

Development of novel porous materials via polymer self-assembly and phase separation



A thesis submitted to the School of Chemistry,

Trinity College Dublin,

For the degree of Doctor of Philosophy

By **Nadezda Prochukhan**

2023

Supervisor: Prof. Michael A. Morris

Declaration

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Abstract

Polymer self-assembly is an ever-growing field that is attracting interest from a diverse range of research topics, which include the production of functional devices and membranes for electronic, optical and energy applications, as well as more established areas such as filtration and separation. This interest stems from the environmentally friendly and low-cost nature of the ‘bottom-up’ self-assembly process, when compared to more established top-down techniques. Nonetheless, there remain several challenges to implementing self-assembling systems into conventional manufacturing, especially in the case of novel membranes and nanostructures derived from biopolymers; these include gaps in research on controlling the self-assembly process, along with developing novel applications and devices using self-assembled materials. This thesis aims to address some of these limitations by closely examining the behavior and function of several self-assembling polymer systems.

Chapter 1 details the background and rationale for this research. An overview of polymers, self-assembly, membranes, polymer brushes and block-copolymers (BCPs) which are used in the work are provided. The subsequent chapters look at experimental approaches aimed at tackling some of the challenges associated with membrane and porous film production technologies in an eco-friendly manner.

Chapter 2 examines the problem of large-scale membrane production in a financially and an environmentally viable manner. A widely recycled polymer poly(methyl methacrylate) (PMMA) and a biopolymer chitosan are employed for membrane fabrication. A custom-built apparatus is used to promote membrane formation by thermally induced phase separation (TIPS) and water vapour induced phase separation (VIPS). These methods are designed to limit solvent and material waste and reduce energy costs by using low electricity and temperatures. Furthermore, a strategy to produce thoroughly functionalized PMMA is provided via silanization with (3-aminopropyl)triethoxysilane (APTS). Another challenge is to characterize 3D materials; thus, a Focused Ion Beam (FIB-SEM) tomography is detailed as a method to analyze these morphologically complex systems. These membranes were also tested for their tensile properties

and filtration capability using Evans Blue dye in order to demonstrate their functional capacity.

Chapter 3 focuses primarily on the reproducibility of pore sizes and asymmetry with the aim to fabricate novel porous systems with the least waste possible. A block copolymer polystyrene-*b*-poly(ethylene oxide) (PS-*b*-PEO) self-assembly is investigated using water vapour annealing (WVA) at room conditions as a sustainable processing methodology. The resultant toroidal micelles display pore sizes of ~ 400 – 600 nm with uniform shape-characteristics. To demonstrate a practical application, the micellar morphology is used for pattern transfer to produce silicon nanotube arrays. Despite the low amounts of polymer and solvents being employed, it is crucial to utilize the most ecologically competitive methods and materials.

Chapter 4 takes a similar approach to Chapter 3, but uses lignin, a highly abundant biopolymer, to produce membranes with high fidelity. Chapter 3 details the self-assembly of four different lignin materials into membranes facilitated by the WVA. The membrane systems are optimized for production of black silicon (BSi) which exhibits low reflectivity in the visible region. This approach opens up avenues for large-scale biopolymer membrane fabrication using cheap and abundant chemicals (lignin and water) for solar cell technology and potentially other applications.

Chapter 5 outlines the main findings in this work in context of the goals and achievements in this thesis. A future perspective and direction for research is provided with the aim of focusing on environmentally sustainable methods from the onset of material design.

Acknowledgements

I would like to thank my supervisor Prof. Mick Morris for the opportunity to complete my PhD in such an exciting and interesting field. His guidance, advice and feedback during the four years was invaluable. I am also grateful to Prof. Morris for backing my ideas and allowing me to develop other skills outside research.

I am grateful to the Morris group researchers for helping with tips along the way as well as organizing fun outings. I would like to thank Andrew Selkirk in particular as he contributed majorly to my research and also gave indispensable advice in general. Thanks for all the not so fun proofreading and being a great friend, Andrew! A special thanks to Ross Lundy for advice on science and theories and explaining how things work in the field. I would like to thank Elsa Giraud and Tom O'Mahony for helping with research, especially at the start of the PhD. Thanks to Eleanor Mullen for all the laughs and random experiments we conducted in the lab (and soap making at home). Thanks to Sukhananazerin Abdulla for deleting all the unnecessary blank pages and allowing me to submit! I am thankful to the other colleagues in the group for the advice, the coffees and the pints, including Pravind, Aislan, Bríd, Jhonattan, June, Lipeeka, Arantxa, Phil, Tandra, Suhana, Lydia, Abbie, Dave, Sibü, Niall, Sumit, Sajan. I would also like to thank Ram, Saranya and Jessica in the Ramesh Babu group for all the help. I would also like to thank the staff in AML (Megan, Dermot, Clive, Cathal), CRANN (Aran, Riley, Neal and others), Chemistry dept (Manuel and John), UL (Sergey) for the help with research and instrumentation. Thanks to the other researchers that I have worked with in TCD and other universities (too many to mention) for all the help!

I would like to say thanks to my friend in TCD and elsewhere, Andrew, Eleanor, Leigh, Joanne, Anfisa, June, Natalia, Éadaoin, Mariah, Alan, Bozhena, Marie, Célia and others, (sorry if I haven't mentioned you), for continuous support during the PhD. Thanks for all the useful advice on admin issues, other research related stuff and all the encouragement!

Last but not least, I would like to thank my family for all the support along the way, I wouldn't have been able to pursue the PhD without such a great family. Thanks to my mother Tatiana for always being encouraging and supportive in everything

I do. Thanks to my grandmother Nina for always keeping in touch and always being optimistic and motivating. Thanks to my sister Mariia for the support, bringing me groceries when I was too lazy and occasional outings. Thanks to my mother's partner Conrado (Pio) for all the great cooking and advice! Thanks to my late aunt Lida for being supportive and always keeping in touch. I would also like to thank my late grandfather Vladimir for introducing me to science early in life and encouraging me to pursue research as well as being my best friend. I am grateful to my late father Yunes for making sure Mariia and I had a great childhood and also thanks for always being supportive.

Abbreviations

3D	Three dimensional
AcOH	Acetic acid
AFM	Atomic force microscopy
APTS	(3-aminopropyl)triethoxysilane
BCP	Block copolymer
BET	Brunauer-Emmet Teller
CA	Contact Angle
CFT	Capillary flow time
CP/MAS	Cross-Polarization Magic Angle Spinning
DSC	Dynamic scanning calorimetry
EtOH	Ethanol
FIB	Focused ion beam
FTIR	Fourier transform infrared spectroscopy
Gly	Glycerol
GPC	Gel permeation chromatography
ICP – RIE	Inductively coupled plasma – reactive ion etch
LSCM	Laser scanning confocal microscopy
MIP	Mercury intrusion porosimetry
NMR	Nuclear magnetic resonance
PDI	Polydispersity index
PEG	Polyethylene glycol
PEO	Polyethylene oxide
PMMA	Poly(methyl methacrylate)
ppm	Parts per million
PS	Polystyrene
PS-<i>b</i>-PEO	Polystyrene- <i>block</i> -poly(ethylene oxide)
SDBS	Sodium dodecyl benzene sulphonate
SE	Surface Energy
SEM	Scanning electron microscopy
Si	Silicon

TEM	Transmission electron microscopy
TGA	Thermogravimetric analysis
THF	Tetrahydrofuran
TIPS	Thermally induced phase separation
UV	Ultraviolet
UVO	UV/ozone
UV-Vis	Ultraviolet-visible spectroscopy
VIPS	Vapour induced phase separation
wt%	Weight percent
WVA	Water vapour annealing
XPS	X-ray photoelectron spectroscopy

Notes on Publications

Certain parts of this work have been published in peer-reviewed journals prior to submission of this thesis.

Sections of chapter 3 were published in the article “Large-Area Fabrication of Vertical Silicon Nanotube Arrays via Toroidal Micelle Self-Assembly”, co-authored with Andrew Selkirk, Ross Lundy, Elsa C. Giraud, Tandra Ghoshal, Clive Downing, and Michael A. Morris.

Sections of chapter 4 were published in the article “Room Temperature Fabrication of Macroporous Lignin Membranes for the Scalable Production of Black Silicon”, co-authored with Stephen A. O'Brien, Arantxa Davó-Quiñonero, Anna Trubetskaya, Eoin Cotter, Andrew Selkirk, Ramsankar Senthamaraikannan, Manuel Ruether, David McCloskey, and Michael A. Morris.

Certain parts of chapter 2 are in preparation for submission entitled “Development and application of a 3D image analysis strategy for FIB-SEM tomography of porous soft materials”. Other sections of chapter 2 are under preparation for submission under the working title “Optimization of self-assembled monolayers of (3-Aminopropyl)triethoxysilane on polymer brushes”.

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1. Introduction

1.1. Motivation and Background

Polymer self-assembly offers an attractive bottom-up strategy for the development of novel functional materials, enabling significant reductions in production costs along with high potential scalability.^{1,2} Possible areas of application include membranes,^{3,4} patterned nanodevices,⁵ selective coatings^{6,7} and drug delivery by encapsulating the drug inside self-assembled micelles⁸ among others. Nonetheless, there remain significant obstacles to the implementation of self-assembly methodologies in conventional industrial processes; these include potential environmental impact such as toxic solvents and nonbiodegradable materials use that require post processing for recycling.

One crucial source of the environmental concern is the widespread use of toxic solvents and non-recyclable materials in self-assembly strategies. Hence, it is essential to develop novel methodologies that reduce solvent use and utilise alternative biodegradable materials. For example, thermally induced phase separation (TIPS) for membrane fabrication uses less solvents than conventional self-assembly strategies.⁹ Another example is using block copolymer (BCP) self-assembly to produce large scale nanopatterned films without the need of costly machinery.^{5,10} In comparison to other self-assembly strategies, these processes require little solvent vapour and are capable of producing large-area, uniform features within seconds.^{11,12}

As previously mentioned, one area of application that may particularly benefit from the implementation of green materials is membrane fabrication. This is a rapidly growing field due to the avoidance of massive costs associated with alternative waste separation methods such as high-performance liquid chromatography (HPLC), electrostatic separation, magnetic density separation, flotation, and sensor-based sorting.^{13–16} Hence, there is a societal and industrial value in producing novel porous materials, particularly biodegradable membranes.^{17–19} Porous materials are also utilized in a variety of sensing and catalysis applications due to their large surface areas.^{20–22} One such material is a biopolymer known as lignin, which is derived from wood.²³ Lignin has potential uses in membrane fabrication,^{24,25} functional composite materials^{26,27} and

functional device applications such as energy storage,²⁸ wearable electronic devices²⁹ and transient devices.³⁰ Chitosan is another biodegradable material derived from the shells of crustaceans.³¹ Similarly, chitosan is oftentimes used in membrane production,³² food packaging³³ and antimicrobial coatings.³⁴

Despite recent progress, there remain a number of barriers that must be overcome for the industrial adaptation of these green materials and methods to be successful. These roadblocks include optimisation of greener methodologies for large scale production as well as control and reproducibility. Currently the field of biopolymer self-assembly research is increasing and gaining visibility, however, it is still at its early stages. Conventional methods without environmental assessment remain more widely used largely due to extensive documentation, available machinery and well-understood theories.^{35,36} Even though those methods come with a high environmental and financial cost,³⁷ they are presently easier to implement in industry due to high process controllability and lower risk of process failure.³⁸ Thus, it is important to fully optimise self-assembly of green materials such as lignin to compete with current methods^{39–41} and to develop alternative sustainable and scalable methods for material design such as membrane production.⁴²

The aim of this thesis is to address these issues by investigating greener methodologies to material production and biopolymer self-assembly for fabrication of porous films. Ecofriendly annealing methods are employed, including self-assembly enhanced by water vapour along with ambient conditions such as annealing at or close to room temperature. Various polymers (both synthetic and bio-derived) are explored such as poly(methyl methacrylate) (PMMA), chitosan, polystyrene-*b*-poly(ethylene oxide) (PS-*b*-PEO) and lignin to form porous structures such as membranes, nanotubes and other morphologies for applications such as filtration, patterning and optics.

1.2. Aims and Context of the Thesis

My thesis work focused on two main goals (**Figure 1.1**): (1) to choose the most environmentally friendly available polymer-solvent system and (2) to make the process of membrane fabrication as eco-friendly as possible. Stemming from the

two main objectives, each of the results chapters investigates various issues associated with porous film production, namely reproducibility, scalability, applicability to various areas and issues with characterization of novel materials.

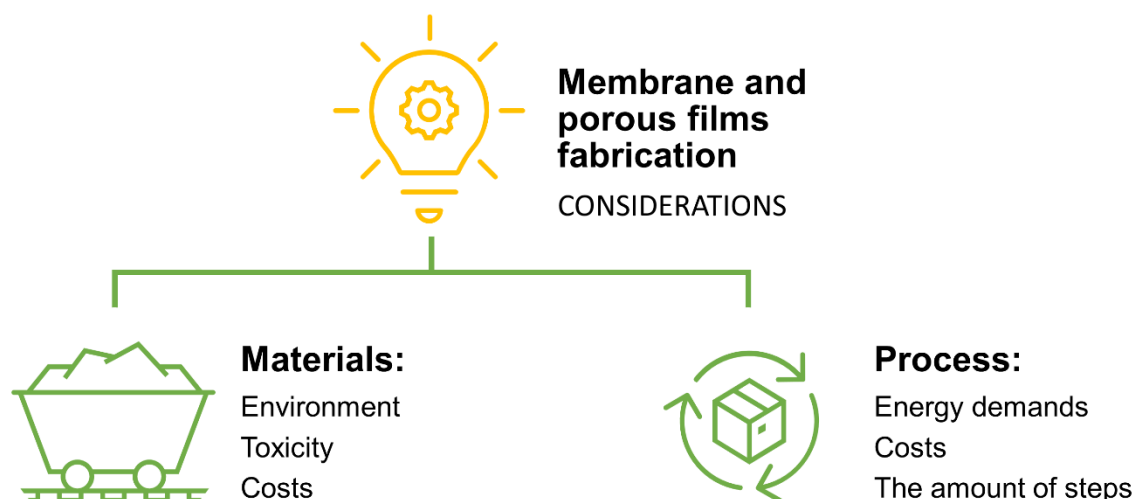


Figure 1.1. Main considerations whilst designing a new porous material.

The specific experimental chapters detail different polymer systems (synthetic, block copolymer and biopolymer) and inherent challenges related to porous film production. The primary goals in each chapter were to design systems and processes with low financial and environmental demands, which include thermal and vapour annealing (chapters 2 – 4), biopolymers (chitosan and lignin – chapters 2 and 4) and low temperatures (chapters 2 – 4). Other aspects that were investigated are large-scale production capability (chapters 2 and 4), reproducibility of morphology (chapters 3 and 4), pattern transfer (chapters 3 and 4) and functionality (chapter 2 – filtration and chapter 4 – optics).

The polymer systems were chosen as either a widely recycled polymer (PMMA), a commonly used block copolymer (PS-*b*-PEO) and abundant biopolymers (chitosan and lignin). The aim was to use what is already widely available (materials and machinery) and methods that can be transferred to an industrial setting. In summary, dry phase separation and water vapour annealing were

deduced to be the easiest to implement in terms of available technology, machinery, steps, costs and environmental concerns. Thus, the following chapters investigate those systems in terms of membrane and porous film forming capability as well as potential functionality. **Table 1.1** details the overall goals associated with individual experimental chapters.

Table 1.1. Overall and specific goals associated with the results chapters in this thesis.

	Aims
Chapter 2	Overall goal: Provide a method for large-scale membrane production with low-cost methodology, where pore sizes and shapes can be variable across membrane material. • Reduce solvent waste i.e., TIPS and VIPS methods. • Employ eco-friendly materials such as biopolymers and green solvents • Reduce energy costs, i.e., accessible temperatures. • Develop a fully functionalised membrane with moieties available for binding of peptides and other chemicals. • Develop a methodology to characterize membranes in 3D in terms of pore size and shape characteristics. • Investigate pore size and shape reproducibility and tensile properties.
Chapter 3	Overall goal: Tackle the issue of pore size and shape reproducibility associated with conventional methods such as phase separation. • Fabricate porous structures with a narrow pore size distribution and reproducible shapes by using a block copolymer system. • Employ an environmentally viable annealing method – water vapour facilitated annealing. • Investigate factors affecting thin film morphology – surface energy, thickness etc. • Develop a method to transfer the pattern on a different substrate such as etching onto silicon
Chapter 4	Overall goal: Develop an easy, scalable, environmentally friendly approach for membrane production using an abundant biopolymer. • Employ the methodology in chapter 4 to anneal a biopolymer system (lignin). • Investigate the reproducibility of the methodology – stability over time, use of different biopolymer sources and substrates. • Examine the possibility of an application – for example pattern transfer and investigate the optical properties.

1.3. Polymer Theory

1.3.1. Polymer Structures and Families

To design suitable polymer self-assembling systems with precise control over morphology, it is important to understand polymer types and properties. Polymers are long chain molecules of repeating units called monomers. There are several ways by which polymers can be classified based on their properties, nature of material, or structure; at a fundamental level, polymers can be described by a four level system: primary (atomic composition), secondary (geometry), tertiary (folding) and quaternary structures (overall structure or morphology).⁴³ Another type of classification includes the source of the polymer – whether that be synthetic or biopolymer. With regards to structures, polymers can be classified into four major categories: linear, branched, crosslinked and network polymers, as seen in **Figure 1.2**. Linear and branched polymers can then be further divided by isomerism, such as *cis* and *trans*, as well as tacticity or stereo arrangement around the backbone: isotactic (groups always on the same side), syndiotactic (groups alternating sides) and atactic (random arrangement in space).^{43,44}

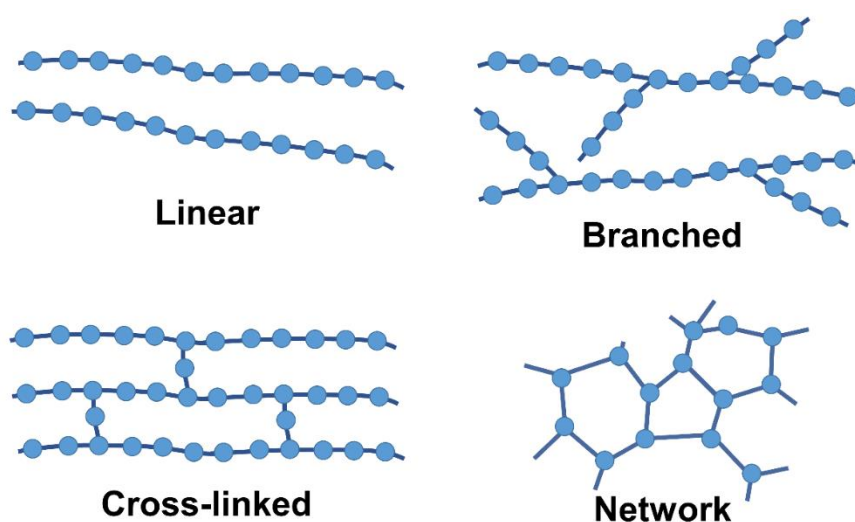


Figure 1.2. The four structural classes of polymers. Adapted from Callister (2001).⁴⁴

Polymers can also be defined by the chemical nature of the monomers – the same monomer throughout makes up a homopolymer, whereas different

monomers in a single chain comprise a heteropolymer.⁴⁵ A regularly repeating pattern of more than one type of monomers is referred to as a copolymer.^{45,46} The arrangements of different monomers in a chain are classified as random, alternating, block and graft copolymers, as seen in **Figure 1.3**.^{46,47} Alternating copolymers' structural unit is simply two or more monomers that regularly alternate down the chain, whereas random copolymers are defined by a random arrangement of monomers.⁴⁶ A graft copolymer, as the name implies, has a homopolymer chain backbone with other monomers grafted onto it.⁴⁶ Lastly, a block copolymer is a linear chain of different homopolymer blocks.⁴⁶

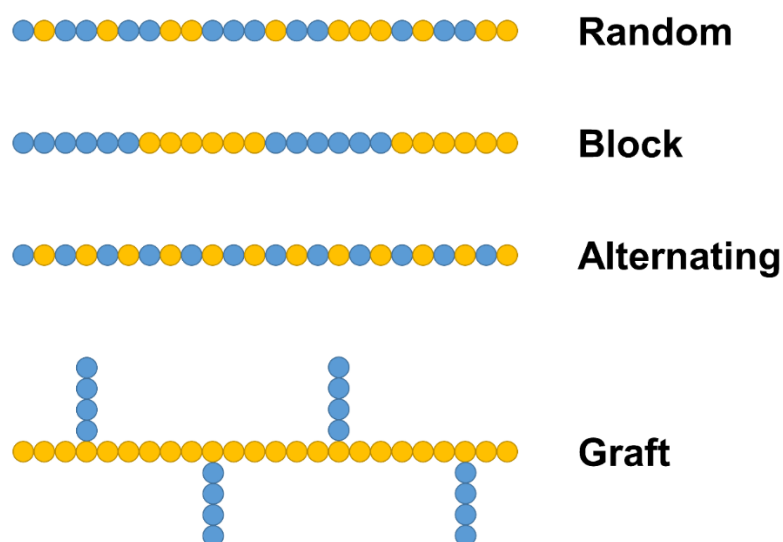


Figure 1.3. Representation of possible copolymer arrangements. Adapted from Callister (2001) and Gromadzki (2010).^{44,47}

In general, the chemical nature of the backbone and the spatial arrangement of groups define the interactions that occur between polymer units and the surrounding environment and hence affect the resulting properties of the polymer material.

1.3.2. Polymer Interactions

The architecture of a polymer and its regularity determines the interactions it can display with itself and moieties around it. The polymer interactions can be modeled using respective monomers present, using interaction energy as a function of their separation. A small repulsive component exists at very short distances ($\sim r^{-12}$ dependence),⁴⁸ therefore the main interactions of interest are intermolecular interactions such as dispersive, dipole-dipole and hydrogen bonding.⁴³

Dipole-dipole interactions can be either between permanent dipoles, i.e. polar groups, or induced dipoles as a result of a polar moiety inducing a dipole on a non-polar group.^{49,50} The charge differences across covalent bonds in polymers give rise to permanent dipoles observed in polar groups. This gives rise to intermolecular attraction due to oppositely charged groups. Note, however, that these interactions are a minor component of the overall polymer-polymer attractive forces due to the hydrocarbon backbone. Dispersive forces on the other hand, account for major interactions in hydrocarbon polymers, especially in the absence of permanent dipoles.⁴⁹ Dispersive forces or London dispersion forces are in fact a component of van der Waals interactions, however for polymeric systems it is useful to consider it separately due to it often being the major interaction.^{51,52} Dispersion forces arise due to the time component of the electron positions, which give rise to time-dependent temporary dipoles.⁵³ Thus, even in non-polar groups there is an intermolecular attraction due to dispersive forces. Another major source of interaction is hydrogen bonding, however this only occurs in the presence of a proton donor and a proton acceptor such as a hydroxyl or carboxyl oxygen.^{49,54} All those forces explain intermolecular attraction between polymers and polymer-solvent interactions. Nevertheless, some polymers display low miscibility in certain solvents due to chemical dissimilarities. Those differences can be quantified using intermolecular forces as a basis.

1.3.3. Polymer Solubility Theory

Solvent-polymer and polymer-polymer interactions play a central role in the self-assembly process; hence, it is important to understand how to quantify such

interactions. Hildebrand and Scott initially defined the solubility parameter, δ , as the square root of cohesive energy density (CED):^{52,55,56}

$$\delta = \sqrt{CED} = \sqrt{\frac{\Delta U}{V}} = \sqrt{\frac{\Delta H^{vap} - RT}{V}} \quad [1.1]$$

where ΔU is molar internal energy, ΔH^{vap} is the enthalpy of vaporization, V is molar volume, T is the temperature in Kelvin and R is the universal gas constant.^{52,55,56} However, it is important to describe the interaction parameter empirically. Thus, a more useful approach developed by Hansen is to consider individual intermolecular interactions separately, where the total (Hildebrand) solubility parameter δ is described in terms of atomic dispersion forces (δ_D), permanent dipole-dipole forces (δ_P) and hydrogen bonding (δ_H) as contributors to total cohesive energy:⁵²

$$\delta^2 = \delta_D^2 + \delta_P^2 + \delta_H^2 \quad [1.2]$$

The solubility of 2 components can be systematically defined by distance Ra developed by Skaarup:⁵²

$$(Ra)^2 = 4(\delta_{D1} - \delta_{D2})^2 + (\delta_{P1} - \delta_{P2})^2 + (\delta_{H1} - \delta_{H2})^2 \quad [1.3]$$

where 1 and 2 are indices representing the 2 components. This approach represents solubility points as a sphere in 3D space where shorter distance essentially means better solubility.⁵²

It is important to define the polymer-solvent system behaviour quantitatively for practical applications. The Flory-Huggins model defines χ as the solvent-polymer interaction parameter.⁵⁷ The conventional solubility theory relates Hildebrand parameters to χ , however Hansen parameters give a better representation:⁵⁸

$$\chi_{12} = \alpha \frac{V}{4RT} (4(\delta_{D1} - \delta_{D2})^2 + (\delta_{P1} - \delta_{P2})^2 + (\delta_{H1} - \delta_{H2})^2) \quad [1.4]$$

where V is molar volume of solution (approximated as the molar volume of the solvent for dilute solutions), subscripts 1 and 2 represent the polymer (its respective monomer) and the solvent, α is a constant and it is assumed to be $\alpha = 1$ for systems whereby dispersion forces are dominant, R is the ideal gas constant, T represents the temperature in Kelvin.^{52,58} The solvent and polymer

are completely miscible if $\chi_{12} \leq 0.5$ as described by the Flory-Huggins model.^{52,58} This model is often used to design solvent systems for polymer materials under investigation.^{59,60}

The same principle can be used to study polymer-polymer interactions, in which case the V in **Equation 1.5** instead becomes the geometric mean of monomer volumes:

$$V = \bar{V}_{12} = \sqrt{(v_1 M_2)(v_2 M_1)} \quad [1.5]$$

where subscripts 1 and 2 represent the monomers of polymer 1 and polymer 2 respectively, v is the monomer specific volume and M is the monomer molecular weight.⁵² Polymer-polymer interactions become important when considering chemically dissimilar monomers in one chain (such as is the case for block copolymers). The Hansen parameters and molar volumes used in this work are shown in **Table 1.2**.

Table 1.2. Hansen Solubility Parameters as obtained from the Hansen Solubility parameters and molar volumes of selected systems used in this work.

Compound	Hansen Solubility Parameters			Molar Volume, V_m (cm ³ mol ⁻¹) at 25 °C
	δd (MPa ^{0.5})	δp (MPa ^{0.5})	δh (MPa ^{0.5})	
Methyl methacrylate	18.6	10.5	5.7	87.1
Styrene	18.6	1.0	4.1	98.8
Ethylene oxide	15.6	10.0	11.0	39.3
Acetone	15.5	10.4	7.0	74.0
Ethanol	15.8	8.8	19.4	58.5
Water	15.5	16.0	42.3	18.0
Chloroform	17.8	3.1	5.7	80.7
Tetrahydrofuran	16.8	5.7	8.0	81.7
Toluene	18.0	1.4	2.0	106.8

The nature of chemical groups, the monomeric arrangement and the degree of polymerization directly affect the structure or conformation that the polymer adopts.⁴⁵ For a linear polymer chain in solution, the size of the polymer (end-to-end length) can be described as:

$$R \sim N^\nu \quad [1.6]$$

where N is the degree of polymerization (or the number of monomers) and ν is the Flory exponent which is related to fractal dimension as $D = 1/\nu$.^{45,61} Thus, the end-to-end length is dependent on factors such as temperature and the quality of solvent. In the case of either lower temperature or low solvent-polymer interaction, the chain contracts to form globules.⁴⁵ Likewise, high temperatures and high polymer-solvent interaction will lead to the dissolution of globules and thus chain elongation. Therefore, the nature of solvent affects the resultant bulk polymer material morphology, which thereby enables the formation of repeating self-assembled patterns.

1.3.4. Polymer Properties

Polymer interactions affect the resultant properties of materials such as crystallinity and phase transitions of polymers. Polymer behaviour is largely governed by chain length and the nature of the functional groups in the repeating monomeric block. The fact that the polymer is a long chain of chemically bonded monomers makes it inherently different from its monomer. Polymers are therefore characterized by the degree of polymerization or the number of monomers N and the molar mass M , which are related as follows:

$$N = \frac{M}{M_{monomer}} \quad [1.7]$$

where $M_{monomer}$ is the molar mass of the respective monomer.⁴⁵ The degree of polymerization can affect properties such as transition temperatures, e.g. the glass transition temperature and softening point, as well as the tensile properties of the material.⁴³

The polymer chain behaviour heavily depends on the length, as at a certain degree of polymerization or molecular weight the chains begin to entangle. This is important as upon entanglement, the polymer behaviour becomes cooperative or dependent on other chains.^{43,62} Therefore, viscosity or impediment to flow is directly affected by this critical chain length.^{43,63} For shorter chains, the viscosity η is linearly proportional to molecular weight M , whereas for entangled polymers the relationship becomes $\eta \sim M^{3.4}$.⁴⁵ A long-chain polymer “reptates” along a so-called confining tube rather than flowing freely.⁴⁵ Thus, polymer bulk properties

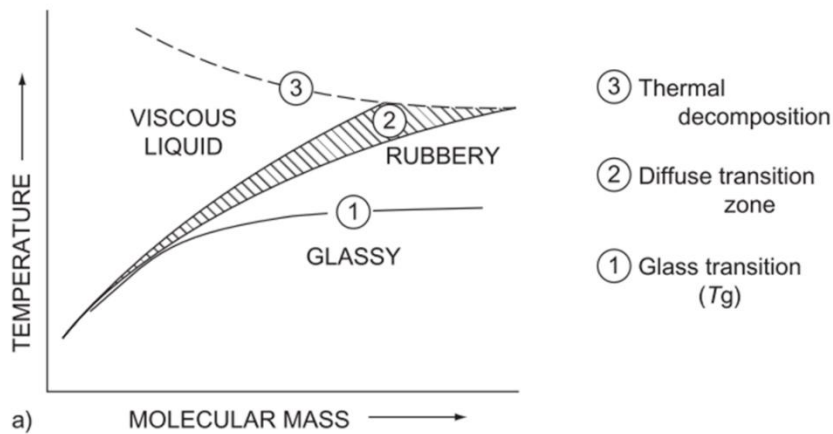
and solution behaviour depends on chain length; however different regions in bulk material can also display different qualities due to differences in external conditions and chain packing.

Polymer behaviour is also largely governed by crystallinity and the available range of ordered morphologies. The usual degree of crystallinity is defined as the ratio of amorphous regions (random coil in glassy or rubbery state) to crystalline regions (ordered lamellar structures).^{43,46} A polymer, unlike its monomeric counterpart, undergoes a number of phase transitions represented by **Figure 1.4**, which are dependent on ordering as well as molar mass or degree of polymerization.⁴⁶ Thus, for higher molar mass, transition temperatures tend to be higher but decomposition temperature is lower.

Generally, polymers are subdivided into three major classes governed by mechanical properties – thermoplastics, thermosets and elastomers. Thermoplastics are amorphous or semi-crystalline with a certain degree of flow or plasticity and high hardness on cooling.⁴⁶ Thermosets are cross-linked polymers which means that they do not soften upon heating as free flow is hindered.^{43,46} Elastomers, as the name implies, they are highly elastic, i.e. flexible, and the deformations are reversible.⁶⁴ It is important to note that thermoplastics are primarily used in this work and thus, they will be focused on.

These aforementioned properties are important when designing a polymer system. Other properties to consider include mechanical properties such as elasticity and tensile strength. In general, thermoplastics can fail due to brittle behaviour or loss of ductility.⁴⁶ This can be alleviated by cross-linking.⁴³ The glass transition temperature T_g is another predictor of how the polymer will behave. It is defined as the transition of amorphous regions from a glassy state (hard state) to a rubbery state (viscous state).⁴⁶ At temperatures below T_g , thermoplastics tend to be brittle but above the T_g the chains can flow.⁶⁵ Thus, knowing T_g is essential to understand the onset of self-assembly and polymer chain alignment in other processes such as polymer membrane fabrication.

Amorphous polymer



Semi-crystalline polymer

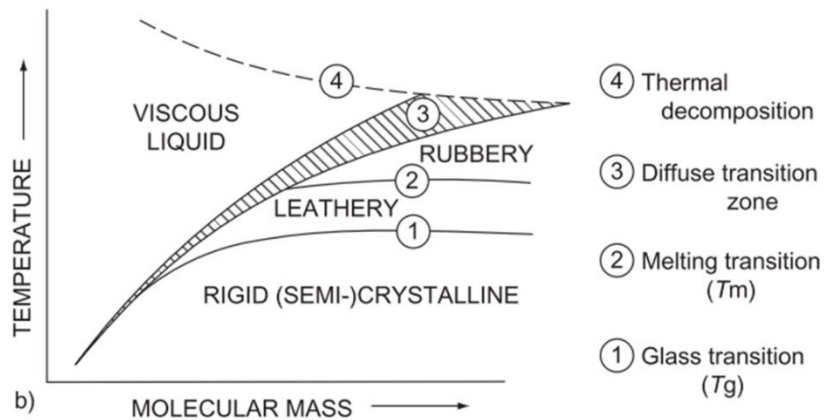


Figure 1.4. Temperature vs molecular mass dependence for amorphous and semi-crystalline thermoplastic polymers. Adapted from Van Krevelen and Te Nijenhuis (2009).⁴⁶

1.4. Membrane Theory

1.4.1. Membrane Classification

A membrane can be defined as a thin film that allows for the selective transport of materials across its structure. Membranes provide an easy, low-cost method for the separation of materials, with applications in areas such as bio-separation, water purification, microelectronics and various others.⁶⁶

Membranes can be classified by their porosity and mechanism of separation. Typically, pressure-driven filtration membranes are subdivided into categories such as microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) membranes.^{67,68} Those categories are represented in **Figure 1.5**, where the pore size defines the separation method. Apart from conventional dead-end filtration processes, cross-flow (i.e., the feed flow travels tangentially across the filter surface)⁶⁹ and lateral flow assays (i.e., the feed enters the membrane but it travels through the membrane along its length, usually positioned horizontally) are also utilised.^{68,70} Another broader way to classify porous materials according to pore size is IUPAC notation, which includes three categories: microporous (pore < 2 nm), mesoporous (pore size between 2 and 50 nm) and macroporous (pore size ~over 50 nm).⁷¹

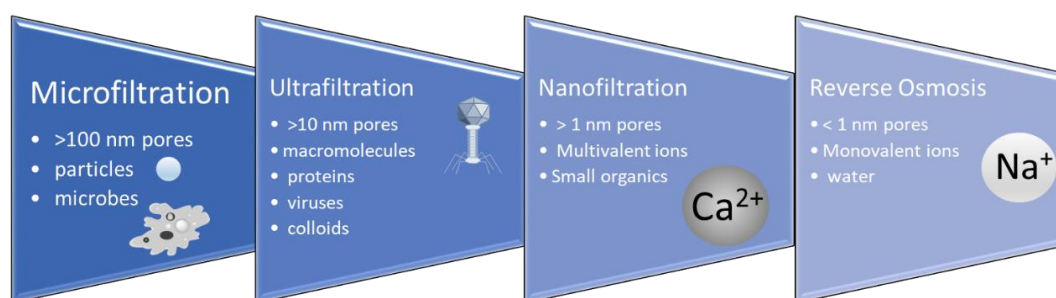


Figure 1.5. Representation of pressure-driven filtration methods and related pore sizes. Adapted from Van der Bruggen (2018) and Baker (2012).^{68,72}

Membranes can be additionally classified by structure or isotropy.⁷² Isotropic membranes have a uniform density, chemical composition and morphology throughout the structure.⁷² It is feasible to prepare isotropic membranes *via* pore etching whereby a hard mask template is commonly used.^{72,73} Anisotropic membranes display variable density, porosity and composition.⁷² Membranes produced *via* phase separation techniques are typically anisotropic, where the top skin layer is typically selective and the layers below down to the bottom layer (belt layer) are highly porous.^{72,74}

1.4.2. Membrane Transport Theory

The transfer of material through a membrane is governed by the laws of diffusion, where individual theories exist for each type of filtration. For the purposes of biomolecule separation, both microfiltration and ultrafiltration are applicable. The phases in a filtration system are defined to exist in an equilibrium state by electrochemical potential:

$$\mu_i = \mu_i^\circ + RT \ln \alpha_i + V_i(p - p_i^\circ) + (z_i F \psi) \quad [1.8]$$

where, μ_i is the electrochemical potential of component i , μ_i° is the chemical potential of component i at reference pressure, p_i° , R is the ideal gas constant, T is temperature, α_i is the activity of component i , V_i is the molar volume of component i and p is the pressure.^{68,72} For charged components, the $z_i F \psi$ part applies, where z_i is the ion valence (0 for uncharged compounds), F is the Faraday constant and ψ is the electrical potential.⁶⁸ **Equation 1.8** holds true for incompressible phases such as membranes.⁷² It is possible to express the driving force in terms of chemical potential to yield flux:

$$J_i = -L_i \frac{d\mu_i}{dx} \quad [1.9]$$

where J_i and $\frac{d\mu_i}{dx}$ are the molar flux and the chemical potential gradient of component i and L_i is the proportionality coefficient.⁷² Alternatively, assuming only pressure driven process applies in absence of concentration gradient,⁷² the flux simplifies to:

$$J_i = -L_i V_i \frac{dP}{dx} \quad [1.10]$$

where $\frac{dP}{dx}$ is simply the pressure gradient.⁶⁸ **Equation 1.9** is more general, taking into account different driving forces such as concentration gradients and electrical potential and not just the pressure gradient (unlike **Equation 1.10**). The solution-diffusion model used to describe dense membranes does not apply to highly porous structures.⁷² It is thus more useful to define flux in terms of pressure:

$$J_i = \frac{P_{M,i}}{l_M} \Delta P \quad [1.11]$$

where $P_{M,i}$ is permeability, l_M is membrane thickness and ΔP is the pressure difference between feed and permeate side assuming the membrane is sufficiently thin.⁶⁸ The flux of a pure solvent is simply:

$$J = \frac{1}{R_M} \frac{1}{\eta} \Delta P \quad [1.12]$$

where R_M is hydraulic resistance and η is the solvent viscosity.⁶⁸

For microfiltration membranes, a laminal flow process applies as pores are sufficiently large, which can be explained by Hangen-Poiseuille's law.^{68,75}

$$v = \frac{d^2}{32\eta L} (P_0 - P) \quad [1.13]$$

where v is bulk flow, d is the pore diameter, L is the length of the pore and $P_0 - P$ is the pressure drop.⁶⁸ Only the surface fraction containing pores, ε with n pores is responsible for flow:⁶⁸

$$\varepsilon = \frac{n\pi d^2}{4} \quad [1.14]$$

Thus, flux can be defined as:

$$J = v\varepsilon\rho \left(\frac{1}{\tau}\right) = \frac{n\pi\rho d^4}{128\eta(\tau)L} (P_0 - P) \quad [1.15]$$

where ρ is density and τ is the tortuosity i.e. the average pore length compared to thickness of the membrane or ratio of real to minimum pore length.^{68,72,75} Cylindrical pores perpendicular to the membrane surface plane have $\tau = 1$.⁷² More complex formulas exist but it is more comprehensive to consider that either constant pressure filtration or constant flux are possible depending on the set-up.⁶⁸ Furthermore, fouling of the membrane and cake formation should be considered as these are often the most important considerations in large scale use of membranes for separation.⁷⁶

The retention of solute R is a simple parameter describing membrane performance, which can be defined as:

$$R = \left(1 - \frac{C_p}{C_f}\right) \times 100\% \quad [1.16]$$

where C_p and C_f are the permeate and feed concentrations respectively.^{68,77} Rejection or retention is a more useful experimental descriptor of membrane function rather than flux for most applications.

1.4.3. Pore Structure and Asymmetry

Pore structure directly affects membrane properties and applications. The first aspect in defining pores is to consider the tortuosity of cylindrical pores. Tortuosity is the ratio of the geodesic length (the shortest path across the surface) over the Euclidean length (the straight line distance) between two points in a connected pore path.⁷⁸ **Figure 1.6** illustrates how the tortuosity of a membrane can be defined. Tortuosity is shown to correlate with particle capture as particles are more likely to impact the pore walls given increased tortuosity.^{72,79} Porosity is another important criterion of membrane structure as defined by **Equation 1.14**.



Figure 1.6. Cross-section of membranes showing varying tortuosity. Adapted from Baker (2012).⁷²

Furthermore, if the pore diameter and solute rejection rates are known, it is feasible to calculate the solute diameter as demonstrated by the works of Ferry and Renkin.^{80,81} This model implies that the effective area, A available for solute transport is smaller than that for solvent transport, A_0 .⁸¹ The relationship states that:

$$\left(\frac{A}{A_0}\right)' = 2\left(1 - \frac{a}{r}\right)^2 - \left(1 - \frac{a}{r}\right)^4 \quad [1.17]$$

where $\left(\frac{A}{A_0}\right)'$ accounts for fluid velocity through the pore and is given as effective fractional pore area, a is the solute radius and r is the pore radius.⁸¹ $\left(\frac{A}{A_0}\right)'$ is equivalent to the ratio of filtrate or permeate and feed concentrations, which are directly related to **Equation 1.16**.^{72,81} Thus, rejection R is defined as:⁷²

$$R = \left[1 - 2 \left(1 - \frac{a}{r} \right)^2 + \left(1 - \frac{a}{r} \right)^4 \right] \times 100\% \quad [1.18]$$

Overall, tortuosity is used as the main descriptor of pore structure in 3D space, as cylindrical pores are defined as $\tau = 1$ and non-cylindrical pores can be defined by extent of tortuosity.^{72,82} If a membrane has a high degree of tortuosity i.e., above 1, the solute rejection rate would increase and so would the membrane performance.^{83–85} Therefore, a crosslinked or network membrane structure means higher rejection rates. Aside from pore shape, membranes typically display anisotropic pore size distribution; macrovoids or finger-like pores are also possible especially for large-scale membrane fabrication.⁷²

1.4.4. Membrane Preparation by Phase Inversion

Phase inversion is a well-known method for asymmetric membrane fabrication, i.e., a membranes formed by this method displays varying morphology across its thickness.^{74,86–88} It can be described as a demixing process, where a polymer solution undergoes conversion from liquid to solid state to form a membrane under controlled conditions.⁸⁹ Wet phase inversion involves the immersion of a polymer casting solution into a nonsolvent coagulation bath.^{74,77,90} This method can yield a desired membrane structure by controlling phase separation conditions.^{91,92} The focus of this project is primarily on air cast thermally induced phase inversion (TIPS) or dry phase inversion, whereby a casting solution containing both solvent and nonsolvent is used.^{88,93,94} This method is advantageous as solvent waste and processing times are reduced.

The theory of various phase inversion techniques can be summarised by a ternary phase diagram, as shown in **Figure 1.7**.^{74,86–88,95} The basis for definitions of solvent and nonsolvent employed in this work is the Flory-Huggins interaction parameter χ described above (**Equation 1.4**). The vertices of the triangle in the

phase diagram represent the components of the ternary system: polymer, solvent and nonsolvent. Each point inside the triangle represents a specific composition. The binodal boundary denotes the liquid-liquid separation where polymer-rich and polymer-poor phases coexist in thermodynamic equilibrium.^{74,86} Tie lines connect the pairs of those compositions at equilibrium.^{86,95} The polymer poor phase nucleates and forms the pores of the resultant membrane.⁷⁴ The spinodal boundary represents the region where demixing occurs spontaneously.⁹⁴ It is implied by various studies that solvent and nonsolvent with regards to the polymer in question must have high affinity to each other in order to obtain a porous structure.^{74,86,88,93,94,96} Furthermore, there must be sufficient time for solvent exchange to occur, otherwise dense “skin” (dense top layer) formation takes place for air cast TIPS membranes.^{74,86,88,93,94,96}

The TIPS method is used in this work to prepare poly(methyl methacrylate) (PMMA) membranes from acetone/ethanol solutions as a test system. Previous works either employed PMMA in TIPS with other more expensive or toxic solvents such as *tert*-butyl alcohol and sulfolane⁹⁷ or cyclohexanol and methanol.⁹⁸ Other polymers such as polyvinylidene fluoride (PVDF) were also used with PMMA as a blend^{99,100} or a combination of techniques was utilised.⁹⁸ Currently, PMMA is used in a solvent/non-solvent TIPS system with additives added during casting, which simplifies the technique overall and yields better control over the phase inversion process.

Another approach is vapour induced phase inversion (VIPS), which is a variation of the TIPS method.¹⁰¹ In this work, VIPS is used for chitosan membranes whereby water vapour shifts the composition of chitosan in aqueous acetic acid (AcOH) towards a desirable membrane formation state. Similar methods were used in previous studies to make membranes from polymers such as polyacrylonitrile,¹⁰² poly(etherimide),¹⁰³ polyethersulfone¹⁰⁴ and PVDF.^{105,106} Chitosan membranes have been previously prepared by thermal phase separation, in particular freeze and cryogenic induced separation,^{107,108} immersion phase separation¹⁰⁹ and a combination of the two methods.¹¹⁰ Herein, only water and acetic AcOH are required at temperatures close to standard (ca 30°C), which again reduced energy and material consumption during the process.

