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**Development of a Scaleable “Breath-figure” Type
Polymer Thin Film Patterning Process *via*
Controlled Vapour Swelling of Thin Films**

A thesis presented to the University of Dublin for the degree of

Doctor of Philosophy

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Declaration

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Philip Darragh

Abstract

Development of a Scaleable “Breath-figure” type Polymer Thin Film Patterning Process via Controlled Vapour Swelling of Thin Films

Philip Darragh

Efficient production of microporous polymeric films can be rapidly synthesised by changing the thermodynamics of a polymeric solution in a humid atmosphere. This conventional method, known as “breath figure” (BF), involves drop casting a volatile polymer solution on to a flat surface and results in an evaporative cooling effect. Once the temperature of the polymer solution reaches the dew point, water droplets begin to condense on to the surface and their morphology dictates the micropore’s density and size that exist within the polymer film. The BF method has received significant attention in respect to the process creating homogenous porosity in polymer thin films in less than 5 minutes. However, the conventional method has its flaws in respect to reproducibility and defects over large surface areas. Here a new method is outlined using a customised piece of apparatus that can create various film porosity by precisely controlling and automating all variables that occur within the BF process, solvent saturation, relative humidity, temperature, and polymer type.

The polymer of interest that has been studied in significant detail is polystyrene (PS), a low-cost polymer that has high spin-coating thickness uniformity, process stability and functions as a dry etch resist. By swelling the PS film of uniform thickness in a favourable solvent, the viscosity can be decreased creating a viscoelastic mouldable film that can be templated by water droplets at the temperature dew point. This process can remove the problems with fluid dynamics, by controlling the swelling of the film through temperature control and the in-situ swelling can be characterised by reflectometry. This approach can allow us to understand the role of thermodynamics on water droplet templating and interpret the effects of polymer swelling on the production of the microporous materials. Using these concepts, a fast method for producing different sizes of microporous PS resists can be assessed. These templates can function as pattern-transfer templates for countless lithographic techniques and methodologies.

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Publications

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COVID Impact Statement

The emergence of a global pandemic such as COVID-19 had severe negative effects on the PhD programme from Feb 2020 - April 2022. As a result, the scope of the PhD project changed concerning:

- **The reduction of lab time**

Due to the campus closure, the lab was inaccessible from March 13th 2020 to June 8th 2020. Further to this, from June 8th, access to the lab was limited to 25% of regular access (i.e. only 1.5 days of access per week to the lab) and for the consecutive months due to social distancing measures in place, lab access was restricted to 50% capacity up to Jan 2021, with restrictions easing over time. After this date, lab masks were required in the lab, and if any COVID cases were reported within the group, all lab members were expected to isolate at home.

- **Reduction of use of equipment and training**

Since the project heavily relied on lab work and equipment, COVID-19 resulted in less experimental work being carried out. In addition, the closure of Trinity College Dublin affected the training programmes in the AML and CRANN Cleanroom. (ICP Etcher, Temescal, SEM, AFM and XPS).

- **Illness & isolation requirements**

In 2022, I was diagnosed with COVID- 19 and was expected to isolate for two weeks. Furthermore, a severe ankle injury (Grade 2 ankle sprain) occurred in February, which required resting, and I was informed to work from home.

Abbreviations

Chapter 1

SDGs = Sustainable Development Goals

EUVL = Extreme UV Lithography

ALD = Atomic Layer Deposition

CVD = Chemical Vapour Deposition

BCPSA= Block copolymer self-assembly

SVA = Solvent Vapour Annealing

BF= Breath Figure

CS₂ = Carbon disulphide

KE = Kinetic Energy

CHCl₃= Chloroform

kJ = Kilojoules

P = Pressure

V = Volume

ΔE = Energy Barrier

SLV= solid- liquid-vapour

D = Diffusion coefficient

C = Concentration

Δ = Length scale

BCP = Block copolymer

PS-b-PPP = Polystyrene-*block*-

polyphenylene

PS-b-PDMS = Polystyrene-*block*-

polydimethylsiloxane

PS-b-PEEA = Polystyrene-*block*-

poly(ethoxy-ethyl-acrylate)

PS-b-PMMA = Polystyrene-*block*-

polymethyl methacrylate

PS-b-PAA = Polystyrene-*block*-acrylic

acid

PS-b-PVP = Polystyrene-*block*-

polyvinyl pyridine

PS-b-PEO = Polystyrene-*block*-

polyethylene oxide

PMMA = Polymethyl methacrylate

PVC = Polyvinyl chloride

PDMS = Poly-dimethyl silane

PB = Polybutadiene

MeOH = Methanol

RH = Relative humidity

NIPS = Non-induced phase separation

SVBF = Solvent vapour annealing

PS = Polystyrene

Chapter 2

nm = nanometres

T_g = Glass transition temperature

V_w = Van der Waals

V_{occ} = Occupied volume

V_{hole} = Hole free volume	$^{\circ}\text{C}$ = Degrees Celsius
κ = Fluid constant	T = Shear stress
H = Film thickness	F = Force
Ω = Fluid density	A = Cross-sectional Area of Fluid
H = Fluid viscosity	Z = Polymer coil size
E = Evaporation rate	M_c = Critical molecular weight
Q = Wave vector	T = Temperature
τ_r = Relaxation rate	N = Polymerisation index
N = Refractive index	Θ = Theta solvent
Φ = Volume fraction	c^* = Critical entanglement length
SR = Swelling ratio	c^{**} = Highly concentrated entanglement concentration
d_o = Initial film thickness	ΔP = Laplace pressure
d_s = Swollen film thickness	PDI = Polydispersity Index
P_{sat} = Saturated vapour pressure	$w/v \%$ = Weight per volume (%)
$ActVP$ = Actual vapour pressure	C_p = Centipoise
HSP = Hansen solubility parameters	$Pa. S$ = Viscosity
R_o = Specific interaction radius	γ = Surface tension / surface energy
RED = Relative Energy Difference	R = Roughness
FH = Flory Huggins	T_{dew} = Dew temperature
X = Flory Huggins Interaction Parameter	LW = Lifshitz van der Waal
Eos = Equation of State	LIS = Lubricant Infused Surfaces
N = Degree of Polymerisation	CB = Cassie Baxter
J = Flux	S = Spread
C = Concentration gradient	$PS-OH$ = Hydroxyl terminated polystyrene
D = Diffusion coefficient	
θ = Contact angle ($^{\circ}$)	

κ^{-1} = Capillary length

e_c = Critical film thickness

Chapter 3

PDI = Polydispersity index

T_g = Glass transition temperature

DSC = Differential Scanning Calorimetry

g mol^{-1} = Grams per Mole

HPLC Grade = High performance liquid chromatography grade

PS-OH = Hydroxylated polystyrene

IPA = Isopropyl alcohol

THF = Tetrahydrofuran

CHCl_3 = Chloroform

w/w.% = weight %

PS = Polystyrene

Rpm = Rotations per minute

kHz = Kilohertz

W = Watts

$^{\circ}\text{C}$ = Degrees Celsius

AFM = Atomic force microscopy

NCM = Non-contact mode

nm = Nanometre

N m^{-1} = Force constant

SEM = Scanning electron microscopy

kV = Kilovolt

$^{\circ}$ = Degree

FIB = Focused ion beam

pA = Picoamps

PS-b-P4VP = Polystyrene-*block*- poly-4-vinylpyridine

N_2 = Nitrogen

THF = Tetrahydrofuran

T_{bub} = Bubbler temperature

T_{stage} = Stage temperature

S = Saturation (%)

BCP = Block copolymer

$^{\circ}\text{C}$ = Degrees Celsius

V_c = Chamber volume

RTD = Resistance temperature detector

PID = Proportional integral derivative

TEC = Thermoelectric cooling

OD = Outer diameter

PEEK = Polyether-ether-ketone

CAD = Computer aided design

SVBF = Solvent vapour breath figure

S = Saturation

P_{sat} = Saturation pressure

RH% = Relative humidity

BF = Breath figure

MPa = Megapascal

C_v = Flow coefficient

PTFE = Polytetrafluoroethylene
 CHCl₃ = Chloroform
 THF = Tetrahydrofuran
 NPT = National pipe tapered threads
 $e(t)$ = Error
 VAC = Voltage alternating current
 SP = Setpoint
 AP = Actual point
 Ω = Ohms (resistance)
 V = Volts
 A = Amps
 RH₁ = Humidity probe 1
 RH₂ = Humidity probe 2
 T = Temperature
 AcVP = Actual vapour pressure
 P_{sat} = Saturated vapour pressure
 d_0 = Initial film thickness
 d_s = Swollen film thickness
 SR = Swelling ratio
 nm = Nanometres
 ϕ_p = Volume fraction of polymer

Chapter 5

BF = Breath Figure
 PS = Polystyrene
 g mol^{-1} = grams per mole

THF = Tetrahydrofuran
 T_g = Glass transition temperature
 T_m = Melting point temperature
 SiO₂ = Silica
 μm = micrometres (micron)
 RMS = Root mean squared roughness
 mJ m^{-2} = Surface energy (Milijoules per metre squared)
 w/w. % = weight percent
 PTFE = Polytetrafluoroethylene
 S = Saturation (%)
 ΔT = Temperature difference
 STP = Standard temperature and pressure
 Cc/min = Flow rate
 kPa = Kilopascal
 n = Refractive index

