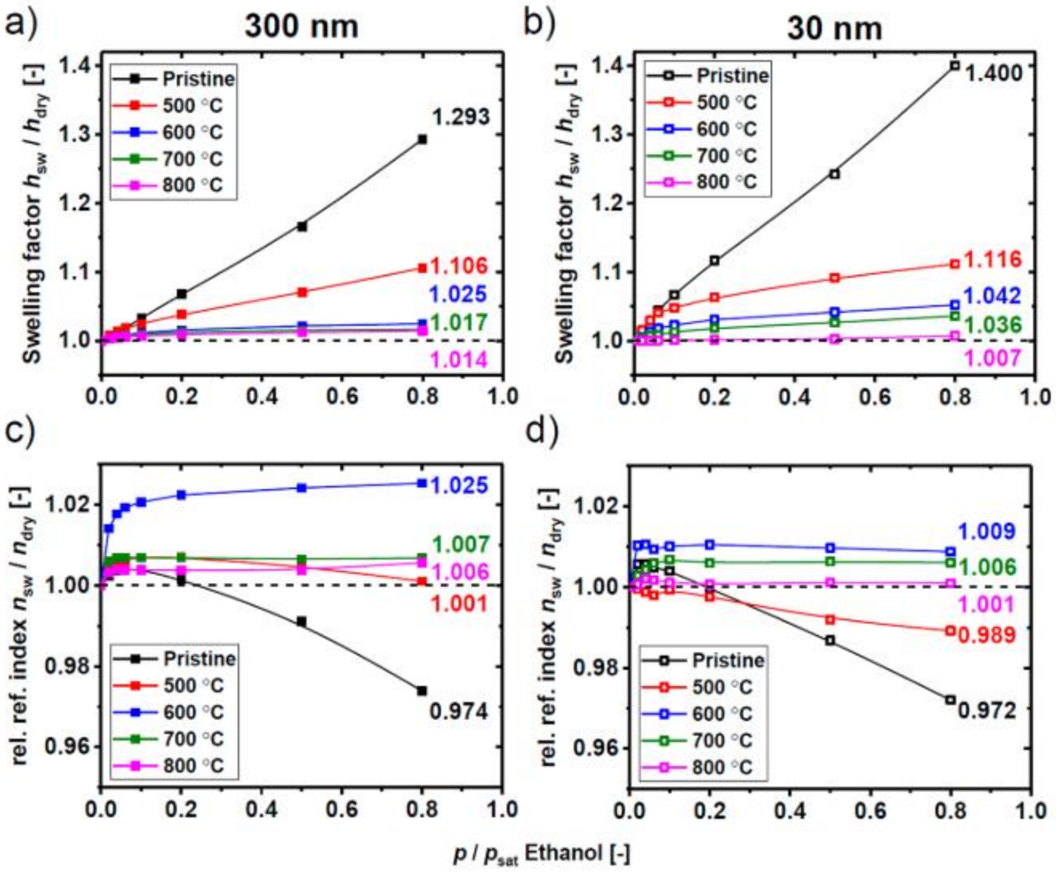

Figure 28 Ethanol vapor exposure of the thin (~300 nm) and ultra-thin (~30 nm) CMS films and the resulting swelling (a and b), and refractive index (c and d). Reproduced with permission.

Subsequent in-situ ellipsometry experiments which investigated swelling of the layers exposed to ethanol vapor corroborated the previous findings and showed that much less microporosity was left available for the organic vapor sorption in the ultra-thin (~30 nm) layers as compared with the thin films (~300 nm), Figure 28. On the other hand, the thinner films were found slightly more prone to swelling which would presumably also lead to further deterioration of their molecular separation properties for fluids with significant swelling and plasticization potential.

b) Nano-hybrid carbon molecular sieve membranes – vapor phase infiltration technique

To address the undesired nano-confinement-related collapse of the ultra-thin carbons we have developed a novel technique of nano-doping of the CMS precursor structure with molecularly dispersed aluminum oxide by performing vapor phase infiltration (VPI) process prior to pyrolysis [H12][35].