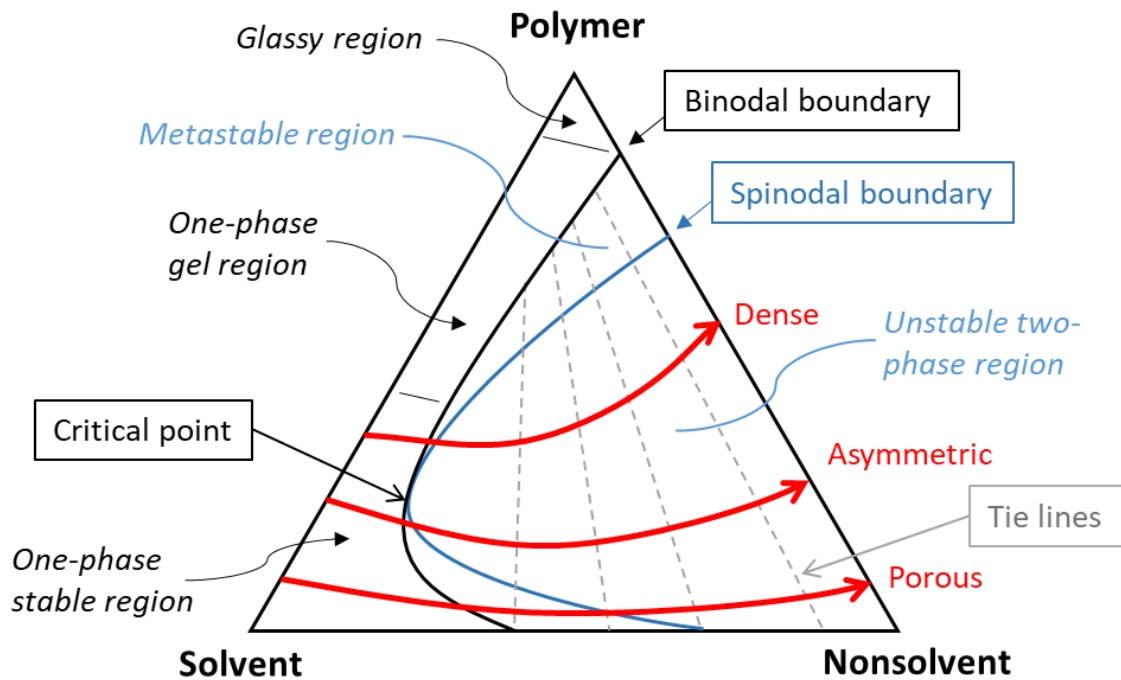


Figure 1.7. Ternary phase diagram for phase inversion process. Red arrows represent trajectories of compositions during phase inversion. Adapted from Caneba and Soong (1985) and Purkait et al (2018).^{88,95}

1.5. Thin film lithography

1.5.1. Polymer brush theory

The thin films employed in this work were used as model porous systems and as materials for bulk surface modification. Polymer brushes, i.e. thin polymer films covalently bonded to a surface, have been used as such to investigate surface properties, wherein bulk membrane morphology cannot be tested due to roughness effects. Polymer brushes are useful as they can be bound to a surface chemically and adopt the surface roughness of the substrate.¹¹¹

As the name polymer “brush” implies, they form a structure like a molecular brush with polymer chains sticking out (as shown in **Figure 1.8**). Generally, polymer brushes can be defined by reduced tethered density (Σ) which describes brush packing density and morphology as follows:

$$\Sigma = \sigma \pi R_g \quad [1.19]$$

where σ is the grafting density, and R_g is the radius of gyration of a tethered chain at defined temperature and for specific solvent.¹¹² The parameter Σ is also indicative of the brush morphology, i.e., there are three brush regimes: the “mushroom” regime (Σ less than 1), the crossover regime (Σ equal to 1), and the highly stretched regime (Σ greater than 1).¹¹³ The architecture of the three regimes is depicted in **Figure 1.8**. The true brush regime, i.e. where the polymer brush is elongated perpendicularly to the substrate, however, is widely reported as $\Sigma > 5$.¹¹²

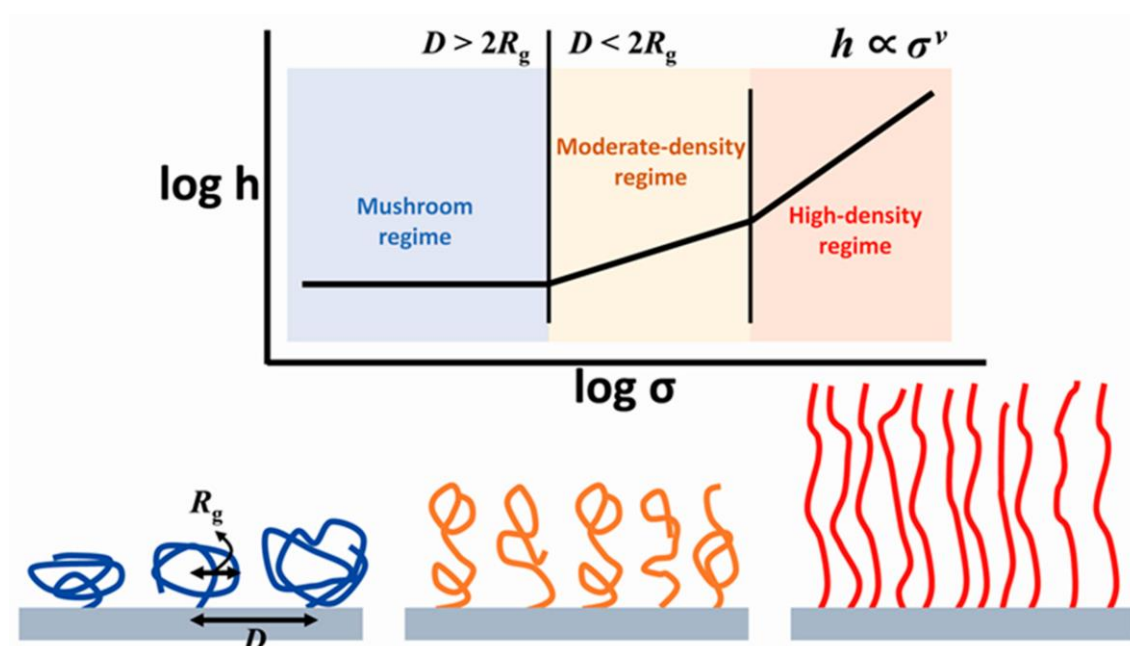


Figure 1.8. Depiction of the mushroom regime, cross-over or moderate density regime and the stretched or high-density regime. h represents the height of the brush, D is the distance between grafting points,¹¹² v is the slope of the $\log h$ vs. $\log \sigma$ plot.⁷ Reproduced from Kim et al (2015).⁷

The radius of gyration, and by extension the local conformation of the polymer brush, are highly dependent on the solvent. In a good solvent where the polymer dissolves well, the chains elongate or stretch ($h < R_g$), while in a poor solvent the chains collapse ($h < R_g$).¹¹³ In general, solvents can be used to selectively swell the brush layers and identify the parameter Σ , while at ambient conditions σ is more often relevant and reported widely.¹¹³

Multiple grafting techniques exist, which include growing the polymer layers directly on the substrate or depositing the polymer brush and chemically bonding to the surface.^{114–116} Surface initiated polymerization (SIP) has many variations, which in commonality have some form of an initiator and polymer precursor where the reaction results in polymer grafting with controlled chain length.¹¹⁷ However, such processes are oftentimes more energy and chemical intensive than using an end-functionalized polymer such as hydroxyl or amine terminated homopolymer brushes. The end moiety can selectively graft to specific substrates upon thermal treatment such as hydroxyl groups to silicon dioxide layers and thiol groups to copper substrates.^{111,114,118} Herein, polymer brushes with end functional groups are employed to modify the substrate surface energy (SE) properties and for modelling surfaces for analysis whereby the subject of study is too rough and hard to assess for properties.

1.5.2. Block copolymer microphase separation

As defined in **section 1.3**, a block copolymer (BCP) consists of two or more distinct monomers that follow a repeating pattern when grouped by segments or “blocks”.^{119,120} This gives rise to many possible self-assembly conformations based on block chemistry and miscibility during microphase separation.¹²¹ The basis for self-assembly is governed by the equilibrium between repulsive and attractive forces between components.¹²¹ In terms of thermodynamics, it can be defined in terms of the Gibbs Free Energy of mixing, where the enthalpy term must be negative in order to overcome the usually observed entropy decrease during self-assembly.^{121,122}

Flory-Huggins theory is particularly applicable here, as it can be used to explain the self-assembly process and preferable pattern formation.¹²¹ If a diblock copolymer is considered with block A and B, a model can be constructed in terms of degree of polymerisation N , volume fraction f and Flory-Huggins parameter χ .¹²² The degree of polymerization is simply the number of monomer units defined as $N = N_A + N_B$. The volume fraction for each block is defined as the ratio of monomers inside the block to the total number of monomers to yield a relationship

$f_A + f_B = 1$.¹²² The Gibbs Free Energy of mixing (ΔG_{mix}) for the blocks can thus be defined as:

$$\frac{\Delta G_{mix}}{RT} = f_A f_B \chi + \frac{1}{N_A} \ln f_A + \frac{1}{N_B} \ln f_B \quad [1.19]$$

where R is the ideal gas constant and T is the temperature in Kelvin. $f_A f_B \chi RT$ is simply defined as the enthalpy of mixing thus the remaining terms in the equation portray the reduction in entropy.¹²¹ The microphase separation process occurs when ΔG_{mix} is minimised but given that χ is usually positive, ΔG_{mix} is likely to be positive as well.¹²¹ Thus, microphase separation is controlled by the segregation product χN as χ here defines the miscibility of the blocks:¹²³

$$\chi(T) = \chi_S + \frac{\chi_H}{T} \quad [1.20]$$

where χ_S is the temperature-independent entropic term and $\frac{\chi_H}{T}$ is the temperature-dependent enthalpic term. The values of the enthalpic and entropic terms are typically determined experimentally.^{124–126} If the components of the BCP are chemically dissimilar, the enthalpic term will dominate, allowing experimental control of χ by varying the temperature.¹²⁴ Further developing on this theory, the parameter χN and volume fraction can be used to design a phase diagram for microphase separation (an example of which is shown in **Figure 1.9**).¹²²

The phases in **Figure 1.9** are denoted as follows: S and S' = body-centered cubic spheres, C and C' = hexagonally packed cylinders, G and G' = bicontinuous gyroids, and L = lamellae, CPS and CPS' = closely packed spheres and PL = perforated lamellae.¹²² The diagram demonstrates that for lamellar BCPs or equal volume fraction BCP below χN of 10.5 the structure is disordered.¹²¹ It can also be observed that lamellar pattern dominates, i.e. the free energy of mixing is minimised in a lamellar pattern as block motion is limited by the covalent bond. Note that many historical variations of diblock BCP phase diagrams exist such as those developed by Matsen¹²⁷ among other versions.^{128,129} Many of these phase diagrams contain rarer phases (such as orthorhombic or *Fddd*) that occur near the boundaries of the common phases.¹²⁷

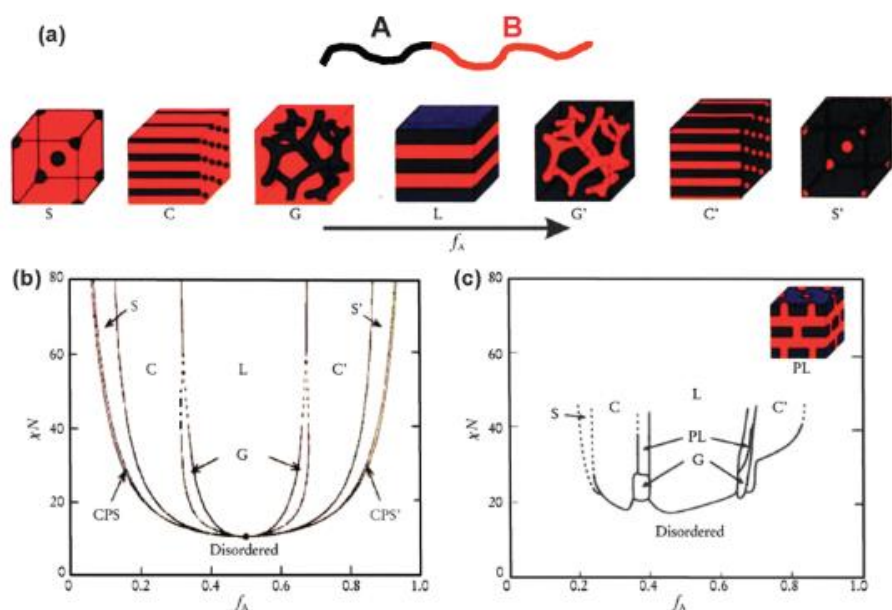


Figure 1.9. (a) Equilibrium morphologies of AB diblock copolymers in bulk; (b) Theoretical phase diagram of AB diblocks predicted by the self-consistent mean-field theory, depending on volume fraction (f) of the blocks and the segregation parameter, χN ; (c) Experimental phase diagram of polystyrene-*b*-polyisoprene copolymers, in which f_A represents the volume fraction of polyisoprene. Reproduced from Mai and Eisenberg (2012).¹²²

Aside from microphase separation, other types of processes can influence the surface morphology of BCP films. For example, dewetting which is defined as a process by which liquid films rupture when they do not wet the substrate, and eventually form droplets on the surface.¹³⁰ Dewetting can also be utilised and controlled to form repeating structures.^{131,132} For example, PMMA cylinders can form perpendicular or parallel with respect to the substrate due to variation in local thickness as reported by Brassat et al.¹³³ Furthermore, micelle formation should also be regarded as a separate process, defined as the self-assembly of amphiphilic BCP in a solvent medium to form a structure typically with a core and corona.¹³⁴

Film thickness also affects microphase separation, in particular for ultrathin BCP films. Confinement effects are usually observed in cases where the film thickness t is less than the domain spacing L_0 . The polymer film can be exposed to two

interfaces and thus, there are two confinement types – hard (polymer film between two rigid interfaces) and soft (polymer film between a rigid interface or substrate and air). In this work, polymer films are subject to soft confinement and thus, the substrate type is important. For example, if the polymer film thickness is incommensurable with the domain spacing and the substrate SE is unfavourable, the film will deviate from predicted packing.¹³⁵ For lamellae, defects such as dislocation dipoles, undulated lamellae, and tilted lamellae can be observed.¹³⁶ If the substrate SE is in fact favourable, the BCP film will preferentially adhere to the substrate if the film is incommensurable, forming defects like islands or holes as to locally adjust thickness to the natural domain spacing.¹³⁷ Smooth defect-free films are feasible if $h = nL_0$ and if no interface is preferential, where n is some integer value. Similarly, $h = (n + 0.5)L_0$ if interfaces display different favourability.¹³⁸ Thus, even with predicted SVA morphology, thickness effects in particular for thin films are substantial.

Thicknesses can be modified by varying polymer solution concentrations and deposition methodology such as spin-coating or dip-coating.³⁵ Furthermore, by carefully choosing the substrate, precise thickness control can be achieved due to variation of the contact angle of the polymer solution on the substrate.¹³⁹ As discussed previously, brush layers can help adjust the SE to make the substrate preferential or not.¹⁴⁰ Random copolymer brushes are often used for BCP self-assembly to eliminate the substrate effect.^{141–143} The resulting film morphology will entirely depend on the annealing conditions and film thickness.

1.5.3. Annealing techniques

BCP microphase separation is generally improved where systems display a high χ parameter. As stated above, temperature is inversely related to the interaction parameter; thus, thermal annealing is often employed.^{123,144} However, annealing times can be lengthy if block diffusivity is low.¹⁴⁵ Furthermore, increasing temperature beyond the glass transition to the degradation point can result in the destruction of the BCP system. Thus, another approach is solvent vapour annealing (SVA).¹⁴⁵ The solvent vapour can selectively swell one or all of the blocks, which is measured by the χ parameter.^{73,145} This process creates free

volume and improves chain mobility.⁷³ This is also described as plasticization, or the effective reduction in glass transition temperature and effective interaction parameter χ_{eff} defined as:¹⁴⁶

$$\chi_{eff} = \chi \phi_{BCP}^{\beta} \quad [1.21]$$

where χ is the Flory–Huggins interaction parameter for the non-swollen BCP film, ϕ_{BCP} is the polymer concentration of the swollen film, and β is an exponent factor with a value between 1 and 2 derived for the film.^{10,147,148} ϕ_{BCP} is simply measured as the ratio of the initial film thickness to the swollen film thickness.¹⁰ Thus, annealing times can be greatly reduced for high χ systems.¹⁴⁵ If the diblock copolymer film thickness is below the bulk lamellar period thickness, it can undergo spinodal dewetting when annealed above a certain microphase separation temperature.^{145,149} Furthermore, solvent vapour condensation can also result in film dewetting.

During film deposition, surface effects such as substrate surface energy should also be considered as well as the casting solvent.¹⁵⁰ Parameters such as the concentration and temperature of solutions prior to casting, micelle formation in solution, deposition technique and annealing conditions all affect the resulting morphology.¹³⁷ It is important to note that polymer films can also be grown by polymerization on the substrate or by chemical vapour deposition (CVD).^{151–153} However, in this work spin-coating was used to deposit thin films due to low processing times and high reproducibility of the results.¹⁵⁴ Spin-coating involves dropping a polymer solution on a flat substrate to coat it and then spinning it at high speeds such as 3,000 rpm.¹⁵⁵ The substrate is coated by centrifugal force as the solvent evaporates to yield a thin film of uniform thickness throughout the sample.¹⁵⁵

1.5.4. Infiltration and pattern transfer

The domains in thin films such as homopolymer and BCP films often contain functional moieties. Those regions can be used to coordinate metal ions or conversely, block the infiltration.^{111,156} The moieties can be manipulated to include specific ions from precursors such as nickel nitrate or iron nitrate salts.¹⁵⁷

Therefore, polymer lithography is feasible where metals can be incorporated with further post-treatment, while the polymer film can be removed or retained.

The most common mechanism of metal ion incorporation is coordination to a polymer via available lone pairs on oxygenated or nitrogenated groups.⁷³ Some examples of polymer systems with available coordination groups include PMMA and poly(ethylene oxide) (PEO) with oxygenated coordination groups and poly(2-vinylpyridine) (P2VP) and poly(4-vinylpyridine) (P4VP) with pyridine groups.¹⁵⁸ The lone pair coordination holds the ion in place, which allows the metal to adopt the architecture of the polymer film.²⁵ The metal precursor can be deposited via spin-coating, dipping or chemical deposition methods such as CVD and atomic layer deposition (ALD) with variations of the methods.^{111,114,159,160} Alternatively, metallic state precursors can be incorporated by physical vapour deposition or magnetron sputtering, where the mechanism of incorporation is determined by adatom mobility and diffusion.^{161,162} In those cases, metals adhere selectively to domains where the mobility is lower. However, upon deposition of high levels of metal via sputtering, the metals would begin to aggregate independent of the surface beneath. The bound metals ions or metallic structures can be further processed for the desired application.

The post-processing steps in polymer lithography include polymer removal and metallic state manipulation. The polymer film is often degraded thermally by light such as UV/ozone (UVO) treatment¹⁶³ or various cold plasmas such as oxygen plasma ashing or etching.^{164,165} Polymer removal methodology is carefully tailored so as not to obstruct the resultant nanopatterned metallic architecture.¹⁶⁶ Similarly, metals ions can undergo changes during polymer removal such as conversion to metal oxides in UVO or oxygen plasma treatments.¹⁶⁷ Heating can also cause calcination and film densification.¹⁶⁸ Other post treatments can include Ar/H₂ plasma to reduce oxidised metal films.¹⁶⁹ In general, metallic films can be tailored via choice of post treatment for the desired composition and purpose.

The metal films can be employed directly for electronic or sensing applications or further used as a mask for etching.^{5,170} The process of utilizing a metal film as a mask is called pattern transfer.¹⁷¹ Interestingly, dry etching is feasible using metallic masks under certain plasmas such as CHF₃/SF₆ and other combinations using C₄F₈, Ar, CF₄ and O₂ gasses among other gasses to etch silicon substrates,

for example.^{172–174} Herein, Inductively Coupled Plasma - Reactive Ion Etching (ICP-RIE) was employed, whereby RIE conducts the etch but ICP considerably accelerates the process. The removal of any residual metal film post pattern transfer¹⁷⁵ produces a nanopatterned substrate. Furthermore, it is possible to coat the structure after pattern transfer, such as gold deposition upon nanopatterned pillars for surface enhance raman spectroscopy (SERS).¹⁷⁴ These metallic architectures or patterned substrates can be then used for optical, electronic, sensing and catalysis applications.^{171,174,176,177}

1.6. Thesis overview

This work covers the areas of surface modification and self-assembly for porous material synthesis. The aim is to produce novel porous materials and utilize advanced characterization techniques to describe them. The produced materials are then used to assess filtration capabilities, pattern transfer and etching and optical properties.

Initially, membrane systems in bulk are investigated, namely chitosan and PMMA membranes as detailed in **Chapter 2**. Surface modifications of PMMA with (3-aminopropyl)triethoxysilane (APTS) are also investigated for the purpose of modifying flow rates during filtration. The main aim is to design membranes *via* a cheap self-assembly process, namely phase inversion, as described above. The dye retention and tensile properties are investigated, and a 3D FIB reconstruction methodology is adopted to assess the membrane morphology. Nadezda Prochukhan conceived and coordinated the study, along with performing the membrane synthesis, membrane functionalisation, spectroscopy, dye retention analysis, tensile measurements and brush optimisation. The custom membrane apparatus was designed by Niall Murphy. Polymer brush sample preparation was performed by Pravind Yadav and Nadezda Prochukhan. Saranya Rameshkumar performed the GPC. Jessica De Micco performed the TGA and DSC. BET analysis was conducted by John Hanrahan (Glantreo, Cork). MIP was performed by Aran Rafferty. Viscosity and turbidity measurements were conducted by Sukhananazerin Abdulla. AFM, SEM imaging and FIB-SEM reconstruction as well as data analyses were performed by Nadezda Prochukhan.

In **chapter 3**, Polystyrene-*b*-Poly(ethylene oxide) (PS-*b*-PEO) (24k-24.5k) is employed as an amphiphilic test system for macroporous surface fabrication *via* water vapour annealing (WVA). A PS polymer brush system is adapted to modify surface properties of the substrate. The toroidal micelles were used to produce silicon nanotube arrays *via* pattern transfer and ICP RIE treatment. Nadezda Prochukhan conceived the experiments and performed sample preparation. Polymer brush preparation was performed by Pravind Yadav and Nadezda Prochukhan. Etching was performed by Nadezda Prochukhan and Andrew Selkirk. XPS was performed by Andrew Selkirk and XPS analysis was conducted by Nadezda Prochukhan. Jessica De Micco performed the TGA and DSC. TEM was performed by Clive Downing. Other characterization and data analyses were performed by Nadezda Prochukhan.

Furthermore, the synthesis of lignin biopolymer membrane thin films *via* a similar method of WVA is outlined in **Chapter 4**. Four different lignins are assessed for pore forming capabilities *via* WVA at room temperature for membranes of various thicknesses. Pattern transfer and ICP RIE were used to produce silicon membranes, which are then further used to investigate the optical properties of the produced black silicon (BSi). Nadezda Prochukhan conceived and coordinated the research and conducted sample preparation. Ramsankar Senthamaraikannan conducted TGA and DSC, Manuel Ruether conducted the NMR. Stephen O'Brien, Eoin Cotter and David McCloskey conducted optical measurements and analyses. Anna Trubetskaya conducted the proximate and ultimate analysis of lignins and Leonidas Matsakas performed the GPC of lignins. XPS was performed by Arantxa Davó-Quiñonero and XPS analysis was conducted by Nadezda Prochukhan and Arantxa Davó-Quiñonero. Etching, imaging and data analysis was performed by Nadezda Prochukhan.

Multiple polymer systems are investigated in this work in order to optimise surface morphology, functionality, structure and chemical properties for membrane fabrication. The structures of the polymers used in this project, PMMA, chitosan, polystyrene-*b*-poly(ethylene oxide) (PS-*b*-PEO) and lignin as well as other molecules are depicted in **Figure 1.10**.

Finally, **Chapter 5** outlines the summary of the results and provides an overall evaluation, along with detailing a future perspective of the field.

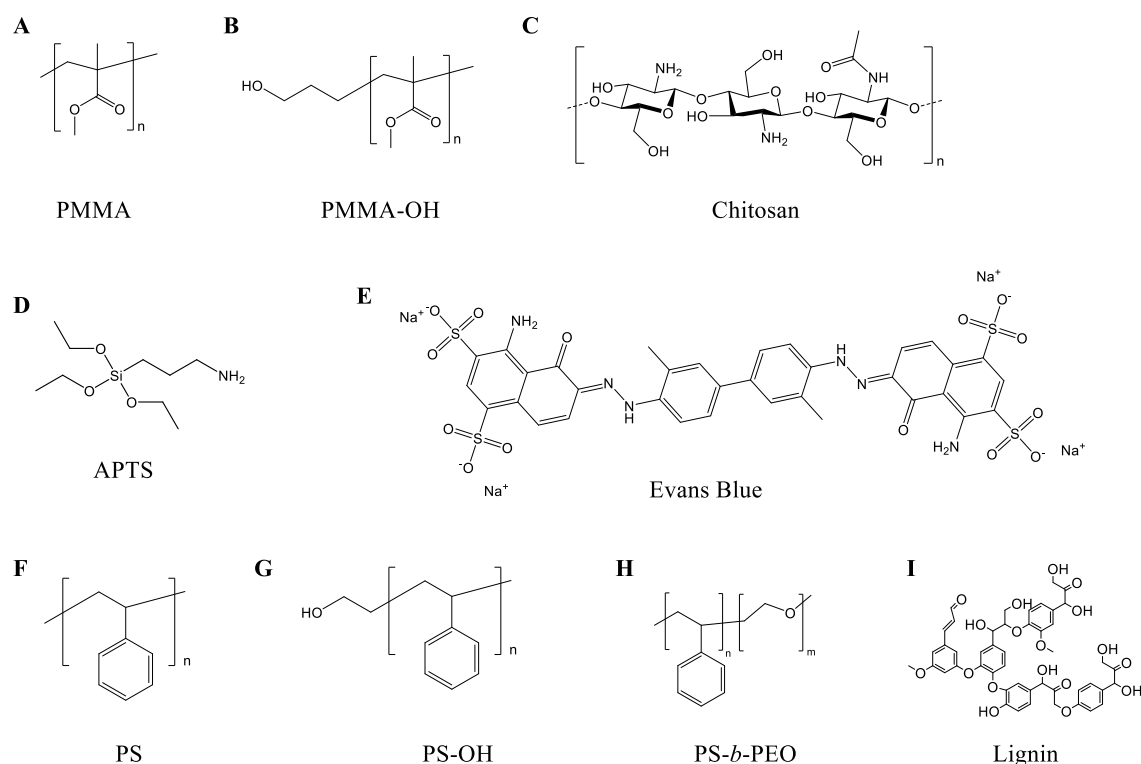


Figure 1.10. Representation of polymers and chemicals used in this work.

1.7. References

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2. Chapter 2. Poly(methyl methacrylate) and chitosan membrane fabrication and functionalisation

2.1. Introduction

Membrane technology has grown in importance recently largely as a response to ever increasing pollution and the need for mitigation strategies. The need for waste separation and purification of waste streams has become indisputable, owing to the continued growth of industrial waste volumes as the world population increases. It is critically important to develop effective and robust systems for the disposal and reuse of chemicals. The aim of this work is to produce a novel membrane system with controlled and tailorable porosity and selectivity (via chemical functionalization) for effective separation. Membrane fabrication methods also need to be carefully designed as large quantities of solvents and chemicals (including water) are commonly used unsustainably in their synthesis. Dry thermally driven phase inversion or vapour enhanced phase inversion can be utilised to overcome some environmental limitations as well as yield better control over the phase inversion process.^{1,2}

Membranes are typically produced via phase separation, whereby the membrane film is immersed in a non-solvent bath to allow for pores to form. Immersion phase separation is complex and difficult to model, as it is important to consider kinetics, diffusion, layers and concentration gradients.³ Such processes are also wasteful and hard to control; thus an alternative approach was developed – thermally induced phase separation (TIPS).⁴ TIPS involves casting a heated polymer solution containing a solvent and a non-solvent, which is then cooled to induce demixing.⁵ The polymer-solvent form the polymer rich phase and later the membrane matrix, while the polymer-non solvent or the polymer poor phase form the pores. The solvents are then removed via evaporation resulting in pore formation. Air or vapour such as water vapour can be used to improve phase separation kinetics; in the case where vapour is used, the process is similarly called vapour induced phase separation (VIPS).⁶ These methods use minimal amounts of non-solvent versus the conventional method of bath immersion. Other methods of membrane preparation exist such as electrospinning,⁷ however those

methods also have associated disadvantages such as high-power demand, i.e., high voltages.⁸ Furthermore, phase separation is easy to modify and control as the mechanism is simple. The mechanism of phase separation is discussed in the **Introduction** chapter in more detail.

The primary aim of this project is to investigate filtration capabilities of phase separation membranes. We will examine membranes that are conventionally used for dead-end filtration; whereby size exclusion mechanism plays a key role to allow selective retention. Herein, mainly microfiltration (pore size > 100 nm) and ultrafiltration (pore size > 10 nm) membranes are explored.^{9,10} Microfiltration is typically used to remove large particles such as dust, algae or bacteria,¹¹ however oils can also be removed from water effectively by micrometre dimension pores.¹² Ultrafiltration can be used to remove smaller particles such as viruses and colloids, along with macromolecules such as polymers and dyes.¹³ Both modes are useful to clean waste water from foulant while useful electrolytes are retained.¹³ Furthermore, membranes can also be used for lateral flow analysis, which have become increasingly important through their use as pregnancy tests¹⁴ or COVID-19 lateral flow tests.¹⁵ The mechanism of lateral flow is simply capillary action as the interconnected pores allow for fluid to flow.¹⁶ The adhesive forces between the liquid and the membrane can be altered, for example by adding surface functionality¹⁷ or changing pore size, structure or density.^{18,19} The constituent materials of the membrane can also influence its resultant properties and applicability.

The specific systems chosen for this study are PMMA cast from acetone (solvent)/ethanol (non-solvent) via an air-cast TIPS method. The chitosan membranes are used to show VIPS methodology where water vapour acts as a pore former. These solvent and non-solvent systems were chosen based on Flory-Huggins theory, which is discussed in detail in the **Introduction** chapter. In TIPS, the membrane system firstly undergoes a transition to a binodal phase, then subsequently to a spinodal phase due to temperature change.⁵ In the binodal phase, the polymer rich (solvent-polymer) and polymer poor (nonsolvent-polymer) phases coexist in equilibrium.⁴ However, upon passing the spinodal boundary, the membrane “crashes out” and solidifies.²⁰ The net composition is theoretically plotted on a 3-point phase diagram (see for example **Figure 1.6**).

For VIPS systems the process is similar in that temperature is also used to drive the formation process, however the nonsolvent is instead in the vapour phase.²¹ The resultant membranes are commonly asymmetric, however general pore size range helps to determine the application of the membrane.²²

Poly(methyl methacrylate) (PMMA) was chosen as the initial test polymer due to its thermoplastic properties and high glass transition temperature.²³ PMMA is cheap and ubiquitous in everyday use plastics and thus can be recycled and used for membrane fabrication. Chitosan was chosen as, similarly to PMMA, it is cheap and stable in aqueous environments. It also has the advantage as a biopolymer due to its biocompatible nature. Chitosan is easy to process and also displays antimicrobial and metal binding properties.^{24–26} Hence, chitosan is an attractive candidate for biomolecule filtration applications. The main aim was to design membranes via a cheap self-assembly process – namely phase inversion, as described above.

In this study, PMMA and chitosan membrane fabrication are studied using TIPS and VIPS in order to compare the resultant morphology, tensile properties and dye retention capabilities. The membrane morphology data was quantitatively analysed firstly using scanning electron microscopy (SEM) and atomic force microscopy (AFM), and secondly, via attempting membrane reconstructions on phase inversion PMMA and chitosan membranes using laser scanning confocal microscopy (LSCM) and focused ion beam (FIB). Quantitative data such as pore volume and connectivity were extracted from FIB models in order to understand in situ membrane architecture and how it relates to filtration capability. Evans Blue filtration was used as an initial indicative test of membrane performance. Surface functionalisation with (3-aminopropyl)triethoxysilane was also investigated to understand surface energy effects via contact angle (CA) measurements and their resulting influence on filtration performance. The deposition was optimised to achieve vapour deposition near standard conditions. An APTS-PMMA pre-functionalised membrane was also fabricated in attempt to create a selective separation medium.

2.2. Experimental

2.2.1. Materials

(3-aminopropyl)triethoxysilane (APTS) 99%, acetone, acetic acid (AcOH), ethanol (EtOH) and the Ninhydrin reagent (2% solution) were supplied by Sigma Aldrich.

Hydroxy-terminated poly(methyl methacrylate) (PMMA-OH) (number average molecular weight, $M_n = 6.3 \text{ kg mol}^{-1}$, $M_w/M_n = 1.06$, M_w : weight-average molecular weight), was purchased from Polymer Source Inc. and was used without further purification. Silicon <100> p-type wafers with a native oxide layer were used as substrates for PMMA-OH and APTS deposition.

PMMA was purchased from Altuglas (BS572), number average molecular weight, $M_n = 440.5 \text{ kg mol}^{-1}$, $M_w/M_n = 1.04$ (where M_w is the weight-average molecular weight as measured by Gel-Permeation Chromatography (GPC)). Chitosan was purchased from Acros Organic. The chitosan molecular weight was measured via GPC, $M_n = 26.93 \text{ kg mol}^{-1}$, $M_w/M_n = 2.90$.

2.2.2. PMMA casting solution preparation.

A range of PMMA solutions were tested from 3 to 6 wt% in acetone and ethanol solvent systems. Membranes with PMMA content below 5 wt% were too thin and thus compositions were adjusted (**Table 2.1**). 6 wt% PMMA solutions are not reported as it was found that the PMMA solubility reduced, which resulted in the formation of membranes which exhibited extremely dense skin layers. The PMMA solutions were left to stir at 30°C overnight prior to casting.

Table 2.1. Composition of PMMA membrane casting solutions.

PMMA (wt%)	Acetone (wt%)	Ethanol (wt%)	Glycerol (wt%)
5.0	40.0	55	-
5.0	40.0	54.0	1.0
5.5	45.0	49.5	-
5.5	45.0	48.5	1.0

2.2.3. Membrane formation via Air-cast Thermal Induced Phase inversion (Air-cast TIPS).

Membranes were prepared via the apparatus shown in **Figure 2.1**.

The casting conditions were kept constant and monitored via temperature and humidity sensors (Easylog EL-21CFR-LCD). The air was supplied by a Kaiser AIRCENTER SX3 compressor. Incoming desiccant air flow was maintained at flow rate of 1.5 L s^{-1} (as measured by the Omega FL-2064 air flow controller) and air was removed at a rate of 1 L s^{-1} as measured with an anemometer at the solvent vent. The solvent vent was attached to a fumehood. The air was initially heated by an air-heater jet (Radionics RS 860-7198). A proportional–integral–derivative (PID) controller and a resistance temperature detector (RTD) probe was used in tandem to set and control the temperature in the chambers. The RTDs were attached to baffles (flaps) at the exits of air-jets, used to control air flow direction.

Melinex (polyester, DuPont Teijin Films) backing film was attached to the conveyor and the motor speed was set to $3 \times 10^{-2} \text{ ms}^{-1}$. The conveyor temperature was maintained using water baths (Grant JBA 5 Academy), the heated water was pumped (using KNF NF300 KT.18s pumps) through copper piping inside an aluminium array which make up the bed or the conveyor.

The cutting knife at solution inlet was set at a height of 1 mm over the Melinex backing film. The slot die assembly (FOM Technologies) with the cutting knife is shown in **Figure 2.1 B**, the back spacer and the other spacer both have thicknesses of 200 μm . A silicone heat pad was attached to the back of the slot die assembly, and PID and RTD were used to control the temperature of the slot die. The membrane solution was pumped with a peristaltic pump (FASTLoad Manual control peristaltic pump) using BioPharmaSil Tubing 6.4x1.6mm (ca 1 m long) at 100 to 150 mL min^{-1} for the PMMA solutions and at 50 to 100 mL min^{-1} for the chitosan solutions. The tubing passed from a membrane containing bottle (100 mL Duran jar) through the peristaltic pump and connected to the slot die assembly through the central hole in front plate with an adapter. Each membrane required approx. 100 g of polymer solution material to produce a membrane of

over 1 m long and over 20 cm in width. The membrane solution was pumped into a $\sim 25 \text{ cm}^2$ area and subsequently extruded and cut with the knife.

The air temperatures in the curing and drying chambers were adjusted to 25°C initially for 30 mins, and then gradually raised to 30°C to ensure solvent removal. The conveyor belt temperature was adjusted to 20°C and kept constant. Drying at temperatures up to 50°C was tested. The membranes were recovered after approximately 90 mins from the beginning of casting.

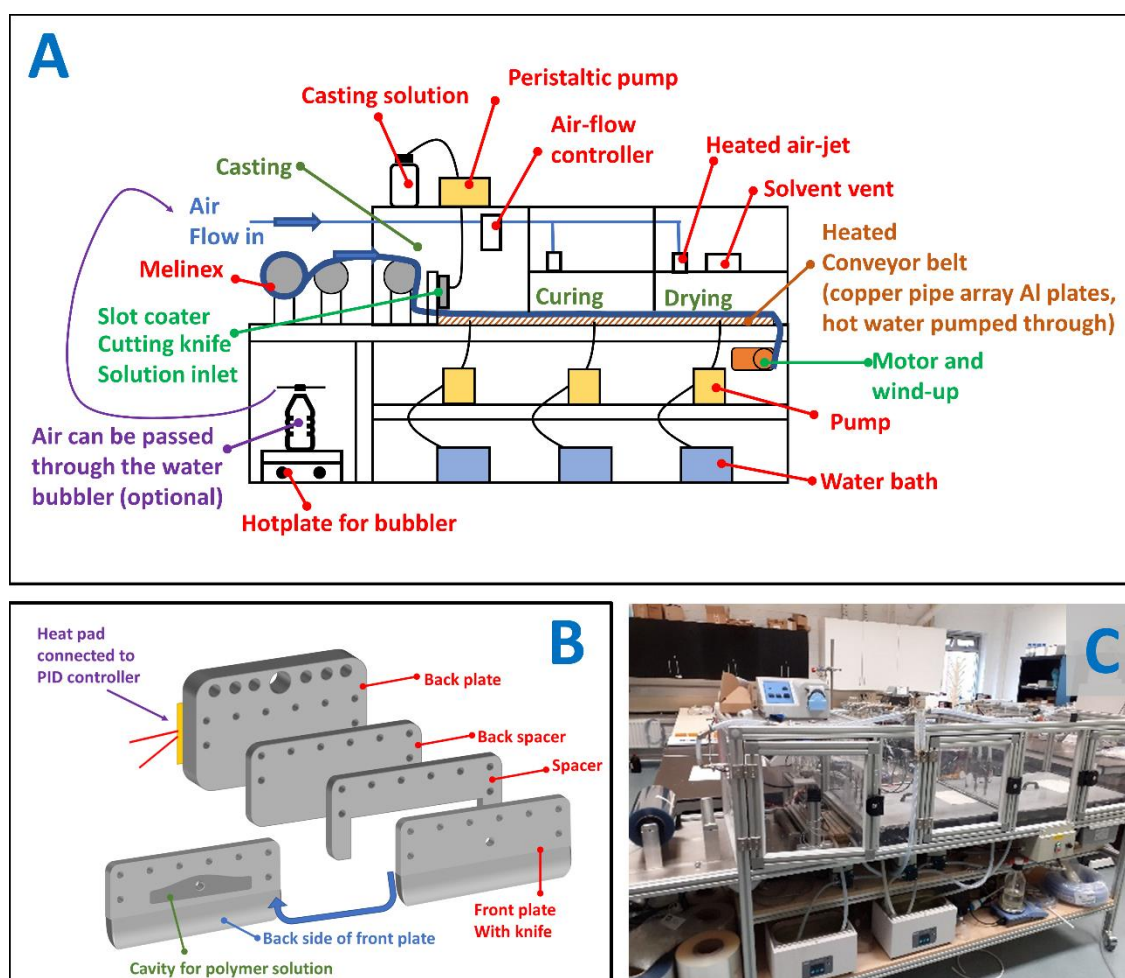


Figure 2.1. The membrane casting apparatus. **A.** Schematic representation, **B.** slot coater detailed schematic and **C.** a photograph of the set-up.

2.2.4. PMMA functionalization with APTS

It was found that PMMA functionalization was achievable after or prior to casting. The initial step involved UV ozone (UVO) activation of PMMA. The PMMA

membrane sheet or PMMA powder was then placed into a Novascan PSD pro series UV Ozone system for 45 mins, approx. 40 mm away from the UV source. APTS liquid deposition experiments were conducted with 1 to 10% v/v APTS/water solutions. The PMMA sheet (20 mm x 20 mm) was immersed in solutions for 30 mins at 80°C. Subsequently the PMMA sheet was washed with 2-propanol and DI water. Samples were placed at 90°C to ensure complete silanization of the surface. These methods are adapted from various previous studies.^{27,28}

APTS vapour deposition experiments were conducted in a vacuum oven at 110°C, 200 mbar (contained in a fumehood) using a modified method as reported by Zang *et al.*²⁹ An open vial containing 50 µL APTS was placed inside a jar with the UVO activated PMMA (0.5 g) or 2 cm³ x 2 cm³ membrane strip and sealed before being placed inside the vacuum oven. The setup was left for 3 to 8 hrs.

Quantification of APTS was conducted via a Ninhydrin test.³⁰ The APTS-PMMA sample of interest (0.5 g) or 2 x 2 cm² membrane strip was immersed in a sealed vial containing Ninhydrin reagent (2% solution, 1 mL) and water (2 mL). The solutions with the samples were heated to 70°C for 15 mins. A similar procedure was conducted for pure APTS to construct a calibration curve for known APTS concentrations of up to 5 µM. The solid samples were extracted by filtration and the solutions were diluted to a volume of 100 mL using volumetric flasks. The absorbance at 570 nm was measured, and the degree of APTS functionalisation was quantified from the standard calibration plot. APTS functionalisation was also characterised via FTIR.

2.2.5. APTS coverage of PMMA analysis by contact angle

PMMA-OH brushes were used as a flat model of a PMMA-APTS membrane system. Brush optimisation was conducted according to the method reported by Lundy *et al.*³¹ Silicon substrates were cleaned in toluene by sonication for 20 minutes and dried with N₂ gas. Substrate surfaces were further cleaned, and hydroxyl functionalised via oxygen plasma for 3 mins (40 kHz, 120 W, Barrel Asher). The substrates were spin-coated (3200 rpm, 25 seconds, 5 seconds ramp) with a 0.6 wt% PMMA-OH brush solution in toluene (stirred for 1 hr). The polymer brush was annealed on a hot plate at 200 °C for 5 mins. Subsequently,

the substrates were sonicated in toluene for 20 mins twice in order to remove any physisorbed layers.

The produced PMMA brush was exposed to UVO for 45 sec and APTS vapour as detailed above for membrane samples, in order to measure the contact angles (CAs) and surface energy (SE) of the system. An APTS brush was produced on Si after plasma treatment as described for the PMMA brush.

2.2.6. Chitosan membranes fabrication via Water Vapour Phase Inversion (Water VIPS)

Chitosan solutions of 2 and 3 wt% chitosan were prepared in 1 wt% aqueous acetic acid (aq. AcOH), while 4 and 5 wt% chitosan were prepared in 2 wt% aq. AcOH. Glycerol (gly) was added to a final concentration of 1 wt% to improve membrane elasticity. Solutions were left to stir at 60°C overnight. The membrane casting method was comparable to PMMA except water vapour was used to improve membrane formation. As shown in **Figure 2.1 A**, a water bubbler was attached to the compressed air and connected to the air inlet in the apparatus. The bubbler was placed on a hotplate (IKA RET) at 100°C in order to promote higher humidity values and to heat the humid air before it arrives at heated air-jets. Conditions were adjusted to maintain 60% relative humidity. Membranes were left to air dry for a month to remove residual AcOH prior to testing. Air temperatures were maintained at 30-35°C during membrane casting/drying.

2.2.7. Tensile strength analysis

Tensile strength and Young's modulus measurements were performed using a Mechanical Analysis machine (Zwick Roell - Instron) with a 100N load cell, and grip to grip separation set to 41 mm. PMMA and chitosan samples were cut with a dumbbell mould with dimensions of 50 mm in length and 4 mm width. The strain increase rate was set to 2 mm min⁻¹. The experiment was set to stop after membrane fracture. The test was repeated 6 times for each membrane sample.

2.2.8. Filtration experiments

Vacuum filtration experiments were conducted with flat sheets of chitosan and PMMA cut to 45 mm diameter rings to fit the filter funnel. 15 mM Evans Blue aqueous solutions were filtered through the membranes and UV-vis spectra of

the feed and filtrates was recorded. The efficiency of membrane filtration was quantified via %retention according to **Equation 1.16** in the **Introduction**.

Capillary flow times (CFTs) were calculated as the time taken for water to traverse 40 mm laterally through the membrane. Membranes were sectioned into 40 mm × 15 mm strips and soaked in 0.1 wt% sodium dodecyl benzene sulphonate (SDBS) solution in water and dried overnight at ambient conditions. Subsequently, membranes were positioned vertically in reservoir (with a 150 µL well) and 300 µL eosin dye solution was added. The time taken for complete wetting of the membrane strip was recorded as CFT.

2.2.9. FIB-SEM tomography

FIB-SEM tomography (Zeiss AURIGA) was performed at a tilt angle of 54° (tilt correction 36° for SEM), 5 mm working distance (eucentric point, i.e., when both FIB and SEM beams are focused on the same spot). Samples were gold-coated and copper tape was used in proximity of the area of interest. SEM imaging was conducted with an accelerating voltage of 5 kV for PMMA and 2 kV for chitosan samples. SEM images were acquired using 60 µm aperture and high current option for all samples. FIB trenches were prepared at 30 kV and 10 nA beam voltage and current at the edge of sample. FIB current was reduced to 1 nA during milling and secondary electron (SE2) image collection. PMMA membrane images were collected as slices determined by the *ZEISS Auriga FIB* at intervals of 1 as pre-set in the *FIB Control* menu, *Options* tab in the *SMART SEM* software, (the intervals are the voxel depth or z-resolution, i.e., the distance between each milled in the z-direction for those samples). Chitosan membrane data collection was performed using *ZEISS Atlas 5* interfaces as the sample was comparatively denser than the PMMA sample and it was possible to deposit a Pt protective layer. Pt protective pad and C tracker lines were deposited using GIS (Gas Injection System) using a 30 kV 1 nA beam with a pad thickness of ~ 2 µm. The tracking lines allowed for automatic adjustment for drift during milling. Trenches were prepared by the *ZEISS Atlas* software; images were collected for the selected sample area and slice intervals were determined by the software.

2.2.10. FIB reconstruction and data processing.

The software and plugins used for FIB-SEM tomography is italicized for reference. The image stack was aligned via *Linear Stack Alignment with SIFT, Registration* plugin on *Fiji/ImageJ*³² setting translation in XY as the only transformation.^{33,34} Subsequently the stack was cropped. The filtering and thresholding was conducted differently on each stack due to differences in artifacts present and feature sizes and shapes under consideration as follows:

PMMA sample: a bandpass FFT filter and Otsu threshold was applied (on a stack histogram) to yield binary images for all samples. The porosity of sample volume was measured from binary image stacks i.e., pores or cavities were set to 0 intensity (black) and membrane structure was set as 255 (white).

Chitosan membrane: a median filter (3D) was applied with a radius of 1 pixel in each direction, subsequently Otsu threshold and then *Purify, BoneJ*³⁵ was used to remove small disconnected particles.

The samples were analyzed with various *Fiji/ImageJ*³² plugins and other software. *3D object counter* was used to analyse disconnected pore volume in PMMA.³⁶ *Skeletonise* and *Analyse Skeleton* plugins were used as part of *BoneJ* plugin to measure membrane branch length and pore tortuosity.^{37–39} *Purify* plugin was used to remove unconnected particles for *Connectivity* analysis.³⁵ Pore size distributions were obtained from *thickness, BoneJ*^{37,40,41} and pore size distribution, *xlib*^{42,43} plugins; MIP simulations were additionally conducted via *xlib*. (*xlib* PSDs and skeleton analysis of the chitosan sample were obtained after the pixel size of the stack in XY was reduced 4-fold (to 20 nm × 20 nm) due to the lack of computational power). Surfaces of binarized samples were exported from *3D Viewer* on *Fiji/ImageJ*.⁴⁴ 3D rendering is performed via *Blender*,⁴⁵ (loose objects were removed for all samples). Thickness 3D maps were constructed in *Blender* normal to the surfaces (using normal dependent depth open shading language script⁴⁶). Segmentation was performed with *Fiji/ImageJ* using *MorpholibJ*⁴⁷ and *Labeling 2D 3D* on *xlib*⁴² and assessed with *3D Manager, 3D Suite*.⁴⁸ Connected pore volume visualisation is performed using *Volume Viewer* plugin⁴⁹ on *Fiji/ImageJ*. Gaussian curvature maps were constructed from sample surface meshes via *MorphoGraphX 2.0*.⁵⁰

2.2.11. Characterization

UV-Vis spectroscopy was performed using a Perkin Elmer/Lambda 35 spectrophotometer. Fourier Transform Infrared Spectroscopy (FTIR) was performed using PerkinElmer Spectrum 100 FT-IR spectrometer with ATR.