Chapter 6

SVBF = Solvent vapour breath figure
 Φ_{coverage} = Polymer coverage (%)
 d_f = Feret diameter
 RMS = Root mean squared roughness
 RGB = Red green blue
 AFM = Atomic Force Microscopy
 FIB = Focused ion beam
 SEM = Scanning electron microscopy

PS-COOH – Dicarboxy-terminated
polystyrene

Chapter 7

PVD = Physical vapour deposition

CVD = Chemical vapour deposition

ED = Electrodeposition

DRIE = Deep reactive ion etching

MEMS = Micro-electronic-mechanical
systems

HF = Hydrofluoric acid

BCPSA = Block copolymer self-assembly

PS-*b*-P4VP = Polystyrene-*block*- poly-4-
vinylpyridine

Ce(III).NO₃.6H₂O = Cerium nitrate
hexahydrate

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Chapter 1

A Comprehensive Literature Review on Breath Figure Templating

1.1 Motivation

Increasing demand for new bottom-up fabrication strategies, has incited a large interest in self-assembly processes, especially in the field of nanotechnology. This seems more appropriate and needed more than ever. These processes can replace energy and process intensive fabrication methods with quick, green synthetic methods to create complex products with a series of different functionalities¹. The negative impacts of human activity on the environment have led to a commitment to follow and deliver a series of U.N sustainable development goals (SDGs). Recently, the EU has proposed a “European Green Deal” to accelerate a decarbonized society and invent new methods for creating new green, energy-saving processes². Simple bottom-up processes and fabrication methods may be a way to decrease these carbon loads.

For technological reasons, in the industrial field of nanotechnology, bottom-up techniques and processes are becoming more favourable to top-down methods where patterning is achieved through molecular interactions and driven by thermodynamics and self-assembly³. Bottom-up methods are preferable, owing to their time efficiency, low cost and ability to synthesise complex hierarchical structures⁴. Moreover, by achieving a concise understanding of the overall mechanism of self-assembly processes, old processes can complement new methods and provide new advantageous routes in creating various types of templates for numerous applications.

The nanoelectronic industry has traditionally preferred top-down approaches because of reliability and reproducibility; however, optical lithography is beginning to reach its wavelength limitations and more expensive techniques are required⁵. Higher precision using extreme UV lithography (EUVL) with a wavelength of light at 10-50 nm have been implemented into existing lithography processes however, these techniques are costly and require a large amount of raw energy consumption⁹. Top-down processes focus on developing “masks” that etch bulk material to produce patterns.

Top-down methods are a multi-step process that rely on multiple steps. For example, a typical process is comprised of several steps such as:

- (1) substrate modification,
- (2) resist (i.e. material used to form the mask) deposition,
- (3) resist patterning,
- (4) pattern transfer to the substrate and
- (5) resist removal

A thin film of resist is usually a chemical resistant polymer that can be produced by spin coating¹⁰. The resist can be either positive or negative, depending on the nature of the polymer. A positive resist is a light-sensitive material that, when exposed to light, becomes soluble in a photoresist developer, and is removed. In contrast, a negative resist is when the polymer is exposed to light and cross-links becoming chemically resistant to the developer and will not be removed. Once the pattern on the resist has been created, the substrate surface is now exposed; this can be selectively etched or deposited with material by methods such as atomic layer deposition (ALD)¹¹, chemical vapour deposition^{12–15} (CVD) and electrodeposition^{16–18} (ED).

Top-down processes are high-volume with multiple steps and are generally quite toxic as many lithography processes use solvents such as N-methyl-2-pyrrolidone (NMP)¹⁹ and are expensive to run. Therefore, the industry would, if possible, favour the bottom-up process paradigm, which is a quick, simple, one-step process⁴ as shown in **Figure 1.1**.

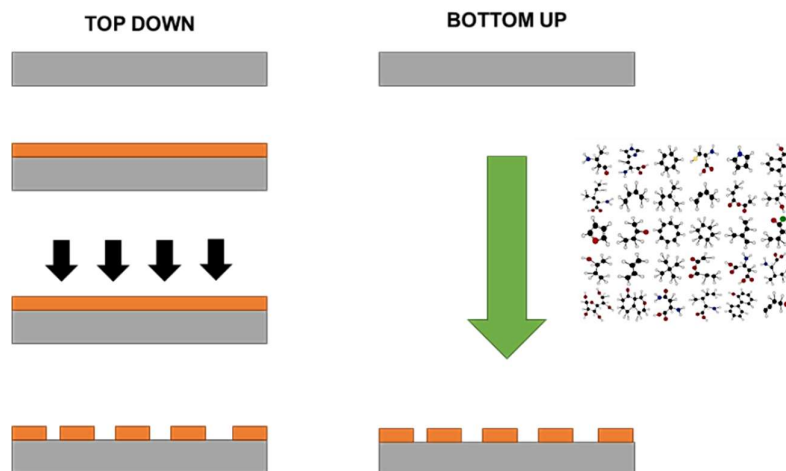


Figure 1.1 - Top-down vs Bottom-Up Approach.

New advances in bottom-up processing, mainly, block copolymer self-assembly (BCPSA)^{11,20–23}, can now produce feature sizes in sub-10 nm range. In addition, various BCP morphologies can be produced by changing molecular weight and solvent through solvent vapour annealing (SVA) processes²⁴.

This research project aims to design a novel bottom-up method for creating highly ordered microporous polymer resists that can be used for pattern transfers in lithography. Microporous systems are of interest because of the importance of that scale regime, where self-assembly is possible at micron sizes but is usually primarily induced by phase separation. An example is inverse phase separations in porous polymer films. Here this type of self-assembly will be examined for ultra-thin ($< 1 \text{ } \mu\text{m}$) films. Techniques such as breath

figure methods (detailed in next section) could be utilised but are usually applied to thicker films where the substrate is not exposed. *In this thesis, we want to examine if the breath figure methodology can (a) be included for thin films and (b) be better controlled for up-scaling.*

1.2 Breath Figure Templating

Highly ordered porous polymeric membranes are of increasing interest due to their potential applications in areas such as membranes²⁵, cell scaffolds for tissue engineering²⁶, biomimetics²⁷ and microelectronics²⁸. The use of various amphiphilic block copolymers²⁹ and polymer surfactants added to polymeric solutions^{30,31} has improved the ordering and pore density of porous materials. The self-assembly and organisation processes of breath figure (BF) arrays is the main process under investigation for producing honeycomb-shaped pores at the micron scale. The mechanism of the water droplet self-assembly was firstly discovered by simply breathing onto a cold surface. In 1895 Aitken studied this phenomenon³², followed by Rayleigh in 1911³³. They both found that when water condenses onto a cold, clean glass surface, it aligns into a series of tiny lenses. Surprisingly, these lenses were highly uniform on the surface and created a well-ordered droplet array on the surface of the glass³³.

In 1994, Francois developed a new polymer templating technique, where he could encapsulate the shape breath figures *via* a quick and simple process. He used block-copolymer, polystyrene-*block*-polyphenylene (PS-*b*-PPP) to create an ordered honeycomb film as presented in **Figure 1.2**.

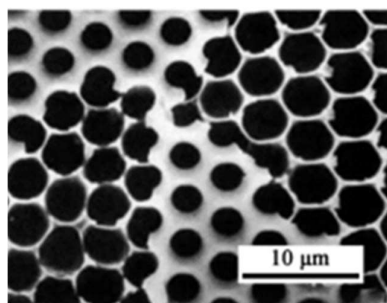


Figure 1.2- SEM images of the honeycomb films fabricated using PS-*b*-PPP to produce breath figures arrays.³⁴

The polymer was dissolved in a carbon disulfide (CS_2) solution and resulted in the formation of honeycomb-shaped pores when drop-cast in a humid atmosphere³⁵. The conventional method to produce breath figures is to drop cast a volatile polymer solution onto a flat substrate in a humid atmosphere which produces ordered microporous polymeric films when the solvent is removed, as seen in **Figure 1.3**.

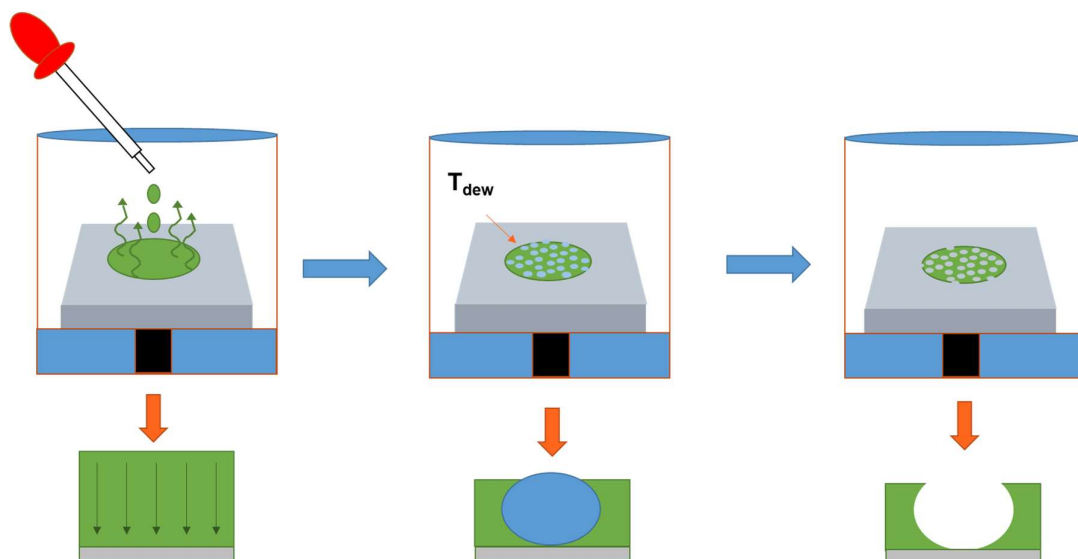


Figure 1.3- A static drop-cast process for producing breath figures.

