GROWING

TO SHRINK

Grafting alumina mesopores
for molecular separations

RENAUD B. MERLET

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DISSERTATION

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Renaud Benoit Merlet

born on the 18th of November 1986
in Paris, France

This dissertation has been approved by supervisors:

Prof. Dr. Ir. A. Nijmeijer

and

Prof. Dr. A.J.A. Winnubst

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Summary

Hybrid, ceramic-based membranes combine the stability of porous ceramic oxides with the functionality of polymers. The wide range of polymers allows for tailor-made materials matching the requirements of the target application. This thesis expands upon the materials, fabrication techniques and potential applications of hybrid, ceramic-based membranes.

Chapter 2 first gives an overview of the recent progress in grafted ceramics for organic solvent nanofiltration (OSN) applications. It provides an overview of suitable organic-inorganic linking functions, reviews the strategies to tune the pore surface and compares the resulting membranes. Also discussed are the capabilities and shortcomings of both the characterization tools and the transport models used to describe this class of membranes. The link between material chemistry, grafting technique and performance is established as the challenges awaiting the researcher of hybrid, ceramic-based membranes are identified. This chapter serves to frame the advances presented in the following Chapters for the reader.

Chapter 3 presents the grafting-from technique applied to the confined mesopores of γ -alumina. It is the first instance of controlled polymerization initiated from the surface of a high-curvature concave geometry. Polystyrene was grown inside 5 nm diameter pores to shrink to a desired degree, demonstrating the ability to tune the membrane selectivity. The parameters choices of the method used - surface-initiated, activators-regenerated-by-electron-transfer, atom-transfer radical polymerization (SI-ARGET-ATRP) – are detailed. The graft is characterized by TGA, AFM, and FTIR, and it is shown that the graft length is solvent-dependent. Also demonstrated is the application potential of this new class of hybrid, ceramic-based membrane as an organic solvent nanofiltration membrane. The top performing membrane exhibited a toluene permeability of $2.0 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$ accompanied by a 90% retention of diphenylanthracene ($\text{MW } 330 \text{ g mol}^{-1}$).

Chapter 4 features further development of the grafting-from method with a novel material and for a different application, poly(ionic liquid) [StyMim][Tf₂N] for CO₂ separation. The same support substrate as Chapter 3 was used for SI-ARGET-ATRP, although adjustments to the reaction reagents and parameters were required. These are explained alongside the gas transport behavior through membranes made by successive polymerizations. The dense-pore gas separation membrane is characterized by means of AFM, XPS, SEM/EDS, and FTIR. A CO₂ permeance of 0.47×10^{-7} (mol.m⁻²s⁻¹Pa⁻¹) and a CO₂/N₂ permselectivity of 14 was achieved, providing an encouraging beginning for development of this new membrane class.

Chapter 5 presents two new unique achievements: a thioether-based aromatic crosslinked selective layer, and a green interfacial polymerization (IP) technique. Before this work, toxic solvents were used for the production of chemically and thermally resistant nanofiltration membranes. The use of non-toxic solvents for the synthesis of these membranes was achieved by adapting thio-bromo click biochemistry to fabrication of a nanofiltration membrane. The selective layer was formed on a pre-functionalized porous ceramic surface via a novel, vapor-liquid interfacial polymerization method. No harmful solvents and minimal reagents were used to fabricate stable, 40 nm-thin films covalently attached to a porous, alumina support. The properties of the membrane selective-layer and its free-standing equivalent were characterized by means of FTIR, TGA/MS, NMR and FE-SEM. Thin layer stability in acid, base, hypochlorite, non-polar solvents and up to 150°C was established. The potential as a nanofiltration membrane was evaluated in water and multiple solvents, exhibiting a PEG in water molecular weight cut-off of 700 g mol⁻¹.

Chapter 6 describes the retention behavior of PDMS-grafted alumina membranes. Their dye-retention performance in several solvents is described and modeled here. In contrast to pure PDMS polymeric membranes, higher retentions were found in nonpolar solvents than in polar solvents. This is attributed to a solvent-induced pore-constriction behavior: confined swelling of PDMS, grafted into the membrane pores, was found to increase retention. To model this hypothesis, pore sizes were calculated by the Ferry, Verniory and steric hindrance pore (SHP) equations and integrated into the Spiegler-Kedem-Katchalsky (SKK)

model to predict dye retention. Ultimately, a diffusion pore size was introduced in the SKK model to reflect the ability of the solute to diffuse through the swollen PDMS graft. A better understanding of the transport mechanisms impacting performance was gained by incorporating the unique pore structure of these ceramic-based hybrid membranes into the SKK model.

Chapter 7 is a collaboration between several academic and industrial partners analyzing the separation performance of three model process mixtures of multiple commercial and laboratory-made membranes, including those described in Chapter 3. The mixtures were chosen specifically to mimic challenges relevant to today's industrial processes: a relatively low MWCO and high temperature. First, a fair comparison of data sets is established by a round-robin test of the same membrane across all test setups used. Next, the results of selected membranes are presented case-by-case. Though all membrane types suffered from the inevitable retention-permeability tradeoff, permeabilities greater than $2 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$ with a MWCO of 330 Da or less were obtained by several membranes in two out of the three cases. This collaboration is a first step towards the industrial validation of the membranes developed in Chapter 3. Promising results encourage the further development of grafted-from hybrid ceramic membranes for OSN.

Chapter 8 provides perspective and commentary on the work done in this thesis as a whole. The materials and membrane fabrication techniques developed in Chapters 3 through 5 are critically assessed. The merits and shortcomings of the model developed in Chapter 6 and the screening methodology of Chapter 7 as tools for the identification of candidate membranes for scale-up are discussed. Several conclusions are drawn, principally the need for support diversification and the necessity of both fundamental study and application-targeted development of the membrane types of Chapters 3 through 5. The crosslinked thioether membranes of Chapter 5 are identified as ideal candidates for development and eventual scale-up.

Samenvatting

Hybride, op keramiek gebaseerde membranen, zoals beschreven in dit proefschrift, combineren de stabiliteit van poreuze keramische oxiden met de functionaliteit van polymeren. Het brede scala aan polymeren maakt het mogelijk om op maat gemaakte membranen te maken die voldoen aan de vereisten van de beoogde toepassing. Dit proefschrift gaat dieper in op de materialen, fabricagetechnieken en mogelijke toepassingen van deze hybride membranen voor nanofiltratie van organische oplosmiddelen (OSN: Organic Solvent Nanofiltration).

Hoofdstuk 2 gaat in op de recente ontwikkelingen op het gebied van het chemisch modifieren (of ‘graften’) van keramische membranen met organische moleculen. Een overzicht wordt gegeven van geschikte moleculen die het (anorganische) keramiek kunnen verbinden met het organisch molecuul. Ook wordt ingegaan op strategieën om het inwendig oppervlak van de poriën zodanig chemisch te modifieren, dat de gewenste membraan eigenschappen worden verkregen. De mogelijkheden en tekortkomingen worden besproken van zowel de karakteriseringstools als de transportmodellen die worden gebruikt om deze klasse membranen te beschrijven. Verbanden worden gelegd tussen de materiaalchemie, het graften en de membraanprestaties en de uitdagingen worden geïdentificeerd voor onderzoek aan hybride op keramiek gebaseerde membranen. Dit hoofdstuk kan ook gezien worden als een verantwoording voor hetgeen in de volgende hoofdstukken wordt beschreven.

Hoofdstuk 3 presenteert het graften in de 5 nm (meso)poriën van gamma-aluminiumoxide. Hier wordt voor het eerst een gecontroleerde polymerisatie beschreven vanaf een anorganisch oppervlak met concave geometrie en hoge kromming (kleine straal). Het graften van polystyreen in de poriën kan hier gecontroleerd worden, waardoor de initiële diameter van 5 nm van het de gamma-alumina porie tot een gewenst afmeting krimpt. Dit biedt de mogelijkheid om de selectiviteit van het membraan te controleren. De synthese methode die hiervoor gebruikt wordt is SI-ARGET-ATRP (Surface-Initiated, Activators-Regenerated-by-Electron-Transfer, Atom-Transfer Radical Polymerization, oftewel: oppervlakte-geïnitieerde, activatoren-geregenereerd-door-elektronenoverdracht,

atoomoverdracht radicaal polymerisatie). De invloed van verschillende synthese parameters op poriemorfologie en membraan eigenschappen wordt uitgebreid beschreven. Karakterisering van de mate van grafting is uitgevoerd met TGA, AFM en FTIR. Daarnaast is aangetoond dat het krimpen van de gamma-alumina porie niet alleen afhankelijk is van de synthese parameters, maar ook van het oplosmiddel, dat gebruikt wordt voor de filtratie experimenten. De potentiële toepassing van deze nieuwe klasse van hybride membranen als nanofiltratie membraan voor organische oplosmiddel oplosmiddelen is aangetoond. Het best presterende membraan vertoonde een toluen permeabiliteit van $2,0 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ gepaard met 90% retentie van difenylantracene (molecuulgewicht: 330 g mol^{-1}).

Hoofdstuk 4 gaat in op een verdere ontwikkeling van deze SI-ARGET-ATRP graft methode. Hier wordt deze methode toegepast voor het maken van een poly-ionische vloeistof (“poly-ionic liquid”) [StyMim] [Tf₂N] membraan voor CO₂-scheiding. Hetzelfde keramische substraat als in hoofdstuk 3 werd gebruikt, en de synthese parameters zijn aangepast om de gewenste resultaten te verkrijgen. Naast het gastransport door deze membranen, is de micro- en chemische structuur geanalyseerd met AFM, XPS, SEM / EDS en FTIR. Een CO₂-permeantie van $0,47 \times 10^{-7} \text{ (mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1})$ en een CO₂/N₂ permselectiviteit van 14 werd bereikt, wat een bemoedigend begin vormt voor de ontwikkeling van deze nieuwe membraanklasse.

Hoofdstuk 5 beschrijft twee nieuwe unieke resultaten: een op thioether gebaseerde aromatisch verknoopte (“cross-linked”) selectieve laag en een groene grensvlak polymerisatie (“Interfacial Polymerization” IP) techniek. In de meeste gevallen wordt bij de productie van chemisch en thermisch resistente nanofiltratie membranen giftige oplosmiddelen gebruikt. Het gebruik van niet-toxische oplosmiddelen voor de synthese van deze membranen wordt bereikt door de thio-bromo click-biochemie aan te passen aan de fabricage van een nanofiltratie membraan. De selectieve laag wordt gevormd op een poreus keramisch oppervlak via een nieuwe, damp-vloeistof grensvlak-polymerisatie methode. Hier worden geen schadelijke oplosmiddelen en een minimale hoeveelheid reagentia gebruikt om stabiele, 40 nm dunne, films te vervaardigen die covalent zijn gebonden aan een poreuze aluminiumoxide-drager. De structuur en eigenschappen van de

selectieve membraanlaag en het vrijstaande equivalent ervan zijn gekarakteriseerd door middel van FTIR, TGA / MS, NMR en FE-SEM. De stabiliteit van deze lagen zijn vastgesteld in zuur, base, hypochloriet en niet-polaire oplosmiddelen en tot temperaturen van 150 °C. Nanofiltratie voor dit membraan is bestudeerd in water en meerdere oplosmiddelen. In water is een retentie gevonden voor PEG met een molecuulgewicht van 700 g mol⁻¹.

Hoofdstuk 6 gaat in op de retentie van met PDMS geïmpregneerde aluminiumoxide membranen. De retentie van verschillende kleurstoffen in verschillende oplosmiddelen wordt hier beschreven en gemodelleerd. In tegenstelling tot 100 % PDMS-polymere membranen zijn voor deze PDMS-geïmpregneerde membranen hogere retenties gevonden in niet-polaire oplosmiddelen in vergelijking met polaire oplosmiddelen. Dit wordt toegeschreven aan een oplosmiddel-geïnduceerd poriekrimp gedrag. Er vindt een beperkte zwelling van het PDMS plaats in de robuuste keramische poriën, wat resulteert in een verhoging van de retentie van een kleurstof. Om deze hypothese te modelleren, zijn de poriegroottes berekend met de Ferry, Verniory en sterische hinder porie (SHP) vergelijkingen en geïntegreerd in het Spiegler-Kedem-Katchalsky (SKK) model om op deze manier de retentie van kleurstoffen te kunnen voorspellen. Uiteindelijk is in het SKK-model een diffusie poriegrootte geïntroduceerd om de mogelijkheid weer te geven, dat de opgeloste kleurstof door het gezwollen PDMS-graft kan diffunderen. Door de unieke poriestructuur van deze hybride membranen in het SKK-model op te nemen is een beter begrip verkregen van de mechanismen die het transport beïnvloeden.

Hoofdstuk 7 beschrijft de samenwerking tussen verschillende academische en industriële partners, waarbij de scheidingsprestaties worden geanalyseerd van drie model procesmengsels door meerdere commerciële en in het laboratorium gemaakte membranen, inclusief het membraan, zoals beschreven in hoofdstuk 3. De mengsels werden zodanig gekozen om situaties na te bootsen die relevant zijn voor de industriële processen van vandaag: een relatief lage MWCO (Molecular Weight Cutt-Off) en hoge temperatuur. Eerst is een eerlijke vergelijking van datasets gemaakt door een round-robin test uit te voeren van hetzelfde membraan over alle gebruikte testopstellingen. Vervolgens worden per geval de resultaten van geselecteerde membranen gepresenteerd. Hoewel alle membraantypes te

maken hebben met de onvermijdelijke wisselwerking tussen retentie en permeabiliteit, zijn permeabiliteit waardes groter dan $2 \text{ L m}^{-2}\text{h}^{-1}\text{bar}^{-1}$ met een MWCO van 330 Da of minder verkregen door verschillende membranen in twee van de drie gevallen. Deze samenwerking is een eerste stap op weg naar de industriële validatie van de membranen die in hoofdstuk 3 zijn ontwikkeld. Veelbelovende resultaten stimuleren de verdere ontwikkeling van gegrachte hybride keramische membranen voor OSN.

Hoofdstuk 8 tenslotte geeft een evaluatie van het werk dat in dit proefschrift is beschreven en geeft perspectieven voor potentiële toepassingen van de membranen. Daarnaast worden suggesties voor verder onderzoek gegeven. De in hoofdstukken 3 tot en met 5 ontwikkelde materialen en synthese methoden voor de fabricage van hybride keramische membranen worden kritisch beoordeeld. Ook is ingegaan op de mogelijkheden en tekortkomingen van het in hoofdstuk 6 ontwikkelde transportmodel. De methodologie van screening om de juiste membranen te kiezen voor opschaling, zoals beschreven in hoofdstuk 7, als hulpmiddelen voor de identificatie van kandidaat membranen voor opschaling wordt geëvalueerd. Met name het op thioether gebaseerde membraan, zoals beschreven in hoofdstuk 5, wordt gezien als een ideale kandidaat voor verdere ontwikkeling en opschaling.

CHAPTER ONE

Introduction

Membrane technology is the application of a selective barrier to separate components of interest, creating a product of added value for the user. A driving force, such as a pressure difference, separates the product from the feed mixture. Much of the research in membrane technology has focused on aqueous-based separations, for example, desalination or wastewater treatment [1-2]. However, upon exposure to feed streams containing organic solvents, typical membranes have not possessed the required durability or performance. Development of new membrane types destined for such harsh conditions has been spurred by interest from industry and academia alike [3]. This field is termed organic solvent nanofiltration (OSN), also referred to as solvent resistant nanofiltration (SRNF). As shown in Figure 1.1Figure 2.1, OSN is a young yet growing research field. The attention OSN has drawn is due to its competitive advantages over traditional molecular separation processes: less energy consumed, ease of scale up, relatively mild operating conditions, and compatibility with heat-sensitive compounds [4-5].

Figure 1.1. Number of publications per year for either or both keywords “Organic Solvent Nanofiltration” and “Solvent Resistant Nanofiltration,” as found by Scopus (April 2019).

The term “nanofiltration” describes a pressure-driven membrane process which will reject solutes below 2 nm in diameter [6], or, alternatively, <1000 Da in mass. Unlike aqueous-based nanofiltration processes, such as desalination, OSN does not refer to a specific application and purpose, it is rather an umbrella term for an assortment of chemical-related separations, for example, quinine catalyst purification in ethanol [7] or the deacidification of waste oils in n-hexane [8]. As a result, there is no “ideal” OSN membrane to be developed, meaning the advancement of the field as a whole lies not in the pursuit of incremental improvements, but rather in developing membrane materials which are resilient to a broad set of conditions and can easily be tuned for a wide range of applications.

To this end, membrane researchers continue to develop new polymeric and ceramic membranes. Each membrane type has advantages and drawbacks. Whereas polymeric membranes are widely available and easily modified, they can also be unstable in organic solvents, especially in nonpolar solvents. Ceramics are costlier than polymers, and the hydrophilic surface of ceramic mesopores inhibits the passage of many solvents, yet their chemical inertness and structural rigidity is appealing. Efforts to combine the robustness of porous ceramics with the tunability of organic materials have led to the emergence of a new class of membranes. It is the focus of this thesis: novel, hybrid ceramic-based membranes for challenging molecular separations.

1.1 THE CASE FOR THE FUNCTIONALIZATION OF POROUS CERAMICS

Functionalization of a porous ceramic with an organic molecule can drastically change the behavior of ceramic membranes. One of the first effective surface chemical modifications of ceramic membranes was reported by Van Gestel et al. [9], as illustrated in Figure 1.2. The grafting (creation of covalent bonds) between an alkoxysilane compound and the surface of γ -alumina support increased hexane permeability from 0.0 to 6.1 L.m⁻²h⁻¹bar⁻¹, while the same treatment reduced water permeability from 4.0 to 0.0 L.m⁻²h⁻¹bar⁻¹. Ever since, a plethora of existing chemistries have been ingeniously adapted to modify porous ceramic membranes

for OSN, resulting in hybrid membranes with excellent permeation and retention properties.

Several types of hybrid ceramic-based membranes have been developed, each with their own strength and weaknesses, as detailed in **Chapter 2**. Researchers of these innovative membrane types seek low (< 400 Da) molecular weight cut-offs (MWCO), despite the limited pore size selection of unmodified ceramic membranes, and to apply the same strong performance across as large as possible a range of solvent-solute combinations. The advances in OSN membranes presented in Chapter 2 and continued in this thesis are inextricably linked to the development of novel membrane material combinations and innovative fabrication techniques.

Figure 1.2. The reversal of permeability behavior of a typical porous ceramic as a result of hybridization.

Figure 1.3. Grafting-from vs. grafting-to. Grafting-from is the polymerization of monomer from a surface-bound initiator, while grafting-to is the linking of ready-made polymer chains onto the ceramic substrate.

1.2 INNOVATIVE CHEMISTRY AND FABRICATION TECHNIQUES FOR MOLECULAR SEPARATIONS

Chapters 3 & 4 pioneer and expand upon the grafting-from method as applied to the confined mesopores of 5 nm diameter γ -alumina. Grafting-from is the process of growing polymer chains from an initiator covalently bound to its substrate, as opposed to grafting-to which is the linking of pre-synthesized polymer chains onto a surface (Figure 1.3). Grafting-from allows a greater variety of polymer grafts, and just as importantly, the *in situ* tuning of the polymer length. The implied benefit for membrane technologists is the potential to tailor both the surface properties and pore size of the ceramic support in one reaction.

Such a benefit is demonstrated in **Chapter 3** with the surface-initiated growth of polystyrene chains. The grafting-from of polystyrene transforms the alumina ceramic support to an OSN membrane for non-polar solvents. The length of the grafted-from polystyrene is shown to be adjustable, thereby giving the ability to choose the MWCO (down to 330 Da). **Chapter 4** expands the grafting-from technique of Chapter 3 to not only adapting the grafting-from procedure to another polymer, poly(ionic liquid) [StyMIM][Tf₂N], but also by showing the potential of this technique in another field, CO₂ separation from flue gas. The

grafting-from technique was applied in a new, confined geometry to two different materials, yielding performing membranes for both OSN and gas separation.

Chapter 5 introduces both a new membrane material and a new, green membrane fabrication method. A thioether-based crosslinked thin film was fabricated on top of γ -alumina. This material is shown to be stable in acid, basic, bleach, and organic solvent media, as well as environments up to 150°C. The membrane fabrication method is a green evolution of the interfacial polymerization technique. Taking advantage of an air-liquid interface, it eliminates hazardous solvent use and stops the disproportionate amounts of reagent waste found in interfacial polymerization techniques.

Chapters 3 and 4 deal with new material combinations and the adaptation of a cutting-edge polymerization techniques to fabricate tunable and versatile membranes. Chapter 5 develops both a new membrane material and green membrane fabrication method. Each is an example of the potential that can be achieved by incorporating new chemistries and techniques to membrane fabrication.

1.3 OSN MEMBRANES AND THEIR POTENTIAL

The ultimate goal of the research engineer is to create a product of added value for society. As this introduction has remarked and Chapter 2 fully reviews, there are numerous OSN membrane types which show this potential, the potential for eventual adoption into industrial applications. Without the ability to predict membrane performance or systematically benchmark membranes for a given application, research output is effectively limited. The diversity of OSN membrane applications means only a few membrane types are likely appropriate for a given application. The first approach, modelling transport behavior across the membrane, is the topic of **Chapter 6**.

The ability to mathematically describe the mass transport of a solution across a membrane can allow for the prediction of transport of another solvent-solute combination, or, alternatively, of a related membrane. A predictive model encompassing multiple membrane classes does not yet exist, however, insights gained during modelling attempts yield valuable information. Chapter 6 shows

that the solute retention is solvent dependent (as the solvent permeability was shown to be [10]). It establishes a model that predicts permeability and retention for ideal solutes (dyes) in a given solvent. It does this correctly by allowing for the diffusion of solutes through the graft.

Chapter 7 is a collaboration between several producers of cutting-edge OSN membranes to compare the performance of membranes in model solutions representing challenging industrial mixtures. Comparability of results among the plethora of published OSN literature (Figure 1.1) is sometimes dubious: different test variables introduce doubt. Test parameters of laboratory-produced membranes, such as equipment configuration, pressure, temperature, etc., to name only a few, are not uniform. Chapter 7 establishes that a fair comparison can be made when comparing the same solvent-solute combination, regardless of dead-end or crossflow configurations and other setup parameters. It shows that performance of a given membrane class can vary widely between even similar cases, e.g. the solute diphenyl anthracene dissolved in toluene versus heptane. For three industrially relevant mixtures top performing membranes are established and therefore recommended to the industrial partners of the study for further investigation.

Both the screening of seemingly suitable membranes for industrial applications and efforts towards producing predictive OSN models are worthwhile pursuits. Progress in these approaches will accelerate the adoption of membranes into industrial processes.

1.4 OUTLINE OF DISSERTATION CHAPTERS

Chapter 2 first gives an overview of the recent progress in grafted ceramics for organic solvent nanofiltration (OSN) applications. It provides an overview of suitable organic-inorganic linking functions, reviews the strategies to tune the pore surface and compares the resulting membranes. Also discussed are the capabilities and shortcomings of both the characterization tools and the transport models used to describe this class of membranes. The link between material chemistry, grafting technique and performance is established as the challenges awaiting the researcher of hybrid, ceramic-based membranes are identified. This

chapter serves to frame the advances presented in the following chapters in the context of the state-of-the-art.

Chapter 3 presents the grafting-from technique applied to the confined mesopores of γ -alumina. It is the first instance of controlled polymerization initiated from the surface of a high-curvature concave geometry. Polystyrene was grown inside 5 nm diameter pores to shrink to a desired degree, demonstrating the ability to tune the membrane selectivity. The parameters choices of the method used - surface-initiated, activators-regenerated-by-electron-transfer, atom-transfer radical polymerization (SI-ARGET-ATRP) – are detailed. The graft is characterized by TGA, AFM, and FTIR. Also demonstrated is the application potential of this new class of hybrid, ceramic-based membrane as an organic solvent nanofiltration membrane..

Chapter 4 features further development of the grafting-from method with a novel material and for a different application, poly(ionic liquid) [StyMim][Tf₂N] for CO₂ separation. The same support substrate as chapter 3 was used for SI-ARGET-ATRP, although adjustments to the reaction reagents and parameters were required. These are explained alongside the gas transport behavior through successive polymerizations. The closed-pore gas separation membrane is characterized by means of AFM, XPS, SEM and EDS, and FTIR.

Chapter 5 presents two new unique achievements: a thioether-based aromatic crosslinked selective layer, and a green interfacial polymerization (IP) technique. Before this work, no nanofiltration membrane fabrication method used non-toxic solvents to produce a chemically and thermally resistant membrane. This was achieved by adapting thio-bromo click biochemistry to fabrication of a nanofiltration membrane. A selective thin layer was formed on a pre-functionalized porous ceramic surface via a novel, vapor-liquid interfacial polymerization method while no harmful solvents and minimal reagents were used. The properties of the membrane selective-layer and its free-standing equivalent were characterized by means of FTIR, TGA/MS, NMR and FE-SEM. Thin layer stability in acid, base, hypochlorite, non-polar solvents and up to 150°C were studied. The potential as a nanofiltration membrane was evaluated in water and multiple solvents.

Chapter 6 studies the retention behavior of PDMS-grafted alumina membranes. Their dye-retention performance in several solvents is described and modeled here. A solvent-induced pore-constriction behavior is introduced, taking into account the confined swelling of PDMS, as grafted into the membrane pores. To model this hypothesis, pore sizes were obtained by the Ferry, Verniory and steric hindrance pore (SHP) equations and integrated into the Spiegler-Kedem-Katchalsky (SKK) model to predict dye retention. Ultimately, a diffusion pore size was introduced in the SKK model to reflect the ability of the solute to diffuse through the swollen PDMS graft.

Chapter 7 describes the separation performance of multiple commercial and laboratory-made membranes, including those produced in Chapter 3, by using three model process mixtures. The mixtures were chosen specifically to mimic challenges relevant to today's industrial processes: a relatively low MWCO and high temperature. First, a fair comparison of data sets is established by a round-robin test of the same membrane across all test setups used. Next, the results of selected membranes are presented case-by-case. This collaboration is a first step towards the industrial validation of the membranes developed in Chapter 2. Promising results encourage the further development of grafted-from hybrid ceramic membranes for OSN.

Chapter 8 critically assesses the materials and membrane fabrication techniques developed in Chapters 2-5, providing perspective and commentary on the work done in this thesis as a whole. The need for support diversification, continuation of specific research lines, and ideal candidates for scale-up are identified and discussed.

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CHAPTER TWO

Hybrid Ceramic Membranes for Organic Solvent Nanofiltration: State-of-the-Art and Challenges

ABSTRACT

Uniquely suited to organic solvent nanofiltration (OSN) are hybrid, ceramic-based membranes. The stability of these membranes in the harsh solvents and conditions of industrial process streams is due to the sturdy and inert architecture of the ceramic, while the organic functionalization is responsible for surface and pore properties of the membrane, and hence its performance. Recently, this kind of inorganic-organic union has produced a plethora of stable and high-performance membranes in a variety of OSN conditions - the topic of this review. This work details and compares the surface modification methods used to fabricate these membranes and their resulting performance. Also, we discuss the capabilities and shortcomings of both the characterization tools and the transport models used to describe this class of membranes. Throughout we aim to provide insight into the challenges awaiting the researcher of hybrid, ceramic-based membranes for OSN.

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2.1 INTRODUCTION

Membrane technology is the application of a selective barrier to separate components of interest, creating a product of added value for the user. A driving force, such as a pressure difference, separates the product from the feed mixture. Much of the research in membrane technology has focused on aqueous-based separations, for example, desalination or wastewater treatment [1-2]. However, upon exposure to organic solvent solutions most of these membranes do not possess the required durability or performance. Development of a new class of membranes destined for such harsh conditions has been spurred by interest from industry and academia alike [3]. This field is termed organic solvent nanofiltration (OSN), also referred to as solvent resistant nanofiltration (SRNF). As shown in Figure 2.1, OSN is a young yet growing research field. The attention OSN has drawn is due to its competitive advantages over traditional chemical separation processes: less energy consumed, ease of scale up, relatively mild operating conditions, and compatibility with heat-sensitive compounds [4-5].

Figure 2.1. Number of publications per year for either or both keywords “Organic Solvent Nanofiltration” and “Solvent Resistant Nanofiltration,” as found by Scopus (April 2019).

The term “nanofiltration” describes a pressure-driven membrane process which will reject solutes below 2 nm in diameter [6], or, alternatively, $< \sim 1000$ Da in mass. Unlike aqueous-based nanofiltration processes, such as desalination, OSN does not refer to a specific application and purpose, it is rather an umbrella term for an assortment of industrial separations, for example, quinine catalyst purification in ethanol [7] or the deacidification of waste oils in n-hexane [8]. As a result, there is no “ideal” OSN membrane to be developed, meaning the advancement of the field as a whole lies not in the pursuit of incremental improvements, but rather in developing the knowledge base necessary for the rapid conception and manufacture of custom-made membranes.

To this end, membrane researchers have and continue to develop new polymeric and ceramic membranes. Each membrane type has advantages and drawbacks. Whereas polymeric membranes are widely available and easily modified, they can also be unstable in organic solvents, especially in nonpolar solvents. Ceramics are more expensive than polymers, and the hydrophilic surface of ceramic mesopores inhibits the passage of many solvents, yet their chemical inertness and structural rigidity is appealing. Efforts to combine the advantages of porous ceramics with the tunability of organic material has led to the emergence of a new class of membranes. It is the focus of this review: the recent developments and promising research directions of hybrid ceramic-based membranes for OSN.

Functionalization of a porous ceramic with an organic molecule can drastically change the behavior of ceramic membranes. One of the first effective surface chemical modifications of ceramic membranes was reported by Van Gestel et al. [9], as illustrated in Figure 2.2. The grafting of alkoxysilane compounds onto a γ -alumina top layer increased hexane permeability from 0.0 to $6.1 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$, while the same treatment reduced water permeability from 4.0 to $0.0 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$. Ever since, a plethora of existing chemistries have been ingeniously adapted to modify porous ceramic membranes for OSN, resulting in hybrid membranes which can maintain excellent permeation and retention properties.

Figure 2.2. The reversal of permeability behavior of a typical porous ceramic as a result of hybridization

Not only do we detail the fabrication, characterization methods and transport modeling of these membranes in this review, we have also analyzed and identified, to the best of our ability, the advantages and constraints of each, as well as the challenges that await the field of OSN as a whole. Both precise pore modification and the prediction of membrane performance remain challenging to the researchers of hybrid ceramic-based membranes for OSN. Specifically, there are two main obstacles: i) obtaining a consistently low (< 400 Da) molecular weight cut-off (MWCO) despite the limited pore size selection of unmodified ceramic membranes, and, ii) understanding the relations between membrane, solvents and solutes to accurately predict membrane performances. The formulation of a predictive transport model would enable a facile starting point for custom membrane fabrication; reaching a target retention would become a matter of fine-tuning the graft. Complicating this is the increased demand to be able to process solvent-containing aqueous streams such as produced water from natural gas fields. This emerging topic in OSN is called organic solvent tolerant nanofiltration (OSTN). Treating mixed water-solvent streams combines the requirements of both water-based and OSN applications. There are no publications specifically on this topic, though several academic research groups have recently become involved.

Naturally, the wide field of OSN has been examined in years past, either in a broader context than this review, or focusing on another sub-field of OSN. The reader is invited to the following for an exhaustive overview of past research in this field. Marchetti et al. [3] thoroughly described advances from 2008 until 2014 in all of OSN, including the various efforts to model transport across these membranes. A review by Cheng et al. [10] reported the advances until 2014 of polymeric OSN membranes; Hermans et al. [11] covered a narrower subset of these, TFC membranes, in 2015. OSN membranes having found use in the pharmaceutical industry were detailed by Buonomenna et al. [12] in 2014. A review by Szekely et al. [5] evaluated the sustainability of OSN technology. Ahmad et al. [13] reviewed the preparation of hydrophobic membranes for diverse applications, while Amirilargani [14] reviewed the various ways to modify and functionalize both polymeric and ceramic membrane surfaces for OSN in 2016. Relevant to this review are two reviews by Buekenhoudt et al. [15-16], published in 2012 and 2014, respectively, detailing the methods used to diversify ceramic surfaces and their performance in OSN, gas separation and pervaporation applications.

As stated, the aim of this review is to provide a summary of the state-of-the-art of ceramic-based hybrid OSN membranes and insights into promising avenues of research. First, the methods used to modify porous ceramic and the resulting OSN membranes are presented in Section 2.2. The characterization techniques and tools of both graft and membrane follows in Section 2.3. Section 2.5 reviews the mathematical models that attempt to describe and predict the transport behavior of solvent and solute through OSN membranes.

2.2 THE CASE FOR HYBRID, CERAMIC-BASED MEMBRANES IN OSN

The composition of a membrane, from the selective layer – the most discriminating layer of the membrane – to the support layer(s), can be divided into one of three material classes: either polymer (organic), ceramic (inorganic), or a hybrid consisting of both. Polymers commonly used in polymeric OSN include polyamide-imides [17], polydimethylsiloxane (PDMS) [18], polyacrylonitrile (PAN) [19], poly(ether ether ketones) (PEEK) [20],

polysulfones [21], polyaniline (PANI) [22], polybenzimidazole (PBI) [23] and blends [24] of the above. The cited examples have all shown some degree of resistance to organic-solvent-induced degradation, although additional enhancement steps, such as crosslinking, are often required [25]. Polymeric membranes have generally shown the most success, in terms of permeability and retention, with polar organic solvents such as alcohols or THF. However, solutions of non-polar solvents can be more troublesome, liable to either chemically degrade the membrane or physically distort the membrane geometry [3,10,11,26]. These disadvantages can be avoided altogether with ceramic membranes.

The porous ceramics for nanofiltration are composed of oxide materials, with either a symmetric or asymmetric architecture, various pore size distributions, porous structures and overall different geometries. Depending on the material and preparation method, porous oxide ceramics can present surface hydroxyl groups and acidic sites, enabling surface modification with an active species, as found for instance in either gas separation or heterogeneous catalysis [27-28]. Porous ceramic membranes are typically multi-layered structures. These layers are classified according to their pore diameter (IUPAC): microporous (<2 nm), mesoporous (2-50 nm) and macroporous (>50 nm) [29]. Generally, macroporous support will provide structural strength to a thinner, selective, meso- or microporous layer. Ceramics are an ideal material to withstand harsh environments due to their resilience to high operating temperatures and common industrial organic solvents [30], especially when compared against polymeric membranes. However, the filtration of non-polar solvents through these hydrophilic membranes is challenging. This was evident as early as the turn of the century: a 90% flux reduction and a tenfold decrease in retention was witnessed for TiO₂ membranes by Voigt et al. [31] when comparing the retention of dyes dissolved in water with the same dyes dissolved in toluene. Similar flux drops were observed by Tsuru et al. [32] and Guizard et al. [33] across a multitude of other ceramic membranes: silica-zirconia, alumina-zirconia and silica-titania with pore sizes ranging from 1-5 nm.

Naturally, hybrid materials have been developed, striving to combine the best aspects of each class of materials. When inorganic material is dispersed

throughout a polymeric selective layer, a mixed matrix membrane (MMM) is formed. This blend of materials can reduce the compaction effects plaguing polymeric membranes [34]. However, it remains to be seen whether the issues traditionally associated with MMMs can be eliminated: instability of dispersed inorganic particles (agglomeration, leaching), lower selectivity due to macrovoids, lower permeability at higher pressures, and poor thermal stability. [35-38].

Another option is to introduce organics directly into the ceramic sol-gel mixture. In one instance, Tsuru et al. [39] coated a methylated SiO_2 colloidal solution onto an α -alumina support with pores of 120 nm which was then calcined in a N_2 atmosphere. Permporometry showed pores ranging from 2 to 4 nm in diameter as well as hydrophobic water contact angles. A n-hexane permeability of $7.2 \text{ L} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{bar}^{-1}$ and a 90% retention of 1200 Da polyolefin was reported, slightly above the upper limit for nanofiltration. Another in-situ hydrophobization by Zeidler et al. [40] of $\text{TiO}_2/\text{ZrO}_2$ membranes was carried out in a similar fashion. Complexing agents were introduced to the sol system, either diethanolamine (DEA) or phenolic resin. Supports were coated with the modified sol and again calcined in a N_2 atmosphere; the ceramic surface was then covered with carbon instead of hydroxyl groups, and thus hydrophobic. No contact angle measurements were given, but permeability and retention measurements, using polystyrene in 3 different solvents, show increasing retention and permeability for polar aprotic solvents ($\text{n-heptane} < \text{ethanol} < \text{THF}$). It should be noted that the findings of Zeidler and co-workers [40] acknowledged a lack of reproducibility stemming from defects in the experimental layer. A transport model was then developed especially to accommodate the defects of these membranes, as discussed in Section 2.5. In the examples covered [39-40], grafting is precluded as the surface sites formed are largely inert.

Alternatively, incorporating organic moieties into a ceramic architecture avoids many of the drawbacks typically experienced by polymeric membranes and MMMs while allowing for the oleophilization and fine-tuning of the ceramic pore. A number of studies have shown that the wetting properties of porous ceramic membranes are easily altered by attaching functional groups onto their pore surface [41]. However, there is also a need for pore size alteration to make

Table 2.1. Reliable fabrication methods have evolved for ceramic membranes. Listed below is a partial list manufacturers marketing aqueous nanofiltration ceramic membranes and their standard pore sizes.