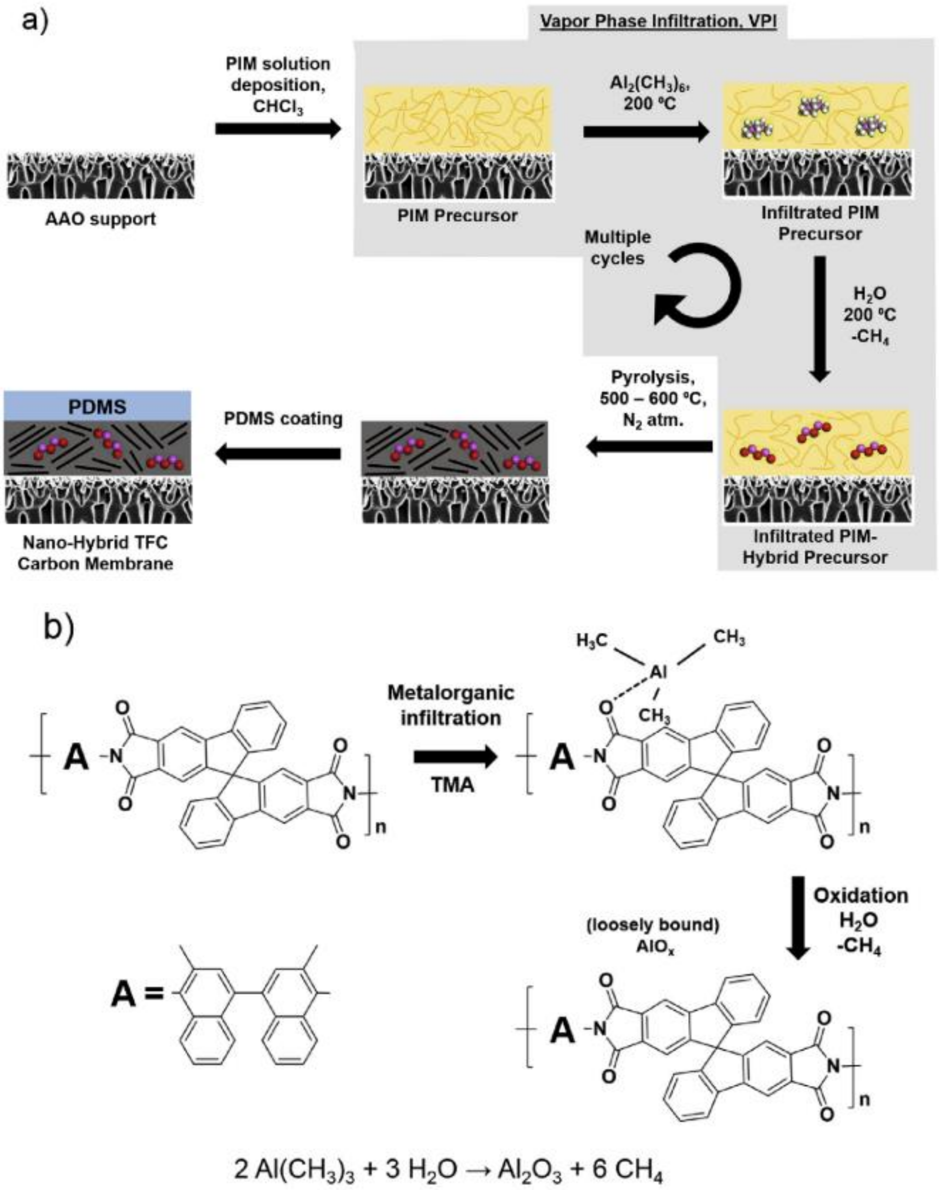

Figure 29 (a) scheme of the vapor phase infiltration (VPI) process followed by the pyrolysis to create nano-hybrid TFC carbon membranes doped with molecularly dispersed aluminum oxide molecules (b) a proposed complexation reaction of the chosen PIM-PI precursor with the VPI precursor. Reproduced with permission from ref[35]