The accidental discovery of BF patterns led to new methods for producing honeycomb-shaped structures with favourable properties such as low weight, stiffness, and a large variation in porosity³⁶. Honeycomb morphologies have sparked interest as they have an efficient hexagonal packing configuration that improves its structural rigidity. By having a honeycomb morphology, the porous material's strength is increased in comparison to other pore networks³⁷.

The BF process heavily relies on the effect of droplet morphology and experimental conditions, there are still uncertainties and conflicting views on how the process occurs in

humid atmospheres³⁸. The generally accepted mechanism to produce breath figures on a flat surface is shown in **Figure 1.4**.

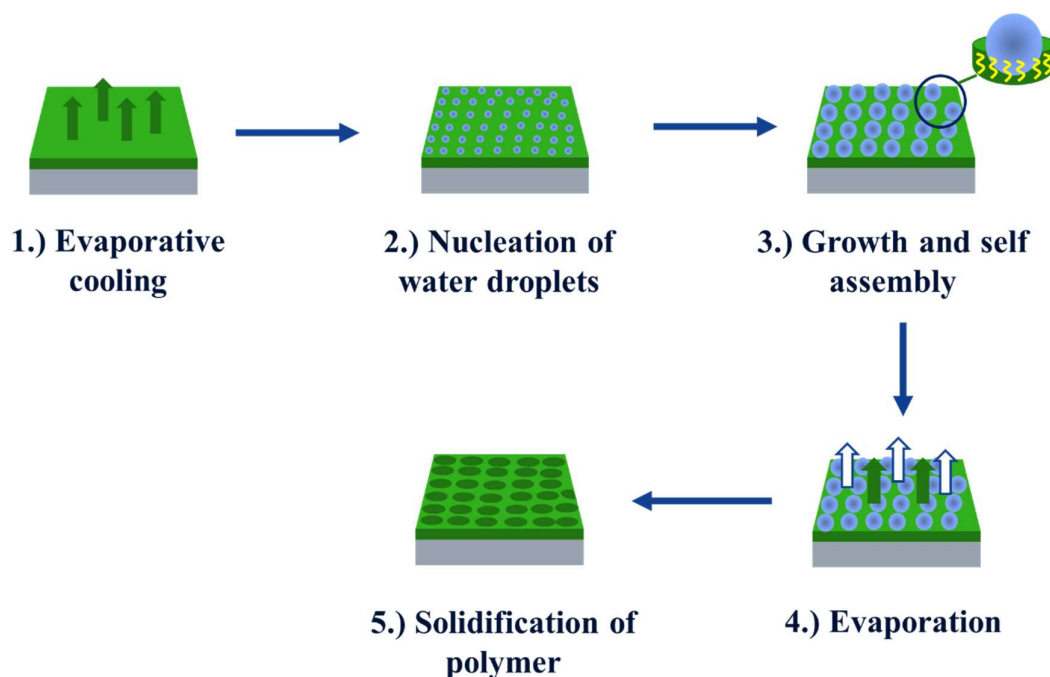


Figure 1.4 Postulated mechanism for breath figure. See text below for details.

Where;

- 1.) The volatile solvent begins to evaporate at room temperature due to evaporative cooling³⁹. When the solution begins to cool, a temperature gradient occurs between the surface and the ambient.
- 2.) Because of cooling, water droplets nucleate onto the polymer solution in a random dispersion. Water molecules begin to nucleate into tiny droplets (where the temperature of the solution is cooler than the ambient temperature).
- 3.) The water droplets begin to grow and form ordered arrangements but do not coalesce due to the changes in surface tension gradients. Marangoni convectional forces⁴⁰

prevent the merging of the droplets and this results in the formation of hexagonally close packed water droplet arrays.

- 4.) The evaporation of solvent causes polymer precipitation to occur, encapsulating the water droplet shape. Once the temperature is above the dew point, the water droplets stop growing and evaporate.
- 5.) When all fluids have evaporated from the substrate, the viscosity of the solution increases and solidifies, creating a thin polymer film with a porous honeycomb pattern.

Certain humidity requirements ($> 60\%$ RH) are needed to drive breath figure formation. The mechanism of BF formation is dependent on polymer-solvent interaction, water droplet self-assembly and surface tension/temperature gradients. This is all detailed in Zhang's review²⁸. The main motivation of this thesis is to as understand the complexity of the BF process and identify a new route in optimising the process for industrial scaled applications. Critical factors that determine droplet templating will be studied; these are solvent effects, surface wetting, the role of droplet growth and self-assembly, and polymer of choice. For the breath figure to occur, the solvent must have a high evaporative rate to cool the surface and have good miscibility with the polymer before drop-casting.

1.2.1 Evaporation

Evaporation is the well-known effect of converting a liquid to a vapour and is a heat transfer mechanism. The molecules near the liquid-gas interface have sufficient kinetic energy (KE) to break the liquid phase's intermolecular forces and release as a gas molecule⁴¹. In surface

chemistry, Hertz-Knudsen (**Equation 1.1**) describes the evaporation rates of various solvents where J is the flux of the solvent (units : $\text{mol m}^{-2} \text{s}^{-1}$)⁴².

$$\frac{1}{A} \frac{dN}{dt} = J \quad \text{[Equation 1.1]}$$

Where A is the surface area, N is the number of molecules and t is the time. *Evaporative cooling* is the cooling of the liquid solvent when it evaporates. The heat exchange is vital in producing breath figures, as the enthalpy of vaporisation of solvents is the driving force to cool the surface of the liquid. This is the amount of heat required to convert 1 g of a liquid to a vapour in an isothermal system, i.e. the temperature remains constant⁴³. **Equation 1.2** indicates that the system's enthalpy depends on the pressure, volume, and internal energy difference between the vapour and the liquid phase.

$$\Delta H_{vap} = \Delta U_{vap} + P\Delta V \quad \text{[Equation 1.2]}$$

The physical properties of the various BF solvents used in the literature were collected from the Dortmund Data Bank⁴⁴ and the National Institute of Standards and Technology (NIST) Chemistry WebBook⁴⁵ (**Table 1.1**). Carbon disulfide⁴⁶ (CS_2), chloroform²⁰ (CHCl_3) and toluene⁴⁷ (C_7H_8) were the ideal solvents mentioned in the literature, which produce good breath figures and various pore morphologies.

Table 1.1 Common Breath Figure Solvents.

Solvents	Molar Mass (g/mol)	Liquid density, (g/cm ³)	Vapour Pressure at 20°C (kPa)	Enthalpy of vaporization at 298.15 K ΔH_{vap} (kJ/mol)
Carbon Disulfide ⁴⁶ (CS ₂)	76.0	1.26	48.05	27.5 ± 0.6
Chloroform ⁴⁸ (CHCl ₃)	119	1.49	26.66	31.20 ± 0.08
Toluene ⁴⁹ (C ₇ H ₈)	92.0	0.87	3.786 ⁵⁰	38.1 ± 0.1

CS₂ is the most evaporative solvent with a vapour pressure of 48.05 kPa at room temperature having, an enthalpy of vaporisation of $\sim 27.5 \text{ kJ mol}^{-1}$. It was reported that the rapid evaporation of volatile solvents can cool the liquid surface to reach temperatures of -6 °C using CS₂⁵¹ and between 0 to 6°C for chloroform⁵². This cooling effect of the solvent can drive water droplets to condense rapidly onto the surface of the polymer-solvent solution and can begin to grow once the temperature has reached the dew point (T_{dew}). **Figure 1.5** shows the morphologies of all the different BF structures using the solvents mentioned.

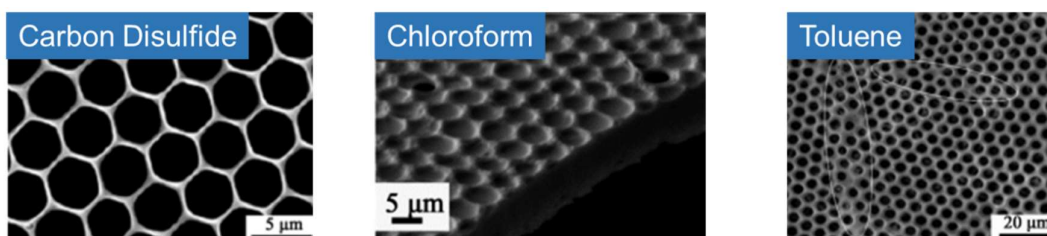


Figure 1.5- SEM images of various breath figures array produced using different solutions of solvents. (a) A solution of CS₂ and PS-NHCH₂CH₂OH (2 mg mL⁻¹)⁵³ (b) Cross-linked poly-isopropylene immersed in CHCl₃ for 1 minute after cross-linking⁵⁴ (c) BFA film produced using PSF/ toluene solution.⁴⁷

1.2.2 Nucleation of water droplets

The nucleation of water vapour is the mechanism that allows the growth of water droplets, with the temperature differential driving the growth of the water droplets at the solution interface. Two types of nucleation can occur, as suggested by Nepomnyaschy *et al.*⁵⁵. These are homogenous nucleation and heterogeneous nucleation. The homogenous process is where the water molecules nucleate at the cold surface, and heterogeneous nucleation is where the water nucleus is formed at the solution-vapour interface, as shown in **Figure 1.6**.