Tradename / Manufacturer	Material	Pore sizes (nm)
Inopor GmbH / Rauschert [42]	TiO ₂	10.0, 5.0, 1.0, 0.9
Inopor GmbH / Rauschert [42]	SiO ₂	1.0
Inopor GmbH / Rauschert [42]	ZrO ₂	3.0
Inopor GmbH / Rauschert [42]	γ -Al ₂ O ₃	5.0, 10.0
Membralox / Pall Corporation [43]	TiO ₂	5.0
Pervatech B.V. [44]	TiO ₂	0.9, 3.5
Pervatech B.V. [44]	γ -Al ₂ O ₃	5.0
Media and Process Technology Inc.	γ -Al ₂ O ₃	4.0, 10.0

ceramic membranes pertinent to a broad range of nanofiltration applications. As shown in Table 2.1, the commercial availability of ceramics with pores between 0.9 nm to 5 nm is discontinuous, i.e. only a few sizes are available in the nanofiltration range. The multitude of potential OSN applications requires alteration of the membrane to fit the circumstances. It is then evident that there is not only a need to alter the surface properties (i.e. hydrophilic nature) but also the size of the pores. Both of these changes can be achieved by grafting a molecule or a polymer of the correct type and size onto the pore wall. In this review, grafting is defined as the formation of strong chemical bonds (i.e. covalent and coordination bonds) between an inorganic substrate and an organic compound. Surface modification of ceramic oxides

2.2.1 Pore surface modification: chemisorption vs. physisorption

The term surface modification refers to the deliberate attachment or deposition of (macro)molecules to the surface of a ceramic oxide to change its physical or chemical properties [45]. It is important to distinguish deposition by physisorption from attachment by chemisorption (Figure 2.3). Physisorption (Figure 2.3, right) corresponds to the physical deposition of species to the surface by electrostatic or Van der Waals interaction, such as polyelectrolyte layering

[46]. For a physisorbed species to have a stable, strong attachment – a bonding strength comparable to covalent or coordination bonds – there must be multiple electrostatic interactions per molecule. Practically, this means employing high molecular-weight polyelectrolytes (> 30 kDa). The minimum pore size these large polyelectrolytes can enter is not smaller than 200 nm in diameter [47], far outside the nanofiltration range. Layering polyelectrolyte on a support with smaller pores results in a membrane performance similar to coated membranes [47]. Therefore, neither polyelectrolyte nor coated membranes will be covered; the focus will be surface modification of nanofiltration membranes by chemisorption. Attachment by chemisorption, i.e. grafting (Figure 2.3, left) implies the formation of covalent or coordinated bonds between the support surface and the organic compound. Surface modification by grafting offers a multitude of possible functionalization, finer control over the pore size, and a sturdy covalent attachment, yet is more challenging. The chemical reaction at the support surface requires the optimization of reaction conditions to control surface and pore coverage (i.e., grafting density, monolayer), and to avoid unwanted secondary reactions (i.e., clustering due to polymerization). [45]

Grafting can be roughly categorized according to two approaches: either grafting-to or grafting-from, as shown in Figure 2.4. Grafting-to refers to a one-step reaction in which an already-synthesized molecule or polymer, containing an inorganic-organic “linking” function, is directly bonded to the support surface. The main advantage of grafting-to is the control over the graft, since the graft is fabricated beforehand. Grafting-from, also termed graft polymerization, occurs when polymerization begins from a grafted initiator at the pore surface. In this second category, the presence of the initiator on the pore surface implies the use of the grafting-to procedure in first step. In contrast to grafting-from, grafting-to of ready-made polymer chains can lead to a lower graft density, as polymer chains attach and sterically hinder neighboring linking sites. Conversely, grafting-from can provide a more uniform and denser coverage due to the ease of diffusion of smaller monomers. Grafting-from at a mesoporous length scale implies the use of a specialized polymerization technique that can exercise a high degree of control over the degree of polymerization, as covered in Section 2.2.5. A series of grafting-to reactions is also possible, this approach is described in 2.2.4, Step-by-step grafting.

Figure 2.3. Schematic illustration of the surface modification by either physisorption or grafting of a porous ceramic oxide.

Figure 2.4. Schematic representation of the grafting-from and grafting-to.

Many of the grafting chemistries and methods presented in the following sections were first adapted from developments in other fields (e.g. sensors, coatings, polymer chemistry). Due to the extensive reach of these fields, this review will not be covering those associated publications. If the reader wishes a broader overview of grafting chemistries, focused on flat and particle geometries, we recommend the review of Pujari and co-workers [45]. The following sections focus on grafted porous ceramic oxide surfaces used as membrane to purify organic solvents. Specialized grating techniques, their advantages and disadvantages, as well as the performances of the resulting membranes, are all covered.

Figure 2.5. On the upper left, schematic of a grafted molecule (blue) bonded to the ceramic oxide selective layer (grey) by a linking function (pink). The upper right shows the conceptual sections of a linker. In the lower half examples of different attachment chemistries are shown: organosilane (A), organophosphate (B), and organometallic Grignard reagent (C).

2.2.2 Inorganic-organic linking functions

A linking function is the chemical group which allows the chemical attachment of (macro)molecules onto oxides. As represented schematically in Figure 2.5, the linking function bonds to the ceramic surface, and the functional group. The functionalized surface is either the final modification or the starting point for further modification. Many classes of linking functions have been shown to create covalent bonds between a metal oxide surface and a functional group [45]. Among the different attachment chemistries that have been used to graft (macro)molecules onto oxides, only few have been employed to prepare grafted-ceramic membranes: organosilanes, organophosphonates, and organometallic Grignard reagents. Each attachment chemistry and their compatibility with various ceramic oxides are detailed below.

2.2.2.1 Organosilanes: alkoxysilane and silyl halide linking functions

Within organosilane linking functions, both alkoxysilanes and silyl halides are routinely employed. A general formula for an organosilane linking agent is as follows: $(R)_{4-n}Si(X)_n$, where n , the number of linking groups, ranges from 1 to 3, and X represent either the alkoxy leaving group, typically a methoxy or ethoxy group, or a halide, typically a chloride. The functional group R will drive the

interaction of the membrane with the solute and solvent or be used as a starting point for further modification. The formation of bonds between the OH-bearing surface of the ceramic oxide and the linking function occurs via hydrolysis (for alkoxy silanes) and condensation, resulting in the formation of M-O-Si covalent bonds. It must be noted that the number and type of hydrolysable groups (n) impacts both the grafting density, attachment strength, and the ability of the alkoxy silane to polycondensate. For instance, silyl halide linking functions are usually employed for their high reactivity, and consequently restricted to one link per functional group ($n = 1$). On the other hand, alkoxy silanes can provide multiple attachment ($n = 2,3$) per functional group, although in that case water content has to be regulated. The presence of water is necessary, though a maximum of 1 to 3 pre-adsorbed monolayers of water on the pore surface is ideal for the formation of a dense monolayer [48]. An excess of water causes the formation of Si-O-Si bonds, leading to the formation of organosilane multilayers [49–53]. Other factors found to have an influence are the temperature, solvent, reaction time, and the size and concentration of the linker, among others, which must be tuned for best coverage [54–58].

Figure 2.6. Proposed 3-step mechanism for alkoxy silane. Unregulated conditions can result in multi-layering of the silane (bottom left), whereas optimized conditions will promote monolayer formation (bottom right). Adapted from [45] with permission.

Grafting of alkoxysilane and silyl halide can be achieved via solution phase deposition (SPD), where an (anhydrous) solvent serves as a reaction medium. Toluene has resulted in high density coverage for a variety of silanes in this role [59]. An alternate method is to employ vapor phase deposition (VPD), bypassing the need for a solvent. This method has proven effective in suppressing the formation of multilayers while yielding uniform, dense grafts, and is usually performed at higher temperatures than SPD [60–62]. Figure 2.6 shows a representation of the commonly-grafted (3-aminopropyl)triethoxysilane (APTES) onto a hydroxyl-terminated surface.

2.2.2.2 *Organophosphorus linking functions*

Phosphonic acids $[R'-P(O)(OH)_2]$ and their phosphonate derivatives $[R'-P(O)(OR)_2]$ (R = alkyl, aryl or trimethylsilyl groups) are increasingly being used for controlling surface and interface properties in hybrid or composite materials [63] (Figure 2.5B). The fourth component (R') is an organic carbonated moiety linked to phosphorus with a P-C bond. Organophosphorus linking agents are famous for their versatile coordination chemistry, allowing them to react with different metal ions via P-O-metal ionocovalent bonds. Furthermore, unlike organosilanes linking function, phosphonic acids their phosphonate derivatives are not subjected to homocondensation reactions. This allows the controlled formation of organic monolayers of grafted phosphonate molecules on the surface of inorganic supports [63-64].

When using an organophosphonic acid ($X = H$), the reaction may easily be performed in water, and the resulting monolayer is also stable in aqueous conditions, unlike many silane-grafted ceramics [64]. Some organophosphorus-modified surfaces have also shown high temperature stability, up to 400°C, due to the strength of the M-O-P and P-C bond while the alkoxysilanes usually decompose around 200-250°C [51,64].

2.2.2.3 *Organometallic Grignard linking functions*

Grignard reagents (alkyl, vinyl, or aryl magnesium halides, e.g. Figure 2.5C, have long been used to form carbon-carbon bonds. They can also form a M-C bond

when M is part of a titania or zirconia matrix, as was demonstrated by Buekenhoudt and co-workers [65-66] with the grafting of 1 and 3 nm pore sizes. The Grignard linking function has not been demonstrated on other substrates. The reaction requires oxygen, water-free conditions, and several days, to yield a partially covered surface, i.e. not a full hydrophobization [66]. Their thermal stability has not been reported, though they are stable in water [67] and a range of polar, aprotic and apolar solvents [68].

2.2.2.4 Strengths and weaknesses

Compatibility, advantages and disadvantages of the organosilane, organophosphorus and organometallic Grignard linking functions are summarized in Table 2.2. As it can be seen, not all porous ceramic oxide are compatible with these linking functions. For example, phosphorous-based linking agents have yielded uniform monolayers on porous zirconia, alumina [51,69,70] and titania [67,71], while organosilanes have been widely used on silica and alumina [45,72-75]. Silylation on γ -alumina or silica surfaces has overwhelmingly been chosen as the first, and sometimes only, grafting step. Comparatively to organosilanes, relatively few examples of organophosphorus grafting exist [76-77]. The authors believe this can be attributed to the non-reactivity of phosphonates towards silica surfaces [64,71], which is a common material in many other research areas, such as microfluidics or electronics. However, organophosphorus compounds continue to be an attractive yet relatively unapplied linker chemistry for alumina membranes [78-80]. The grafting of organometallic Grignard linking agents has only been reported on titania and zirconia porous ceramic support.

Thus during the selection of the linking function, one should refer not only to the compatibility with the metal oxide ceramic support but also the surface bonding (number of possible bonds), the yielding grafting density, and the possibility to form a monolayer. This is important when trying to impart a customizable functionality to the selective layer, as covered in the following sections. First grafting-to membranes are detailed, then grafting-from and its potential as a tunable OSN membrane production method, and also membranes modified by step-by-step grafting. Finally the merits and disadvantages of these three membrane modification methods are compared to one another.

Existing fabrication processes for porous silica, titania and zirconia can yield stable layers with a pore diameter equal to or less than 3 nm [81-82]. Since grafting in these small mesopores or micropores is sterically hindered, it is generally the only modification step. However, with mesopores of at least 5 nm in diameter, there can be further modification via the functional group of the linker, either by grafting-from or grafting-to.

2.2.3 Grafting-to

Grafting-to refers to a one-step reaction in which an already-synthesized molecule or polymer is directly bonded to the support surface. A well-known grafting-to functionalization is the attachment of perfluoroalkylsilanes (FAS), a fluorinated alkyl molecule terminated with an organosilane linking function. It has been grafted onto various substrates for a variety of separation applications: emulsion separation [41], membrane distillation [83] and pervaporation [3], among others [84-85]. The draw of the FAS grafted molecules is the ability to impart hydrophobicity in one, simple grafting step. Tuning the fluorinated alkyl chain length (from 1 to 12 carbons), degree of fluorine substitution, and reaction conditions have all shown an impact on performance [86]. Studies appear to be limited to a chain length of 12 or fewer carbons; this reflects the range of commercially available FAS. However, one-step surface tuning, i.e. when the (macro)molecule already contains a linking function, is not always achievable or practical. Oftentimes, the functional group of the linking agent is purposed to react with a second reagent, which will in turn dictate the pore size and surface properties. Together, these two reactions are also referred to as grafting-to (see Figure 2.4).

The following sections explore the advances in grafting-to as applied to OSN ceramic membranes. First presented are various hybridizations of the alumina membrane mesopores, followed by Grignard-grafted titania and zirconia membranes. We emphasize that linking functions are not restricted to the chemistries presented in Section 2.2.2. As inorganic-organic linking chemistry has only recently been adapted to the field of OSN, new applications of existing chemistries are regularly implemented and published. This is exemplified by a newly adapted linking functionality, detailed in the section after Grignard-grafted membranes: maleic anhydride copolymer grafting.

Table 2.2. Summary of linkers and substrates: Advantages, disadvantages, characteristics & compatibility.

Linking function	Organosilane	Organophosphorus	Organometallic Grignard reagents
Porous ceramic oxide compatibility	Al ₂ O ₃	✓✓	unknown
	TiO ₂	✓✓	✓
	ZrO ₂	✓✓	✓
	SiO ₂	X	unknown
Bond type	M-O-Si,	M-O-P,	M-R,
Possible bond number	up to 3	up to 3	only 1
Controlled monolayer formation	~	✓✓	~
Hydrolytic stability	~	✓	✓
Max. grafting density	Medium	Medium/High	Partial surface coverage
Comments	Hydrothermal stability depends on substrate	Potential dissolution and precipitation of the substrate depending on pH	Demanding reaction conditions: multiple days and steps, oxygen-free and water-free [77]

2.2.3.1 Alkoxysilane grafted-to membranes

Gamma alumina (γ -Al₂O₃) is a mesoporous phase of alumina. When used as the membrane selective layer, it is typically deposited on an α -alumina support. Pinheiro et al. and Tanardi et al. used organosilanes as the linking agents between γ -alumina of a 5 nm native pore size and chains of mono-functional-terminated PDMS with an average degree of polymerization (n) equal to 10 or 39, as shown in Figure 2.7. The PDMS rendered the surface hydrophobic, shifting the contact angle from $\sim$ 0-30 to 90-99° [87]. High fluxes and dye retentions were found for these PDMS-grafted membranes as shown in Table 2.3. The permeability of the PDMS $n=10$ membrane was found to be stable for at least 170 days in toluene, showing no significant change in permeability [88,89], though no retention tests were conducted over this time-frame.

These values are competitive with polymeric membranes: most OSN studies report toluene permeabilities in the range of 0.3-1.0 L.m⁻²h⁻¹bar⁻¹ [3], with a reported high of 3.6 L.m⁻²h⁻¹bar⁻¹ for doped Lenzing P84 polyimide membranes, though the permeance of that specific membrane degraded with time or increasing pressure [90].

Figure 2.7. Two-step process for the grafting-to of PDMS onto an alumina pore surface, as in [87-89]. (A) the linking agent 3-aminopropyltriethoxysilane (APTES) is grafted. (B) Mono-epoxy terminated PDMS is reacted with the amine functional group to further modify the pore.

A follow-up study explored the introduction of crosslinking PDMS inside the pores of the alumina. Di-functional PDMS ($n = 10$) mixed with a tetra-functional crosslinker were grafted onto 5 nm γ -alumina organosilane-functionalized surface [88,89]. As shown in Table 2.3, the resulting membranes demonstrated higher retentions with reasonable permeabilities [91].

The studies detailing and testing PDMS-grafted alumina membranes found that permeability and retention were dependent on graft swelling, i.e. the swollen graft constricted the pore, reducing permeability and increasing retention [91,92]. This swelling was constrained to the individual pores of the ceramic architecture, as the overall membrane size and shape remained stable. No evidence was found for compaction of the swollen graft under the pressures tested, as solvent fluxes remained linear with respect to the applied pressure [93]. Localized swelling and no compaction distinguish the PDMS-grafted membranes from other PDMS-based OSN membranes, whose performance suffers from these effects, especially in nonpolar solvents such as toluene [94].

Further research by Tanardi et al. investigated the grafting of polyethylene glycol (PEG), with an organosilane linking function into the same γ -alumina 5 nm pores. The organosilanes linker and PEG chain were bonded together before grafting, and subsequently as a whole, into the membrane pores and surface. These membranes were hydrophilic as evidenced by the water contact angle of 38° (Table 2). Only the PEG-grafted membrane with the highest graft density was selected for performance testing. Results are shown in Table 2.3. [95]

2.2.3.2 *Phosphonate-grafted ceramic membranes*

Though no phosphonate-grafted membranes exist for OSN, the use of this linking chemistry has begun to be applied in other membrane separation fields. The treatment of titania with phosphoric acid terminated alkyls was found impart fouling resistance during the ultrafiltration of BSA proteins in water in the form of longer consistent fluxes and retentions [96]. Similar fouling resistance was witnessed found when grafting porous titania or zirconia with phosphonate or phosphinate terminated alkyl or phenyl groups [66]. Ionic liquids grafted via a phosphonate linking function onto γ -alumina for CO_2 selective-membranes have demonstrated potential in gas separation applications with a high ideal CO_2/N_2

Figure 2.8. Grignard functionalization of a ceramic oxide surface showing partial surface coverage. [99]

selectivity (~144) yet low flux (130 Barrer) [27]. As the hydrolytic stability of phosphonate-based coupling has been demonstrated to be greater than alkoxy-based linking functions [63], the authors believe phosphonate-grafted ceramic membranes to be an unexplored approach for the treatment of mixed aqueous-solvent or ‘wet’ gas streams, as often found in the oil and gas industry.

2.2.3.3 Grignard-grafted ceramic membranes

Buekenhoudt et al. recently introduced Grignard-grafted membranes [65,77]. The eponymous reaction to fabricate these membranes requires a strictly inert, water-free atmosphere and yields membranes showcasing direct M-C bonds, M representing a titanium or zirconium ceramic surface atom and C representing the terminal carbon atom of an alkyl chain or phenyl group, as shown in Figure 2.8. Although Grignard-grafting bypasses the need for a separate linker, it results only in partial surface coverage of the ceramic, imparting an amphiphilic character to the membrane [99]. A continued investigation of these membranes [98] evaluated membrane performance in either acetone or toluene solutions, the solutes were either polystyrene (PS) chains, PEG chains or 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl (BINAP) ligands. The membranes were grafted with varying *n*-alkyl groups (*n* = 1, 5, 8, or 12); selected results are shown in Table 2.4.

Table 2.3. Permeability in various solvents and retention of Sudan Black B (neutral dye, MW = 457 Da) across various organically-grafted γ -alumina membranes.

Membrane	WCA	Solvent (polar)	Permeability (L.m ⁻² h ⁻¹ bar ⁻¹)	R (%) 457 Da	Solvent (apolar)	Permeability (L.m ⁻² h ⁻¹ bar ⁻¹)	R (%) 457 Da	Ref.
PDMS $n = 10$	94°	Isopropanol	0.9	55	toluene	3.1	72	[74]
PDMS $n = 39$	95°	Isopropanol	0.75	66	toluene	2.1	83	[74]
Crosslinked PDMS	108°	Isopropanol	0.4	80	toluene	1.3	95	[91]
PEG $n = 10$	38 °	Ethanol	0.78	89	hexane	3.7	54	[75]
p(MA-alt-1-decene)	74°	Ethyl acetate	1.7	90	toluene	1.8	98	[97]

Table 2.4. Permeability and retention of oligomer solutes across Grignard-modified (8-carbon alkyl chain) 1-nm diameter TiO₂ membranes [98].

Solvent	Polystyrene			Polyethylene glycol		
	Permeability (L.m ⁻² h ⁻¹ bar ⁻¹)	R (%) 580 Da	R (%) 1500 Da	Permeability (L.m ⁻² h ⁻¹ bar ⁻¹)	R (%) 600 Da	R (%) 1500Da
Acetone	9.5	85	92	5.0	55	81
Toluene	3.0	55	63	1.5	-5	46

Negative retentions of PEG in toluene have been previously observed and explained as stemming from a raised PEG concentration at the membrane surface due to a high membrane-solute affinity (hydrogen bonding) [68]. Negative retention can occur when the solute-membrane affinity is stronger than the solvent-membrane affinity, as is the case with PEG in toluene. Size exclusion effects are then readily apparent, as is the case with PEG retention in toluene. As shown in

Table 2.4, the PEG retention in toluene jumps from -5% to 46% as the PEG increases in molecular weight. As described by Hosseinabadi and co-workers [98], size exclusion in Grignard membranes could be a combination of pore-shrinkage and pore entrance blockage. As the alkyl chain length increased pore entrances may become obstructed, yet less of the inside of the pore is modified due to reduced graft penetration by steric hindrance, thereby explaining the relative difference in permeabilities: unmodified > C12 > C1 > C8 > C5.

2.2.3.4 Maleic anhydride copolymer grafts

Amirilargani et al. [97] have bypassed the need for a traditional linker. Instead, the maleic anhydride (MA) ring opening moieties of an alternating copolymer, poly(MA-alt-1-alkene) directly bond to the surface hydroxyl groups of γ -alumina, as shown in Figure 2.9. This pre-synthesized polymer was found too bulky (Mn: 17 - 23 kDa) to significantly penetrate into the 5.0 nm pores of the γ -alumina, meaning a new selective layer was formed on the external surface of the support. While the MA provides the linking functionality, the alkane chains were found to dictate the performance of the membrane. When varying the length of the 1-alkene monomer $n = 6$ to $n = 18$ carbons, the solvent permeabilities peaked at $n = 10$ (toluene, $1.8 \text{ L.m}^{-2}\text{h}^{-1}\text{bar}^{-1}$; ethyl acetate, $1.9 \text{ L.m}^{-2}\text{h}^{-1}\text{bar}^{-1}$), double that of the second-best sample. Retentions of Sudan Black B (MW = 450 g.mol^{-1}) did not depend on alkene monomer length, staying remarkably high and constant, between 90 and 94%. The results are shown in Table 2.3.

Swelling of the graft did not seem to be an issue, likely due to the multiple attachment points per chain grafted. Noted was the significant adsorption of solute onto the un-grafted pore surface sites. As this membrane is a recent development, its long-term graft stability is yet unreported. The authors of this

review speculate that the MA linking function is stable in the long-term in most organic solvents, although the ester linkage may be vulnerable to nucleophilic attack, making it unsuitable for a minority of environments, for example, extreme-pH aqueous mediums.

2.2.4 Step-by-step grafting

Step-by-step grafting is the modification of a selective layer by the stepwise addition of monomers, i.e. a series of grafting-to reactions. In each separate reaction, the monomers supplied react to form covalent bonds with the previous layer of monomer applied, forming chains extending away from the substrate. Attachment to the substrate is typically done beforehand by grafting a monomer as the functional group of a linking agent. Described below are two examples of step-by-step grafting.

Figure 2.9. Schematic representation of a maleic anhydride (MA) ring opening moieties of an alternating copolymer, poly(MA-alt-1-alkene) directly bond to the surface hydroxyl groups of a porous γ -alumina support. [97]

Pinheiro [100] grafted, step-by-step, one of each of the following polyamide monomers onto 5 nm or 9 nm pores of γ -alumina: benzophenonetetracarboxylic acid and 3,3'-diaminodiphenyl ether. The 9 nm γ -alumina showed a pore shrinkage to 2.4 nm, and permeabilities of $1.7 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$ in toluene and $3.9 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$ in hexane. For these membranes, a MWCO of 850 Da was determined by the filtration of polyisobutylenes in toluene. However, the membrane degraded after 29 days, becoming impermeable to hexane and decreasing its toluene permeability. The blocking of solvent transport was attributed to capillary condensation of water inside the pores. Fluorinated monomer equivalents were also grafted in the same manner [100]. However, the only permeable membranes obtained were those grafted on α -alumina pores of 70 nm, resulting in membranes with toluene permeabilities of 8-9 $\text{L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$ and untested, though likely poor, retentions.

Amelio et al. [101] cycled the addition of monomers trimesoyl chloride and m-phenylenediamine to an APTES-functionalized, anodized-alumina substrate. The resulting membranes were only tested for salt retention, retention peaking at 5 layers with 76% NaCl retention with a water permeability of $0.6 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$. However, layer growth was observed only on the external surface of the membrane, not in the pores. The external layer did not extend from the surface uniformly after 3.5 cycles of monomer addition. This membrane type has not yet been tested on organic solvents, though without improvements its performance will likely fall short of its chemical equivalent prepared by interfacial polymerization (IP) on polymeric supports [102].

2.2.5 Grafting-from

Grafting-from is a newly developed approach for the functionalization of nanofiltration mesopores [103]. It is the process of growing polymer chains from a porous substrate, via a grafted molecule which contains both the linking function and polymerization initiator. Only recent advances in controlled polymerization techniques have made such synthesis approachable to material scientists and engineers, as well as tunable at the nanoscale [104]. Grafting-from has been mainly used to fabricate polymer brushes – chains grown in high density – from flat or convex geometries (e.g. sheets, nanoparticles), and less from concave surfaces, such as the inside of a tube or pore [105]. Accordingly, there

exists few examples of grafting-from inside membrane pores. More common are polymer brushes on the external membrane surface for added functionalization [14].

Brushes on ceramic oxide membranes have mainly been used as a means to create a new layer or to modify large macropores. In one instance, acrylic acid was polymerized into polyacrylic acid brushes on the surface of α -alumina membranes (3 μm pore diameter) to reduce fouling during the ultrafiltration of aqueous solutions. These brushes were pH responsive, compacting at a pH smaller than 1.1 and extending at pH 5.5. Compacted brushes increased the flux ~ 15 times [106-107]. In another example, the free-radical polymerization of vinylpyrrolidone or vinyl acetate on top of silica surfaces was performed to make a pervaporation membrane for the separation of methanol and methyl tert-butyl ether. The polyvinyl acetate (PVAc) and polyvinyl pyrrolidone (PVP) brushes were found to be 39 nm thick and 26 nm, respectively [108]. The molecular weight of each brush was claimed to depend roughly on monomer concentration and temperature, though no tuning of brush height was demonstrated [109-110].

The two examples listed in the previous paragraph are dealing with brushes much larger than the mesopores of ceramic oxides destined for nanofiltration. Comparing the starting pore size of ceramic oxides mesopores ($\text{\O pores} \approx 5 \text{ nm}$) with the backbone unit length of vinyl polymers ($(\text{C-C-}) n = 0.25 \text{ nm}$), we can understand the need for a brush whose degree of polymerization can be controlled in the range of 4-20 monomers. Conventional radical polymerization yields polymers with hundreds or thousands of repeating units, so controlled polymerization techniques are needed to achieve precise control over the degree of polymerization of the graft.

For this reason, controlled polymerization techniques such as atom-transfer radical polymerization (ATRP) or nitroxide-mediated polymerization (NMP) are now used to grow polymers of low specific molecular weights [111]. This can be done from ceramic surfaces by immobilizing an initiator on the surface (e.g., with a peroxy carbonate initiator onto silica nanoparticles [112], an azo initiator on ferrite, titania and silica particles [113], or an ATRP initiator onto the 5 nm pores of γ -alumina [103]).

Figure 2.10. General scheme showcasing the facile grating approach of ATRP. Reprinted with permission from [114]. © 2007 American Chemical Society.

The ATRP-initiator of [103] was composed of an organosilane linking function, and was used to grow polystyrene chains from the pore surface. This resulted in shrunken and hydrophobic membrane pores, which gave a toluene permeability of $2.0 \text{ L.m}^{-2}\text{h}^{-1}\text{bar}^{-1}$ while reaching 90% retention of diphenylanthracene ($\text{MW} = 330 \text{ g.mol}^{-1}$). This membrane needed plasma etching, post-initiator and pre-polymerization, to remove external-facing initiator not in the pore. Chain length control, and thus the tuning of effective pore size, was achieved by varying the reaction time as well as the monomer:initiator ratio of the reaction, activators-regenerated-by-electron-transfer (ARGET)-ATRP.

ARGET-ATRP is ATRP with the incorporation of a reducing agent, allowing for (ppm) levels of catalyst, as well as easier maintenance of oxygen-free conditions. This enables practical implementation of grafting-from on surface areas larger than laboratory wafers, such as a membrane [114-115]. Its ease-of-use is depicted in Figure 2.10. Though Merlet and coworkers [103] reported the first use of ATRP to shrink and modify nanofiltration pores, it was also used to graft ultrafiltration membranes [116] and free-floating, 14 nm mesopores [117]. Using surface-initiated ATRP, Chu et al. [116] polymerized poly(3-(N-2-methacryloyloxyethyl-N,N-dimethyl)ammoniatopropanesulfonate) (PMAPS) from an initiator bonded on the surface of 200 nm diameter pores of anodic aluminum oxide. The study reported no impact on chain growth due to the concave geometry, though the retardation of monomer to growing chains in the center of the pores was noted. In [117] mesoporous silica particles of diameter

~15 nm were grafted, with polyacrylonitrile (PAN) of varying lengths. These silica mesopores were however free standing porous structures, not aligned and packed together as a membrane.

2.2.6 Evaluation & Comparison

The potential of grafting-to has been realized across a variety of ceramic oxides. The advantages and disadvantages of several grafting-to methods and grafting-from are summarized in Table 2.5. The PDMS-grafted alumina membranes developed by Tanardi and Pinheiro [88,89] exhibit competitive separation properties for non-polar organic solvent solutions, whereas the amphiphilic character of the Grignard-grafted membranes developed at VITO [98] renders them competitive when dealing with separations of polar organic solvents with solutes which are less polar than the solvent. The grafted-from membranes of [103] are easily tuned and have demonstrated a MWCO down to 300 Da. In each case, swelling of the polymeric graft is not an issue, as it is attached to a rigid, solvent-resistant, ceramic architecture. In the PDMS-grafted alumina membranes swelling is localized to the pores, actually increasing the selectivity, whereas swelling was not observed in Grignard-grafted membranes, since the graft only partially covers the surface. Just as the Grignard-grafted membranes, the p(MA-alt-1-decene) membranes of [97] are linkerless. They also show promise for both the filtration of polar and non-polar organic solvents. Step-by-step grafting for OSN has been used to make two different membranes. The approach taken by Pinheiro [100] is difficult within narrow 5 nm mesopores because of the bulky, rigid polyamide monomers used. Though the macropores in the α -alumina are large enough to accommodate these monomers, no data was published on either the retention or stability of such membranes. The work presented by Amelio et al. [101] shows scant evidence of pore modification but is instead focused on the creation of a layer on top of the alumina support, which is likely to suffer from the same problems of polyimides layers that are exposed to non-polar solvents. In a broader context, the step-by-step approach has several drawbacks compared to grafting-from or grafting-to. Repeated, separate steps, including each monomer reaction, membrane washing, and thermal treatment, take time and resources. Step-by-step grafting has also not demonstrated the performance of grafting-to membranes.

Table 2.5. Pros and cons of the grafting-to and grafting-from methods.

Method	Grafted membrane	Advantages	Disadvantages
Grafting-to	[74] PDMS on γ -alumina	Tunability: permeability-retention tradeoff by adjusting PDMS graft length, well-suited to non-polar solvent nanofiltration	Mono-functionally terminated PDMS required, low swelling of graft means low retention, linker required
Grignard grafting-to	[98] alkyl on titania	Best performance with polar solvents	Poor retention when combining non-polar solvent with polar solutes
Linkerless Grafting-to	[97] Maleic anhydride copolymer on γ -alumina	Linkerless, high retentions (90% + in toluene and acetone). Potential to tailor alkene monomer for target application.	Requires copolymer fabrication step
Grafting-from	[103] Polystyrene on γ -alumina	Tunability of pore shrinkage by adjusting reaction parameters	Not (yet) expanded to other polymers and polymer architectures

So far, only three distinct grafting-to methods and one grafting-from method have yielded performing membranes. Many approaches have yet to be tried. The advantages of grafting onto ceramic membranes have been shown: tunability of the graft, versatile grafts, and a sturdy architecture. Combined with the wealth of unexplored grafting chemistries, hybrid ceramic-based membranes for OSN continues to be a promising research avenue.

2.3 GRAFT & PORE CHARACTERIZATION

In the previous sections, the effect of surface modification of porous ceramic supports was analyzed based on the results from contact angle, cyclohexane pmporometry, and, most importantly, membrane performance (solvent flux, solute retention). The combination of these results indicates successful surface modification but does not actually confirm the formation of chemical bonds between the support and the (macro)molecule. Indeed, a host of other valuable information is absent, such as grafting density, homogeneity and the local environment of the grafted species. These are useful data which serve to understand and predict the membrane performances and stability. Thankfully, several analytical techniques are available for the direct evaluation of the (macro)molecule concentration on a metal oxide surface. However, these characterization methods are challenging or ill-suited to hybrid ceramic membranes due to two factors: i) the relatively low amount of grafted species, ii) the porous structure of the ceramic support [91,103]. Indeed, the grafted species which are confined in the mesopores represent less than 1% by weight or volume of the total sample. The macroporous support layer makes up the majority of the support (99.5+ %, by weight or volume), and is generally unreactive, with a low specific surface area [30]. This section explores the adaptations in characterization techniques that have made direct graft characterization possible

2.3.1.1 *Direct graft characterization: spectroscopic methods*

X-ray photoelectron spectroscopy (XPS) has proven to be useful to estimate the grafting density at the surface of the ceramic support [118]. However, due to the rough and porous nature of the support, the results are less accurate compared to a flat and dense support. To circumvent these issues, porous particles of the same material as the selective layer can be used as a model system. This method

eliminates the inactive substrate that otherwise diminishes the sample signal and allows the estimation of grafting density by coupling TGA and N₂ sorption analysis [91,103]. Another method is to cyclically measure and etch from the surface of the membrane to obtain atomic depth profiles. Difficulties associated with this method include imprecise etching rates, the contamination of the pores underneath by etched material, and the destruction of the sample [118].

In many cases, IR spectroscopy can be useful to demonstrate and distinguish between the presence of physisorbed or grafted species on or near the external surface of modified membranes. For example, the degree of protonation of the phosphonate linking function can be, as a first attempt, investigated by IR spectroscopy [64,69,79,119]. In the case of Grignard-functionalized membranes, Micro-ATR/FTIR spectroscopy was used directly on the external surface of the membrane to demonstrate the presence of alkyl groups [99]. Compared to standard FTIR spectroscopy, this technique has an increased signal to noise ratio because more reflected light is received by the detector. A less considered alternative, Raman spectroscopy can also be used as a complementary tool to assess the local environment of the grafted species. Raman spectroscopy may detect other bonds not clearly shown by FTIR [120], and has the ability to scan for organic species as a function of depth (micrometers) into the porous ceramic support [121].

In addition, solid state NMR is one of the techniques which can provide detailed information on the grafting mode of the linking function. For example, after a grafting-to reaction with an alkoxysilane linking function, the degree of silanol attachment to the metal oxide surface can be determined by measuring the ²⁹Si chemical shift by performing ²⁹Si → ¹H cross-polarization (CP) MAS experiments [97]. Furthermore, it has been shown that ¹³C-CP/MAS NMR experiments can directly prove the formation of C-O-Ti bonds between alkyl Grignard reagent and TiO₂ [65]. Unfortunately, given the poor sensitivity of the carbon and silicon nuclei and the relatively low amount of grafted species compare to the bulk, such experiments have only been carried out so far on richly-grafted, model mesoporous particles. Recently, ¹H, ¹³C, ¹⁹F and ³¹P one pulse High Resolution MAS NMR experiment on a phosphonate-based ionic liquid ceramic membrane was conducted directly on pieces of ceramic support

immersed in D₂O [69]. Using this technique, the authors were able to detect and distinguish between the presence of both grafted and physisorbed species in the hybrid ceramic membrane. This confirmed that significant spectra resolution of HR-MAS NMR experiments can be obtained even at moderate spinning rates, hence providing valuable information over the membrane hybridization [122]. As HR-MAS NMR was only recently (successfully) adapted to the study of grafted ceramic membrane, we expect the use of this technique to become more accessible in the future.

2.3.1.2 Between graft and membrane: Pore characterization techniques

Equally important is the characterization of the pores to determine the graft distribution, the pore size distribution, general surface properties and, also, the presence of defects. Small mesopores and micropores exclude pore-sizing techniques long used in membrane technology: scanning electron microscopy (SEM), bubble point test method, mercury intrusion porosimetry, and permoporometry. Each of these techniques has its limitation. The magnification capability of standard SEMs will not, for example, display 3 nm TiO₂ pores, nor the molecules grafted inside. The lower detection limits of the bubble point method and mercury intrusion porosimetry do not reach down to small mesopores. The pore diameters of conventional mesoporous ceramic supports can be determined by permoporometry only down to 2 nm and up to 50 nm [123-124]. The 2 nm diameter detection limit of this technique restricts its use in the characterization of grafted pores [123-124]. These methods can however often detect the following information: i) the presence of a graft, if the change from support to grafted sample is noticeable, ii) the properties of the ungrafted sample and, importantly, iii) the presence of defects. Less considered, the nanopermoporometry technique can measure nanosized pores ranging from 0.6 to 30 nm, though both the accuracy and lower detection limit are dependent on the solvent and the properties of the membrane surface [125].

Another new accurate technique was developed for the analysis of micropores <1 nm to expand the range of conventional adsorption isotherm analysis. This technique combines the information from thermogravimetry and pycnometry data. Thermogravimetric data is employed to assess the uptake of solvent vapors into the microporous structures of the sample at room temperature. Together with

qualitative information on surface chemistries, quantitative micropore volumes and minimum pore entrance sizes are derived. In conjunction, the pycnometer is employed to measure the uptake and adsorption of inert gas into the structure at room temperature. From these data, semiquantitative surface-to-volume ratios, surface areas and micropore cavity sizes are derived as well as qualitative information on surface chemistry of the sample. This technique, until now only used on zeolite is very promising for grafted ceramic membrane pore characterization.

Together, graft and pore characterization provide crucial insights and parameters which help the membrane researcher to predict membrane performance via transport models, allowing for the tuning of graft, solvent, and solute interactions. Inversely, the membrane performance can also yield information about the membrane structure. A model is then needed to translate permeability and retention measurements into pore size and other parameters the model may call for, such as tortuosity. The following section studies OSN models for ceramics and grafted ceramics.