Dynamic contact angle (CA) measurements (custom built system) were recorded on five different regions of each sample using a high-speed camera (60 Hz sampling rate) to capture the advancing and receding CAs of three probe liquids (water, diiodomethane and glycerol).³¹ Liquids were dispensed with flow rates of 10 nLs⁻¹ using a 35-gauge needle (Ø135 µm OD) with droplet volume of ~100 nL. Surface energy analysis was determined from the advancing CAs of the three probe liquids using the Lifshitz-van der Waals/acid-base approach.⁵¹ Contact angles were quantified on ImageJ using “drop snake” plugin.^{52,53}

PMMA homopolymer was used to fabricate pure PMMA substrates. The powders were dry-pressed into disc-shaped pellets ≈2 mm thick at a pressure of 350 MPa in a 13 mm diameter steel pellet die (Specac, 13 mm evacuable pellet die). The as pressed pellets were exposed to toluene solvent vapour until a smooth mirror-like surface was produced. APTS melt was deposited onto Si substrates to produce flat substrates for CA measurements.

Thermogravimetric Analysis (TGA) was conducted via PerkinElmer Pyris 1 at a temperature range of 30 °C to 800 °C at a rate of 10 °C min⁻¹ under nitrogen atmosphere. Differential Scanning Calorimetry (DSC, PerkinElmer Pyris Diamond) was conducted from 20 to 250 °C at a rate of 10 °C min⁻¹.

Scanning electron microscopy (SEM, Zeiss Ultra Plus) images were recorded at an accelerating voltage of 2 kV and a working distance of 4 to 5 mm. SEM cross-sections of macro membranes were obtained at a 90° angle. PMMA membranes were cleaved after freezing in liquid nitrogen in order to preserve morphology. Other membranes were cleaved with a knife. Cross-sections of samples on Si wafers were obtained at 70° tilt angle. Polymer membranes were gold-coated prior to analysis on SEM to prevent charging effects.

Turbidity measurements were recorded for PMMA solutions at 25°C and 30°C using a Lovibond TB 100 tintometer.

Viscosity for casting solutions of PMMA (at 25°C and 30°C) and chitosan (at 25°C and 60°C) was measured over a period of 15 min at intervals of 30 s using a Brookfield DVI-Prime Viscometer and an LV-3 spindle.

Laser scanning confocal microscopy (LSCM) was performed on Rhodamine B (Rh B) stained PMMA membranes using a Leica SP8 Inverted scanning confocal microscope. Rh B was added to polymer solutions to yield 1 µM concentration. Images were obtained via LAS X software. Subsequent processing was conducted on ImageJ.

Atomic force microscopy (AFM) (Park systems, XE7) was operated in NCM (non-contact mode) under ambient conditions using silicon microcantilever probe tip (force constant of 42 Nm⁻¹).

Brunauer-Emmet-Teller (BET) analysis was carried out using Micromeritics Tristar II surface area analyser. The specific surface area was calculated using the multi-point BET method in the relative pressure range of $P/P_0 = 0.05-0.3$ using nitrogen gas at 77 K.

Mercury intrusion porosimetry (MIP) was conducted via Autoscan-33 porosimeter (Quantachrome) in order to measure a wider range of pore sizes. The pore diameter D was calculated according to:⁵⁴

$$D = \frac{-4\gamma\cos\theta}{P} \quad [2.1]$$

where θ is the contact angle between the solid and mercury, γ is the surface tension of mercury (485 dyne cm⁻¹),⁵⁵ and P is the hydraulic pressure applied to force penetration of the mercury into the pores, the larger pores are filled first and the smaller pores are filled as the pressure increases. $\theta = 150^\circ$ is used for PMMA samples and $\theta = 130^\circ$ is used for chitosan samples.

(Where applicable, values are reported as sample mean value $\pm 1s$, where s stands for sample standard deviation).

2.3. Results and Discussion

2.3.1. PMMA membranes fabrication and morphology

PMMA membranes were produced as described in the introduction and experimental sections via the air-cast TIPS method. The main aim was to test the reproducibility and control of the air-cast process prior to casting biopolymer membranes. Acetone and ethanol were the solvent and non-solvent of choice due to their miscibility and relatively low boiling points. Acetone is also cheaper versus other solvents used for PMMA such as butanol. Both acetone and ethanol are considered to be green solvents due to low environmental risk.⁵⁶ Furthermore, the toxicity of ethanol and acetone are relatively similar.⁵⁷ Acetone is a good solvent for PMMA ($\chi = 0.30$, i.e., $\chi < 0.5$) whereas ethanol promotes pore formation ($\chi = 1.30$, $\chi > 1$), where χ is the Flory-Huggins parameter from **Equation 1.4** ($\alpha = 1$) and the Hansen parameters are shown in **Table 1.1**.

The casting conditions were chosen close to room conditions (temperatures of 25–50°C and pressures of 1 atm) in order to minimize costs and environmental impacts. Melinex polyester backing was used due to high chemical and thermal resistance and low water absorptivity.

5 wt% PMMA membrane morphology is shown in **Figure 2.2**. Other 5 wt% and 5.5 wt% membranes at different conditions are shown in **Figures 2.3** and **2.4**. Glycerol (gly) doesn't exhibit visible effects on membrane architecture, but we anticipate that it will affect water permeability and tensile properties of the membranes. However, higher drying temperatures result in lower porosity and pore density in the skin layer.

The average pore sizes for the 5 wt% membrane in **Figure 2.2** are 3.07 ± 1.38 μm for skin and 3.80 ± 1.41 μm for belt as determined from SEM. Membrane thickness was estimated from SEM as 77.64 ± 2.31 μm . It can be seen that the pore sizes are rather variable. A higher content of PMMA and ethanol are expected to result in lower pore size distributions. Nonetheless, the belt side remains highly porous and hence such membranes should be used with skin side as the selective surface to control rejection of solutes.

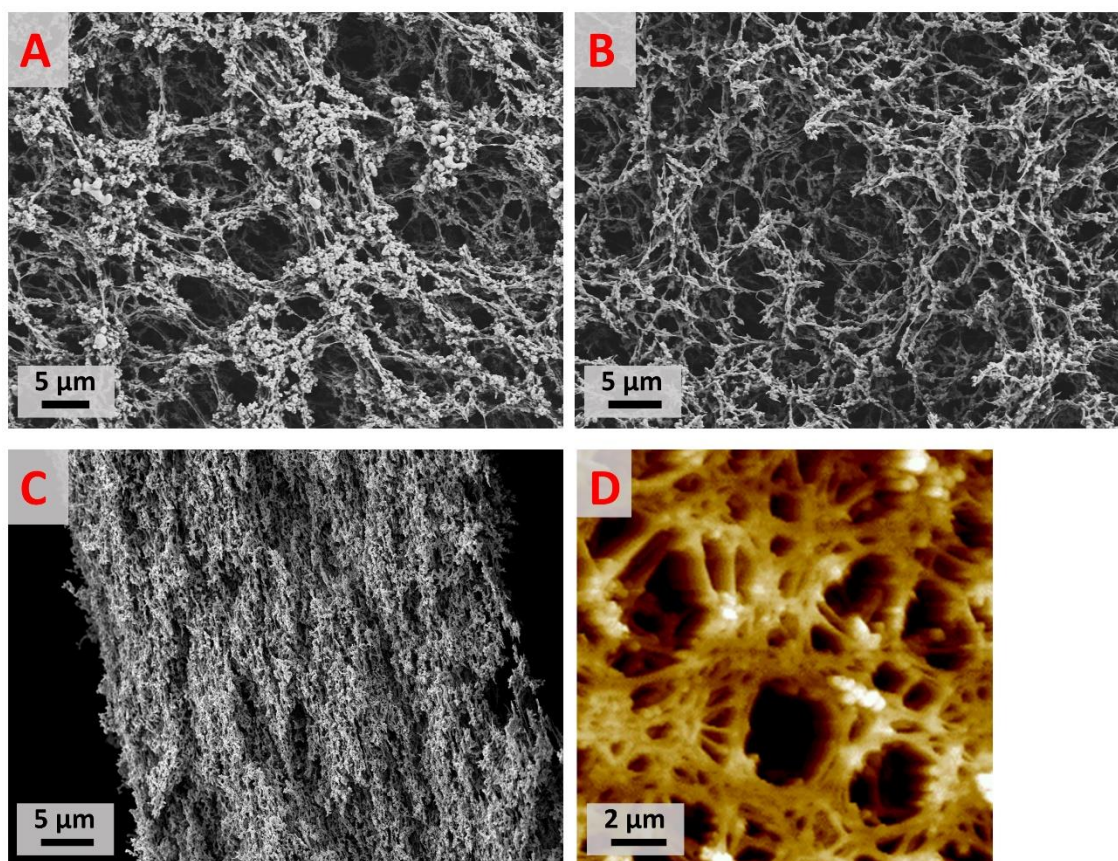


Figure 2.2. A,B,C. SEM images of skin (top), belt (conveyor-side) layers and cross-section of 5 wt% PMMA membrane dried at 30°C. D. 15 μm x 15 μm AFM image of the skin layer.

Brunauer-Emmett-Teller (BET) analysis was inconclusive as only surface area was measurable and not the pore sizes (**Appendix 2.5.2 Table A2.1**). A hysteresis was not observed as expected as the samples are macroporous. However, there is a weak correlation of surface area to pore size. The MIP graphs shows more relevant pore size information in **Appendix Figure A2.4**. The pore sizes match the observed smaller pore sizes within fibres on SEM between 20 to 40 nm and slightly larger pores with peak diameter of ~0.7 μm for 5% PMMA, APTS functionalised 5% PMMA and 5.5% PMMA membranes. However, again pore sizes observed on the SEM (above 10 μm) are beyond the porosimetry range. Thus, SEM analysis remains a more practical tool for macroporous membranes.

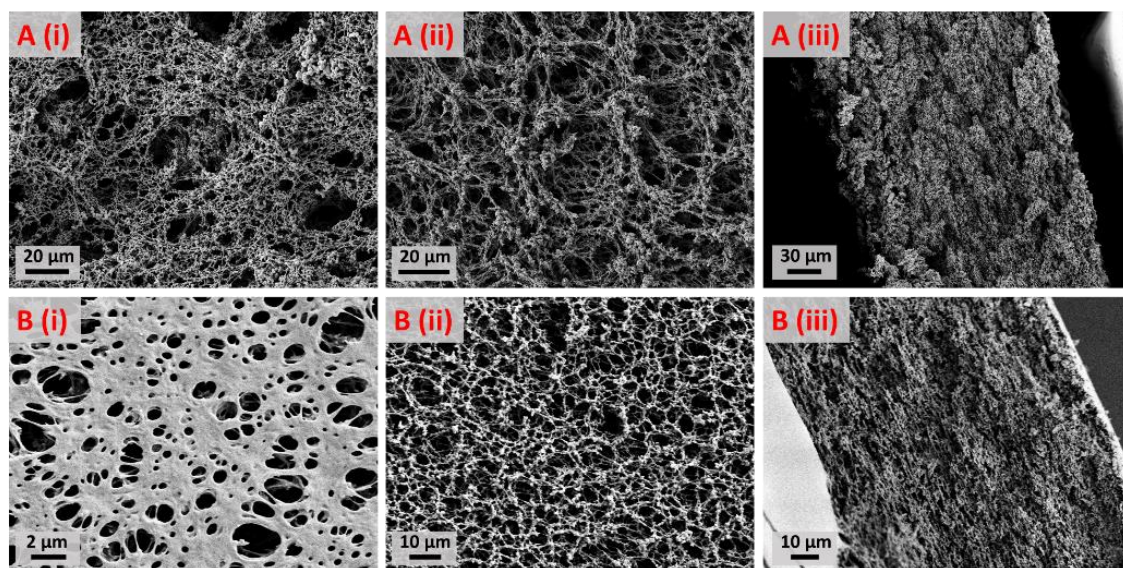


Figure 2.3. 5 wt% PMMA membranes: **A.** containing 1 wt% gly dried at 30°C and **B.** not containing gly dried at 50°C; **(i)**, **(ii)** and **(iii)** represent the skin, belt and cross-section respectively.

Porosity was estimated from Focused Ion Beam (FIB) cross-sections obtained from a 5 wt% PMMA membrane sample. The sample was sputter coated with gold/palladium prior to milling. Resin embedding was not employed as the sample displays low tensile properties such as tensile strength below 2 MPa as shown in **Figure A2.18 B**. For highly porous structures such as the ones discussed in this study, resin infiltration can modify the pore morphology^{58–60} and as such, minimal sample manipulation is used. **Appendix Figure A2.1** shows a schematic representation of FIB milling and SEM imaging as well as FIB and SEM views prior to milling. Trenches were milled around the area of interest to avoid interference and allow for smooth image collection. The secondary electron detector (SE2) was used in order to obtain direct topography of each slice. Slices were collected at intervals determined by *ZEISS Auriga* for the selected sample volume to be milled. Measurements were performed with *Fiji/ImageJ*³² with combinations of various plugins and thresholding methods.

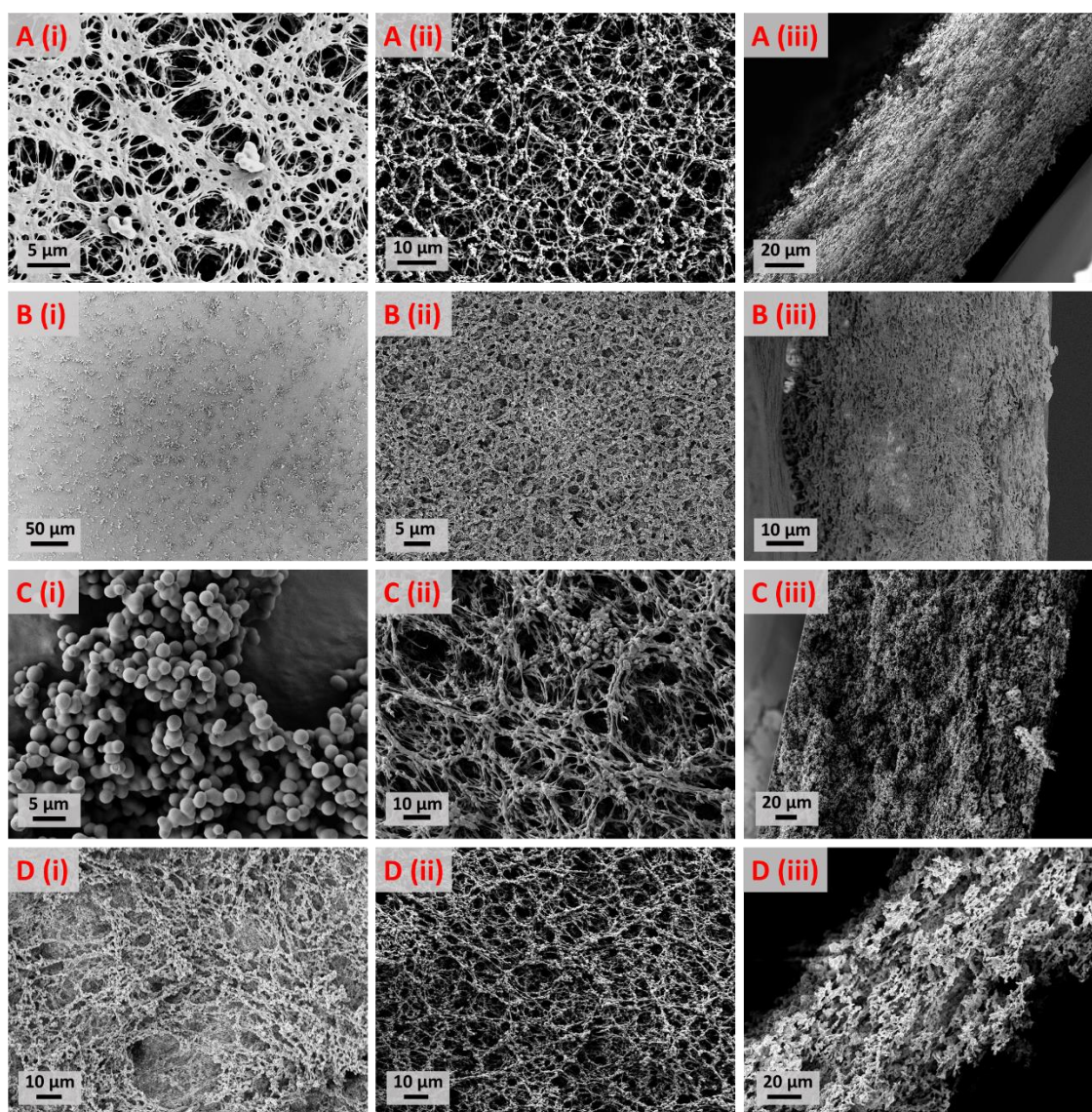


Figure 2.4. 5.5 wt% PMMA membranes without gly **A.** dried at 30°C and **B.** at 50°C. **C.** 5.5 wt% PMMA membrane containing 1 wt% gly dried at 30°C and **D.** APTS pre-functionalised 5.5 wt% PMMA membrane dried at 30°C; **(i), (ii)** and **(iii)** represent the skin, belt and cross-section respectively.

Focused Ion Beam (FIB) reconstruction of Fast Fourier Transform (FFT) filtered image stack is displayed in **Figure 2.5**. The stages of initial image preparation are outlined in **Appendix Figure A2.2**. The threshold and bandpass filter was applied according to Neusser et al.³⁴ Initially, the stack is processed with a Fast Fourier Transform (FFT) bandpass filter (**Appendix Figure A2.2 B**) and subsequently the stack is binarized (**Appendix Figure A2.2 C**). The filtering adjusts the intensity levels and filters out structures by size in order to obtain

uniform brightness in all images in the stack. Binarization allows for differentiation between pores or empty space versus the membrane branches. The threshold application (Otsu)⁶¹ distinguishes between background and foreground features well in this case. The porosity for the sample volume as shown in **Figure 2 D** ($16682.4 \mu\text{m}^3$) is measured as $70.50 \pm 4.50 \%$. The sample volume under investigation represents a section of the membrane midway between the skin and conveyor sections and only shows a small portion of the real membrane.

Skeletonise and *Analyse Skeleton* plugins were used to estimate branch length of membrane fibres. The average branch length for the sample is $1.03 \pm 0.79 \mu\text{m}$ while the maximum and minimum lengths are 8.04 and $0.04 \mu\text{m}$ respectively. The number of branches and junctions are estimated as $1.95 \text{ branches } \mu\text{m}^{-3}$ and $1.05 \text{ junctions } \mu\text{m}^{-3}$. However, when the connectivity plugin is used the number of connected branches per μm^3 is just 0.5 . The low branch junction density per volume is expected for these highly porous network membranes. The pore connectivity is similarly $\sim 0.5 \mu\text{m}^{-3}$. The matching connectivity of branches and pores show that the membrane indeed forms a porous structure. It is interesting to note that for membranes where pores are not cylindrical, tortuosity (real over minimum pore length) is used to measure flux.⁶² The *Analyse Skeleton* plugin can also be used to estimate tortuosity of pores from Euclidian distance and actual branch or pore length in 3D for pores ($\tau = 1.43 \pm 0.81$ in this example). This tortuosity relates to individual branches rather than the overall membrane thickness. Nevertheless, it provides an indication of solute and solvent path during filtration, and it is more a representative local measure of pore shape rather than simple pore size or volume measurements.

The above results, however, are very general and might not apply to the overall membrane structure. However, FIB reconstruction provides a good method to visualise and understand how morphology correlates with function. Ideally, multiple reconstructions should be analysed but the process is slow and costly. The *3D Objects Counter* plugin was used to analyse porosity, however only 163 pores were detected that are not touching the edges, (with minimum pore size set as 10 voxels). This is due to minimal size detection setting as well as the definition of what a pore represents for a branched (or sponge like) structure. Most of the membrane is interconnected pore space and only non-connected

objects were identified. The average isolated pore volume detected is $0.011 \mu\text{m}^3$ but the standard deviation is high $\sim 0.017 \mu\text{m}^3$. The smallest pore detected is $2.00 \times 10^{-3} \mu\text{m}^3$ and the largest is $0.123 \mu\text{m}^3$ which explains the large variance. The mean distance from geometrical centre to the surface for 3D objects was estimated as $0.113 \mu\text{m}$ which is similar to object radius. It is evident that setting the detection limit any lower would not yield meaningful results as the resolution of the images in the stack is $35.71 \text{ nm pixel}^{-1}$ in XY and voxel depth is 154.24 nm in this case. This process does not detect large inter-connected spaces as “pores”.

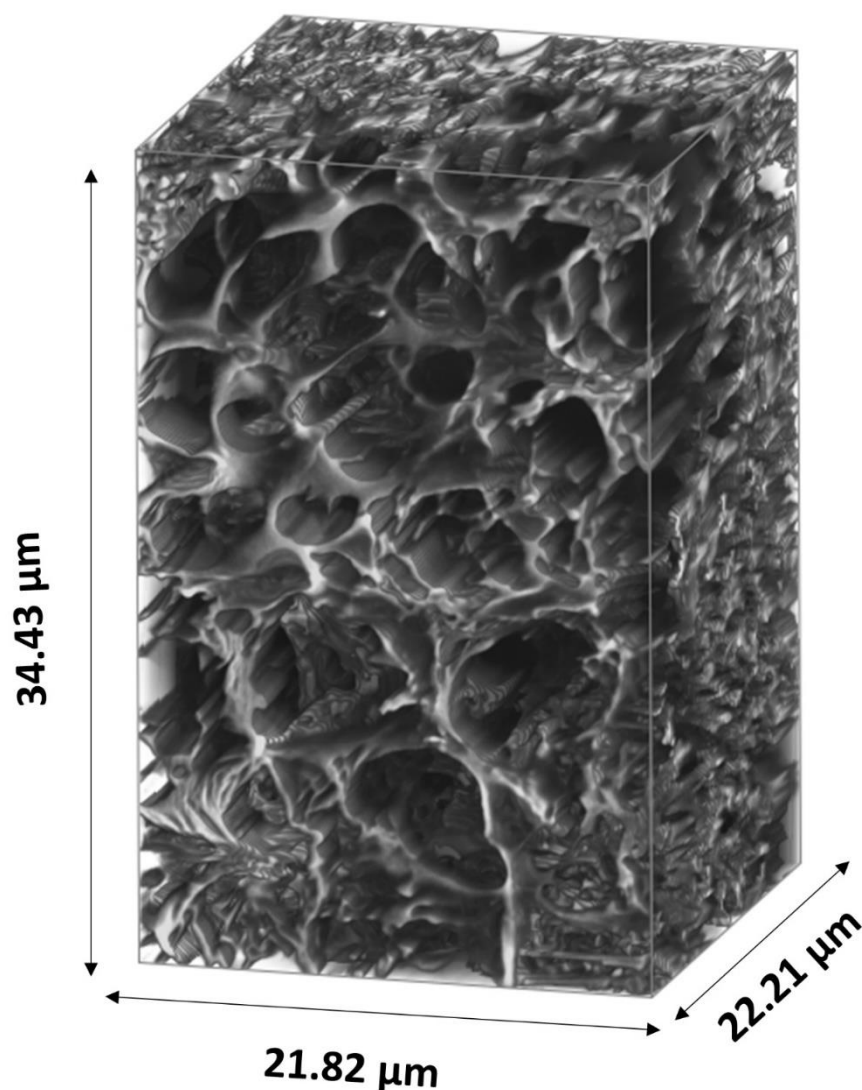


Figure 2.5. 3D volume of 5 wt% PMMA sample.

The pore size distribution of overall pore space was analysed using *thickness* and *xlib* pore size distributions (PSDs). Cumulative pore distributions are displayed in **Appendix Figure A2.3**. *Thickness* assumes spherical pores and fits those to the pore space with a maximum size detected over 3 μm in diameter. Pores detected via *xlib* display a higher diameter up to approx. 5 μm . The mechanism of pore detection is different as *thickness* plugin is more suitable for isotropic stacks, some error can be incurred. However, PSD calculations via *xlib* are slower as more iterations are required. The PSD distributions (*thickness* and continuous PSD via *xlib*) display a similar shape showing a similar pore volume continuity throughout the sample volume. The average diameter detected via *thickness* is 1.11 μm and 1.68 μm via *xlib* plugins. The size variation is not huge, however both values display high sample deviations of 0.66 μm and 1.10 μm respectively. Nevertheless, the PSDs offer a good indication of pore size and pore sizes spread throughout the sample. The average max feret diameter in 2D XY plane is 1.47 μm which is close to the estimation by *xlib*, while the min feret diameter is 0.81 μm which is closer to the *thickness* estimation in this case. Furthermore, a MIP simulation was run with intrusion start area for intrusion set as the XY plane, yielding a mean diameter of 1.10 μm which matches the estimate of *thickness* closely. The MIP PSD displays steps indicative of several peak pore diameters, for example at 1.0, 1.4 and 3.0 μm signifying that the distribution is anisotropic. The PMMA sample analysis tomographic PSD measurements were close to the measurements via experimental MIP with average pore sizes $\sim 0.71 \mu\text{m}$. The average is close to the measurement via *thickness* plugin and the MIP simulation via *xlib*. Therefore, tomography via FIB-SEM gives an estimate of porosity and provides visual and quantitative structural representation of the 5% PMMA membrane.

The rendered 3D models via *Blender*⁴⁵ with thickness maps normal to the surfaces⁴⁶ are shown in **Figure 2.6**. Furthermore, connected pore regions were also obtained via *Labeling 2D 3D* in *xlib*⁴² and visualised via *Volume Viewer*⁴⁹ in ImageJ (**Appendix Figure 2.4 A**). The connected components are displayed in the same colour. The analysis was conducted using *3D Manager* as part of *3D Suite*.⁴⁸ For PMMA a total of 501 different phases were identified i.e., 500 disconnected particles which account for approx. 0.03% of the total volume.

Gaussian curvature 3D maps were obtained via *MorphoGraphX 2.0*⁵⁰ as shown in **Appendix Figures 2.4 B and C** with a neighbourhood of 1 μm . Gaussian curvature is useful as it is intrinsic to the surface independent of deformation.⁶³ The curvature helps to visually interpret whether the surface is flat (a 0 value curvature) or not (positive values indicating peaks or local valleys and negative values indicating saddle points).⁶⁴

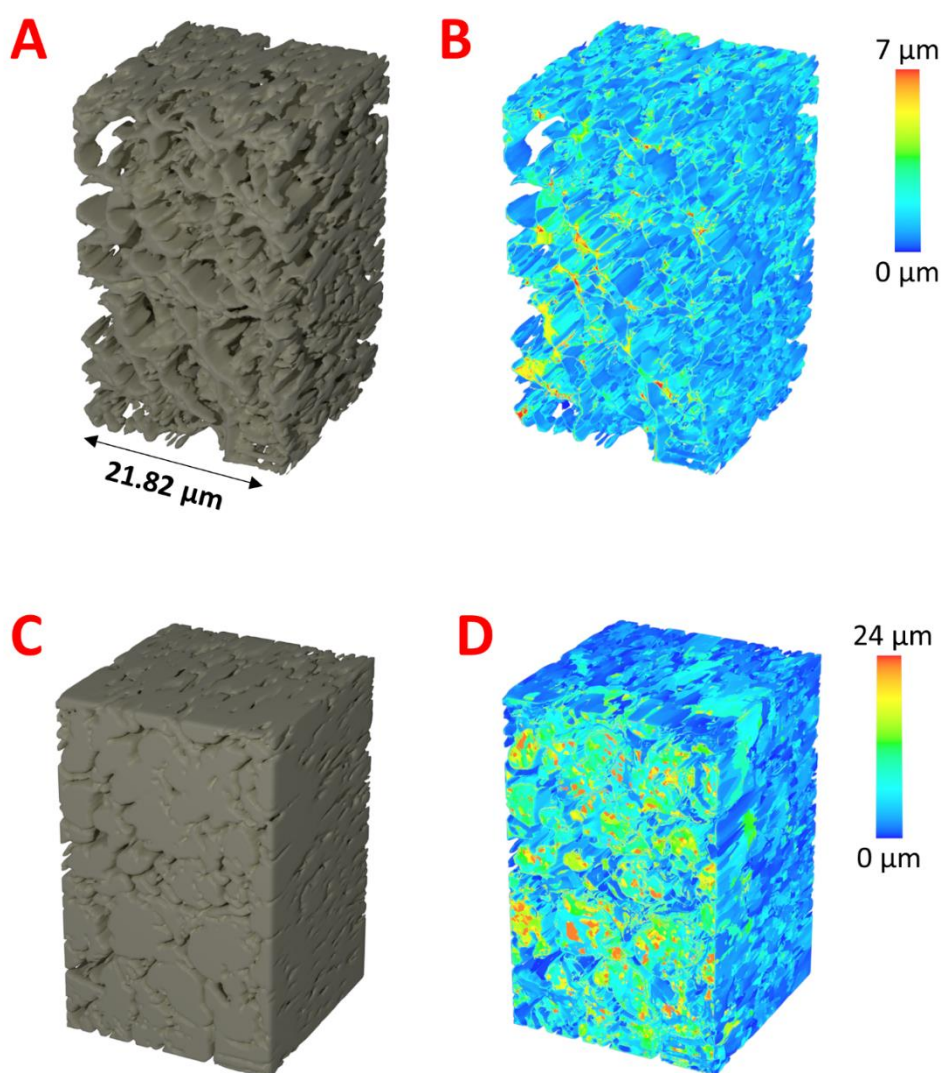
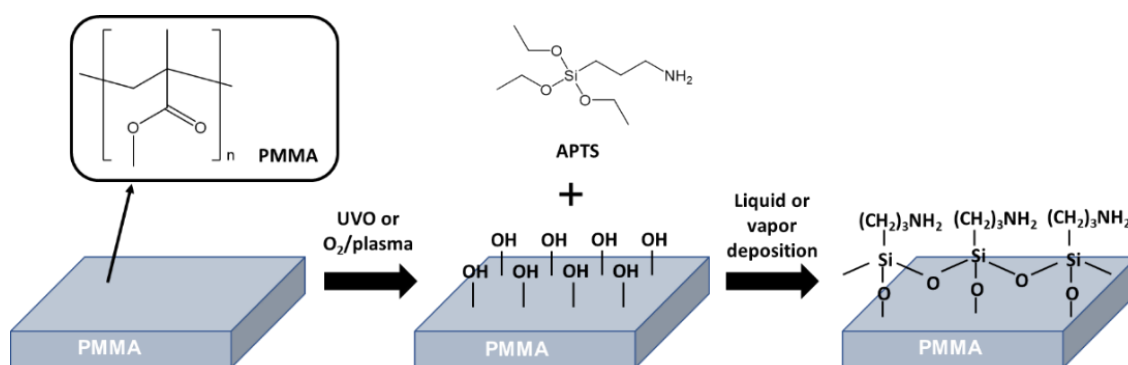


Figure 2.6. Rendered 3D models for membrane samples. **A – D.** show the PMMA membrane, branch thickness map, membrane pore space and pore space density map respectively.

2.3.2. Functionalization with APTS and its effect on membrane properties

APTS functionalization was achieved according to **Scheme 2.1**. Preliminary liquid based APTS deposition was employed but the degree of functionalization was not significant, possibly due to long deposition time and high temperatures required for condensation reaction (**Appendix 2.5.3**). Furthermore, there is a kinetic constraint during liquid deposition as PMMA is a large molecule and thus APTS needs time to orient correctly for bonds to form. Alternatively vapour based deposition in a vacuum oven at 200 mbar, 110°C yielded higher deposition rates as seen from Ninhydrin tests (**Appendix 2.5.3**). The chosen conditions were deduced from the Antoine Equation as shown in **Appendix 2.5.3** and are optimal for lab based vapour deposition avoiding low pressures.⁶⁵



Scheme 2.1. Functionalisation of PMMA with APTS.

The morphology of the pre-functionalised PMMA membranes does not vary significantly compared to the non-functionalised membranes (**Figure 2.7**). Pore sizes are $5.86 \pm 2.86 \mu\text{m}$ and $18.56 \pm 15.50 \mu\text{m}$ for skin and belt respectively with estimated thicknesses of $192.57 \pm 14.84 \mu\text{m}$ from SEM. The contact angle (CA) test is not a useful technique here as the high membrane porosity obscures the measurement. The relationship between surface roughness and CA as defined by Wenzel relates the apparent or measured CA (θ_{apparent}) to actual contact angle (θ) given smooth surface:⁶⁶

$$\theta_{\text{apparent}} = r \cos \theta \quad [2.2]$$

where r is simply the roughness factor defined as the surface area divided by geometric surface area.⁶⁶

Therefore, the measured CA can be overestimated as the surface roughness is not well defined for microporous membranes. As an alternative, a PMMA brush was used to optimise CA measurements shown in **Appendix 2.5.3**. The PMMA brush deposition was adopted from a method reported by Lundy *et al.*³¹ The APTS-PMMA brush shows similar CA value to the APTS brush atop silicon.

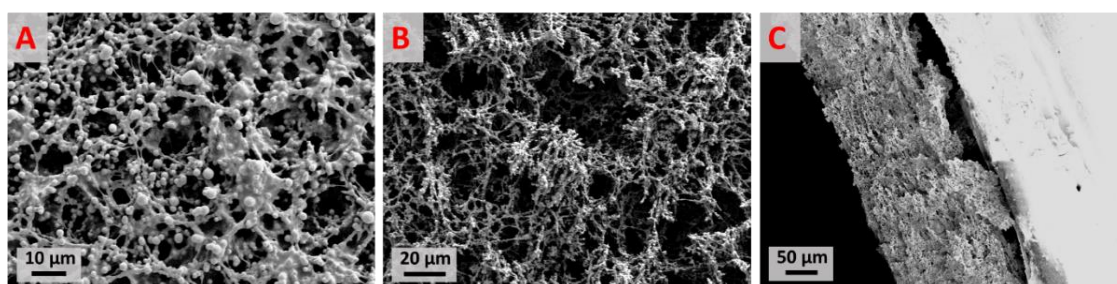


Figure 2.7. SEM micrographs of **A.** skin, **B.** belt, **C.** cross-section of 5 wt% APTS pre-functionalised PMMA membrane dried at 30°C.

The main advantage of casting a pre-functionalised material is that the membrane is modified throughout the matrix and APTS groups should be exposed inside the pore surface. Despite the morphology of the membranes not changing after functionalization of PMMA with APTS, the hydrophilicity of the membranes increases. A capillary flow time (CFT) test was used to qualitatively determine degree of water permeability. The CFT across a 40 mm length of APTS functionalised PMMA is approx. 4 mins, whereas non-functionalised PMMA shows a time of over 10 mins. This effect is attributed to the amine moiety facilitating water adhesion to the membrane and thus improving the flow rate. A comparison between PMMA morphology is summarised in **Figure 2.8**. Pore sizes for APTS pre-functionalised membranes are higher than for non-functionalised counterparts. This is explained by APTS miscibility with the acetone/ethanol solvent system. The allyl amine end group of APTS shows $\chi = 0.26$ and 0.51 for acetone and ethanol respectively.

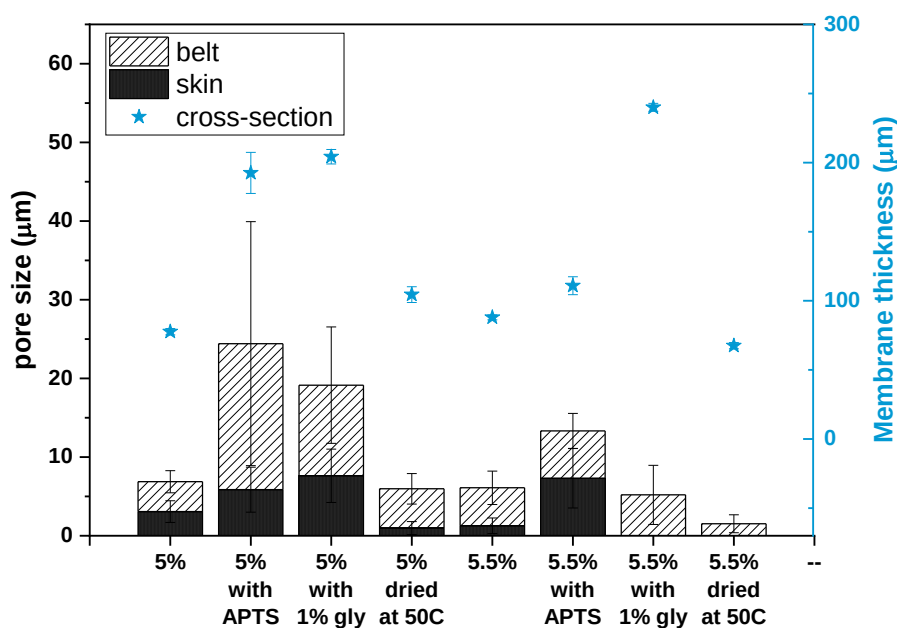


Figure 2.8. Pore size and cross-section thickness for cast PMMA membranes.

Drying at 50°C results in reduced pore size and dense skin formation if more PMMA is incorporated, as seen from 5.5 wt% samples. Higher temperatures result in faster drying and acetone evaporating and thus there is insufficient time for phase inversion to occur as explained by the ternary phase diagram. The 5.5 wt% samples display considerably lower porosity, especially for the skin where it was a dense nonporous layer. This structure can be useful for screening solutes. The membrane thickness is also proposed to have some effect on porosity but the high variance in results cannot yield conclusive interpretation for pore size. Thus, the dry phase inversion method does not exhibit a lot of controllability in the final outcome. It is important to note that functionalisation of PMMA with APTS led to membrane brittleness and it was impossible to prepare APTS-PMMA membranes for tensile analysis. This shows that the tensile strength of APTS-PMMA is much lower than that of PMMA membranes alone (~ 5 MPa for 5 wt% PMMA membranes).

2.3.3. Chitosan membranes

Chitosan membranes were fabricated similarly to the PMMA membranes; however, water vapour was used to promote chitosan demixing from the aqueous acetic acid (aq. AcOH) solvent system. This process is called water VIPS.⁶⁷ The lower the amount of chitosan in the film, the higher the porosity, which can be explained by the density of fibres in the membrane. (A comparison between conditions in the curing chamber for PMMA and chitosan membranes can be found in **Appendix 2.5.4, Figure A2.12**). Chitosan is weakly basic and does not dissolve in water at pH 7, thus AcOH was added in small quantities to promote dissolution. 1 wt% and 2 wt% chitosan solutions in water display pH values of 2.8 and 2.6 respectively, thus chitosan dissolves readily. In this case, acetic acid is considered a relatively green solvent while water is inherently green.⁵⁶ The addition of water (nonsolvent) to the system should logically result in the reduced chitosan solubility, hence in order to reduce waste during the curing process, water was used in vapour form. Furthermore, if water was to be added in liquid form during curing, the membrane phase separation could very rapid, and the membranes could crack due to rapid changes in the local pH. The VIPS processes also reduces solvent waste overall compared to conventional wet or immersion phase inversion methods as no coagulation nonsolvent bath is required.

The chitosan casting solutions display higher viscosity compared to PMMA solutions at room temperature ~ 25°C, i.e., for PMMA solutions the viscosity values are below 100 cP and for chitosan solutions the viscosity is over 2000 cP as seen in **Appendix Figure A2.13**. Furthermore, at comparative casting temperatures, 30°C for PMMA and 60°C for chitosan, the viscosity of chitosan solutions remains high for 4 wt% and 5 wt% chitosan solutions. At 60°C 2 wt% and 3 wt% chitosan solutions display viscosities below 1000 cP. Thus, membranes derived from those solutions are expected to be more porous than 4 wt% and 5 wt% chitosan membranes due to improved solvent exchange. The turbidity of chitosan solutions was not recorded as the solutions are coloured and the turbidity value would be exaggerated, however turbidity data for PMMA solutions is shown in **Appendix Table A2.4** as an example. Only a marginal

difference is observed between 25°C and 30°C for all PMMA solutions as expected.

Chitosan membranes were prepared at low temperatures ~30–35°C in order to reduce energy costs associated with high temperature processing. SEM micrographs of 2, 3 and 4 wt% chitosan membranes are shown in **Figure 2.9**. The measured pore sizes for the 2 wt% chitosan membranes shown are $6.78 \pm 4.71 \mu\text{m}$ for skin and $10.56 \pm 5.11 \mu\text{m}$ for belt and the thickness is $36.43 \pm 0.93 \mu\text{m}$. A 2 wt% chitosan FIB reconstruction is shown in **Figure 2.10**.

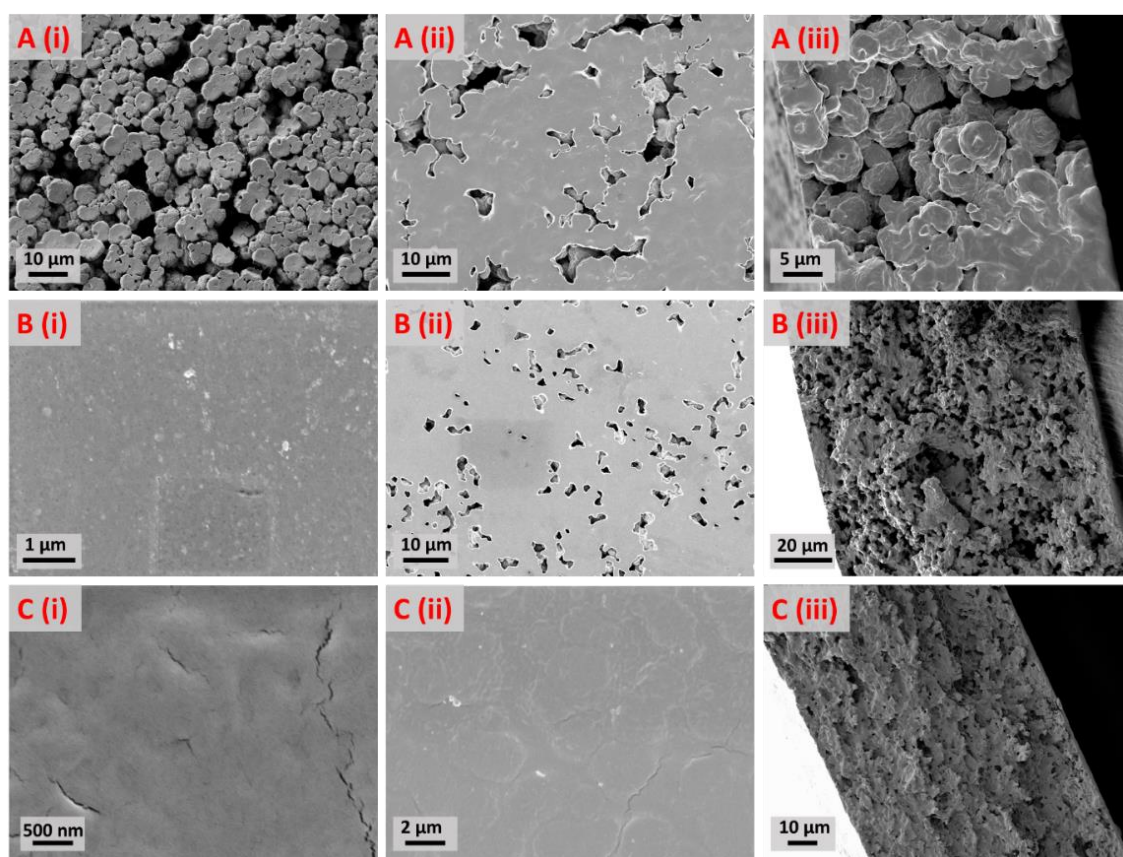


Figure 2.9. SEM images of **A.** 2 wt%, **B.** 3 wt% and **C.** 4 wt% chitosan membranes respectively; (i), (ii) and (iii) represent the skin, belt and cross-section respectively.

BET analysis (**Appendix 2.5.2. Table A2.1**) showed low surface area for all samples as expected as the chitosan films are dense. 2 wt% chitosan sample was expected to show a larger than $0.01 \text{ m}^2 \text{ g}^{-1}$ surface area value, but possibly

due to highly dense belt layer the recorded surface area is low. The MIP analysis for 3 to 5 wt% chitosan membranes showed no porosity, however the 2 wt% membrane (**Appendix Figure A2.5 D**) displays majority of pores in the range of > 1000 nm as expected from the SEM data.

The 2 wt% chitosan sample was reconstructed via FIB-SEM similarly to PMMA in order to understand the inner structure of the pores. Herein, *ZEISS Atlas* was employed as the sample displayed comparatively flat and smooth regions and it was possible to deposit a platinum layer with carbon tracking lines (see the **Experimental section 2.2.9**). The *ZEISS Atlas* software allows for real time z-tracking and for shift corrections in XY during milling. Furthermore, imaging parameters can be automatically adjusted by the software and the data collection is fully automated once the desired sample area is selected. The stages of FIB tomography using the *ZEISS Atlas* software for the chitosan sample are displayed in **Appendix Figure A2.14**. The *ZEISS Atlas* interface allows for better tracking in z-plane and image alignment in XY during the scan. The software allowed for spatial location checking during the scan with the aid of carbon tracking lines. The *ZEISS Atlas* software provides improved image resolution compared to conventional slice collection at arbitrary intervals as the resolution is 5 nm pixel⁻¹ in XY and voxel depth is 22.25 nm. However, images were still aligned for translations in XY plane post slice collection.

A similar post-processing methodology to the PMMA sample was then applied to the chitosan membranes as shown in **Appendix Figure A2.15**. The chitosan membrane images were processed using a median 3D filter as the FFT bandpass identified features hidden in the layers below the XY plane (**Appendix Figure A2.15 B**). This highlights the necessity to compare the original stack to post processing images as certain bias may be incurred in the final result (**Appendix Figure A2.15 C**).

A volume of ~489.9 μm^3 of the 2 wt% chitosan sample was reconstructed via FIB-SEM tomography as described in the experimental section and shown in **Figure 2.10**. The measured porosity is $63.18 \pm 3.40\%$. Furthermore, the produced chitosan membranes, unlike PMMA, have finger-like pores or macrovoids (**Appendix 2.5.6**) and thus a different mechanism of filtration. It would be difficult

to observe this pore structure via conventional SEM cross-sections due to membrane fracturing if sample preparation is inadequate.

The number of connected branches is estimated as 393.3 branches per μm^3 , thus the specimen is significantly denser packed than the PMMA membrane sample. The average feret diameter of the finger-like pore if viewed top-down and averaged through the z-plane is 236 nm at maximum distance and 82 nm at minimum. The standard error is not shown as it is higher than the feret diameter due to large range of values. The circularity of those finger-like pore cavities is low and estimated as 0.55 ± 0.27 .