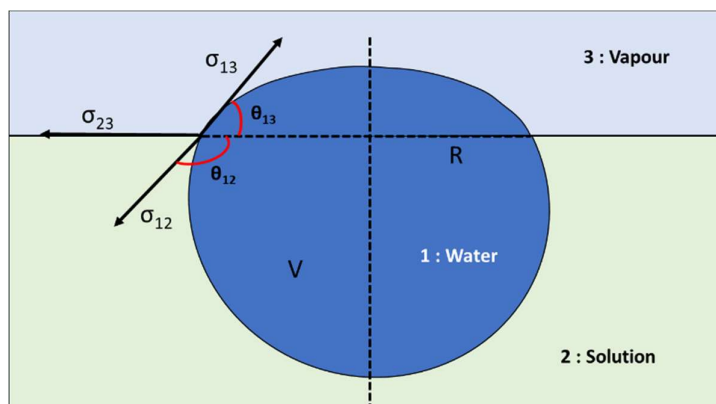


Figure 1.6 A simplified sketch of a liquid water droplet at a solution-liquid-vapour (SLV) interface where nucleation occurs.⁵⁵

Equations 1.3 and **1.4** describe the energy barriers (ΔE) for homogenous and heterogeneous nucleation to occur respectively⁵⁵.

$$\Delta E = -(P' - P)V + \sigma_{13}A_{13} \quad \text{[Equation 1.3]}$$

$$\Delta E = -(P' - P)V + \sigma_{13}A_{13} + \sigma_{12}A_{12} - \sigma_{23}\pi R^2 \quad \text{[Equation 1.4]}$$

Where $(P' - P)$ is the pressure difference, V is the volume, A is the surface area where σ are the interfacial tensions of the (1) droplet with radius R , (2) solvent-polymer solution and

(3) the vapour. For homogenous nucleation, the nucleation of water droplets is located at the water-vapour interface, but for heterogenous, nucleation is also dictated by the interaction of the polymeric-solution. These processes describe the overall energy needed to overcome the activation barrier allowing nucleation to occur. The free energy barrier for heterogeneous nucleation is always smaller than the homogenous nucleation, as heterogeneous nucleation is more likely to occur at the solution-liquid-vapour (SLV) interface to form breath figures. The experimental analysis confirmed that the water deposited in a paraffin oil bath formed at the liquid-gas interface⁵⁶.

1.2.3 Droplet Growth

At steady state, where the temperature is unchanged, the droplet growth rate is controlled by the vapour pressure of the water with respect to the ambient temperature and the temperature of the surface of the polymeric solution. **Equation 1.5** describes the growth process, where the droplet volume increases with respect to time (t)⁵⁶.

$$\frac{dV}{dt} = D\Delta p C_o \delta^{-1} \quad \text{[Equation 1.5]}$$

Where D is the diffusion coefficient of water, (Δp) is the saturation pressure difference, C_o is the concentration of water in the gas phase, and δ is the length scale of the condensation gradient related to the viscosity of the solution. Relative humidity and temperature are proportional to changing the droplet volume and were confirmed as essential factors for droplet growth using a cold stage. The reduction of the solution temperature converted the water rapidly from a gas to a liquid through cooling⁵⁷. In summary, the longer the growth time, the larger the pore size; however, when neighbouring droplets reach a critical distance, coalescence will occur as the water droplet interaction will be increased and droplet merging will occur⁵⁸.

1.2.4 Water Droplet Assembly

The nucleation of water droplets occurs in a random order; however, when they grow to a critical size, they sink into the solution and self-assemble. Convective currents carry the water droplets to the base of the polymer-solvent solution and result in the close packing of the water droplets. The Marangoni effect is the reasoning behind the non-coalescence phenomenon, which results in optimal close packing (**Figure 1.7**)⁴⁰. Baroud *et al.* defined this as a “mass transfer effect along with the interface of two fluids due to the surface tension gradients”. The difference in surface tensions between the organic solvent and water is one factor that gives rise to the closely packed honeycomb arrangement.

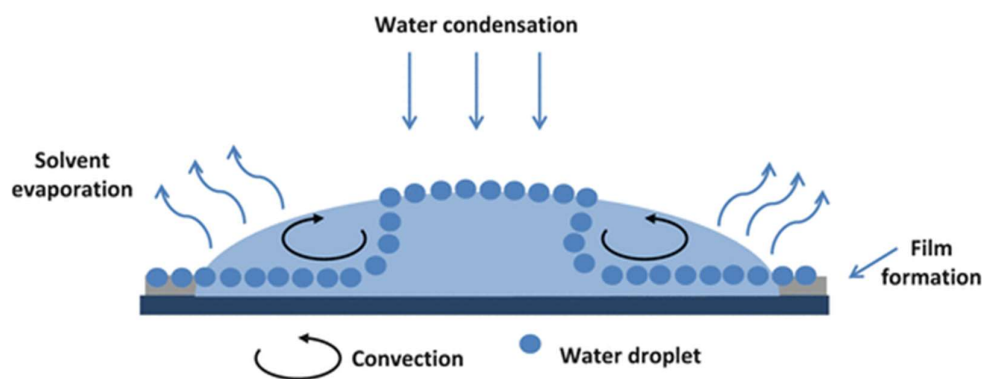


Figure 1.7– Schematic showing the water droplet assembly.⁵⁹

The precipitation of the polymer around the droplets stabilises and encapsulates their shape, thus preserving the porous structure during the evaporation phase of BF. If the droplet fails to emerge before the drying of the polymer solution, no porosity will occur.

1.2.5 Polymer Choice

Polymers are considered ideal for producing BF arrays as they easily dissolve in a wide range of organic solvents, are malleable at high temperatures, and most types are insoluble

in water. Since the 2000s, countless studies have been carried out on various polymeric materials to produce contrasting topological features. A review by Zhang *et al.* discusses all the different processes and materials that have been studied to create ordered honeycomb patterns²⁸. Using water as a non-solvent, allows for the formation of BF as water is immiscible in all organic solvents. If a polymer is dissolved in an organic solution, it will only affect the stability of the water droplet shape and will not dissolve in aqueous media.

1.2.5.1 Linear Block Copolymers

Block copolymers (BCPs) consist of a linear arrangement of polymer “blocks” where block A and block B are bound end-to-end by a covalent bond, as presented in **Figure 1.8**.

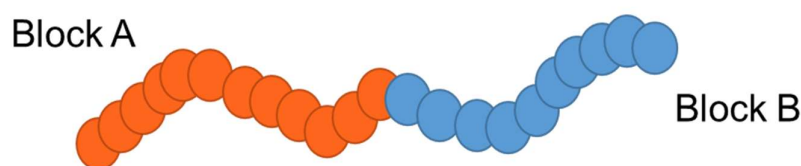


Figure 1.8 Block copolymer chain structure.

Linear BCPs have been shown to quickly produce ordered BFAs due to their unique self-assembly behaviour in solutions and interfaces. Multiple efforts have been made to understand the self-assembly behaviour of BCPs and how the chains interact with the water droplets. BCPs can be categorised into two types, amphiphilic and non-amphiphilic. Amphiphilic BCPs possess both hydrophilic and hydrophobic properties, while non-amphiphilic BCPs only have hydrophobic or hydrophilic properties, with their templating relying solely on the precipitation of the polymer during solvent removal.

The first breath figure array (BFA) film was prepared using non-amphiphilic diblock copolymer polystyrene-*block*-polyphenylene (PS-*b*-PPP) as described in section 1.1³⁵. This

work involved dissolving the PS block in carbon disulfide (CS_2) solvent while the PPP was insoluble, forming quasi-spherical micelles with the PPP forming the core and PS acting as a ligand. Francois *et al.* states that the star-shaped aggregates of PS-*b*-PPP were crucial for BF formation as they possessed high segment density and prevented the droplets from coalescing³⁵. Additional studies using other non-amphiphiles such as polystyrene-block-polydimethylsiloxane (PS-*b*-PDMS)⁶⁰, polystyrene-block-poly (ethoxy ethyl acrylate) (PS-*b*-PEEA)⁶¹ and polystyrene-block-methyl methacrylate (PS-*b*-PMMA)²⁰ have also been used as materials to produce ordered BFA arrays (**Figure 1.9**). Highly ordered BFAs can be produced using PS-PDMS at a concentration of 40 mg mL^{-1} ; however, at higher concentrations, the ordering is reduced⁶⁰.

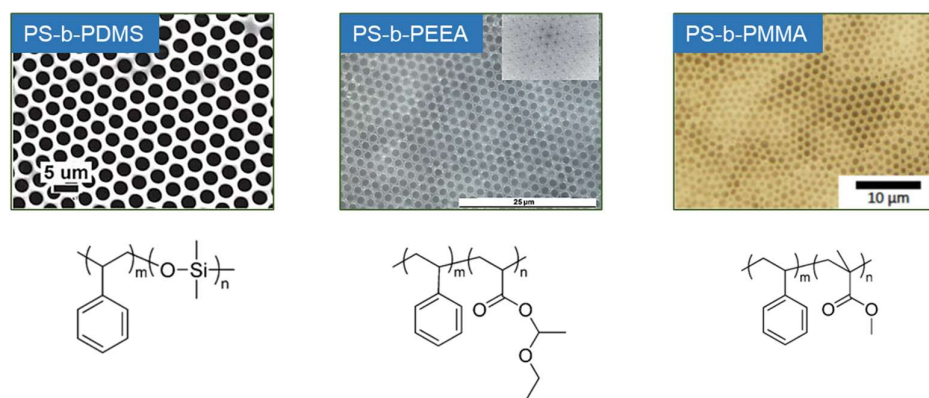


Figure 1.9 Breath figure arrays produced using PS-*b*-PDMS⁶⁰, PS-*b*-PEEA⁶¹ and PS-*b*-PMMA²⁰. The chemical structures of the polymer units are shown underneath each of the images.