2.4 MEASURING PERFORMANCE

Membrane performance is defined by two main metrics: its throughput, expressed as permeability, and its selectivity, expressed as retention. The permeability, P ($\text{L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$), is equal to the pressure-normalized flow through a unit area of the membrane, as shown in Equation (1). The retention of a solute, also referred to as rejection, is usually expressed as a percentage, R (%), as shown in Equation (2).

$$P = \frac{J}{\Delta p} \quad (1)$$

$$R = \left(1 - \frac{c_p}{c_f}\right) * 100 \quad (2)$$

where J is the flux and Δp is the pressure applied across the membrane (also known as trans-membrane pressure, TMP), and where c_p and c_f are the permeate and feed concentrations, respectively, of the solute. A common metric ascribed to membranes is the molecular weight cut-off (MWCO), defined as the molecular

weight that reaches 90% retention across the membrane. In the field of OSN, this metric does not accurately describe the retention capability of a given membrane, as the MWCO is often different when examining retention of the same solute in different solvents, and also varies across different solutes of the same molecular weight [126-127]. Regardless of the non-specific nature of the MWCO in OSN, a sharp difference in the retention of two molecules of similar molecular weight is advantageous, as it enables the separation of multi-solute mixtures. This ability allows a nanofiltration membrane to compete with traditional separation processes such as distillation.

Many solutes have been proposed and advocated as model testing solutes. Due to the simplicity of light absorbance testing and the molecular weight range of nanofiltration solutes, dyes are often used in retention tests. Their advantage is also their disadvantage, as their overlapping absorption spectrums makes testing of multiple dyes at once impossible. Commonly used dyes and their properties are listed in Table 2.6. Besides dyes, at least three separate studies have advocated the use of various polymers as “model solutes” for testing membranes in organic solvents. These polymers include polyethylene glycol (PEG) [128], polystyrene (PS) [129], and polypropylene glycol (PPG) [130] as ideal testing solutes, also listed in Table 2.6. Though each solute has its merits, it remains difficult to translate molecular weight across solvents, as changing the solvents will change the retention of the same oligomer. Predicting the retention of other solutes from the retention of one, even in the same solvent, has not yet been achieved. In short, rather than proposing an ideal solute class, it is our view that new membranes should be evaluated by a class of solutes representative of the target application rather than by any semi-arbitrary standard.

If there were a single predictive model for all OSN membranes, such as the solution-diffusion model for reverse osmosis membranes, a standardized testing method would make sense. However, this ideal has yet to be formulated. The models describing transport through aqueous-application membranes are not directly applicable to OSN, as retention is a function of not only the membrane but also of complex membrane-solute-solvent interactions [126-127]. For instance, polymers, either as part of the membrane or as a solute, are susceptible

Table 2.6. Commonly used solutes, their molecular weight, or repeat unit molecular weight (n), along with notable properties. HPLC = high performance liquid chromatography, ELSD = evaporative light scattering detector, TOC = total organic carbon. [128-130]

Solute	Mol. wt. (g.mol ⁻¹)	Selected properties
Rose Bengal, dye	974	Neutral, insoluble in hexane, toluene
Methyl Orange, dye	327	(-) charge, Insoluble in diethyl ether
Sudan Black B, dye	457	neutral, widely soluble
Bromothymol Blue, dye	624	Neutral, limited solubility in nonpolar solvents
Brilliant Blue R, dye	826	Zwitterionic, limited to no solubility in nonpolar solvents
Orange II, dye	350	(-) charge, limited solubility in nonpolar solvents
Safranin O, dye	350	(+) charge, limited solubility in nonpolar solvents
9,10-Diphenyl anthracene	330	Nonpolar UV-visible aromatic hydrocarbon
Alkane oligomers (C _n H _{2n+2})	<400	Limited solubility in polar solvents, availability is impure > 400 Da, detected via gas chromatography
PS oligomers	n • 104	Expensive, limited solubility in polar solvents, measured via HPLC
PEG oligomers	n • 44	Insoluble in many non-polar solvents, limited accuracy, measured via GPC or HPLC with ELSD or TOC analysis
PPG oligomers	n • 58	Soluble in a wide range of solvents, limited accuracy, measured with HPLC with ELSD

to solvent effects. They have been shown to change their size and conformation based on the solvent(s) present [131-132]. These effects can, for example, create, restrict, or enlarge pores [88,133]. Other interactions between the solvent, solute and membrane have led to negative retentions, as reported in several publications

[17,134-135]. The search for a single model is naturally continuing, recent or notable models for OSN ceramic membranes are listed in Table 2.7, each described in the following section.

2.5 TRANSPORT THROUGH POROUS CERAMIC MEMBRANES

There are generally three types of models describing transport through membranes. The first type is models based on irreversible thermodynamics, treating the membrane as a “black box”, meaning membrane properties are excluded. The second is pore-flow models (for porous membranes) which incorporate membrane properties. Third are solution-diffusion models, for dense membranes.

The first two model types can describe transport through porous ceramics. Solution-diffusion type models aptly describe dense membranes [136] and are hence not reflective of the transport mechanics through porous ceramics.

The transport model by Kedem and Katchalsky [137] is one of the first of the thermodynamic models for membrane transport and is still used in various forms today. This model excludes any membrane-specific properties such as tortuosity or porosity, and was later expanded upon by Spiegler and Kedem [138] to Equations (3) and (4).

$$R = \frac{\sigma(1-F)}{1-\sigma F} \quad (3)$$

$$F = \exp \left(-(1 - \sigma) \frac{J_v}{P_s} \right) \quad (4)$$

where the volumetric flux, J_v , and retention, R , are related through two constants: the membrane reflection coefficient, σ , and the solute permeability, P_s . The reflection coefficient is a measure for the retention of a solute under purely convective influence. P_s is the diffusion-driven permeability of solute across the membrane, and thus varies with the solute-solvent combination [139]. This model has explained the behavior of aqueous-applications membranes well, such as salt

retention, and has been used to predict the effect of operating parameters such as trans-membrane pressure [140].

One of the first models describing the size exclusion mechanism across porous membranes was the “Theory of Sieving” proposed by Ferry [141] in 1936 for ultrafiltration. Its underlying concept is that there is a statistical distribution of retained solutes that are smaller than the pores of a given membrane. Assuming spherical solutes, an isoporous membrane, cylindrical pores oriented normal to the membrane surface, and a homogenous (bulk) solution at the pore entrance, retention was expressed in the following way, where d_c is the solute diameter and d_p the membrane pore diameter, for $d_c \leq d_p$:

$$R = \left(\frac{d_c}{d_p} \left(\frac{d_c}{d_p} - 2 \right) \right)^2 \quad (5)$$

Though filtration by steric hindrance, i.e. sieving, undeniably plays a role in the retention of solutes through pores, affinity and membrane surface effects play an increasingly important role as mesopores shrink to nanofiltration range. Interactions are further complicated when water is replaced with organic solvents or a mixture of liquids. Marchetti et al. [142] studied the retention of solutes which are significantly smaller than the pore and similar in size to the solvent (e.g. salts). The retention is determined by the preferential affinity of the membrane surface to either the solute or solvent, as illustrated in Figure 2.11. The same work showed that if no preferential affinity exists, the retention is near zero (if $d_c \ll d_p$). It was also shown that the addition of water to an organic solvent can change the interaction as preferential solvation of the solute can change its interaction with the membrane surface. These findings, among others, helped qualitatively explain observed negative retentions in terms of membrane-solute-solvent interactions in a number of studies [98,143-144]. It has become clear that any comprehensive model describing nanofiltration through pores should include both bulk and surface effects.

Qualitative evaluation and performance prediction of porous, non-swelling membranes was undertaken using Hansen solubility parameters (HSPs) [145]. The relative affinity between solvent and membrane (SM) and the difference in the relative affinities between solvent-membrane and solute-membrane (SM-

SoM) were calculated and visualized by employing ternary HSP plots. The membranes used were the 0.9 nm TiO₂ Grignard-grafted membranes from VITO described in section 2.3.2. A clear relationship was shown between the SM parameter and relative solvent flux, when corrected for viscosity. Visually, it is seen as the lower the affinity, the higher the distance on the ternary plot, and therefore the lower the expected flux.

It was also claimed that a low SM-SoM (i.e. stronger solute-membrane than solvent-membrane affinity) indicated an increased likelihood of low or even negative retentions. The HSP method [145] presents a useful tool for maximizing the performance for non-swelling porous membranes. It should be considered when modifying the surface hydrophilicity of a porous ceramic for a given application. However, the retention indication parameter (SM-SoM) has no input from the relative size of the solute to the membrane pore, and should therefore be carefully applied.

Figure 2.11. a) Membrane surface effects in nanofiltration versus ultrafiltration b) In nanofiltration, higher solute or solvent flux due to either preferential solute-membrane or solvent-membrane affinity, respectively. Adapted from [142].

Other solute-membrane interaction terms have been used besides HSPs. For the nanofiltration of aqueous solutions, solute-membrane interaction terms are found in porous models, for example in sieving models modified by empirically-determined correction factors [146-147], and also in the Donnan-Steric Pore Model (DSPM) [148]. These and other models have been adapted from aqueous membrane applications to describe the transport of organic solvent solutions through nanofiltration membranes; they are described in the next two sections. The first section describes OSN models for transport through unmodified ceramic membranes. These models have been derived from transport studies across hydrophilic (unmodified) ceramic membranes, nonetheless their behavior can be used as a basis to understand transport through modified ceramics. The second section describes models for grafted ceramics. Many of the models presented focus only on explaining or predicting solvent permeability and do not include solute transport. Ungrafted ceramic membranes

The models used to describe the transport of organic solvent solutions through porous ceramics have generally been derived from existing models for aqueous applications. Table 6, as well as this section, begins with models describing the passage of solvent and solute through porous ceramics. The following section continues with those models generated to describe transport through grafted ceramics.

The unique permeation characteristics of organic solvents passing through a ceramic nanofiltration membrane were detailed by Tsuru et al. in two papers published at the outset of OSN in 2000 [32,154]. A set of alcohols permeating through $\text{SiO}_2/\text{ZrO}_2$ membranes (pore diameters 1-5nm) was found to deviate from the Hagen-Poiseuille model. Though viscosity was still the major solvent parameter impacting flux, permeability was facilitated by an increase in temperature (after correcting for viscosity) while negatively affected by solvent size. The study concluded that permeation through pores of 1 – 5 nm required a higher activation energy for larger molecules [32]. Next, permeation of alcohols and sugars at different temperatures was analyzed by the Spiegler-Kedem model and corroborates the proposition of a size-dependent activation energy [154]. These studies established the different character of porous nanofiltration membranes from their ultrafiltration counterparts.

Table 2.7. Models used to interpret or predict solvent and solute transport across OSN ceramic-based membranes.

Ref.	Capability	Model basis	# of fitted variables	Parameters	Model agreement with experimental data
[149]	Pure solvent permeability	SD with pore-like imperfections	2	Solvent viscosity, dielectric constants of solvent & reference solvent, surface tension of solvent & reference solvent	Overall agreement with 3 membranes tested, Koch MPF-50, Solsep-030505, HITK 27, of which alone HITK is ceramic
[150]	Pure solvent permeability	Coupled resistances	3	Solvent viscosity, dielectric constants of solvent & reference solvent, surface tension of solvent & reference solvent, solvent size pore size	Agreement with 2 ceramic membranes tested, HITK 275 and HITK2750.
[151]	Solvent (pure & mixtures) permeability	Modified pore flow	3	Solvent surface tension, contact angle between membrane and solvent, solvent dipole moment, polarizability of the membrane as calculated by Carré's theory of surface polarizability, solvent size, pore size	Agreement except for acetonitrile/water mixtures. Membranes tested Inopor Nano 450, Inopor Nano 750, Sulzer 1000, Inopor Ultra 2000
[152]	Pure solvent permeability	Empirical fit to Hansen solubility parameters	1	Hansen solubility parameters of solvent and reference liquid (water)	Agreement with 3 Inopor membranes (pore sizes 0.9, 1 and 5 nm)

(Continued on next page)

(continued)

[93]	Pure solvent permeability	Modified pore flow with swelling parameter	1	Swelling degree for PDMS in solvent, swelling degree for PDMS in reference solvent, solvent viscosity	Agreement with PDMS-grafted membranes (2 sizes of PDMS, $n = 10, 39$)
[92]	Permeability & retention	Modified Spiegler Kedem	2	Pore size, diffusion pore size, solute size, membrane thickness	Agreement with PDMS-grafted membranes (2 sizes of PDMS, $n = 10, 39$)
[73]	Permeability & retention	Spiegler Kedem model	2	none	Fitted to Grignard-grafted membranes, better agreement for high polarity solvents and at higher pressures
[153]	Permeability & retention	Modified Bowen-Welfoot	0	Solvent viscosity, Solvent size, solute size, pore size, solute molecular weight	No agreement except for retention of polystyrenes in THF

In 2009, Darvishmanesh et al. [149] published a solution-diffusion model with imperfections adapted to pure solvent permeability. In addition to diffusive transport within the membrane, an extra term takes into account the viscous transport through the imperfections located in the membrane itself:

$$J_i = \frac{a_0 \alpha}{\mu \exp(1-\beta)} (\Delta p - \Delta p_\pi) + \frac{b_0}{\mu \exp(1-\beta)} (\Delta p) \quad (6)$$

where a_0 and b_0 are fitted diffusivity and permeability parameters, respectively, for a given membrane, μ is the viscosity, p is the pressure, p_π is the osmotic pressure, α is the dielectric constant ratio (relative to water for hydrophilic membranes, and to hexane for hydrophobic membranes) and β is either the surface tension ratio of the solvent to the hydrophilic membrane or the surface tension ratio of the hydrophobic membrane to the solvent's. A range of organic solvents was tested on two commercial membranes, a hydrophilic ceramic membrane, HITK 275 (TiO_2), and a hydrophobic PDMS polymeric membrane, MPF 50. The fitted parameters of the model were reported to agree within 5% error. This model confirmed earlier findings showing the inverse relation between single-solvent permeability and viscosity as well as molar volume [18,32,154-155], and also continued to emphasize the impact solvent-membrane affinity has on permeability [156-157].

Shortly following the previously discussed study, Darvishmanesh et al. published a coupled series-parallel resistance model (CSR) specific to inorganic membranes [150]. The model was tested on HITK275 (0.9nm diameter, TiO_2) and HITK2750 (3.0nm, ZrO_2) only with pure solvents. The three resistances consisted of a surface resistance, R_s , connected in series to two parallel resistances: the membrane resistance, R_m , and the pore resistance, R_p . The α and β parameters are the same as Equation (8). The r_s and r_p are solvent and pore radius, respectively, and k_s , k_m and k_p are parameters to be fitted for each membrane. These resistances are combined to give flux equation (13).

$$R_s = k_s \left(\frac{r_s}{r_p} \right)^2 \exp(1 - \beta); R_m = k_m \left(\frac{\mu}{\alpha} \right); R_p = k_p \mu \left(\frac{r_s}{r_p} \right)^2 \quad (7)$$

$$J_i = \frac{\Delta P}{R_{\text{overall}}} \quad (8)$$

This model again gives fitting results with a reported error of less than 5%. Here the surface affinity between solvent and membrane are taken into account by incorporating the dielectric constants and surface tensions of both the solvent and membrane as parameters. Unfortunately, neither of these models were tested on solvent mixtures or solutions. Marchetti et al. [151] proposed in 2012 a corrected pore-flow model, which has four parameters to be fitted. Only three, K_{HP} , $f_{capillary}$ and f_{steric} were found necessary for model validity.

$$J_i = \frac{K_{HP}\Delta p}{\mu} (1 + f_c) \quad (9)$$

$$f_c = f_{capillary} + f_{dipole} + f_{steric} = C_1 \frac{2\gamma_{LV} \cos \theta}{r_p} + C_2 |\delta_i - k_{pol}| + C_3 \left(\frac{r_s}{r_p}\right)^2 \quad (10)$$

where θ is the contact angle between membrane and solvent, δ_i is the solvent's dipole moment, k_{pol} is the polarizability of the membrane as calculated by Carré's theory of surface polarizability [158]. The dipole moment was chosen over the dielectric constant as a better indicator of molecular (versus bulk) properties. This model was tested on a range of TiO_2 and ZrO_2 membranes with solvent and solvent mixtures and compared against the classic Hagen-Poiseuille equation and coupled resistances model [150]. The Hagen-Poiseuille equation failed to accurately predict some solvent permeabilities through microporous membranes, while the coupled resistance model suffered the same shortcoming for mesoporous membranes. The corrected pore flow model was found to be accurate (within 5%) through pore sizes of 0.9 nm to 3 nm, and the parameters taken to vary linearly with composition for most solvent mixtures.

A model derived by Buekenhoudt et al. [152] in 2013 uses the empirically determined linear relation between the Hansen solvent solubility parameter and its viscosity-corrected flux. The derived equation is shown below,

$$\frac{J_i \mu_i}{J_{water} \mu_{water}} = \frac{S_{Hansen,i}}{S_{Hansen,water}} C + (1 - C) \quad (11)$$

where S_{Hansen} is the total Hansen solubility parameter and C is the only parameter to be fitted. The product of viscosity and flux is normalized to that of water, just as the Hansen solubility parameter of the solvent is normalized to water. When tested on inorganic membranes, it was shown that for the given

material (TiO_2) the C parameter has an exponential relationship with the pore diameter and found to be valid from 0.9 nm to 100 nm, using different solvents and solvent mixtures. This model that accurately describes solvent flux through both ultrafiltration and nanofiltration pores is remarkable, however, no effort has been made to describe retention using this model or its ‘C’ parameter. This publication tentatively proposes that the observed affinity difference between the membrane and solvent is in fact between the membrane and a thin water layer adsorbed onto the hydrophilic membrane surface. Extension of this simple model to modified hydrophobic surfaces may prove to be more complex, as the Hansen solubility parameter at the membrane surface would depend on the solvent or solute preferentially adsorbed to the membrane surface.

A transport analysis [153] of in-situ modified membranes whose fabrication method [40] is described in Section 2.6 was published in early 2016. The membrane selective layer was composed of hydrophobic 1.0 nm diameter pores of ZrO_2 . The retention of styrene oligomers of low molecular weight with varying endgroup polarities were tested. The authors modified the model of Bowen and Welfoot [159] to include a pore size dependent viscosity, due to the presence of an absorbed layer at pore surface, and a pore size distribution to accommodate defects in the top layer. The applicability of the resulting model is poor, as it is only valid for the retentions of polystyrene in one solvent, THF. When using other solvents, such as ethanol or n-heptane, retentions are significantly over-predicted. The model also over-predicts solvent fluxes by at least an order of magnitude, and fails to accommodate membrane defects. A purely theoretical model with no fitted parameters is ideal, however, this attempt falls short. Though the applicability of pore size dependent viscosity as applied in [153] is probably not applicable to the “soft surface” of grafted ceramic pores, it may still be possible to incorporate, in another way, the impact of defects on retention and permeability.

2.5.1.1 Grafted ceramic membranes

Now described are the few models for grafted ceramic membranes. These models have been used to gain an understanding of the transport phenomena occurring through the grafted membranes and then predict general behavior. First described

are two PDMS-grafted membrane studies [92-93] followed by a study detailing transport through Grignard-grafted membranes [68].

Tanardi et al. [93] developed an organic solvent permeability model specific to grafted ceramic membranes. Derived from the pore flow (Hagen-Poiseuille) model, this approach equates the viscosity-corrected flux to a permeability which takes into account the swelling degree of the grafted moiety, assumed to be responsible for shrinking the pore. A linear relationship between graft swelling and solvent permeability is described in the equations below.

$$P_i = P_{\text{ref}} (A - BV'_i) \quad (12)$$

$$J_i \times \mu = P_{\text{ref}} (A - BV'_i) \Delta p \quad (13)$$

$$V'_i = \frac{V_i}{V_{\text{ref}}}; \quad (14)$$

$$P'_i = \frac{P_i}{P_{\text{ref}}}; \quad (15)$$

where P_{ref} is the permeability of a reference solvent, V_{ref} is the amount of sorbed reference solvent per gram of grafted moiety, P_i and V_i are the permeability and sorbed solvent per gram of graft of the solvent in question, respectively, and P'_i and V'_i are the normalized values of these, and are equal to 1 when $P_i = P_{\text{ref}}$ and $V_i = V_{\text{ref}}$. The membrane-specific constants A and B are empirically determined by the linear relationship between P'_i and V'_i . This model was tested on 2 different PDMS-grafted ($n = 10, 39$) γ -alumina membranes in a temperature range of 20°C - 70°C. Noting that the linear relationship between P'_i and V'_i always passes through the point (1,1) implies the possible reduction of this model to 1 fitted constant:

$$J_i \times \mu = P_{\text{ref}} (B - BV'_i + 1) \Delta p \quad (16)$$

The permeability of the reference solvent, hexane, was obtained along with values of V'_i , as determined through simple sorption experiments of free-standing PDMS [93]. Equation (16) correctly predicted the permeabilities of six other solvents, as shown in Table 2.8.

Table 2.8. Permeabilities (P) of PDMS ($n = 10$) grafted membranes for each solvent, with permeabilities corrected for viscosity and permeabilities corrected for viscosity and PDMS swelling. Correcting for both swelling and viscosity gives a uniform permeability. $B = 0.68$ for PDMS $n = 10$ grafted membrane. [93]

Solvent	μ (mPa.s)	V_i^*	Permeability ($L.m^{-2}.h^{-1}.bar^{-1}$)	$P^*\mu$	$P^*\mu /$ ($B.BV_i^*+1$)
Isopropanol	2.39	1.00	0.9	2.2	2.2
Ethyl acetate	0.45	1.02	4.6	2.1	2.1
Octane	0.54	1.12	3.4	1.8	2.0
Toluene	0.59	1.15	3.1	1.8	2.0
p-xylene	0.64	1.34	2.7	1.7	2.2
Hexane	0.31	1.40	4.8	1.5	2.0
Cyclooctane	2.13	1.48	0.6	1.3	2.0

Figure 2.12. Retention as a function of solute size for a series of neutral dyes. The points are experimental data and the lines from the modified Spiegler-Kedem model of [92].

Merlet et al. [92] modeled the retention performance of these same PDMS-grafted membranes with a modified Spiegler-Kedem (SK) model. The retention of neutral dyes of molecular weights ranging from 322 g.mol^{-1} to 973 g.mol^{-1} in a variety of solvents were reported, as shown in Figure 2.12. Building upon previous work [160], the Ferry sieving model, Einstein-Stokes diffusion equation and Renkin equation (hindered diffusion in a cylinder) were used to make the original model parameters, σ and P (Equations 3 and 4), a function of the ratio of the solute size to the pore size. This alteration to the SK model allowed for the diffusion of solutes through the graft by introducing a “diffusion pore size”, equal to the original diameter minus the monolayer of organosilane linker on the γ -alumina pore, resulting in a diffusion pore size of 4.1 nm. The end result is a model that requires two fitted parameters, one obtained from a permeation and retention experiment through a given solvent-membrane pair, the second being membrane-dependent and easily obtainable by permoporometry. This model does not include any specific affinity interactions between the solute and either the membrane or solvent, yet still correctly predicts permeation because in this work it tests only one class of solutes, namely neutral dyes. Despite this limited scope of this model, it shows the need to consider the diffusion of solutes through the graft when evaluating or modeling these types of membranes.

While solvents clearly swelled and changed the performance of the PDMS-grafted membranes described in the model above, solutes with a high or low graft affinity may influence their own retention as well. Besides the pronounced surface effects in the nanofiltration pore that influence solute retention [142], it is possible for the solute to affect the graft swelling. Postel et al. [161] as well as Ogieglo et al. [162] have determined that solutes with an affinity for PDMS, as determined by Hansen solubility parameters, will additionally swell PDMS that was already saturated with a given organic solvent. Further studies of PDMS-grafted membranes with different types of solutes, not only neutral dyes, would elucidate this relationship.

A different behavior is seen for TiO₂ Grignard-grafted membranes, as the graft partially covers the surface and has not been observed to swell. In a comprehensive study of these membranes [68], the permeabilities in a range of solvents, from polar to nonpolar, was obtained. Retention was also measured, both by PEG chains of similar molecular weight but with endgroups of varying polarity, and by a series of PS oligomers. Results were analyzed via the Spiegler-Kedem model and in terms of the affinity of the solvent and solute, as measured by Hansen solubility parameters. Observed were two classes of solvents: high polarity solvents, where solute retention is independent of pressure, and low polarity solvents, where retention shows a pressure dependence. As observed in previous studies of Grignard grafted membranes [98], these polar solvents also had higher fluxes (DMF: 2.6 L.m⁻²h⁻¹bar⁻¹, THF: 2.7 L.m⁻²h⁻¹bar⁻¹). This was likely due to the partial graft coverage, which imparts only an amphiphilic character to the membrane surface. The membrane surface then prefers polar compounds over non-polar ones, which translates into higher fluxes for polar solvents. When analyzed through the Spiegler Kedem model, solutions of polar solvents were found to be in a convection-dominated regime. While in this regime, diffusion of solutes through the membrane is negligible. The study concludes that the retention mechanism in these polar solvents is therefore intrinsic to a size exclusion mechanism, i.e. by the reflection coefficient of the Spiegler-Kedem model (Equations 3 and 4), while those solutions of solvents below a certain affinity, as measured by Hansen solubility parameters, will show lower retentions. These retentions especially decreased with an increase in solute polarity or a decrease of applied pressure. Through Hansen solubility parameters

and the Spiegler-Kedem model this study gains an understanding of the performance Grignard-grafted membranes in the context of solvent-solute-membrane affinities.

Both PDMS-grafted and Grignard-grafted ceramic membranes are similar in many respects, as each is a grafted ceramic designed for OSN. Upon comparison of their transport studies via the Spiegler-Kedem model we perceive that their different graft styles lead to different transport behaviors. The best performance of PDMS-grafted membranes in non-polar solvents can largely be explained by examining the graft swelling, which is maximized in non-polar solvents, while the amphiphilic character imparted by the partial surface coverage of the Grignard-graft makes those membranes especially suitable for polar solvent nanofiltration. Both PDMS-grafted and Grignard-grafted ceramic membranes show competitive separation in organic solvents, yet transport through either is not yet fully understood. For the PDMS-grafted membranes the effect of solute type was not studied nor modelled as only one type of solute has been used [92]. For Grignard-grafted membranes, the effect of solute affinity is only qualitatively understood, by either placing the solute in an affinity-independent region (polar solvents) or in an affinity-dependent region (less polar solvents) and identifying trends in each region [68]. In each case a qualitative, predictive model is missing, which would allow for confident estimations of membrane performance than the informed guesses we can currently make.

A recurring theme of the transport models described in the last two sections is choosing solvent properties as baselines to normalize various parameters. Examples include the dielectric constant of either water or n-hexane [149], the flux and solubility parameters of water [152] and the swelling degree of PDMS in cyclooctane [93]. Choosing water as a baseline is not logical for the filtration of organic solvents through hydrophobic membranes. A rational alternative is to normalize properties to a representative hydrophobic solvent, such as hexane. Besides the ambiguity of the term “representative hydrophobic solvent,” this approach prevents the formulation of a unified transport theory for both hydrophilic and hydrophobic membranes. It also raises the question of how to model those membranes termed amphiphilic, as determined either by their water contact angle (70° - 90°) or by their varied functional surface groups (e.g. a

mixture of hydroxyl and alkyl groups). Since it is the relative affinities of the solvent, solute and membrane to one another that influence performance, a better approach is to use the membrane properties to normalize various parameters, as with the corrected pore flow model [151], where the solvent's dipole moment is normalized to the polarizability of the membrane.

As discussed in the introduction, the research, development and production of polymeric membranes outnumbers that of ceramic membranes. Naturally, models describing polymeric membranes also exceed models for ceramic membranes. However, no model has proven superior for both membrane types. Different models work best for different combinations of solvent, solute, and membrane [156,163-166]. The few models tailored to ungrafted or grafted ceramic OSN membranes are either descriptive, i.e. not predictive, or do not adequately predict performance across several types of membranes. The complexity of a theory that can cover both types of membranes may be too unwieldy and complicated, or existing in different forms depending on the membrane structure. Additionally, if any model describing ceramics OSN membranes makes use of physical characteristics of the membrane, such as pore size, hydrophobicity, etc., then it will likely not be applicable to most polymeric membranes. From this we conclude that the focus should shift towards finding models describing a set of membranes with a similar structure, such as a single model well-describing porous ceramics.

2.6 CONCLUSION

Grafted ceramics are a promising class of materials for OSN. While to-date much research is focused on polymeric membranes, the advantages of tailoring porous ceramics with polymers are clear. The inherent chemical and mechanical resistance of ceramics coupled with the multitude of possible grafts translates into three major benefits: long membrane lifetimes, suitability to harsh conditions, and the ability to be tailored to a large range of applications. This potential, the facile tuning of separation properties, has started to be realized. A sharp and low MWCO in the range of 250-450 Da would potentially enable solute-solute discrimination, opening up new applications. This challenge can be overcome by exploring and expanding the many grafting chemistries and techniques available, notably surface-initiated polymerization. Recent developments, such as linker-less grafting of an alternating copolymer [97] and the grafting-from of polystyrene [103], show how known chemistries can be applied to the fabrication of ceramic-based hybrid membranes.

Developing performance-predicting models valid for a range of grafted ceramics would allow for facile membrane customizations, as grafts could then be tailored to target applications with a reasonable expectation of success. Currently, only a partial grasp of the complex solvent-solute-membrane relationship is present. Research efforts to quantitatively model these interactions could yield the much needed greater understanding needed for predictive modeling as well as naturally attract further interest from industry. OSN technology is young yet advancing rapidly, and the sub-field of grafted ceramics for OSN even more so, propelled by its recent advancements that encourage further development.

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CHAPTER THREE

Growing to shrink:
nano-tunable polystyrene
brushes inside 5 nm mesopores

ABSTRACT

The development of controlled polymerization techniques in the last decade has enabled polymer brushes to be grown from inorganic substrates with precision. Less studied are brushes grown from concave geometries of high curvature, such as mesopores, despite their application potential in the separation sciences. The method used here, surface-initiated, activators-regenerated-by-electron-transfer, atom-transfer radical polymerization (SI-ARGET-ATRP), is used to grow a polystyrene brush from aluminum oxide pores of 5 nm diameter, to-date the most confined geometry in which ATRP has been conducted. The brush is characterized by TGA, AFM, and FTIR, the latter two methods applied specifically to the external brush. Additionally, permoporometry as well as permeability and retention measurements are used to characterize the graft within the mesopores. We show that the brush length is tunable, that the brush length is solvent-dependent, and we also demonstrate the application potential of this hybrid material as an organic solvent nanofiltration membrane. This new class of membranes shows excellent performance: a toluene permeability of $2.0 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$ accompanied by a 90% retention of diphenylanthracene (MW 330 $\text{g}\cdot\text{mol}^{-1}$).

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3.1 INTRODUCTION

The union of inorganic and organic substances to realize hybrid materials of designed functionalities continues to attract interest from both industry and academia [1]. The application of polymer brushes on inorganic surfaces has proven a popular way to modify substrate surface properties. As scientists and engineers have developed finer control over the chemical composition, thickness, and architecture of polymer brushes, the number of possibilities and applications have grown. Highly specific hybrid materials have been created, examples include thermo-responsive, fluorescent nanocrystals and light-activated gates on the surface of mesoporous, hybrid-silica films. [2-3]

To create polymer brushes from inorganic substrates, one of two approaches can be applied. The first is to polymerize the brush from a surface-bound initiator molecule, this is called grafting-from. The other approach, termed grafting-to, is the binding of a pre-fabricated chain onto the target surface, often done with the help of an inorganic-organic linker already deposited on this surface. One of the main advantages of grafting-from over grafting-to is that there is no separate polymer synthesis step prior to grafting, decreasing the number of synthesis steps or dependence on a specialized commercial product. Another advantage are higher graft densities. This is due to the hindered diffusion of whole polymer chains to surface binding sites during grafting-to, while during grafting-from the monomer is relatively free to diffuse to active surface sites [1,4-5]. Before the advent of controlled polymerization methods, the separate synthesis step required by the grafting-to method meant greater control over the brush height and uniformity than could be achieved by a single grafting-from reaction. Nowadays, with controlled polymerization methods such as atom-transfer radical polymerization (ATRP), researchers are making dense, precisely-tuned brushes by grafting-from. [6-7]

The basis of ATRP lies in a high ratio of dormant chains to active chains, as seen in Scheme 1, where the equilibrium favors the left-hand side. This equilibrium requires the strict absence of oxygen, which if present will oxidize the metal complex. The benefits of this equilibrium are not only to slow down the reaction, resulting in lower, controllable molecular weights, but also to reduce the number

of chain–chain terminations. However, inter-chain terminations still take place, removing the catalyst from the equilibrium cycle, as seen in Scheme 3.2.

ATRP –grown brushes on inorganic substrates are not new. For instance, PMMA was grown on the outside of imogolite cylinders [10] and patterning techniques have been developed for the selective growth of polymer on silicon wafers [11]. However, relative to grafting-from on planar to convex geometries, such as a wafer or nanoparticle, there exist only few examples of brush polymerization from concave surfaces, such as the inside of a pore, and even fewer of those are in the mesoporous (IUPAC: $2 < \phi \leq 50$ nm, ϕ = pore diameter) range [12-14]. As the radius of curvature becomes more extreme, the growing brush becomes increasingly confined. Chu et al.[15] grew poly(3-(N-2-methacryloyloxyethyl-N,N-dimethyl) ammoniatopropanesulfonate) (PMAPS)

Scheme 3.1. Dormant / active chain equilibrium of ATRP, where k_{a} and k_{da} are the activation and deactivation rates, respectively, M is a transition metal ion, L the ligand, I the initiator, P_n the dormant chain, and $\text{P}_n^\bullet$ the active chain. When the chain is active, there is a chance that one or more monomers will add to the chain. Adapted with permission, copyright (2006) American Chemical Society.[8]

Scheme 3.2. ARGET-ATRP, where the deactivated catalyst is regenerated both by the equilibrium reaction and by the reducing agent. The chain-chain termination rate constant is k_{t} . Adapted with permission copyright (2006) American Chemical Society [8].

brushes via ATRP from an initiator bound onto the surface of 200 nm diameter pores of anodic aluminum oxide. The study claims no impact on chain growth kinetics due to the concave geometry, though the retardation of monomer to chains growing in the center of the pores was noted. ARGET-ATRP was used by Cao et al. to grow poly(N-isopropylacrylamide) (PNIPAAm) from silica mesopores of 29 nm diameter [16]. Until now, the smallest concave surface successfully polymerized-from without eliminating the pore volume was the inside of mesoporous silica particles with a pore diameter of 15 nm [5]. The brush height could be varied within 1 - 2 nm, with a minimum attainable pore diameter of 6 nm. This was demonstrated with 3 different polymer brushes, polymethacrylate (PMMA), polyacrylonitrile (PAN) and polystyrene (PS), all on mesoporous (ϕ 15 nm) silica particles dispersed in solution [17-18].

Here, we have grown brushes inside the smaller pores of 5 nm diameter of gamma aluminum oxide (γ -alumina, γ -Al₂O₃) particles and membranes. We demonstrate tunable pore shrinking by the controlled growth of polystyrene from surface-immobilized initiators. Styrene is polymerized via ARGET-ATRP, and we show that the reaction kinetics are affected not only by the reaction time and monomer concentration, but are also faster outside the confined, concave pore geometry. The pore diameter can be shrunk down to values below 2.0 nm, though this pore size is shown to be dependent on the solvent the polystyrene brush is in contact with. Emphasized is that the term “pore size” refers here to the openings created by the rapidly moving grafted polymer chains in the pores, which can be physically interpreted as the average diameter of the free volume elements represented as a cylinder [19]. The mesoporous brushes developed here are used to change the surface property of the ceramic alumina. Possible industrial applications of mesoporous brushes include catalysis, as in [17-18], however here this new hybrid material is used as a membrane, a selectively barrier separating solutes of 330 g mol⁻¹ from a given solvent.

Accordingly, the majority of γ -alumina samples used in this publication are not free-floating hollow cylinder particles as the examples cited above [5,17-18], but a collection of pores calcined together to form a uniform and selective layer, or mesoporous membrane. These pores are not perfectly cylindrical but rather a stacking of alumina particulates, creating a tortuous path through the selective

membrane layer. By tuning the polystyrene brush growth in these 5-nm pores we show the application potential of bespoke organic solvent nanofiltration (OSN) membranes.

The membrane technology field termed organic solvent nanofiltration (OSN) strives to purify or concentrate compounds between 200-1000 g.mol⁻¹ from organic solvents. Since its inception in the early 2000s, marked by its first commercial success, the “max-dewax” process [20], OSN has received growing attention from the chemical industry and academia alike [21]. A focal point is membrane material development, fabricating membranes that can withstand organic solvents and elevated temperatures while maximizing performance. The advantage of ceramic membranes over polymeric membranes are their inertness to most organic solvents, notably apolar solvents such as toluene, which often chemically degrade or physically deform polymeric membranes or their supports [21]. However, the highly hydrophilic surfaces of ceramic oxides makes them ill-suited to OSN applications, and as such the surface modification of porous ceramic oxides with apolar groups has found success, such as the grafting-to of PDMS [19] and the Grignard-grafting of alkanes or phenyl group [22]. However, grafting-from of the ceramic mesopores and its potential advantages - facile tunability of both the brush size and its chemical character in one synthesis step - remain unexplored until now [23]. The two key metrics for membrane performance, permeability and retention, are measured in this work by the permeability of toluene and the retention of 9,10-diphenylanthracene (DPA, $MW = 330$ g.mol⁻¹). From these results we demonstrate the promising application potential of grafted-from mesopores in membrane technology, specifically in the field of organic solvent nanofiltration.

3.2 EXPERIMENTAL

3.2.1 Materials

The solvents toluene (anhydrous, 99.8%), anisole (anhydrous, 99.7%), isopropyl alcohol (99.5%), ethanol (absolute) and hexane (anhydrous, 95%); the chemicals copper(II) chloride (99.999%), 4,4'-dinonyl-2,2'-dipyridyl (dNbpy, 97%) chlorotrimethylsilane (TMCS, $\geq 99\%$), tin(II) 2-ethylhexanoate (Sn(EH)₂, 92.5-100.0%) and 9,10-diphenylanthracene (DPA, 97%) were all purchased from

Sigma-Aldrich and used as received. Styrene ($\geq 99\%$, containing 50 ppm of 4-tert-butylcatechol inhibitor) was purified using a basic alumina column. (3-Trimethoxysilyl)propyl 2-bromo-2-methylpropionate (initiator) was purchased from Gelest. All water used is MilliQ water.