VPI is based on the exposure of the high free volume precursor polymer (PIM-PI) to trimethylaluminum (TMA) in a gas phase, diffusion/complexation within the polymer structure, and subsequent oxidation with water vapors. High-temperature treatment (pyrolysis) in the last step leads to the creation of the nano-hybrid CMS membranes where their micropores are partially filled with rigid aluminum oxide aglomerates. As a result, both the collapse of the structure (reflected in their physical aging) and gas sieving properties are significantly improved, Figure 30.

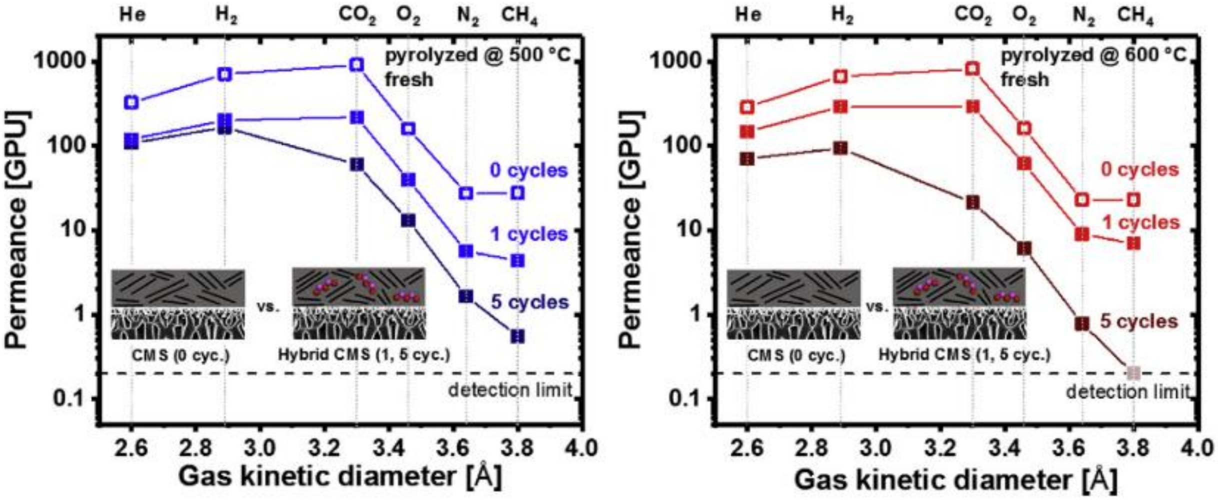

Figure 30 Gas permeance of the nano-hybrid CMS membranes pyrolyzed at 500 °C (left) and 600 °C (right) as a function of the doping level in comparison with the pristine, undoped membranes. Reproduced with permission from ref[35]

The nano-hybrid CMS films possess excellent gas separation properties which are equivalent to undoped CMS membranes pyrolyzed at 200-300 °C higher temperatures. This feature has significant favorable practical consequences in avoiding risks of high pyrolysis temperatures as well as allows for a much broader choice of suitable membrane supports. There is also significant flexibility in the choice of a dopant, including but not limited to, aluminum oxide, zinc oxide, or titanium oxide. We have recently been granted a US patent as a result of this work.

c) Carbon molecular sieve membranes – scale-up

In the past 2 years, I have focused much more on the early attempts to transfer the CMS membrane technology from the laboratory scale to the industry. This work has been performed within several AMPM Center-funded projects and one translational research project at my employer (KAUST) which were granted to my supervisor Prof. Ingo Pinnau.