Amphiphilic block copolymers are a class of polymers that stabilise the water droplets through chemical interactions. The polymer chain's hydrophilic moiety is attracted to the water, resulting in self-assembling around the water droplet, as shown in **Figure 1.10**.

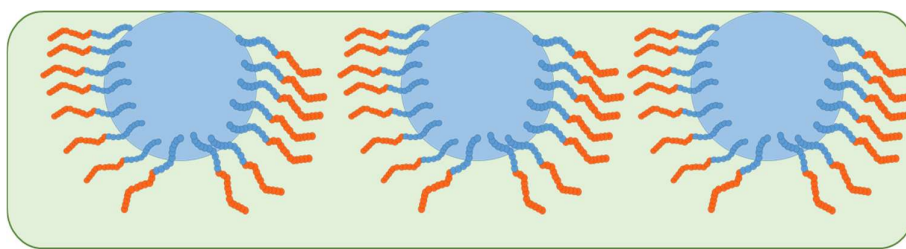


Figure 1.10 Schematic showing the affinity of specific blocks of polymer chains stabilising droplets in the polymer solution.

Numerous amphiphilic BCPs can create microporosity by efficiently stabilising the droplets on the polymer-solvent interfaces^{29,30,57,62–65}. The most popular amphiphilic BCPs have polystyrene (PS) as one of the blocks, as it can easily phase separate from hydrophilic polymer groups, generating ordered porosity in thin films. For example, polystyrene-block-acrylic acid (PS-b-PAA)⁶⁴, polystyrene-block- polyvinyl pyridine (PS-b-PVP)^{65,66} and polystyrene-block- polyethylene oxide (PS-b-PEO)⁶⁷ can create uniform honeycomb porosities as shown in **Figure 1.11**.

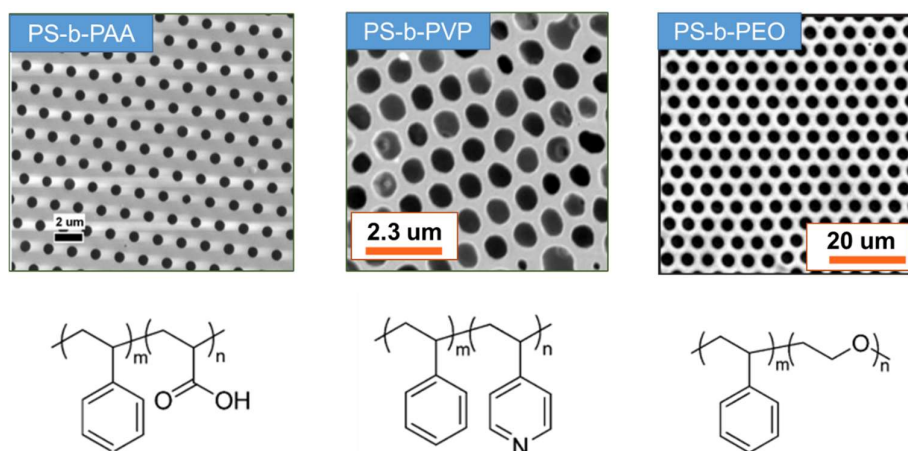


Figure 1.11 Breath figure arrays produced using PS-b-PAA⁶⁴, PS-b-PVP⁶⁸ and PS-b-PEO⁶⁷. The chemical structures of the polymers are shown underneath each of the images.

1.2.5.2 Linear Homopolymers

It was initially thought that only star-shaped and branched polymers can create regular BFA patterns²⁹. This is because they have high segment density and easily precipitate around the water droplets, stabilising their shape⁶⁹. However, star and branched polymers and block copolymers are expensive to purchase due to their complex synthesis and shape (polystyrene, 3-Arm Star polymer (P1005-3S), \$1400/g, polystyrene-*block*-poly (2-vinyl pyridine) (P4802-S2VP), \$500/g, Polymer Source). However, linear homopolymers are cheaper to acquire (polystyrene, \$60/g, Polymer Source) and are easy to synthesise and functionalise. The more specialised the polymer, the more challenging it can be to access from suppliers, which also includes long wait times (> 2 months).

A large amount of effort has been devoted to fabricating well-ordered BFA patterns with simple homopolymer chains, as shown in **Figure 1.12**.

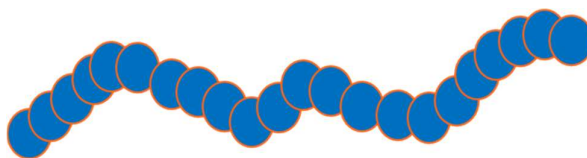


Figure 1.12 Homopolymer chain structure.

The monomers are bound end-to-end and are identical to one another. The most widely used homopolymer is linear polystyrene (PS) which is easy to synthesise and modify. The chemical structure of PS is shown in **Figure 1.13**.

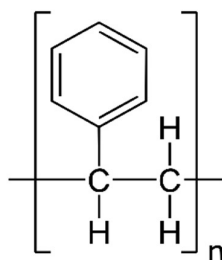


Figure 1.13 Chemical structure of polystyrene

PS is a hydrophobic polymer with no bonding ability. BF solely relies on the precipitation of the polymer thus encapsulating the shape of the water droplet. Solvents that have viable swelling interaction with PS are high in dispersive forces. The type of interaction that PS and swelling solvents such as toluene, THF and CHCl_3 would mainly be Van-der-Waal or π - π interactions⁷⁰, with respect to the bulky phenyl rings in its structure.

It has been reported that PS can produce ordered porous films across a molecular weight (M_w) range of 15K to 214K. For a dynamic BF process, very specific conditions are needed to produce BFA's as the water droplet packing is influenced by the polar end groups, molecular weight, and the casting solvents^{47,53,71,72}. PS without polar end groups can also form well-ordered BFA at a range of temperatures, concentrated solutions, and molecular weights, as shown in **Figure 1.14**⁷³.

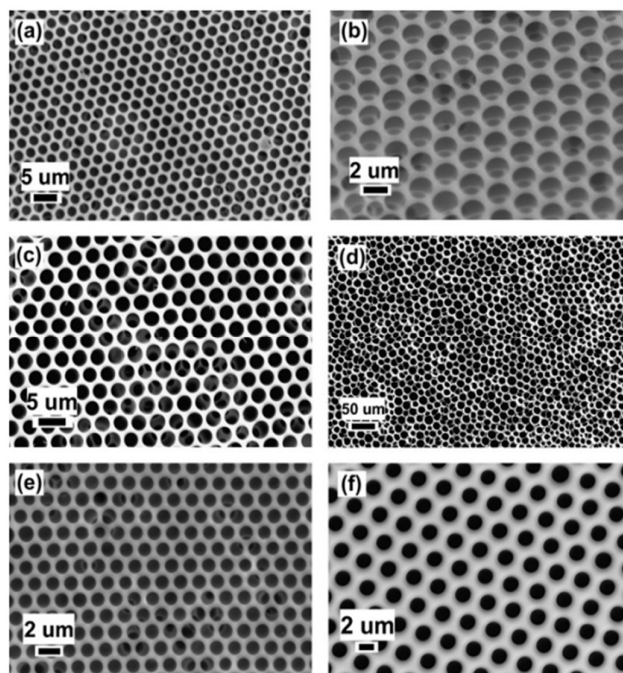


Figure 1.14 SEM images of PS films prepared under various conditions (a) $M_w = 214.8K$, 12 mg mL^{-1} (b) $M_w = 214.8K$, 35 mg mL^{-1} , 4°C (c) $M_w = 214.8K$, 60 mg mL^{-1} (d) $M_w = 214.8K$, 120 mg mL^{-1} (e) $M_w = 40K$, 50 mg mL^{-1} (f) $M_w = 15K$, 90 mg mL^{-1} .⁶¹

Other types of homopolymers such as polymethyl methacrylate (PMMA)⁶⁸, polyvinyl chloride (PVC)⁷⁴, poly-dimethyl silane (PDMS)⁷⁵ and polybutadiene (PB)⁷⁶ have also been shown to produce ordered BFAs, and are also cheap alternatives.

1.3 Recent Advances in Upscaling Breath Figures

Capabilities to produce new bottom-up templates are in high demand because of top-down costs and manufacturing process limitations for large volume production. BF requires specially constructed polymeric systems and well-designed process controls (humidity levels, temperature and solvent saturation are the main factors that affect porosity, density, and size³⁸. Bui *et al.* have reported a route for promoting BF arrangements in polymer solutions by firstly producing a uniform thin film of polylactic acid (PLA) on a substrate^{77,78}. The main interest in patterning PLA is its excellent biocompatibility and biodegradability⁷⁹. PLA films were dip-coated in a volatile solvent (CHCl_3) and non-solvent (MeOH) to produce a well-ordered BF film. Pattern morphology was altered by controlling non-solvent concentration, humidity, and temperature. Varying the volume of methanol added to the PLA/chloroform solution resulted in a change in contact angle, changing the wettability of porous surfaces *via* Cassie Baxter analysis⁸⁰. High humidity levels resulted in larger roughness values, thus increasing the contact angle. This explains the common issue of coalescence of droplets at high RH values⁸¹.