Alpha-alumina supports ($\alpha\text{-Al}_2\text{O}_3$, ϕ 3.9 mm, 2 mm thick) were purchased from Pervatech B.V., The Netherlands. Two layers of gamma-alumina ($\gamma\text{-Al}_2\text{O}_3$) were applied on the $\alpha\text{-Al}_2\text{O}_3$ discs by dip-coating a boehmite sol and calcined at 650°C during 3 hours to create a $3\text{ }\mu\text{m}$ -thick selective layer with an average pore size of 5 nm. Fabrication and characterization details of this layer can be found elsewhere [24-25]. Porous gamma-alumina particles were fabricated by calcining 15 mL of the same sol solution with the same temperature treatment as used for the gamma-alumina layers. The γ -alumina surfaces of both disc and particles are conceptually described as being either ‘internal’ or ‘external’, internal referring to the (internal) pore surface while external being the surface facing the exterior.

3.2.2 Methods

The standard rinse-and-soak that was performed after each reaction is described here. Samples were rinsed three times with the same solvent of the reaction and then left to soak in the same solvent of the reaction for at least 8 h before drying in a vacuum oven at 50°C for at least 12 h. All sample storage, prior to and between grafting reactions, was in a humidity-free nitrogen atmosphere.

3.2.2.1 Initiator grafting

Prior to the vapor phase deposition of initiator, samples (either porous particles or discs) were submerged in a 2:1 v/v water-ethanol solution for 8 hours and then dried in a vacuum oven at 50°C overnight. Afterwards a 30 mM solution of initiator in 50 mL of toluene was stirred and heated to 75°C for 6 h in a nitrogen atmosphere, 3 cm above which the sample was suspended, all of which is contained in a sealed round-bottom flask.

3.2.2.2 Plasma Etching

In some cases, post initiator grafting, samples were plasma etched for 40 sec at 100 W with 40 standard cubic centimeter per minute (sccm) of O₂. These were then soaked in ethanol for 1 h and dried in the vacuum oven at 50°C for 2 h.

3.2.2.3 TMCS grafting

Samples were immersed in a 2% v/v solution of TMCS in hexane, prepared and sealed in a dry atmosphere. The solution was stirred and heated to 65°C for 20 h, after which the sample was removed, rinsed in hexane and dried.

3.2.2.4 Surface-initiated polymerization

The sample (disc-shaped substrate or porous particles) was submerged in a solution of 100 mL of anhydrous anisole in a nitrogen glovebox. Styrene (0.060 mL, 0.53 mmol) was added to the sample solution, then 2 mL of an anisole solution of catalyst and ligand, CuBr₂ (3.0 mg, 21 μmol) and dNbpy (21 mg, 52 μmol), respectively, was added. The reaction vessel was sealed and heated to 75°C, at which time a 2 mL solution of tin(II) 2-ethylhexanoate (12 mg, 0.03 mmol) was injected through a septum. After a set reaction time, the flask was opened and exposed to air, thereby stopping the reaction. The sample underwent the standard rinsing and soaking in toluene rather than anisole, and was then dried in the vacuum oven at 50°C for at least 12 hours.

3.2.2.5 Characterization

Contact angle measurements were performed by the sessile drop method, 2.0 μL Milli-q water drops dispensed at a speed of 0.5 μL.s⁻¹. Contact angle was calculated 1.0 second after drop contact with the surface. Atomic force microscopy (AFM) imaging was carried out in intermittent-contact mode in air with AFM instrument Molecular Force Probe 3D (MFP-3D) (Asylum Research, Santa Barbara, CA) using cantilevers (Nanoworld®, Neuchâtel, Switzerland) with a force constant of approximately 2 N.m⁻¹ and a resonance frequency of 85 kHz at a scan rate of 0.5 Hz. The root-mean-square (RMS) roughness of the substrates was determined by imaging 1 μm² of each sample.

Permoporometry measures the oxygen permeance through a membrane as a function of the vapor pressure of a condensable gas, cyclohexane in this case. At 15°C, a stepwise decrease of the cyclohexane partial pressure causes cyclohexane layers to desorb from the pores, opening the pores in order of decreasing diameter. The pore size distribution is calculated by relating the flux of oxygen at each partial pressure through the Kelvin equation. This technique can accurately measure pore radii between 1.0 nm - the thickness of an absorbed cyclohexane layer around the pore circumference - and 50 nm [25].

Thermogravimetric Analysis (TGA) was done on a STA 449 F3 Jupiter®, NETZSCH. The samples were heated to 800°C with a heating rate of 10°C.min⁻¹ and under a 70 mL min⁻¹ flow of N₂. A blank correction run using an empty sample holder was carried out beforehand. All samples were kept in a vacuum oven at 50°C for 2 h prior to measurement.

Nitrogen adsorption/desorption isotherms were collected at 77 K using a Gemini System VII from Micromeritics Instruments Corp. (USA) under nitrogen flow of 50 mL.min⁻¹. Specific surface areas were calculated by using the Brunauer-Emmett-Teller (BET) model in the relative pressure range of $p/p_0 = 0.05-0.2$. Pore size distributions were evaluated from the desorption data of the N₂ isotherms by the Barrett-Halenda-Joyner (BJH) model between relative pressures $p/p_0 = 0.35-0.9$, and the pore sizes were estimated from the peak positions of the BJH pore size distribution curves.

3.2.2.6 Membrane permeability and retention

Permeability is the flux of a given solvent across a membrane per unit driving force, here expressed as liters of solvent per square meter of membrane (active membrane area = 1.2 cm²) per hour per bar of pressure applied across the membrane (L.m⁻².h⁻¹.bar⁻¹). Flux was measured with a custom-made dead-end setup, consisting of a nitrogen tank pressurizing a feed vessel with a valve to regulate pressure. The feed vessel was connected to the inlet of the membrane module, which led to the active membrane area. Permeate was collected and weighed at timed intervals while applying a pressure of 8, 12, or 16 bar above atmospheric pressure, abbreviated as TMP (trans-membrane pressure). Permeability was then calculated as the slope of the flux as a function of pressure.

All slopes were found to be linear unless otherwise noted. A permeability of 0.0 indicates no solvent permeation during 24 hours of operation at a TMP of 16 bar.

Retention measurements of 9,10-diphenylanthracene in toluene were done in a cross-flow setup at applied pressures of 10 and 30 bar. Both outputs, the permeate and retentate, were recycled back into the feed, thus recovery is assumed to be at 100% and the feed was kept at a constant concentration of 60 ppm. Aliquots of permeate were analyzed with a Perkin-Elmer λ 12 UV-Vis spectrophotometer at the wavelength of 375 nm. The retention was calculated by the following equation, $R = (1 - C_p/C_f)$, where C_p and C_f are the permeate and feed concentrations, respectively. After each set of retention measurements, samples were cleaned by 15 min of sonication in neat toluene with a Bransonic 1510-EDTH.

3.3 RESULTS & DISCUSSION

The same set of reactions was performed on two porous substrate geometries, γ -alumina discs and γ -alumina particles. The discs consist of 2 layers, on top is a thin selective layer of 3 μ m-thick γ -alumina with pores of $\phi = 5.6$ nm, as measured by permoporometry, supported underneath by 2 mm of α -aluminum oxide with $\phi = 80$ nm pores. The particles are porous particles entirely composed of γ -alumina. The average pore diameter of the ungrafted particles was calculated by the Brunauer–Emmett–Teller (BET) theory as 5.1 nm. Both the nitrogen adsorption/desorption and permoporometry data are available in the SI.

The reactions were done on particles to allow characterization by TGA, FTIR, and nitrogen adsorption/desorption. Not only is the size of an alumina disc incompatible with those instruments, the relative amount of graft is lower per unit volume of sample. This is because the α -alumina portion of the disc (99.8% per unit volume) is a largely inert surface with a relatively low surface area [12]. On the other hand, it is safe to assume that the following set of reactions only took place on the γ -alumina surface.

3.3.1 Initiator & TMCS grafting

Both the γ -alumina particles and discs underwent vapor phase deposition of the initiator, (3-trimethoxysilyl)propyl 2-bromo-2-methylpropionate (initiator), 329 g.mol^{-1} . The grafted $\gamma\text{-Al}_2\text{O}_3$ particles showed a surface coverage of $1.6 \text{ }\mu\text{mol.m}^{-2}$ ($0.9 \text{ molecule.nm}^{-2}$) as calculated from a weight loss of 12.1% (TGA, shown in Figure 3.1) and an ungrafted surface area of $240 \text{ m}^2.\text{g}^{-1}$ ($\text{N}_2 \text{ ad/des}$). This interpretation assumes negligible inter-silane condensation, a benefit of the vapor phase deposition method which has shown to yield uniform monolayers compared to solution phase deposition [26]. Similar grafting densities were expected on the discs, which is supported by a shrinkage in pore diameter of 0.8 nm, giving an average of $5.2 \pm 0.1 \text{ nm}$ as calculated by permoporometry. This is a similar value to the shrinkage observed when grafting a monolayer of the common inorganic-organic linker (3-aminopropyl)triethoxysilane (APTES, 221 g.mol^{-1}) onto γ -alumina discs. [27]

Subsequent to the initiator grafting, both disc and particle samples were reacted with chlorotrimethylsilane (TMCS, 109 g.mol^{-1}). The small size and mono-reactivity of the TMCS molecule is suitable for the bonding to and blocking of previously unreacted surface hydroxyl groups of γ -alumina. According to Kruk

Figure 3.1. Weight loss by TGA of γ -alumina particles grafted with initiator and subsequently with TMCS

et al.[18],the additional TMCS grafting serves to hinder the complexation of the Cu(II) catalyst, needed in the following polymerization step, with unbound surface hydroxyl groups of the alumina surface. Whereas the pore size remained unchanged for both discs and particles, TGA analysis of the particles revealed a successful graft of TMCS with an additional 3.7% weight loss, which translates to a surface coverage of $1.7 \mu\text{mol.m}^{-2}$ of γ -alumina. These results were expected, as TMCS was expected to react with remaining free hydroxyl surface groups as well as unbound silane methoxy moieties of the initiator (perhaps already hydrolyzed). Both these types of groups are found at the alumina surface and not further inside the pore. Samples unreacted with TMCS did not show polymerization. The above results confirm the discussion as reported in Kruk et al. [18]; TMCS ‘caps’ the unreacted hydroxyl groups, no further pore shrinkage occurs, and catalyst complexation with the surface is thus prevented.

3.3.2 Polymerization

The ARGET-ATRP of styrene will grow PS chains from surface-immobilized initiators [7]. Styrene was selected as a monomer because it is a well-studied system in ATRP literature, and as polystyrene it will have a high affinity towards the non-polar solvent it will be in contact with during nanofiltration, namely toluene. To attempt mesoporous brush formation, polymerization was carried out on both particles and discs, under the same conditions, and with the same reactant molar ratios, i.e., a monomer:initiator:catalyst:ligand:reducing agent ratio of 400:1:0.80:1.4:8. When selecting the initial reaction system, slow reaction times were targeted for two reasons: the target chain length is low compared to literature recipes [7,28], and the monomer should have sufficient time to diffuse into the pore during the reaction. Table 3.1 provides further details on each reaction parameter.

The pore sizes were measured before and after the polymerization, and the obtained results are shown in Table 3.2. Although the pores of the discs shrunk increasingly with reaction time, the pores of the particles show no significant shrinkage. It is important to note that pore diameters of discs below 2.0 nm cannot be determined as this is the measurement limit of permoporometry, corresponding to a single adsorbed monolayer of the condensable gas, cyclohexane, around the

Table 3.1. Justification for initial reaction conditions

Reaction parameter	Value	Rationale	(Negative) results
Monomer	Styrene	Well-studied, many starting points available [7], high affinity towards non-polar solvents	No other monomer tried
Solvent	Anisole	Reaction speed increases with solvent polarity [29], dissolves styrene	Toluene: solubility issues with other components
Catalyst	CuBr ₂	CuCl ₂ is less active than CuBr ₂ [30], but found to be too slow	When using CuCl ₂ no pore shrinkage or contact angle change observed after 8 hours of reaction
Ligand	dNbpy	High deactivation rate and medium activation rate (Scheme 1, k_{da} and k_a) [30]	Me6TREN, another commonly used ligand, suffers from low solubility in anisole
Initiator	Tert. α -bromo-esters	Average activation rate [31], commercially available with silane functionality	No other initiators tried
Temperature	75°C	the higher the T the faster the polymerization, 75°C is relatively low [8]	At 65°C, no pore shrinkage or contact angle change observed after 8 hours of reaction
Stirring	No	Stirring was found, in one instance, to slow the reaction [7]	Stirring was tried, no difference (permporometry, contact angle) was detected
Monomer: initiator ratio	1:400	Partial monomer conversion was estimated to yield short chains ($n = 10-50$) within 2-4 hours of reaction time, assuming standard ATRP first order kinetics [7]	Other ratios are explored in the text (800:1, 200:1). 5000:1 was tried and gives a surface PS layer with no separation properties of interest, no pore shrinkage. 20:1 shows no observed reaction over 24 hours.
Initiator: catalyst ratio	1:80	120 ppm of catalyst deemed safe to account for uncovered alumina hydroxyl sites, any impurities. ARGET-ATRP minimum as low as 5 ppm [16]	Polymerization successful with 9 ppm of catalyst, though pore shrinkage was imprecise to the point of irreproducibility.
Catalyst:ligand: reducing agent ratio	0.80:1.4:8	Based on literature [7,16]	10x decrease in reducing agent yields no observed pore shrinkage

circumference of the pore [25]. As shown in Table 3.2, this detection limit was passed for the 240 min reaction, therefore a pore shrinkage larger than 3.2 nm was calculated. Despite no indication of brush polymerization within the pores of the particles, TGA showed an additional weight loss, beyond the initiator & TMCS grafting, of $9 \pm 4\%$. The variation in weight loss had no discernable dependence on time reacted, varying within a sample set. The FTIR spectra of the particles, post initiator/TMCS grafting and post polymerization, are shown in Figure 3.2 along with peak descriptions in Table 3.3. The two spectra share common features, as the carbonyl functional group of the initiator and TMCS are present in both. The common bands are the C-H bending at 2945 cm^{-1} , the C=O ester stretch at 1733 cm^{-1} , the C-H bending at 1455 cm^{-1} , as well as the ester C-O stretches at 1278 , 1163 and 1080 cm^{-1} . Features indicating the presence of polystyrene are the aromatic C-H stretch at 2924 cm^{-1} , the C=C aromatic stretch overtones from 1490 - 1630 cm^{-1} , and the distinct C-H bend peak of mono-substituted aromatics at 696 cm^{-1} . Carbonyls, including esters, are one of the strongest IR absorbing groups, which explains their relative intensity compared to more numerous polystyrene groups [32].

The results from Table 3.2, in conjunction with those of TGA and FTIR, indicate that particle brush growth took place on the external particle surface but not inside the pores. The interpretation of this result is that the substrate morphology matters, specifically the ratio of external to internal surface area. A particle has more external surface area than a flat, porous disc, and hence more initiator grafted on its outside. This can translate into a reduced polymerization rate inside particle pores because the reactant monomer is 1) consumed at the external surface sites before it can diffuse inside the pores and 2) the consequentially faster-growing brush on the outside then hinders diffusion of monomer into the particle pores. An attempt to decouple external and internal brush growth is described in a following subsection.

Whatever the reason, the results in Table 3.2 show that the reaction rate inside the pores of each sample type are not equivalent. The particles were used to confirm successful initiator and TMCS grafts and (external) polystyrene growth, however, since the novelty and application potential lies in brushes grown from a plane of mesopores forming a selective barrier, the remainder of this work focuses on tunable polystyrene brushes grown inside porous ceramic discs and its potential application as a membrane.

Table 3.2. Pore shrinkage of particles and discs for increasing reaction times. The reactant molar ratios of monomer:initiator:catalyst:ligand:reducing agent are 400:1:0.80:1.4:8. Each set of conditions was repeated 3 times. Pore size shrinkage was calculated by subtracting the post-polymerization pore size from the pore size measured post-TMCS grafting. Particle pores were characterized by N₂ ad/des while disc pores were characterized by permoporometry.

Sample	Time (min)	Pore shrinkage (nm)
Particles	40	0.1 ± 0.1
Particles	120	0.1 ± 0.1
Particles	240	0.1 ± 0.1
Disc	40	1.3 ± 0.2
Disc	120	3.1 ± 0.1
Disc	240	> 3.2

Figure 3.2. FTIR spectra of particles initiator/TMCS-grafted (bottom red line) and PS-grafted particles ($t=240$ min, top blue line). The spectra were obtained by subtracting the spectrum of bare γ -alumina from each measurement. Peak attributions are given in Table 3.3. A reference polystyrene spectra is given in Figure S3.4.

Table 3.3. Peak positions and attributions of the associated FTIR spectra of Figure 3.2. A reference polystyrene spectra is given in Figure S3.4.

Initiator & TMCS	PS	Wavenumber (cm ⁻¹)	Peak attribution
x	x	2945	C-H stretch
	x	2924	aromatic C-H stretch
x	x	1733	ester C=O stretch
	x	1490-1630	C=C aromatic stretch
x	x	1455	-C-H bending
x	x	1278, 1163, 1080	C-O ester stretch
		696	C-H bend of mono-substituted aromatic
	x		

3.3.2.1 Brush height tunability

Figure 3.3 shows the pore size and permeability of γ -alumina discs as a function of reaction time, reacted with the same molar ratios given in Table 3.2 of the previous section. The figure shows a decreasing pore size with time: at $t=240$ min the pores become impermeable to toluene and the pore diameters are below 2.0 nm. The water contact angle was $72^\circ \pm 6$ for all polymerized samples (ungrafted γ -alumina support: 0°).

To allow more insight into the near-zero permeability of toluene when the pore diameter is still measured to be around 2 nm, the findings from previous studies [19,33] of grafted-to γ -alumina membranes are now briefly outlined. Polydimethylsiloxane (PDMS) chains of length (n) of either $n = 10$ or $n = 39$ repeating units were grafted into the same type of γ -alumina membrane discs as used in this work. When in contact with an organic solvent, this PDMS brush swelled, constricting the pores and thereby decreasing the membrane permeability. The degree of swelling, and hence pore constriction, was dependent on the solvent, following the same trend as free-standing PDMS. These insights are applied here to the polystyrene grafted-from brushes and their characterization by permoporometry and solvent permeability.

Figure 3.3. Pore diameters and toluene permeabilities of γ -alumina discs as a function of reaction time. Molar ratios are the same as those in Table 3.2, i.e., monomer:initiator: catalyst:ligand:reducing agent ratios of 400:1:0.8:1.4:8. Pore diameter was determined by permoporometry. An empty bar indicates a pore diameter below the 2.0 nm

Figure 3.4. Pore diameters and toluene permeabilities of γ -alumina discs as a function of reaction time. Monomer concentration is doubled with respect to the conditions related to Table 3.2 (see also Figure 3.3), i.e., monomer:initiator:catalyst:ligand:reducing agent is 800:1:0.8:1.4:8. Pore diameter was determined by permoporometry. Each reaction time was tested at least 3 times. Permeability error bars indicate the low and high values of each sample set while pore size error bars are standard deviations.

Figure 3.5. (a) AFM image of a bare γ -alumina surface, RMS = 40.7 nm, and (b) the height profile of the cross section denoted by the red line. (c) and (d) The same surface of a sample reacted for $t = 120$ min under the conditions in Table 3.2. Pore shrinkage of particles and discs for increasing reaction times. The reactant molar ratios of monomer:initiator:catalyst:ligand:reducing agent are 400:1:0.80:1.4:8. Each set of conditions was repeated 3 times. Pore size shrinkage was calculated by subtracting the post-polymerization pore size from the pore size measured post-TMCS grafting. Particle pores were characterized by N_2 ad/des while disc pores were characterized by permoporometry., with (c) having the same scale as (a) for comparison, while (d) under an adjusted scale, RMS = 3.1 nm.

Polymer brush height scaling laws have been long established and verified [34-35] to describe the swelling behavior of polymer brushes in organic solvents. In a good solvent, the height, H , of the brush scales with both the length (n) and the grafting density, σ , ($H \propto n \cdot \sigma$), while for theta and poor solvents the dependency on grafting density drops ($H \propto n \cdot \sigma^{0.5}$ and $H \propto n \cdot \sigma^{0.33}$, respectively). Cyclohexane at 15°C is a ‘poor’ solvent for polystyrene [36], below the cyclohexane-polystyrene theta temperature of 34.5°C, while toluene is a ‘good’ solvent [37], which leads to greater swelling of a polystyrene brush in toluene than in cyclohexane at 15°C (the condensable gas of the permoporometer). Therefore, it

was not surprising that for the same sample set in Figure 3.1 at $t = 120$ min cyclohexane did not swell the pore shut, yet toluene could not permeate. Hence, the pore diameters measured by permoporometry should only be taken as the pore diameters when the brush is swollen in cyclohexane. The pore size, and therefore permeability, is solvent-dependent.

The AFM images of Figure 3.5 show the external surface of a γ -alumina disc before and after polymerization ($t = 120$ min). When comparing Figure 3.5a and 5c, it can be seen that enough polystyrene was grown on the external surface of the samples to reduce the RMS roughness by an order of magnitude, from 40.7 nm to 3.1 nm, thereby concealing topographical features of the bare γ -alumina. This requires that the brush grown on the external surface of the γ -alumina consists of, on average, much longer chains than the brush in the pore, a variation beyond polydispersities typical of ARGET-ATRP [8].

From this AFM analysis as well as the particle polymerization data, we conclude that the internal and external rates of polymerization differ, that the brush height growth is slower inside the pores. To further investigate the link between external brush growth and brush growth from the inner walls of the pores, ARGET-ATRP experiments were done with a higher monomer:initiator ratio, those results are presented next.

Figure 3.4, just as in Figure 3.3, shows the pore size and toluene permeability as a function of reaction time, however, the monomer concentration of all reaction mixtures was doubled. The toluene permeability drops to 0.0 at $t = 360$ min, yet the pore diameter was not found to shrink below 4.1 nm. The brush growth on the external surface of the membrane, rather than inside the pores, is thought to be responsible for the reduction in permeability. This is hypothetically attributed to the acceleration in reaction kinetics when the monomer concentration is increased relative to the other reactants [8]. Greater monomer consumption at the external surface would retard the passage of monomer to the inside of the pores, thus slowing or altogether halting polymerization inside the pore. This same mechanism is proposed in the previous section to explain the difference in internal (pore) brush growth between particles and discs.

3.3.2.2 *Internal and external brush growth*

Pore brush growth has now been found to be dependent on the substrate geometry – particle vs. disc – as well as the monomer concentration, and therefore the reaction speed. Polystyrene brush growth is overall slower inside the pores, sometimes so slow as to be negligible. The brush growth at the external surface is hypothesized to be the culprit, by means of both monomer uptake and steric hindrance. The external brush is then seen as a surface layer obstructing the penetration of monomer into the pores. In an attempt to decouple the contribution of external brush growth from internal brush growth, samples were plasma etched post initiator-grafting but pre TMCS-grafting as to reduce the initiator functionality only at the external disc surface. From these etched discs, brushes were grown from three different polymerization mixtures with monomer:initiator concentrations varying from 200:1, 400:1 to 800:1, and compared to their unetched counterparts.

During plasma etching, the static water contact angle of the initiator-grafted membranes fell from $31^\circ \pm 13^\circ$ to $15^\circ \pm 8^\circ$. Since the surface is porous and hydrophilic, water drops were quickly absorbed into the sample, contributing to the error. In order to verify expectations of plasma etching only the external surface and not the inside of the pores, the same plasma treatment was performed on the hydrophobic PDMS-grafted membranes described in the previous section and in references [19,33,38]. Upon grafting the static water contact angle was raised from $\sim 0^\circ$ to $110^\circ \pm 7^\circ$. Upon plasma etching, the static water contact angle decreased to $30^\circ \pm 5^\circ$, while the membrane retained water impermeability. This indicates a substantial oxidation or eradication of the external PDMS graft while leaving the pore-confined PDMS largely unaffected. It is therefore expected that the same plasma treatment, applied post-initiator grafting, diminished the initiator functionality at the membrane surface.

The exception is for etched samples 200:1, where the brush almost closes the pore, and therefore the permeability drops to $0.1 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$. Curiously, the peak permeability of etched samples reached at the 800:1 samples, which have a smaller pore size than the 400:1 samples. Based on the pore size alone, the 400:1 would be expected to have a greater permeability. To explain this apparent contradiction, the same monomer-barrier mechanism of the previous sections is

proposed. The faster reaction kinetics due to the high 800:1 monomer:initiator ratio likely cause a monomer diffusion barrier at the mouth of the pore. This would mean a taller brush at the mouth of the pore, whereas the brush deeper inside the pore, i.e. further away from the monomer choke point at the pore mouth, would suffer from reduced monomer availability and therefore polymerize less. Consequently, the effective thickness of the membrane separation layer (layer with the smallest pores) shrinks, therefore increasing permeability.[39] Permporometry, by its nature, measures only the smallest pore diameter within the length of a pore, explaining the diameter of 2.0 nm for the 800:1 sample.

Upon comparison of the unetched and etched samples, a trend is seen: etched samples generally have greater permeability for the same pore size, which is attributed to the diminished external brush growth. The next section shows the application potential of these grafted discs, both etched and unetched, as membranes for organic solvent nanofiltration.

3.3.3 Application potential as a membrane

The two metrics of a membrane that define its performance are its throughput, expressed as permeability, and its selectivity, expressed as the retention of a specified solute in a given solvent. To visually sort the performance of the membranes fabricated, Figure 3.6 shows the retention of 9,10-diphenylanthracene in toluene as a function of permeability for all grafted sample sets. The open circle and open triangle of Figure 3.6 are the most competitive membranes, corresponding to etched discs reacted for 120 min with 200:1 (circle) and 800:1 (triangle) monomer:initiator concentrations. Although the unetched 800:1 barely outperformed its unetched the etched 200:1 significantly improves its selectivity over its unetched counterparts. It is possible that the (partial) removal of surface initiator by plasma etching was more effective in reducing surface layer growth at the lower reaction speeds of the 200:1 monomer:initiator concentrations.

Table 3.4. Average toluene permeabilities and pore diameters of regular (unetched) and plasma-etched discs for a polystyrene brush-growth time of $t = 120$ min.

Monomer:initiator ratio		200:1	400:1	800:1
Unetched	Pore ϕ (nm)	2.1	2.1	4.2
	Permeability (L.m ⁻² h ⁻¹ bar ⁻¹)	1.4	0.0	0.0
Etched	Pore ϕ (nm)	< 2.0	3.5	2.0
	Permeability (L.m ⁻² h ⁻¹ bar ⁻¹)	0.1	2.0	3.2

Table 3.5. Membranes listed below are those with equal toluene permeabilities, or equal pore sizes. Retentions of DPA are compared. Retentions are ± 0.01 at 30 bar of applied pressure. M:I = monomer:initiator ratio, E = etched sample set.

Sample set	ϕ (nm)	Membrane Performance		Experimental Conditions	
		Permeability (L.m ⁻² h ⁻¹ bar ⁻¹)	Time (min)	M:I	Retention (%)
ungrafted	5.2	7.9	0	-	10
A	2.8	0.6	90	400:1	86
B	4.4	0.6	240	800:1	55
C	2.1	1.4	120	200:1	39
D	2.1	0.0	120	400:1	-
E	2.0	3.2	120	800:1	78

Figure 3.6. Retention of 9,10-diphenylanthracene ($MW = 330 \text{ g.mol}^{-1}$) in toluene as a function of toluene permeability for the grafted γ -alumina membranes with non-zero permeabilities. Solid markers correspond to unetched samples while open markers correspond to plasma-etched samples. The ratios given are monomer:initiator molar ratios. For unetched samples with monomer:initiator ratio 800:1 (▲) and 400:1 (■) multiple data points are given. These data series indicate that with increasing reaction time permeability decreases. Retentions are measured at 30 bar of applied pressure and deviate within ± 0.01 .

The bottom half of Table 3.5 compares etched and unetched samples C, D and E, which have the same pore size, yet the retentions and permeabilities are not the same. The same explanation used for A and B is used here to explain the different permeabilities of C, D and E. The monomer:initiator ratio is doubled from C to D, resulting in a longer external brush for D and consequently reducing its permeability to 0.0. This is in contrast to E, where plasma etching initiator from the surface reduced the external brush size, thereby increasing permeability. Comparing these results it can be seen that increasing the pore shrinkage increases the selectivity while decreasing the membrane permeability, which is consistent with conventional porous membranes. The presence of an external brush is thought to lower the membrane permeability, due to increased resistance, and to sometimes indirectly decrease the retention of the membrane when inhibiting the brush growth inside the pore during polymerization.

Table 3.6 compares the most selective membrane of this work (etched, toluene permeability $2.0 \text{ L.m}^{-2}\text{h}^{-1}\text{bar}^{-1}$, 90% retention. i.e. the open circle data point in Figure 3.6) with other grafted ceramic membranes for OSN as well as commercially available polymeric membranes claimed stable in toluene. The performance of the selected membrane in this work is competitive: only one membrane listed (P84) is more selective, yet not as permeable. The nature of the grafting-from pore-tuning method developed here implies that a MWCO similar to P84 is achievable by adapting the reaction conditions to obtain longer grafted chains. A slight drop in permeability is predicted to accompany this hypothetical, more selective membranes.

There are 2 other types of hybrid, ceramic-based membranes for OSN, PDMS grafted-to on $\gamma\text{-Al}_2\text{O}_3$ membranes and alkanes or aromatic groups Grignard-grafted onto TiO_2 . The PDMS graft is done via the attachment of a whole PDMS chain onto a silane linking agent, meaning the polymer has to be pre-synthesized and cannot be tuned in-situ. Various lengths and crosslinkers of PDMS are commercially available, and consequently different membranes have been fabricated, 2 of which are shown in Table 3.6.

Grignard-grafted membranes are also stable, the source is the strong, direct titania-carbon bond, stable up to at least 150°C . The Grignard reaction however limits the graft choices to alkanes and phenyl groups [22]. The surface coverage yield from this method is partial, and the resulting amphiphilic surface is well-suited to the nanofiltration of polar solvents. In contrast PDMS-grafted membranes are best-suited to the nanofiltration of non-polar solvent, in which selectivity is higher. Our work has shown that by means of SI-ATRP the grafted polymer length, and hence membrane performance, can be tuned. In combination with the existing wealth of inorganic-organic grafting and SI-ATRP literature, excellent starting points are now available for the polymerization of other vinyl groups from any suitable oxide surface. This implies the ability to fabricate bespoke OSN membranes from a wider combination of materials – organic moiety and inorganic substrate both - than previously thought possible, for a range of applications.

Table 3.6. Permeability and retention comparison with other grafted ceramic membranes and commercial polymeric membranes.
TOABr = Tetraoctylammonium bromide

Membrane type	Ref.	Toluene Permeability (L.m ⁻² h ⁻¹ bar ⁻¹)	Solute, MW (g.mol ⁻¹)	Retention (%)
This work	-	2.0	DPA, 330	90
PDMS grafted-to on 5.0 nm γ -Al ₂ O ₃	[19]	2.5	Sudan Black B, 457	83
PDMS grafted-to & crosslinked on 5.0 nm γ -Al ₂ O ₃	[40]	1.3	Sudan Black B, 457	95
C1 grignard-grafted on 0.9 nm TiO ₂	[22]	0.4	Polystyrene, 580	36
C8 grignard-grafted on 1.0 nm TiO ₂	[22]	1.5	Polystyrene, 580	55
Phenyl grignard-grafted on 1.0 nm TiO ₂	[41]	1.0	Polystyrene, 580	91
Evonik P84 (commercial)	[42]	0.86	Pristane, 268	95
Starmem122 (commercial)	[43]	0.92	TOABr, 547	99

3.4 CONCLUSION

For the first time, tunable brushes were grown from the mesopores (pore size 5.2 nm) of γ -alumina membranes. By means of ARGET-ATRP reactions, polystyrene brushes were grown on both particles and discs of γ -alumina. The different geometries caused different results: opposite to the discs, there was almost no brush growth inside the pores of the γ -alumina particles at the same reaction conditions. Inside the pores of the discs and for a given monomer to initiator ratio (400:1), the amount of polystyrene grown from the pore surface was shown to be directly related to the reaction time. The pore diameter shrank from 5.2 nm to 2.0 nm and below. At a pore size below 2 nm the membranes become impermeable to toluene. The pore brush showed solvent-dependent swelling, meaning the pore size is solvent-dependent. This explained the disparity between a 2.0 nm pore as measured by cyclohexane-permporometry and closed (impermeable) pore when testing toluene permeability.

AFM showed that the surface roughness lowered from 40.7 to 3.1 nm upon polymerization, a reduction indicating taller brushes on the external surface than inside the 5 nm pores. From this we deduce a higher polymerization rate on the external surface than on the internal pore surface of the γ -alumina disc. We proposed that during the reaction, the external brush is thought to hinder the diffusion of monomer to growing chains in the pore, both by steric hindrance and by chemically consuming the monomer. This is supported by obtaining generally smaller pores (i.e. taller brushes) when submitting samples to plasma etching on the external surface area before polymerization, which diminished the initiator concentration on the surface but not inside the pores.

The application potential of these grafted γ -alumina discs as membrane for organic solvent nanofiltration is demonstrated. A toluene permeability of 2.0 L.m⁻²h⁻¹bar⁻¹ accompanied by a 90% retention of 9,10-diphenylanthracene (MW = 330 g.mol⁻¹) is obtained and compared to other OSN membranes exhibiting a competitive membrane suited for OSN.

3.5 SUPPORTING INFORMATION

Figure S3.1. N₂ adsorption/desorption measurements of pure and grafted γ -alumina flakes. For each sample a type IV hysteresis loop is obtained, indicating the presence of mesopores. Initiator = (3-trimethoxysilyl)propyl 2-bromo-2-methylpropionate, TMCS = Chlorotrimethylsilane

Figure S3.2. Pore size distribution as obtained by N₂ adsorption/desorption analysis of pure and grafted γ -alumina flakes. For each sample the pore size distribution is shown. Initiator = (3-trimethoxysilyl)propyl 2-bromo-2-methylpropionate, TMCS = Chlorotrimethylsilane

Figure S3.3. Permporometer analyses of the same γ -alumina disc before and after initiator and TCMS reactions. The average pore diameters for each sample are 6.0, 5.4 and 5.2 nm for the “Ungrafted,” “Initiator,” “Initiator & TCMS,” respectively. Initiator = (3-trimethoxysilyl)propyl 2-bromo-2-methylpropionate, TCMS = Chlorotrimethylsilane.

Figure S3.4. Reference IR spectra of polystyrene from the National Institute of Standards and Technology (NIST).

<https://webbook.nist.gov/cgi/cbook.cgi?ID=C100425&Mask=80#IR-Spec>
(Accessed 19-10-2018)

3.6 REFERENCES

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CHAPTER FOUR

Growing to shrink: Poly(ionic liquid)
brushes confined to mesopores for
CO₂/light gas separation

ABSTRACT

Atmospheric CO₂ is a major contributor to climate change and its global concentration continues to rise. The development of efficient and sturdy CO₂ capture and storage technologies is therefore increasingly crucial. Promising advances in CO₂ post combustion capture have involved ionic liquids and poly(ionic liquid)s (ILs/PILs) for the separation of CO₂ at its emission points.

Here we demonstrate the tunable growth of poly(imidazolium styrene) brushes containing exclusively Tf₂N anions ([StyMim][Tf₂N]) from the 5 nm-diameter mesopore surface of γ -alumina support to obtain an optimum CO₂ permeance and CO₂/light gas selectivity. The pore is closed by repeated ARGET-ATRP from an organosilane surface-bound initiator. The resulting hybrid membrane is characterized by means of AFM, surface XPS, cross-sectional EDS, and FTIR, confirming the presence of PIL brush confined to the support pore as well as surface aggregates of the tin-based reducing agent. A CO₂ permeance of 0.5×10^{-7} mol.m⁻²s⁻¹Pa⁻¹ and CO₂/N₂ & CO₂/CH₄ permselectivities of 14 and 13 were achieved, providing an encouraging start to the development of this new membrane class.

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4.1 INTRODUCTION

Atmospheric CO₂ concentrations continue to increase, contributing to climate change, acidifying oceans, and otherwise damaging our global ecosystem [1]. Halting this increase calls for the efficient capture and storage of CO₂ at its emission sources. A widely implemented solution in industrial and power-generation plants is post combustion capture (PCC) using amine-based absorbents [2]. Though modular by nature and easily retrofitted onto existing installations, this is an expensive and energy-intensive solution. Furthermore, the amine solvents used in PCC are volatile and easily degrade, corroding and polluting their environment. Therefore, new approaches for PCC have focused on increased efficiency and environmentally-friendliness [3-4].

Promising new avenues for CO₂ PCC have an inextricable link between material and process. New adsorption processes try to employ custom solid porous materials such as zeolites or metal-organic frameworks (MOFs), but are however limited by their production cost and stability [5-6]. Membrane technology has emerged as an attractive option for CO₂ separation due to lower energy consumption and operating costs. However, obtaining highly permeable selective membranes, with resistance to the conditions commonly found in flue gas remain challenging [7]. Ideally, a CO₂-selective membrane could withstand high temperatures (50-100°C), applied pressures of at least 2 bar, and the presence of traces NO_x and H₂O while maintaining a stable selectivity over its lifetime. [8-9]

An attractive class of materials for PCC and CO₂ separation are poly(ionic liquids) (PILs) and their building blocks, ionic liquids (ILs). This class of materials encompasses a range of organic salts, composed of cations and anions whose chemistries have been diversified and tuned for a wide range of applications [10]. Here, the specific appeal of ILs and PILs, besides their general low toxicity, high thermal stability and non-volatility, is their high CO₂ solubility compared to other gases such as CH₄ or N₂. As a result, many IL/PIL-based CO₂-selective membranes have been fabricated and optimized for PCC [11-15].