The main efforts of my current work are directed toward the development of pilot-scale modules with several hundreds of cm^2 membrane areas, Figure 31. Both ceramic, as well as metallic supports[36], are being used. So far, we have managed to produce several membrane modules that could reproduce the excellent CMS gas separation properties at relatively low pressures. Currently, we are working on the fabrication of high-pressure, cross-flow modules with large membrane areas that could be tested at relevant high pressures and in mixed gas conditions.

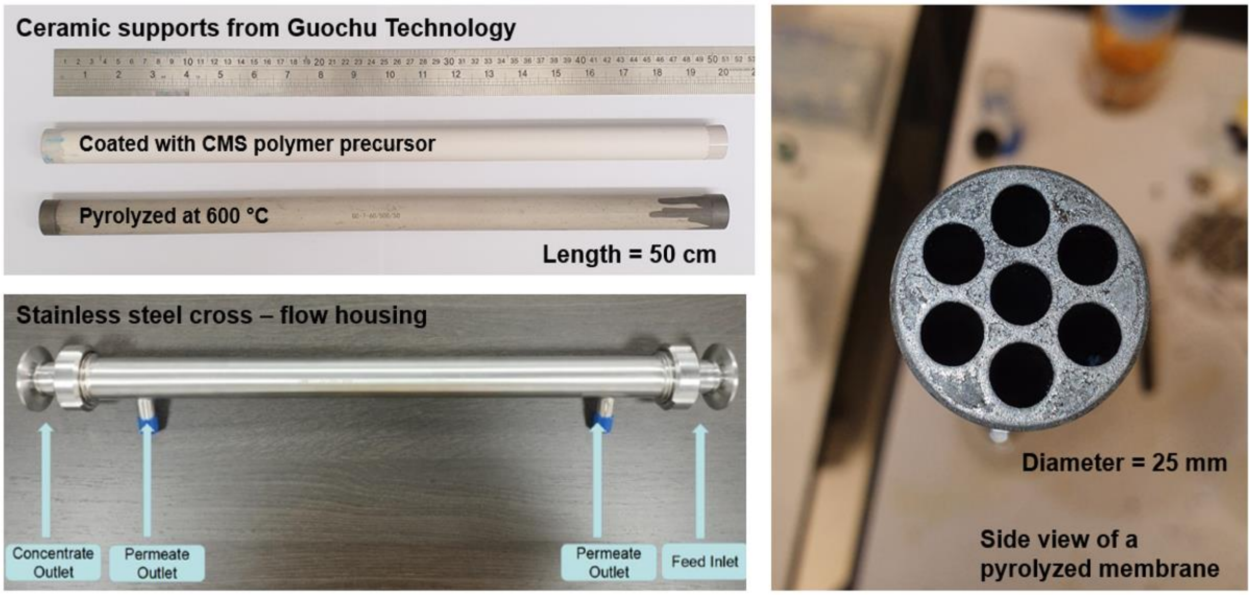

Figure 31 Pilot-scale multi-channel ceramic modules serving as supports for CMS membranes based on PIM-PI polymers

Section III: Summary of achievements

- *Successful fabrication of small, lab-scale thin-film composite CMS membranes based on novel polyimide of intrinsic microporosity (PIM-PIs) precursors as well as comprehensive characterization of their structural and gas separation properties as a function of pyrolysis temperature.*
- *Generation of abundant evidence on the extensive, undesired collapse of ultra-thin CMS layers (significantly below 1 µm) leading to an important counter-intuitive conclusion that such thin CMS layers are actually much less productive as molecular separation membranes than their thicker (several micron) counterparts.*
- *Introduction of a new concept of nano-hybrid CMS membranes with molecularly dispersed inorganic oxides serving as dopants that modify their gas separation properties. Such membranes can provide excellent gas separation properties typical of high-temperature CMS membranes at, however, much lower pyrolysis temperatures. This feature is extremely important from the practical point of view leading to reduced risks of defects as well as broadening the choice of a substrate. In addition, the physical aging characteristics of the nano-hybrid CMS membranes are more favorable than of the undoped CMS membranes.*
- *Significant advances in the translation of the CMS membranes based on PIM-PI technology from lab scale into the pilot scale.*