Bui also prepared PLA solution with a CHCl_3 / MeOH volume ratio (85/15) under ambient conditions (60% RH at 20°C)⁷⁷. It was shown that using solvents with differing evaporation rates can lead to well-ordered polymeric films. Bui *et al.* spin coated a polymer film onto a substrate and subsequently dip-coated the substrate in the binary mixture of solvent and non-solvent, which results in a highly ordered honeycomb structure as shown in **Figure 1.15**.

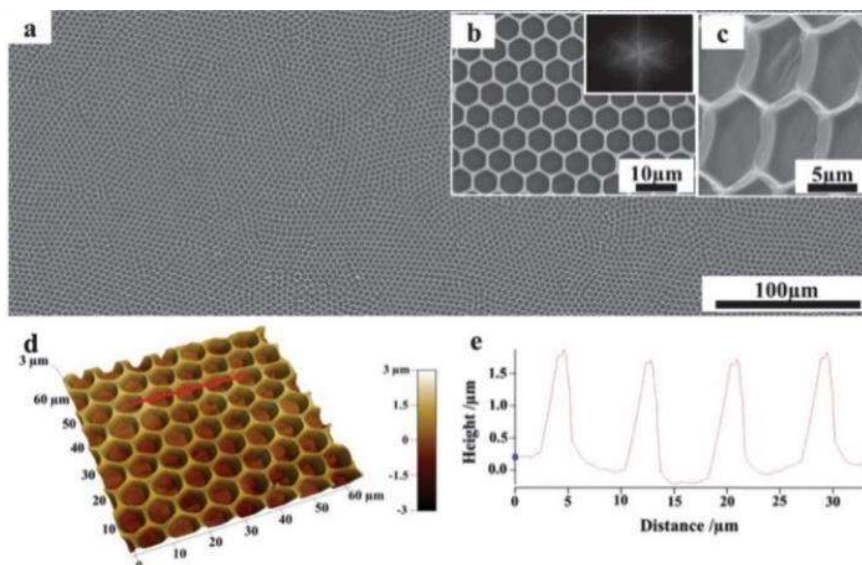


Figure 1.15 SEM/ AFM images of poly-lactic acid (PLA) patterned films prepared with solvent/non-solvent volume ratio of 85/15 at (a) low magnification, (b) high magnification with an inserted FFT pattern, (c) tilt angle of 60 degrees, (d) AFM image and (e) AFM cross-section analysis⁷⁷.

By solvent swelling the PLA film in humid environments, the morphology of breath figure arrays can be produced. This approach could be further optimised using a non-solvent induced phase separation (NIPS) approach to draw the water droplets to the MeOH rich phase⁷⁷. Using non-solvents such as methanol can influence the polymer to stabilise the droplets, which enhances the lateral capillary forces between the droplets and the solution⁷⁸. An increase in MeOH surface tension was reported during the solvent evaporation process. The water droplets self-pack under the influence of these capillary forces resulting in the formation of the honeycomb structure. If there is an excess in methanol content ($> 17\%$), the patterned films become very rough; however, at 16%, it is a well-ordered film⁷⁷. In 2022, methanol assisted studies have also been carried out using bioresorbable polycaprolactone films⁸².

Dextran sulphate, heparin and dihexadecyl dimethylammonium were treated with BF and used as cell scaffolds to improve the binding of proteins by the materials as they have lactose moieties that can bind to lectin⁸³. Furthermore, the proteins were successfully immobilised at the substrate indicating that the honeycomb morphology works as an efficient binding site for cells. Recent advances in cell scaffolding with breath figures have shown great potential in tissue engineering and stem cell applications⁸⁴⁻⁸⁶. Porosity is reported as crucial for cell migration and nutrient delivery in the 3D scaffolds⁸⁴.

In 2014, Shimomura and co-workers identified that the addition of surfactants (small amounts of polyacrylamide derivatives) to the polystyrene solution reduced line defects, and the honeycomb patterns could be upscaled to A4 sized PET films, as presented in **Figure 1.16**⁸⁷.

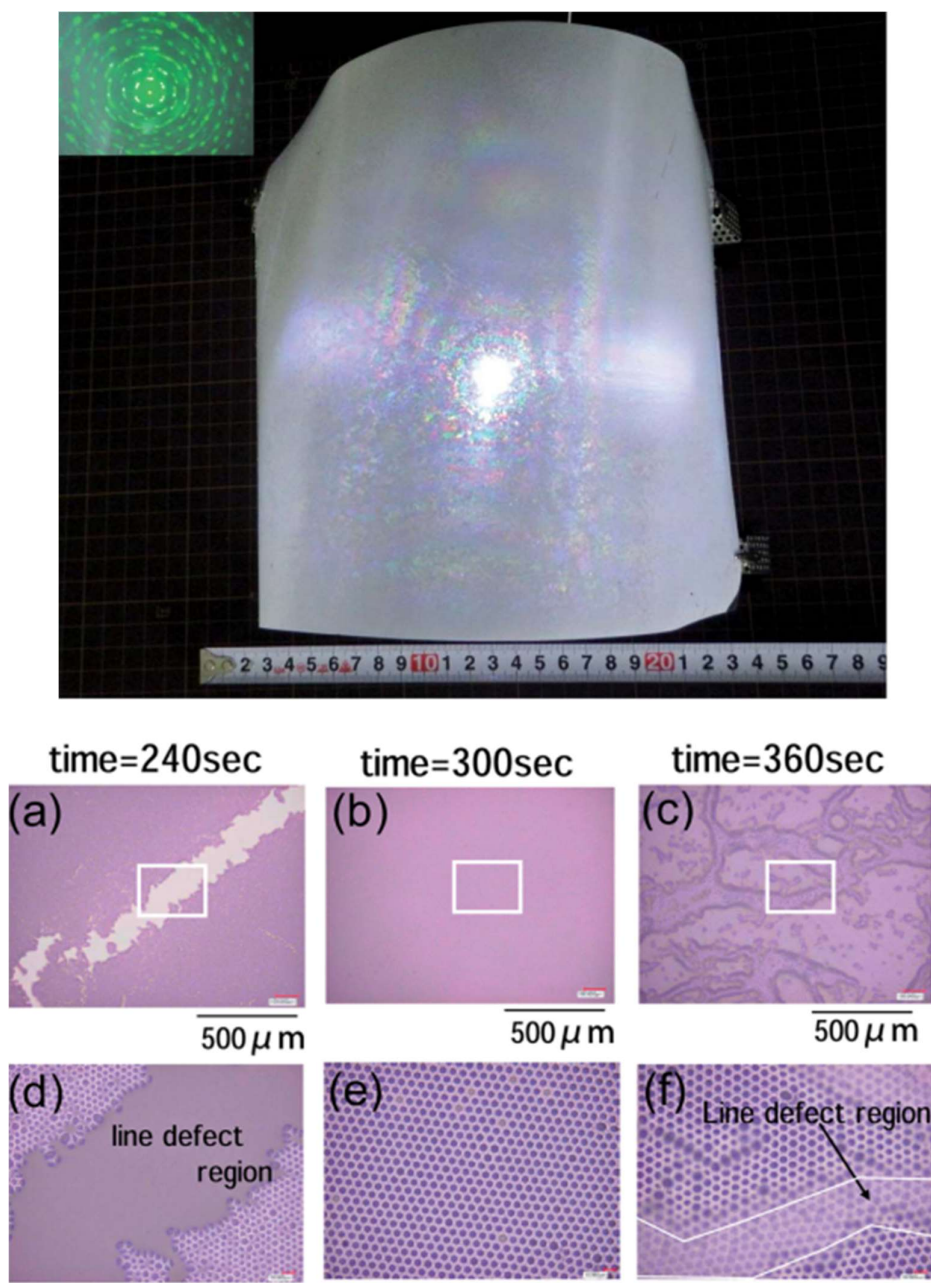


Figure 1.16. Photograph of A4 sized PET sheet with an inset image of a laser diffraction pattern⁸⁷. (a-f) Breath figure patterns with line defects (a, d, c, f) reduced at a growth time of 300 secs (b, e). Scale bar at 50 μm.

1.4 Large-Scale Production

The processing capabilities to produce new bottom-up templates are in high demand, as discussed previously in **Section 1.1**. It was reported that to upscale the breath figure process, it must be separated into three different chamber setups: the casting zone, humidification zone and drying zone (**Figure 1.17**), where the substrate would be carried through the chamber using a belt drive².

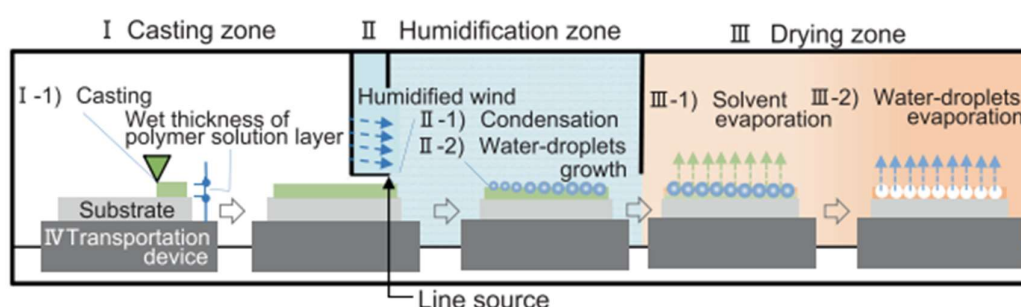


Figure 1.17. Schematic for Up-scaling Breath Figure Polymer Templating².