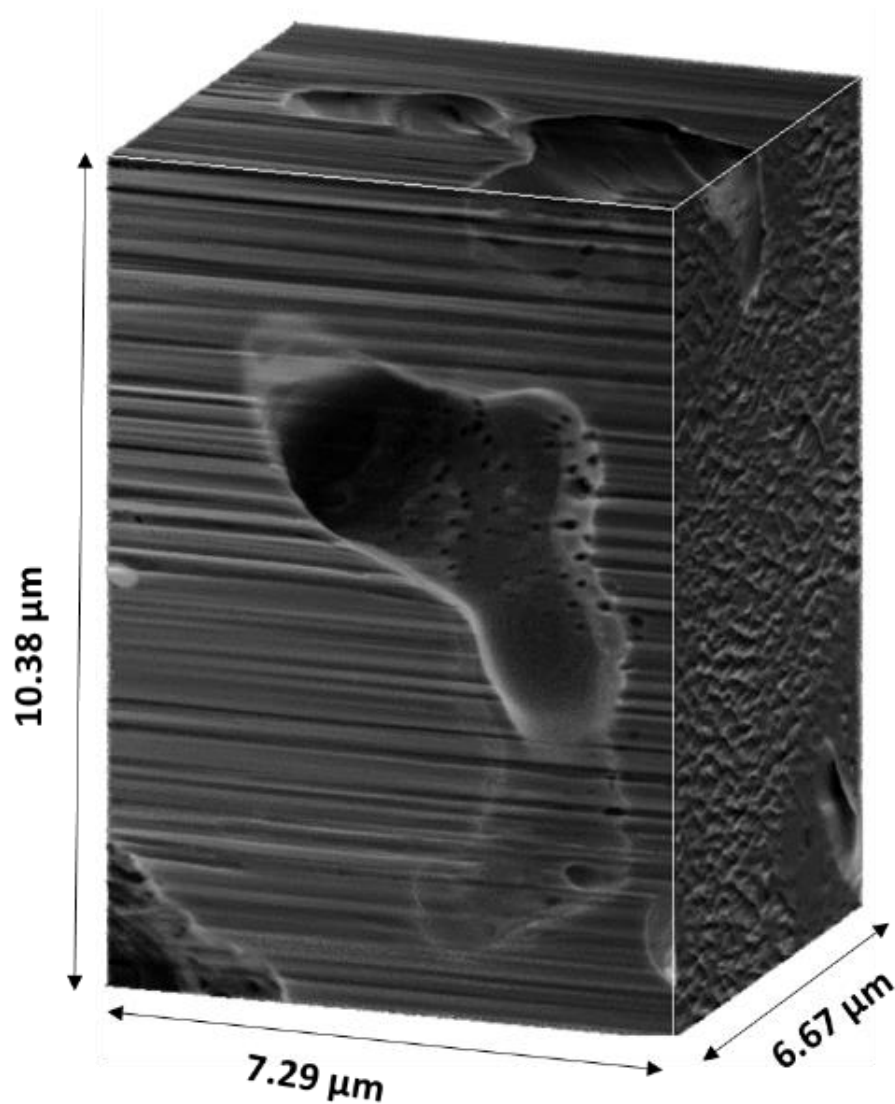


Figure 2.10. FIB reconstruction of the 2 wt% chitosan membrane.

The PSD distributions were measured similar to the PMMA sample as seen in **Appendix Figure A2.16**. As before the *xlib* PSD detects a higher pore diameter than the *thickness* plugin. The average pore diameter via *thickness* is 128 nm which is two times lower than *xlib* estimation of 302 nm. The overall distribution shapes are the same as before, showing smooth shapes and thus isotropic pore size distributions. The *xlib* plugin estimation is closer to the maximum feret diameter in 2D plane for the chitosan sample and is thus more indicative of maximum pore size. The MIP simulation yields an estimated pore diameter of 130 nm on average which is again closely matching the *thickness* value like for the PMMA membrane. In this case, MIP infiltration direction was set as the top through the XZ plane following the direction of finger-like pores. The experimental MIP technique in detects large cavities in the chitosan sample at peak diameters of 2.27 μm and 5.33 μm , which are close to SEM measurements. However, a small peak at 308 nm is close to the estimated average via the *thickness* plugin and the MIP simulation as for PMMA. Other MIP peaks at 17, 20 and 32 nm are not well detected via FIB-SEM tomography as the resolution in z for chitosan was ~ 20 nm. A peak at 547 nm is also not evident from tomography, however this could be due to large spread of PSD distributions obtained via FIB-SEM. Thus, in this case the difference between tomography and MIP is large possibly due to sample region selection for FIB-SEM. For PMMA a section midway between the top and the conveyor sides was reconstructed, but for chitosan a section at the top layer was selected.

The tortuosity of the pores was measures as 1.35 ± 0.53 from the skeletonized pores which is higher than expected, but it is likely skewed by the presence of large cavities as well as cylindrical pores. Furthermore, pore connectivity is approx. $137.5 \mu\text{m}^{-3}$. The chitosan membrane has a much higher density of interconnected branches than pores (2-fold difference), showing that the structure does not form a network but rather disconnected voids. The rendered 3D model via *Blender* is shown in **Figure 2.11**. The connected pore space and gaussian curvature maps are shown in **Appendix Figure A2.17** similarly to the PMMA sample. The chitosan sample contains 692 objects and 691 disconnected particles ($\sim 0.30\%$ of the total volume). Thus, the structure shows higher discontinuity than PMMA as expected.

The degree of deacetylation of chitosan is measured via Fourier Transform Infrared (FTIR) to be ~77.7% as described by Brugnerotto *et al* (**Appendix 2.5.7. Figure A2.18 A**).⁶⁸ The formula used takes into account bands in the fingerprint region (1320 cm^{-1} and 1420 cm^{-1}) and thus water content does not affect the measurements.

Chitosan membrane tensile properties improve with increased chitosan content as observed from tensile strength analysis (**Appendix Figure A2.18 B**), however as a test an air cast-TIPS produced 3 wt% chitosan membrane was also examined. A substantial improvement in Young's modulus is observed if VIPS method is used (**Figure 2.12**). However, tensile strength for all chitosan films is below 20 MPa as shown in **Appendix Figure A2.18 B**. Thus, in general chitosan membranes only survive filtration at ambient conditions.

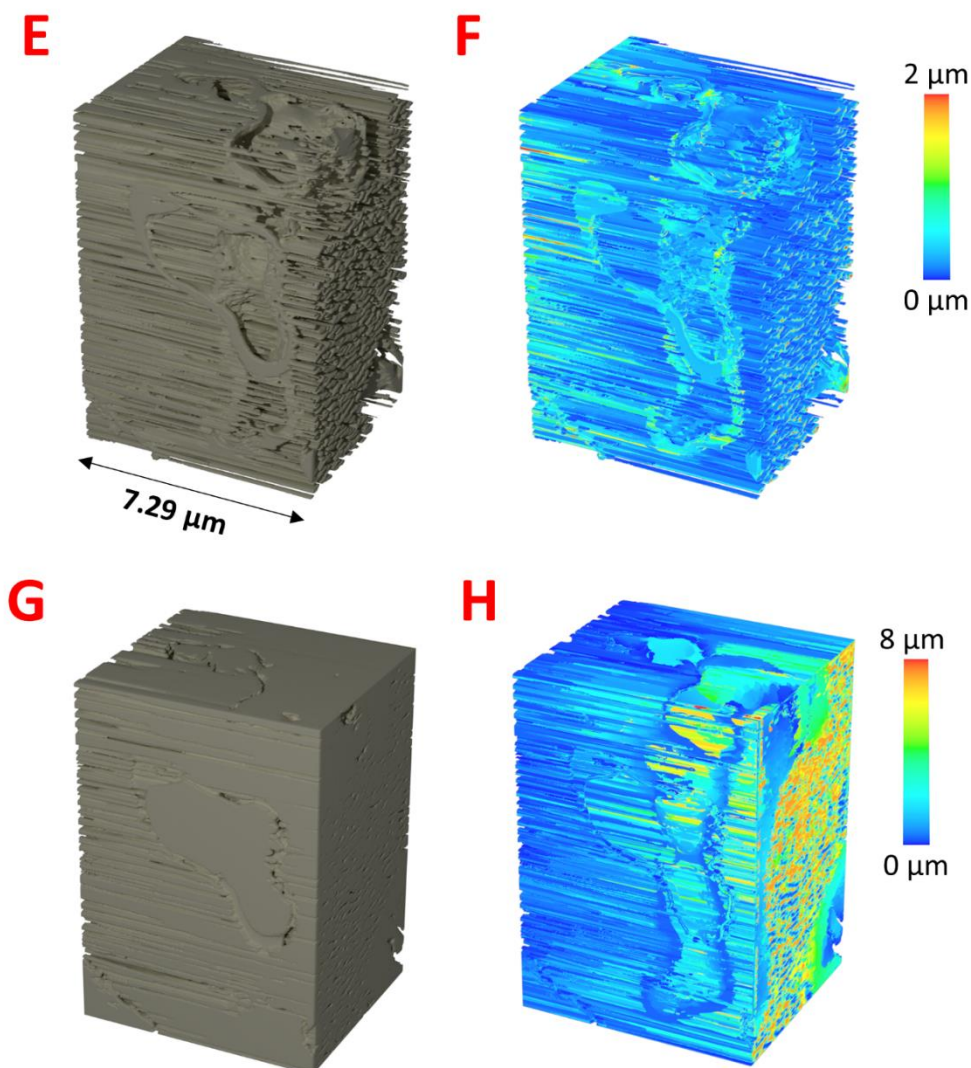


Figure 2.11. Rendered 3D models for membrane samples. **A – D.** represent the chitosan membrane, membrane thickness map, membrane pore space and void space density respectively.

2.3.4. Phase Inversion Membranes Comparison

The advantage of chitosan over PMMA is that it is inherently a more sustainable choice as membrane material. However, modifying chitosan porosity by the phase inversion method is not as straightforward as for PMMA. Chitosan membranes appear denser and display higher elasticity and dye retention compared to PMMA membranes. The summary of select PMMA and chitosan membranes is depicted in **Figure 2.12**. The 5 wt% PMMA membrane has a

comparatively low Young's modulus $\sim 74.43 \pm 0.19$ MPa in comparison to chitosan membranes. This is likely due to higher porosity of the fabricated PMMA membranes. It is interesting to note that the 3 wt% chitosan sample produced without water vapour shows a significantly lower Young's modulus compared to its water VIPS produced counterpart (132.46 ± 56.41 MPa compared to 194.85 ± 27.23 MPa). Tensile strength, although higher for chitosan membranes (~ 18 MPa) compared to PMMA membranes (~ 5 MPa) is still low. This explains fracturing of the membrane during filtration if vacuum suction was applied.

Dye retention is calculated according to **Equation 1.16** from UV-Vis studies. Chitosan membranes display a considerably higher retention ($\sim 40 - 60\%$) than PMMA ($\sim 20 - 30\%$) given their dense structure as expected.

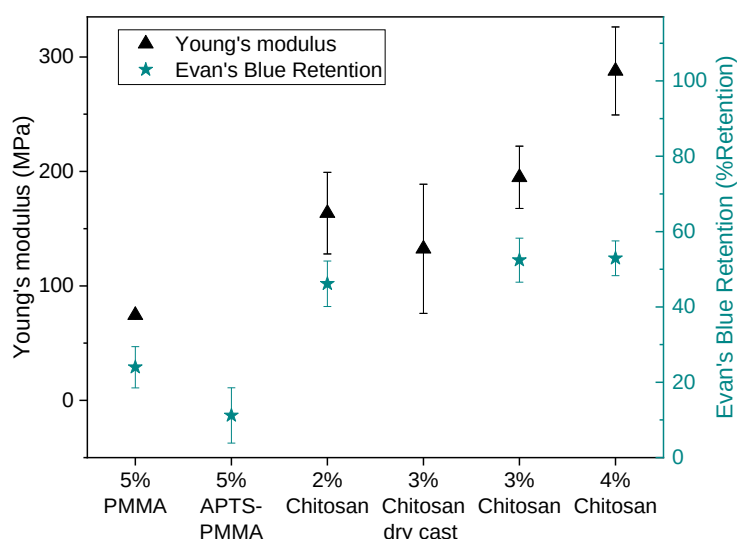


Figure 2.12. Young's modulus and Evan's Blue retention data for select PMMA and chitosan membranes.

Another interesting observation is that %retention of Evan's Blue is nearly 2 times lower for APTS pre-functionalised PMMA compared to non-functionalised membrane. This is explainable by higher pore sizes for APTS-PMMA. However, APTS moiety is also more hydrophilic than PMMA and thus it should improve water permeability as well.

Apart from tensile and dye retention properties, the membranes display physical and chemical differences. Chitosan films appear smoother as seen from AFM images in **Appendix Figure A2.19** as well as less porous than PMMA films (**Figure 2.2 D**). Furthermore, it was possible to obtain a Laser Confocal Scanning Microscopy (LCSM) reconstruction of the 5 wt% PMMA membrane (**Appendix Figure A2.20**) as rhodamine B (RhB) dye penetrated the structure, while chitosan does not incorporate the dye well. LCSM also needs deconvolution and thus FIB-SEM reconstruction is superior as no fluorophore is required to provide architectural characterization of the membranes.

In terms of thermal stability, both chitosan and PMMA have high degradation temperatures of over 300 °C as seen from TGA in **Appendix Figure A2.21** (376°C for PMMA and 310°C for chitosan). Thus, the temperature stability is only slightly different for both. DSC in **Appendix Figure A2.22** shows that both polymers have similar glass transition temperature i.e., approx. 78 °C for PMMA and 87 °C for chitosan. Therefore, in terms of processing and thermal stability both polymer systems can be treated similarly and provide a good synthetic polymer versus biopolymer comparison.

Photographs of the membranes in **Appendix Figure A2.23** show that PMMA membranes are visually more porous than their chitosan counterparts, which appear shiny; this is indicative of a denser packed structure as proven by SEM analysis. Furthermore, several centimetre dimension membrane sheets are feasible as shown. However, membranes tend to be brittle, and it is hard to prepare evenly cut sheets as seen in the photograph.

The dry phase inversion method is a facile approach for membrane fabrication, but the lack of controllability makes it a rather unreliable method for precise pore control as observed from the overall PMMA and chitosan results. Whereby dense or microporous microfiltration membranes are required, this method proves to be useful as the costs and efficiency of production are balanced. However, a more systematic approach with set input conditions and output membrane parameters is required for biomolecule filtration.

2.4. Conclusions

In this study, we have examined the feasibility and performance of APTS functionalised PMMA membranes constructed using an air-cast TIPS method. The performance of the PMMA membranes was measured via comparison to chitosan membranes constructed using the VIPS method, demonstrating that both the TIPS and VIPS techniques are viable options for large-scale membrane fabrication.

Pre-functionalisation of the polymer mix is possible prior to casting, hence removing the necessity for post processing. However, due to the asymmetric nature of the membranes produced via this technique, conventional pore size quantification is difficult. Thus, a protocol for successful SEM and FIB-SEM 3D reconstruction was designed to identify descriptors such as pore diameter and volume, porosity and tortuosity. Furthermore, this allows to visualise the true pore structure with nanoscale precision, which is not accessible via BET, mercury porosimetry or LCSM.

APTS modification allowed for improved lateral flow as assessed by CFT with a 4-fold improved flow rate. This shows that surface functionalisation has an effect on flow capabilities and that pre-functionalisation is successful via vapour deposition methodology. Nevertheless, the addition of APTS led to reduced tensile properties as the membranes were too brittle for tensile tests. However, crosslinking or the addition of plasticizer can potentially improve the quality of the APTS-PMMA membrane.

Chitosan membranes were adopted for VIPS, however only the 2 wt% chitosan membrane displayed visually distinct pores. VIPS was shown to improve tensile properties of 3 wt% chitosan membrane versus TIPS methodology. FIB reconstruction was adapted similar to PMMA to provide insight into pore structure. Conversely to PMMA, chitosan films displayed finger-like pores. Furthermore, the tensile properties of chitosan are shown to be better than PMMA, such as improved tensile strength and Young's modulus. Dye retention is over 20% higher for chitosan membranes for Evans Blue, which is consistent with pore size.

Both tensile properties and dye retention is expected to improve for all membranes if crosslinking is applied. However, this will be the focus of future work and entails a set of entirely different studies.

In summary, our work demonstrates that APTS vapour deposition can be successfully performed on PMMA brushes and rough membrane surfaces alike, which can be used to modify material applications. We have also shown that a 3D reconstruction and analysis technique can be applied to membrane characterization when other techniques are not feasible; we anticipate that this technique may find further application to materials beyond membranes in fields such as electronics, sensing and diagnostics. Overall, our membrane production methodology and characterization routes provide novel processing tools for future membrane technology.

2.5. Chapter 2 Appendix

Appendix 2.5.1. Focused Ion Beam preparation and data processing.

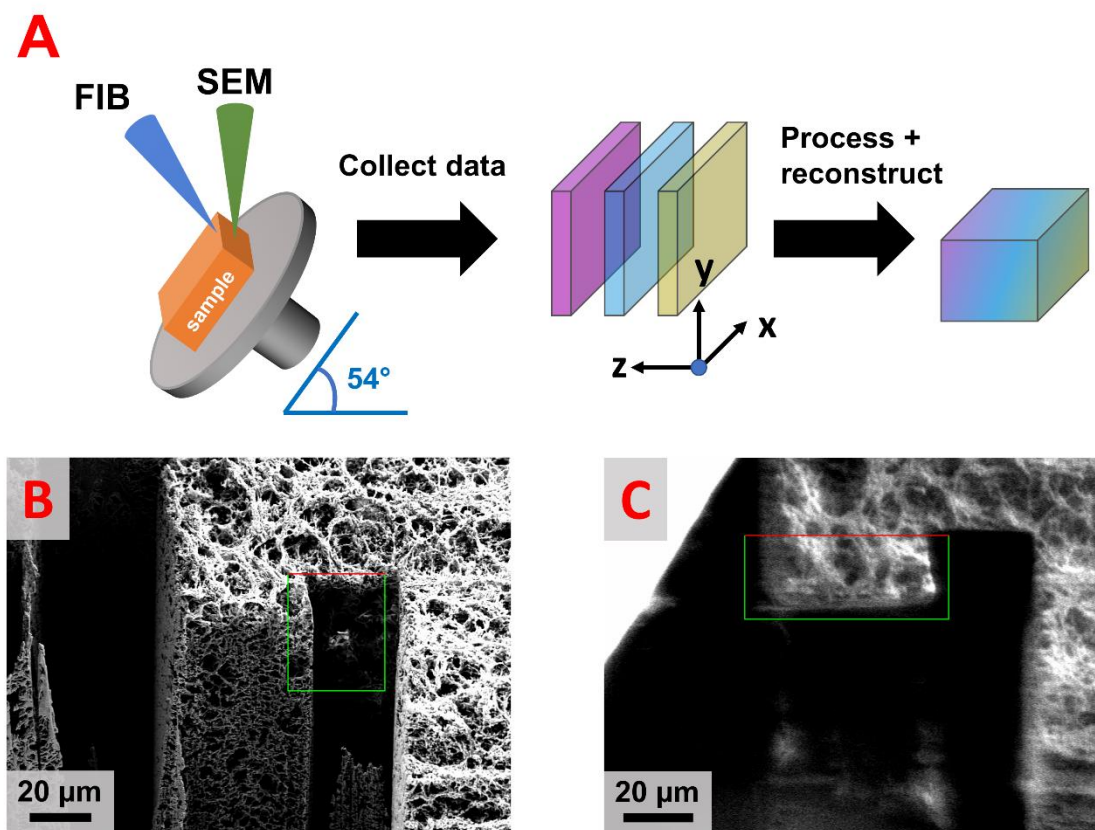


Figure A2.1. A. schematic of the FIB-SEM tomography and reconstruction. Trench prior to FIB reconstruction of PMMA membrane: **B.** SEM micrograph (5kV, 60 μm aperture) of the trench to be milled. **C.** FIB micrograph (30kV, 4nA) with the area to be milled enclosed in rectangle selection.

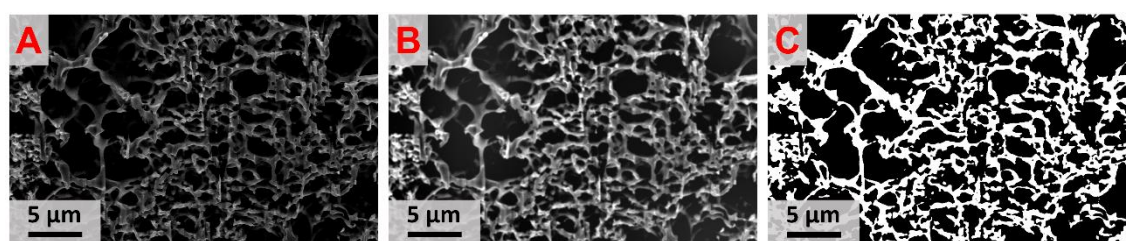


Figure A2.2. Image processing representation applied to image stack after FIB mill and SEM recording. **A.** Raw 5 wt% PMMA SEM image. **B.** FFT bandpass filtered image. **C.** Binarised image.

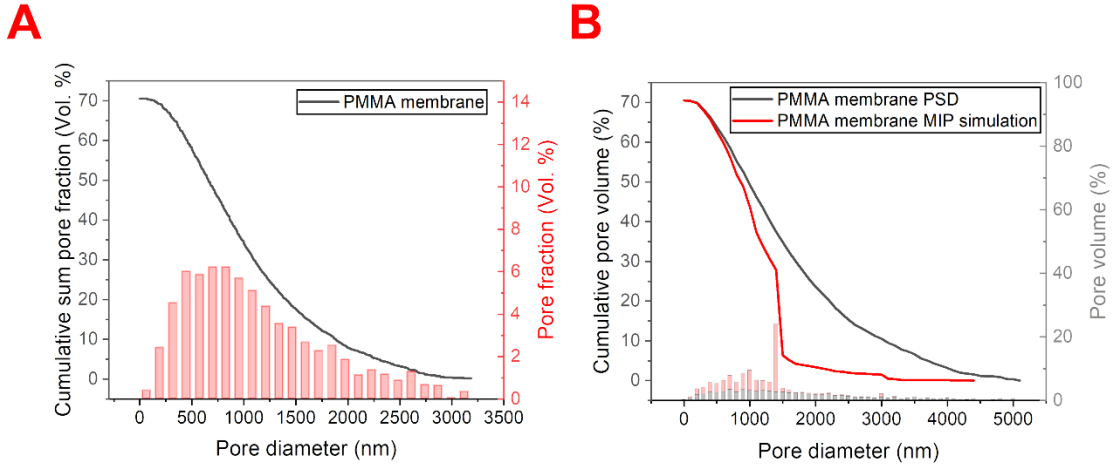


Figure A2.3. A. pore size distribution using *thickness*, *BoneJ* plugin and B. continuous pore size distribution and MIP simulation via *xlib* plugin.

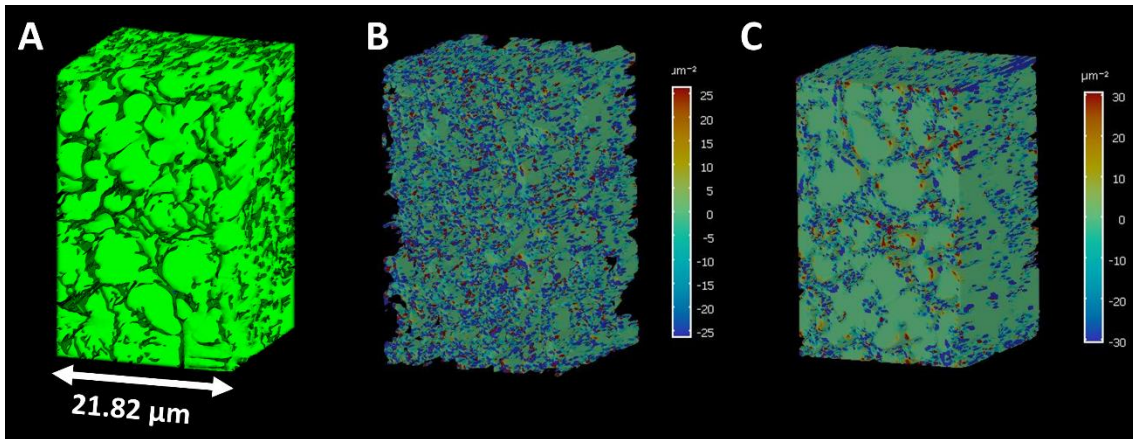


Figure A2.4. A. Connected components maps obtained via *Labeling 2D 3D*, *xlib*⁴² through volume for the PMMA membrane. Gaussian curvature maps obtained via *MorphographX 2.0*⁵⁰ for B. and C. the PMMA sample and its voids.

Appendix 2.5.2. Summary of the BET and mercury porosimetry results

Table A2.1. Summary of BET results for select membranes. Only surface area was measurable (commercial analysis conducted by Glantreo™).

Sample	BET Surface area (m ² g ⁻¹)
5% PMMA	2.290
5% PMMA with APTS	5.806
5.5% PMMA	<0.01
2% chitosan	<0.01
3% chitosan	0.0170
4% chitosan	<0.01

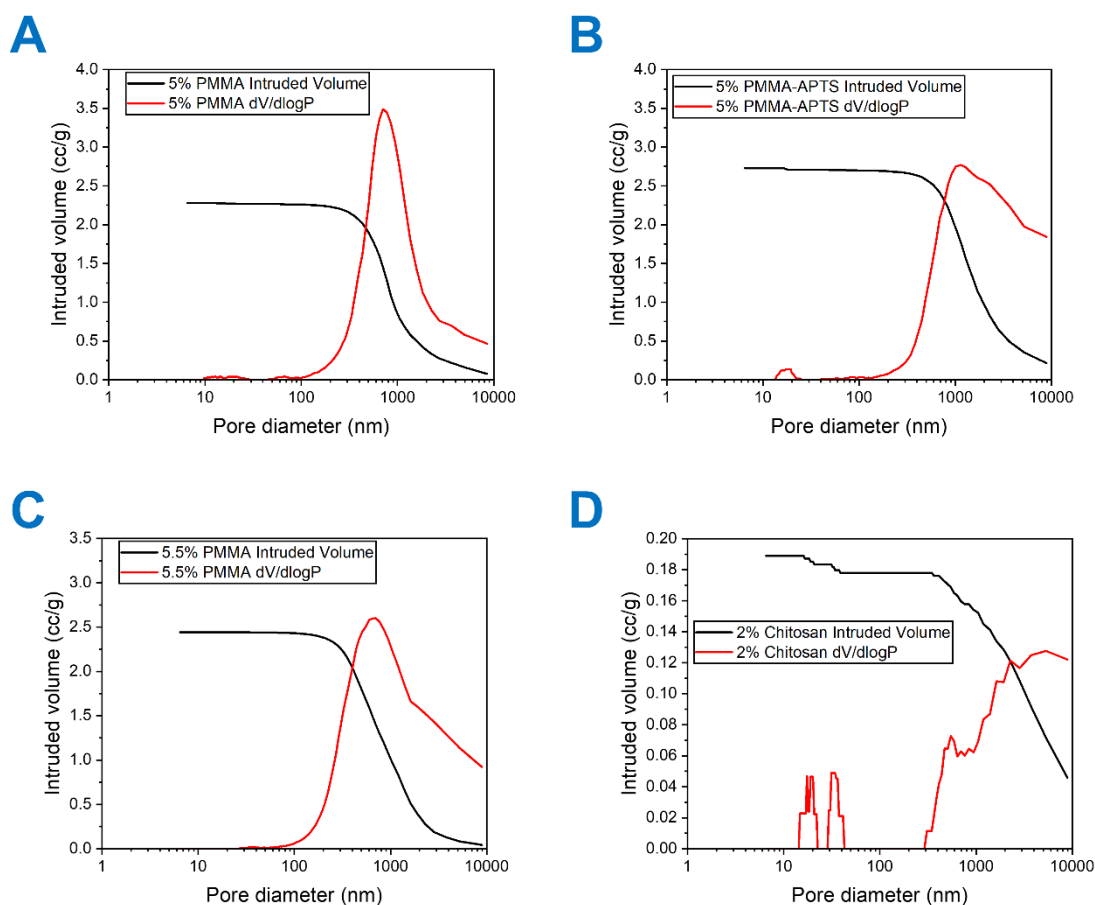


Figure A2.5. Mercury porosimetry data for select membranes: **A.** 5% PMMA membrane **B.** 5% PMMA-APTS membrane, **C.** 5.5% PMMA membrane and **D.** 2% chitosan membrane.

Appendix 2.5.3. APTS liquid based and vapour deposition optimisation.

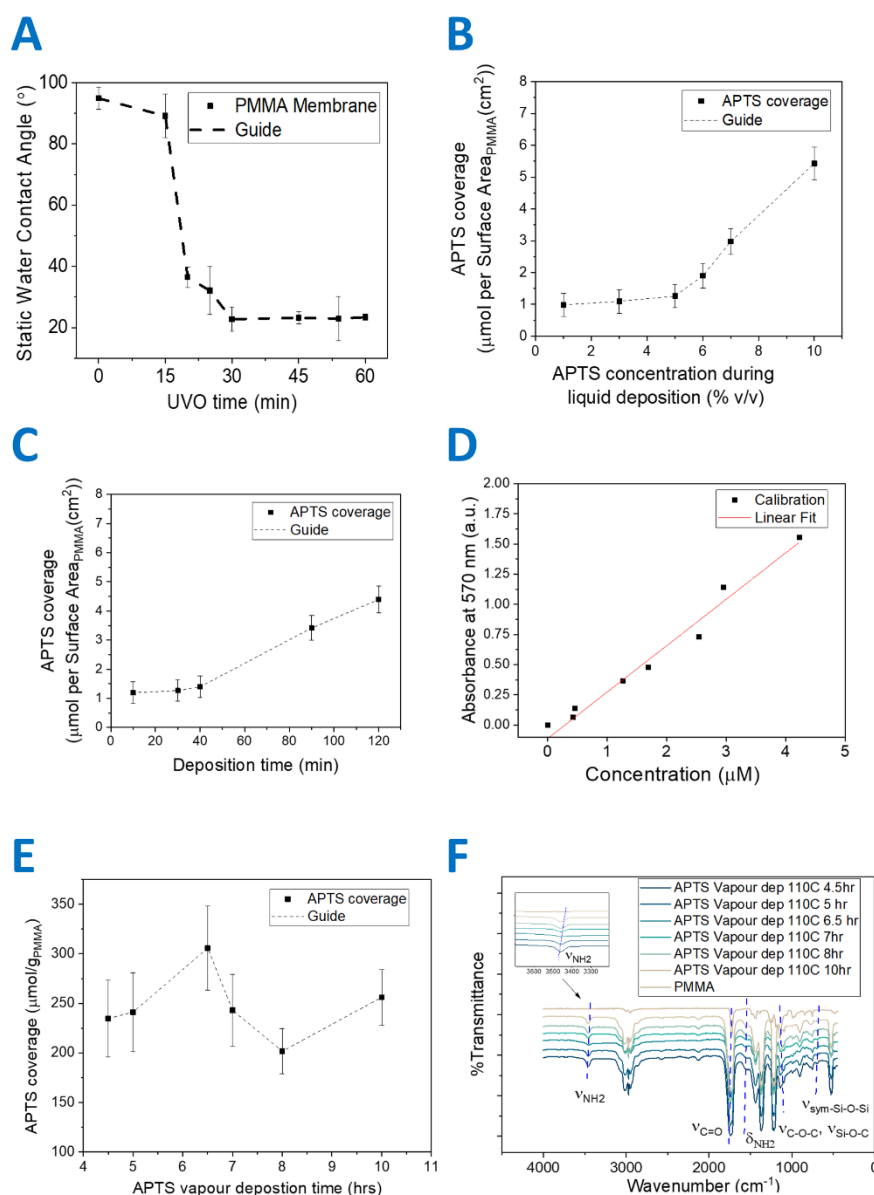


Figure A2.6. **A.** Relationship between UVO exposure times and static contact angle of PMMA. **B.** APTS coverage on PMMA after 30 mins liquid deposition vs APTS solution concentration. **C.** APTS coverage on PMMA over time using 5% v/v APTS solution. **D.** Calibration plot for APTS quantification via Ninhydrin assay. **E.** Coverage after Vapour Deposition. **F.** FTIR spectra of PMMA and APTS-PMMA.

Determination of APTS coverage was conducted via Ninhydrin test. APTS concentration was calibrated from absorbance at 570 nm with a series of aqueous solutions and a calibration plot was obtained (correlation coefficient = 0.987).

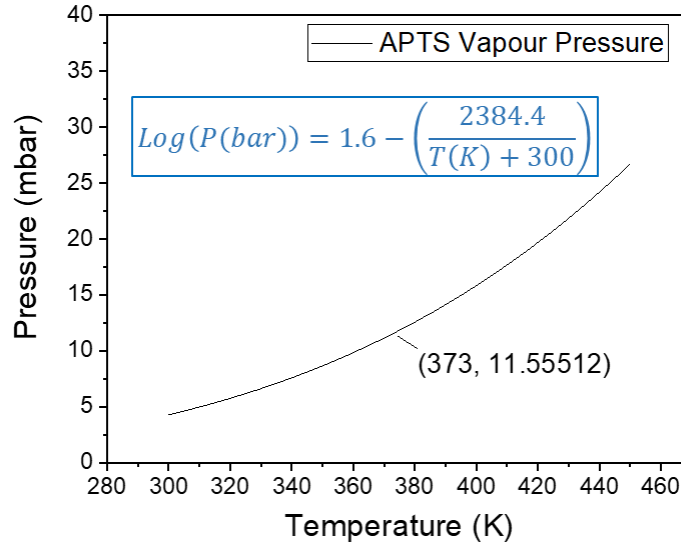


Figure A2.7. APTS Antoine Equation parameters⁶⁵ used to design deposition conditions (300-390 K range).

PMMA brush optimisation was conducted from advancing water contact angle measurements. The coverage Φ was quantified from:³¹

$$\Phi = \left(\frac{\cos \theta_{Brush}}{\cos \theta_{SiO_2}} - 1 \right) / \left(\frac{\cos \theta_{max}}{\cos \theta_{SiO_2}} - 1 \right) \quad [A2.1]$$

where Φ measures coverage from 0 to 1 (full coverage), θ_{Brush} is the advancing water CA at a given PMMA-OH concentration, θ_{SiO_2} is Si substrate CA after same pre-treatment as the brush samples and θ_{max} is the CA of the PMMA pellet. θ_{SiO_2} is $6.63 \pm 0.39^\circ$ and θ_{max} is $77.64 \pm 1.46^\circ$.

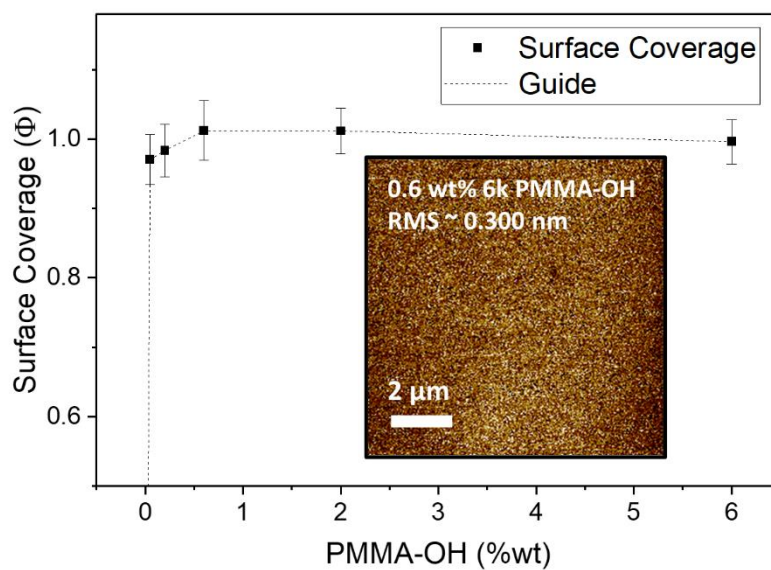


Figure A2.8. 6k PMMA brush coverage as a function of precursor concentration with associated AFM image of the brush at lowest full coverage concentration.

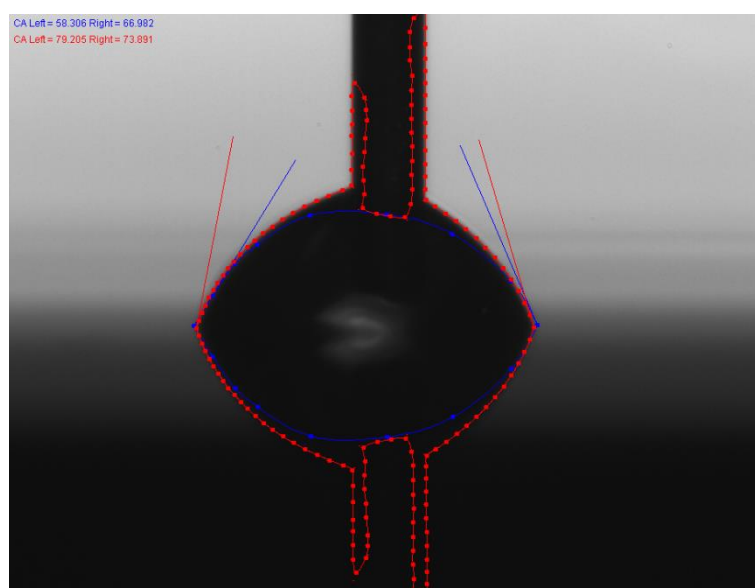


Figure A2.9. Representation of water advancing contact angle measurements with drop-snake plugin on ImageJ on a PMMA brush.

Surface energy was quantified from a 3 liquid system (water-glycerol-diodomethane) via van Oss–Chaudhury–Good (vOCG) method.⁵¹ Surface energy components of the liquids are described in **Table A2.2**.

Table A2.2. Surface Energy components for liquids used to calculate SE.

Liquid	Surface Energy Component			
	Total	Lifshitz–van Waals (γ_{LW})	Lewis Acid (γ_s^+)	Lewis Base (γ_s^-)
Water	72.80	21.80	25.50	25.50
Glycerol	64.00	34.00	3.92	57.40
Diodomethane	50.80	50.80	0.00	0.00

UVO studies on PMMA brushes were conducted via AFM and CA analysis as portrayed in **Figure A2.10** and **Figure A2.11**. The hysteresis was calculated as the difference between cosine of receding and advancing water contact angles in radians.

A UVO time of 45 sec was found to be optimal as the contact angle displays reduction and the hysteresis is low, indicating a smooth surface. Furthermore, the AFM root-mean squared (RMS) roughness after 45 sec UVO is minimal (~0.320 nm) which exceeds RMS of 5 nm upon UVO exposure of 1 min.

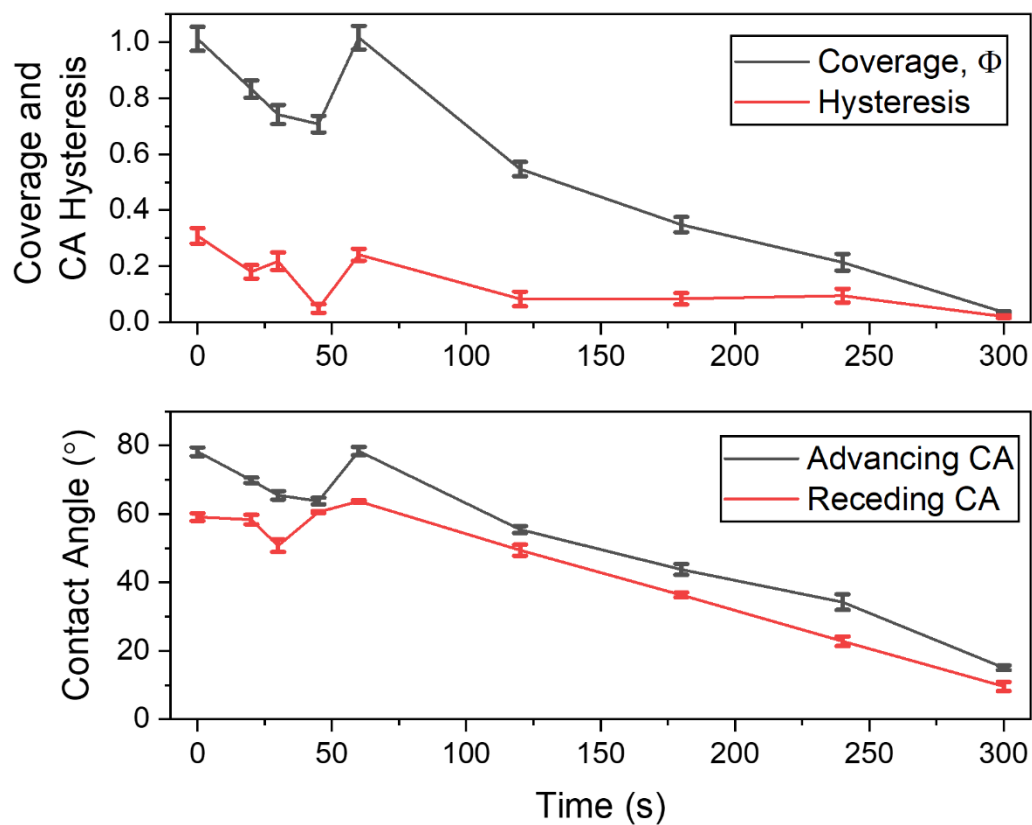


Figure A2.10. PMMA brush exposure to UVO treatment as a function of time. The advancing and receding water contact angles on PMMA brushes and associated coverage and contact angle hystereses are displayed.

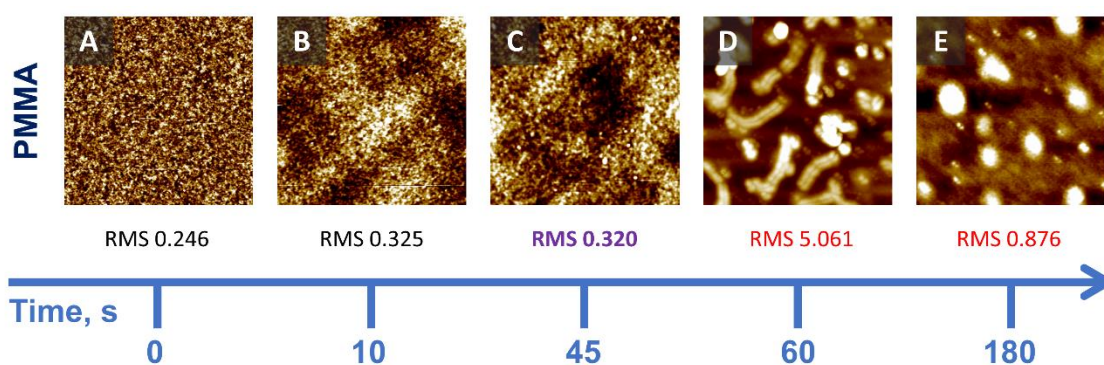


Figure A2.11. AFM micrographs ($1 \times 1 \mu\text{m}$) of UVO treated PMMA brushes with associated UVO times and RMS roughness values indicated below.

Contact Angle measurements for PMMA brush, APTS brush, APTS melt and APTS-PMMA sample after UVO and 7 hr deposition of APTS are shown in **Table A2.3**.

Table A2.3. CA measurements for preliminary APTS deposition investigation.

Sample	Advancing Water Contact Angle (°)
PMMA brush (0.6 wt%)	78.19 ± 1.30
APTS brush	36.21 ± 4.93
APTS melt	87.93 ± 0.92
APTS-PMMA	36.36 ± 0.67

Appendix 2.5.4. Comparison between conditions in the curing chamber during casting of PMMA and chitosan membranes.

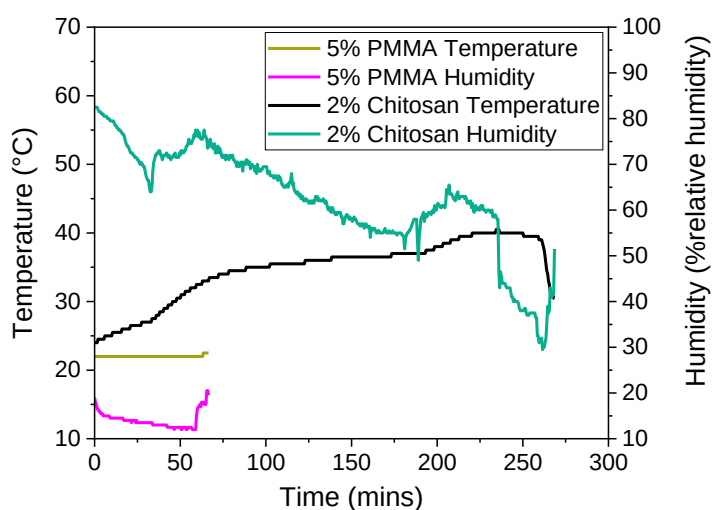


Figure A2.12. Temperature and humidity conditions during 5% PMMA (dried at 30 °C) and 2% chitosan membranes casting versus time.

Appendix 2.5.5. Casting solution characterization.

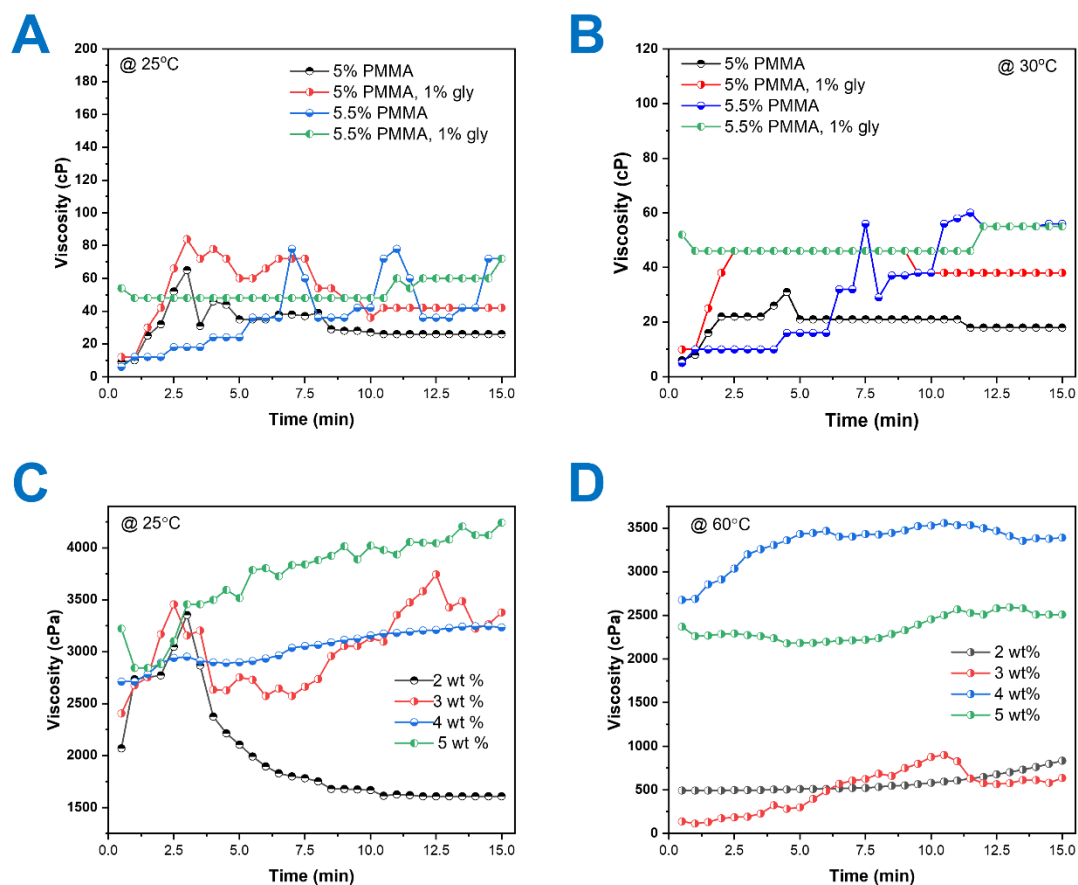


Figure A2.13. Viscosity data for membrane casting solutions: **A.** PMMA solutions at 25°C **B.** PMMA solutions at 30°C, **C.** Chitosan solutions at 25°C and **D.** Chitosan solutions at 60°C.