Other scientific and research achievements

Scientific activity before obtaining the doctoral degree (2007 – 2014)

During my undergraduate studies at Cracow University of Technology (Poland), I participated in a student's research club (2007) under the supervision of prof. dr. hab. inż. Dariusz Bogdał. The activities within that club raised my interest in scientific research in a broad discipline of chemical engineering and enabled my successful application to the student exchange program ERASMUS with Münster University of Applied Sciences (Germany) as the host institution (2008). Afterward, I was able to successfully apply for a double diploma program which resulted in a double MSc degree (with distinction, 2009) from both Cracow University of Technology (Poland) and Münster University of Applied Sciences (Germany), supervised by prof. dr. hab. inż. Jan Pielichowski and Prof. Dr. rer. nat. Martin Kreyenschmidt. The MSc Thesis titled: "*Investigation of interactions between ultraviolet laser beam and polymer matrices with a use of Total Organic Carbon and Laser Ablation ICP-MS*" had a highly interdisciplinary character and sparked my interest in advanced analytical techniques.

Following my M.Sc., I got accepted for a 4-year doctoral program (2010 – 2013) at the University of Twente (the Netherlands) under the supervision of a world-renowned membrane expert Prof. Dr.-Ing. Matthias Wessling and the excellent mentorship of Prof. dr. ir. N.E. Benes with a topic related to the superposition of nanoconfinement effects and penetrants in membrane science. During my PhD studies, I was able to participate in multiple technical and non-technical courses. In particular, I was able to finish the 4 prestigious RPK Polymer Science courses at PTN Research School, the Netherlands. I graduated with PhD (*cum laude,* with distinction) in 2014 and my PhD Thesis was awarded 2nd place of the Dutch Challa Polymeer Prijs 2015 for the best PhD dissertation in the field of polymer chemistry/technology in the Netherlands for years 2013 and 2014. I received Paul Drude Medal (2012) awarded to young scientists for their contributions in the field of spectroscopic ellipsometry at 7th Workshop Ellipsometry (Lepizig, Germany) as well as the Best Oral Presentation prize at Euromembrane (2012) (London, UK). In 2013, I was a finalist of the LANXESS Talent Award at DWI/RWTH (Aachen, Germany). Overall, my PhD work resulted in authoring and co-authoring of 20 articles published in top peer-reviewed international journals (published between 2012 and 2019). The articles tied directly to my PhD studies have been collectively cited over 400 times (as of August 2022).

The focus of my PhD work has been on the fundamental behavior of predominantly model macromolecular systems in a form of thin films when exposed to interacting penetrants. For this purpose, I helped develop, adapt, and optimize the in-situ spectroscopic ellipsometry technique to study thin films and membranes under realistic process conditions. The breakthroughs related with the introduction of ellipsometry into membrane science allowed unprecedented characterization possibilities of thin-film membranes where the behavior of the selective layer (even ultra-thin, <100 nm) in contact with fluid could be accessed in a non-destructive, dynamic manner.

In addition, during my work as a PhD student I was able to gain hands on experience of multiple membrane and thin film characterization techniques, such as spin-coating, dip-coating, phase separation, scanning and transmission electron microscopy (SEM, TEM), atomic force microscopy (AFM), dielectric relaxation spectroscopy (DRS), or porosimetry.

Being part of one of the best membrane science research groups in the world at the University of Twente allowed me the development strong fundamentals of membrane fabrication (both organic and inorganic), transport theory and practice, as well as exposed me to experts from all around the world during multiple international and national meetings. Although, my research had a highly fundamental character, I also gained the basic ideas behind membrane development which helped me appreciate the challenges that lie in the technology transfer from the lab into the industry.