The supported ionic liquid membranes (SILM) were the first type of IL-based membranes developed and consisted of an ionic liquid impregnated in a polymer or inorganic porous support. Though selective, their general industrial potential

is limited, as at an applied pressure above the Laplace pressure characteristic to the IL and support, the physisorbed ionic liquid is not contained within the support and desorbs from the support. As pioneered by Vangeli et al. [16] and Pizzoccaro et al. [17], a sturdier attachment, consisting of covalent bonds between a porous ceramic substrate and the ionic liquid, yields a grafted ionic liquid membrane (GILM). The covalent attachment to the ceramic support imparts the mechanical robustness of the ceramic support to the ionic liquid-based membrane. However, the permeances obtained by Pizzoccaro et al. (CO_2 : $1.32 \times 10^{-9} \text{ mol.m}^{-2}\text{s}^{-2}\text{Pa}^{-1}$) were not as attractive as a SILM membrane. To surpass the performances of SILM-based CO_2 membranes, PIL membranes have been explored. PILs were shown to have higher CO_2 capture efficiencies than their IL monomeric counterparts [18], yet this has not yet been translated into higher membrane permeances and selectivities. Crosslinked PIL films embedded with IL have been developed by Cowan et al. [19] and Tome et al. [15,20], yet these membranes are sensitive to higher transmembrane pressures where leaching of the embedded IL can occur [19]. Each class of IL or PIL membrane has its shortcomings, namely the selectivity-permeance tradeoff found for all membrane types, and the performance-mechanical stability tradeoff particular to IL/PIL membranes [10].

The approach here is to confine PIL brushes inside mesopores, controlling the confinement of the PIL and pore free volume to increase the CO_2 /light gas selectivity while maximizing CO_2 permeability. The combined mechanical robustness of a ceramic support with the CO_2 solubility of PIL brushes composed of the 1-(4-vinylbenzyl)-3-methylimidazolium cation [StyMIM] and the bis(trifluoromethylsulfonyl)imide anion [Tf_2N] was therefore proposed. Recent work by Merlet et al. [21] demonstrated the controlled growth of a polystyrene brushes within 5 nm diameter mesopores. ILs confined inside ceramic pores have shown enhanced CO_2 permeability together with high CO_2/N_2 separation capacity [22]. We propose here that a PIL grown to a chosen degree and covalently linked by an alkoxy silane grafting agent to the pore surface of a well-defined support yields a CO_2 selective membrane. The porous support is composed of a 3 μm -thick γ -alumina layer of 5 nm-diameter mesopores on a 2 mm-thick α -alumina macroporous support. Living, controlled polymerization of the IL monomer [StyMIM][Tf_2N] was initiated from an initiator covalently bound to the pore

surface. The polymerization technique used is ARGET-ATRP (activators regenerated by electron transfer, atom transfer radical polymerization), which enabled repeated and controlled polymerizations, closing the mesopore and reducing its free volume to an optimum for CO₂ membrane separation.

4.2 EXPERIMENTAL

4.2.1 Materials

The solvents diethyl ether (anhydrous, 99%), acetonitrile (98%), anisole (anhydrous, 99.7%), ethanol (dried), ethyl acetate (anhydrous, 99.8%) and chloroform-d (99.8%) along with the reagents 1-methylimidazole (99%), 4-vinylbenzyl chloride (90%), copper(II) chloride (99.999%), 4,4'-dinonyl-2,2'-dipyridyl (dNbpy, 97%) chlorotrimethylsilane (TMCS, $\geq 99\%$), and tin(II) 2-ethylhexanoate (Sn(EH)₂, $\geq 92.5\%$) were purchased from Merck, Netherlands. Lithium bis(trifluoromethane) sulfonimide (99%) was purchased from Solvionic. Toluene (anhydrous) was purchased from VWR Chemicals, and n-Hexane (anhydrous) was purchased from Alfa Aesar. (3-Trimethoxysilyl)propyl 2-bromo-2-methylpropionate (BiB-Si, 99%) was purchased from Gelest. All water used is MilliQ water. All chemicals were used as received.

Alpha-alumina supports (α -Al₂O₃, diameter of 3.9 mm, 2 mm thick, 80 nm diameter pores) were purchased from Pervatech B.V., Netherlands. Two layers of γ -Al₂O₃ boehmite sol were dip-coated onto α -Al₂O₃ discs and calcined at 650 °C yielding a 3 μ m thick selective layer with an average pore diameter of 5 nm. Fabrication and characterization details of this layer can be found elsewhere [23-24].

4.2.2 Ionic liquid monomer syntheses

4.2.2.1 1-[(4-ethenylphenyl)methyl]-3-methylimidazolium chloride [StyMIM][Cl]

10.26 g (125 mmol) of 1-methylimidazole was added to 30 mL of CH₃CN. Then 4-chloromethylstyrene (19.5 mL, 139 mmol) was added to the mixture and heated at 50 °C while stirring overnight under N₂ atmosphere. At the end of the reaction, the mixture was poured into 250 mL of diethyl ether, and the mixture was stirred

until complete precipitation of the PIL monomer. The product was placed in a freezer for 1.5 h after which the diethyl ether phase was decanted, removed and the product was then dissolved in 125 mL of MilliQ water. The aqueous phase was washed 3 times with 100 mL of ethyl acetate. The final aqueous solution of [StyMIM][Cl] was directly used to prepare the [StyMIM][Tf₂N] PIL monomer after characterization by liquid NMR. The ¹H and ¹³C liquid NMR results are in accordance with published values.

¹H NMR (CDCl₃): δ(ppm) 10.35 (1H, s), 7.42 (1H, s), 7.38 (1H, s), 7.34 (2H, br), 7.28 (2H, m), 6.64 (1H, m), 5.73 (1H, d), 5.52 (1H, d), 5.24 (2H, s), 4.00 (3H, s).

¹³C NMR (CDCl₃): δ(ppm) 138.6, 135.8, 132.7, 128.3, 123.5, 121.6, 115.3, 52.9, 36.7

4.2.2.2 1-[(4-Ethenylphenyl)methyl]-3-methyl-imidazolium bis(trifluoromethane) sulfonimides [StyMIM][Tf₂N]

Lithium bis(trifluoromethane)sulfonimide (LiTf₂N) (36.17 g, 125.0 mmol) was added to the [StyMIM][Cl] aqueous phase, and an oily phase was immediately observed. The mixture was stirred for 1h at room temperature. The oily phase was extracted into ethyl acetate (250 mL) and washed with MilliQ water (3 × 100 mL). The organic phase was dried with anhydrous MgSO₄, and the resulting organic phase reduced by rotary evaporation. The remaining solvent was removed under vacuum while stirring at 40°C overnight. The ¹H, ¹³C and ¹⁹F liquid NMR results are in accordance with published values.

¹H NMR (CDCl₃): δ(ppm) 8.63 (1H, s), 7.36 (1H, s), 7.33 (1H, s), 7.22 (2H, m), 7.12 (2H, m), 6.64 (1H, m), 5.71 (1H, d), 5.24 (1H, d), 5.18 (2H, s), 3.81 (3H, s).

¹³C NMR (CDCl₃): δ(ppm) 139.0, 135.9, 135.7, 129.2, 127.2, 124.5, 118.1, 114.9, 53.2, 36.3

¹⁹F NMR (CDCl₃): δ(ppm) -79.2

4.2.3 Support pre-functionalization

4.2.3.1 *Grafting of the initiator on the γ -Al₂O₃ supports (S-ini)*

Prior to the vapor phase deposition of the initiator, (3-Trimethoxysilyl)propyl 2-bromo-2-methylpropionate (BiB-Si), γ -Al₂O₃ supports were submerged in a 2:1 v/v water-ethanol solution for at least 8h and then dried under vacuum at 50 °C overnight. Afterwards a 15 mM solution of initiator in 100 mL of toluene was stirred and heated to 105 °C for 4 h in a N₂ atmosphere, 3 cm above which the sample was suspended. Initiator-grafted porous supports (S-ini) were rinsed and washed with 50 mL of toluene and stored at 50°C under vacuum.

4.2.3.2 *Plasma etching (S-ini-P)*

S-ini samples were plasma etched for 3 min at 100 W with 20 standard cubic centimeter per minute (sccm) flow of O₂. The supports were then soaked in toluene for 1h and dried at 50 °C under vacuum for 2 h.

4.2.3.3 *TMCS grafting (S-ini-P-T)*

S-ini-P samples were immersed in a 1% v/v solution of chlorotrimethylsilane (TMCS) in n-hexane. The solution was stirred and heated at 75 °C for 20 h, after which the supports were removed, soaked in n-hexane for 30 min and dried at 50 °C in under vacuum for 2 h.

4.2.4 Surface-initiated ionic liquid polymerization

S-ini-P-T samples were submerged in a solution of anisole under a dry N₂ atmosphere. [StyMIM][Tf₂N] (0.057 mL, 0.31 mmol) was added to the solution, then CuBr₂ (1.37 mg, 6.1 μ mol) and 4,4'-dinonyl-2,2'-dipyridyl (dNbpy) (6.28 mg, 15.4 μ mol) were added. The reaction vessel was sealed and heated to 90 °C, at which time tin(II) 2-ethylhexanoate (Sn(EH)₂) (18.69 mg, 46.1 μ mol) was injected through a septum. After 24 h, the flask was opened and exposed to air, thereby stopping the reaction. The samples underwent rinsing and soaking for 30 minutes in ethanol and subsequent drying at 50 °C under vacuum for 2 h. Before each successive polymerization step (the repetition of this procedure) the membrane was dried at 50°C under vacuum for 2 hours. Samples are defined by the number of repeated polymerizations, e.g. P3 means three successive, repeated polymerizations.

4.2.5 Characterization methods

^1H , ^{13}C , ^{19}F NMR spectra were recorded using a Bruker 400 MHz NMR spectrometer at respective frequencies of 400, 100, and 376 MHz in chloroform-*d*. Chemical shifts were expressed in parts per million (ppm, δ) downfield from tetramethylsilane.

FTIR analyses of the pure reactants and PIL monomers was conducted on a Bruker Tensor 27 spectrophotometer. Spectra were recorded in the 4000–400 cm^{-1} range using 16 scans at a resolution of 4 cm^{-1} . **ATR-FTIR** analysis of the membranes was conducted using a PerkinElmer Spectrum 100 spectrophotometer. Spectra were recorded in the 4000–600 cm^{-1} range using 32 scans at a resolution of 4 cm^{-1} in ATR mode ($\gamma\text{-Al}_2\text{O}_3$ was used as a background).

Water contact angle measurements were performed by the sessile drop method, 2.0 μL Milli-Q water drops were dispensed, and the contact angle was calculated 1.0 s after the drop contacted the surface.

Permporometry was conducted using an in-house built permporometer. Permporometry relates the diameter of mesopores to cyclohexane partial pressures via the Kelvin equation. The permeance of oxygen through a selective layer is measured as a function of the vapor pressure of a condensable gas (cyclohexane). At 15 $^\circ\text{C}$, a stepwise decrease of the cyclohexane partial pressure causes cyclohexane layers to desorb from the pores, opening the pores in order of decreasing diameter. This technique can accurately measure pore radii between 1.0 nm - the thickness of an absorbed cyclohexane layer around the pore circumference - and 50 nm.

AFM imaging of the surface of the membrane was carried out on a Multimode 8 AFM with a NanoScope V controller and a JV vertical engage scanner using tapping mode. Aluminum-coated cantilevers were purchased from Olympus. The resonance frequency of the cantilevers was ~ 70 kHz, with the force constant of 2 N/m. The friction was measured by sliding the cantilever through the samples in the lateral direction (with the scan angle: 90°) over a sliding size 10 μm using a velocity of 10 $\mu\text{m/s}$.

Energy dispersive X-ray (EDS) was conducted in high-vacuum at 10 kV using a JEOL 6010 LA scanning electron microscopy (SEM).

X-ray Photoelectron Spectroscopy (XPS) was used to determine the chemical composition of the selective layer of the membrane. The measurements were carried out on a Quantera Scanning XPS Microprobe from Physical Electronics with a monochromatic Al K α X-ray source (1486.6 eV photons). All binding energies were referenced to the C_{1s} hydrocarbon peak at 284.8 eV. An argon sputtering gun of variable intensity was used to etch into the sample to obtain atomic depth profiles. The sputter depth of the beam was calculated based on the sputter rate of SiO₂ (~ 100 nm/min) and it was converted to the sputter rate of Al₂O₃ (~ 40 nm/min).

4.2.6 Membrane permeance and selectivity

The permeance of a given gas i is expressed as (P_i) according to

$$P_i = \frac{J_i}{\Delta P} \quad (1)$$

where J is the steady-state gas flux per unit area of membrane under a trans-membrane pressure drop (ΔP) and normalized to the unit thickness of the membrane (l). Permeance will be given in $\times 10^{-7}$ mol.m⁻²s⁻¹Pa⁻¹. The ideal gas selectivity or permselectivity of two gases, $\alpha_{i/j}$, is defined as

$$\alpha_{i/j} = \frac{P_i}{P_j} \quad (2)$$

Gas permeance measurements were carried out on a Convergence OSMO single gas permeation set-up, which works in a dead-end mode during which the selective layer of the membrane is exposed to the gas feed. The effective membrane surface area was defined by the Viton-51414 O-rings of diameter 15.5 mm. During the measurements, the feed pressure and the permeate pressure were kept at 3 and 1 bar, respectively, yielding a 2 bar transmembrane pressure at room temperature. The gases were measured in the given order (gas kinetic diameter): H₂ (0.289 nm), N₂ (0.364 nm), CH₄ (0.389 nm), and CO₂ (0.33 nm). The gas

Figure 4.1. Equipment flowchart of the single gas permeation set-up. Adapted from [25].

permeation data were recorded for each gas at steady state. The permselectivity was calculated based on equation (2). A schematic representation of the experimental set-up is shown in Figure 4.1.

4.3 RESULTS & DISCUSSION

The aim of confining a controlled polymerization of PIL monomer to the 5 nm-diameter γ -alumina mesopores was to obtain a CO₂-selective and permeable membrane. The intrinsic CO₂ solubility of the PIL monomer combined with the added benefit of confinement should lead to a high CO₂/light gas selectivity for the resulting PIL/ γ -alumina-closed pores compared to an unmodified support. High CO₂/light gas selectivity is theoretically achieved when enough disconnected free volume elements remain to let the PIL brushes orient themselves beneficially and favor CO₂ transport through the membrane [22]. Concerning the nanoconfinement, such a specific arrangement in well-defined micro and mesopores has been suggested to explain the impressive experimental results of several IL-based CO₂-selective membranes [17,22,26].

Pores of γ -alumina are closed by the controlled, surface-initiated polymerization of PIL monomers. The cation 1-(4-vinylbenzyl)-3-methylimidazolium [StyMIM]

and anion bis(trifluoromethanesulfonimide) [Tf₂N] were chosen. The cation has two moieties imparting two functions, one is the well-studied styrene monomer [Sty] and the other is the well-known IL-based cation of 1-methylimidazolium [MIM]. The anion [Tf₂N] was selected for its ability to increase the PIL CO₂ solubility [27-28] and previously demonstrated ability to not interfere with the ARGET-ATRP of cation [StyMIM] [29].

SI-ARGET-ATRP (surface-initiated, activators-regenerated-by-electron-transfer, atom-transfer-radical-polymerization) was chosen as a slow, controllable polymerization technique previously adapted for the controlled shrinkage of mesopores [21,30-31]. ARGET-ATRP has also once been adapted to the bulk polymerization of PIL [29]. These techniques are combined here to yield a CO₂-selective membrane.

4.3.1 PIL monomer synthesis

Before polymerization of PIL from the support surface, the poly(ionic liquid) monomer [StyMIM][Tf₂N] was first synthesized. The poly(ionic liquid) monomer was prepared over a two-step synthesis adopted from existing procedures [32-33]. First, quaternization of 1-methylimidazole with a styrene group yielded a PIL monomer with a chloride anion, [styMIM][Cl]. The [Cl] anion was then exchanged with bis(trifluoromethane) sulfonimide [Tf₂N]. The reaction schemes are shown below in Scheme 4.1 and Scheme 4.2. After each stage, NMR (¹H, ¹³C, ¹⁹F NMR) and FTIR spectra proved comparable with literature, the FTIR is shown in Figure S4.1.

4.3.2 Pre-functionalization of the support

A three-step pre-functionalization of the γ -alumina porous support was necessary to direct PIL growth inside the support pores as shown in Scheme 4.3 [21]. First, a monolayer of alkoxy silane initiator (BiB-Si) was grafted onto the pore and external surface of the γ -alumina support as confirmed by FTIR (Figure S4.1). A brief plasma etching followed, which is necessary to de-functionalize (most of) the initiator on the external surface, thus preventing the growth of PIL brushes normal to the support. The third and final step is the chlorotrimethylsilane (TMCS) grafting, which prevents catalyst complexation and deactivation with the exposed surface hydroxyl groups of the γ -alumina support [31]. Contact angle

measurements match prior results of this established pre-functionalization procedure (Figure S4.2) [21].

4.3.3 PIL-grafted membranes: influence of reaction parameters

This section deals with the optimal polymerization procedure to obtain closed but not overly dense pores. SI-ARGET-ATRP is a type of controlled and living polymerization, enabling repeatable and slow polymerizations growing from

Scheme 4.1. Quaternization reaction of 1-methylimidazole and 4-vinylbenzyl chloride to obtain [StyMIM][Cl].

Scheme 4.2. Ion exchange reaction of [StyMIM][Cl] and [Li][Tf₂N] to obtain [StyMIM][Tf₂N] PIL monomer.

Scheme 4.3. Three-step pre-functionalization of the 5 nm pores of γ -alumina. Sample S is first grafted with a methoxysilane containing an initiator function (Bib-Si). S-ini has initiator plasma etched from its external surface, then sample S-ini-P is grafted with chlorotrimethylsiloxane (TMCS).

surface-bound initiators. A controlled (slow) polymerization is necessary for the chain growth in confined mesopores [31,34]. First-order kinetics are intrinsic to living polymerizations, thus the monomer to initiator ratio (M:I) directly influences the reaction rate and chain length [35]. Besides the M:I, a host of other factors influence the reaction rate of an ARGET-ATRP reaction [36]. These factors include the temperature, monomer, solvent, as well as the catalyst and ligand combination, among others. The polymerization conditions used in this work were composed from, and are therefore compared to, the conditions used in the bulk ARGET-ATRP of [StyMIM][Tf₂N] [37] and in the SI-ARGET-ATRP of styrene in confined mesopores [21]. The reaction parameters are listed in Table 4.1 and discussed in the following paragraphs. The reaction is represented in Scheme 4.4.

Previous work within our group [21] reported significant and tunable shrinkage of the same 5 nm-diameter γ -alumina mesopores using a M:I between 200 and 400. This same work conjectured a diffusion-based limitation of monomer accessible to the growing chains inside the mesopores to explain the disproportionate external surface growth occurring at high M:Is. In other words, it was suggested that too high a bulk concentration monomer caused a rapid polymerization from the external surface, further hindering the diffusion of monomer from bulk to pore, thus preventing pore shrinkage.

Table 4.1. Selected reaction parameters for the ARGET-ATRP of confined [StyMIM][Tf₂N] (this work), bulk [StyMIM][Tf₂N] [29], and confined styrene [21]. The initiator and reducing agents used were identical. TPMA = tris(2-pyridylmethyl)amine, dNbpy = 4,4'-dinonyl-2,2'-dipyridyl

Parameter	Confined [StyMIM][Tf ₂ N] (this work)	Bulk [StyMIM][Tf ₂ N] [29]	Confined Styrene [21]
M:I	20	100-400	200-400
Temperature (°C)	90	90	75
Solvent	Anisole	Pivalonitrile	Anisole
Catalyst/ligand	CuBr ₂ /dNbpy	CuBr ₂ /TPMA	CuBr ₂ /dNbpy
Time (h)	17	4-28	1-8

Scheme 4.4. SI-ARGET-ATRP of sample Si-ini-P-T. The polyionic chains grown from the surface of sample P1 are living, meaning polymerization can be re-initiated from the (Br) at end of the chain.

Surface-initiated polymerization of the [StyMIM][Tf₂N] monomer yielded pore shrinkage only when using a M:I as low as 20. Higher M:I ratios (100, 200, or 400) did not shrink the pore (as measured by permoporometry), yet did show PIL growth as indicated by FTIR and a hydrophobic contact angle of 96°, suggesting too high a reaction rate on the external surface as in [21]. The required use of a low M:I of 20 is believed to be due to the increased monomer size, relative to the styrene monomer used by Merlet et al. [21], and hence increasingly hindered monomer diffusion [38-39] of the IL monomer from the bulk to the pore. The reactivity of the styrene moiety of [StyMIM] is believed to be largely the same compared to unmodified styrene [21], as there is no strong electron-withdrawing or donating group on the styrene, i.e. the imidazolium moiety has a negligible impact on the monomer activity [40].

The next reaction parameter compared in Table 4.1 is the reaction temperature. Since 75°C was found ineffective for the polymerization of [StyMIM][Tf₂N], the value of 90°C was mirrored from the bulk polymerization of [StyMIM][Tf₂N] [29]. The solvents anisole and pivalonitrile are of similar polarizability and are hence believed to have a similar impact on the reaction rate [41]. The ligand dNbpy was used over ligand TPMA because TPMA is known to increase the rate

of polymerization by 2-3 orders of magnitude compared to dNbpy [42]. Therefore, since the target degree of polymerization was low (15~40), dNbpy was selected. Additionally, higher reaction rates are associated with decreased chain-end functionality (CEF) [42]. CEF refers to the fraction of chains retaining the ability to polymerize further, i.e. the fraction of living chains. So a higher reaction rate will increase the chance of chain-chain termination, which is when two growing chains meet and become the next monomer of each other, and hence terminate and become unreactive or 'dead' [43]. When growing from a concave surface and into the same decreasing pore volume, chains face an increased likelihood of growing while adjacent to each other, increasing the likelihood of chain-chain termination [31,34].

The aim of the polymerization was to close the pore of γ -alumina for optimum CO₂ permeance and selectivity. Assuming a dense brush leading to chains extending normal to the pore surface, a single monomer reduces the pore only 0.25 nm [21,31]. With an M:I of 20 and an expected conversion of around 50 % [29,44], the average degree of polymerization was expected to be around 10, which would not be enough for to close the 5 nm mesopore ($10 \times 0.25 \text{ nm} = 4 \text{ nm}$) [45]. Indeed, a total of two successive polymerizations with a M:I of 20 were needed to shrink the pore past the permoporometry detection limit (2 nm diameter), as shown in Table 4.2. The number of polymerizations undergone by a given sample is indicated as the sample name, e.g. P2 = 2 polymerization steps, etc.

Table 4.2. Pore shrinkage for successive [StyMIM][Tf₂N] ARGET-ATRP compared to the neat support, as measured by permoporometry.

Sample	Mean pore diameter (nm)	Pore shrinkage (nm)
pristine porous support	5.6	-
P1	4.5	1.1
P2	< 2	> 3.6
P3...5	< 2	> 3.6

4.3.4 PIL-grafted membranes: characterization

Sample P3 exhibited the best CO₂ permeance and selectivity, as detailed further in the discussion. Therefore, detailed characterizations were carried out on P3 and are presented in this section. The FTIR spectra between 4000 and 2000 cm⁻¹ (I.) and 1800-800 cm⁻¹ (II.) of the PIL monomer [StyMIM][Tf₂N] (a), and the grafted PIL membrane after 1, 3 or 5 polymerization reaction (b, c and d, respectively) are shown in Figure 4.2. The FTIR spectrum of the PIL monomer is characterized by peaks corresponding to the stretching vibrations of the =C-H and -CH₂ groups at 3150, 3102 and 2948 and 2907 cm⁻¹ [46]. In the lower wavenumbers the dominating bands in the spectrum are attributed to the Tf₂N⁻ anion and corresponds to the asymmetric and symmetric -SO₂ stretching vibrations found at 1325–1344, 1184 and 1137 cm⁻¹, and -SNS stretching vibration found at 1055 cm⁻¹ [47]. The bands at 1628 and 1511 cm⁻¹ are attributed to the stretching vibration of the C=C alkenyl and C=C aromatic groups, respectively. Similarly to the neat PIL monomer, the grafted PIL membrane presents the bands related to the =C-H and CH₂ groups as well as the bands attributed to the Tf₂N⁻ anion. It must be noted that the intensity of the bands associated to the anion decrease with

each successive polymerization. Also important is the shift in the stretching bands related to the C=C aromatic group (from 1511 to 1557-1609 cm⁻¹) and the quasi absence of the C=C alkenyl band ($\approx$ 1628 cm⁻¹) which confirm the polymerization of the monomer. In addition, similarly to the S-ini sample, a broad band which is attributed to the Al-O-Si bond and centered at 1100 cm⁻¹ is visible in all the spectra [47]. The Al-O-Si band broadens with each polymerization, suggesting an increase of the PIL brush length and a decrease of resolution due to the confinement and densification of the brushes.

Figure 4.3 shows AFM phase surface images of pristine γ -Al₂O₃ (A) compared to the membrane P3 (B). Phase images were used because of their higher resolution than topographic images (those are shown in Figure S4.4). The pristine γ -Al₂O₃ surface shows a smooth, homogeneous surface with a roughness in the order of a few nanometers, as also seen by Merlet et al. [21], and Amirilargani et al. [48]. However, the extreme change in surface morphology from Figure 4.3A to B was not observed in those works when grafting and surface polymerization

Figure 4.2. FTIR spectra between 4000 and 2000 cm^{-1} (I.) and 1800-800 cm^{-1} (II.) of the PIL monomer [StyMIM][Tf₂N] (a), and the grafted PIL membrane after 1, 3 or 5 polymerization reaction (b, c and d). The symbol * and • in the spectrum of [StyMIM][Tf₂N] attribute, respectively, the bands to the stretching vibrations of the Tf₂N⁻ anion and the C=O ester function of the solvent used for the washing procedure (ethyl acetate).

Figure 4.3. AFM phase images of 5x5 μm area of unmodified γ -alumina (A) and P3 (B).

reactions were conducted. After the SI-ARGET-ATRP of styrene brushes, Merlet et al. measured a decrease in roughness when performing grafting from, while the roughness of the surfaces studied by Amirilargani et al. almost did not change after polymer grafting. Neither the grafted surfaces of [21] nor of [48] resemble the rougher (by an order of magnitude) surface of P3. Figure 4.3B and a surface X-ray photoelectron spectroscopy scan (XPS, Figure S4.5) strongly suggest that the particle morphology seen on the surface of P3 are aggregates of tin. Tin(II) ethyl hexanoate is the reducing agent dosed periodically during the polymerizations and likely the source of tin surface aggregates. It was not possible to deconvolute the XPS signal to obtain the species of tin, though it is likely present as tin oxide and perhaps also as Sn(IV) – the oxidized species of the reducing agent. The presence of significant amounts of tin on the surface could be an indication that polymerization did not proceed as efficiently as possible, and also could have interfered with the reducing agent of subsequent polymerizations, lowering their efficiencies.

Tin is also present throughout the γ -alumina layer, as presented in the EDS line-scan analysis of P3, shown in Figure 4.4. Also present and expected in the EDS analysis are the chemical species related to the grafted initiator (Si) and the PIL brushes (N, S and F). The atomic ratio of F to S (both found in the anion) should be 3:1, if these atoms solely come from the Tf_2N^- anion, although it is calculated to be around 2.2:1 (Figure 4.5A). This difference is attributed to measurement error due to the relatively low quantities of each. The nitrogen, present in both cation and anion, and sulfur, present in the anion, stay at constant ratio of 1.5:1, indicating near equal amounts of polymerized cation [StyMIM] to anion [Tf_2N].

The presence of significant amounts of chlorine, however, was unexpected. It is likely due to the entrapment of the LiCl by-product present in the PIL monomer (LiCl salt is produced during the anion exchange reaction, Scheme 4.2). Chloride will interfere with polymerization as it can complex with the copper catalyst or substitute on the growing chain end in place of bromide, lowering both catalyst and chain activity [29,31], hence slowing down polymerization.

The results of the line-scan of Figure 4.4 correspond to two further EDS area-scan analyses done on the cross-section of P3 (Figure S4.6). The combined cross-sectional analyses do not indicate the thickness of the selective layer. Though there clearly is poly(ionic liquid) within the pore, we are unable to estimate for a given depth whether the pore is closed and therefore strongly CO₂-selective rather than open (microporous). Therefore membrane gas permeability could not be estimated, as opposed to permance.

Figure 4.4. EDS line-scan (A) of the γ -alumina support into the α -alumina as pictured in (B). Twenty points along the linear line of (B) are scanned to build a depth profile, shown in (A). The x-axis corresponds to the distance from the top surface. Carbon, aluminum and oxygen are not shown.

4.3.5 Gas transport behavior of P1-P5

As previously discussed, the PIL monomer [StyMIM][Tf₂N] was chosen for its established gas separation properties when used in composite membrane [49]. Gas permeation measurements were performed to evaluate the gas permeance and selectivity of the membranes from the polymerization P1 to P5. Table 4.3 shows the single gas permeation of CO₂, CH₄ and N₂ as well as the CO₂/CH₄ and CO₂/N₂ permselectivities (ideal selectivities) of P2 to P5. The first polymerization, P1, is omitted from Table 4.3 as neither permeances nor permselectivities changed significantly from the neat support (Table S4.1). This was expected from permoporometry results of Table 4.2, as gas transport through 2-5 nm alumina mesopores (P1) is governed by Knudsen diffusion [50-51]. Full permeance and selectivity results are available in Table S4.1. Significant permselectivities were expected from P2 onwards, again based on the permoporometry results of Table 4.2.

The second polymerization step shrank the membrane pores past the mesoporous region (Table 4.2, < 2.0 pore diameter) and a drastic CO₂ permeance drop of 98 % from P1 is seen. The CO₂ selectivities are not anymore in the Knudsen regime: 6.2 and 11, respectively, for CO₂/CH₄ and CO₂/N₂ for sample P2. After the third polymerization step (sample P3), the CO₂ permeance peaks at 0.47×10^{-7} mol. m⁻²s⁻¹Pa⁻¹ and the CO₂/N₂ selectivity at 14. This is attributed to the further growth of PIL brushes, which increases the membrane affinity to CO₂. After the fourth polymerization step, all permeances decrease while selectivities remain about constant. This is attributed to the continued densification of the brushes in the pore as well as the external-surface growth of PIL brushes, each contributing to gas transport resistance. Additionally, loss of CEF (chain-chain terminations) likely further reduces the overall mobility of the chains, also hindering gas transport [52]. It is noted that only one sample of P4 and P5 was tested as opposed to three samples for P1 to P3.

Overall membranes P3 and P4 show the best performance and establish the potential of PIL-grafted ceramic mesopores as CO₂ separation membranes. Compared to IL/PIL-based membranes presented in the literature, the membranes developed here exhibit much higher permeabilities but lower selectivities: Pure PIL membranes [53], SILM [54] and GILM [17] all reported CO₂ permeances

between 0.01×10^{-7} and 0.03×10^{-7} mol.m⁻²s⁻¹Pa⁻¹, while in our work the CO₂ permeances varied between 0.08×10^{-7} (P2) and 0.47×10^{-7} mol.m⁻²s⁻¹Pa⁻¹ (P3). However, in those publications, CO₂/N₂ and CO₂/CH₄ permselectivities between 30 and 60 were reported, while in our case, maximums of 14 (P3, P4) and 13 (P4) were found, respectively. An IL/PIL membrane made from the same [StyMIM][Tf₂N] monomer as a standalone thin film (Bara et al. [33]) exhibited a CO₂/N₂ ideal selectivity of 32 and a CO₂/CH₄ ideal selectivity of 39 with single gas permeances $< 0.02 \times 10^{-7}$ mol.m⁻²s⁻¹Pa⁻¹. As discussed in the following paragraph, we assume contamination from either or both chloride and tin to be the source of the reduced selectivities.

The CO₂/N₂ and CO₂/CH₄ permselectivities remain constant between 14 and 9 for samples P2-P5. This was interpreted as an unchanging confined PIL brushes structure and homogeneity in membranes P2 through P5, affecting the transport of gases in the same way [55]. The lower permselectivities for P2-P5, as compared to literature data, are likely due to the presence of [Cl] anion within PIL as detected by EDS (Figure 4.4). IL cations exhibit 2-3 times more CO₂ adsorbance when coupled to specialized anions such as [Tf₂N] rather than [Cl] [56]. The unexpected increase in permeance of all gases from P2 to P3 could be due to interactions of the PIL brushes with the tin oxide aggregates or chloride ions reducing all gas solubilities. Complexation of the reducing agent, PIL monomer or even the catalyst with tin aggregates is likely interfering with all polymerizations. Chloride, besides interfering with polymerization, is an inferior anion to [Tf₂N], with overall reduced gas solubility [57-58]. The P2-P3 permeance jump is however not attributed to the possibility of entrapped PIL monomer within the PIL brush. The presence of free PIL monomer should have increased both the CO₂ permeance and selectivity as was observed in IL/PIL ion gel membranes [19,59]. To confirm the absence of entrapped PIL monomer, a ¹⁹F HRMAS NMR analysis could be conducted directly on the membranes P1-P5 to qualitatively estimate the percentage of physisorbed species to polymer brushes [17].

Table 4.3. Permeance of CO₂, CH₄ and N₂ and CO₂/CH₄ and CO₂/N₂ permselectivities after each repeated polymerization step P2-P5. Three samples were tested for P2 and P3. * one sample for P4 and P5 were tested.

Sample	Permeance ($\times 10^{-7}$ mol.m ⁻² .s ⁻¹ .Pa ⁻¹)		Permselectivity	
	CO ₂	CH ₄	CO ₂ /CH ₄	CO ₂ /N ₂
P2	0.08 ± 0.008	0.013 ± 0.013	0.0072 ± 0.002	11
P3	0.47 ± 0.140	0.096 ± 0.021	0.033 ± 0.003	14
P4*	0.14	0.0083	0.0065	14
P5*	0.17	0.026	0.019	8.9

4.4 CONCLUSION

The 5 nm-diameter pores of pre-functionalized γ -alumina were closed by PILs to fabricate a CO₂-selective membrane. This was done via repeated SI-ARGET-ATRP polymerizations to optimize the pore free-volume loss and hence maximize CO₂ permeance. FTIR spectra establish the presence of the polymerization initiator as well as the PIL chains grown from the mesopores. AFM, EDS and XPS confirm the presence of PIL and indicate residual tin particles on the external membrane surface as well as residual chloride ions. An optimum CO₂ permeance of $0.47 \times 10^{-7} \text{ mol.m}^{-2}\text{s}^{-1}\text{Pa}^{-1}$ was obtained after 3 polymerization steps. A top CO₂/N₂ permselectivity of 14 and a CO₂/CH₄ permselectivity of 13 were achieved. While the CO₂ permeance increased by a factor of more than 16 compared to current published IL/PIL membranes [17,53-54], the presence of chloride ions likely suppresses the full selectivity potential of the membrane. PIL-grafted alumina membranes manifest a promising performance and establish potential for further development.

4.5 SUPPLEMENTARY INFORMATION

Figure S4.1. FTIR spectra between 4000 and 2000 cm^{-1} (I.) and 1800–800 cm^{-1} (II.) of the precursors: 1-methylimidazole (a), 4-vinylbenzyl chloride (b), LiTF_2N (c), and the PIL monomer $[\text{StyMIM}][\text{TF}_2\text{N}]$ (d). The symbol * and • in the spectrum of $[\text{StyMIM}][\text{TF}_2\text{N}]$ described respectively the bands attributed to the stretching vibrations of the TF_2N^- anion and the C=O ester function of the solvent used for the washing procedure (ethyl acetate).

Figure S4.2. FTIR results of the (I) neat initiator and (II) grafted porous support with the initiator. The spectrum of the neat initiator is dominated by the $-\text{Si-O-CH}_3$ band at 1078 cm^{-1} (I) which is replaced by the Si-O-Al band between 1012 and 1039 cm^{-1} (II). In addition, C=O stretching at 1732 cm^{-1} and $-\text{CH}_2$ stretching at 1158 cm^{-1} and 1272 cm^{-1} are also visible on each spectra.

Figure S4.3. Water contact angle measurements (sessile drop) for the pre-functionalized support compared to Merlet et al. [21]

Figure S4.4. AFM surface topographies, 5x5 μ m, of A) neat γ -Al₂O₃ and B) P3.

Figure S4.5. Elemental mapping by an XPS surface scan of P3. Significant tin is detected.

Area	Element									
	Al	O	C	Sn	S	F	Si	Cl	N	
20	20.9	48.1	21.9	1.0	0.4	1.4	0.8	1.5	3.8	
21	28.2	51.4	11.7	1.5	0.3	1.2	0.4	2.4	2.8	
22	29.7	52.1	11.3	1.2	0.4	0.9	0.3	2.1	2.0	
23	29.9	49.5	10.8	1.3	0.4	1.4	0.5	1.9	4.1	
24	39.8	60.2	-	-	-	-	-	-	-

Area	Element									
	Al	O	C	Sn	S	F	Si	Cl	N	
25	20.7	47.6	22.3	0.7	0.1	1.9	0.8	1.4	3.9	
26	24.3	48.0	17.5	1.3	0.4	1.1	0.6	2.4	3.4	
27	29.0	51.5	12.0	1.4	0.4	1.0	0.3	2.2	2.3	
28	28.6	53.4	12.4	1.0	0.2	1.2	0.4	1.3	0.8	
29	38.6	57.0	4.4	-	-	-	-	-	-

Figure S4.6. Elemental area analysis by EDS on the cross-section of P3 and associated percentages by area. The top ~3 μm are γ -alumina, while the granular material below is α -alumina.

Table S4.1. Single gas permeance and CO₂/CH₄ and CO₂/N₂ permselectivities for unmodified γ -alumina and PILs-grafted samples P1-P5.