Table A2.4. PMMA solutions turbidity data.

Sample details (wt %)				Turbidity (NTU) @25°C	Turbidity (NTU) @60°C
PMMA	EtOH	Acetone	Glycerol		
5	40	55	0	20.5	32
5	40	54	1	56.8	114
5.5	45	49.5	0	30.8	24.1
5.5	45	48.5	1	75	82.8

Appendix 2.5.6. FIB preparation and reconstruction of 2 wt% chitosan membrane.

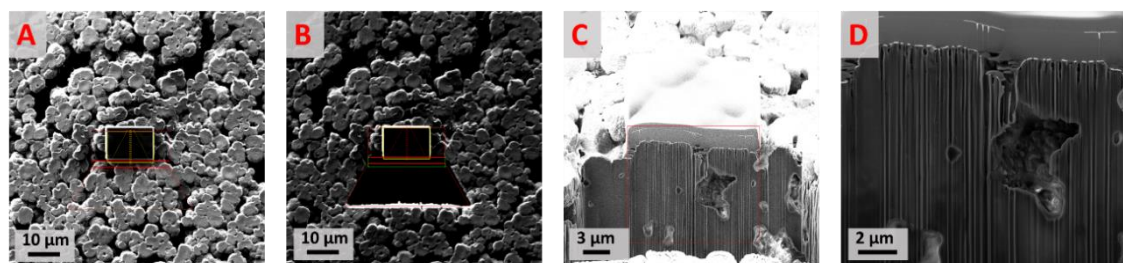


Figure A2.14. **A.** FIB image (30 kV, 600 pA) of pre-mill platinum coating, carbon tracking lines and platinum coating on top with positions displayed. **B.** FIB image (30 kV, 2nA) of trench preparation. **C.** SEM image (3 kV, high current) of prepared trench with protective layer and tracking lines. **D.** SEM image obtained during mill from Atlas 3D interface.



Figure A2.15. ImageJ processing summary. **A.** Raw SEM image. **B.** after median 3D filter. **C.** Binarised image.

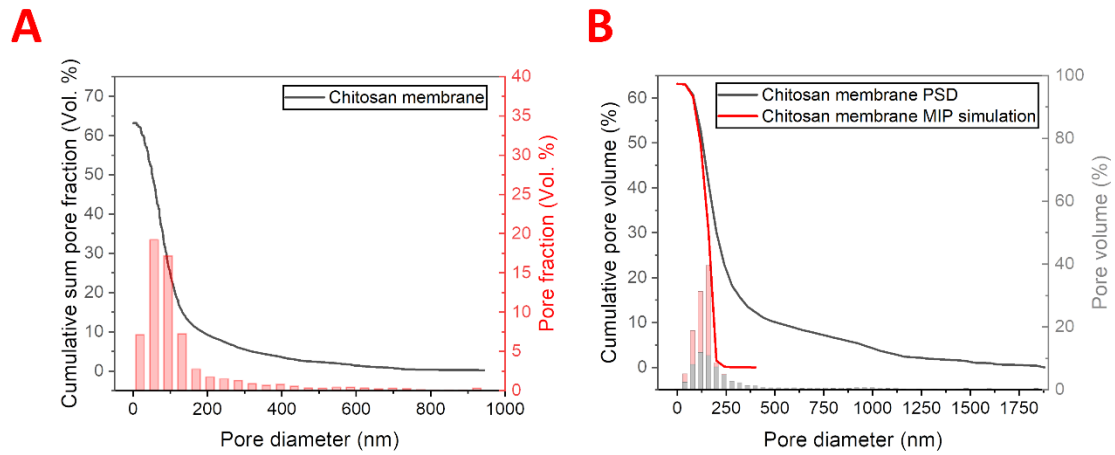


Figure A2.16. A. pore size distribution using *thickness*, *BoneJ* plugin and B. continuous pore size and MIP simulation via *xlib* plugin for the 2 wt% chitosan membrane.

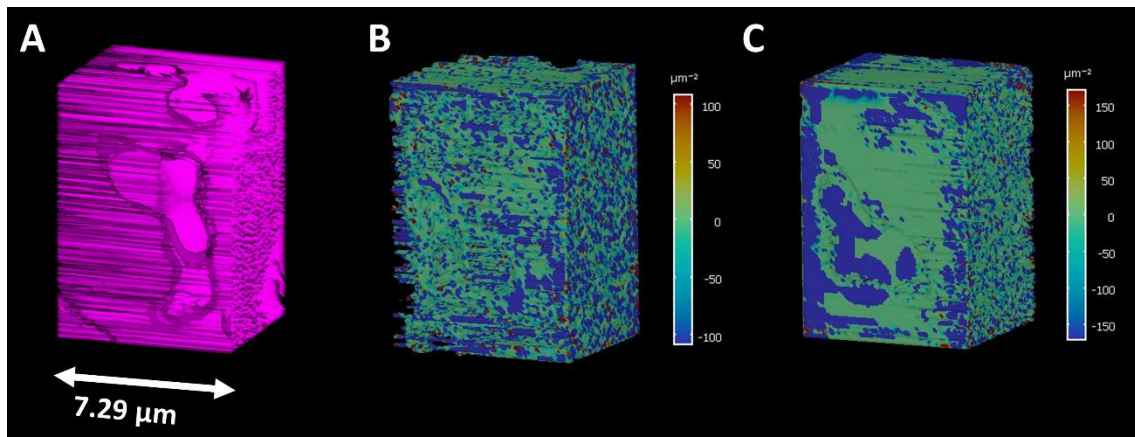


Figure A2.17. A. Connected components maps obtained via *Labeling 2D 3D*, *xlib*⁴² through volume for chitosan membrane. Gaussian curvature maps obtained via *MorphographX 2.0*⁵⁰ for B. and C. the chitosan sample and its voids,

Appendix 2.5.7. Additional chitosan and PMMA characterization.

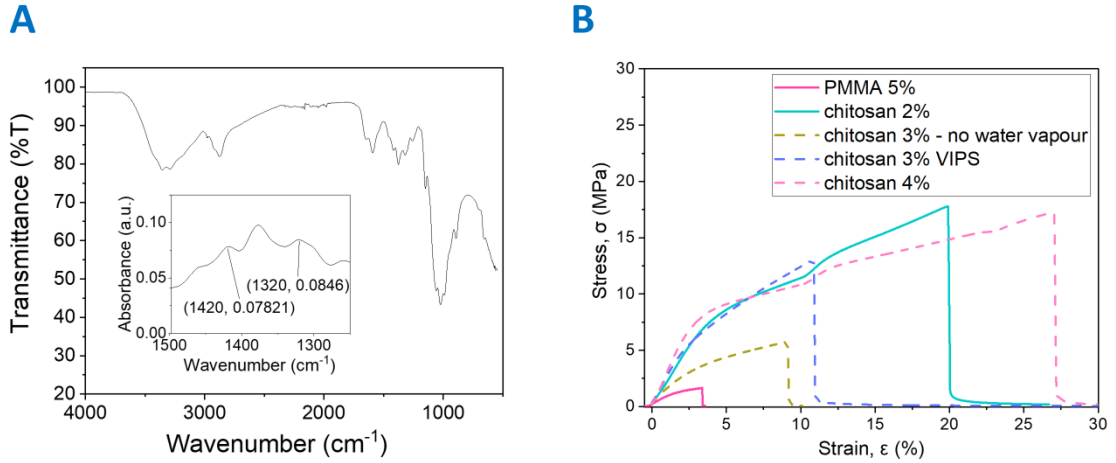


Figure A2.18. A. FTIR spectra of chitosan. B. Tensile strength curves for chitosan and PMMA.

Absorbance values at 1320 cm⁻¹ (A_{1320}) and 1420 cm⁻¹ (A_{1420}) were used to estimate the %Deacetylation of chitosan as explained by Brugnerotto *et al.*:⁶⁸

$$A_{1320}/A_{1420} = 0.3822 + 0.03133DA \quad [A2.2]$$

where DA is degree of acetylation and the degree of deacetylation is given by: 100% – DA .

Absorbance (A) obtained from FTIR transmittance (% T) graph via the relationship:

$$A = 2 - \log(\%T) \quad [A2.3]$$

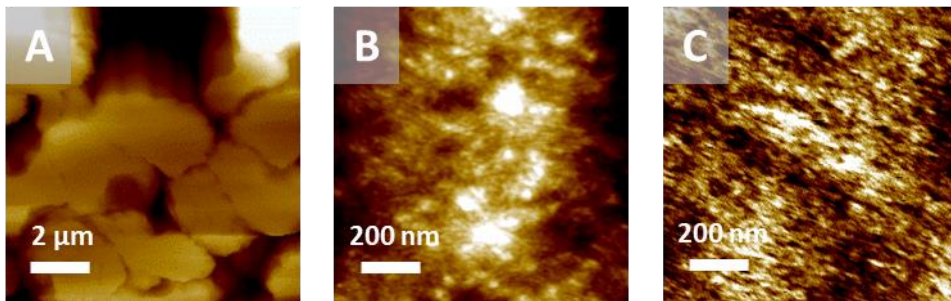


Figure A2.19. AFM images of chitosan membranes. A. 2 wt% skin. B. 3 wt% skin. C. 3 wt% belt.

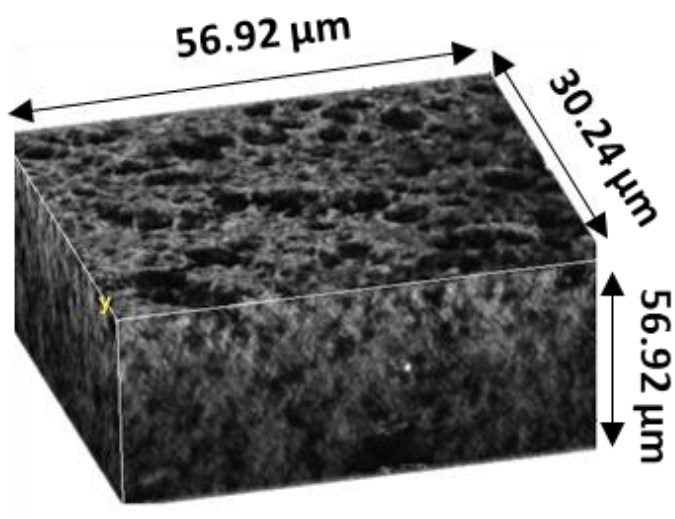


Figure A2.20. LCSM reconstruction of 5 wt% PMMA membrane

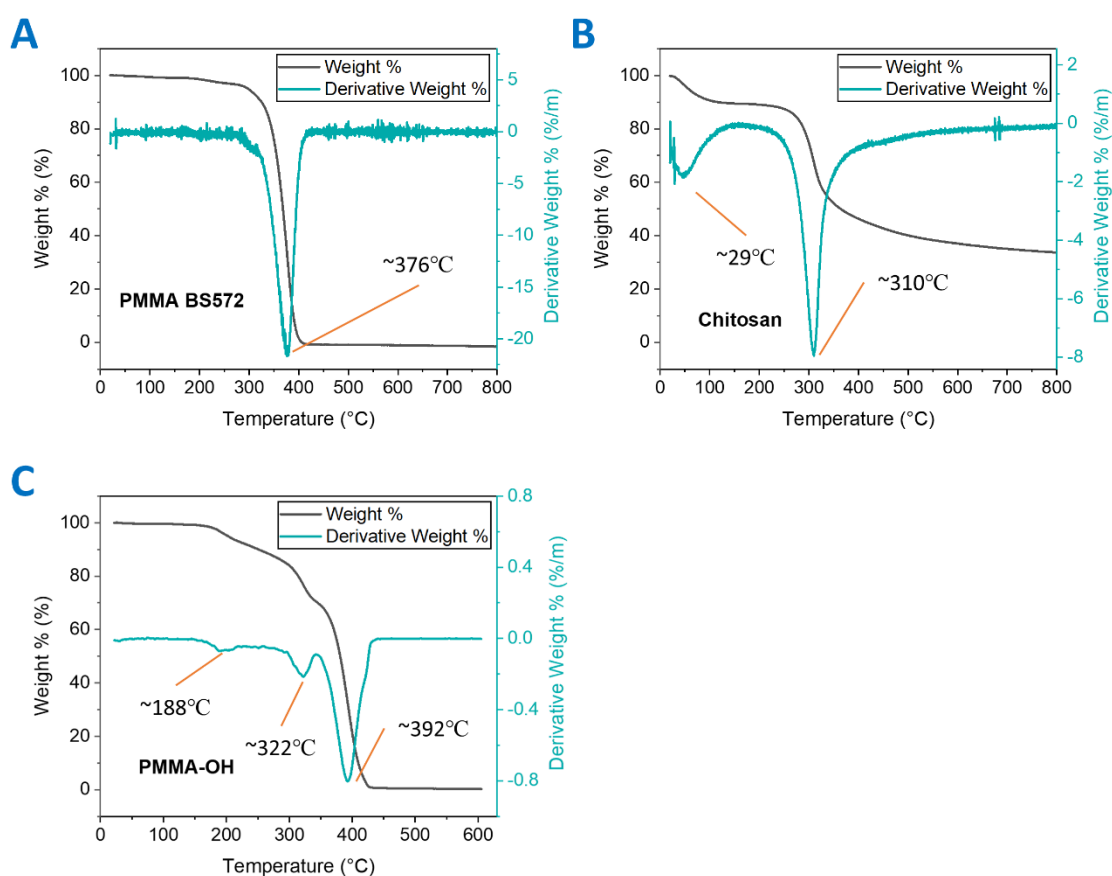


Figure A2.21. TGA data of **A.** PMMA material used for membranes, **B.** chitosan material used for membranes and **C.** PMMA-OH brush used as a model system.

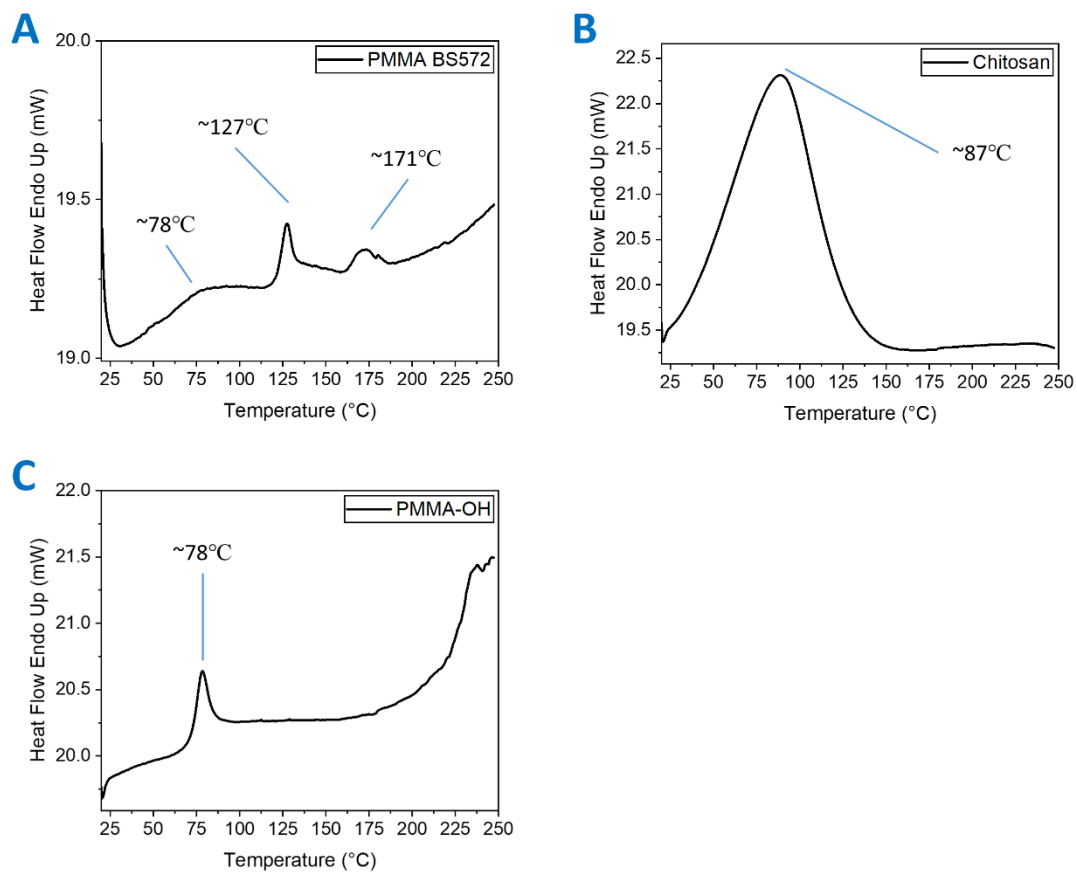


Figure A2.22. DSC data of **A.** PMMA material used for membranes, **B.** chitosan material used for membranes and **C.** PMMA-OH brush used as a model system.

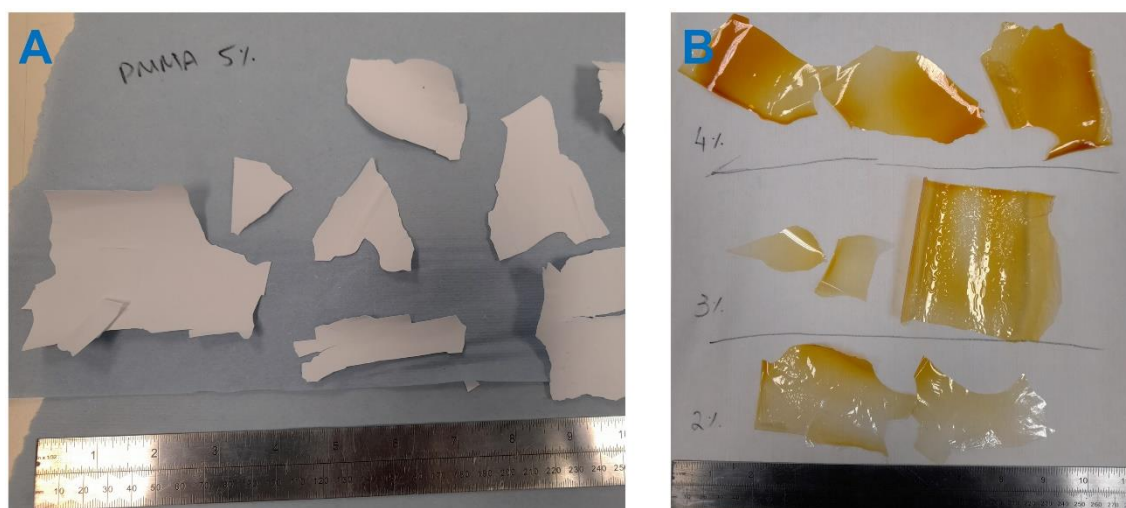


Figure A2.23. Photograph of **A.** 5% PMMA membrane **B.** 2%, 3% and 4% chitosan membranes.

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3. Chapter 3. Large-Area Fabrication of Vertical Silicon Nanotube Arrays via Toroidal Micelle Self-Assembly

3.1. Introduction

Block copolymer (BCP) self-assembly provides an avenue for the formation of a myriad of nano-scale morphologies, with applications such as optoelectronics, biosensing, filtration, bioactive surfaces, surface coatings and magnetic applications, among others.^{1–10} More usual microphase separated self-assembled architectures include lamellar, cylindrical, spherical and gyroidal structures as well as various micellar based morphologies such as helices, tubes, disks and toroids.^{11–13} Micelle formation is defined as the self-assembly of an amphiphilic BCP in a solvent medium to form a structure typically with a core and corona.^{11,14} Of the myriad of available micellar structures, toroidal micelles, in particular, have garnered interest owing to their proven applicability in synthesizing a range of nanostructured materials with unique plasmonic and magnetic properties.^{15,16} Such structures are typically fabricated *via* incorporating various metals and metal oxides, which upon removal of the polymer matrix produce metallic toroidal or nanoring structures.¹⁷ These metal/metal oxide structures have also been utilised as hard masks for patterning underlying silicon substrates, yielding high aspect ratio nanotube arrays.^{18,19} Nonetheless, one notable drawback of toroidal micelles obtained *via* BCP or triblock copolymer self-assembly is that the size distributions of the structures are often too large for optoelectronic applications.¹³

In this work, we describe a novel strategy to address this issue by controlling the formation of large toroidal structures *via* water vapour annealing (WVA) of a polystyrene-*b*-poly(ethylene oxide) (PS-*b*-PEO) diblock copolymer system atop a PS modified substrate. Vapor annealing is a common technique employed to direct BCP self-assembly *via* polymer swelling.^{20,21} Solvent vapor can selectively swell one or more blocks (thereby affecting morphology) and the propensity to swell can be estimated by the Flory-Huggins interaction parameter χ .^{18,21} The solvent vapor driven swelling creates free volume increasing chain mobility.¹⁸ This is also described as plasticization and results in effective reduction of the

glass transition temperature and effective χ parameter.²² Thus, annealing times can be significantly reduced for high χ systems.²¹ Previously, WVA treatment has been employed to modify silk material or perovskite structures,^{23–26} however, water was only used as a facilitating solvent during BCP annealing rather than a unique swelling solvent.^{27,28}

Furthermore, aside from the influence of the affinity of each block to the annealing solvent, substrate effects can also substantially impact the resulting BCP pattern.^{29–31} The application of a polymer brush enables the tailoring of the surface energy (SE) of the substrate influencing the BCP morphology.³² In this case, a PS brush is utilized to control the self-assembly of a lamellar PS-*b*-PEO system. The pre-treatment of the Si substrate with a PS brush favors PS block segregation to the brush/BCP interface.²⁹ Qiu *et al.* demonstrated a similar approach to generate toroidal micelles in solution whereby a homopolymer was added to a BCP solution in various mass ratios in order to control the size of the micelle.³³ The addition of a homopolymer to a BCP system requires careful tailoring; in addition to varying the micelle sizes, it can also result in the alteration of the shapes of the resulting micelles.^{11,33–35} Previous studies on toroidal micelle fabrication use highly acidic conditions to drive ring micelle formation at surfaces or variation of solvent composition of BCP in solution,^{13,15} and/or homopolymer addition to BCP solutions.³³ Contrastingly, in this methodology we achieve such structures *via* simple surface modification.

The general mechanism by which toroid structures form from spherical or cylindrical micelles is described by Cui *et al.*, whereby high interfacial curvature of spheres or high energy endcaps of cylinders result in transition to more stable toroid systems with lower free energy.³⁶ In binary systems, toroids are generally not observed as the statistical probability of toroid formation is lower than the growth of rods as explained by Porte.³⁷ The reason is simply that open shapes like rods have considerably more bent conformations possible than closed rings, even though rings should be more energetically favourable.³⁷ Therefore, in this case, toroid formation in BCP system only occurs when polymer blocks are sufficiently flexible and self-attraction between blocks is considerable to form toroids from cylinders,^{35–37} such as is the case for PEO.³⁸

Our process establishes that a homopolymer pre-treatment of the substrate can influence the onset of toroidal micellization of the BCPs within minutes of BCP deposition (< 5 mins). We use the resulting morphology to demonstrate a simple, yet original strategy for production of vertical silicon nanotube arrays (diameter = 355 ± 73 nm, height after 2 mins etch = 355 ± 36 nm) *via* WVA (~ 60 mins), metal ion inclusion and Inductively Coupled Plasma (ICP) Reactive Ion Etch (RIE). We use the term array to describe a densely packed arrangement of structures with little periodicity as no single self-assembled entities are observed. Traditional methods for silicon nanotube growth often include extensive chemical steps or require toxic chemicals such as silanes, acidic conditions and high processing temperatures.^{39–41} Therefore, our methods are relatively facile compared to existent methods of production of metallic nanorings and vertical silicon nanotube vertical arrays, which usually involve complicated multistep synthesis and top-down approaches such as wet chemistry synthesis, Chemical Vapor Deposition (CVD), various lithographic approaches and use of multiple resist layers and materials.^{19,42–46} Additionally, WVA treatment is a low-cost and environmentally-friendly fabrication method. One of the critical advantages of our approach is the formation of large feature size patterns by utilizing a highly controlled micelle approach to compliment smaller feature sizes produced by microphase separation of the systems. Morphology formation is simple and scalable, generating toroidal nanostructure arrays over short timescales. We expect that the versatility of this patterning approach can be transferred to a range of PS-treated substrates to produce metallic nanorings or etched structures.

3.2. Experimental

3.2.1. Materials

Hydroxy-terminated polystyrene (PS-OH) (number average molecular weight, $M_n = 10$ kg mol⁻¹, $M_w/M_n = 1.09$, M_w : weight-average molecular weight), PS-*b*-PEO diblock copolymer ($M_{nPS} = 24$ kg mol⁻¹, $M_{nPEO} = 24.5$ kg mol⁻¹, $M_w/M_n = 1.09$, $f_{PS} = 0.49$), PS ($M_n = 16$ kg mol⁻¹, $M_w/M_n = 1.03$) and PEG ($M_n = 10$ kg mol⁻¹, $M_w/M_n = 1.01$) were purchased from Polymer Source Inc. and were used without further purification. Silicon <100> p-type wafers with a native oxide layer were used as

substrates. $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (iron(iii) nitrate nonahydrate), $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (nickel hydrate hexahydrate), toluene (CHROMASOLV, for HPLC, 99.9%), ethanol (dehydrated, 200 proof) were purchased from Sigma-Aldrich and used without further purification unless otherwise stated. De-ionized (DI) water was used wherever necessary.

3.2.2. Polymer Brush Preparation

Brush optimisation is conducted according to the method reported by Lundy *et al.*^{47,48} Silicon substrates were cut into $2 \times 2 \text{ cm}^2$ pieces, cleaned in toluene by sonication for 20 mins and dried with N_2 gas. Substrate surfaces were further cleaned, and hydroxyl functionalized *via* oxygen plasma for 3 mins (40 kHz, 120 W, Barrel Asher). The substrates were spin coated (3000 rpm, 25 seconds, 5 seconds ramp) with 0.2 wt% PS-OH brush solution in toluene ($\sim 100 \mu\text{L}$ per sample, stirred for 1 hour). The polymer brush was annealed on a hot plate at 200°C for 5 mins. Subsequently substrates were sonicated in toluene for 20 mins twice in order to remove any physisorbed layers and dried in dry N_2 gas afterwards.

3.2.3. Block copolymer film preparation and solvent vapor annealing

2 wt% solutions of PS-*b*-PEO BCP were prepared in toluene and stirred at 35°C for 24 hrs. BCP solutions ($\sim 100 \mu\text{L}$ per sample) were spin-coated onto PS brush substrates at 3200 rpm for 25 seconds with a ramp of 5 seconds. WVA was conducted in a glass jar (150 mL) containing the sample and a small vial (50 mm x 12 mm x 4 mL) of water (3 mL) for 60 mins at 25°C . Samples were recovered from the jars and allowed to stand in air for the trapped solvent to evaporate.

3.2.4. Metal ion inclusion

Metal inclusion and pattern transfer were conducted according to methods reported by various researchers.^{1,18,27,49} $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solutions of 0.8 wt% were prepared in ethanol. The metal ion solutions ($\sim 100 \mu\text{L}$ per sample) were spin-coated onto samples at 3200 rpm for 25 seconds with a 5 second ramp. UV/ozone treatment for 3 hrs was employed to oxidize the precursor and remove the polymer *via* UV/ozone system (PSD Pro Series Digital UV Ozone System; Novascan Technologies, Inc., USA). Samples were then

calcined in a tube furnace at 800°C for 1 hr in order to promote metal densification and remove cross-linked polymer residue.

3.2.5. Pattern transfer

Iron and nickel oxide were used as hard masks for pattern transfer *via* Oxford Instruments Plasma Technology Plasmalab System100 ICP180 etch tool. Substrates were etched using an ICP Power of 1200 W, RIE power of 20 W, etch time of 1 to 4 minutes, CHF₃ (80 sccm) and SF₆ (15 sccm) gasses at 20 mTorr. Following pattern transfer remaining iron oxide and nickel oxide hard masks were removed *via* oxalic acid treatment.^{50,51}

3.2.6. Characterization

Atomic force microscopy (AFM) (Park systems, XE7) was operated in NCM (non-contact mode) under ambient conditions using a silicon microcantilever probe tip (force constant of 42 Nm⁻¹). Scanning electron microscopy (SEM, Zeiss Ultra Plus) images were recorded at an accelerating voltage of 2 kV and working distance of 4 to 5 mm. SEM cross sections were obtained from samples cleaved in half and perpendicularly positioned to the incident electron beam with a tilt angle of 20° (70° to the incident beam). The film thicknesses were measured by reflectometry (Filmetrics F20) and electron microscopy.

TEM imaging and analysis were acquired using an FEI Titan operating at 300kV. Electron energy loss spectroscopy (EELS) and Energy Dispersive X-Ray (EDX) analysis was performed using a Gatan Tridium EEL spectrometer and Edax EDX detector respectively.

Dynamic contact angle (CA) measurements were recorded using a custom-built system on three different regions of each sample using a 60 Hz camera to capture the advancing CAs of three probe liquids (water, diiodomethane and glycerol).^{47,48} Liquids were dispensed with flow rates of 10 nLs⁻¹ using a 35-gauge needle (Ø135 µm OD) with droplet volumes between 70 to 100 nL. SE was calculated using the advancing CAs *via* the Lifshitz-van der Waals/acid-base approach.⁵² Contact angles were measured on ImageJ using the “drop snake” plugin.^{53,54} SE was recorded for the BCP films and compared to the PS pellet and the polyethylene glycol (PEG) melt. PS pellet was pressed according to Lundy *et*

al.,⁴⁷ PEG was directly melted onto Si wafers at 70°C and tilted at 90° while cooling to produce a flat film.

Thermogravimetric analysis (TGA, PerkinElmer Pyris 1) was conducted using approx. 3 mg of each sample in a platinum pan. The spectrum was recorded from 30 °C to 800 °C at the rate of 10 °C/min under nitrogen atmosphere.

Differential Scanning Calorimetry (DSC, PerkinElmer Pyris Diamond) was used to study glass transition behaviour of polymers. The machine was calibrated using indium standards. The samples (~3 mg) were sealed in aluminium pans and heated from 20 to 250 °C at a rate of 10 °C/min.

X-ray photoelectron spectroscopy (XPS, VG Scientific ESCA^{lab} Mk II) was performed under ultrahigh vacuum conditions ($<5 \times 10^{-10}$ mbar) using a hemispherical analyzer and Al K α X-rays (1486.6 eV).⁴⁷ The emitted photoelectrons were collected at a take-off angle of 90° from the sample surface. The analyzer pass energies were set to 100 eV for survey scans and 40 eV for high-resolution core scans. Photoemission peak positions were corrected to C 1s at a binding energy of 284.8 eV.⁵⁵

(Where applicable, values are reported as sample mean value $\pm 1s$, where s stands for sample standard deviation).

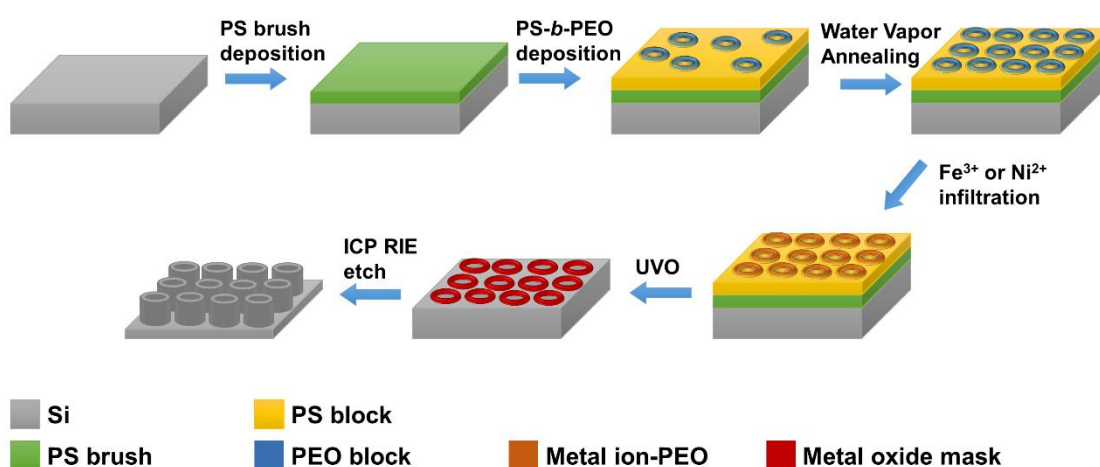
3.3. Results and Discussion

3.3.1. Pattern Formation

We chose a lamellar PS-*b*-PEO (24-24.5k) system in order to investigate whether surface pre-treatment and WVA can influence the resultant film morphology. The overall experiment is outlined in **Scheme 3.1**. In summary, we spin-cast PS-*b*-PEO/toluene solutions onto the PS pre-treated substrates. Subsequently, a WVA step was employed for an hour at 25°C followed by metal ion liquid phase infiltration and pattern transfer.

Toluene was the solvent of choice as it is one of the best solvents for PS-*b*-PEO, $\chi_{S-Tol} = 0.06$ and $\chi_{EO-Tol} = 1.92$ as measured via **Equation 1.4** at 25°C if $\alpha = 1$.⁵⁸ The polystyrene interaction with toluene is extremely good, thus PS-*b*-PEO dissolves readily even though poly(ethylene oxide) on its own dissolves poorly in

toluene. Other solvents trialled, such as green solvents like 2-methyltetrahydrofuran and ethyl lactate, led to poor dissolution of the polymer system. Tetrahydrofuran (THF) was found to be miscible with PS-*b*-PEO ($\chi_{S-THF} = 0.41$ and $\chi_{EO-Tol} = 0.27$), however the solutions were less stable due to aggregation of the polymer in solution over time versus toluene-PS-*b*-PEO solutions. In terms of waste, a minimal amount of solution (ca 100 μ L) is enough to coat a sample (ca 2×2 cm²). WVA was employed as an eco-friendly method at room temperatures $\sim 25^{\circ}\text{C}$ in order to minimize energy demands.



Scheme 3.1. Toroidal micelle formation process and etch pattern formation.

We observed the formation of a toroidal micelle-like pattern where PEO forms a circular micelle on a PS brush surface as seen from **Figure 3.1 B, D and E**. This approximates to previous work by Wang *et al.*, where a toroidal pattern was formed using a BCP system with a relatively similar volume fractions of the block.⁵⁶ However these workers used an ethanol induced reconstruction to produce open micelle structures or toroidal structures from an initial spherical micelle array.

The attachment of a brush shown in **Figure 3.1 A** is critical in tuning the surface energy such that micellar toroid-like surface features are obtained rather than microphase separated structures.¹⁵ Spin-coating onto a PS brush immediately leads to the formation of micelles without the need of annealing, signifying the

importance of the PS pre-treatment for the formation of micelle pattern (**Figure 3.1 B**).

The toroidal pattern formation was promoted by selective swelling of the hydrophilic PEO block *via* exposure to water vapor. It is important to note that spin-coating the 2 wt% PS-*b*-PEO BCP solutions directly onto silicon (Si) substrates yields disordered micelles upon WVA (**Figure 3.1 C**). Thus, effectively the PS brush promotes toroid micelle formation by matching surface energies between the BCP and the substrate. The availability of the brush thereby increases the PS ratio or the core volume of the micelle as expected, with the PEO block forming a corona around the PS core.^{33,34}

Figure 3.1 D and **E** display the morphology of the BCP films on PS substrates after WVA. The PS-*b*-PEO film thickness (including the PS brush) is approx. 86 ± 1 nm for water annealed film as measured by reflectometry and the average “pore” or feature size is 364 ± 101 nm. Annealing films with water for less than an hour provides poor pattern homogeneity, whereas times of 60 minutes or longer result in a more evenly distributed BCP pattern. WVA considerably improves the toroid pattern packing but the question is what mechanisms are at play?

To explain WVA in a quantitative way, we calculated the Flory-Huggins χ parameters for solvent-polymer interactions using the Hansen approach according to **Equation 1.4**.^{57,58} Solvent and polymer are completely miscible if $\chi_{12} \leq 0.5$ as described by the Flory-Huggins model.^{57,58} Water is not theoretically selective for either of the blocks, i.e. $\chi > 1$. PEO miscibility with water is largely underestimated by Flory-Huggins parameter, however it is more important to consider the difference in polymer-solvent interaction parameters between the PS and PEO blocks. $\chi_{S-H_2O} = 3.11$ and $\chi_{EO-H_2O} = 1.84$ as estimated from **Equation 1.4** at 25°C and with appropriate solubility parameters if $\alpha = 1$.⁵⁸ We can thus postulate that the PEO block is responsible for the majority of microphase separation during WVA, as well as for formation of micelles. Additionally, the extremely low solubility of the PS block in water is another significant factor. It means that introducing minimal amounts of water to the BCP system would result in substantial increase in the interfacial free energy, thereby promoting micellization as observed.¹⁴

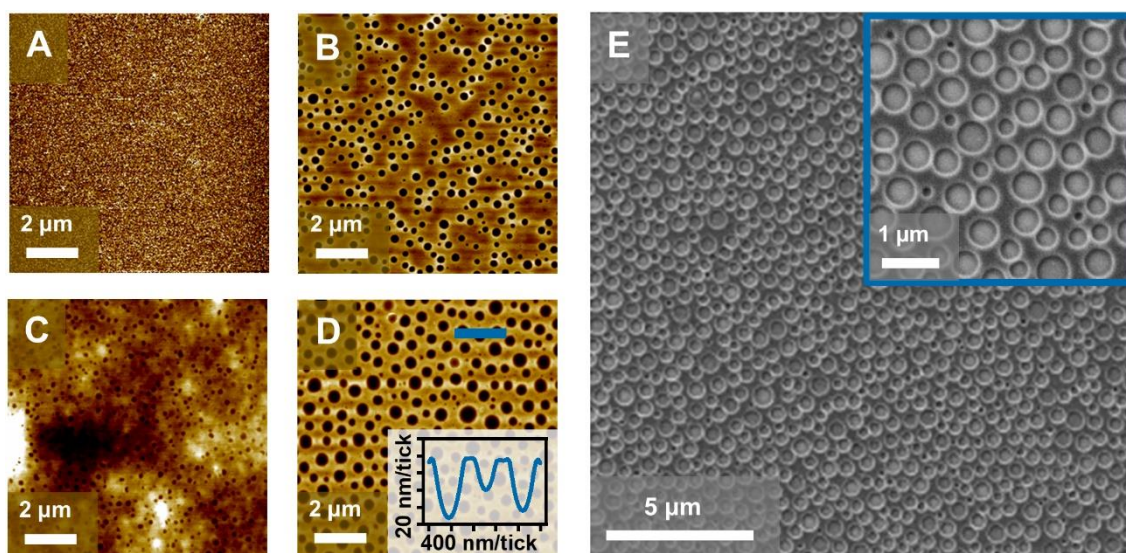


Figure 3.1. Atomic force microscopy (AFM) images of: **A.** 10k PS brush optimized according to Lundy *et al.*^{47,48}, **B.** 2 wt% PS-*b*-PEO on brush as spun on without annealing shows disordered micelle formation after 1-5 mins after spin-coating, **C.** 2 wt% PS-*b*-PEO on Si after WVA, **D.** 2 wt% PS-*b*-PEO on PS brush after WVA. **E.** Large-area scanning electron microscopy (SEM) image of 2 wt% PS-*b*-PEO on PS brush after WVA with a magnified image inset.

We also looked at film thickness and SE effects on the observed morphology in order to investigate the onset of toroid formation as summarised in **Figure 3.2**. The films produced from 0.2 wt% and 0.5 wt% solutions (**Figure 3.2 A and B**) display no obvious micellar pattern. The 0.8 wt% water annealed samples form a similar structure to 2 wt% samples as seen in **Figure 3.2 C**. However, the 0.8 wt% samples do not display a nanoring morphology after metal infiltration and UV/ozone (UVO) treatment (**Appendix 3.5.5. Figure A3.2**). **Figure 3.2 D** also shows no observable ordered pattern for a 1 wt% film. Only upon reaching the thickness of 86 ± 1 nm, toroidal micelle formation becomes evident as observed for a 2 wt% sample in **Figure 3.2 E**. We can thus deduce that a minimal thickness of approx. 86 nm is required for micelle evolution in this system. The results reveal that the morphology of micelles in thin films depends on the thickness of the thin films and the selectivity of the confining surfaces. It is well-known that film thickness can affect the resulting micelle morphology.⁵⁹ To complement these findings, we estimated the SE of the films to try to understand the relative block composition at the surface. The SE was measured from advancing contact angles

with diiodomethane, water and glycerol as test liquids and the calculation is outlined in **Appendix Section 3.5.2**. The 2 wt% water annealed films display SE of 47.6 mJ m^{-2} . This is comparably higher than the PS pellet SE of 42.5 mJ m^{-2} but lower than the SE displayed by poly(ethylene glycol) (PEG) melt of 54.8 mJ m^{-2} indicating the presence of both blocks at the surface.

It is also important to note that PS-*b*-PEO and PS-OH are stable during the process, as seen from TGA in **Appendix Figure A3.3 A** and **B** as the degradation temperature for both is over 400°C . Furthermore, PS-OH brush annealing occurs over the glass transition temperature as seen from DSC (**Appendix Figure A3.3 D**). However, PS-*b*-PEO is annealed below T_g of 60°C (**Appendix Figure A3.3 C**). Therefore, it is evident that water vapour, in fact, promotes self-assembly into toroids.

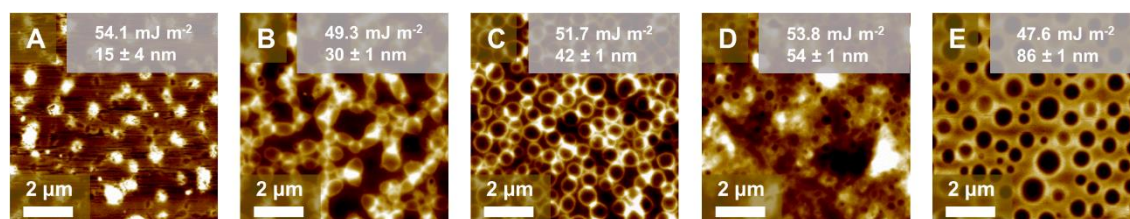


Figure 3.2. AFM images of PS-*b*-PEO on PS brush after WVA cast from different concentration polymer solutions with associated SE and thickness (measured by reflectometry). Morphology of the films produced from **A.** 0.2 wt%, **B.** 0.5 wt%, **C.** 0.8 wt%, **D.** 1 wt% and **E.** 2 wt% polymer solutions after WVA.

3.3.2. Metal Ion Inclusion

These self-assembled toroidal structures offer an ideal template to facilitate the formation of a Si nanotube array, using a well-developed BCP lithographic strategy of liquid phase selective infiltration and using a resultant metal oxide pattern as a mask in an etch process.^{18,50} The PEO domain readily coordinates various metals such as iron or nickel ions which, after processing, in turn act as a hard mask for ICP etching.^{50,60}

Following WVA, metal ion inclusion was conducted by spin-coating ethanolic iron and nickel nitrate solutions on the polymer films. UVO treatment was employed

to remove the polymer template as well as to convert the salt to a metal oxide. Samples were calcined in a tube furnace at 800°C prior to etching to promote densification of the metal oxide and to remove residual polymeric material or convert the metal oxide film into a desirable state, (i.e., to promote production of only one type of metal oxide if several oxide states are present).²⁸ **Figure 3.3** depicts the iron and nickel oxide nanoring arrays post UVO and calcination. The resultant patterns retain uniformity as the feature sizes of the BCP films and metal oxide masks closely follow normal distributions (**Appendix Figure A3.7**). The micelle pattern is obvious from the metal oxide masks as only the PEO domain should incorporate the metal ion precursors. The outer nanoring diameters for iron and nickel oxide masks are 430 ± 113 nm and 423 ± 77 nm respectively and are both approx. 50 nm thick, which is favourable for sensing applications if feature spacing and size is optimised.^{61,62}

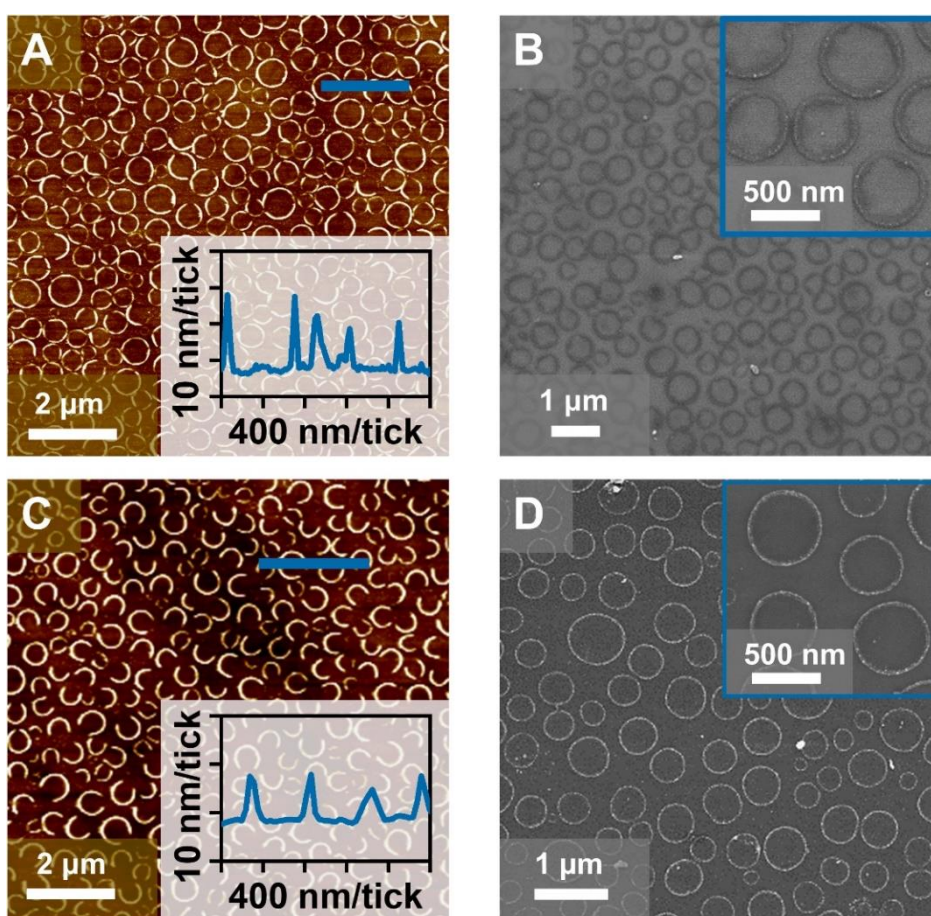


Figure 3.3. A. and B. iron oxide mask AFM and SEM micrographs respectively. C. and D. nickel oxide mask AFM and SEM images respectively.