1. Casting zone – The polymer solution is cast evenly onto the substrate. The zone is maintained at a low temperature to avoid any premature solvent evaporation.
2. Humidification - Initiation of condensation on to the thin films and growth of water droplets. Temperature, exposure time and chamber humidity is monitored to allow for even distribution of water droplet density and size across the entire substrate area.
3. Drying zone – Solvent evaporation drives the polymer to solidify and must be controlled via temperature controls or rely on the solvent's evaporative effects. Water will evaporate to produce thin, porous films consequently.

4. Belt drive – Controlling the speed of the belt is essential for determining how long the exposed polymer solution should be in each of the chambers. Strict monitoring of belt temperature is also important.

Fuji Film Co. commercialised the honeycomb patterning method and patented it in 2012 to produce optical films with a liquid crystal display as shown in **Figure 1.18**⁸⁸. Temperature and humidity conditions were monitored and maintained using stage temperature control and an air-controlled nozzle for spraying onto the thin films.

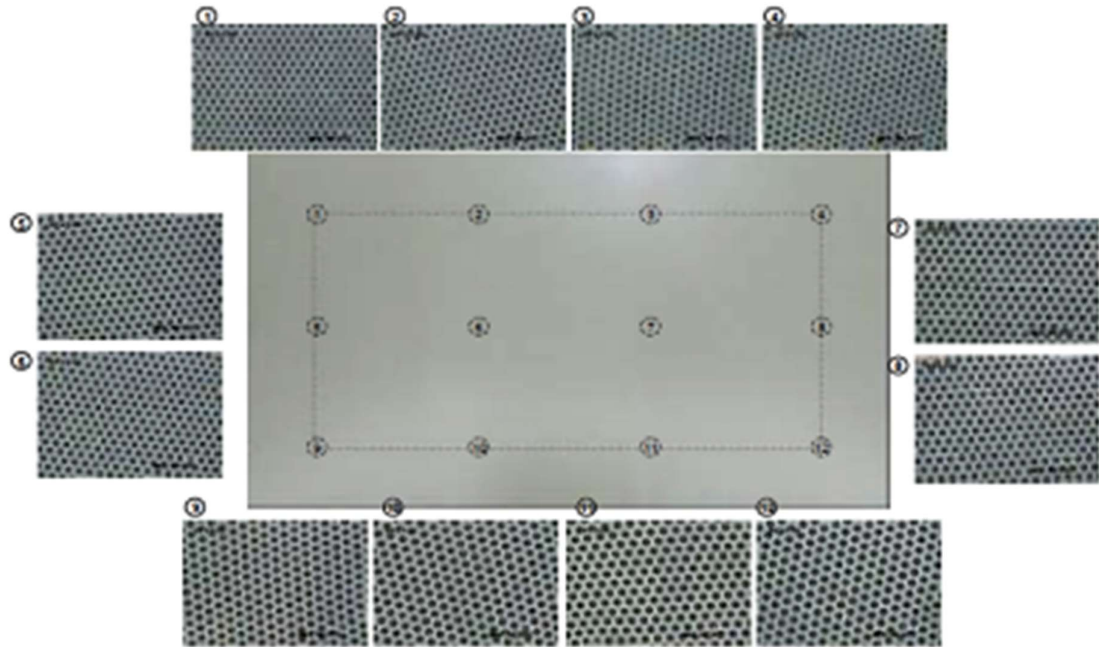


Figure 1.18. Large size “honeycomb” films using the Fujifilm developed process. The area covered was 200 mm x 300 mm with a mean distance of 14.8 μm and a coefficient variance of 3.7 %.⁸⁸

However, it is important to note that all work on scale-up is based on thicker films of 1 μm and above. Therefore, the body of this work details how the BF process can be applied to

thin films (sub-micron) exposing the substrate, thus enabling functionality as lithographic resists.

1.5 A Novel Approach – Solvent Vapour Breath Figure

Current issues in forming BFs are primarily concerned with defect densities and poor polymer viscoelastic control through droplet templating methodologies²⁸. To improve control, a novel approach was proposed which allowed controlled swelling of the film by a vapour phase solvent. This allows ‘tuning’ of the viscoelastic properties of the film. This novel approach is known as the solvent vapour breath figure (SVBF) process, which is presented in **Figure 1.19** and was developed as a major part of this thesis.

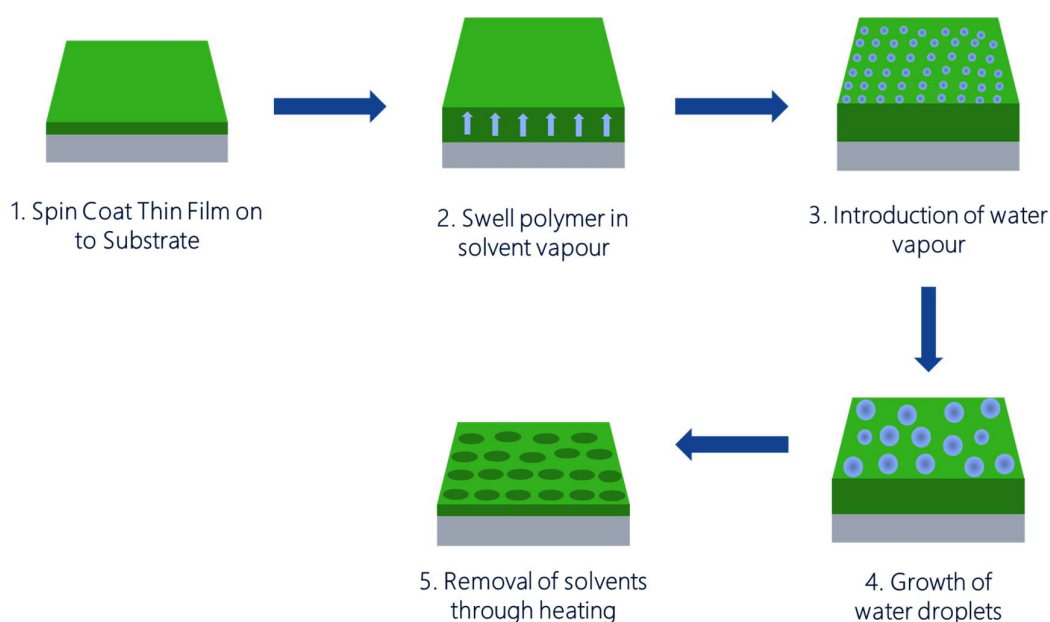


Figure 1.19 An illustration detailing each part of the SVBF approach.

Breaking down each part of the BF process, will define new routes and methods for producing well-ordered patterns in a controlled manner, using an innovative state-of-the-art piece of apparatus, and following the steps:

Step 1: Thin polymeric films are produced *via* the spin coating method, creating a uniform polymer film of known thickness that is coherent across the entire substrate.

Step 2: The polymer film is swollen to a viscous-like state *via* polymer swelling. The chains can move within the swollen film, and the swelling ratio can be controlled by temperature control. This will also remove any film thickness variation along the substrate associated with the drop cast method, as discussed in **Section 1.2**, where no clear indicator of film thickness uniformity is confirmed²⁸.

Steps 3 and 4: Relative humidity (RH) is controlled using a water bubbler and can be fine-tuned by changing the temperature and flow rate of the water. This dynamic process indicates that the solvent and water vapour are transferred by N₂ flow. By controlling the condensation rate and time, the controlled growth of the droplets can increase, resulting in various dimensions in porosity size and density.

Step 5: Solvent and water can be easily removed from the swollen polymer matrix by heating the solution. By driving off the solvent vapour, the polymer film solidifies, and upon removal of the water droplets, a porous pattern emerges.

The final part of the project is the theoretical analysis of the polymeric system and refining the understanding of BF formation in thin films. The rheology of the polymeric solution will be assessed, in addition to the overall stability of the thin film during the swelling process. The polymer system that is studied throughout the rest of this research project is polystyrene (PS). PS can be a challenging polymer for BF formation as it relies solely on polymer precipitation to form the porous structure. It has been noted that adding functional groups to the polymer improves the ordering of the droplets⁵³. Numerous theoretical studies of PS rheology and swelling⁸⁹ are found in the literature, indicating it may be an ideal

polymer to work within the preliminary stages of assessing the capabilities of the novel SVBF method.

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Chapter 2

Development of Quantitative Theory and Modelling for Thin Film Templating

2.1 Thin Film Swelling

To understand the complex dynamics of thin film self-assembly in BF-type studies, a significant focus of the work was developing a theoretical platform that could inform detailed interpretation of the work. This perspective is used to explain the data presented in later chapters.

In our everyday lives, thin polymer films are often encountered (as well as fabricated parts, bodies and packaging) as coatings or adhesives that can provide mechanical surface protection and advances such as sensors and detectors in numerous applications^{1,2}. A thin film can be described as a “very thin layer of a substance on a supporting material”³. Although it is never explicit what the thickness range is, it can vary between a few nanometres to several micrometres. The film can be described as ultra-thin when the thickness is below ~ 100 nm. In this work, sub-100 nm thickness ranges will be discussed where the polymer confinement at the substrate can possess contrasting physical properties that deviate from bulk behaviour concerning film uniformity, stability and substrate effects^{4,5}.