Sample	Permeance ($\times 10^{-7}$ mol.m ⁻² s ⁻¹ Pa ⁻¹)			Permselectivity	
	CO ₂	CH ₄	N ₂	CO ₂ /CH ₄	CO ₂ /N ₂
γ -Al ₂ O ₃	5.2	8.4	5.0	0.62	1.0
P1	3.95	6.1	3.5	0.6	1.1
P2	0.08	0.013	0.0072	6.2	11
P3	0.47	0.096	0.033	4.9	14
P4	0.14	0.0083	0.0065	17	22
P5	0.17	0.026	0.019	6.5	8.9

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CHAPTER FIVE

A new and green thioether-based
crosslinked membrane for
nanofiltration applications

ABSTRACT

As nanofiltration applications increase in diversity, there is need for not only chemically and thermally stable membranes but also for environmentally-friendly fabrication methods. No current nanofiltration membrane fabrication method uses non-toxic solvents while producing a chemically and thermally resistant membrane. In this work, thio-bromo click chemistry was adapted for the fabrication of a nanofiltration membrane. The selective layer was formed on a pre-functionalized porous ceramic surface via a novel, vapor-liquid interfacial polymerization method. No harmful solvents and minimal reagents were used to fabricate stable, 40 nm-thin films covalently attached to a porous, alumina support. The properties of the membrane selective-layer and its free-standing equivalent were characterized by means of FTIR, TGA/MS, NMR and FE-SEM. Thin layer stability in acid, base, hypochlorite, non-polar solvents and up to 150°C was established. The potential as a nanofiltration membrane was evaluated in water and multiple solvents, exhibiting a PEG in water molecular weight cut-off of 700 g.mol⁻¹.

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5.1 INTRODUCTION

Separation, recovery, and disposal of organic solvents in the chemical and pharmaceutical industries account for 40–70% of both capital and operating costs [1-2]. Nowadays, membrane-based technology has been demonstrated as an effective alternative or complement to conventional purification and separation processes (e.g. distillation, extraction, chromatography, etc.) for the purification of water or organic solvents. This is due to the nature of their simple processes, high separation efficiencies, low energy consumption, and eco-friendliness [3]. The size of most aqueous and organic contaminants or active molecules such as antibiotics, amino acids, and catalysts is between 0.5 and 5 nm. Ideal membrane-based separation techniques to isolate these molecules are the processes of nanofiltration (NF) and ultrafiltration (UF).

Recent advances in the design of polymer structures have resulted in ultrathin selective layers. Highly structured networks, such as covalent organic frameworks (COFs) [4], polymers with intrinsic microporosity (PIMs) [5] and biomimetic membranes [6], have each been used to fabricate membranes with interconnected networks, enhancing solvent transport and solute retention [7]. However, these membranes use traditional, toxic membrane fabrication methods [8]. Such a well-known method is interfacial polymerization (IP) [9], a reaction at the interface of two immiscible phases between the monomers of each phase. The two phases usually consist of water and a hazardous solvent such as hexane or toluene. In addition, only a fraction of the monomers present in the starting solutions are consumed, with typical concentrations ranging from 1 to 3 wt.% [10].

The IP process has demonstrated its ability to produce ultrathin selective layers, for instance, with the fabrication of extremely permeable nanofiltration, 10 nm-thick, films [11]. There are, however, scarce attempts to reduce the environmental impact of the IP process due to its intrinsic nature. The only instance found in literature was the formation of a thin nanofiltration layer from catechin and chitosan, networked together by amide and imine groups [12]. While this one-step approach resulted in a ~99% retention of Na_2SO_4 with a water permeation flux of $45 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ at 0.6 MPa, the amide- and imine-based network unfortunately suffered from the same drawbacks as the original polyamide membranes

produced by IP. Though stable in many organic solvents, these membranes cannot withstand strong acids, bases, or hypochlorite-based cleaning treatments. This makes them unsuitable for certain applications, for instance those encountering heavy biofouling or highly acidic or basic media [13-14]. In nanofiltration, the ability of a membrane to withstand harsh feed streams, whether due to their chemical or thermal nature, is rarefied and hence valued [1].

To overcome the chemical and thermal stability shortcomings, commonly suffered by nanofiltration membranes while eliminating toxic chemicals from the IP process, recently developed organic networks are attractive candidates to make nanofiltration membranes. For example, in 2005 a click-chemistry reaction was demonstrated by Timmerman et al. between peptide thiol groups and benzylic halide groups for the multi-cyclization of peptides [15]. This bio-inspired reaction was demonstrated to be quick with a high-yield, and a metal-free reaction producing thioether bonds under mild conditions (pH~8) [16]. Additionally, in 2015 Monnereau et al. described a series of thioether and disulfide hyper-crosslinked porous polymers based on tetra-functional thiol and dihalide monomers [17]. The authors were able to use the same nucleophilic substitution between multifunctional thiols and halides as Timmerman et al. to generate organic frameworks. These frameworks were shown to be insoluble in common organic solvents as well as stable up to 500°C. This established the combined potential of high chemical and thermal stability and environmentally benign reaction conditions.

Here a novel strategy is proposed to prepare a green thioether-based crosslinked membrane inspired from the biochemical peptide work of Timmerman et al. and the polymer work of Monnereau et al.. It relies on the use of dithiol and tribromide aromatic monomers (1,3-benzenedithiol & 1,3,5-tris(bromomethyl)benzene) and a single green solvent, anisole. The membrane synthesis is realized at the vapor-liquid interface on top of a pre-functionalized porous ceramic support (Figure 5.1). The support top-surface serves not only as a starting point of the thioether network polymerization but also acts as an interface between the two immiscible vapor and liquid phases. Herein, a special effort was devoted to prepare, in a green manner, a thioether-based network by a quick and high-yield reaction using vapor of 1,3-benzenedithiol (2SH) and a basic anisole solution of 1,3,5-

tris(bromomethyl)benzene (3Br). The influence of the surface pretreatment during the membrane formation was investigated as well as the thermal and chemical stability of this new system. The system reported here serves as a proof-of-concept to develop a thioether-based membrane for a wide range of NF applications.

Synthesis of thioether-based hyper-crosslinked membrane

Figure 5.1. A schematic representation of the interfacial vapor-liquid polymerization synthesis used to prepare a green thioether-based hyper cross-linked NF membrane.

5.2 EXPERIMENTAL

5.2.1 Materials

Solvents used were ethanol (technical grade >95%), toluene ($\geq 99.5\%$, Merck, NL), anisole (>99%, Merck, NL), deuterium oxide (99.9 % deuterium, Merck, NL), anhydrous toluene- d_8 (100%, Merck, NL) deuterium (99.96%, Merck, NL) and water (MilliQ). Chemicals used were glycerol (anhydrous, Merck, NL), 1,3,5-tris(bromomethyl)benzene (3Br) (>97%, Fluorochem, UK), (3-mercaptopropyl)trimethoxysilane (MPTMS) (>95%, Merck, NL), 1,3-benzenedithiol (2SH) (>99%, Merck, NL), triethylamine (>99.5%, Merck, NL), and triethanolamine (>99.5%, Merck). The chemical structures and abbreviations can be found in Figure S5.1. Ceramic α -alumina porous supports (discs of 39 mm in diameter, 2 mm thick, $\varnothing_{\text{pore}} \approx 80$ nm) were purchased from Pervatech, NL. Two layers of γ -alumina were dip-coated and calcined onto the α -alumina ceramic support to form a 3 μm thick layer with 5 nm of pores diameter (Figure S5.2). Details on fabrication and characterization can be found elsewhere [18-19].

5.2.2 Methods

5.2.2.1 Thioether-based cross-linked film preparation

A polymeric thin (free-standing) film was prepared via interfacial polymerization. In a glass vial, 17 mg (0.12 mmol, 1 eq) of 1,3-benzenedithiol (2SH) and 20 μL (0.14 mmol, 0.6 eq) of triethylamine (Et_3N) was dissolved in 10 mL of MilliQ water under stirring for 30 min. In a separate vial, 26 mg (0.073 mmol, 0.9 eq) of 1,3,5-tris(bromomethyl)benzene (3Br) was stirred until complete dissolution in 10 mL of toluene. Then, in the glass vial containing the basic aqueous solution, a small amount of neat toluene was added slowly to prevent mixing of the two phases (≈ 1 mL). Then, the 3Br organic solution was added dropwise to the same vial. The heterogeneous mixture was left over night to ensure the formation of a homogeneous layer (Figure S5.3). Afterwards, the layer was removed with a pincer and washed with 10 mL of first water, then ethanol and finally acetone under sonication for 30 min. Finally, the layer was dried at 50 $^{\circ}\text{C}$ under vacuum.

5.2.2.2 Thioether-based cross-linked membrane preparation

Prior to use the mesoporous γ -alumina supports, each substrate was soaked in an water/ethanol mixture (v/v = 2:1) for 8 h before drying under vacuum at 50°C. The synthesis of the Thioether-based cross-linked membrane is divided in three steps as described in Figure 5.1.

Porous support pre-functionalization

The grafting of (3-mercaptopropyl)trimethoxysilane (MPTMS) was conducted using the vapor phase grafting method. Prior the synthesis, γ -alumina support was filled with glycerol by rubbing a drop (≈ 1 mL) onto the substrate surface and after 10 min of rest, dabbed with a tissue. Vapor phase grafting was conducted by placing a glycerol-filled γ -alumina support (top-surface facing down) 3 cm above 50 mL of a 25 mM anisole solution of MPTMS at 105°C for 3h. Afterwards, the pre-functionalized porous support was washed in 20 mL of anisole for 1h under sonication to remove the physisorbed species and dried overnight at 50°C under vacuum.

Click-reaction

Following the MPTMS grafting step, the pre-functionalized porous support was soaked for 2 minutes in 10 mL of an anisole solution containing 0.22 mmol of 1,3,5-tris(bromomethyl)benzene (3Br) and 0.16 mmol of triethanolamine (TEOA). Then, compressed air was gently blown across the surface of the support to remove any solvent visible to the eye. Samples obtained at this stage were denoted CR-support.

Interfacial liquid-vapor polymerization

The thioether-based cross-linked membrane was then prepared by vapor phase reaction at 80°C for 4h using 20 μ L (0.17 mmol) of 1,3-benzenedithiol (2SH) under stirring with the CR-support surface (top-surface facing down). Finally, the resulting membrane was washed twice in 20 mL of ethanol for 30 min under sonication before drying treatment at 50°C under vacuum.

5.2.3 Characterization

5.2.3.1 ATR-FTIR.

A Perkin Elmer spectrum 100 was used to perform all ATR-FTIR presented spectra. Wavenumbers between 4000 and 550 cm^{-1} were scanned in reflectance mode at a resolution of 4 cm^{-1} for a minimum of 16 scans.

5.2.3.2 ^1H Liquid NMR

A Bruker AscendTM 400 MHz NMR spectrometer was used to perform ^1H liquid-state nuclear magnetic resonance (NMR) measurements in either D_2O or toluene d_8 . Chemical shifts were expressed in parts per million (ppm, δ) downfield from tetramethylsilane.

5.2.3.3 FE-SEM

Field-emission scanning electron microscopy images were obtained with a Zeiss MERLIN high-resolution scanning electron microscope using an accelerating voltage of 1.4 kV. FE-SEM samples were sputtered with 2 nm of chromium to avoid sample charging.

5.2.3.4 Thermal characterization

Thermogravimetric analysis (TGA) coupled with differential scanning calorimetry (DSC) and mass spectroscopy (MS) was performed using an STA 449 F3 Jupiter (Netzsch), equipped with a dual TG/DSC sample/reference holder. Measurements were performed under 55 mL min^{-1} N_2 and 15 mL min^{-1} O_2 flow with a heating rate of 10 $^\circ\text{C min}^{-1}$ from 40 to 800 $^\circ\text{C}$. Calibrations were performed using melting standards. Measurements were run sample-temperature controlled. The sample masses were determined using an internal balance 30 min after inserting the sample. The gases evolved during TGA analysis were transferred to a mass spectrometer (QMS 403 D Aëolos, Netzsch). TGA and MS start times were synchronized, but no correction was applied for the time offset caused by the transfer line time (estimated <30 s, systematic offset). A bar graph scan for $m/z = 1\text{--}110$ amu was recorded for all samples to determine the evolving m/z numbers.

5.2.4 Membrane screening and performance tests

Permeability and retention data were collected with a custom-made, dead-end filtration setup, consisting of a nitrogen tank pressurizing a feed vessel with a valve to regulate pressure. Permeability is the flux of a given water or solvent across a membrane per unit driving force, here expressed as liters per square meter of exposed membrane area (9.1 cm^2) per hour per bar of pressure applied across the membrane ($\text{L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$). Permeability data were collected by weighing the flow of permeate at timed intervals at three applied transmembrane pressures between 8 and 15 bar and taking the slope of a linear fit of the collected data. All slopes were found to be linear unless otherwise noted. A permeability of 0.0 indicates no detected solvent permeation during 17 h of operation at an applied pressure greater than 14 bar.

Retentions (R) of either Sudan Black B (SBB, $\text{MW} = 457 \text{ g}\cdot\text{mol}^{-1}$) or PEG oligomers ($\text{MW} = 300, 600, 1000, 1500 \text{ g}\cdot\text{mol}^{-1}$) were calculated by the equation $R = 1 - c_p/c_f$, where c_p and c_f are the permeate and feed concentrations of solute, respectively. Retentions samples were obtained between 15-25% recovery. SBB concentrations were calculated by Perkin-Elmer $\lambda 12$ UV-Vis spectrophotometer at the characteristic wavelength of 604 nm. PEG concentrations were determined by gel permeation chromatography (GPC). The GPC setup consisted of two SUPREMA 100 Å columns from PSS Polymer Standards Service GmbH (Germany), an HPLC pump from Waters (Millipore B.V., The Netherlands) and a Shodex RI-Detector from Showa Denko GmbH (Germany). The columns were calibrated using the same PEG standards.

5.2.5 Chemical resistance tests

The thioether-based cross-linked films were subjected to soaking in either 1M sodium hydroxide (NaOH), 1M nitric acid (HNO_3), or 10% hypochlorite (NaOCl) solution for 5 days, then dried at 50°C under vacuum.

5.3 RESULTS & DISCUSSION

5.3.1 Porous support pre-functionalization

In order to prepare the thioether-based cross-linked membrane, the top-surface of the porous support was pre-functionalized with a thiol propyl alkoxysilane to serve as a starting point for the membrane formation. A 2 mm thick porous α -alumina support ($\varnothing_{\text{pore}} \approx 80$ nm) coated with a 3 μm thick, well-defined mesoporous γ -alumina layer ($\varnothing_{\text{pore}} \approx 5$ nm) was used as a substrate (Figure S5.1). The hydroxylated porous surface of the γ -alumina layer can easily be functionalized by grafting and thus is a promising starting point for the formation of a covalently attached surface layer [20]. To guide the grafting reaction on the support top-surface and not inside the mesopores [21], the substrate was filled with a pore-filling agent (glycerol), and then functionalized with (3-mercaptopropyl)trimethoxysilane (MPTMS) via vapor phase deposition. In this manner, the alkoxysilane linker reacts with the hydroxylated surface by hydrolysis and condensation leading to a homogeneous monolayer coverage without polycondensation of the organosilane [22]. Before proceeding with the click-reaction, the support was characterized by FTIR spectroscopy (Figure S5.4b). This analysis is commonly used to demonstrate the grafting of molecules as well as the presence of physisorbed species. The FTIR spectra of the pre-functionalized support present a band at 2550 cm^{-1} attributed to the -SH group. The bands in the $2850\text{--}2950\text{ cm}^{-1}$ region correspond to the symmetric and antisymmetric C-H stretching vibration of the aliphatic -CH₂ function. Moreover, the bands corresponding to the stretching vibrations of the alkoxysilane coupling function ($1090\text{--}1020\text{ cm}^{-1}$) are present but with a low intensity, suggesting only residual -Si-OCH₃ function and a high grafting efficiency, as also demonstrated by the presence of the broad band centered at 1050 cm^{-1} , ascribed to the formation of Si-O-Al bonds during grafting [23].

5.3.2 Formation of the thioether-based hyper cross-linked film and membrane

The thioether-based hyper-crosslinked film presented here is an insoluble network prepared by the conventional interfacial polymerization (IP) of 1,3-benzenedithiol (2SH) monomer and 1,3,5-tris(bromomethyl)benzene (3Br) at the interface of two immiscible liquid phases. This film is prepared as a proof-of-

concept as well as to determine the physico-chemical properties of the final membrane. Compared to a synthesis in a single solvent, the IP method allows the formation of a well-defined organic network [24].

Scheme 5.1 shows the molecular structure of the compounds used as well as a schematic representation of the reactions occurring in the aqueous phase and at the interface. The use of a base in the 2SH phase was needed to deprotonate the thiol groups of the monomer leading to the thiolate dianions (Figure S5.7 to S5.10). The pH of the aqueous phase was ~ 7.4 and aromatic thiols such as 2SH are known to possess low pK_a values, usually in the range from 6.0 to 7.0 [25]. The degree of monomer conversion to film depends on the degree of thiol conversion into thiolate, as these latter species possess a higher nucleophilicity. However, it must be noted that the formation of a disulfide bond between 2 monomers via an oxidation reaction in the aqueous phase cannot be precluded, as illustrated in Scheme 5.1 [17]. At the interface of the aqueous phase (2SH) and the organic phase (3Br), the thiolate reacted with the bromide group by nucleophilic substitution leading to the formation of a C-S-C bond (Scheme 5.1). This was observed about 15 minutes after the two phases were brought into contact; a thin homogeneous polymeric film became visible to the eye (Figure S5.3). The system yielded thicker layers the longer it was left to react.

Thin thioether-based cross-linked membranes were prepared by a click-chemistry and interfacial vapor-liquid polymerization on top the pre-functionalized porous ceramic support. The pre-functionalized support was first dipped in an anisole solution of 3Br and triethanolamine. As illustrated in Scheme 5.1, the presence of the base in the anisole solution allowed for the deprotonation of the thiol group, present on the porous surface, leading to the thio-bromo click reaction of the thiolate with the tribromide monomer (3Br) to form an initial surface monolayer of thioether-connected di-functional bromides.

To avoid the formation of disulfide connections during membrane fabrication, the base was contained within the 3Br organic phase. This action was taken to prevent framework depolymerization, since disulfide connections (in the presence of base) were detected by liquid ^1H NMR (Figure S5.8), and these are easily cleaved by mild chemical reagents [26] or even mechanical stresses [27]. In addition, triethanolamine was used as an environmentally friendlier alternative base

instead of trimethylamine. Following the click-reaction step, the support was exposed to dithiol monomer (2SH) vapor, leading to the progressive formation of the thioether-based hyper-crosslinked membrane.

① Water phase – Deprotonation reaction

② Water phase – Disulfide bond formation

③ Water/toluene interphase – Nucleophilic Substitution ($\text{S}_{\text{N}}2$)

Scheme 5.1. Schematic representation of the reactions in the water phase (1, 2) and at the interface of the aqueous and toluene phases (3). The aromatic dithiol is first converted to an aromatic thiolate and can then proceed by nucleophilic substitution to form a thioether bond at the interphase.

To identify the reaction parameters influencing the membrane fabrication, a quick screening was conducted across different reaction conditions, reaction times, and monomer concentrations. Both water or ethanol permeation and SBB retention in ethanol were used to provide an indication of the membrane performance and quality (e.g. selectivity and presence of defects) and compared to those of a neat porous ceramic support. The role of the pore-filling solvent during the grafting of MPTMS was found to be crucial to avoid network formation inside the pores of the ceramic support. The membrane prepared without pore-filling solvent did not present any water flux under a pressure of 16 bar, even after 17 h of testing. Membrane impermeability suggested the formation of a hyper-crosslinked network inside the mesoporous γ -alumina support. Exposure of the 2SH to an elevated temperature was found essential for the liquid-vapor IP procedure (Figure 5.1, step 3), as neither room temperature nor vacuum yielded significant performance improvements (SBB retention < 5%). Finally, both the 3Br concentration, 2SH amount and the vapor-liquid IP reaction time were varied, as shown in Table 5.1. When the monomers (3Br/2SH) molar ratio increase from 0.64 to 1.29, the formation of a layer is suggested due to the increase of SBB retention (up to 50%). However, when the ratio is increased up to 1.94, a hyper cross-linked network is formed as evidenced by the absence of solvent flux at elevated pressure. The formation of a similar network was obtained by increasing the vapor-liquid IP reaction time from 4 to 24h, the same. The results indicate that membrane formation was found to be quite sensitive to the monomers molar ratio and reaction time used which were thus fixed respectively at 1.29 and 4 h to prepare the membrane denoted TE-memb.

Whereas traditional IP fabrication methods rely on a two-phase aqueous-organic interface, the series of steps shown here uses only one green solvent and minimizes reactants usage. Glycerol, the pore-filling agent is “*generally recognized as safe*” by the FDA as well as a biodiesel production waste product [28], while the solvent anisole is classified as a green solvent [29]. Furthermore, the monomer amounts used in this work (Table 5.1) are minuscule when compared to concentrations used in typical IP procedures, typically from 1 to 3 wt.% [10].

Table 5.1. Vapor-liquid IP reaction parameters influencing the formation of a thioether-based hyper-crosslinked membrane: 3Br/2SH molar ratio, reaction duration and Sudan Black B retention results. The symbol * denotes the absence of permeate after 17h of water or ethanol flux measurements at a pressure of 16 bar.

3Br/2SH molar ratio	Vapor-liquid IP reaction time	SBB retention (%)	Summary
0.64	4h	< 5	No separative layer
1.29	4h	≈ 50	Layer suggested
1.94	4h	No permeate*	Impermeable layer
2.44	4h	< 5	No separative layer
1.29	24h	No permeate*	Impermeable layer

5.3.3 Physico-chemical properties of the membrane and film

A spectroscopic comparison of the thioether-based membrane (TE-memb) and film (TE-film) was conducted to ensure fair comparison. Figure 5.2 shows the FTIR spectra of the reactants (2SH, 3Br), TE-film and TE-memb between 4000 and 2000 cm^{-1} (A) and 1700-550 cm^{-1} (B). All the spectra show the bands attributed to the C=C stretching vibrations of the aromatic rings around 1570 and 1600 cm^{-1} , as well as the stretching aromatic C-H band between 3020 and 3060 cm^{-1} . Compared to the reactants, the spectra of the film and membrane present few shifts in the overall bands attributed to the vibrations of the aromatic group. As an example, the band at 1208 cm^{-1} in the spectrum of 3Br is attributed to the C-H bending vibrations of the benzylic carbons is shifted in the spectra of the TE network to 1231 cm^{-1} as the bromine is replaced by sulfur [30]. In the 4000-2000 cm^{-1} spectra, the stretching vibration of the free thiol group is particularly visible at 2561 cm^{-1} in the spectrum of 2SH. This band is not visible in the spectra of the thioether cross-linked film and membrane. This is explained by the combination of low thiol signal intensities and the minimal presence of such groups in the final network due to the formation of a thioether bond (C-S-C). In addition, bending vibration attributed to the C-Br group at 580 cm^{-1} is absent in the spectra of the film and the membrane, which suggests few to none unreacted functional groups in the final product. As the spectroscopic characteristics of the film and membrane are identical, we can assume that the physico-chemical properties of the film and membrane are identical.

Figure 5.2. FTIR spectra of the IP reactants (3Br, 2SH) and the thioether cross-linked film (TE-film) and membrane (TE-memb) between 4000 and 2000 cm^{-1} (A.) and 1700-550 cm^{-1} (B.).

To confirm the presence of a distinct layer, TE-memb was further characterized by FE-SEM analysis. Figure 5.3A shows a cross-section with the α -alumina and γ -alumina layers consistent with reported characterization [18-19]. No organic layer was observed on the top surface until higher magnification, as shown in Figure 5.3B, where a thin organic layer is evident. The minimum and maximum thickness of the layer was estimated to be between 30 and 60 nm. The organic layer was in direct contact with the γ -alumina support, at times seeming to sink or embed itself into the support.

Figure 5.3. FE-SEM images of the thin IP layer on gamma-alumina supported by α -alumina.

Figure 5.4. A. Mass loss up to 800°C and energy input as a function of temperature for the thioether-based film under air, obtained with a heating rate of 10°C/min, B. Mass spectrometer signal upon heating for the thioether-based film. The release of CO₂ (solid line, $m/z = 44$) and SO₂ (dashed line, $m/z = 64$) is shown as function of temperature.

5.3.4 Membrane performance

The membranes achieved permeabilities of 0.5 and 0.6 L.m⁻²h⁻¹bar⁻¹ in ethanol and water (Table S5.1). The retention of the thioether membrane was tested in two solutions, i.e. PEG oligomers (200, 600, 1000 and 1500 g.mol⁻¹) in water and Sudan Black B (SBB, MW = 457 g.mol⁻¹) in ethanol. PEG-water results are shown in Figure 5.5. The molecular weight cut-off, where retention reaches 90%, is approximated to be 700 g.mol⁻¹, well within nanofiltration range (≤ 1000 g.mol⁻¹). This is much lower than the MWCO of unmodified gamma-alumina, around 2500 g.mol⁻¹ [32]. It can be seen in Figure 5.5 that the maximum retention reached for a PEG molecular weight of 1500 g.mol⁻¹ is 98%, suggesting the presence of a minor number of small defects in the film or a small calibration error of the GPC. The ethanol retention of SBB averaged $50 \pm 2\%$, roughly matching the retention from the PEG-water retention curve. Post SBB/ethanol filtration the membranes remained white: no visible fouling had occurred, and contrary to the defective trial membranes produced earlier during the study, no dye dots or stains were observed (Figure S5.3). The observed retentions are therefore not due to dye adsorption but result from a molecular sieving mechanism. Furthermore, the lack of any dye adsorption on the layer during filtration indicates fouling-resistance.

Figure 5.5. Retention of PEG oligomers in water through the thioether-based crosslinked membrane. The molecular weight cut-off (90% retention, dashed line) was estimated to be ~ 700 g.mol⁻¹. The lines only serve as guides to the eye.

5.3.5 Stability of thioether-based crosslinked membrane

As Figure 5.6 shows, the permeability of the membrane in water remains stable after exposure to ethanol, toluene, hexane, or heat (150°C in air for 48 hours). The membrane is impermeable to hexane and toluene. Unfortunately, the gamma-alumina support is not resistant to highly acidic or basic environments and therefore the membrane could not be tested in those media. However, the chemical resilience of the thioether-based cross-linked film could be investigated further by means of FTIR. After 5 days of exposure to 1 M acid, base, 10% sodium hypochlorite, and 48 hours at 150°C (bleach, common disinfectant and membrane cleaner), FTIR spectra were taken of each film and compared against the original. The results are shown in Figure 5.7. The spectra are quite similar, though weak bands tend to appear at 2500, 1500 and 1150 cm^{-1} in the case of the TE-film exposed to the thermal treatment. These bands indicate a possible slight oxidation of the film. However, it must be noted that none of the samples changed visually over the course of exposure.

Figure 5.6. The permeability of various solvents through the same membrane over time and exposure to heat over 2 days. The water permeability remained constant ($0.60 \pm 0.05 \text{ L.m}^{-2}\text{h}^{-1}\text{bar}^{-1}$) throughout. The sample was dried overnight at 50°C under vacuum between each solvent.

Figure 5.7. ATR-FTIR spectra of original film and after exposure to HNO_3 (pH~0), NaOH (pH~14), hypochlorite and after a thermal treatment at 150°C . The * denotes the new bands present after the thermal treatment at 150°C .

5.4 CONCLUSION

Demonstrated is a new and green IP methodology and membrane chemistry. Selective thioether NF membranes are prepared by a vapor-liquid IP process. The aromatic thioether network formed via a click reaction between di-functional thiol monomers and tri-functional bromide monomers. Both the toxicity and quantity of waste is reduced with only one solvent, classified as green [29], and 100 times less monomer use than conventional IP. A thin selective layer (40-60 nm) covalently attached to a pre-functionalized porous support exhibits high chemical stability in organic solvents (ethanol, hexane, toluene), acid and basic media (pH ~0, ~14), and in sodium hypochlorite solution (10% aqueous). Onset of thermal degradation did not start before 300 °C.

Permeabilities of 0.6 and 0.5 L.m⁻²h⁻¹bar⁻¹ in water and ethanol, respectively, were achieved, with a PEG MWCO of 700 g.mol⁻¹ in water. The membrane was found to be impermeable yet stable to two apolar solvents, toluene and hexane, and permeable to ethanol and water. Based on this proof-of-concept, the development of thioether-based films can be expanded to a variety of membranes. The interfacial liquid-vapor polymerization method presented is a highly effective and easy method which shows significant advantages over conventional IP method.

5.5 SUPPORTING INFORMATION

Figure S5.1. Abbreviation and chemical structure of: 1,3,5-tris(bromomethyl)-benzene (3Br), 1,3-benzenedithiol (2SH), trimethylamine (TEA), triethanolamine (TEOA), mercaptopropyl trimethoxysilane (MPTMS), Sudan black B (SBB) and polyethylene glycol (PEG) where $n = 6, 13, 22$ or 33 , approximately $300, 600, 1000$ and 1500 g.mol^{-1} .

Figure S5.2. FE-SEM image of the unmodified γ -alumina mesoporous support.

Figure S5.3. Schematic representation of the thioether-based cross-linked film formation by conventional interfacial polymerization.

Figure S5.4. FTIR spectra of the precursor MPTMS (a) and of the support pre-functionalized with MPTMS (b).

Table S5.1. Permeability and retention data for ethanol/SBB tests.

Sample	Permeability ($\text{L.m}^{-2}\text{h}^{-1}\text{bar}^{-1}$)	Retention (%)
1	0.52	48.00
2	0.48	50.00
3	0.50	51.00
Average	0.50	49.67
St. deviation	0.02	0.01

Figure S5.5. Pictures of the pristine support and two selected TE-membranes after the SBB retention test.

Figure S5.6. The crucible used during the TGA/DSC analysis was re-run without sample, showing an early mass gain, as observed in the main text.

Over the ^1H NMR of Figures S5.9 and S5.10

Preparation procedure: In the tube containing 2SH and the deuterium solvent (either anhydrous toluene- d_8 (Figure S5.9) or D_2O (Figure S5.10), a drop of Et_3N was added. The ^1H NMR was recorded after 15 min of the Et_3N addition. The newly appeared peaks can be attributed to the formation of disulfide bridges in the presence of base and are more visible when the D_2O solvent is used. Due to the random configuration of these molecules renders the elucidation of the spectrum impossible with merely ^1H NMR.

Figure S5.7. ^1H liquid NMR spectrum of 2SH in water. Asterisk (*) denotes solvent peak (D_2O).

Figure S5.8. ¹H NMR spectrum of 2SH in toluene. Asterisks (*) denote solvent peaks (C₇D₈).

Figure S5.9. ¹H liquid NMR Spectrum of the reaction product of 2SH and TEA. Asterisks (*) denote solvent peaks (C₇D₈).

Figure S5.10. ¹H-NMR Spectrum of 2SH and TEA. Asterisks (*) denote solvent peaks (D₂O).

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CHAPTER SIX

Interpreting rejection in OSN
across grafted ceramic membranes
through the Spiegler-Kedem Model

ABSTRACT

PDMS-grafted alumina membranes have already demonstrated high organic solvent permeabilities; described and modeled in this paper are their retention capabilities. In contrast to pure PDMS polymeric membranes, higher retentions were found in nonpolar solvents than in polar solvents. This is attributed to a solvent-induced pore-constriction behavior: confined swelling of PDMS, grafted into the membrane pores, was found to increase retention. To test this hypothesis, pore sizes were obtained by integrating the Ferry, Verniory and steric hindrance pore (SHP) equations into the Spiegler Kedem Katchalsky (SKK) model in order to predict the retention of dyes. Ultimately, a diffusion pore size was introduced into the SKK model to reflect the ability of the solute to diffuse through the swollen PDMS graft. A better understanding of the transport mechanisms that impact performance was achieved by incorporating the unique pore structure of these ceramic-based hybrid membranes into the SKK model.

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6.1 INTRODUCTION

Solvent resistant nanofiltration (SRNF), also known as organic solvent nanofiltration (OSN), is a useful tool for separations in organic media, such as the removal of impurities from used solvents, recycling of solvents or the recovery of products from reaction mixtures in the chemical, petrochemical, and pharmaceutical industries [1, 2]. For these kinds of applications, continuous exposure towards organic solvents is expected, which has generated a need for robust membranes. To meet this need, research has primarily focused on developing suitable polymeric membranes [3, 4] rather than ceramic-based membranes. Ceramic membranes are more expensive but do not suffer from compaction effects or aging [5]. Consequently, the study of transport through SRNF membranes has also mainly dealt with polymeric membranes and the complex membrane-solvent-solute interactions that are unique to SRNF [6, 7]. To enable process modelling and to facilitate the design of SRNF processes using ceramic-based membranes, the major parameters and transport mechanisms that influence the transport of solvents and solutes through the membrane must be quantified. This study investigates the retention behavior and transport mechanisms of a promising hybrid ceramic-based membrane in order to facilitate future applications of ceramic-based membranes for SRNF.

Membrane preparation by means of grafting polymer chains into the pores of a rigid ceramic membrane offers the opportunity to integrate pore size tuning and surface wettability/functionality into a single modification step, while avoiding the effects of swelling and aging typically experienced by purely polymeric membranes. Several instances of porous inorganic membranes modified by grafting have been employed in various applications [8-13] demonstrating the potential for grafting as a method to prepare selective and chemically stable membranes.

However, to date only a few studies have attempted to elucidate the rejection behavior of ceramic membranes for OSN. One such study dealt with a purely ceramic membrane, a $\text{ZrO}_2/\text{TiO}_2$ hydrophobic membrane produced by a modified sol-gel technique and pyrolysis in an inert atmosphere [14]. A modified pore-flow model, based on the work of Bowen and Welfoot [15], was used to describe the transport through these membranes [16], though the model was found to be valid

for only one solvent, THF. Another type of ceramic membrane, produced by Hosseinabadi et. al. [17], consists of short alkyl and phenyl oligomers which were Grignard-grafted into the pores of 1 nm TiO_2 and 3 nm ZrO_2 membranes. This reaction yielded a partial surface coverage, giving the membranes an amphiphilic character and high selectivity in various organic solvents. The transport of polyethylene glycol (PEG) and polystyrene (PS) oligomers in a variety of solvents was explained by fitting the Spiegler Kedem model to the retention data [18]. Those solvents were divided into two classes: (1) those with low polarity, experiencing low retentions varying with pressure; and (2) those with high polarity, experiencing high retentions independent of pressure. It was concluded that solutes in high polarity solvents are transported mainly by convection, implying a size-rejection mechanism. Solute transport in low polarity solvents was concluded to be significantly impacted by diffusion, meaning the applied pressure and polarity of solutes played a role in rejection.

Unlike the ceramic membranes used by Blumenschein et al. or Hosseinabadi et al., the membranes investigated here have been modified by the immobilization of short PDMS chains into the 5 nm pores of $\gamma\text{-Al}_2\text{O}_3$ membranes. Modified in this way, the alumina membrane retains its porous character; its pores are shrunk and now suited to SRNF due to their newfound hydrophobicity. When in contact with a solvent, the PDMS can only swell away from the pore wall, towards the center of the pore, effectively shrinking the pore. The benefit of confining PDMS is apparent when compared against a “free” PDMS polymeric membrane. When in contact with a highly-swelling solvent, free PDMS membranes showed reduced retention and increased permeability [19], while PDMS-grafted alumina membranes showed decreased permeability [20].

Tanardi et. al. [20] identified solvent viscosity and the effect of solvent sorption as the major parameters influencing the transport of pure solvents through PDMS-grafted 5 nm $\gamma\text{-Al}_2\text{O}_3$ membranes. Specifically, solvent permeation through these membranes was described as following a pore flow behavior, and a linear relationship between graft sorption and viscosity-corrected membrane permeability was established. This relationship between swelling and permeability is illustrated in Figure 6.1.

Figure 6.1 Normalized, viscosity-corrected permeabilities of the M2 membranes and PDMS sorption data for different solvents [20]. Specific values can be found in Table 6.1. Accompanying the graph is a conceptual diagram of a PDMS-grafted pore (top-down view) in contact with a weakly-swelling solvent (left) and a strongly-swelling solvent (right).

Gamma-alumina with a native pore size of 5nm was grafted with two PDMS graft sizes, whose lengths are defined by their number-average of repeating monomer units, $n = 10$ or $n = 39$. First, Sudan Black B was chosen as a probe solute, and its retention in seven different organic solvents as a function of pressure was collected and analyzed. The impact of feed pressure on dye rejection is discussed, followed by an estimation of the pore size for each membrane. It should be emphasized that the term “pore size” refers here to the openings created by the rapidly moving grafted polymer chains, which can be physically interpreted as the average diameter of the free volume elements represented as a cylinder. Subsequently, dyes varying in molecular weight were tested in a hydrophilic

Table 6.1: The rejection (R) of Sudan Black B in different solvents for M1 and M2 membranes at TMP of 20 bar at 50% recovery along with solvent properties and permeabilities from [20].

Solvent	μ (mPa.s)	S (cm ³ .g ⁻¹)	J M1 (L.m ⁻² h ⁻¹ bar ⁻¹)	J M2 (L.m ⁻² h ⁻¹ bar ⁻¹)	R M1 (%)	R M2 (%)
Isopropanol	2.39	0.47	0.9 ± 0.1	0.8 ± 0.1	55 ± 1	66 ± 1
Ethyl acetate	0.45	0.48	4.6 ± 0.1	3.7 ± 0.1	64 ± 1	75 ± 1
Octane	0.54	0.54	3.4 ± 0.1	2.9 ± 0.1	71 ± 1	80 ± 1
Toluene	0.59	0.53	3.1 ± 0.1	2.5 ± 0.1	72 ± 1	83 ± 1
p-xylene	0.64	0.63	2.7 ± 0.1	1.6 ± 0.1	75 ± 1	87 ± 1
Hexane	0.31	0.66	4.8 ± 0.1	2.8 ± 0.1	78 ± 1	88 ± 1
Cyclooctane	2.13	0.70	0.6 ± 0.1	0.3 ± 0.1	82 ± 1	93 ± 1

(isopropanol) and a hydrophobic (toluene) solvent to investigate the effect of solvent-membrane affinity on the observed membrane rejection. Throughout, the applicability of the Spiegler-Kedem-Katchalsky (SKK) model as a solute rejection model to accurately describe the rejection behavior of the PDMS-grafted ceramic membranes is considered. A modification to the SKK model is made to accommodate the unique characteristics of these membranes. The resulting model agrees well with the experimental data.