X-ray photoelectron spectroscopy (XPS) is essential to verify the chemical composition of the nanoring arrays produced from metal ion inclusion (**Appendix 3.5.3 Figure A3.5 and Figure 3.4**). XPS spectra of metal oxide films were investigated to determine if the content of polymer or carbon had reduced upon calcination; it shows an approximate 3 times decrease in carbon content (**Figure 3.4 C**). This verifies that UVO alone might not be enough to remove the polymer, which is undesirable if the nanoring array is purposed for optoelectronic applications. The chemical composition of the iron oxide is predominantly Fe_3O_4 upon UVO which converts to Fe_2O_3 after calcination as reported by Ghoshal *et al.*² This is evident as Fe 2p core level spectrum of iron oxide after UVO consists of broad Fe 2p_{3/2} (711.6 eV) and Fe 2p_{1/2} (725.4 eV) peaks indicating the presence of both Fe^{2+} and Fe^{3+} ions (**Figure 3.4 A**). The curve fitted (Gaussian-Lorentzian) binding energies for Fe 2p_{1/2} and Fe 2p_{3/2} are 710.3 eV and 723.7 eV attributed to Fe^{2+} and 711.9 eV and 725.8 eV assigned to Fe^{3+} . The ratio of the curve-fitted peak areas $\text{Fe}^{3+}/\text{Fe}^{2+}$ is approximately 2 to 1, which is expected for Fe_3O_4 . After calcination the Fe 2p core level consists of sharper peaks: Fe 2p_{3/2} (711.0 eV), Fe 2p_{1/2} (725.1 eV) and high binding energy satellites signifying the presence of only Fe^{3+} ions as anticipated for Fe_2O_3 as observed from **Figure 3.4 B**. Nickel oxide mask consists of both Ni^{2+} and Ni^{3+} before calcination and upon annealing changes to NiO (**Figure 3.4 D and E**).⁶⁰

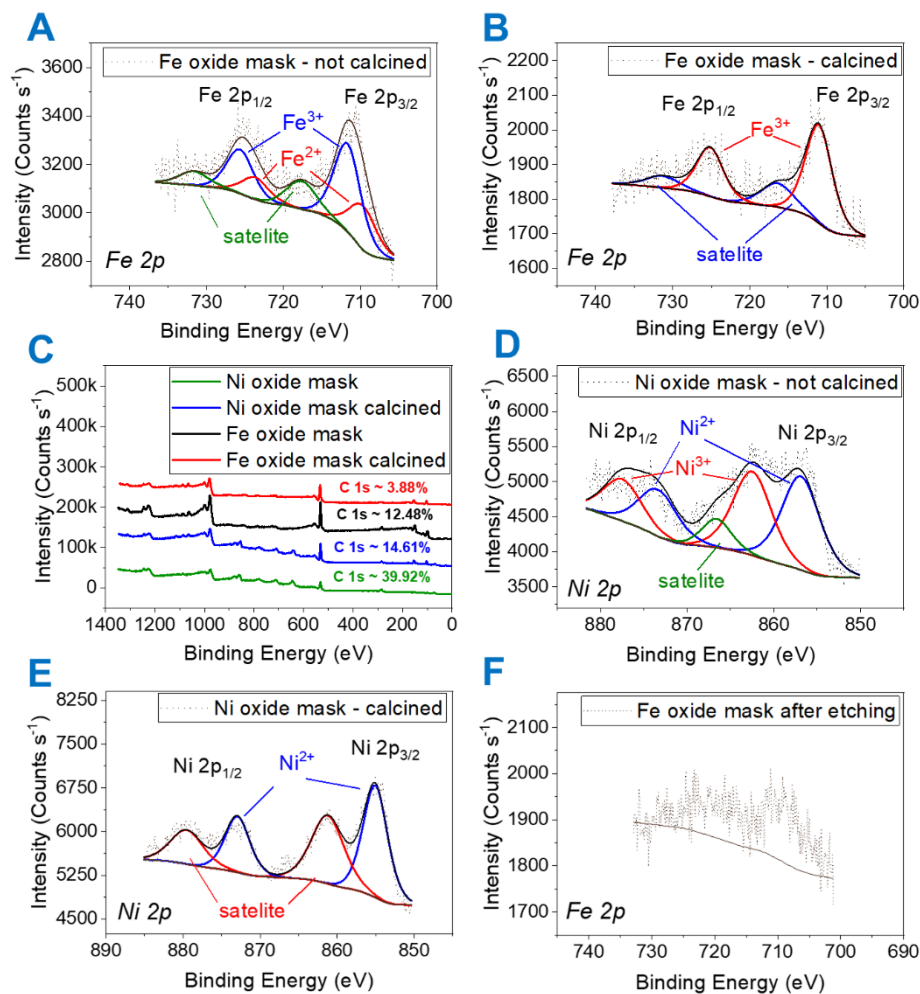


Figure 3.4. XPS spectra of metal oxide masks post UVO treatment: **A.** iron oxide mask, **B.** iron oxide mask after calcination, **C.** Comparison of survey spectra of metal oxide mask and their relative carbon content, **D.** nickel oxide mask, **E.** nickel oxide mask after calcination, **F.** iron oxide mask after ICP RIE (3-minute) showing negligible iron content.

3.3.3. Pattern Transfer

In order to translate the metal oxide nanorings into 3D structures, we utilized a well-studied pattern transfer method.⁵⁰ The ICP RIE method is outlined in the **Section 3.2.5**. We employed a CHF₃-SF₆ Si etch recipe without a native oxide etch step in order to preserve the integrity of the metal oxide mask during the aggressive etch. The advantage of this recipe is that the silicon tube walls are perpendicular to the substrate without the scalloping of the side walls commonly

observed for other silicon ICP etch methods (see tilted cross-section SEM inserts in **Figure 3.5**).^{18,50,63} Nickel oxide masks produce better results after etching compared to iron oxide masks (**Appendix 3.5.4. Figure A3.6**). Therefore, the nickel oxide mask method was repeated for several etch times (1 – 4 mins). Top-down and cross-sectional SEM micrographs in **Figure 3.5** demonstrate defined large-scale silicon nanotube arrays post ICP etching. The resulting nanotube pattern after etching of the calcined nickel mask displays considerably lower feature heights as seen in **Figure 3.5 E, F, G** as compared to non-calcined mask in **Figure 3.5 A, B and C**. This could be attributed to lower stability of calcined nickel oxide mask during this particular etch method, but more research is essential to verify whether the chemical composition of the nickel oxide mask gives rise to considerable differences during etching. For non-calcined nickel oxide mask, etch times of 3 minutes or longer result in lower feature height (209 ± 108 nm) than 1 or 2 minute etch times (214 ± 24 nm and 355 ± 36 nm respectively) due to nickel oxide mask removal during the ICP etch process. Furthermore, a 4-minute etch leads to mask disintegration for both calcined and non-calcined masks and yields a disordered etched silicon film as seen from cross-sections in **Figure 3.5 D and H**. The removal of the metal oxide mask during etching is supported by XPS in **Figure 3.4 F** as the iron content after 3-minute ICP RIE reduces considerably.

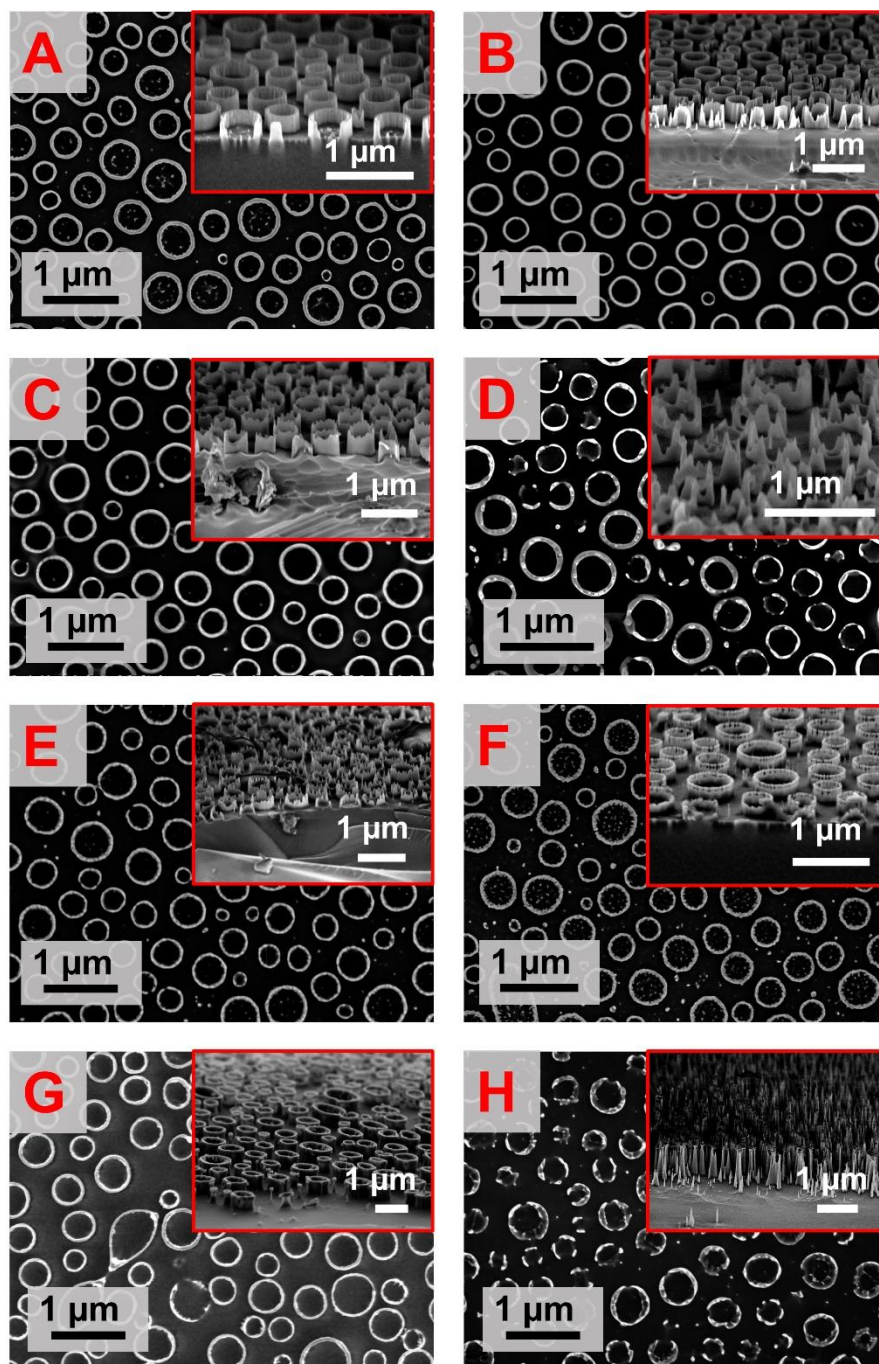


Figure 3.5. SEM micrographs (top-down and associated cross-section at 70°) of patterned Si wafers. Morphology produced from nickel oxide mask (not calcined) after: **A.** 1 min etch, **B.** 2 min etch, **C.** 3 min etch, **D.** 4 min etch. Pattern produced nickel oxide mask (calcined) after: **E.** 1 min etch, **F.** 2 min etch, **G.** 3 min etch, **H.** 4 min etch.

The feature sizes associated with the etched structures fabricated from nickel oxide nanorings (not calcined) are summarised in **Figure 3.6**. Overall, the feature

sizes follow a normal distribution relatively well, however the degree of uniformity remains considerably low. Nonetheless, we anticipate that a more ordered pattern may be yielded with further optimization and fine-tuning of the annealing conditions. Lower etch times of 1 or 2 minutes display a more uniform height distribution (**Figure 3.6 B and C**) whereas longer times result not only in reduced height but a more irregular height distribution attributed to the onset of mask degradation (3-minute etch in **Figure 3.6 D**). Thus, the dry etch itself introduces more irregularity as the heights vary more with increasing etch time signifying lack of control. We expect that further optimization of the etch recipe and gas chemistries may alleviate such issues. The nanotube array displays high porosity and large surface area (height of silicon nanotubes is 355 ± 36 nm after 2 minutes ICP RIE and relative diameter distribution and wall thickness are the same as before the etch as seen in **Figure 3.6 A** and **Appendix 3.5.5. Figure A3.7 E – G**). The nanotube diameter (359 ± 73 nm) and wall thickness (55 ± 11 nm) follow a normal distribution profile as shown in **Figure 3.6 A** and **Figure A3.7 G** respectively. Therefore, we propose that the vertical silicon nanotube array described herein can find application in catalysis and sensing.^{44,45,64} The nanotube array itself can be modified, for example, as demonstrated by Fan and co-workers whereby an O₂ environment at high temperatures is employed to oxidise Si to SiO₂.⁴⁴

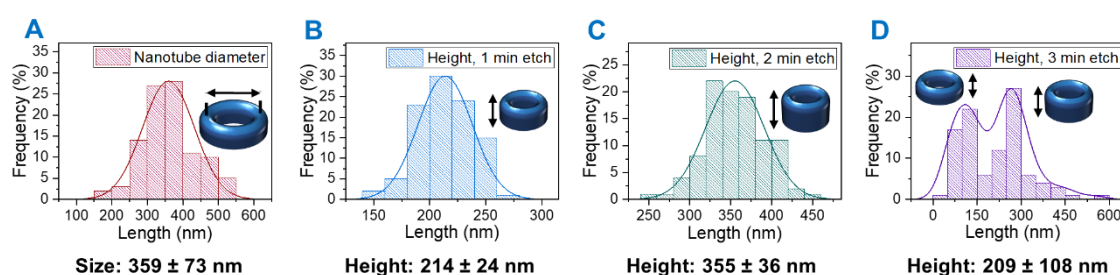


Figure 3.6. Size distributions of silicon nanotubes produced from the nickel oxide mask (not calcined): **A.** nanotube diameter, **B.** feature height after 1 min etch, **C.** feature height after 2 min etch, **D.** feature height after 3 min etch.

3.4. Conclusions

In this work, we successfully obtained a silicon nanotube array using a PS-*b*-PEO (24-24.5 kg mol⁻¹) toroidal micelle motif as a template for ICP RIE. The PS-*b*-PEO film readily self-assembled into toroidal micelles on a PS brush surface after spin coating. Additionally, film ordering was enhanced *via* WVA of the PEO block for an hour. The toroidal micelles displayed a size distribution of 400 – 600 nm, with an average micelle “pore” or inner diameter of 364 ± 101 nm. Although a notable variation in uniformity was observed, we suggest that this may be improved upon *via* co-casting the BCP with a PS homopolymer onto a PS brush substrate.^{33,65,66} Dynamic WVA could also be used to promote pattern uniformity across the film.²¹ Nevertheless, the method we employed in this work is a very attractive route to generate a relatively close packed toroidal micelle array on the substrate.

Subsequently, we demonstrated the production of metal oxide nanoring array (NiO and Fe_xO_y) by integrating metal ion precursors into the PEO corona of the toroidal micelle structure. We emphasise the versatility of this method as numerous different metals or moieties can be incorporated into the PEO domain with subsequent alterations such as calcining under different atmospheres to yield different metal state nanoring arrays.⁶⁷ Various substrates can be employed for selective etching, however for simplicity we chose a silicon substrate to show vertical Si nanotube fabrication.

The resulting metal oxide structures yielded an array of Si nanotubes with feature diameter of 359 ± 73 nm, thickness of 55 ± 11 nm and heights of >300 nm after a 2-minute ICP RIE process. Despite the clear success of this pattern transfer, we anticipate even further improvement may be possible through additional refinement of the etch recipe.

Overall, we report a facile and scalable self-assembly method for generating arrays of Si nanotubes. The cost-effectiveness and time-efficiency of this strategy yields significant advantages over conventional top-down lithographic techniques, which we expect will find uses in materials and electronic applications such as transistors, sensors and optoelectronic devices.⁶⁸

3.5. Chapter 3 Appendix

Appendix 3.5.1. Additional PS brush and PS-*b*-PEO optimization data

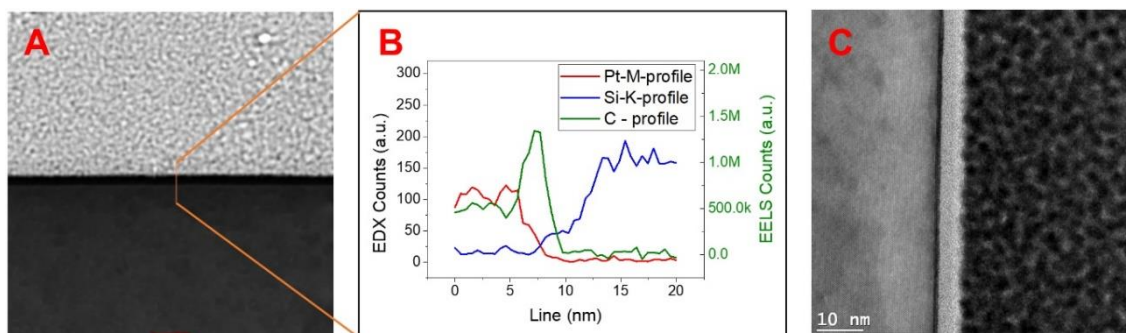


Figure A3.1. A. and C. TEM images of the PS-brush, thickness is approx. 5 nm. B. shows EDX and EELS profile of the line in A.

The rationale for using a PS brush: A physisorbed PS layer can be used instead of a brush, however a covalently grafted brush eliminates dewetting and provides a smoother surface by allowing washing to ensure single molecule polymer thickness. Root-mean square roughness (RMS roughness) of the brush ranges 0.2 to 0.8 nm, which is comparable to a clean Si surface (ca 0.2-0.5 nm) as estimated from AFM; therefore, it is assumed that roughness effects are negligible in pattern formation.

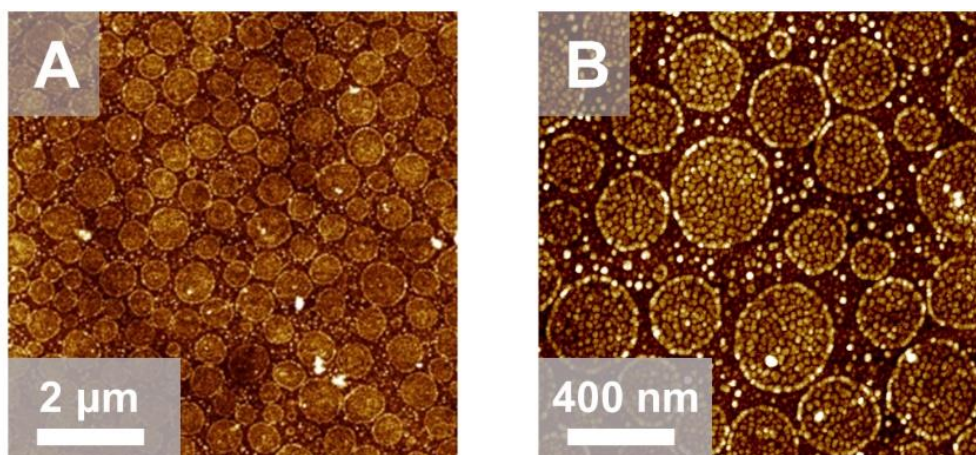


Figure A3.2. A. and B. 0.8 wt% water annealed PS-*b*-PEO film after Fe ion inclusion and UVO.

Grafting density σ of the PS brush is estimated as 0.32 chains per nm².⁶⁹

$$\sigma = \frac{h_d \rho N_a}{M_n} \quad [A3.1]$$

where h_d is the dry height of the brush (≈ 5 nm, estimated from TEM), ρ is the PS polymer density (1.05 g/cm³), N_a is the Avogadro's number, and M_n is the number average molecular weight (≈ 10 kg mol⁻¹).

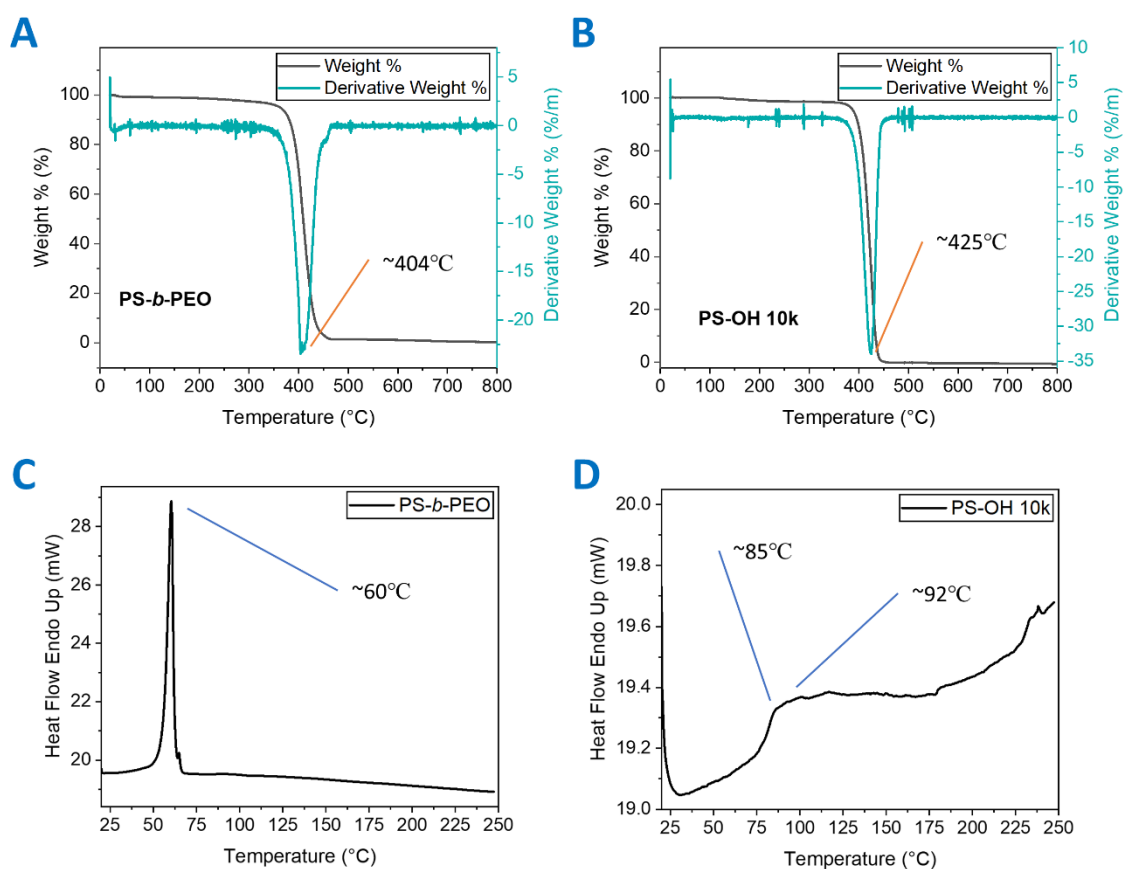


Figure A3.3. TGA data and DSC data of **A.** and **C.** PS-b-PEO and **B.** and **D.** PS-OH respectively.

Appendix 3.5.2. Surface Energy measurements

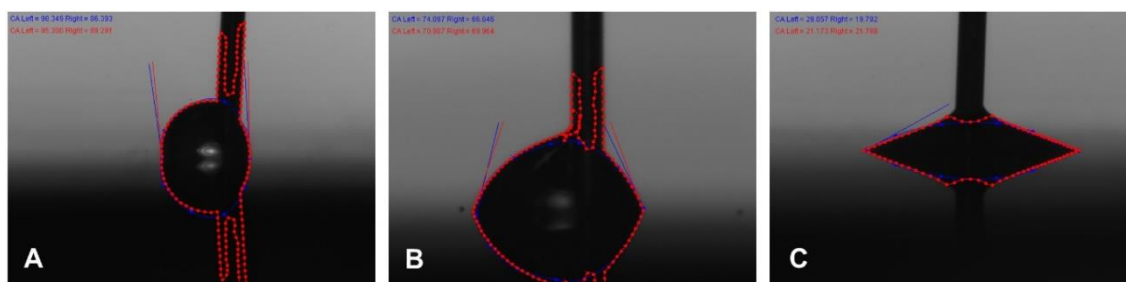


Figure A3.4. Representation of advancing contact angle (CA) measurements with drop-snake plugin on ImageJ for water annealed BCP sample for SE estimation. **A.** Water CA. **B.** Glycerol CA. **C.** Diiodomethane CA.

Surface energy was quantified from a 3 liquid system (water-glycerol-diiodomethane) *via* van Oss–Chaudhury–Good (vOCG) method.⁵² Surface energy components of the liquids are described in **Table A3.1**.

Table A3.1. Surface Energy components for liquids used to calculate SE.

Liquid	Surface Energy Component				
	Total	Lifshitz–van der Waals (γ_{LW})	Lewis (γ^+)	Acid	Lewis Base (γ^-)
Water	72.80	21.80	25.50		25.50
Glycerol	64.00	34.00	3.92		57.40
Diiodomethane	50.80	50.80	0.00		0.00

Surface energy was calculated by solving a system of linear equations:⁵²

$$(\gamma_{S,LW}\gamma_{W,LW})^{0.5} + (\gamma_S^+\gamma_W^-)^{0.5} + (\gamma_S^-\gamma_W^+)^{0.5} = 0.5\gamma_W(1 + \cos\theta_w) \quad [A3.2]$$

$$(\gamma_{S,LW}\gamma_{G,LW})^{0.5} + (\gamma_S^+\gamma_G^-)^{0.5} + (\gamma_S^-\gamma_G^+)^{0.5} = 0.5\gamma_G(1 + \cos\theta_G) \quad [A3.3]$$

$$(\gamma_{S,LW}\gamma_{D,LW})^{0.5} + (\gamma_S^+\gamma_D^-)^{0.5} + (\gamma_S^-\gamma_D^+)^{0.5} = 0.5\gamma_D(1 + \cos\theta_D) \quad [A3.4]$$

$$\gamma_{S,AB} = 2(\gamma_S^-\gamma_W^+)^{0.5} \quad [A3.5]$$

$$\gamma_S = \gamma_{S,LW} + \gamma_{S,AB} \quad [A3.6]$$

where γ are the SE components with subscripts S – solid, W – water, G – glycerol, D – diiodomethane, LW - Lifshitz–van der Waals, AB – acid-base and superscripts + and - signify acid and base respectively.

Appendix 3.5.3. XPS

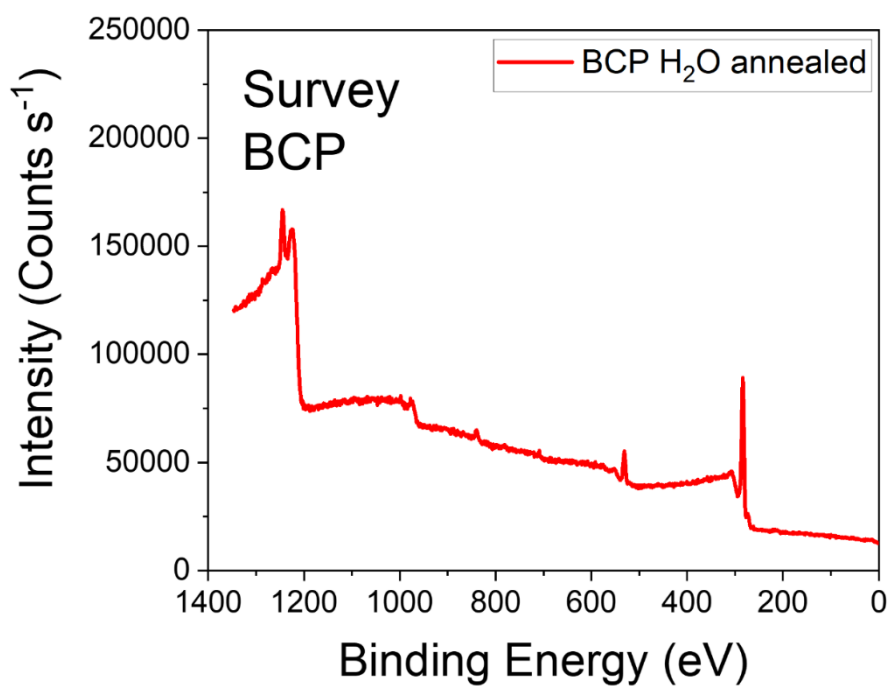


Figure A3.5. XPS survey spectra of PS-*b*-PEO films.

Appendix 3.5.4. Etch data

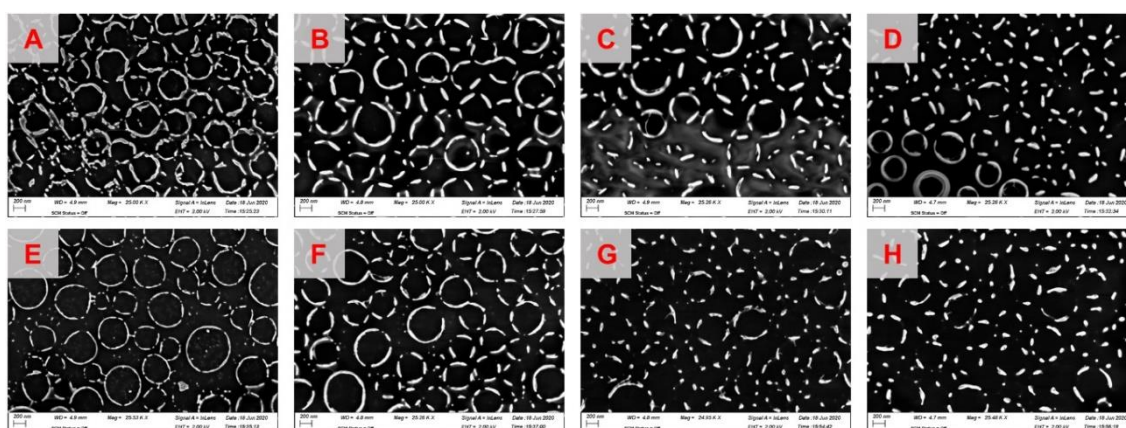


Figure A3.6. Etch pattern from H₂O annealed BCP Fe oxide mask (not calcined) after etching for **A.** 1 min, **B.** 2 min, **C.** 3 min, **D.** 4 min. Etch pattern from H₂O annealed BCP Fe oxide mask (calcined) after: **E.** 1 min, **F.** 2 min, **G.** 3 min, **H.** 4 min.

Appendix 3.5.5. Feature sizes

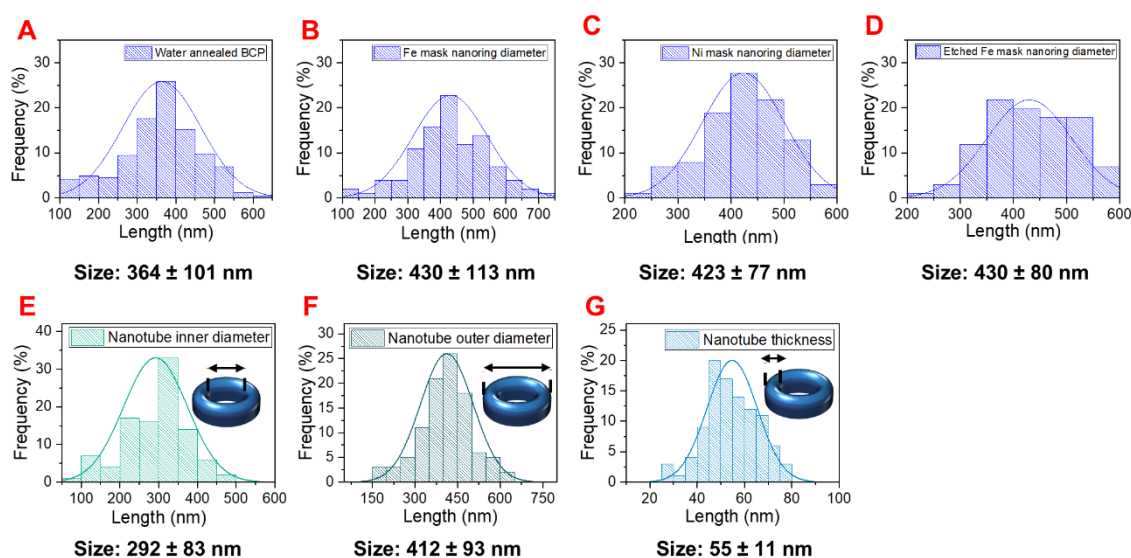


Figure A3.7. Feature sizes: “pore” diameters for PS-*b*-PEO water vapor annealed films and outer toroid diameter sizes for metal oxide masks: **A.** BCP film, **B.** Fe oxide mask, **C.** Ni oxide mask, and **D.** etched Fe oxide mask sample (1 min etch). After etching: **E.** nanotube inner diameter, **F.** nanotube outer diameter, **G.** nanotube thickness.

Appendix 3.5.6. Film Thickness data

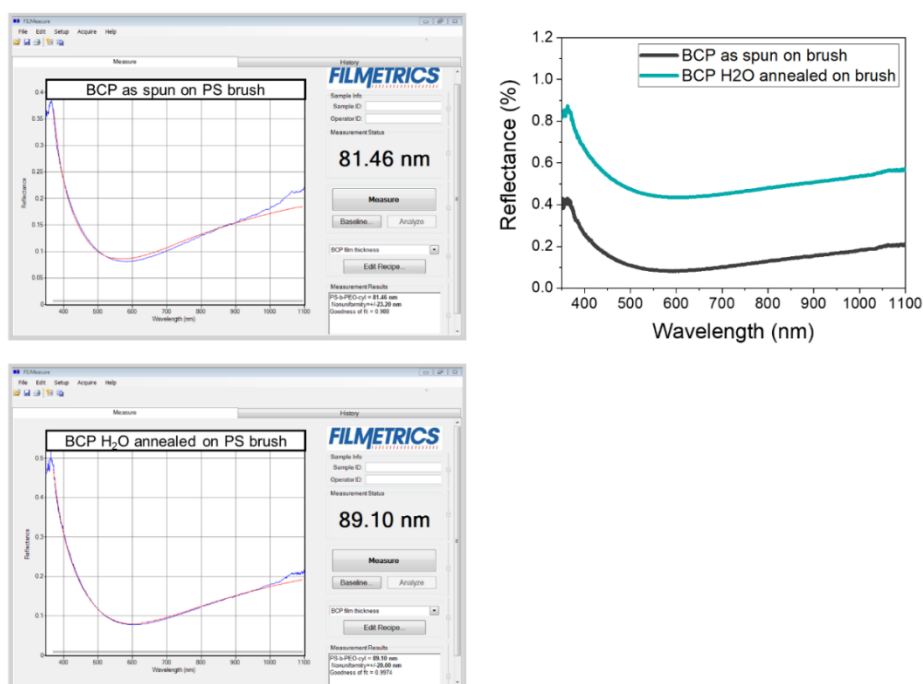


Figure A3.8. Examples of reflectometry fits for BCP films (labelled).

Appendix 3.5.7. Chloroform annealing preliminary experiments

The process in the paper was repeated according to the experimental section using chloroform (Chl) (for HPLC, $\geq 99.9\%$, contains 0.5–1.0% ethanol as stabilizer, Sigma-Aldrich) instead of water as an annealing solvent. Chloroform solvent vapour annealing (SVA) was conducted at 4°C and the next steps were the same as WVA.

PS-*b*-PEO BCP solutions directly onto silicon substrates (Si) yields two different outcomes depending on the annealing solvent: disordered micelles and less ordered micelle structures with water, or structures in a dewetted film with chloroform. This can be attributed to lower film stability on Si and to the sensitivity of the lamellar BCP to substrate SE (poor wetting).^{32,70} The morphology of the Chl SVA films is shown in **Figure A3.9 A – D**.

Chl favours the styrene block over ethylene oxide, $\chi_{S-Chl} = 0.08$ compared to $\chi_{EO-Chl} = 0.77$ as calculated from **Equation 1.4** at 25°C and with appropriate solubility parameters.⁴⁵ This small difference in selectivity facilitates the motion of both blocks as well as phase separation. PS-*b*-PEO film thickness (including the PS

brush) is approx. 88 ± 1 nm for chloroform (Chl) annealed films as measured by reflectometry. The average “pore” or feature size is 390 ± 179 nm for Chl SVA respectively.

The SE of the film annealed with Chl is similar to the SE of PEO. BCP films obtained from 1 wt% solutions, however, have much lower SE comparable to the pure PS film. The SE calculation is outlined in **Appendix 3.5.2**, where the Chl annealed film displays SE of 50.92 mJ/m^2 . This is comparably higher than the PS pellet SE of 42.58 mJ/m^2 but lower than the SE displayed by poly(ethylene glycol) (PEG) melt of 54.85 mJ/m^2 .

The chloroform annealed samples show a more membrane-like pattern than after WVA (**Figure A3.9**). The iron oxide mask for the Chl annealed film evidently shows low iron ion inclusion as seen from height profile in **Figure A3.9 E**. The observed film morphology is consistent with inadequate phase separation, with a matrix composed of both PS and PEO blocks in a disordered configuration and onset of film dewetting. The Chl annealed BCP nickel oxide mask however shows extremely high features due to incomplete removal of the BCP as the images shown are non-calcined masks. The morphology of the iron and nickel oxide masks derived from Chl SVA PS-*b*-PEO is shown in **Figure A3.9 E – H**.

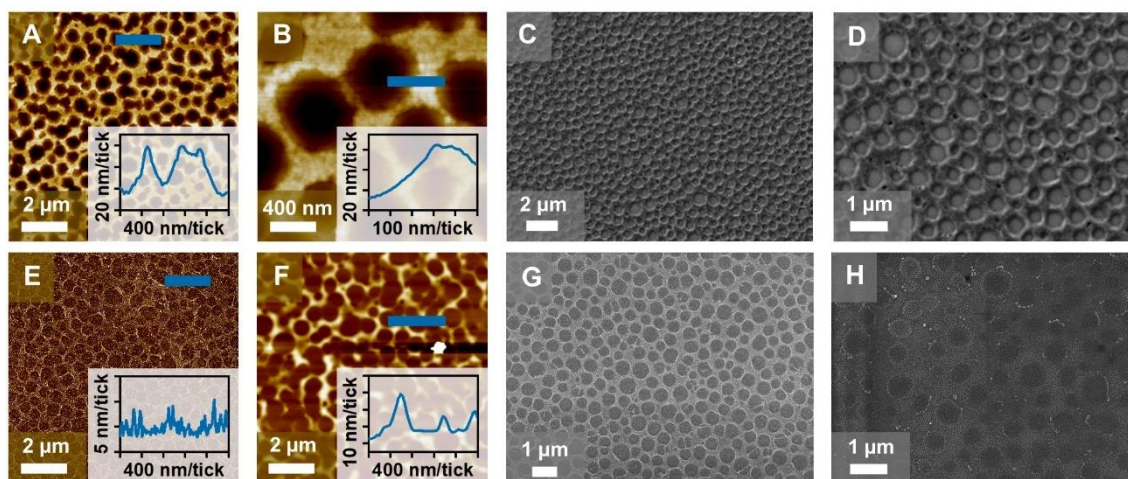


Figure A3.9. Chl annealed PS-*b*-PEO. **A, B.** AFM and **C, D.** SEM images respectively. Metal oxide masks after UVO treatment: **E.** iron oxide mask and **F.** nickel oxide mask AFM images with height profile inserts; **G, H.** SEM images of iron oxide and nickel oxide mask respectively.

In summary, the chloroform annealed masks did not yield good results, which is mainly due to the narrow feature characteristic of the mask and low metal content. This is demonstrated by **Figure A3.10** where the “pore” size is summarised and in the disordered etch result shown in in **Figure A3.11**.

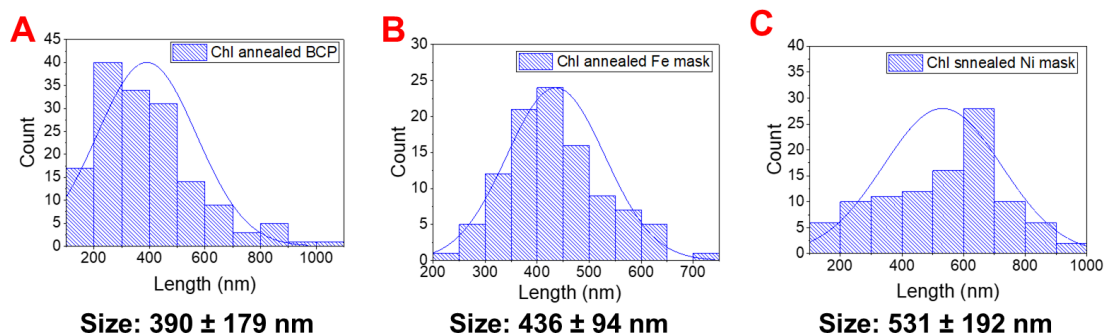


Figure A3.10. Feature “pore” size for PS-*b*-PEO Chl vapour annealed film: **A.** BCP film, **B.** Fe oxide mask and **C.** Ni oxide mask.

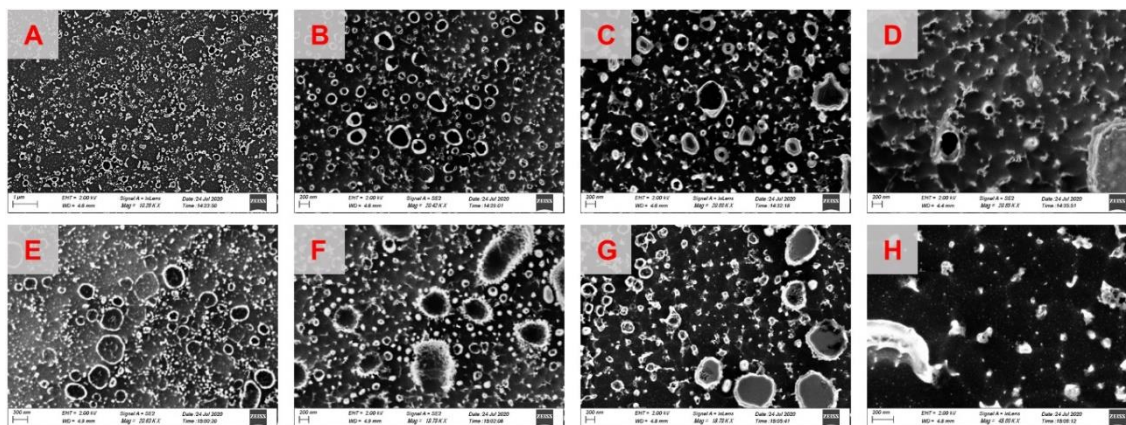


Figure A3.11. Etch pattern from Chl annealed BCP Fe oxide mask (not calcined) after etching for **A.** 1 min, **B.** 2 min, **C.** 3 min, **D.** 4 min. Etch pattern from Chl annealed BCP Ni oxide mask (not calcined) after: **E.** 1 min, **F.** 2 min, **G.** 3 min, **H.** 4 min.

3.6. References

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4. Chapter 4. Room Temperature Fabrication of Macroporous Lignin Membranes for the Scalable Production of Black Silicon.

4.1. Introduction

Anthropogenically induced environmental changes have raised awareness about the harmful effects of non-biodegradable materials. Biopolymer research, in particular related to plant-derived materials such as cellulose and lignin, research has thus garnered attraction. Lignin is a biopolymer, second only in abundance to cellulose; nevertheless, it remains largely underutilized and often treated as a byproduct.^{1–3} The main advantages of lignin are biocompatibility, low toxicity, biodegradability, high carbon content and also carbon-neutrality.^{4,5} Lignin is mainly used as a biofuel, an additive for composite materials and the production of added-value chemicals.^{4,6,7} However, lignin membrane technology is currently limited to lignin composite materials, where lignin is not the sole constituent. Therefore, stand-alone lignin materials are of high commercial and environmental relevance.

The chemical composition of lignin is particularly interesting as it is plentiful with alcohol and methoxy groups allowing for hydrogen-bonding interactions. Lignin is composed of three polymeric units (monolignols), namely syringyl, guaiacyl, and p-hydroxyphenyl, which in turn consist of sinapyl, coniferyl, and p-coumaryl alcohols respectively, linked via ether and C–C bonds.⁸ The alcohol groups, in particular the phenolic hydroxyl groups and carbonyl groups, can interact with water and act as active water sorption sites.⁹ The sites of lignin-water interaction can form pore like features as described by Vu et al and Wang et al.^{10,11} Therefore, a macroscale porous structure can be obtained given that the surface area for water exposure is high, i.e., the membranes must be below a certain critical thickness.

Lignin is often used as an additive to enhance the tensile strength and rigidity of materials such as membranes.^{12,13} However, to-date there has not been any report on stand-alone lignin membranes without additives. Owing to the highly

branched structure of lignin rich with aromatic groups and the large shear modulus ($\sim$ GPa range),¹⁴ lignin-majority membranes tend to be brittle.¹⁵ Thus, lignin films can be supported on a substrate to overcome this drawback. In the present study, lignin films on silicon (Si) substrates are demonstrated to form porous nanoscale membranes under controlled humidity. Water vapour can act as a non-solvent promoting pore formation as described by various researchers.^{16–18} Interactions such as hydrogen bonding and hydrophobic effects result in lignin aggregation, leading to the formations of holes that we refer to as pores.¹⁸ This process can be called water vapour annealing (WVA) as lignin assembles into porous networks.¹⁹ Herein, we describe a novel process of sub-micron thickness membrane fabrication from four organosolv lignin materials cast on silicon substrates using only water vapour as a membrane forming agent. The organosolv term refers to a pulping method which consists of two stages: the catalytic hydrolysis of the wood material and the solubilization of lignin in organic solvent(s) at high temperatures.^{20,21} Thus, lignins sourced by this method are referred to as organosolv lignins.

Furthermore, the abundance of alcohol groups and methoxy groups in lignin makes it convenient for metal ion coordination and production of metal oxides. The metal nitrate salts are particularly useful as they dissolve in eco-friendly ethanol or ethanol/water mixtures.²² The metal ions then can readily coordinate to the available oxygen lone pairs on lignin upon liquid deposition of metal salt ethanolic solutions. Thus, the lignin structure can be implemented as a template for metal oxide membrane formation. Henceforth, the possible applications could be innumerable ranging from pattern transfer to production of metal oxide membranes with antimicrobial, sensing or catalytic properties. The highly uniformly distributed lignin membrane structure yields a nickel oxide membrane upon Ni^{2+} coordination and UVO treatment.^{23,24}

Additionally, the nickel oxide membrane can act as an effective Inductively Coupled Plasma (ICP) Reactive Ion Etch (RIE) mask.²⁵ Silicon substrates can thus be patterned to create a silicon membrane, which, if the pores are deep enough, forms black silicon (BSi).²⁶ The micro- or nano-structured surface on BSi promotes light scattering and absorption as well as reducing reflection losses, thus the surface of BSi appears black.²⁷ BSi is therefore highly useful in a wide

range of fields spanning from sensing, catalysis to optoelectronic applications and it is particularly popular in solar cell technology.²⁸ Conventional BSi production methods report the use of laser irradiation, metal-assisted chemical etching (MACE), wet etching such as HF etching, reactive ion etching (RIE) used herein among other methods.²⁹ RIE processes typically require the use of photoresists or some form of masking material. Therefore, in this work we demonstrate how a bioavailable and nontoxic lignin material can be used to form the template for pattern transfer without the use of extensive machinery or high costs. Thus, we demonstrate how a so-called byproduct can be used to produce solar cell materials.