During my PhD, I also had a pleasure to co-supervise several BSc and MSc students who all graduated with excellent Theses and their work resulted in significant contributions to two publications. Many of them continued to pursue their PhD, as well.

The interdisciplinary focus of my work is also highlighted by the activity in both membrane and ellipsometry societies. In 2011, I participated in the organization of ICOM (the largest membrane conference) in Amsterdam (the Netherlands). In 2015, I managed the submissions, venue, and website of the 9th Workshop Ellipsometry in Enschede (the Netherlands).

Scientific activity after obtaining the doctoral degree (2014 - 2022)

In January 2014, I transitioned from a PhD student to a postdoctoral fellow and worked on a project sponsored by the Dutch ISPT Institute related with the development of gas and organic solvent separation membranes based on hybrid POSS-related materials which targeted harsh conditions (elevated temperatures and pressures). This work gave me a chance to apply the unique analytical techniques developed during my PhD to much more application-oriented problems.

In March 2015 I was offered a postdoctoral position at RWTH Aachen University, Germany. During that stay, I significantly broadened my expertise related to analytical and fabrication techniques used in membrane science and engineering. In particular, I developed a strong understanding of X-Ray Reflectometry, 3D printing, or Quartz Crystal Microbalance with Dissipation. I also significantly broadened my understanding of cutting-edge developments in chemical separation engineering, not strictly related to membranes, e.g. redox flow batteries, module design, block co-polymers, advanced bio-sensors, and imaging techniques. In Aachen, I have also continued to supervise Master and Bachelor students who gave me excellent feedback as a supervisor. The majority of those students decided to continue their academic careers and joined PhD programs.

My main focus in Aachen, however, was the application of high-pressure in-situ ellipsometry to a novel class of microporous polymeric materials, polymers of intrinsic microporosity (PIMs). This constituted a collaboration project between RWTH Aachen and King Abdullah University of Science and Technology (KAUST). The project resulted in several publications as well as a book chapter in a book dedicated to spectroscopic ellipsometry. In 2016, I was an invited speaker during several seminars: at ISAS Institute in Berlin, Germany, at IPF Institute in Dresden, as well as at KAUST, Saudi Arabia. I was also an invited speaker and poster presenter at ICSE-7 – the largest ellipsometry conference in the world, and at New Materials Horizon for Energy Intensive Industrial Separations at KAUST (conference by invitation-only). At that conference, I was awarded the best poster award.

In September 2017, I was offered a position of a Research Scientist (R3) in the group of Prof. Ingo Pinnau at Advanced Membranes and Porous Materials Center at KAUST. During my work at KAUST, I have further broadened my focus on amorphous microporous materials used in membrane engineering by including carbon molecular sieve (CMS) membranes. Initially, between

2017-2019, my work had a fundamental character, however, gradually my interest moved to a much more application-focused work related to CMS membrane scale-up (2020-present). I strongly believe that the challenge of scale-up is currently the most urgent issue in bringing the often excellent membrane materials developed in the laboratory to the existing industrial reality. In that spirit, I significantly contributed to two competitive grants awarded within KAUST to the research Center. Currently, I am working within a KAUST Translation Funding project (nearly 900 000 USD) on a scale-up of CMS membranes for energy intensive separations. In July 2022, after receiving excellent performance evaluation for two years in a row, I was promoted to Research Scientist (R4) which is equivalent to an Assistant Research Professor position.

At KAUST, I gained a much better understanding of not only membranes used for gas separation, but also those being developed for water and organic solvent purification. This has resulted in multiple collaboration papers with researchers from KAUST as well as from abroad (USA, Germany). Recently, we have developed an entirely new method of CMS membrane nano-modification by combining atomic layer deposition with pyrolysis which resulted in a successfully granted US patent. Another patent application for an innovative fast pyrolysis process to fabricate CMS membranes have been recently disclosed internally within KAUST PI department. Recently, our work was also recognized by the KAUST Discovery magazine who featured our recent paper in a separate article and a video (https://discovery.kaust.edu.sa/en/article/1140/sweet-spot-for-membrane-thickness-offers-sustainable-separations).