6.2 THE SPIEGLER-KEDEM-KATCHALSKY SOLUTE TRANSPORT MODEL

A general model to describe solute transport for both porous and nonporous membranes is given by Kedem and Katchalsky [21], in which the membrane is considered a black box, comprising a feed and a permeate as the input and output, respectively. The flux of the solute through the membrane is described as:

$$J_c = P_c \Delta x \frac{dc}{dx} + (1 - \sigma) J_v \bar{c} \quad (1)$$

where J_c is the solute flux, P_c the solute permeability, Δx the membrane thickness, $\frac{dc}{dx}$ the concentration gradient over the membrane, σ the reflection coefficient, which is a measure of the selectivity of the membrane towards a specific solute, $\bar{c}$ the logarithmic average of the solute concentration over the membrane and J_v the solvent flux. The solvent flux is defined as:

$$J_v = \Delta P * k_v \quad (2)$$

where k_v is the membrane permeability, specific to a solvent, and ΔP the difference between the feed and permeate pressure, also termed the trans-membrane pressure (TMP). In Equation (1), the first term describes the transport of solutes by a diffusion mechanism, while the second term describes the transport of solutes by a convection mechanism.

The rejection, R , of a solute is obtained experimentally by the following classic equation:

$$R = 1 - \frac{c_p}{c_f} \quad (3)$$

where c_p and c_f are the solute concentrations in permeate and feed solution, respectively.

From Equations (1), (2) and (3), Spiegler and Kedem derived the following two equations to predict rejection [22, 23]:

$$R = \frac{\sigma(1-F)}{1-\sigma F} \quad (4)$$

where F (the flow parameter) is:

$$F = \exp\left(\frac{\sigma-1}{P_c} J_v\right) \quad (5)$$

These equations are a function of the solvent flux, the reflection coefficient, and the solute permeability. Hereafter, equations (1), (4) and (5) will be referred to collectively as the SKK (Spiegler-Kedem-Katchalsky) model.

Originally termed a flow parameter, F indicates which solute transport mechanism, convection or diffusion, is dominant, if any. Since J_v scales with feed

pressure but P_c does not, the applied pressure across the membrane will affect the solute rejection. As the pressure increases, F tends towards zero, and solutes are transported by convective flow rather than by diffusion, so:

$$\frac{J_v}{P_c} \rightarrow \infty ; F \rightarrow 0 ; \sigma \rightarrow R \quad (6)$$

While operating in the convective regime, as defined in Equation (6), the rejection is solely dependent on the reflection coefficient, and is constant for a membrane-solvent pair. However, when F is not near to zero, both the effects of diffusive and convective transport must be taken into account, and rejection remains a function of several parameters as shown in Equation (7).

$$R = F(J_v, P_c, \sigma) = F(\Delta P, k_v, P_c, \sigma) \quad (7)$$

Hence, whether or not experimental rejection values vary with applied pressure will indicate whether the diffusion of solutes across the membrane is influencing membrane performance.

6.2.1.1 *The convection term*

As ΔP increases, the solvent flux increases, and F tends to 0. As described above, the reflection coefficient will then equal rejection (Equation 6), i.e. the convection mechanism becomes dominant and diffusion can be neglected at sufficiently high pressures. The reflection coefficient can then be determined from a simple rejection experiment. This coefficient is related to the ratio of the solute diameter to the pore diameter through the three established models described below.

First, Ferry [24] proposed a solute transport model, which relates the reflection coefficient to the ratio of solute diameter to pore diameter. This model shows increasing rejection as the solute size nears the pore size, and solutes of a larger diameter than the membrane pore diameter are completely rejected. The membrane is assumed to be isoporous, and no interactions between the membrane, solvent and solute are taken into account. Therefore, the pore size obtained in this way is hence no more than the effective radius of an ideal filtration. The reflection coefficient develops from 0 to 1 as the ratio of d_c/d_p increases from 0 to 1, where d_c is the average solute diameter and d_p the mean

pore diameter. This means $\sigma = 1$ when $d_c/d_p \geq 1$ and $\sigma=0$ when $d_c/d_p = 0$. Ferry's model can be expressed in the following way:

$$\sigma = \left(\frac{d_c}{d_p} \left(\frac{d_c}{d_p} - 2\right)\right)^2, \left\{\frac{d_c}{d_p} \in 0 \leq \frac{d_c}{d_p} \leq 1\right\} \quad (8)$$

Second, the Verniory model [25] incorporates wall friction forces occurring between the solute and membrane pore surface, meaning that a given solute particle size is predicted to experience a higher rejection than the Ferry model. The Verniory model can be written as:

$$\sigma = 1 - \left(\frac{1 - \frac{2}{3} \frac{d_c^2}{d_p^2} - 0.2 \frac{d_c^5}{d_p^5}}{1 - 0.76 \frac{d_c^5}{d_p^5}} \right) \left(1 - \frac{d_c}{d_p}\right)^2 \left(2 - \left(1 - \frac{d_c}{d_p}\right)^2\right), \left\{\frac{d_c}{d_p} \in 0 \leq \frac{d_c}{d_p} \leq 1\right\} \quad (9)$$

Third, the steric hindrance pore (SHP) model [26] accounts for a rejection case in which attractive forces between membrane and solute are assumed. Consequently, lower rejections would be calculated for a given solute size than the Ferry size-exclusion model. The SHP model is expressed as:

$$\sigma = 1 - \left(1 + \frac{16}{9} \frac{d_c^2}{d_p^2}\right) \left(1 - \frac{d_c}{d_p}\right)^2 \left(2 - \left(1 - \frac{d_c}{d_p}\right)^2\right), \left\{\frac{d_c}{d_p} \in 0 \leq \frac{d_c}{d_p} \leq 1\right\} \quad (10)$$

The three reflection coefficient models described above assume three different solute-membrane interactions. These models were chosen to screen for significant interactions, other than size-exclusion, that influence the reflection coefficient. Though coupling the reflection coefficient to the ratio of solute diameter to pore diameter prevents the prediction of negative rejections, we expected no negative rejections given the relatively inert nature of the pore surface (PDMS) and solutes (neutral dyes). Using these three models, three

similar pore sizes were obtained from each of the rejection data of various solute-solvent pairs, as presented in Section 6.4.

6.2.1.2 The diffusion term

Here, the solute permeability can be taken as being equal to the diffusivity of the solute through the membrane pore over the thickness of the separation layer [27]:

$$P_c = \frac{D_c}{\Delta x} \quad (11)$$

where Δx is the thickness of the separation layer and D_c the diffusion coefficient of the solute through the pore. The Stokes-Einstein relation predicts an inverse relationship between the solute diameter and its diffusion coefficient as shown in Equation 12.

$$D_c = \frac{kT}{3\pi\mu d_c} \quad (12)$$

where μ is the viscosity, and T the temperature. Van der Bruggen et al. [28] developed a simplification of equations (11) and (12) by extracting the solute diameter, d_c , from Equation (12) and combining the remainder of the diffusivity term and separation layer thickness into one diffusion parameter, ω . This parameter was then applied to the SKK model in order to describe the retention of uncharged solutes in aqueous media as a function of solute size, as shown in Equation 13.

$$P_c = \frac{\omega}{d_c} \quad (13)$$

where ω is empirically determined, specific to a solvent-membrane pair at a constant temperature, and is readily obtainable once the reflection coefficient is known.

Once the reflection coefficient (σ) is obtained, two pieces of information are then available: a pore size from either the Ferry, Verniory or SHP models and the solute permeability parameter, ω . This parameter (ω) allows for a prediction of

rejection of other solute diameters through the same solvent-membrane combination by changing the solute diameter, d_c , in equation (13). However, the filtration experiment may not be operating in the convection-only regime. In that case, it is possible to determine σ by extrapolating the rejection versus pressure curve to an area of higher applied pressure, in which the rejection becomes constant as the solvent flux increases relative to the pressure-independent solute permeability.

The discussion of this work describes the applicability of the SKK model to describe the solute rejection behavior of two types of γ -alumina membranes grafted with either a short or long PDMS chain ($n = 10$ or $n = 39$). Reflection coefficients are either obtained directly from rejection vs pressure experiments, or the data are extrapolated to a region of steady rejection. From these reflection coefficients, pore sizes are calculated using the Ferry, SHP and Verniory model. Once the reflection coefficient is known, ω is calculated, and rejection predictions are then made for various sized solutes in both toluene and isopropanol.

6.3 EXPERIMENTAL

Two types of polydimethylsiloxane (PDMS)-grafted ceramic membranes were studied. The first series of membranes (M1) consisted of macroporous α - Al_2O_3 supports, topped with a 3 μm thick mesoporous (pore size 5 nm) γ - Al_2O_3 layer which was modified with 3-aminopropyltriethoxysilane (APTES) followed by mono(2,3-epoxy)polyetherterminated polydimethylsiloxane ($n = 10$). Details of the membrane modification procedure are described elsewhere [29]. The second series of membranes (M2) consisted of macroporous α - Al_2O_3 supports, topped with an identical 0.3 μm thick mesoporous (pore size 5 nm) γ - Al_2O_3 layer which was modified by using mercaptopropyl triethoxysilane (MPTES) followed by monovinyl terminated polydimethylsiloxane ($n = 39$). Details of this membrane modification procedure can be found in [27]. All membranes were flat discs with a diameter of 20 mm and a thickness of 2.5 mm. The mean pore diameters of the unmodified, APTES-grafted, and MPTES-grafted γ - Al_2O_3 were obtained by permoporometry using cyclohexane as condensable gas [8].

The solvents, namely octane (98% purity), cyclooctane (>99%), p-xylene (>99%), and n-hexane (>99%) were purchased from Sigma-Aldrich. Toluene (100%), ethyl acetate (99.9 %), and isopropanol (100 %) were purchased from VWR. All solvents were dried using zeolite A (molecular mesh 4-8 nm) purchased from Sigma-Aldrich and pretreated for 1 hour at 200°C. Dyes were purchased from Sigma-Aldrich, and their chemical structures are shown in Figure 6.2.

Filtration experiments were performed using a stainless steel dead-end pressure cell. This cell was filled with feed solution and nitrogen was used to pressurize the cell. The feed solution was continuously stirred at a speed of 500 rpm. Filtration experiments were performed at each TMP at 50% recovery. Before each test, the membranes were soaked for 24 h in the solvent to be tested. Between each rejection test, the setup was thoroughly cleaned and the membranes were rinsed with the previous solvent and then cleaned in an ultrasonic bath of fresh ethanol for 10 minutes. After this cleaning treatment, the membranes were dried in a vacuum oven at 80°C for 24 hours before the next test.

The nanofiltration behavior of Sudan Black B was investigated for all solvents. All other dyes (except Rose Bengal) were studied in both toluene and isopropanol. However, Rose Bengal was only studied in isopropanol, due to its insolubility in toluene. The feed solutions consisted of 8000 ppm of dye. All measurements were performed on three different samples for each type of membrane with three measurements per sample.

Dye solute concentrations in the feed and permeate solution were analyzed using a Perkin-Elmer λ 12 UV-Vis Spectrophotometer. The rejection (R) was calculated by the following equation: $R = (1 - C_p/C_f) \times 100\%$, where C_p and C_f are the solute concentrations in permeate and feed solution, respectively. C_f and C_p were determined as a function of total area from a plot of electric potential versus time. To check whether any concentration polarization occurs, the solvent permeation of blank feeds (pure solvents without solutes) and those with solutes were compared using a similar set-up. Permeate fluxes were obtained by measuring the weight of the collected permeate as a function of time. It should be noted that no significant differences were observed between the permeation of blank feeds [20]

and those with solutes, suggesting that no concentration polarization of solutes occurred during the measurements.

The average molecular diameter of the dye solutes (d_c) were calculated by using the *CS 3D Model* software by taking into account the bond length, the corresponding Van der Waals radius, and the bond angle as given in [30, 31]. Since the dye solute can be positioned in various conformations when approaching the membrane pores and assuming that the different conformations may have a similar probability of occurring [32], an average value for each type of dye is used, representing the average size of the solute molecular diameter in the axial, horizontal and lateral direction. These values are given in Figure 6.2.

Figure 6.2 The chemical structures, molar masses and diameters of the dyes used.

6.4 RESULTS & DISCUSSION

6.4.1 The impact of pressure & graft swelling on rejection

Figure 6.3 shows rejection data of Sudan Black B in various solvents as a function of trans-membrane pressure. Please note that plotting rejection against applied pressure and not solvent flux is in order to be able to compare the seven solvents in one figure. It can be seen that, for most cases, dye rejection increased with applied pressure regardless of the type of solvent used. The possibility of deformation (e.g. shear-induced compaction) of the graft under the pressures tested has been discarded, as this would result in a larger membrane pore diameter at higher applied pressures, consequently decreasing rejection and increasing solvent permeability. This is in agreement with the previous observation on the same type of membranes: an absence of shear rate flow induced behavior is attributed to the unyielding nanostructure of the rigid ceramic substrate over the pressure range studied [20].

It can be observed in Figure 6.3 that rejections of Sudan Black B varied according to the solvent used. The highest rejection of Sudan Black B was found in cyclooctane, while the lowest rejection was found in isopropanol. In Table 6.1, the specific rejection values (R) of Sudan Black B at a TMP of 20 bars for M1 and M2 membranes are given. To gauge whether there is a relation between rejection and solvent viscosity, viscosity values are also given in Table 6.1. Another factor which can influence the rejection is the degree of graft swelling, which is a function of the permeating solvent. A measure of polymer swelling is the solvent sorption (S) by the polymer (PDMS) as defined in [20] and therefore, corresponding solvent sorption values are given in Table 6.1.

In a previous study, pure solvent permeation was studied on these same membranes [20]; the permeability data are provided in Table 6.1. In that study, it was shown that both solvent viscosity and sorption of solvent into the grafted moiety determine solvent transport through the membrane. It is logical that the swollen graft does not only influence the solvent transport, but also the solute rejection of the membrane. In this case, the relatively stronger sorption of cyclooctane in the grafted moiety compared to that of isopropanol would be

Figure 6.3 Rejection of Sudan Black B in different solvents versus TMP at room temperature for (A) M1 and (B) M2 membranes.

expected to result in a smaller pore size in the presence of cyclooctane, thus yielding a higher solute rejection in cyclooctane than in isopropanol.

For free (or unconfined) PDMS polymeric membranes, lower rejections are observed in the presence of toluene whereas higher rejections are observed in the presence of isopropanol [33-35]. However, the results of this work, as partially summarized in Table 6.1, show the opposite behavior, meaning a higher solute rejection in toluene than in isopropanol for both types of PDMS grafted ceramic membranes (M1 and M2). This again emphasizes the different behaviors of a “free” PDMS membrane compared to that of membranes in which PDMS is confined to a ceramic matrix. For an unconfined PDMS membrane, the sorption of solvent leads to free swelling, thus a more open membrane structure, while for grafted ceramic membranes, it is suggested that a strongly sorbed solvent leads to a more closed structure of the grafted membranes [20]. This explains the higher solute rejection in the presence of toluene than in the presence of isopropanol.

It can be further observed from Figure 6.3 that rejection increases nonlinearly with TMP regardless of the type of solvent used. From Figure 6.3B, it can be seen that the strongly swelling solvents reach a region of constant rejection; for instance, the change in rejection of Sudan Black B in cyclooctane and p-xylene, by increasing TMP from 15 to 20 bar, is less than the experimental error (± 1). The other solvent-membrane pairs given in Figure 6.3 do not reach this rejection plateau, but do however seem to trend towards a constant rejection value at TMP > 20 bar.

These observations are in agreement with the traditional SKK model: if the diffusion of solutes is independent of pressure, and thus becoming negligible at higher solvent flux, then according to the SKK model the effect of convection becomes dominant. At these feed pressures, the relationship between solute flux and solvent flux becomes constant and thus rejection trends towards a constant value equal to the reflection coefficient, as given in Equations (4) and (5). As previously mentioned, some solvent-membrane combinations reached this constant rejection value; for example, Sudan Black B rejection reached a limiting value of 92% for cyclooctane in M2 (Figure 6.3B). It can therefore be assumed that this value is equal to the reflection coefficient of Sudan Black B in cyclooctane for membrane M2.

Table 6.2 Membrane pore diameters (d_p , in nm) for membrane M1 and M2, calculated from the Ferry, SHP and Verniory models. The reflection coefficients (σ) for membrane-solvent pairs, used for these calculations, are also shown.

Solvent	M1				M2			
	σ	dp (nm)			σ	dp (nm)		
		SHP	Ferry	Verniory		SHP	Ferry	Verniory
Isopropanol	0.54	0.96	1.31	1.43	0.82	0.75	0.82	0.87
Ethyl acetate	0.65	0.90	1.14	1.24	0.85	0.73	0.80	0.84
Toluene	0.79	0.79	0.91	0.97	0.88	0.73	0.79	0.83
Octane	0.77	0.81	0.95	1.02	0.85	0.75	0.83	0.88
p-Xylene	0.78	0.80	0.93	0.99	0.88	0.75	0.82	0.87
n-Hexane	0.81	0.78	0.89	0.95	0.90	0.72	0.78	0.81
Cyclooctane	0.83	0.77	0.87	0.93	0.92	0.71	0.76	0.79

For those solvent-membrane pairs that did not reach a constant rejection value, the existing data points of Figure 6.3 are an input into Equations (4) and (5), and by least-squares fitting (here done using Matlab R2014b) reflection coefficients (σ) are obtained. These σ values, listed in Table 6.2, were then used to calculate

the membrane pore size characteristic of each solvent using the SHP, Ferry and Verniory models. Each solvent-membrane pair therefore yields three pore sizes for each membrane, as shown in Table 6.2. The most precise approximations of σ are obtained for those solvent-membrane pairs whose rejection data are at their high-pressure plateau. As expected from the permeability and swelling data, given in Table 6.1, the pore sizes are inversely proportional to the degree of graft swelling.

The pore diameters listed in Table 6.2 were compared to pore sizes obtained through other characterization methods. The mean pore diameter of the native (non-grafted) γ -Al₂O₃ was confirmed to be 5.0 ± 0.1 nm as measured by permoporometry. The pore diameter was found to be shrinking to 3.0 ± 0.1 nm post-linker grafting for both M1 (APTES linker) and M2 (MPTES linker). Previous analysis [36, 37] of nitrogen adsorption/desorption isotherms on the

native, linker-grafted and PDMS-grafted γ -alumina flakes gave the pore diameters in dry (solvent-free) conditions. Uniform pores were observed that had estimated pore diameters of 4.8 nm for native γ -alumina, 4.2 nm post-APTES grafting, 2.2 nm for the grafted M1 γ -alumina flakes and 1.8 nm for the grafted M2 γ -alumina flakes. As expected, the wet pore sizes given in Table 6.2 are markedly smaller than the native γ -Al₂O₃ pore sizes, also smaller than the linker-grafted pore size, and smaller than the dry-PDMS pore sizes.

6.4.2 Rejection vs. solute diameter: dyes

The rejection of several dyes was studied in toluene and isopropanol for both membranes (M1 and M2), and a summary of the results can be found in Table 6.3. In the previous section, the rejection of Sudan Black B in both toluene and isopropanol at a TMP of 10 bar was found to be in the mixed diffusion-convection regime. Therefore, it was expected that the rejection predictions and rejection data treated in this section would also be in the mixed diffusion-convection regime. To calculate the expected rejection, both the reflection coefficient (σ) and solute permeability (P_c) were calculated as a function of solute size for each membrane-solvent pair tested.

Table 6.3 Hydrodynamic diameters (d_c) of various dye solutes and the experimental rejection values at TMP = 10 bars in toluene or isopropanol for membranes M1 ($=R_{M1}$) and M2 ($=R_{M2}$).

Solutes	d_c (nm)	Toluene		Isopropanol	
		R_{M1}	R_{M2}	R_{M1}	R_{M2}
		(%)	(%)	(%)	(%)
Solvent blue 35	0.58	40 ± 1	55 ± 1	16 ± 1	28 ± 1
Solvent blue 36	0.61	44 ± 1	60 ± 1	18 ± 1	31 ± 1
Solvent red 27	0.63	46 ± 1	62 ± 1	19 ± 1	33 ± 1
Sudan black B	0.65	45 ± 1	64 ± 1	20 ± 1	35 ± 1
Bromothymol blue	0.89	65 ± 1	81 ± 1	31 ± 1	53 ± 1
Rose bengal	1.02	-	-	40 ± 1	65 ± 1

The values of σ and P_c were related to values of d_p and ω , respectively, as a function of solute and pore diameter using the Ferry, SHP and Verniory models (Equations 8, 9 & 10) and the diffusion permeability (Equation 13). The pore size and diffusion parameter were obtained from the Sudan Black B rejection versus pressure data presented in the previous section. Since three pore sizes were obtained (Table 6.2), three sets of rejection values were predicted, from $d_c/d_p = 0$ up to $d_c/d_p = 1$. The solvent permeabilities of membranes M1 and M2 are already known [20] for each solvent-membrane pair. Applying these data, comparisons between experimental and predicted rejection values were made, as shown in Figure 6.4, a to d.

The results shown in Figure 6.4 show that rejection is generally higher in toluene than in isopropanol, which is to be expected from the impact of swelling as previously discussed. Also expected were the higher rejections caused by M2 than M1 in the same solvent, because the pores of M2 are smaller because of the larger PDMS monomer used ($n = 39$ vs. $n = 10$ for M1). Finally, and in accordance with the general behavior of porous membranes, the rejection of dyes is largely a function of their molecular size, and hence of their molecular weight. However, the SKK model predictions are not in accordance with the experimentally observed results on two points specifically: solutes bigger than the calculated pore size are able to permeate through the membrane, and 100% rejection is not reached at the proposed pore size. For example, the SHP pore diameters of M1 and M2 in isopropanol were calculated to be 0.96 nm and 0.75 nm, respectively, and the diameter of Rose Bengal is 1.02 nm and yet its rejections are below 70% for both M1 and M2. To address these issues, we further discuss the unique pore structure of these grafted ceramic membranes. Membranes M1 and M2 benefit from a rigid ceramic architecture, constraining the swelling of the grafted PDMS chains. However, PDMS, especially when swollen, is not a dense material, nor is the interface between the solvent grafted chains especially hard or well-defined [38]. Diffusion of solutes through the membrane has until now been assumed to be subject to the same reduced pore size as the convection of solutes and solvents, but now it can reasonably be assumed the solute can permeate through the free space between the grafted PDMS chains. The remainder of this section describes the integration of a pore size for diffusion (d_d) into the SKK model.

Figure 6.4 Comparison of experimental dye rejection as function of d_c for M1 in (a) toluene and in (b) isopropanol and for M2 in (c) toluene and (d) isopropanol with the predicted SKK rejection values from the Verniory, Ferry and SHP pore sizes. Points represent experimental data; lines the SKK model.

Table 6.4 The ω and d_d values of M1 and M2 used in rejection predictions. The ω value is the diffusion parameter, and the diffusion pore diameter (d_d) is the diameter of the pore after organosilane (linker) attachment, as determined by permporometry. This value does not vary significantly from M1 to M2.

Solvent	ω (L.m ⁻¹ h ⁻¹)		d_d (nm)	
	M1	M2	M1	M2
Isopropanol	1.1×10^{-8}	7.7×10^{-9}	3.0 ± 0.1	3.0 ± 0.1
Toluene	1.7×10^{-8}	7.7×10^{-9}	3.0 ± 0.1	3.0 ± 0.1

The diffusion pore size (d_d) is larger than the convection pore size (d_p) for these ceramic-based hybrid membranes. Since a portion of the solute is able to diffuse through the swollen graft, effectively increasing the apparent pore size for the diffusion mechanism, solutes larger than the convection pore diameter are allowed to permeate through the membrane. The diffusion pore size is taken to be equal to the pore diameter before the grafting of PDMS, measured by permporometry as $3.0 \text{ nm} \pm 0.1$ for both M1 (APTES linker) and M2 (MPTES linker), as shown in Table 6.4.

The fact that the modeled retentions, as given in Figure 6.4, do not reach unity when the pore size equals the solute size is due to the incorporation of the Stokes-Einstein equation to calculate P_s as a function of pore size (Equations 11, 12 & 13). In this case free diffusion is assumed, i.e. diffusion of solutes is unhindered by the pore walls. To account for the hindrance caused by the pore wall, the Renkin equation is used. This expresses the ratio of hindered diffusion, D_c^* , to free diffusion (D_c , Equation 12) of a spherical particle inside a cylinder of known diameter as a function of the ratio of solute to cylinder diameter. Since its introduction in 1954 [39], agreement with experimental data has been observed for both biological and non-biological membranes [40-42]. The Renkin equation is below:

$$\frac{D_c^*}{D_c} = f\left(\frac{d_c}{d_d}\right) = \left(1 - \frac{d_c}{d_d}\right)^2 \left(1 - 2.104 \left(\frac{d_c}{d_d}\right) + 2.09 \left(\frac{d_c}{d_d}\right)^3 - 0.95 \left(\frac{d_c}{d_d}\right)^5\right) \quad (14)$$

Now a new permeability (P_c^*) incorporates d_d through the Renkin equation as shown in Equation (15).

$$P_c^* = \frac{\omega}{d_c} * \left(1 - \frac{d_c}{d_d}\right)^2 \left(1 - 2.104 \left(\frac{d_c}{d_d}\right) + 2.09 \left(\frac{d_c}{d_d}\right)^3 - 0.95 \left(\frac{d_c}{d_d}\right)^5\right) \quad (15)$$

This corrected permeability term was used in the SKK model and is plotted together with the experimental results in Figure 6.5. The reflection coefficient and rejection were bounded as follows: $0 < \sigma < 1$ and $0 \leq R \leq 1$, while for the purposes of clarity and simplicity, only the Ferry pore size, as listed in Table 6.2, was used for d_p . This modified SKK model shows a closer fit to the experimental data, especially for M2. The better fit for M2 may be due to better approximations of the σ values, as more of the solvents of Figure 6.3b reach a constant rejection value (see Figure 6.3b), and, besides, the rejection of Sudan Black B in isopropanol in M1 was only tested at three pressures for membrane M1 rather than four pressures, as for membrane M2.

The modified SKK model shows that the permeability of solutes is now decreased to zero as the solute cross-sectional area nears the diffusion pore size, and that rejection is predicted past the original limit of $d_c/d_p = 1$ up to the new limit, $d_c/d_d = 1$. Figure 6.5 appears to show that rejection does not approach 100% at d_d (3.0 nm), but at smaller solute sizes around $d_c = 2$ nm. This is predicted by the Renkin equation, which calculates the hindered diffusion to be 2% of its original value at $d_c/d_d = 0.66$, limiting the transport of solute across the membrane. Of course, retention experiments with molecules in the 80-100% predicted rejection range would further validate this model, though dyes molecules are generally smaller than these sizes, with Rose Bengal (MW = 973 Da) already one of the largest dyes. Additionally, grafting PDMS into the pores of ceramic membranes of various pore sizes would allow for further testing of this modified SKK model. In its present form, the modified SKK model shows that both diffusion and convection of solutes is significant and do not necessarily operate with the same (pore-size) parameters.

Figure 6.5 Experimental and predicted dye rejection results for (a) M1 and (b) M2 in toluene and isopropanol (IPA) using the modified SKK model.

6.5 CONCLUSION

PDMS-grafted γ -alumina ceramic membranes showed a higher rejection of a certain solute in the presence of nonpolar solvents, such as toluene, than in more polar solvents, such as isopropanol. A relation was observed between solute rejection and the ratio of solute diameter versus membrane pore diameter, indicating that a size-exclusion mechanism is applicable to describe the membrane solute rejection when taking into account pore shrinkage due to graft swelling.

Rejection data as a function of pressure were analyzed in the frameworks applied by the Ferry, Verniory, and SHP size-exclusion models together with the Spiegler-Kedem-Katchalsky (SKK) equations to calculate pore diameters for the various solvents tested, and, subsequently, the solute permeability parameters. It was proposed that a larger pore size is experienced by the diffusion of solutes across the membranes, due to the open structure of the PDMS grafted moiety. The SKK equations were modified in response, proposing the pore size available for diffusion as the pore size of γ -Al₂O₃ before PDMS grafting, as determined by permoporometry measurements. This modified SKK model has a clear physical interpretation and, more importantly, offers accurate rejection predictions.

The testing of solutes of various polarities and shapes, along with solvent mixtures, would doubtless generate an additional layer of complexity when interpreting and modeling results. It remains to be seen whether the SKK model - or a derivative - could accurately predict membrane performance that involve increasingly complex solute-solvent-membrane interactions, though the insight gained from the results here certainly contributes towards understanding the fundamental mechanisms involved in solute transport across polymer-grafted ceramic membranes.

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CHAPTER SEVEN

Evaluation of organic solvent
nanofiltration membranes under
industrially relevant conditions

ABSTRACT

Organic solvent nanofiltration (OSN) is gradually expanding from academic research to industrial implementation. The need for membranes with low and sharp molecular weight cutoffs that are able to operate in aggressive conditions is increasing. However, the lack of comparable and uniform performance data renders screening and membrane selection for the development of specific processes difficult. Here, a collaboration is presented between several academic and industrial partners analyzing the separation performance of multiple membranes, both commercial and laboratory-made, of three model process mixtures. These were chosen specifically to mimic challenges relevant to today's industrial processes: a relatively low MWCO and high temperature.

First, a fair comparison of data sets is established by a round-robin test of the same membrane across all test setups used. Next, the results of selected membranes are presented case-by-case. Though all membrane types suffer from the inevitable retention-permeability tradeoff, permeabilities greater than $2 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$ could be realized with a MWCO of 330 Da or less for two out of three cases. Based on these findings, the comparison of OSN membrane performance across different setup configurations is encouraged while using the same model mixtures.

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7.1 INTRODUCTION

Organic solvent nanofiltration (OSN, also known as solvent resistant nanofiltration (SRNF)), concerns itself with non-aqueous separations via a membrane. An incoming solution, the feed, is pressurized and brought into contact with a selective barrier. The solute, with a molecular weight between 200-1000 g.mol⁻¹, is typically purified or concentrated, creating respectively a permeate or retentate with added value [1-2]. OSN has attracted interest from both academics and businesses since its first proven commercial success, the MAX-DEWAX® process in 2001 [3]. Interest has continued to grow, finding a variety of applications in the chemical-related, pharma and food industries [4-7]. As these varied examples show, the OSN field is not focused on a single application, as desalination, but rather encompasses a wide range of solvents, solutes and process conditions relevant to a variety of industries.

While the width of potential application areas generates diverse interest in OSN, each application brings a different operating environment. This has consequently led to a variety of OSN membranes reported in literature, each designed for optimal performance in specific solvent classes. Accurate comparison of membrane performance data when either or both the solvent and solute are changed is rarely possible, as competing affinities between the membrane, solute and solvent remain too complex to predict or translate to comparable performance data [1,8]. Besides the test solution and membrane, important process parameters such as temperature, cross-flow velocity, recovery and pressure further complicate the comparability of test data. Hence, experimental screening trials are a prerequisite for the scale-up of any laboratory-developed OSN membrane technology.

The challenge is then the screening (or benchmarking) of lab-made membranes. Currently, no widely accepted method for systematic OSN membrane testing is in place. This is not due to a shortage of proposed solutions. Many solutes, mixed with various solvents, have been advocated as cornerstones of ideal standard testing method. Due to the simplicity of light absorbance characterization and the wide range of available molecular weights, dyes such as Rose Bengal are often used in nanofiltration retention tests. However, overlapping absorption spectra makes testing of multiple dyes at once impossible. Oftentimes, dyes suffer from

a limited solubility range, or are charge-carriers, which can make it difficult to distinguish between membrane adsorption and retention [9]. Besides dyes, at least four separate studies have advocated the use of a range of oligomers as “model solutes”. Polyethylene glycol (PEG) [10], polypropylene glycol (PPG) [11] and polystyrene (PS) [12] were all proposed as ideal OSN testing solutes, among a plethora of other widely used solutes (e.g. n-alkanes [13], polyisobutylenes [14-15]). Though each method has its merits and drawbacks, the prediction of Molecular Weight Cut Off (MWCO) in a range of solute-solvent pairs, based on testing with one specific model solute, remains unattained. This means a single screening method cannot represent the interests of all or even most OSN applications. Testing a representative solvent-solute pair, of similar chemical make-up and affinity as the target case(s), is however feasible, and employed in this work.

Apart from the representativeness of solutes and solvents, OSN membranes themselves are diverse and mostly not exchangeable between applications. For example, a membrane that can concentrate peptides in ethanol is not optimized for, or even necessarily stable in, catalyst recovery from an aromatic mixture. Indeed, some of the most challenging membrane separations occur in non-polar solvents, such as aromatics and alkanes. Traditional membrane materials used in aqueous solutions, such as polyamide or cellulose acetate, are not necessarily stable in these solvents. Ceramic membranes, though stable in most solvents, are as such not suited for non-polar solvent filtration due to their highly hydrophilic surface. As a result, a variety of specialized and innovative membrane materials and modification methods have been developed for use in non-polar solvents.

The goal of the study was to fairly compare the performance of emerging OSN membranes developed by five project partners across three model cases, representative of demanding industrial process separations. The model cases were chosen to (a) provide laboratory-safe equivalents of industrial mixtures and (b) to protect proprietary industrial process mixtures. All cases ask for membranes that can separate at the challenging end of the OSN spectrum, i.e. in the molecular weight range of 250-450 g.mol⁻¹, and one case requires performance at high temperatures. These cases are listed in Table 7.1. To accurately compare the permeability and retention of the various membranes and testing equipments used

by the project partners, a round-robin test was first conducted on the same commercial OSN membrane. The analysis ensures that fair comparison of the diverse membrane types is possible.

The material compositions and structures of the membranes used in this study are a diverse selection of innovative membranes developed specifically for use in OSN. The membranes and some of their relevant material properties are summarized in Table 7.2. Further details about the fabrication methods of these membranes and their performance in other media can be found in the references, given in the Materials section. Polymeric selective layers, as found in the KU Leuven, SolSep or UT-POSS membranes (Table 7.2), are typically crosslinked to remain insoluble and limit swelling in organic solvents. Commonly used in OSN are a variety of thin film composite membranes with a PDMS-based top-layer (ECN-PDMS) or integrally skinned polyimide membranes (KUL-PI) [16-17]. Polymeric selective layers are either supported by a solvent-resistant polymeric supports, such as polyacrylonitrile (PAN, as used for UT-POSS), or a meso- or macroporous support such as α -alumina [18-19]. Where micro- or mesoporous ceramics form part of the selective layer, the grafting of chemical species serves to hydrophobize the pore surface and also tune the pore size, as in PDMS-grafted alumina [19-20] or alkyl-grafted titania [21-22]. All of the membranes used in this study were identified as potentially stable and high-performing for one or more of the model cases.

In short, the performance of multiple experimental OSN membranes from five partners was tested and analyzed. To ensure fair comparison across testing equipment, a commercial membrane was first tested on each setup in the conditions of Case 1. Those are the first results presented in Results and Discussion section, followed by the performance of membranes presented by case.

7.2 MATERIALS

The properties and origin of the membranes used are listed in Table 7.2 All membranes used are either commercial, semi-commercial, or lab-scale with

fabrication methods published in peer-reviewed literature. Below are detailed relevant membrane properties, ordered alphabetically by partner.

7.2.1 ECN-TNO

All membranes prepared by ECN-TNO employ the same support. The supports, a 14 mm outer-diameter, porous alumina single-channel tube supplied by Inopor (Germany) with a pore size of about 5 μm , were first coated on the outside with two α -alumina layers of pore size 0.2 μm . Subsequently, a γ -alumina layer with a pore size of 4 nm was applied. Details of this coating process are described by Bonekamp et al. [23].

The hybrid silica based membranes (**ECN-Hybrid**) are based on sol-gel technology. A mixture of bis(triethoxysilyl)ethane (BTESE) precursor and the templating agent cetyl trimethylammonium bromide (CTAB) was prepared based upon the procedure described by Castricum et al. [24]. The composition of the BTESE-CTAB mixture was taken similar to the tetraethylorthosilicate - CTAB sol as described by Klotz et al.[25]. This sol was coated on the outside of the γ -alumina support tube. After coating the BTESE-CTAB layer was dried and calcined at 270°C under nitrogen atmosphere for 1 hour. The polymeric layers were coated on the outside of the γ -alumina support tube by using either a 2 wt.% Polyimide (P84) solution in NMP (**ECN-PI**) or 40 wt.% PDMS + crosslinker (Elastosil M4644A + Elastosil M4644B) in *n*-hexane (**ECN-PDMS**). After coating both polymeric membrane layers were dried in an oven at 100°C for PI and 110 °C for PDMS for 1 hour.

7.2.2 KU Leuven

The preparation of membrane **KUL-PI** is based on a simplified synthesis route described in the literature [26]. Polyimide (PI) powder was first dried overnight in an oven at 100 °C. A homogenous PI solution ranging from 18-22 wt.% (Table 7.3) was prepared in a NMP/THF mixture and left resting overnight to remove air bubbles. The polymer solution was cast at a constant speed of $4.4 \times 10^{-2} \text{ m.s}^{-1}$ and with a wet thickness of 250 μm using an automatic casting device (Porometer, Belgium) on a non-woven impregnated with NMP. After 2 min, to allow THF evaporation from the surface, the film was immersed in a coagulation bath. The coagulation bath consisted of 1,6-hexanediamine (HDA) (2.0 %) in DI water to

Table 7.1. Solvents, solutes and screening conditions of cases 1, 2, and 3. Ideally, the solute is to be retained while the solvent is free to pass through the membrane.

	CASE 1	CASE 2	CASE 3
SOLVENT	Toluene 92 Da	n-Heptane 100 Da	Anisole 108 Da
SOLUTE	9,10-Diphenylanthracene 330 Da, 100 ppm	9,10-Diphenylanthracene 330 Da, 100 ppm	Pentaerythritol tetrabenzoate 553 Da, 0.2 wt.%
CONDITIONS	20°C 20-30 bar	20°C 20-30 bar	50°C 20-30 bar

Table 7.2. Characteristics and provenance of the membrane types tested, ordered alphabetically.