The lignin membranes could find other uses in fields such as filtration and separation of large particles such as bacteria,³⁰ membrane supports for nanofiltration^{31–33} and water purification.³⁴ Furthermore, lignin itself exhibits antimicrobial properties³⁵ and thus, lignin coatings could be adapted to food packaging.³⁶ Similarly to nickel ion inclusion, other species with antimicrobial properties such as silver³⁷ or zinc ions can be incorporated to produce biocompatible antifouling surfaces. Other potential applications of lignin membranes include energy technology,^{38,39} anti-reflective surfaces,⁴⁰ sensing⁴¹ and synthesis of functional materials.³

In this work, we demonstrated the formation of lignin membranes of various thickness on silicon substrates from four different organosolv lignin materials. A method of nickel oxide membrane production is outlined by liquid deposition of nickel nitrate ethanolic solutions onto lignin membranes with subsequent UVO treatment. A simple ICP RIE method on the nickel oxide mask atop silicon is also used to produce silicon membranes or BSi. We expect that our methodologies of lignin membrane, metal oxide membrane and BSi fabrication can be further adapted to satisfy the needs of versatile fields from biosensing to photovoltaics.⁴²

4.2. Experimental

4.2.1. Materials

The organosolv lignin (**L1**) was supplied by Chemical Point UG (Deisenhofen, Germany) and used without any pre-treatment. The softwood lignin (**L2**) and

wheat straw lignin (**L3**) were supplied by BOC Sciences and used without pretreatment. The olive stone lignin (**L4**) was sourced from olive stone from the Mediterranean region and prepared as outlined in previous studies^{43,44} via an organosolv process in a steam explosion reactor at 180 °C without an acid catalyst. The pretreated solid was separated from the liquor by vacuum filtration and recovered from the liquor by centrifugation after ethanol removal in a rotary evaporator. The lignin was finally air-dried and stored at room temperature for 18 months.

Silicon <100> p-type wafers and with a native oxide (NO) layer and silicon wafers with a thermal oxide layer (200 nm) were used as substrates. Ni(NO₃)₂·6H₂O (nickel nitrate hexahydrate), ACS reagent, ≥98%), tetrahydrofuran (THF) (inhibitor free), anhydrous ethanol and acetone (MERCK, Ireland) were high-performance liquid chromatography (HPLC) grade and used as received. Deionized water was used where necessary

4.2.2. Lignin membrane preparation

Silicon substrates were cleaved into 2 × 2 cm² sizes, cleaned in acetone and then in ethanol for 10 minutes each in an ultrasonic bath. The wafers were then dried with N₂ gas. Lignin solutions with concentrations from 0.5 wt% to 3 wt% were prepared in THF and stirred at 20°C for 1 week. The substrates were spin coated with lignin/THF solutions (~100 µL per sample) at 3000 rpm for 25 seconds using a 5 seconds ramp. Water vapour annealing (WVA) was conducted at room temperature for 5 mins to 1 month under ambient atmosphere (20 ± 2 °C, relative humidity ~ 50 ± 10%) and in a sealed chamber for 5 mins to 30 mins under 300 ± 50 mbar, 20 ± 2 °C and a relative humidity of 70 ± 10%.

4.2.3. Metal ion inclusion

Nickel nitrate hexahydrate was dissolved in ethanol to give 0.8 wt% nickel nitrate hexahydrate solution. The nickel nitrate solution (~100 µL) was then spin-cast onto the 0.5 wt% **L1** lignin samples (3000 rpm, 25 seconds, 5 second ramp) similar to the methods reported by various researchers.^{23,24,45} UVO treatment was conducted for 3 hrs via the UV/ozone system (PSD Pro Series Digital UV Ozone System; Novascan Technologies, Inc., USA). Samples were then calcined in a

tube furnace at 800°C for 1 hr to promote metal densification and remove the residual lignin.

4.2.4. Pattern transfer

Pattern transfer was conducted via Oxford Instruments Plasma Technology Plasmalab System100 ICP180 etch tool using nickel oxide as a hard mask. An ICP Power of 1200 W and RIE power of 20 W were used, with gas flow rates of 80 sccm and 20 sccm for CHF₃ and SF₆ respectively. The chamber pressure was maintained at 16 mTorr. The remaining nickel oxide was removed with 1% oxalic acid (7 hrs, 20°C),^{46,47} the samples were rinsed with DI water and dried with N₂ gas.

4.2.5. Characterization

Lignin molecular weight was measured by gel permeation chromatography (GPC) according to the previously reported methods^{7,8} and determined to be $M_n = 1115 \text{ g mol}^{-1}$, $M_w/M_n = 7.64$ for **L1** lignin; $M_n = 980 \text{ g mol}^{-1}$, $M_w/M_n = 7.16$ for **L2** lignin; $M_n = 1484 \text{ g mol}^{-1}$, $M_w/M_n = 10.70$ for **L3** lignin; $M_n = 1050 \text{ g mol}^{-1}$, $M_w/M_n = 4.41$ for **L4** lignin.

Ultimate and proximate analysis were performed for all lignin samples. Moisture content was obtained following overnight drying at 105 °C, whereas ash content was determined at 575 °C for the raw samples, following the ASTM standard E1755-01. Ultimate analysis results (CHN) were acquired using a 2400 CHNS/O Series II (PerkinElmer) elemental analyser, following the procedure in ASTM D5373-02. The oxygen content was calculated by the difference according to previous research.⁴⁸

The thermal stability of Lignin was examined using a PerkinElmer Pyris 1 TGA. Each sample (ca. 3 mg) was loaded in a platinum pan and heated from 30 °C to 800 °C at the rate of 10 °C/min under nitrogen atmosphere.

A PerkinElmer Pyris Diamond Differential Scanning Calorimeter (DSC) was used to understand the crystallization behaviour of the lignin. The machine was calibrated using indium standards. The samples (~3 mg) were sealed in aluminium pans and heated from 20 to 250 °C at a rate of 10 °C/min.

Atomic force microscopy (AFM) (Park systems, XE7) was operated in NCM (non-contact mode) under ambient conditions using a silicon microcantilever probe tip (force constant of 26 Nm^{-1}) in adaptive scan mode (scan rate of 0.2 Hz to 1.0 Hz, error bound of 1 nm).

Solid-state Cross-Polarization Magic Angle Spinning (CP/MAS) Nuclear Magnetic Resonance (NMR) spectra of ^{13}C were acquired at 100.6 MHz while using a Bruker 400 MHz (9.4 T) Avance HD spectrometer equipped with a 3.2 mm HX-CP/MAS probe. The temperature was stabilised at 20°C with a flow rate of 600L/h. ^{13}C spectra were acquired under MAS at 20 kHz, if not otherwise specified, using ramped amplitude cross polarization, and SWFTPPM decoupling with a ^1H -decoupling field of about 100 kHz. A 1 ms contact time and a pulse delay of 4 s were used. Chemical shifts were calibrated setting the ^{13}C low field signal of adamantane to 38.48 ppm

Fourier Transform Infrared (FTIR) spectra were recorded on a PerkinElmer Spectrum 100 equipped with a universal total reflectance (UATR) (Diamond/KRS-5 sandwich assembly) sampling accessory. The spectra were recorded from 4000 cm^{-1} to 400 cm^{-1} , with 16 accumulations and a resolution of 4 cm^{-1} .

Scanning electron microscopy (SEM, Zeiss Ultra Plus) images were recorded at an accelerating voltage of 2 kV, working distance 4 – 5 mm and using a $30 \mu\text{m}$ aperture. SEM cross sections were obtained from the cleaved samples positioned at a tilt angle of 70° , the images were recorded using “tilt correction”. The film thicknesses were measured by electron microscopy. Pore size distributions were analyzed from the secondary electron SE2 detector SEM micrographs via ImageJ by applying an FFT bandpass filter to the images, binarizing the images and using the particle analyzer plugin.

Advancing contact angle (CA) measurements were recorded using water, diiodomethane and glycerol at 3 different spots on each sample for each liquid. The measurements were conducted on a custom-built system using a 60 Hz camera and a 35-gauge needle ($\varnothing 135 \mu\text{m}$ OD) as described in previous studies.^{49,50} The flow rate was set to 10 nL s^{-1} and the droplet volume was between 80 to 100 nL. Contact angles were measured on ImageJ using the “drop

snake” plugin.^{51,52} SE was calculated using the advancing CAs via the Lifshitz-van der Waals/acid-base approach.⁵³

X-ray photoelectron spectroscopy (XPS) analysis was performed under ultra-high vacuum conditions ($<5 \times 10^{-10}$ mbar) with a non-monochromated source of Al K α X-rays (1486.6 eV) operating at 200 W (CTX400, PSP Vacuum Technology). The emitted photoelectrons were collected at a take-off angle of 90° from the sample surface and analysed in a RESOLVE120 spectrometer (PSP Vacuum Technology). XPS spectra were recorded setting the analyser pass energies constant to 100 eV and 50 eV, for the survey and core scans, respectively. The peak positions of the photoemission lines were corrected to the C 1s transition, at a binding energy of 284.8 eV.⁵⁴

4.2.6. Optical measurements on BSi

Reflectance measurements in the visible region (400 – 800 nm) were recorded on BSi samples using a Lambda 650S spectrometer (Perkin Elmer) equipped with an integrating sphere. The spectra resolution of the instrument is 0.17 nm and the measurements were recorded with a 1 nm step.

Angle-resolved reflectivity measurements were carried out using a custom built 2Θ system shown in **Appendix Figure A4.13**. The system consisted of a Thorlabs halogen lamp weakly focused onto a sample positioned on the inner stage of the rotating 2Θ system. The reflected light was collected by means of a collection lens and optical fibre mounted on the outer stage of the system which rotated at twice the rate of the inner stage. The fibre was connected to an Ocean Optics USB4000 visible range spectrometer with a spectral resolution of 0.2 nm. The measurements were carried out with an angular step of 0.5° and for the wavelength range of 400 – 750 nm.

(Where applicable, values are reported as average value $\pm$ 1s, where s stands for sample standard deviation)

4.3. Results and Discussion

4.3.1. Membrane Fabrication and Optimization

In this work, macroporous lignin membranes were produced via spin-coating of four lignin materials onto Si substrates from tetrahydrofuran (THF) solutions. Green solvent alternatives, such as ethyl lactate and 2-Methyltetrahydrofuran, did not lead to good dispersion and dissolution of lignin. Alternatively, acetone could be used but the acetone-lignin solutions were found to be less stable long term than the THF-lignin counterparts.

WVA was applied similarly to our previous work to produce porous films (see **Chapter 3**).²⁴ Water vapour is chosen over a liquid water treatment in order to prevent the structural collapse. Furthermore, water is readily abundant and low-cost, it is known to interact with lignin via hydrogen bonding.⁵⁵ Four different lignins, denoted commercial organosolv (**L1**), softwood (**L2**), wheat straw (**L3**) and olive stone (**L4**) were used to fabricate a range of different pore sizes. **L1**, **L2** and **L3** lignin membranes form readily at 25 ± 1 °C in a WVA assembly²⁴ within 5 mins to an hour, whereas **L4** membranes required higher humidity i.e., the vacuum chamber assembly (~ 300 mbar, ~ 20 °C, $\sim 80\%$ relative humidity, 5 mins) which can be due to differences in chemical structure and composition of the **L4** lignin. If the laboratory conditions matched the swelling conditions the films were observed to spontaneously assemble into porous membranes as in **Figure 4.1** after spin casting and large-scale SEM images are shown in **Appendix Figure A4.1**.

Figure 4.1 portrays the 0.5 wt% lignin membranes derived from **L1**, **L2**, **L3** and **L4** lignins represented in **A**, **B**, **C** and **D** respectively. The thickness of the membranes was estimated from a series of scanning electron microscope (SEM) images as 45 ± 8 nm for **L1**, 43 ± 15 nm for **L2**, 53 ± 4 nm for **L3** and 61 ± 9 nm for **L4** derived lignin membranes. SEM micrographs and relative thicknesses of membranes produced from 0.8 wt% to 3.0 wt% solutions are shown in **Appendix Figure A4.2**, **A4.3**, **A4.4** and **A4.5**. The 0.8 wt% membranes display pore sizes similar to the 0.5 wt% membranes for all lignins but with a higher thickness. Therefore, we can deduce that membranes with a thickness < 100 nm tend to form open pores throughout the structure (**Appendix Figures A4.2 –**

A4.5). The 1 wt% membranes also display a porous network, however with less open pore space than the 0.5 wt% and 0.8 wt% counterparts for each lignin type. The 1.5 wt% membranes begin to appear less porous as the thickness rises, however not substantially over 100 nm for all lignins. For higher lignin concentrations the structures tend towards dense films with less open pore space per volume.

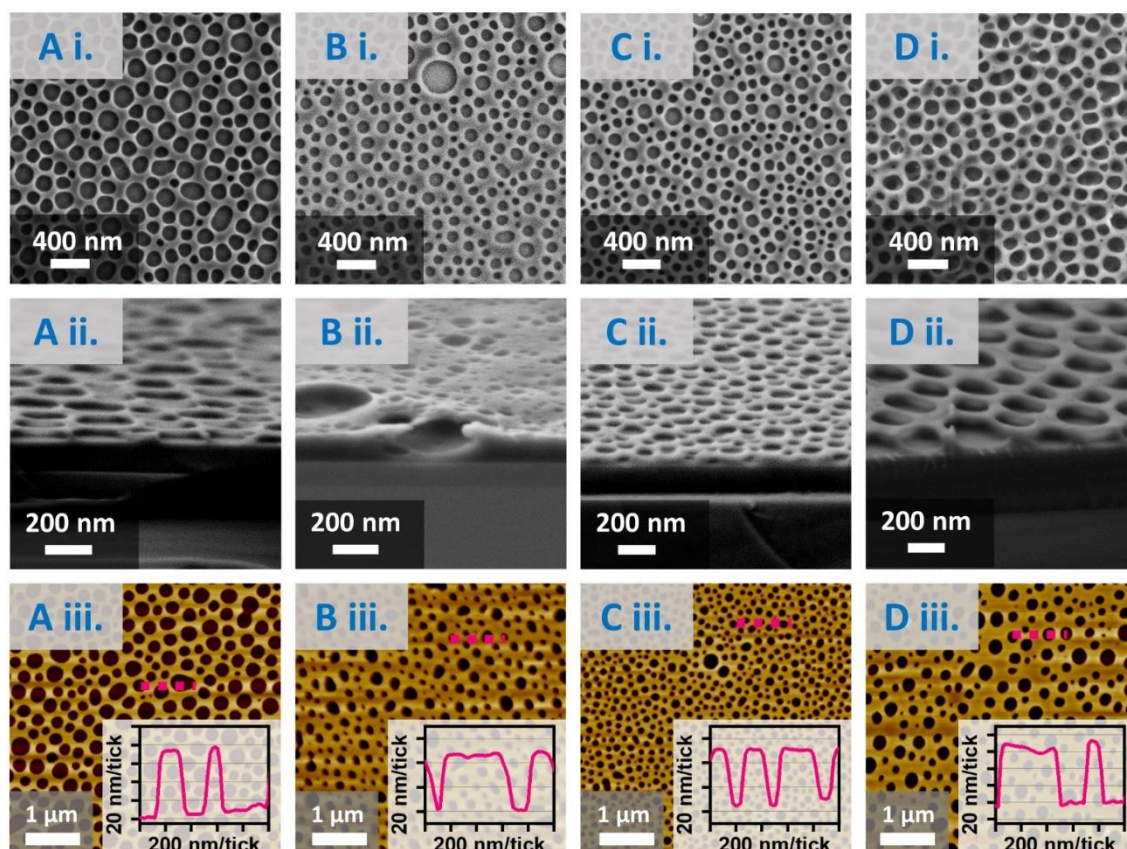


Figure 4.1. Lignin membranes fabricated in a sealed chamber after 5 mins of 0.5 wt% films. **A.** organosolv (**L1**), **B.** softwood (**L2**), **C.** wheat straw (**L3**), **D.** olive stone (**L4**) lignin membranes respectively. **i.**, **ii.** and **iii.** represent the top-down SEM, cross-section SEM and top-down AFM micrographs with line profiles inset respectively.

The pore diameter distributions of the 0.5 wt% membranes are shown in **Figure 4.2 A, B, C and D** for **L1, L2, L3 and L4** lignin membranes respectively. The membranes display similar pore size distributions, i.e., within a 100 nm to 200 nm range. **Appendix Figure A4.6** demonstrates that the relationship

between molecular weight and pore size is minimal, however the range of molecular weights used is narrow and all lignins are derived and supplied from different sources. The investigation of pore size versus molecular weight is thus a subject of a future study when other lignins could be sourced or extracted. Furthermore, we investigated how long the obtained porous films remain stable at laboratory ambient conditions.

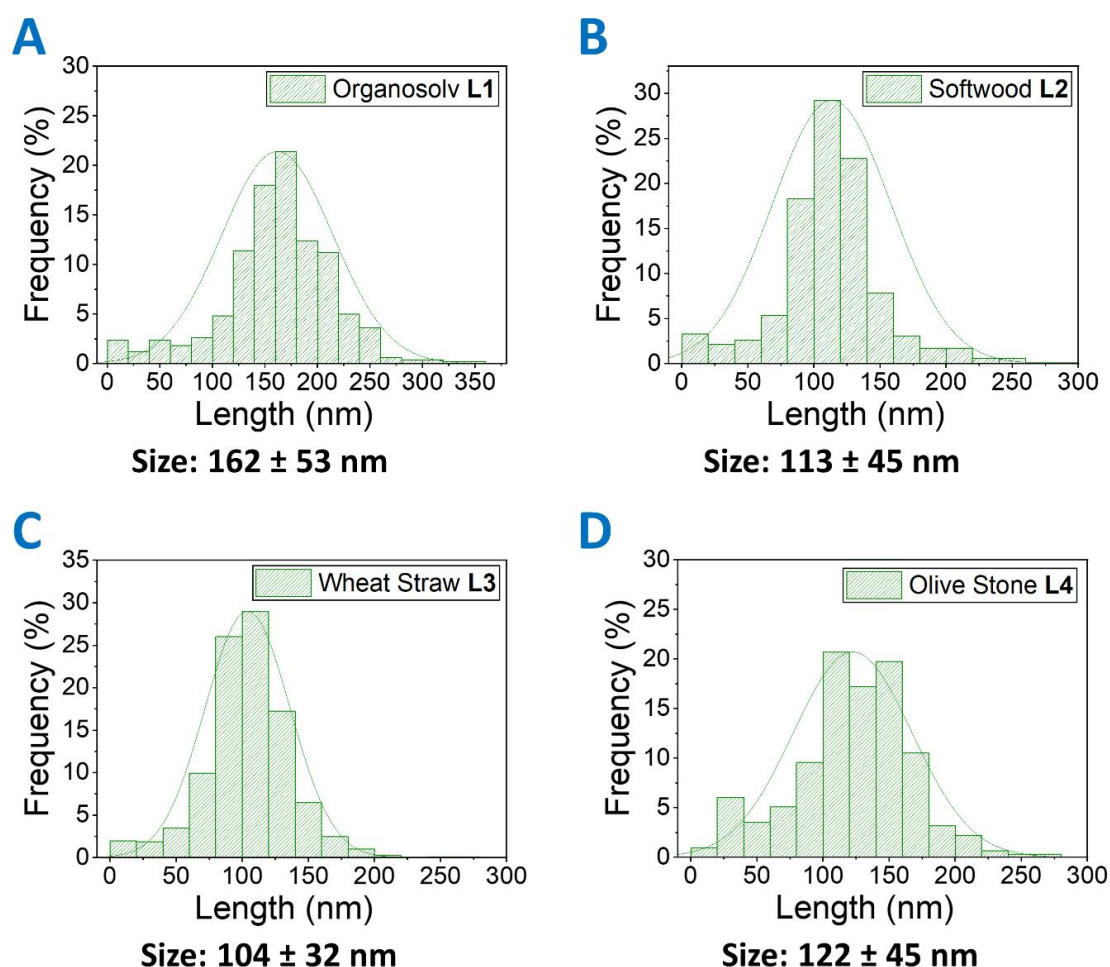


Figure 4.2. Lignin membranes pore size distributions for 0.5 wt% membranes. **A.** organosolv (**L1**), **B.** softwood (**L2**), **C.** wheat straw (**L3**), **D.** olive stone (**L4**) lignin membranes respectively.

To answer the question on how long the membranes remain stable or how long the structure remains uniform, we observed the stability of the membranes over a period of a year on two different substrates: silicon p-type <100> with a NO

layer ($\sim 4 - 6$ nm) and silicon p-type $\langle 100 \rangle$ with a thermal oxide layer (~ 200 nm). The membranes retained the structure on the thermal oxide silicon wafers for 1 to 3 months at ambient conditions ($\sim 20 \pm 2$ °C, relative humidity $\sim 50 \pm 5\%$). However, on the NO silicon wafers the structure undergoes a spontaneous transition to a disordered state, forming islands with smaller pores within 24 hrs to a few days under ambient conditions as shown for **L1** lignin membranes in **Figure 4.3**. Similarly, for SiO₂ substrates, the film starts to deform but the process is much slower, i.e., several weeks to months. Despite having virtually, the same bulk surface energy (SE) after cleaning in acetone and ethanol, (45.80 mJ.m⁻² for NO silicon and 47.90 mJ.m⁻² for thermal oxide silicon as described in **Appendix Table A4.1**), the substrates are slightly chemically dissimilar. Thermal oxide silicon wafers possess only SiO₂ at the surface, however NO is stipulated to contain both SiO and SiO₂, sometimes described as SiO_x ($x < 2$) or SiO-SiO_x.^{56,57} We propose that either of the following two processes are involved. Firstly, lignin might adhere better to a pure SiO₂ surface due to the interactions of the lignin groups, or secondly, the slightly lower surface energy on the NO surfaces might lead to faster disassembly kinetics causing the lignin to bunch into islands under tension. Lignin is a branched polymer and does not display flow-like motion that is exhibited by straight chain polymers, further explaining the film rupturing into islands under prolonged water vapour exposure and due to the surface tension. The **L2**, **L3** and **L4** membranes follow similar membrane formation and disassembly stages over time. Interestingly, the lignin films display vastly different bulk SEs (from 26.38 mJ m⁻² for **L3** to 57.64 mJ m⁻² for **L1** as described in **Appendix Table A4.1**) showing the difference in surface chemistries. Yet all the SE values for lignin membranes are below the water equilibrium surface tension value of 72 mJ m⁻²,⁵⁸ as expected for hydrophobic organosolv lignins. Therefore, despite the difference in SEs, the hydrophobic interactions between water and lignin and the π - π interactions of lignin with itself due to the high abundance of aromatic groups are sufficiently strong to yield similar porous lignin films ubiquitously distributed along the substrate.

The site-specific interactions of lignin with water virtually breaks up the bulk structure and leads to the formation of “pores” due to high surface tension. A more detailed proposed mechanism is as follows: initially, lignin interacts strongly

with itself mainly by π - π stacking as lignin molecules are highly concentrated in aromatic groups and each lignin molecule is proposed to adopt a flat or disk-like configuration in solution.¹⁶ As water permeates through the film, the lignin molecules aggregate together within the internal surface of the dense film due to the hydrophobic effect induced by water and also the lignin π - π interaction with other lignin molecules.^{17,18} This leads to fracturing of the thin layer of the remaining lignin at the outer surface due to a pressure difference, creating the so-called pore. Therefore, a normal phase separation model does not describe the lignin membrane formation well. Under the fluctuations in atmospheric conditions, the lignin films can alter morphology from porous to dense to ruptured porous lignin islands as observed in this work. The formation of islands can be akin to formation of spheres in solution by π - π interactions between the aromatic rings within lignin as described by Li et al and Xiong et al.^{17,18} To establish the real mechanism of macropore formation (pores > 100 nm in diameter), further studies and perhaps novel models of polymer interactions should be designed.

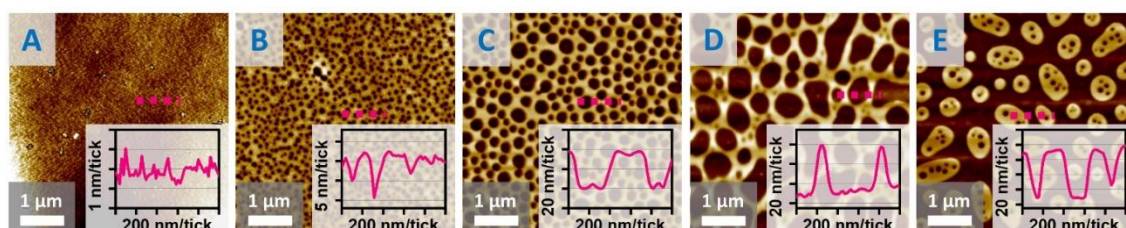


Figure 4.3. AFM images with line profiles inset of 0.5 wt% **L1** membrane self-assembly stages on a NO Si p-type <100> surface. **A.** The as spin-coated film. **B.** The as-cast film starts to form pores upon WVA within a few minutes. **C.** The assembled lignin membrane after 10 mins. **D.** The pore sizes increase and the film becomes disordered (at 20°C, 50% relative humidity) after 30 mins to a few hrs. **E.** The film begins to rupture and form lignin islands with smaller pores after ~ 24 hrs at ambient room conditions (20°C, 50% relative humidity).

The Solid-state Cross-Polarization Magic Angle Spinning (CP/MAS) ¹³C Nuclear Magnetic Resonance (¹³C NMR) spectroscopy, Fourier-Transform Infrared (FTIR) spectroscopy, Thermogravimetric Analysis (TGA) and Differential

Scanning Calorimetry (DSC) characterization of the lignin materials can be found in **Appendix 4.5.2. Figures A4.7, A4.8 and A4.9.**

The four lignin materials used in this study are organosolv lignins with an established general structure.⁴⁴ The main monomers such as syringyl and guaiacyl can be identified from the FTIR and ¹³C CP/MAS NMR spectra with the assignment included in **Appendix Figure A4.7, Appendix Tables A4.2 and A4.3.** The organosolv lignins used in this paper were extensively structurally characterized in previous studies by various researchers.^{59–61} The FTIR and NMR spectra were thus used to verify that the structures of all the organosolv lignins are guaiacyl-syringyl types with predominantly aromatic groups.^{62–64} The **L1** and **L2** lignins were observed to have higher aromaticity than the other two lignins and the **L4** lignin was deduced to have the highest purity. In general, the four lignins behave similarly under WVA, with the assembly mechanism described above pertaining to all the materials. **L4**, however, required a vacuum chamber for self-assembly which is explained by the low aromaticity and high purity, i.e., lower propensity for lignin π - π interactions and reduced hydrophobic effect during WVA. A more detailed structural analysis is included in the SI below **Appendix Tables A4.2 and A4.3.**

The X-ray photoelectron spectroscopy (XPS) survey spectra of the lignin membranes are shown in **Appendix Figure A4.10**, with associated elemental content atop NO silicon wafers. The proximate and ultimate analysis results are displayed in **Appendix Table A4.4.** The elemental composition for all lignins is similar. The DSC analysis shows that L1, L2 and L3 lignins have a glass transition temperature at approx. 60 to 65 °C, whereas the **L4** lignin displays a glass transition temperature T_g of ~ 41°C. The glass transition in this case is observed as an endothermic peak as described by Gordobil et al, whereby enthalpy relaxation takes place.⁶⁵ Those workers postulate that lignin kept for large periods of time at conditions close to glass transition exhibits improved chain mobility, which explains the endothermic peak. All the lignins remain stable up to 200 °C as seen from the TGA in **Appendix Figure A4.8** so there is no thermal degradation during the membrane fabrication process.

4.3.2. Nickel oxide membranes

A well-known metal oxide inclusion methodology (for synthetic polymers but not seen for biopolymers such as lignin) can be adapted to the lignin membranes to yield nickel oxide membrane structures. Lignins are rich with polar groups with lone pairs available for metal coordination such as alcohols, therefore we anticipated incorporation of the metal into the structure ubiquitously. A 0.8 wt% ethanolic solution of nickel nitrate was spun on as in previous studies to fabricate a lignin membrane with coordinated Ni^{2+} ions.²⁴

To investigate the nickel membranes, we selected **L1** 0.5 wt% membranes due to the lowest cost of the source material. After metal inclusion, a UVO treatment was conducted to remove the lignin material and to produce the nickel oxide. A further calcination step, i.e. heating at 800 °C for 1 hr was applied to remove any residual lignin. The nickel oxide membranes show a relatively uniform structure as seen in **Figure 4.4 A** and **B** with a similar pore size (144 ± 37 nm) as the lignin membrane (162 ± 53 nm). The size variation in pore size after nickel oxide infiltration, UVO treatment and calcination compared to the lignin polymer membrane is not significant.

The survey spectra of nickel oxide after UVO treatment and after calcination is shown in **Appendix Figure A4.11 A** and **B**. Prior to calcination, the nickel mask consists of solely NiO (Ni 2p_{1/2} (872.3 eV) and Ni 2p_{3/2} (854.7 eV)) as seen in **Appendix Figure A4.11 C** as opposed to block copolymer nickel oxide masks after UVO (Ni(II) and Ni(III) oxide).²³ We propose that lignin bound Ni^{2+} ions are prevented from further oxidation to Ni^{3+} and thus NiO is the only oxide. The O 1s core spectrum also indicates the presence of only one oxide (NiO) at 530.0 eV as well as C-O (530.9 eV) and Si-O (532.5 eV) bonds.

The chemical composition of the nickel oxide membrane after calcination was determined to be NiO (Ni^{2+}) with a minor amount of nickel metal (Ni^0) as seen from curve fitted binding energies.⁶⁶ After UVO, the NiO has a significant number of surface defects because of the UVO-lignin removal in the surroundings, as described by the “container” effect.⁶⁷ This generates labile oxygen groups that upon heating at 800 °C leads to a partially reduced state i.e., Ni metal formation. **Figure 4.4 C** shows the curve fitted (Gaussian-Lorentzian) binding energies for

nickel oxide are Ni 2p_{1/2} (870.6 eV) and Ni 2p_{3/2} (852.9 eV) assigned to Ni⁰ and Ni 2p_{1/2} (872.8 eV) and Ni 2p_{3/2} (854.8 eV) assigned to Ni²⁺. The O 1s core spectrum shows only C-O (531.1 eV), Si-O (532.2 eV) and Ni-O (529.2 eV) chemical linkages (**Figure 4.4 D**). We expect that the content of nickel metal in the mask facilitates improved etching depth as compared to just solely NiO masks.

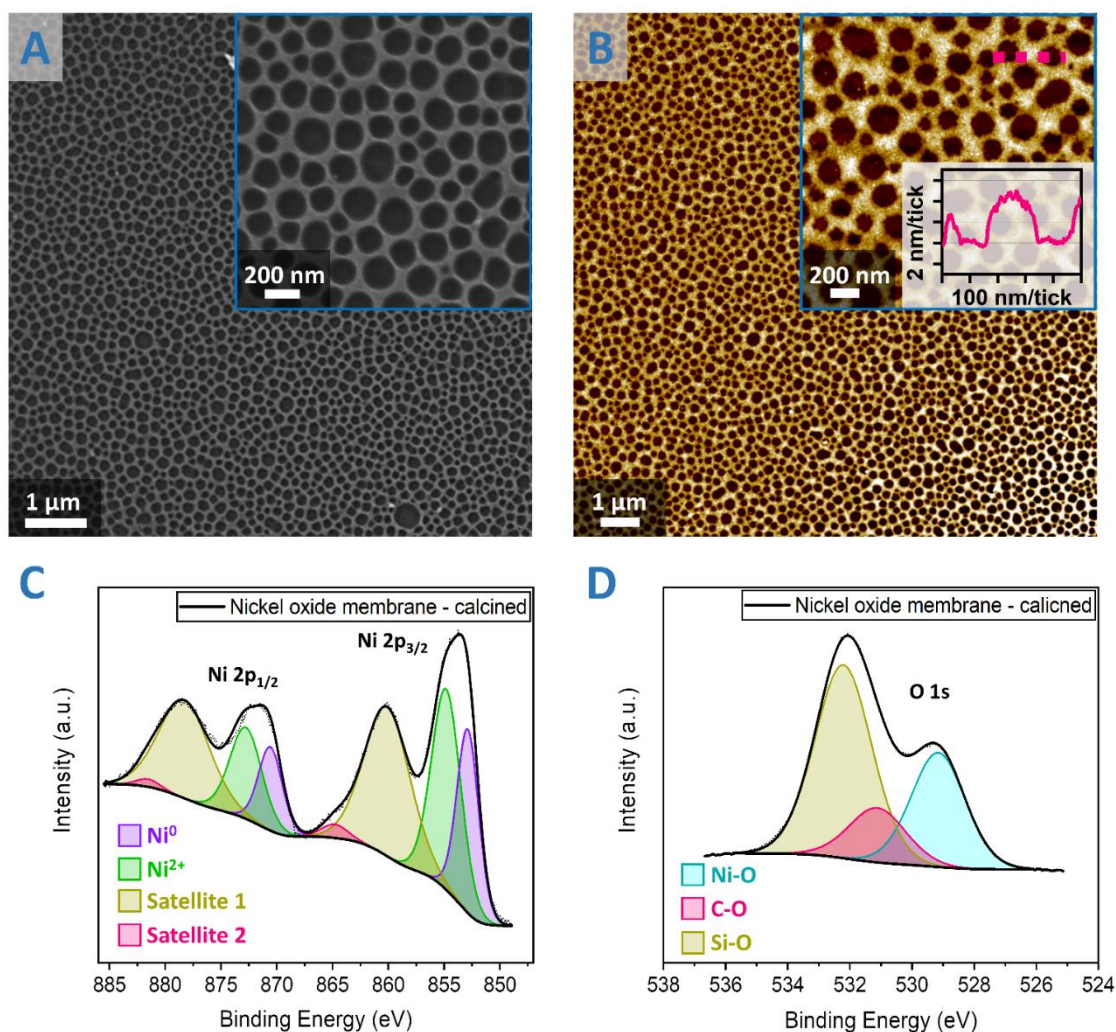


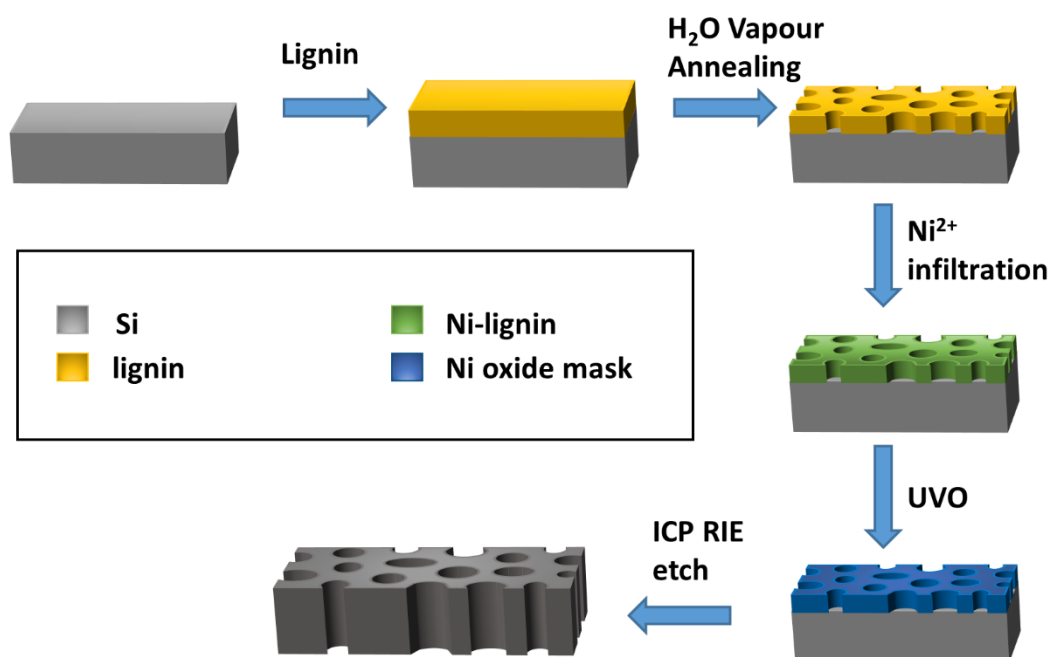
Figure 4.4. Nickel oxide membrane after calcination produced from the **L1** 0.5 wt% lignin membrane: **A.** SEM images and **B.** AFM images with line profiles inset. The XPS high-resolution core scans spectra of **C.** Ni 2p and **D.** O 1s of nickel oxide membrane on NO silicon after calcination.

The method of Ni^{2+} coordination to the lignin substrate can also be used to “store” the structure as the nickel ions tether the lignin in place and prevent polymer motion and disassembly. We applied this method to preserve the structures for several months on either substrate without subsequent UVO treatment as shown in the AFM image in **Appendix Figure A4.12 A** for an **L1** 0.5 wt% sample with incorporated Ni^{2+} ions.

4.3.3. Silicon membranes and optical applications

Pattern transfer was applied to etch the silicon substrates to create an ordered membrane with cylindrical macroscale pores. The full process is described in **Scheme 4.1**. It is asserted that this surface engineering may have many applications in the area of porous silicon surfaces. Here we explore the formation of BSi in particular. Other authors have explored self-assembled structures and pattern transfer to produce BSi. However, these have been through vertical nanowire type structures.²⁷ We suggest that these have limited mechanical robustness. However, by creating BSi from an engineered porous film, we postulate that this increases mechanical strength and adhesion.

The calcined nickel oxide mask was etched for 1 to 4 mins as shown in **Figure 4.5 A – D**. A 1 min etch produces pore etch depth of 150 ± 25 nm and a 4 min etch leads to mask degradation with large variations in feature heights. The 2 and 3 min etch yield a pore depth of 406 ± 66 nm and 1307 ± 201 nm respectively. However, upon the ICP RIE etch the pore diameter increases over a 100 nm in size from 144 ± 37 nm (nickel oxide mask) to 256 ± 64 nm (after 1 min etch) (**Appendix Figure A4.12 B and C**), possibly due to etch mask degradation during etching. The pore size distributions after 1 to 4 min etches are practically the same. For the purpose of BSi production with a large etch depth ($> 1 \mu\text{m}$) the size increase is irrelevant, but where the mask pore size needs to be preserved this aspect should be noted.



Scheme 4.1. Overall lignin-based silicon membrane production process. The lignin is spun from THF solutions onto silicon substrates. The nickel precursor is subsequently deposited, and the lignin is removed via UVO. The pattern is transferred onto the silicon substrate via an ICP RIE etch.

Standard and angle-resolved reflectance measurements were recorded to understand the optical behaviour of the silicon membranes and to determine the suitability of the process to BSi production. **Figure 4.6 A** shows the normal reflection spectra of an unetched silicon sample with NO (4 – 6 nm), compared with samples etched for 1 min, 2 min and 3 min respectively. The average reflection from the NO sample across the visible range at normal incidence is 38%. This is reduced to 18% for the 1 min etch, 7.1% for 2 min etched sample and then <3% for the 3 min etched sample. Furthermore, the 3 min etched sample appears black throughout as seen in the inset photograph in **Figure 4.6 A**. Thus, the extensive distribution of the etch pattern over a macroscale area coupled with the extremely low reflectance in the visible region make the 3 min etch process suitable for large area BSi production.

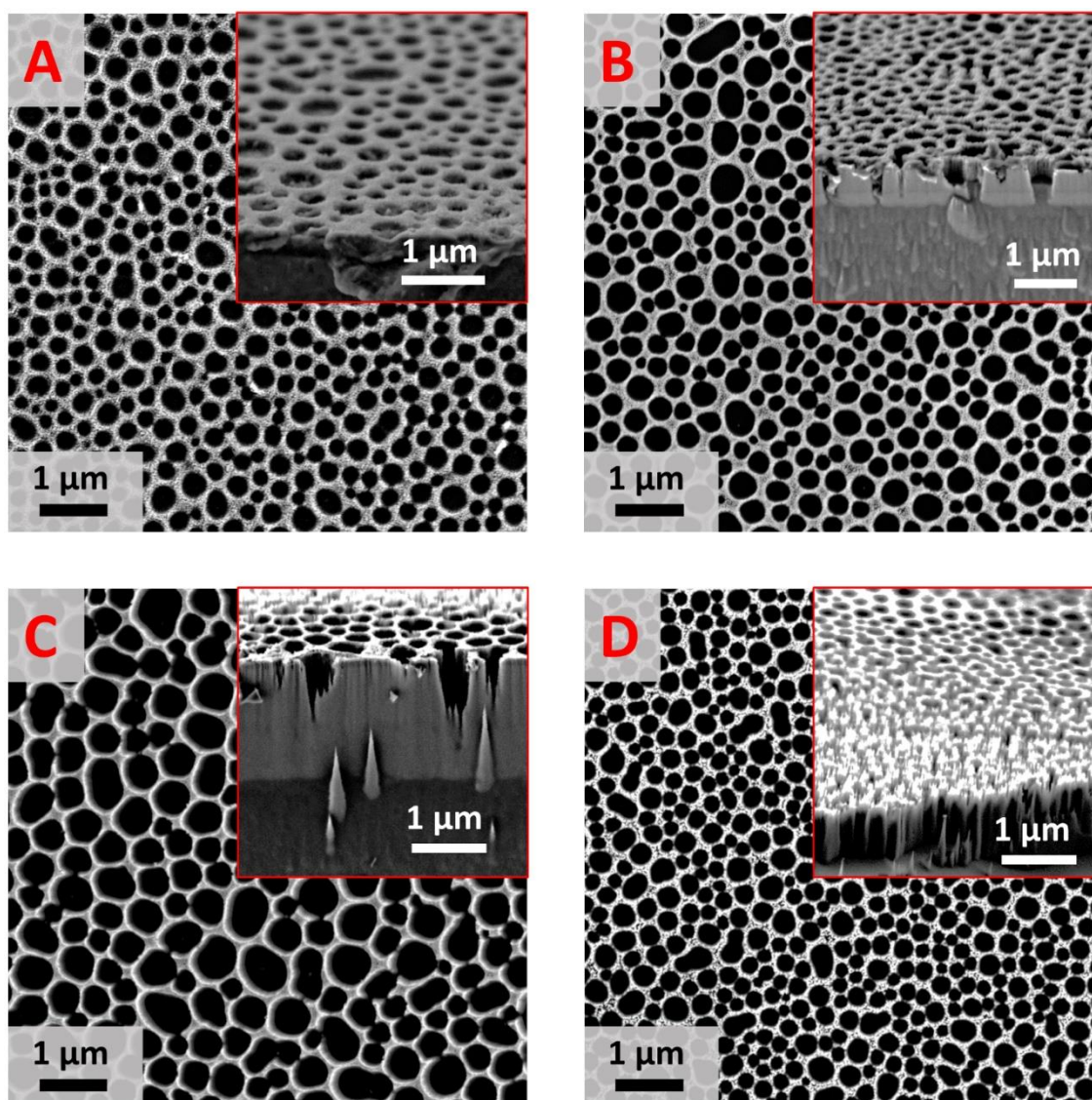


Figure 4.5. SEM images (with cross-section inset) of silicon membranes produced from **L1** 0.5 wt% lignin membrane nickel oxide template after ICP RIE etch after **A.** 1 min **B.** 2 mins **C.** 3 mins and **D.** 4 mins.

It is essential to examine the angle resolved reflectance measurements for our process to be practically useful. The angle dependent reflectivity for the samples were taken using a custom built 2θ system with the setup shown in **Appendix Figure A4.13**. The surface plots show the magnitude of unpolarized reflection as a function of angle on the x-axis and wavelength on the y-axis. In general, we expect to see low reflectivity for a broad range of angles but an increase at higher angles due to Fresnel reflection. The 2 min etch results in lower reflection at normal incidence however still has large reflection at higher angles

(**Figure 4.6 B**). The 3 min etched sample shows a strong reduction in reflection, which persists even at the higher angles (**Figure 4.6 C**).

Previous studies that reported BSi production by ICP RIE methods either used expensive materials such as Pt,⁶⁸ or textured the surface to produce pillars of higher reflectance than reported herein.²⁹ The coating of the textured silicon substrates with Al₂O₃,⁶⁹ NbN⁷⁰ or other materials coupled with the use of highly energy demanding atomic layer deposition (ALD)⁷¹ or other methods improved the reflectance to 3%.²⁹ However, our work shows that BSi can be produced with reflectance lower than 3% in the visible region without the use of costly materials, coatings or machinery. In summary, the 3 min etch sample displays desirable attributes for BSi manufacturing such as low reflection over a broad range of wavelengths and angles and macroscale coverage of the etched structure. Therefore, we recommend our lignin and nickel membrane methodology with the 3 min ICP RIE process as a suitable candidate for solar cell applications.

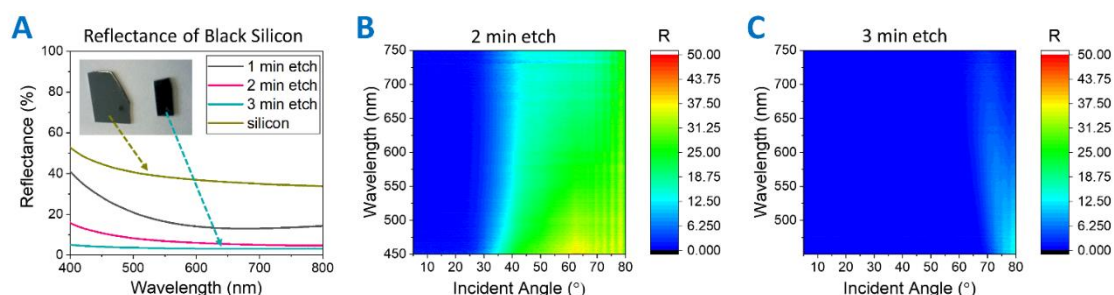


Figure 4.6. **A.** UV-Vis-NIR spectra of NO silicon, 1 min, 2 min and 3 min etch samples, **B.** Angle resolved visible spectrum of 2 min etched sample **C.** Angle resolved visible spectrum of 3 min etched sample.

4.4. Conclusions

We demonstrated a completely novel and highly facile strategy to fabricate large area macroporous membranes derived from lignin without additives. The four chosen lignin materials yielded pores in the range of 100 to 200 nm when the membrane thickness remained below 100 nm. The process is highly scalable and produces large-area porous films as shown. The described lignin membranes are easy to produce on large scale with simple equipment and chemicals. We suggest that this structure can be adapted to incorporate various moieties such as metal oxides for optical, antimicrobial or sensing applications.

Furthermore, we demonstrated nickel oxide membrane production from the lignin templates via a facile method of metal infiltration, UVO treatment and calcination. These metal oxide structures have potential applications in areas such as sensing or catalysis. These metal oxide templates were then utilized as etch masks for the fabrication of silicon membranes (with pore depths of over 1 μm) via a well-established ICP-RIE method. The BSi produced displayed low reflectivity ($< 3\%$ for the 3 min etch sample) in the visible range. We therefore anticipate that the BSi produced by this method can be applied to solar cell technology.

Overall, we believe that this work greatly expands the potential and scope of lignin bulk chemistry and membrane formation processes. This method is comparatively cheaper and more ecofriendly than the existing polymer lithographic techniques as both lignin and water are abundant and ecologically safe. We anticipate that the lignin membranes and methodology described in this work opens a new research direction for the development of a variety of photonic and catalytic applications.