In the past several years, I completed two research stays abroad. In 2019, I executed a 3-week research project at RWTH Aachen University in Germany which was completed with a collaborative publication in Macromolecules in 2020. In 2021, I received a Mobility Grant from the Nicolaus Copernicus University in Toruń, Poland, to perform a 1 month project on pervaporation with CMS membranes. A collaborative (KAUST, UMK Toruń) manuscript resulting from the project is currently under preparation.

I have also continued to develop in-situ spectroscopic ellipsometry, which resulted in breakthrough applications of the technique directly to as-received membranes. It is anticipated, that this technique will have potential large implications to the field of membrane in-situ/in-operando characterization, in particular in one of the largest current membrane markets (interfacially-polymerized membranes for water desalination). To broaden my ellipsometry expertise even further, I developed an understanding of infrared spectroscopic ellipsometry (collaboration project with ISAS Berlin, Dr. Andreas Furchner) and completed an Anisotropy course related to spectroscopic ellipsometry data analysis in 2020.

At KAUST, I have had plenty of interactions with MSc and PhD students who I co-supervised or otherwise assisted. In 2019, I was Assistant Mentor for a youth program (Saudi Research Science Institute, SRSI) which involved very intense daily mentoring of a top Saudi high school (17 year old) student during a 6-week summer project. This involved laboratory work, as well as supervision of writing and communication efforts. The student finished with an excellent result (top 5 of his cohort). More recently in summer 2022, I served on a committee of judges to evaluate 45 reports and presentations from 2022 SRSI edition. In 2020 and in 2022, I was chosen to showcase research done at KAUST in a series of invited internal seminars for chemical engineering students. In addition, twice a year, I present my research at a center seminar with the presence of all faculty (11 research groups) and students/staff (nearly 200 scientists). In 2021, I volunteered for an AMPM Center open day which involved conducting scientific demonstrations and discussions for the general KAUST community. During AMPM Center external accreditation evaluation in 2021, I was selected by the center director to represent Research Scientists staff during a promotional video interview.

I continue to offer service to the broader scientific community as reviewer of peer-reviewed articles by such journals as: Nature Communications, The Journal of Membrane Science, Polymer, Materials Letters, Materials Today Nano, and others. Since 2018, I completed over 30 such reviews. I also continue to be attend (as keynote, invited, or standard speaker) at least 2-3 major membrane and ellipsometry conferences per year. I am a member of the German AKE Drude Ellipsometry professional society (http://www.ake-pdv.org/), as well as the North American Membrane Society (https://membranes.org/).

Further research plans

My recent research allowed me the identification of several major hurdles in the development of practical and efficient membranes that could be used for energy-intensive separations (natural gas purification, olefin-paraffin separations, etc.). These lie in the inherent property of amorphous microporous materials to physically age, in particular when prepared as thin and ultra-thin films.

The physical aging drastically reduced the achievable transport rates in such membranes effectively often rendering them not competitive with the currently existing membranes. I am focused on developing ways to prevent such unwanted effects with some success so far (e.g. via development of nano-hybrid inorganic/organic membranes).

I would also like to expand the capabilities of in-situ spectroscopic ellipsometry to some of the most challenging areas such as the characterization of microporosity distributions in microporous films. Such method would be similar to the existing cryogenic N_2 sorption and NLDFT analysis yet with the important difference of being applicable directly to thin and ultra-thin films.

My future plans also involve development of collaboration efforts with the Membranes and Membrane Techniques group at the Nicolaus Copernicus University in Toruń. In particular, membranes developed at KAUST (my current institution) will be evaluated towards molecular sieving of liquid mixtures via solvent permeation and pervaporation. In a longer perspective, I consider continuation of my academic career at one of the polish universities.

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