Sample family	Partner	Availability	Membrane architecture	Material		Max T [°C]
				Support	Selective layer	
ECN-Hybrid	ECN-TNO	Semi-commercial	Ceramic-based hybrid	α -Al ₂ O ₃ / γ -Al ₂ O ₃	BTESE & CTAB	150
ECN-PDMS	ECN-TNO	Semi-commercial	Ceramic-supported polymer	α -Al ₂ O ₃ / γ -Al ₂ O ₃	Crosslinked PDMS	150
ECN-PI	ECN-TNO	Semi-commercial	Ceramic-supported polymer	α -Al ₂ O ₃ / γ -Al ₂ O ₃	Polyimide	150
KUL-PI	KU Leuven	Laboratory	ISA	Non-woven	Matrimid/polyimide	> 80
Solsep	Solsep™	Custom-made for project	TFC	Polyimide	Proprietary	80-120
TUD/UT-MA	University of Twente / Technical University of Delft	Laboratory	Ceramic-grafted polymer layer	α -Al ₂ O ₃ / γ -Al ₂ O ₃	Poly(alkene-co-maleic acid)	> 50
UT-PS	University of Twente	Laboratory	Ceramic-based hybrid	α -Al ₂ O ₃ / γ -Al ₂ O ₃	Polystyrene grafted-from γ -Al ₂ O ₃	100
UT-POSS	University of Twente	Laboratory	TFC	PAN	polyPOSSamide	160
VITO-GG	VITO (FunMem)	Semi-commercial	Ceramic-based hybrid	TiO ₂	Proprietary Grignard-grafted	120-150

simultaneously perform phase inversion and crosslinking of the membrane. After 30 min, the membrane was removed from the coagulation bath and stored in water until further use. PI (Matrimid® 5218) was purchased from Huntsman (Switzerland). The non-woven poly-propylene-polyethylene fabric Novatex 2471 was provided by Freudenberg (Germany). 1,6-hexanediamine (HDA, 99.5%, Acros) was used for PI membrane crosslinking. The various membranes fabricated and used are shown in Table 7.2.

7.2.3 SolSep

The SolSep membranes used in this work are composites based on proprietary materials. The top layer of the membranes is tunable, aimed for optimal performance in specific solvent-solute-membrane systems. The membranes used here differ from standard SolSep membranes available on an industrial scale.

7.2.4 University of Twente

Three classes of membranes were provided by the University of Twente. The first, **UT-PS**, consists of 2 layers of γ -alumina (3 μ m thick, 5 nm pores) that were dip-coated onto a flat α -alumina substrate (2 mm thick, 39 mm diameter, 80 nm pores) which was obtained from Pervatech, the Netherlands. Polystyrene (PS) chains were polymerized from an initiator covalently bonded to the pore surface

Table 7.3. The membrane fabrication variables and which cases they were used for: PI concentration and casting solution solvent ratios.

Membrane designation	PI concentration (wt%)	Casting ratio NMP:THF	Model case(s) used
KUL-PI-1	22	50:50	Case 1, Case 2
KUL-PI-2	22	40:60	Case 1, Case 2
KUL-PI-3	20	50:50	Case 1, Case 2
KUL-PI-4	20	40:60	Case 1, Case 2
KUL-PI-5	18	50:50	Case 3
KUL-PI-6	19	50:50	Case 3
KUL-PI-7	21	50:50	Case 3

of the γ -alumina, fabricating a hybrid selective layer which shrunk and hydrophobized the pores. These membranes were developed by Merlet et al. [27], where fabrication details can be found. The second set of membranes, **TUD/UT-MA**, uses the same γ -alumina coated α -alumina support as UT-PS. As developed by Amirilargani et al. [9], a pre-synthesized, alternating copolymer of maleic anhydride and 1-alkene is grafted onto the surface of the γ -alumina. The maleic anhydride bonds to the alumina surface providing multiple covalent bonds per chain. The alkane side chain length was optimized to 16 carbons long to yield the best performance, as described in [9].

The third set of membranes, **UT-POSS**, consists of a selective layer fabricated by interfacial polymerization, yielding a 100 nm thick layer of polyPOSSamide [28]. PAN supported films were prepared by impregnating a prewetted commercial ultra-porous polyacrylonitrile membrane, fixed on a perforated plate by vacuum, with an aqueous solution of 0.9 wt % ammonium chloride salt functionalized POSS (OctaAmmonium POSS®, Hybrid Plastics (USA)). The pH was adjusted to 9.7 by adding sodium hydroxide. Subsequently, the membrane was submerged into 0.2 wt.% trimesoyl chloride in n-hexane for 5 minutes. Alpha-alumina supports with 80 nm pore size were purchased from Pervatech (Netherlands). Two layers of γ -alumina were dip-coated and calcined onto the α -alumina ceramic support to form a 3 μ m thick layer with a pore diameter of 5 nm [29-30].

7.2.5 VITO

Tubular 0.9 nm TiO_2 membranes with surface area of $48.4 \times 10^{-4} \text{ m}^2$ length 25 cm, outer diameter 10 mm, inner diameter 7 mm) were purchased from Inopor (Veilsdorf, Germany) and functionalized by grafting organic groups onto the membrane surface using Grignard chemistry (**VITO-GG**). The details of the grafting procedure can be found elsewhere [21,31]; a general description is included below. The support tubes were first properly pretreated to remove adsorbed surface water, after which they were submerged for 48 h into a reaction mixture comprising a specific Grignard reagent in diethylether. The reaction was carried out under dry atmosphere at room temperature and the reaction mixture was filtered through the membrane to maximize the contact with the complete pore surface. MgBr salts, formed as side-product of the reaction, were removed

by a proper washing procedure. After washing, the grafted membranes were dried at 60°C under vacuum.

The solvents used for membrane fabrication and membrane testing were sourced from various manufacturers. Unless otherwise indicated, solvents were analytical grade (99%) or above and used without further purification. The solutes of cases 1, 2 and 3 were 9,10-Diphenylanthracene (Sigma, ≥99%), and Pentaerythritol tetrabenzoate (Sigma, ≥96%), all used without further purification. Solvent, solutes and concentrations used are given in Table 7.1.

7.3 METHODS

A variety of membrane test setups were used. Specification of these setups can be found in the Supporting Information. Both dead-end and crossflow setups were used with tubular or flat membrane geometries. A typical dead-end setup is composed of a nitrogen-pressurized vessel containing the feed, from which the only outlet is fed to the membrane. In a crossflow setup, the membrane feed is pressurized either by a pressurizing pump or by pressurized nitrogen to provide transmembrane pressure. A circulation pump is used to provide a crossflow velocity across the membrane surface. The different setups used are listed in Table 7.4. In each case the permeate is collected and weighed at timed intervals. The permeability, P ($\text{L m}^{-2}\text{h}^{-1}\text{bar}^{-1}$) was calculated using Eq. (1), where V (L) is the permeate volume, A (m^2) the membrane area, t (h) the filtration time and ΔP (bar) the applied pressure difference:

$$P = \frac{V}{A \times t \times \Delta P} \quad (3)$$

Retention, R (%), was calculated according the following equation:

$$R = 1 - \frac{c_p}{c_f} \quad (4)$$

where c_p and c_f are the permeate and feed solute concentrations, respectively. Retention is expressed as a percentage throughout this work. Solute concentrations were determined by measuring the UV-Vis absorbance with a

Table 7.4. Equipment configuration of each partner.

Partner	Cross flow or Dead-end	Geometry
University of Twente	CF	Flat sheet
VITO	CF	Tubular single-channel
ECN-TNO	DE	Tubular single-channel
Solsep	DE	Spiral-wound
KUL	DE, stirred	Flat sheet

spectrophotometer. Standard curves were made to ensure linear fitting over the solute concentration profile. Sample absorption profiles are provided in the Supporting Information, Figures S7.1 and S7.2.

7.4 RESULTS AND DISCUSSION

Before results from different setups can be compared, it is necessary to establish that the setups are equivalent, i.e. that results from one equipment can be fairly compared against the results of the others. The setup configurations employed in this study are diverse, not only in terms of dead-end vs. crossflow, but almost in every aspect, e.g. membrane cell geometry, means of pressurization, control instruments, sampling and test volumes, effective area, membrane pretreatment, etc.

Prior literature comparisons of dead-end vs. crossflow configurations for OSN are scarce. The two analyses found suggest that diverging retention or permeability across different setup configurations is seen at high solute concentrations [32-33]. In one study, the dead-end and crossflow modes were compared for StarMem™ 122, an integrally skinned asymmetric PI-based OSN membrane. Solutions of 50mM of linear-chain trialkylamines in toluene yielded the lower retentions in a crossflow configuration than dead-end [32]. The other

study [33] used DuraMem® membranes, equally PI-based, and showed no significant difference in retention when comparing crossflow and dead-end setups, while permeability generally decreased with increased solute loading in both cases. In this current work, the solute concentrations for Cases 1 and 2 are ~ 5 -10x lower than the examples discussed (100 ppm vs. 270-520 ppm [32] or 1000 ppm [33]), and the solute concentration is kept constant from setup to setup. Therefore, the impact of concentration polarization on either permeability or retention was expected to be minor, and independent of setup configuration. Case 3 used a concentration of 0.2 wt% (2000 ppm) across all setups, and therefore dead-end setups of Case 3 (ECN-TNO, SolSep) may have experienced lower than expected retentions.

Even within the same type of setup configuration, other factors, such as cell shape or crossflow velocity, can impact the membrane performance. However, an extensive study by Böcking et al. [34] on the variance of permeability and retention across crossflow setups from the DuraMem® and PuraMem® Evonik product lines showed that permeability and retention variance were innate to the membrane type for that given feed composition and filtration conditions. Interestingly, the variance of permeability is found to be greater than the retention variance, and each is found to be membrane-dependent.

A larger variance in permeability than in retention was also found during the round-robin analysis of current work. For this analysis, a commercial membrane, provided by SolSep™, was used in the setup of each partner. The round-robin test was carried out with the Case 1 mixture (100 ppm of DPA dissolved in toluene). Overall, retention was constant after discarding the first few milliliters of permeate, and the permeate was periodically recycled into the feed, effectively keeping feed solution at a constant concentration. Tests were done in duplicate on each setup and all results are plotted in Figure 7.1.

In Figure 7.1, crossflow setups are represented by an open square, while the filled squares represent dead-end setups. The mean permeability and retention are $2.80 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$ and 72.5% with standard deviations of 0.89 and 9.4, respectively. The only outlier of Figure 7.1 (marked with an X, $4.7 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$ & 50%) was omitted from the permeability and retention means, as its more reasonable duplicate ($3.9 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$, 65.9%) did not match and was within standard

deviation bounds. The relatively low retention of the outlier also coincided with a higher permeability, suggesting a defective membrane or improper module sealing. The data points of Figure 7.1 at 1.9 and 2.0 $\text{L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$ and 83.4 and 83.5% were obtained from a module designed for dead-end setups but connected to a crossflow setup, hence limited crossflow was expected. As expected, the permeability has a greater spread than the retention [34]. The data suggest that crossflow setups give a better retention at the cost of permeability, though there are too few data points to be conclusive. At significantly higher recoveries, retentions may start to be concentration dependent, especially for dead-end setups. Though the permeability and retention variance are innate to all membranes, we conclude that we can compare the experimental data between setups as presented in the following section, case-by-case.

Retention as a function of permeability are plotted for Cases 1 and 2 in Figures 7.2 and 7.3, respectively. The membrane type best-suited for separation in Case1 (100 ppm of DPA, MW 333 Da, in toluene) is TUD/UT-MA (red triangles) with a permeability of $2.9 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$ and a retention of 91%. The highest

Figure 7.1. Round robin test results of membrane SolSep M tested on a Case 2 feed at 10 bar of transmembrane pressure and room temperature. Open squares represent crossflow setups, filled squares represent dead-end setups. The outlier (X) was discarded when calculating the means and standard deviations.

permeabilities (around $3.2 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$) with retentions greater than 60 %, , were observed for the TUD/UT-MA and UT-PS membranes. The UT-PS data series (red diamonds of Figure 7.2) shows a linear improvement as the grafting-from reaction parameters were optimized to promote pore shrinkage instead of a brush on the external membrane surface. Reaction parameters conducive to slower polymerization enabled polystyrene chain growth inside the pore. It was determined that pore shrinkage, rather than a layer on the external surface of the γ -alumina, is the driving force behind selectivity gains for UT-PS membranes [27]. KUL-PI membranes #1-3 are not shown here due to their negative retentions (from -27 to -33%). Therefore, only KUL-PI-4 is shown. Negative retentions are usually due to higher solute-membrane than solvent-membrane interactions [13,35]. KUL-PI also sees negative retentions in Case 2.

Figure 7.2. Permeability and retention results of Case 1 experiment: Toluene with 100 ppm DPA (333 g mol^{-1}).

Figure 7.3. Case 2 results. Heptane with 100 ppm DPA (333 g mol⁻¹)

Case 2 uses the same solute, 100 ppm of DPA, but now dissolved in heptane. As shown in Figure 7.3, retention greater than 90% is achieved only by a handful of membranes. The membrane of VITO performed similar to the last case: high retention, but low permeabilities. The Solsep NF-TM#1 achieved a permeability of 2 L.m⁻²h⁻¹bar⁻¹ coupled with a retention of 93 %. However, the Solsep membrane NF-TM#2 that performed well in Case 2 (heptane) only yielded a permeability of 0.35 L.m⁻²h⁻¹bar⁻¹ and a retention of 63% in Case 1. Again, the same KUL-PI membranes exhibit negative retentions (from -9 to -16%) and low (<0.1 L.m⁻²h⁻¹bar⁻¹) permeabilities. The UT-PS membrane continues to perform well, with a permeability of 1.8 L.m⁻²h⁻¹bar⁻¹ and retention of 87%, while the best performer is the TUD/UT-MA, with a permeability of 2.5 L.m⁻² h⁻¹ bar⁻¹ and high retention of 92%.

While Case 1 and 2 are similar – both use the same solute dissolved in an aprotic non-polar solvent – the results of the NF-TM#2 Solsep membrane are markedly different from Case 1 to Case 2, while the VITO, UT-PS and TUD/UT-MA membrane results are similar. A highly likely explanation is that toluene swells

the selective, dense polymer layer of the Solsep membrane to a different degree, or differently, than the VITO, UT-PS and TUD/UT-MA membranes, which have a ceramic, porous architecture. The Grignard-graft on the VITO membranes does not swell as it is not a uniform polymer layer [36]. The polystyrene graft on the UT-PS membranes can swell, but the porous ceramic membrane architecture remains inert to swelling. The different swelling degree of the PS graft from solvent to solvent was shown to impact the permeability and retention to a limited degree [37]. The maleic anhydride functional groups of the TUD/UT-MA membranes ensure frequent attachment to the external surface, thus preventing excessive polymer swelling. Whereas the pores constrain the swelling in UT-POSS, here the swelling is limited by the repeated covalent bonds per copolymer chain with the external surface of the γ -alumina layer [9]. The Solsep membranes have no ceramic structure to rely upon and thus are prone to swelling effects, pronounced differently in toluene than heptane. A similar effect was seen with the KUL-PI membranes, which proved to be unsuitable for nanofiltration of this particular solute in toluene and heptane, as all but one exhibit negative retentions, and all with low permeabilities. Even though both toluene and heptane are non-polar solvents, they are quite different: heptane is far less viscous than toluene, and their molecular interactions are different (as calculated, for example, by Hansen solubility parameters [38])

In case 3, the retention of 0.2 wt.% of pentaerythritol tetrabenzoate in anisole was tested at elevated temperatures, and the results are shown in Figure 7.4. The tests at VITO were conducted at 50°C, and the tests at KUL and ECN at 60°C. Not all partners were able to test membranes at such elevated temperature. In general the permeabilities are low, and the best membranes were offered by VITO, with permeabilities of 0.14 and 0.16 L.m⁻².h⁻¹.bar⁻¹ and retentions of 76 and 81%, respectively. The hybrid membrane of ECN showed comparable results, with 0.18 L h⁻¹ bar⁻¹ m⁻² and 69 % retention at 60°C. These results are comparable to the Case 1 and Case 2 results, indicating the thermally stable inorganic-based membranes give reliable performances at higher as well as room temperatures. It should be noted that the membranes of Case 3 were also tested at room temperature instead 50-60°C and had poor performances, exhibiting zero to negligibly low permeabilities.

Figure 7.4. Case 3 results. Anisole with 0.2 wt.% Pentaerythritol tetrabenzoate (MW = 553 g mol⁻¹).

To summarize, Case 1 & 2 were at first glance similar, each containing the same solute, pressure, concentration, temperature, and a non-polar solvent. However, without the distinction of solvent, the membrane selection would not have been the same, and cost additional resources in the next technology development stage. During Case 1 there was the opportunity to tune the UT-PS membrane series, and Case 2 provided additional membrane stability data. Case 3, at elevated temperature, allowed for a selection of membranes that would not have been obvious from the other cases. In general ceramic-based membranes has the lowest performance variation from case to case. As a follow-up to this study, several of the best-performing membranes benchmarked within this study were selected for continued testing on industrial mixtures.

7.5 CONCLUSION

Several OSN membranes were tested on three industrially relevant model mixtures. The mixtures were solutions of non-polar solvents with low molecular weight polyaromatic compounds representative for industrial commodity chemical production processes targeting maximal solute retentions. Presented data are a collaboration between multiple academic and industrial partners, each with a unique setup. The analysis of a round-robin test with the same membrane in each setup configuration confirmed that results could be compared, even between dead-end and cross-flow filtration modes.

The membranes were analyzed, case-by-case, in terms of their retention and permeability. The top performance was not shown by the same membrane type across all three cases. Across all 3 cases, the membranes with polymeric supports had larger performance variations than those membranes with ceramic supports. Some of the polymeric membranes were only chemically stable for a given case but not in another. Until membrane-solvent-solute interactions become predictable, these results demonstrate the need for customized testing with representative synthetic mixtures when benchmarking OSN membranes for an industrial process. We invite others to use these screening solutions for the evaluation of OSN membranes in non-polar test systems.

7.6 ACKNOWLEDGEMENTS

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7.7 ACRONYMS

BTESE: bis(triethoxysilyl)ethane

CTAB: acetyl trimethylammonium bromide

DI: de-ionized

GG: Grignard-grafted

HDA: 1,6-hexanediamine

NMP: N-methyl pyrrolidone

PAN: polyacrylonitrile

PDMS: polydimethylsiloxane

PI: Polyimide

POSS: poly octahedral silsesquioxane

PS: polystyrene

THF: Tetrahydrofuran

TFC: Thin-film composite

7.8 SUPPORTING INFORMATION

7.8.1 UV-Vis spectrum and calibration curves of DPA in toluene (Case 1) and n-heptane (Case 2) from KU Leuven

Fig. S7.1: (a): UV-VIS spectrum of DPA in toluene as a function of concentration; (b): Calibration plot of DPA in toluene at 375 nm (blue arrow on (a)).

Fig. S7.2: (a): UV-VIS spectrum of DPA in heptane as a function of concentration; (b): Calibration plot of DPA in heptane at 372 nm (blue arrow on (a) graph).

7.8.2 Equipment configuration

7.8.2.1 ECN-TNO

The nanofiltration membrane testing at ECN part of TNO was done in a semi-dead-end test set-up. Semi-dead-end in this case means that the feed liquid is pressurised by nitrogen to create a driving force for flux through the membranes,

while a small flow is maintained on the feed side in order not to increase the overall solute concentration on the feed side. The flow used is low and does not give enough shear force to e.g. clean the membrane surface from particles or molecules that could be attached to this surface.

7.8.2.2 *KU Leuven*

The membranes were evaluated in a high-throughput filtration module which allows to run 16 simultaneous dead-end filtrations with applied pressure of 20 bar and different temperature (room temperature to 80 °C). At least two membrane coupons were tested for different type of membranes. The feed solution was stirred at 400 rpm to minimize concentration polarization. The active area of each membrane coupon was $1.54 \times 10^{-4} \text{ m}^2$.

7.8.2.3 *University of Twente*

The crossflow setup used consisted of a 1L feed vessel from which a dedicated HPLC pump pressurized a circulation loop between 10 and 30 bar of applied pressure by means of a backpressure valve. The feed and retentate are thus both pressurized. The crossflow velocity over a flat membrane active area of 2.8 cm^2 was generated by a separate circulation pump. The temperature was kept constant at $20 \pm 1 \text{ }^\circ\text{C}$.

7.8.2.4 *VITO*

A stainless steel high pressure cross-flow filtration test rig was used, consisting of a temperature-controlled feed tank with capacity of approx. 1 L connected to an external heater, a magnetically driven circulation pump (type D-10, Hydra-Cell, USA), a laboratory-built housing for 1-channel ceramic membranes, as well as pressure and temperature transducers. The modified ceramic membranes were sealed into the housing using Kalrez o-rings. Approximately 1 L of test mixture was used and the trials were carried out in batch filtration mode (permeate recovery limited to max. 8%), at a cross flow velocity of approx. 2 m.s^{-1} , test temperatures of 50, 75, 100°C and transmembrane pressures of 10-15 bar. Nitrogen gas was used to pressurize the vessel.

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CHAPTER EIGHT

Perspectives & Reflections

8.1 INTRODUCTION

This thesis deals with porous ceramics hybridized with polymers for molecular separations. A start had already been made within the Inorganic Membranes group here at the University of Twente: the theses of Pinheiro [1] and Tanardi [2] proved the possibility of grafting PDMS and PEG oligomers onto γ -alumina using organosilane linker chemistry. These works furthermore demonstrated the advantages hybridized ceramic-based membranes brought to the field of organic solvent nanofiltration (OSN) applications in terms of performance of stability. From this start, the need for further research became clear, namely:

- 1) Diversification of graft type,
- 2) Exploration of other grafting methods, and
- 3) Investigation of the mass transport behavior through grafted pores.

This chapter reflects on these lines of research as applied in this thesis. Input is briefly given about the membrane support as well as continuing research into transport modelling of membrane performance. The relationship between graft material and membrane application is examined, followed by the surface modification techniques developed for these materials. Throughout, promising research directions and shortcomings of current investigations are suggested and identified.

8.2 A CASE FOR SUPPORT DIVERSIFICATION

All of the work presented in this thesis rests on γ -alumina supports (Figure 8.1). Its 5 nm diameter pores are only slightly larger than nanofiltration pores yet just large enough for the infiltration of grafting agents for pore size shrinkage and tuning of the surface properties. A variety of grafting chemistry is applicable to the surface of γ -alumina owing to the surface hydroxyl groups covering its surface [3]. However, there are drawbacks to using γ -alumina. The thickness of the γ -alumina layer is 3 μm . Grafting in the whole layer yields too thick a selective layer. The reactivity of the hydroxyl groups can also be a hindrance, as witnessed in Chapters 3 and 4: an extra pre-functionalization step with TMCS was needed to block the interference between hydroxyl groups and the polymerization catalyst. Also, γ -alumina is unstable in strong acid or base [4].

Other materials may provide a thinner and more stable support layer on which to graft. Titania mesopores are available and have demonstrated sturdy covalent attachment with phosphonic acid linker groups [5]. Mesoporous silica membranes with a thickness of only 20 nm were recently fabricated [6], grafting from or onto these would yield a thinner hybrid layer and thus lower resistance. The option to bypass the mesoporous layer and directly graft onto a macroporous is also attractive: reduced support costs and less permeability resistance. These are attractive options that would require adapting not only the grafting technique but also the graft characteristics, such as length and architecture.

Figure 8.1. FE-SEM picture of a γ -alumina mesoporous layer supported by a macroporous α -alumina support.

8.3 A UNIVERSAL, PREDICTIVE MODEL

As detailed upon in Chapter 2, a series of mathematical models for the predictive and descriptive transport through ceramic and hybrid, ceramic-based membranes have been proposed. None of these models, including the one in this thesis (Chapter 6), are able to translate the performance data of a solvent-solute pair across a membrane to accurately predict the performance of other solvent-solute pairs across the same membrane. The ultimate goal, a model which can predict the performance of a membrane from its properties, is not within sight.

The difficulties in the way of this seemingly unsurmountable task are clear. Unlike aqueous filtrations, where water is always the solvent, in OSN the solvents (and mixtures thereof) vary widely. This adds another dimension to the interactions (as shown in Figure 8.2), leading to the qualitatively understood competing affinities between solute-solvent-membrane, which have yielded phenomena such as negative retentions [7]. Additionally, both the membrane materials and structures are diverse. The material choice impacts the transport in nanofiltration more than for ultra- or microfiltration due to the increased contribution of surface effects found in nanofiltration (Figure 8.3). The structures of the selective layer have varied from dense thin-film composites to grafted pores and layers containing a high volume of interconnected pores with high free volume elements. Further complicating this is the impact of the solvent which can swell the selective layer material, changing its structure and thereby its transport behavior [8]. If possible, taking into consideration all of these factors in a single transport model would presumably yield an unwieldy set of equations unable to give a quick approximation.

Relevant to the growing interest in OSN from chemical-related industries is the ability to effectively and efficiently screen membranes for specific applications. So far, the best process is the testing of several membranes in model solutions representing the scenario at hand. Chapter 7 details such an attempt, and its findings agree with the literature: even using varied testing equipments, membranes can be compared against one another. This permits the screening of a variety of membranes across different locations and setups. Until now, this remains the best way to screen membranes for specific applications.

Figure 8.2. Solute-solvent-membrane interaction triangle representing some of the complexities found in OSN

Figure 8.3. Increased impact of material surface properties found in nanofiltration pores (left) if compared to ultra- or microfiltration (right)

8.4 GRAFTED MATERIALS FOR TARGETED APPLICATIONS

In organic solvent nanofiltration (OSN), the well-established solute-solvent-membrane affinity relationship asserts that the surface properties of the selective layer will determine its success in a given application. Simply put, for maximum performance the membrane material should have a higher affinity for the solvent than the solute [9]. The membrane gas separation field holds a similar mantra, seeking to maximize the solubility and diffusivity of the target gas across the membrane. In this thesis, diverse polymers were chosen to be grafted onto porous

alumina for equally diverse applications. In this section the rationale for the material choice vis-à-vis the target application is explained, and, with hindsight, the drawbacks and potential avenues of exploration are discussed.

In Chapter 3, polystyrene was explored as a graft for the nanofiltration of non-polar solvents (Figure 8.4). Linear-chain polystyrene is not a conventional membrane material. It possesses neither intrinsic porosity nor any particular membrane-relevant functionality. However, polystyrene does have high thermal and chemical stability. It is also non-polar, much like the solvents that polymeric membranes typically have trouble handling. Furthermore, styrene is frequently employed in literature as a monomer for controlled polymerization methods [10-11]. The insights found in this body of publications provided a specific starting point for how to conduct the controlled polymerization method (ARGET ATRP) from inside the confined mesopores of γ -alumina. Together these factors suggested that polystyrene, when grafted from ceramic mesopores, would yield a stable membrane and serve as an ideal proof-of-concept for the nanofiltration of solutes in aromatic solvents.

Indeed, the outcome was a membrane with a 90% retention of a 330 Da solute in toluene and a toluene permeability of $2.0 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$. The disadvantage of grafting styrene was in the characterization. Purely made up of carbon, it was impossible to quantify the amount of polystyrene inside the pore using methods such as cross-sectional EDS or XPS combined with consecutive etching. Spectroscopic methods such as FTIR only gave an indication of aromatic presence, but not quantity. So far, HR-MAS-NMR tests (unpublished) have suffered from too low a resolution to estimate the degree of polymerization or give direct proof of the covalent attachment of polystyrene to alumina. As an alternative, the same polymerization procedure with fluorinated styrene (2,3,4,5,6-pentafluorostyrene) was tried but unfortunately proved unsuccessful. The ability to easily characterize the confined graft would yield insight into the kinetics of controlled polymerization in confined volumes, such as mesopores, as well as specific information of the resulting graft, such as the fraction of remaining living chains (as a function of graft length) or the mobility of such a confined graft. Combined with performance data, these insights would guide the

Figure 8.4. Schematic representation of a grafted γ -alumina pore, grafted with polystyrene brushes.

material selection and polymerization conditions for a second generation of grafted-from OSN membranes.

The same ARGET-ATRP procedure developed for polystyrene was adapted to a poly(ionic liquid) (PIL) in Chapter 4. The PIL [StyMim][Tf₂N] was chosen as a suitable graft for CO₂ gas separation. It is well-known to have high CO₂ absorbance, and its unpolymerized, grafted IL counterpart has also shown promise as a CO₂ selective membrane. The grafted IL counterpart was hypothesized to fall short of its own potential due to its pores being only partially closed by the graft. Polymerization of the ionic liquid to fully close the alumina mesopore was a natural solution. With the local expertise of Dr. Pizzoccaro-Zilamy in ionic liquid-based gas separation membranes, a top CO₂ permeance of 0.47×10^{-7} (mol.m⁻².s⁻¹.Pa⁻¹) and a CO₂/N₂ permselectivity of 14 were obtained. Unlike the polystyrene-grafted membranes of Chapter 3, this was not an outstanding performance but does serve as a concrete proof-of-concept of PIL-grafted ceramics for CO₂ gas separation. The IL monomer can be improved in specific ways. First the methyl group of the cation [StyMim] can be extended and fluorinated from C1 to C6-8 [12-14], or, alternatively, switched to an ammonium-based cation [15]. Known anion CO₂ sorption capacities suggest [BF₄] or [PF₆] as potentially better performers [16], though their impact compared to the cation has been questioned [17]. These are only starting points, as ionic liquids are highly customizable and a multitude of synthetic methods have been reported, rendering the possibilities infinite [18].

A novel material was synthesized and adapted into a selective layer in Chapter 5. The thioether-based crosslinked aromatic network was inspired from the biochemistry field, specifically the multi-cyclization of peptides using thioether bonds [19]. The material exhibited high chemical and thermal stability in preliminary tests, urging its development to a selective membrane layer. Efforts yielded a thin (40 nm) selective layer covalently attached to γ -alumina. The performance of the resulting membrane was not optimal, though its potential as a new class of membranes is undisputable: high thermal resistance up to 300°C, stability to base, acid, bleach and non-polar solvents exposure. While a polyethylene glycol (PEG) molecular weight cutoff of 700 Da in water qualifies it as a nanofiltration membrane, the relatively low water permeability of 0.5 L. m⁻²h⁻¹bar⁻¹ should be improved. To understand and remedy the low permeability, the link between monomer, layer structure and membrane performance has to be systematically investigated. The 40 nm-thick layer is perhaps too dense, as indicated by the high amount of connections per thioether unit as well as no detection of meso- or microporosity by N₂ ad/desorption. The positioning of the thiol group (meta versus para or ortho), the spacing between aromatic ring and bromo or thiol functional group and varying the number of functional groups per aromatic ring can serve as starting points.

The inspirations for novel membrane materials in this thesis have come from different sources. Nevertheless, whether sourced from written or oral discussion, inspiration always builds upon the work of others. Similarly, improvements and innovation based upon the new hybrid materials presented in this thesis will also fall to others. It should be kept in mind that the building blocks of the polymers presented are not the only influencer of the properties of the final membrane. The surface and pore medication methods play an equally important role, as discussed in the following section.

8.5 SURFACE & PORE MODIFICATION STRATEGIES

This thesis presents numerous methods to modify a porous ceramic support. Chapters 3 and 4 detail the growth of polystyrene and a poly(ionic liquid), respectively, from the surface of 5 nm pores of γ -alumina. This is done in a controlled manner to be able to diminish the free volume of these mesopores in a sufficient, chosen degree. Chapter 5 presents the fabrication of a thin, thioether-

based crosslinked layer on the surface of γ -alumina for the nanofiltration of polar solvents and extreme aqueous streams. All of these polymers are covalently attached to the surface of the γ -alumina. Though at first glance the end result is similar – polymer grafted ceramic membranes – the strategies employed differ widely.

Grafting-from of the mesopore is the natural evolution of the grafting-to technique. Past attempts to modify the pore surface have focused on the grafting of ready-made molecules or polymers with an integrated linking function ready to bind to the (sometimes pre-functionalized) ceramic surface [20-22]. This approach, however, is intrinsically limited to the availability of compatible, functionalized (macro)molecules and thus unable to precisely tune the pore size and surface properties. Over the last two decades, progress in controlled polymerization techniques have permitted the synthesis of polymer brushes from inorganic substrates with well-defined heights and grafting densities [23-24]. Particularly suited to scale-up and adaptation into applied fields is surface-initiated, activators-regenerated-by-electron-transfer, atom-transfer radical polymerization (SI-ARGET-ATRP) [25]. In chapter 3, this method was adapted, for the first time, to mesopores of 5 nm diameter. The difficulties found associated with grafting-from in a confined, high-curvature concave geometry were *i)* the competing polymerization occurring at the external surface of the membrane and *ii)* the narrow set of conditions that allowed this polymerization to proceed. ARGET-ATRP proceeds via a set of interconnected reagents, and not only the selection thereof but also their ratios impact the polymerization kinetics. This allows for reaction tunability but also for a complexity not approachable to the non-scientific, perhaps the cause of the quotations in the title of the recent review *Grafting from surfaces for "everyone": ARGET ATRP in the presence of air*. [25]. The intrinsic complexity of SI-ARGET-ATRP means any reagent or parameter change quickly becomes convoluted. Adapting the SI-ARGET-ATRP procedure from styrene, described in Chapter 4, to the ionic liquid [StyMim][Tf₂N] (Chapter 5) entailed modifying a host of other parameters. These were all necessary changes to obtain the proper amount of pore closure. Generally, the kinetics of ATRP in bulk solution are well-established [26], the grafting-from of convex surfaces are less-well understood, and the polymerization from high-curvature concave surfaces as grafted in Chapters 3 and 4 even less so. Grafting-from of

mesopores is in its infancy, and while it has produced two performing membranes for two widely different applications, further fundamental understanding would lower the technical threshold for its application to other surface functionalizations and applications.

Innovation in polymerization techniques does not necessarily have to come from the advances of the last decade. Chapter 5 took an 80-year old method, interfacial polymerization, and succeeded in converting it to a green method for the fabrication of a sturdy, ultra-thin membrane. The innovative use of an air-liquid interface to eliminate hazardous solvents while minimizing monomer concentrations a hundred-fold yielded a crosslinked, thioether-based aromatic network covalently linked to a γ -alumina support. As with any new method, further improvements are possible. A methodical study of the reaction parameters (such as time, temperature, concentration, etc.) would indicate the optimum(s) at which a uniform layer would be the thinnest as well as quick to form. This technique could also be adapted to other porous supports besides γ -alumina. For instance, this green air-liquid IP performed directly on a macroporous support would theoretically eliminate the need for a mesoporous layer, reducing cost and permeability resistance.

8.6 TOWARDS PILOT-SCALE

Three new membranes types are presented in Chapters 3, 4 and 5. All of these are done on flat sheet membranes with a surface area of 11.9 cm². Assuming sufficient performance improvements in the second generation of these membranes to draw industry interest, pilot-scale membrane trials are the next step. The membrane geometry then shifts to a tubular configuration, and the grafting procedures have to be adopted. Chapter 3 & 4 make use of the same newly developed grafting-from mesopores method, while Chapter 5 renovates the interfacial polymerization concept. The complexity and sensitivity of the grafting-from procedure, described in Chapters 3 & 4, including its three, separate support pre-functionalization steps, will inherently face more challenges and fine-tuning than the newly developed air-liquid IP procedure of Chapter 5. This thioether network fabrication method also benefits from the exclusive use of green solvents and minimal reagents and reagent concentrations. Both its single pre-functionalization by grafting at the air-liquid interface should be

straightforward to replicate in a tubular geometry. In my opinion, this method has greater potential for adoption to upscaled membrane geometries.

8.7 CONCLUSION

The research presented in this thesis continues to explore the potential of polymer-grafted ceramics for molecular separations. A mindset for both materials and fabrication methods with a clear target application are required when developing membrane materials. This has allowed the fabrication of three novel membrane types for three different applications areas. Polymer-grafted ceramics continue to diversify and prove their potential in emerging membrane application fields.

8.8 REFERENCES

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List of Publications

Amirilargani, M., Merlet, R.B., Chu, L., Nijmeijer, A., Winnubst, L., de Smet, L.C.P.M., Sudhölter, E.J.R., Molecular separation using poly (styrene-co-maleic anhydride) grafted to Γ -alumina: Surface versus pore modification (2019) *Journal of Membrane Science*, 582, pp. 298-306.

Merlet, R.B., Amirilargani, M., de Smet, L.C.P.M., Sudhölter, E.J.R., Nijmeijer, A., Winnubst, L. Growing to shrink: Nano-tunable polystyrene brushes inside 5 nm mesopores (2019) *Journal of Membrane Science*, 572, pp. 632-640.

Amirilargani, M., Merlet, R.B., Hedayati, P., Nijmeijer, A., Winnubst, L., De Smet, L.C.P.M., Sudhölter, E.J.R. MIL-53(Al) and NH₂-MIL-53(Al) modified α -alumina membranes for efficient adsorption of dyes from organic solvents (2019) *Chemical Communications*, 55 (28), pp. 4119-4122.

Amirilargani, M., Merlet, R.B., Nijmeijer, A., Winnubst, L., de Smet, L.C.P.M., Sudhölter, E.J.R. Poly (maleic anhydride-alt-1-alkenes) directly grafted to Γ -alumina for high-performance organic solvent nanofiltration membranes. (2018) *Journal of Membrane Science*, 564, pp. 259-266.

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About the Author

Renaud Merlet was born in Paris in 1986. After finishing high school in Newton, MA (USA), he graduated from the Georgia Institute of Technology (Atlanta, GA) with a B.S. in Polymer Engineering. For the next 4 years he worked at Kemira as a specialty chemicals scientist in R&D. It was there he was introduced to membranes, which he continued studying during the European EM3E program (Erasmus Mundus Master's in Membrane

Engineering). This program took him from Montpellier, France (first semester) to Prague (second semester) and finally to Enschede (second year). There he received his M.S. in Chemical Engineering upon completion of his thesis “Self-assembled membranes for water ultrafiltration” under the supervision of Wiebe de Vos at the University of Twente in 2015. Electing to stay at the University of Twente, Renaud started a Ph.D. under the supervision of Louis Winnubst and Arian Nijmeijer. This Ph.D. project, titled “Modular functionalized hybrid organic-inorganic membranes” was in partnership with TU Delft and jointly funded by the Institute for Sustainable Process Technology (ISPT) and the Netherlands Organization for Scientific Research (NWO). On November 1, Renaud started his new role as Process Development Engineer at Corbion in Gorichem, Netherlands.