4.5. Chapter 4 Appendix

Appendix 4.5.1. Lignin membranes of higher thicknesses

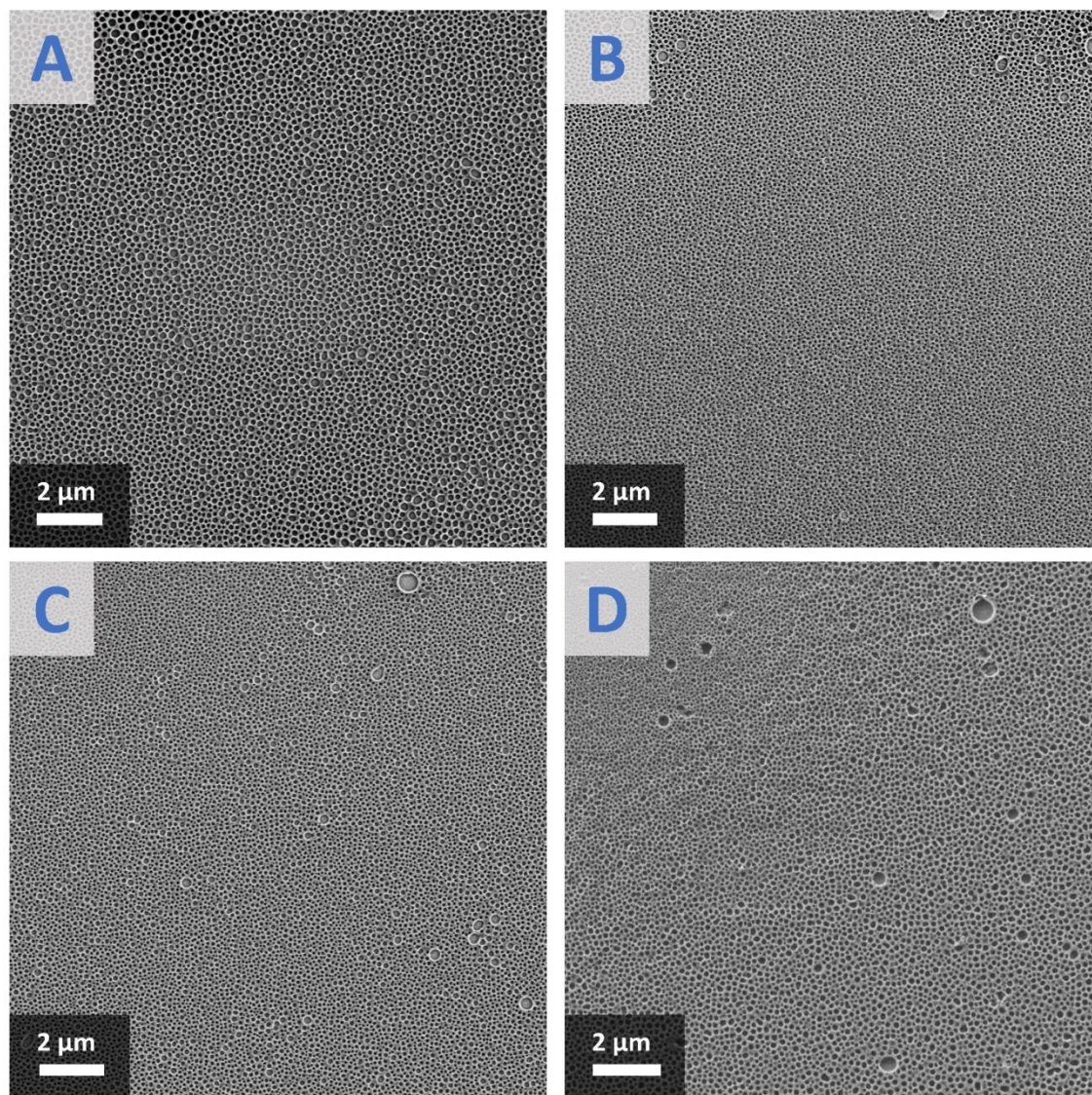


Figure A4.1. Large area SEM micrographs of 0.5 wt% lignin membranes: **A. L1**, **B. L2**, **C. L3** and **D. L4**.

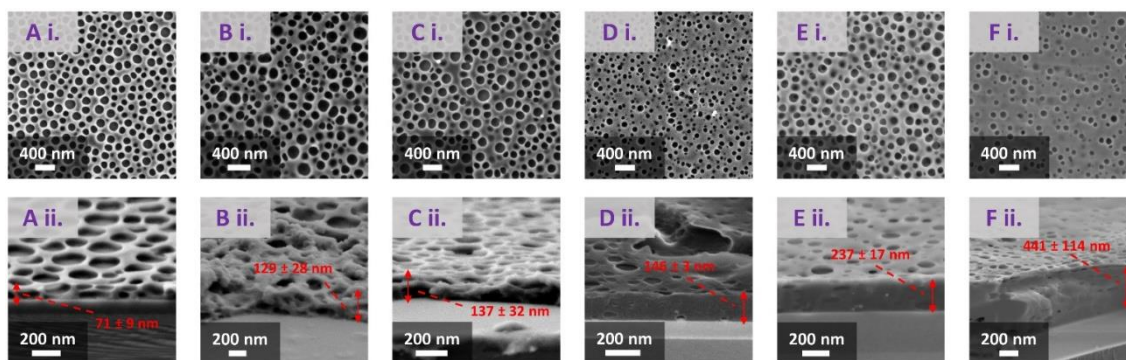


Figure A4.2. SEM micrographs of **L1** lignin membranes where **A** is 0.8 wt%, **B** is 1.0 wt%, **C** is 1.5 wt%, **D** is 2.0 wt%, **E** is 2.5 wt%, **F** is 3 wt% membranes; **i.** represents the top-down SEM and **ii.** represents the cross-section SEM micrographs with associated thicknesses.

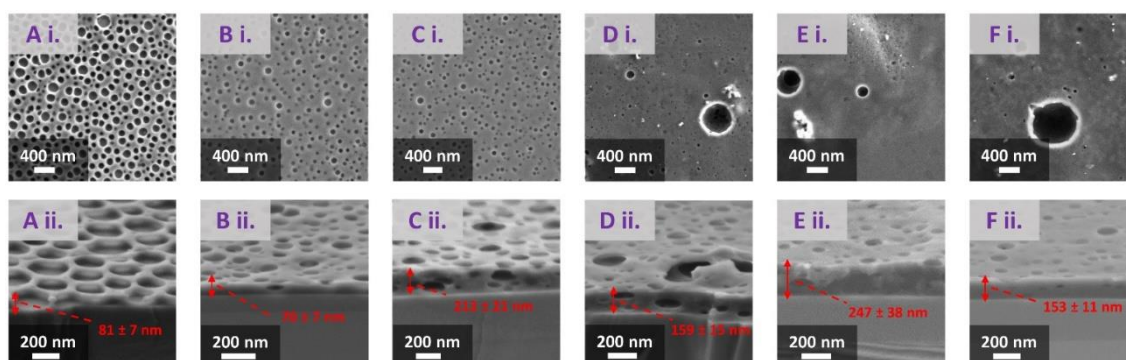


Figure A4.3. SEM micrographs of **L2** lignin membranes where **A** is 0.8 wt%, **B** is 1.0 wt%, **C** is 1.5 wt%, **D** is 2.0 wt%, **E** is 2.5 wt%, **F** is 3 wt% membranes; **i.** represents the top-down SEM and **ii.** represents the cross-section SEM micrographs with associated thicknesses.

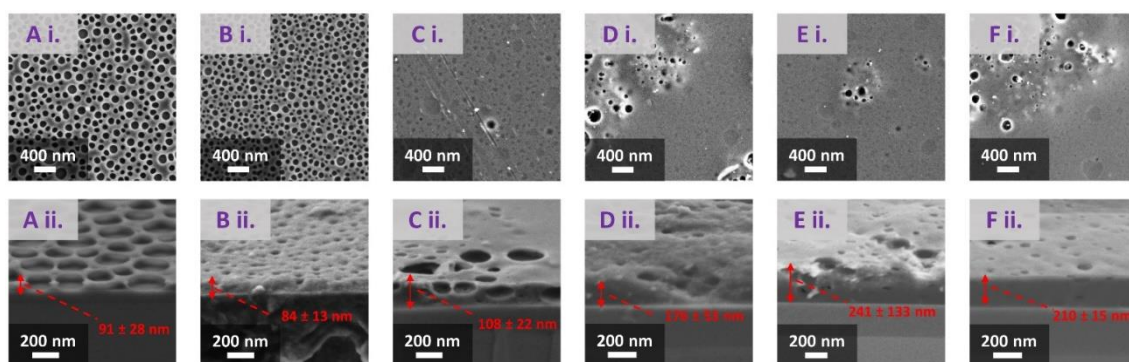


Figure A4.4. SEM micrographs of **L3** lignin membranes where **A** is 0.8 wt%, **B** is 1.0 wt%, **C** is 1.5 wt%, **D** is 2.0 wt%, **E** is 2.5 wt%, **F** is 3 wt% membranes; **i.** represents the top-down SEM and **ii.** represents the cross-section SEM micrographs with associated thicknesses.

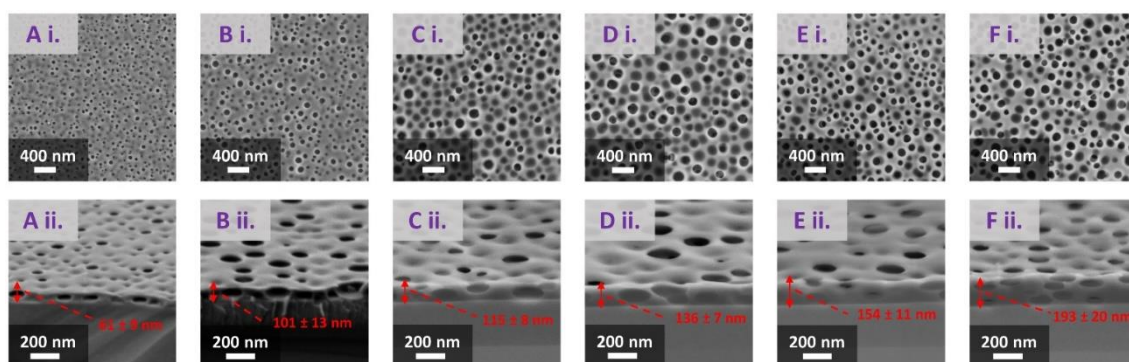


Figure A4.5. SEM micrographs of **L4** lignin membranes where **A** is 0.8 wt%, **B** is 1.0 wt%, **C** is 1.5 wt%, **D** is 2.0 wt%, **E** is 2.5 wt%, **F** is 3 wt% membranes; **i.** represents the top-down SEM and **ii.** represents the cross-section SEM micrographs with associated thicknesses.

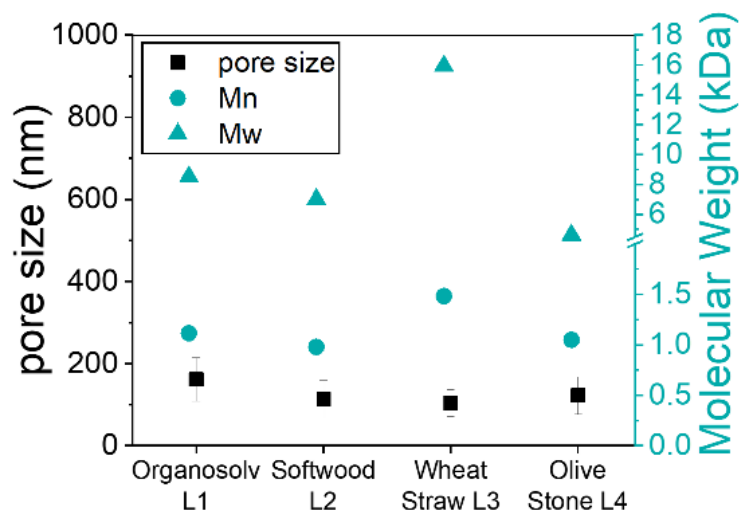


Figure A4.6. The comparison between pore sizes of 0.5 wt% membranes and molecular weight: the number average molecular weight (M_n) and weight average molecular weight (M_w). There appears to be no observable correlation between pore size and molecular weight.

Appendix 4.5.2. Supporting Characterization

Table A4.1. Contact angle and surface energy measurements of 0.5 wt% lignin membranes and silicon substrates.

Sample	Contact angle (°)			Surface Energy (mJ m ⁻²)
	Water	Diiodomethane	Glycerol	
Organosolv L1	70.94 ± 0.75	48.43 ± 0.94	89.82 ± 1.69	57.64
Softwood L2	85.87 ± 1.31	44.63 ± 1.14	80.69 ± 1.47	39.50
Wheat Straw L3	112.01 ± 1.54	70.81 ± 0.61	82.64 ± 0.27	26.38
Olive Stone L4	74.92 ± 0.32	45.28 ± 0.76	65.23 ± 0.87	40.12
Silicon native oxide	52.21 ± 1.37	58.97 ± 0.35	46.53 ± 1.24	45.80
Silicon thermal oxide	54.76 ± 1.20	58.88 ± 0.86	38.81 ± 1.67	47.90

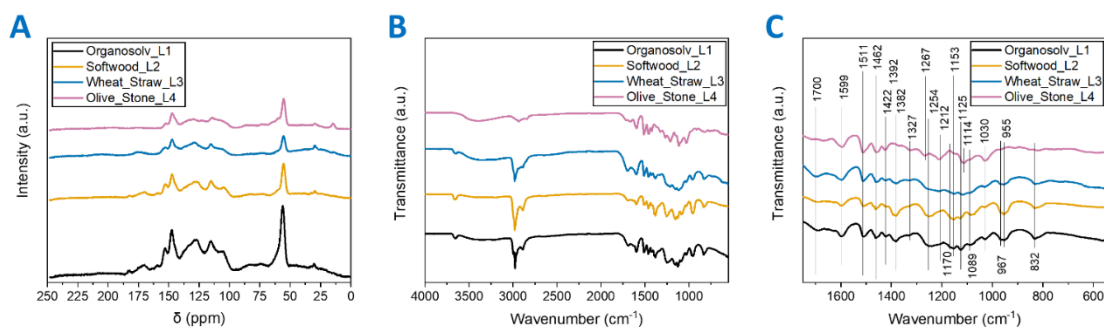


Figure A4.7. A. ^{13}C CP/MAS NMR, B. and C. FTIR spectra of **L1**, **L2**, **L3** and **L4** lignins in the 4000 – 550 cm^{-1} and 1750 – 550 cm^{-1} respectively for clearer interpretation.

Table A4.2. The ^{13}C CP/MAS NMR chemical shifts assignments of the four lignins according to Trubetskaya et al.^{59,60} Abbreviations: S, syringyl; G, guaiacyl; ne, in non-etherified arylglycerol b-aryl ethers; e, in etherified arylglycerol b-aryl ethers.

Chemical shift, ppm	Assignment
170 – 174	Carbohydrate; $-\text{COO}-\text{R}$, $\text{CH}_3-\text{COO}-$
152 – 154	Lignin; S3(e), S5(e)
147 – 148	Lignin; S3(ne), S5(ne), G1(e), G4(e)
133 – 138	Lignin; S1(e), S4(e), G1(e)
127 – 130	Lignin; G6
105 – 116	Carbohydrates; C1, Lignin; S2, S6, G5, G6
89 – 92	C4 in cellulose (cr)
82 – 86	C4 in cellulose (am)
72 – 75	C2, C3 in carbohydrates; C5 in cellulose
55 – 57	Lignin, OCH_3
29 – 40	CH_2 in aliphatics

Table A4.3. The FTIR vibrational bands assignments of the four lignins according to various researchers.^{44,60,64,72,73}

Wavenumber, cm ⁻¹	Assignment
3400	OH stretch
3000 – 2930	-CH ₂ - stretch
2930 – 2830	-CH ₃ - stretch
1700	C=O stretch
1599	C=C aromatic skeletal vibration
1511	C=C aromatic skeletal vibration
1462	C-H asymmetric deformations in CH ₂ and CH ₃ groups
1422	C-H asymmetric deformation in -OCH ₃
1400 – 1360	O-H and C-O of phenol and tertiary alcohol, aliphatic C-H stretch in CH ₃
1327	C-O stretching in syringyl ring breathing
1270 – 1250	C-O stretching in guaiacyl ring breathing
1212	C-O stretching in syringyl and guaiacyl ring breathing
1153	C-H in-plane deformation of guaiacyl ring
1125	C-H in-plane deformation of syringyl ring
1114	C-O deformations of secondary alcohols and aliphatic ethers aromatic C-H in-plane deformation (G > S)
1089	C-O deformation in secondary alcohols and aliphatic esters
1030	C-OH stretching of the side groups and C–O–C and glycosidic bonds
970 – 950	=CH out-of-plane deformation (trans) (guaiacyl)
832	C-H out-of-plane deformation of guaiacyl ring

The NMR characterization of the lignin samples indicates a presence of residual carbohydrates predominantly in the **L1**, **L2** and **L3** lignins. The **L4** sample shows much lower relative intensity in the region of 170 – 174 pm, indicating that the pre-treatment removes most of the impurities. Furthermore, cellulose is also observed in all the lignin materials. The intensity of cellulose peaks are comparatively low in all the lignin samples, indicating a low amount of residual impurities in general. The NMR assignments in **Table A4.2** confirm the presence of both syringyl and guaiacyl units.

The FTIR analysis demonstrates that the lignins **L1**, **L2** and **L3** show guaiacyl ring breathing as a shoulder in the 1250 – 1270 cm⁻¹ region whereas the **L4** lignin has a well-defined peak at 1267 cm⁻¹ indicating higher purity. Furthermore, the signal at 1327 cm⁻¹ responsible for the syringyl ring breathing is better defined for **L4** lignin compared to the other three materials (broad signal), indicating higher purity of **L4**. The C=C presence is confirmed in all four lignins (1599 cm⁻¹ and 1511 cm⁻¹), indicating high content of aromaticity.⁶⁰ The four lignins display

aromatic C-H deformations at 1153 cm^{-1} but **L3** and **L4** have significantly lower signal intensity indicating lower aromatic content than **L2**, which has a slightly less intense signal than **L1**. It is possible to deduce that **L1** has the higher aromatic content than **L2**, and **L3** and **L4** show lower content than both. The **L1** lignin displays an additional peak at 1170 cm^{-1} responsible for C=O vibration of esters⁶⁰ but **L2** has lower intensity with **L3** and **L4** showing no signal.

Guaiacyl and syringyl is identified in all the four lignin samples from both NMR and FTIR. However, it can be observed that **L4** lignin has less impurities than the other three lignin materials. Therefore, the differences in structure i.e., degree of aromaticity and the content of impurities can explain why **L4** lignin requires a vacuum chamber for the self-assembly to occur. This can be due to two factors – either the degree of aromaticity or impurities result in less energy demanding self-assembly onset. The degree of aromaticity improves π - π interactions of lignin with itself and thus enhances the hydrophobic effect of water allowing for easier self-assembly. Furthermore, impurities can act as nucleation sites for pore formation to occur as they break up the lignin aggregated structure and allow for faster self-assembly kinetics.

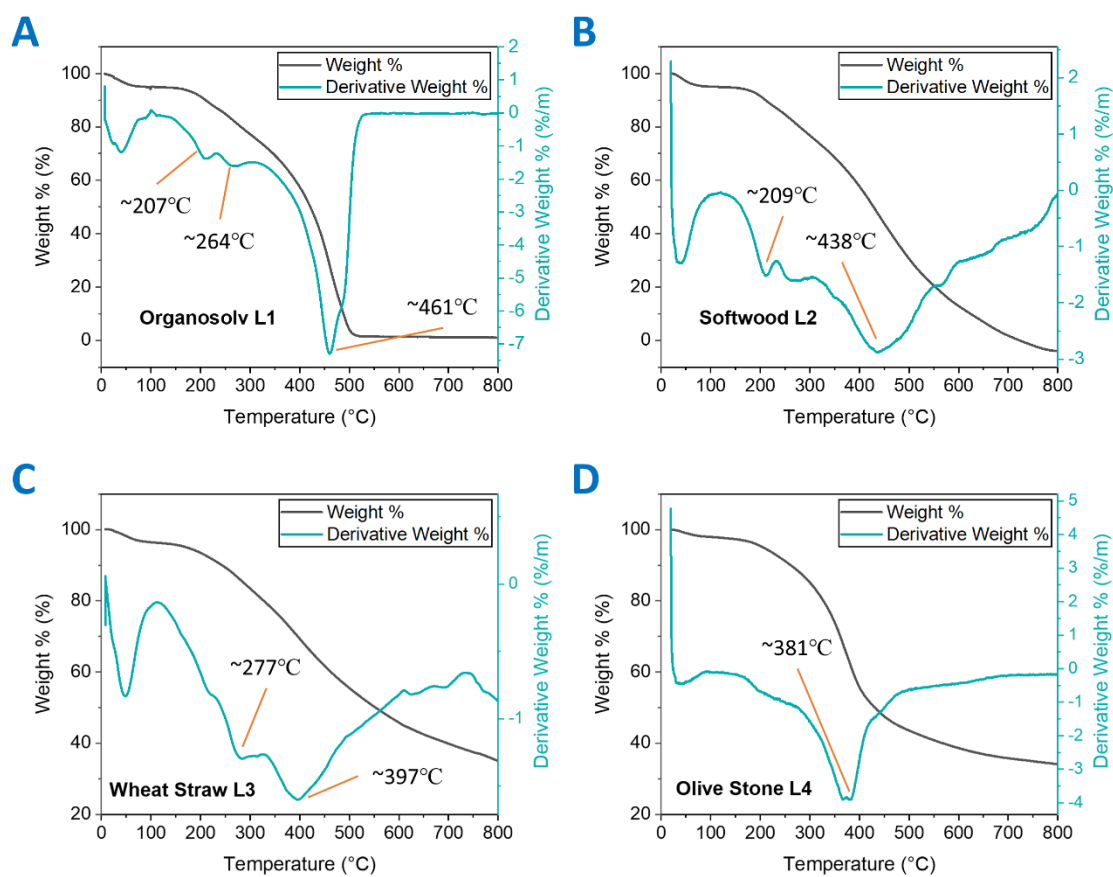


Figure A4.8. TGA data of **A. L1**, **B. L2**, **C. L3** and **D. L4** lignins.

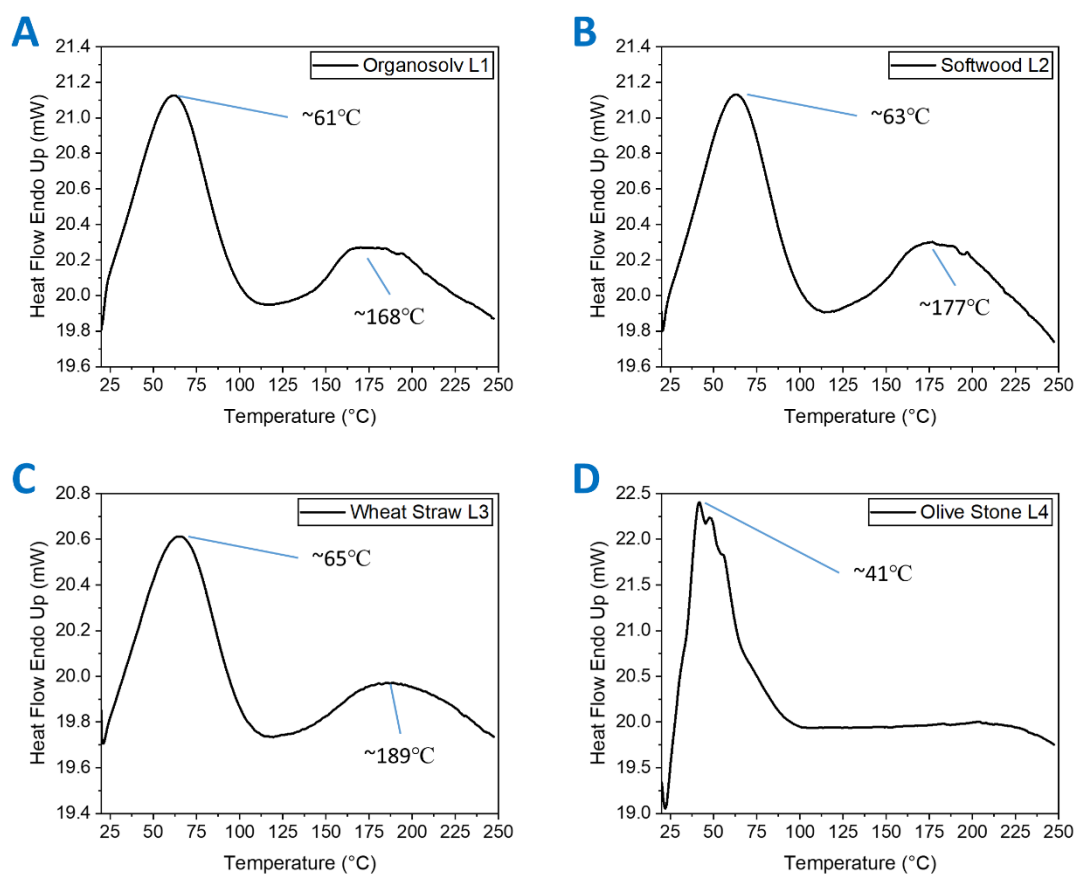


Figure A4.9. DSC data of **A. L1**, **B. L2**, **C. L3** and **D. L4** lignin materials.

Table A4.4. Proximate and ultimate analysis of **L1**, **L2**, **L3** and **L4** lignins.

	Organosolv L1	Softwood L2	Wheat Straw L3	Olive Stone L4
<i>Proximate and ultimate analysis (% on dry basis)</i>				
Moisture	1.5	4.1	3.8	3.7
Ash (550 °C)	3.8	1.5	4.3	1.6
C	61.7	59.9	61.1	64.7
H	5.3	5.5	5.6	5.6
O	28.3	31.9	28.2	27.6
N	0.9	1.2	0.8	1.0

Appendix 4.5.3. Supporting XPS

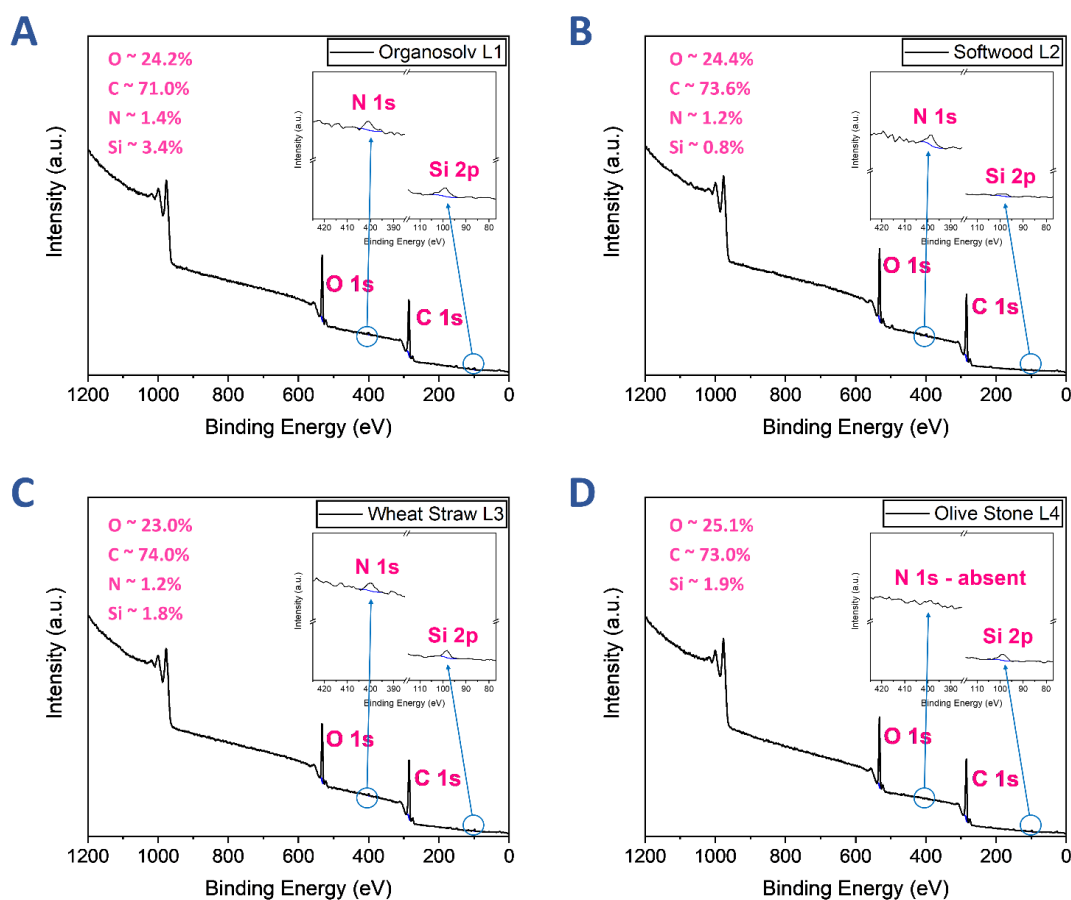


Figure A4.10. Survey XPS spectra and elemental composition of **A. L1**, **B. L2**, **C. L3** and **D. L4** lignin membranes on native oxide silicon wafers.

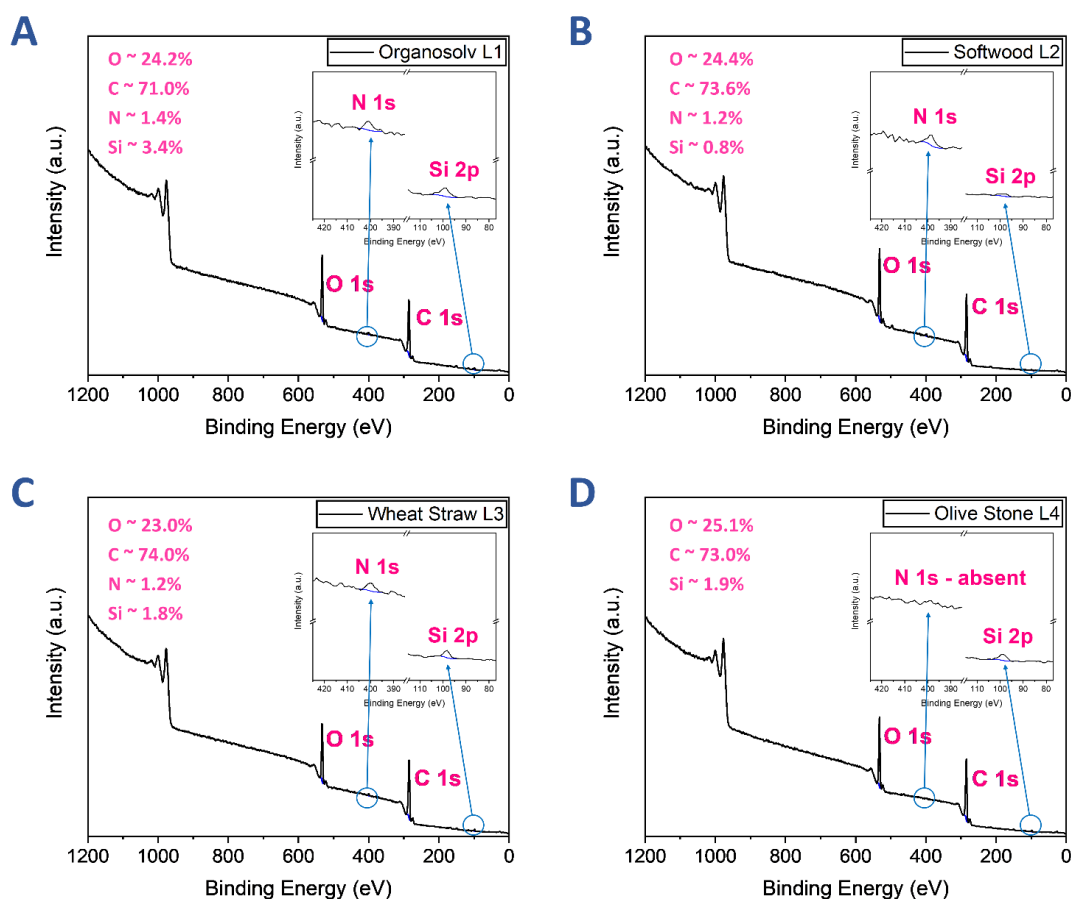


Figure A4.11. Survey XPS spectra of nickel oxide membrane on native oxide silicon wafer **A.** after UVO treatment, **B.** after calcination. XPS high resolution spectra of nickel oxide membrane on native oxide silicon wafer after UVO: **C.** Ni 2p core scan and **D.** O 1s core scan.

Appendix 4.5.4. Pattern transfer and optical setup

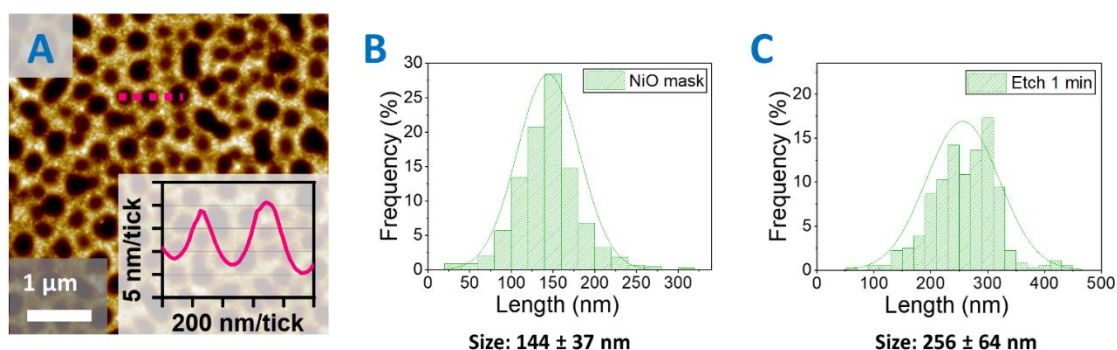


Figure A4.12. A. AFM image of Ni^{2+} bound to lignin **L1** 0.5 wt% membrane on NO silicon substrate after 3 months storage at ambient lab conditions, (no UVO treatment). Pore diameters statistics of **B.** calcined nickel oxide mask and **C.** 1 min etch.

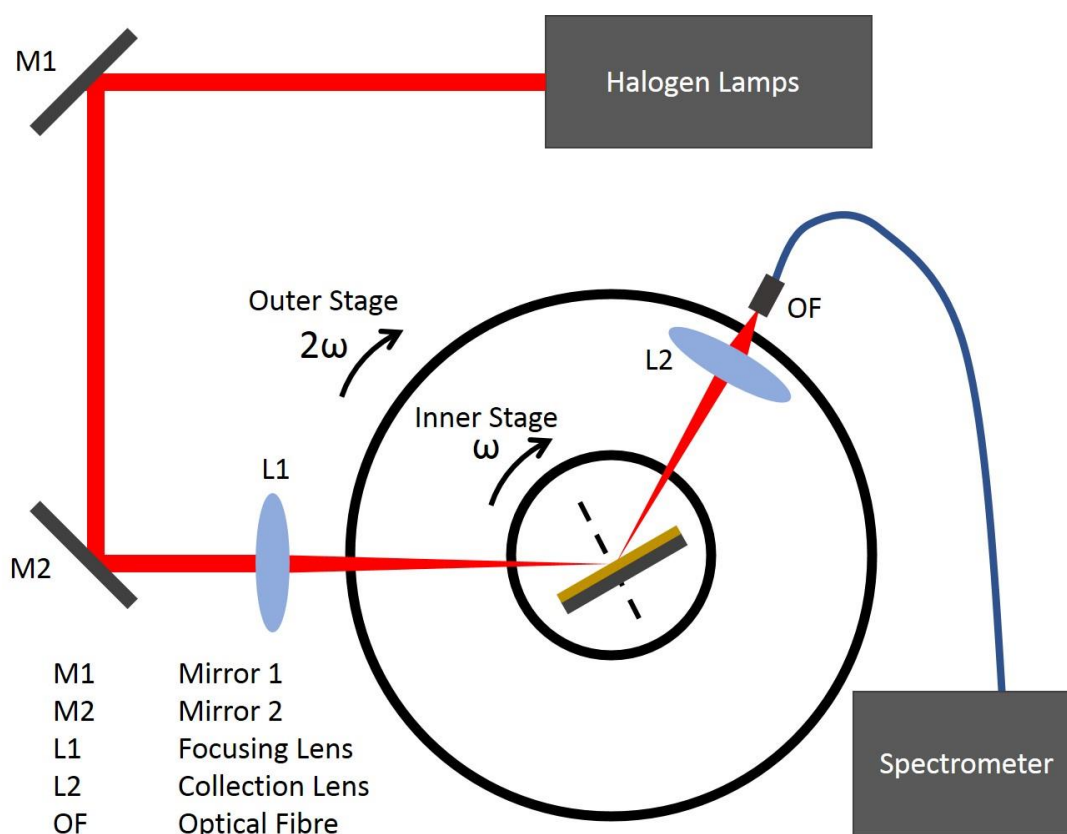


Figure A4.13. Custom built 2θ system schematic for angle-resolved reflectivity measurements as described in the **Experimental section 4.2.6.**

4.6. References

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5. Conclusions and Future Work

5.1. Perspective

Membranes and porous films are the backbone of many established and emerging technologies. This is particularly true in light of increasing environmental demands and the role of membranes in pollution mitigation. However, both the production and processing methods are well developed for polymer systems. This thesis has explored unconventional materials as membranes (chitosan, lignin), unconventional processing (water-solvent vapour annealing, pattern transfer) as well as strategies for surface functionalisation (brush bonding) to control selectivity. All of these have been successful and suggest a range of new methodologies are possible. The development of sustainable systems by design might be possible using approaches outlined here. The results are summarised here and discussed as extensions to the work to allow further development of the concepts outlined.

5.2. Conclusions

The patterning of nanostructures using polymer self-assembly is a growing field, owing to a multitude of reasons that include low cost, low energy consumption, and eco-friendlier bottom-up opportunities. The range of polymer chain lengths, the possibility of using different monomers and various structural arrangements allow for the formation of numerous different nano- and micro- sized features. Herein, multiple systems were investigated for their propensity to form porous materials of various scales. Additionally, alternative characterization approaches were used to investigate a number of applications.

In **Chapter 2**, we explored the possibility of using PMMA as a model system for pore formation via the TIPS method. APTS binding was proven successful to vary capillary flow rates through PMMA membranes, however the implementation of a new moiety results in lower tensile strength. Chitosan was used similarly to investigate phase inversion in the presence of water vapour. However, water was shown to only slightly help pore formation and improve the acetic acid removal during phase separation. The phase separation apparatus was found to be useful

to form bulk materials, but different sections of the membranes displayed variable pore sizes (such as smaller pores on the top layer). This may limit the applicability of the phase separated membranes, thus more research is required to improve membrane uniformity in the future. The asymmetric membranes produced via TIPS or VIPS were utilised for filtration, showing up to a 60% retention for Evans Blue. Thus, the TIPS and VIPS membranes were found to be functional, however it was also important to understand the internal pore structure to characterize the prepared membranes fully.

Due to the difficulty in pore size estimation for asymmetric and macroporous membranes using conventional techniques (such as BET or porosimetry), we adapted a novel FIB reconstruction methodology for studying the internal pore structure, volume, and pore volume distribution of our membranes. Large volumes of several thousands of μm^3 were reconstructed and variability in pore structure can be observed and studied quantitatively. The pore tortuosity was also interpretable. To summarise, we have demonstrated that the FIB technique is highly suitable for bulk asymmetric membrane characterisation. However, a major problem was the investigation of surface properties of asymmetric membranes due to high porosity and roughness in **Chapter 2**. Therefore, polymer brushes were adapted to demonstrate surface behaviour such as surface energy and binding to silanes such as APTS.

In **chapter 3**, we investigated the effect of brush coatings on the self-assembly of a PS-*b*-PEO BCP system. Brushes were found to have a considerable effect on the resultant pattern morphology, as it was observed that PS-*b*-PEO self-assembled into toroidal structures when atop the PS brush. Thus, brushes can allow for BCP self-assembly atop various substrates where brush coatings are possible. This also alleviates the surface incompatibility effects for BCPs if the surface energy of the substrate is vastly different. Moreover, different thicknesses BCP films were found to display varying morphologies atop brushes, as predicted by the commensurability of film thickness and domain size.

We also examined the feasibility of WVA for producing novel nanostructured surfaces; firstly with a PS-PEO system in **Chapter 3**, and secondly using a natural biopolymer, namely lignin in **Chapter 4**. Water was used as the vapour of choice, as the aim of this work is to provide a greener method for polymer self-assembly.

Using water is an attractive option for an annealing strategy as it is the greenest solvent available and causes no environmental concerns. Additionally, both PS-*b*-PEO and lignins readily formed porous structures in the presence of water. Furthermore, using water in vapour form conserves the amount of solvent used, as minimal quantities are needed for large scale annealing. Depending on the nature of the film used, the film thickness, and annealing time, the pore sizes vary drastically after WVA, but all pores obtained were in the macroporous range.

The obtained macroporous materials were employed for pattern transfer in **Chapters 3 and 4**. Both the BCP and lignins contain polar groups, which readily bind to metals such iron and nickel ions to produce iron and nickel oxide films. These metal oxide films are shown useful for pattern transfer during ICP RIE. PS-*b*-PEO was used as a model for testing etching capabilities to produce arrays of structures such as silicon nanotubes. In comparison to the BCP system, the lignins contain more moieties for metal incorporation and thus produced thicker metal oxide masks, meaning that a deeper etch was feasible. The silicon pores of over 1 μm on the lignin samples resulted] in the formation of black silicon (BSi), which showed an average reflectance of 3% in the visible region; this is on par with current methods; however the process is much greener.

In summary, the work outlined in this thesis provides an overview of polymer self-assembly for the production of porous films. Novel phase separation approaches – namely, TIPS and VIPS and WVA – were successfully adopted for our various polymer systems. Eco-friendly alternatives such as chitosan and lignin were employed to demonstrate pore formation in asymmetric membranes and thin films alike. Lignin was adapted to form membrane material for the first time, with only water vapour as a driving factor for self-assembly. The porous materials were not only used as traditional filtration membranes but also for pattern transfer and for optical applications. Thus, this work showcases the versatility of polymer self-assembly as a tool kit for bottom-up opportunities in many fields from separation to solar cell applications. We anticipate that the outcomes of this thesis may prove invaluable in helping to alleviate the environmental impact of microplastics waste.

5.3. Future Work

This thesis has demonstrated the breadth of polymer self-assembly for fabrication of porous materials. However, some suggested enhancements and future tests are necessary to further improve the results and functionality. These are described in detail below.

The phase inversion approach used in **Chapter 2** is useful where large quantities of membranes are required, but the major drawbacks are the membrane morphology reproducibility, broad pore distributions and tensile properties. The apparatus could benefit from a better sealed system with improved air circulation as well as more precise humidity control. The tensile parameters could also be improved by crosslinking or the addition of more plasticizers such as glycerol. This is currently a topic of future work on another project. The water exchange, particularly for chitosan membranes, can also be improved by better circulation and improved humidity sensors. Also, the assessment of the formed 3D morphology can be further improved.

The FIB methodology is currently under further development as milling times are long and energy demands are high. Therefore, methods such as improved coating with conductive materials, resin embedding, and tool optimisation and automation are under research currently.¹⁻³ Nevertheless, this methodology paves a way for understanding the inner workings of a membrane with nanometre resolution. Our future expansion of this work will involve adapting the technique for other soft materials such as wood. Potentially, the insight gained on the nanometre resolved 3D architecture can help build better materials for batteries, membranes and even building materials.

Evidently, the polymer self-assembly as portrayed in **Chapters 2 to 4** plays a key role for formulation of porous materials. The self-assembly approaches may be improved by a better set-up with dynamic control and monitoring. It is feasible to construct an apparatus for the control of BCP self-assembly,^{4,5} however water controls such as humidity require more precise apparatus. Also, reflectometry is hard to optimise where huge changes in refractive indices or liquid condensation take place. Thus, alternative in-situ monitoring real-time monitoring during the annealing process such as real-time AFM, real-time environmental SEM analysis,

in-situ small angle X-ray scattering (SAXS) and other techniques can be adapted or developed from scratch for that purpose.^{6–11} Thin films allow for better control over structure, however the possibility to scale up the thickness of films would be beneficial. This might be achieved by building a swelling or phase inversion apparatus in tandem with multiple controls which will be the subject of future work. It is possible to enhance the control over pore size to yield narrower pore size distributions. Again, this is feasible with better machinery or by carefully adjusting the experimental parameters such as polymer purification, making PDI values closer to 1 and pin-pointing precise conditions for specific self-assembly events.

Another aspect that might be improved is the use of less toxic solvents. Greener alternatives to solvents such as THF, acetone or toluene might be employed, however further study is needed as these conventional solvents still work best for polymer dissolution. Major analysis on environmental aspect of self-assembly approaches needs to be conducted as well as an analysis on the implementation of these methods for industrial scale applications. Currently some research has been published on life cycle assessment of polymer lithography,¹² but further study is required.

In general, the functionality of the materials can also be enhanced. Further testing could be performed on the membranes; for example, membrane performance against other dyes could be explored, provided that the tensile properties are improved. Further filtration tests under pressurised conditions may be implemented, as well as controlled flow rate and flux analysis. For thin films, larger area applicability can be demonstrated such as building a layered working device. Thin films can also be applied to more substrates as well as possibly taken off the substrate by floating on water or other approaches. Thus, the adaptability of thin films described herein as coatings to various materials should be explored. BCP and lignin thin films themselves could also be adapted for applications other than pattern transfer. Metal oxide films might be used for sensing or catalysis on their own. It is possible to investigate separation or catalytic applicability of the silicon nanotubes, while lignin derived silicon membranes have the potential to be used for applications other than optics such as sensing.

Overall, this work described the possible opportunities of porous polymeric materials for various applications as well as possibility of using biopolymers and water vapour during nanofabrication. Future work is essential to further develop those tools and methods such as testing more filtration parameters, improving tensile qualities, and testing the durability of these materials. Applicability can also be explored in more depth such as the design of active membranes and devices such as solar cells or catalytic tools. Further improvements in general could be to include non-fouling or self-cleaning aspect to membranes and thin films and to test the recyclability or reusability as well as life cycle of the processes and materials. Overall, addressing those issues will allow for new research avenues to be explored, as well as the smooth implementation of the polymer self-assembly toolkit into modern technology.

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List of Publications

Publications

Esmeraldo Paiva, A.; Baez Vasquez, J. F.; Selkirk, A.; **Prochukhan, N.**; G. L. Medeiros Borsagli, F.; Morris, M. Highly Ordered Porous Inorganic Structures via Block Copolymer Lithography: An Application of the Versatile and Selective Infiltration of the “Inverse” P2VP-b -PS System. *ACS Appl. Mater. Interfaces* 2022. <https://doi.org/10.1021/acsami.2c10338>

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Conferences

2019:

- “Towards fabrication of functional polymer membranes”, Poster presentation, Micro and Nano Engineering (MNE) Conference, Rhodes, Greece.

2022:

- “Preparation of lateral flow membranes from wood veneers with advanced electron and ion microscopy characterization”, Oral presentation, The North American Membrane Society (NAMS) Conference, Tempe, Arizona, USA (Online)
- “Advanced microscopy methods for structural characterization of soft and organic materials”, Oral presentation, European Materials Research Society (E-MRS) Conference, Virtual conference (Online)