When a thin film is exposed to a suitable solvent, the solvent molecules can diffuse into the polymer matrix and swelling can be observed. For thin polymer films, unidirectional dilation occurs, which restricts the swelling to the perpendicular direction due to substrate confinement⁶. Therefore, it is essential to recognise the difference between dilation and

penetrant mass uptake. Dilation is referred to an increase in polymer volume resulting from solvent molecules that occupy free space in the polymer matrix. Penetrant mass uptake refers to the concentration of penetrant within the polymer matrix; however, no change in volume is observed. The schematic shown in **Figure 2.1** shows the 3 effects of swelling for (i) penetrant mass uptake, (ii) 3D polymer swelling and (iii) 1-D perpendicular swelling.

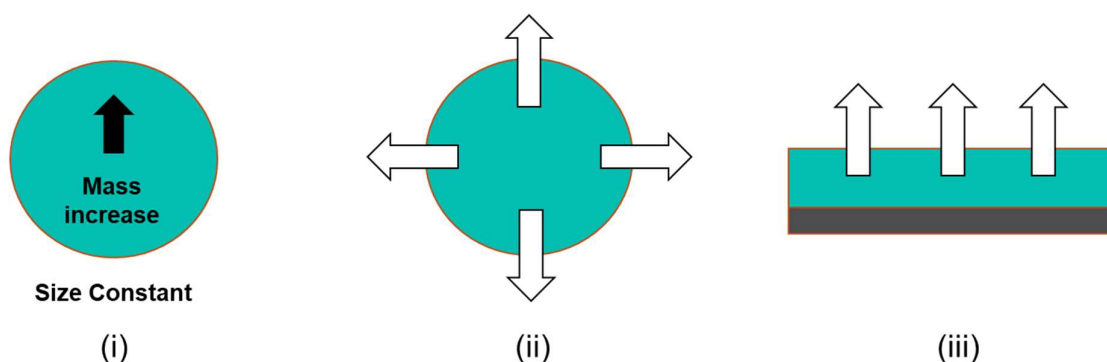


Figure 2.1 Schematic representation of (i) mass uptake, (ii) 3D dilation (middle) and (iii) 1D dilation for thin polymer films.

3-D dilation is where molecules can swell in all directions along the x, y and z axis. An example of this type of swelling would be polymer microspheres swelling in a suitable solvent⁷. The swelling of thin polymer films is restricted to only swell in 1 direction: in this case, vertically.

2.1.1 The Glass Transition

The thermodynamic state of a polymer and its properties are affected not only by the polymer's chemical makeup but the polymer's processing parameters⁸. Polymer films are usually processed by either dissolving the polymer in a suitable solvent or by melting the

polymer to a liquid state. In the case of melt processing, upon cooling, the molecular motions of the chains slow down and reduce to a level when the polymer returns to its solid-state. A point at which the crystalline solid is converted to a liquid is known as the melting point and is a first-order transition. In contrast, a glassy solid to a liquid is considered a second-order transition. Both transitions are shown in **Figure 2.2** A second order transition is where the system's entropy, volume and energy change gradually whereas a first order transition occurs abruptly with no prior fluctuations

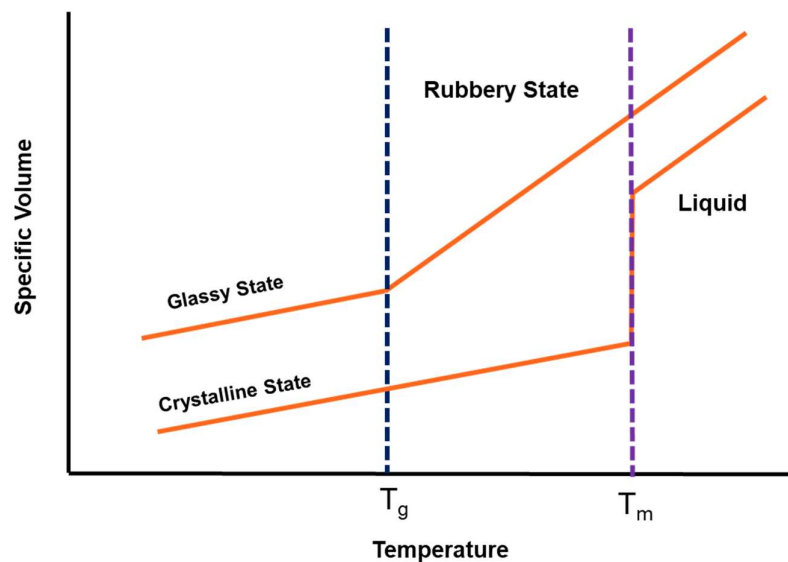


Figure 2.2 Liquid-solid transition for a polymer where T_g is denoted as the temperature where the polymer becomes rubbery, and T_m is the melting point of the polymer.

When a polymer melt is cooled, the rapid decrease in polymer chain mobility will create a solid that is either an amorphous or crystalline, depending on the rate of cooling. The point at which the polymer chain motion is frozen in place is known as the glass transition temperature. For thermoplastics, this is a reversible transition where the polymer transforms from a hard brittle plastic to a viscous, rubbery material. For thermosetting polymers, the

process is not reversible due to cross-linking of the polymer molecules. The glass transition is one of the most important physical properties of an amorphous solid as crossing this boundary can influence properties of the material such as viscosity, heat capacity, optical, and mechanical properties.⁸

The specific volume of a glassy polymer is directly proportional to its mass and packing density and influences the penetrant sorption, elastic modulus, and viscosity. The specific volume in a rubbery material consists of 4 types. The van der Waal's volume is the space occupied by the molecule and is impenetrable to other molecules⁹. The second type is the packing volume or additional space imposed by the packing constraints of the molecules (as empty spaces exist from the packing of spheres). Together, the van der Waals and volume packing sums up the occupied volume of the polymer. The molar volume and Van der Waal volume of glassy amorphous polystyrene at 25 °C is 99 cm³/ mol and 62.9 cm³/ mol, respectively⁹. This gives an overall packing ratio of 1.58.

Expansion volume, vibrational volume, or interstitial volume is the third type. This is the free volume spread amongst all molecules and is created by the thermal motion of the atoms, which is temperature dependent. Hole-free volume (V_{hole}) is the final contributor and is the space between the non-ideal packing of the polymer chains. A localised volume element can be redistributed due to the polymer chain motion^{10,11}. The following section will discuss how thin films are made and the theory behind creating highly uniform polymer thin films.

2.1.2 Thin Film Production – Spin coating

Spin coating is a valuable method for producing uniform thin polymer films with thicknesses ranging from nanometres to several microns. The spin coating technique is widely used in industry to produce thin films that function as photoresists for lithography¹² and microelectronic applications¹³. The method is shown in **Figure 2.3**.

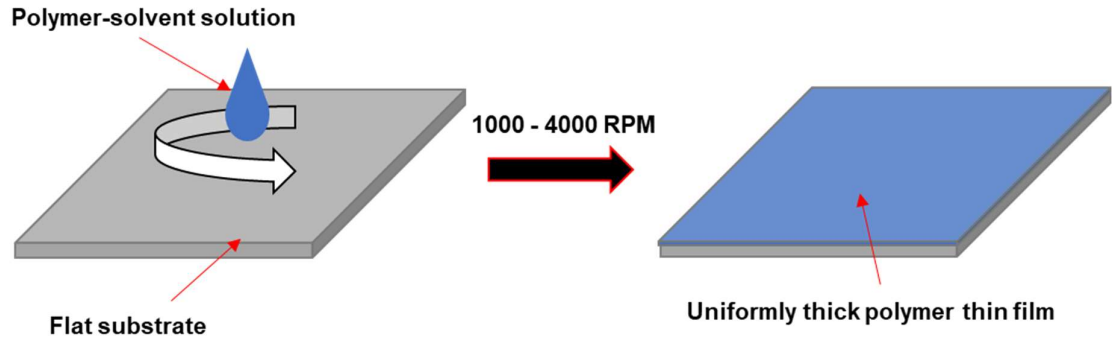


Figure 2.3 Spin-coating method for producing polymer thin films.

By spin casting polymer solutions onto flat substrates such as silicon wafers spun at high velocities, the thickness of the films can be precisely controlled. Parameters such as evaporation rate and chemistry of the solvent, spin speed, temperature, substrate chemistry and polymer-solvent interactions are variables that affect film quality during the spin-coating process.

Spin-coating was first modelled by Emslie, Bonner and Peck (EBP) in 1958¹⁴. They describe the flow of a Newtonian fluid on a rotating disk and how the centrifugation effect does not disturb the uniformity of the fluid. As defined by Newton, a Newtonian fluid is where the viscosity is independent of the shear rate¹⁵. In 1978, Meyerhofer was the first to consider the evaporation rate and how it affects the spin coating model¹⁶. He simply added “e”, the evaporation rate, to the EBP’s model to generate **Equation 2.1**.

$$\frac{dh}{dt} = -2kh^3 - e \quad \text{[Equation 2.1]}$$

Where h is the film thickness at any time, t , during spinning, k is the fluid constant, and e is the evaporative rate. The fluid constant (k) is determined using **Equation 2.2**.

$$k = \frac{p\omega^2}{3\eta} \quad [\text{Equation 2.2}]$$

Where p is the fluid density, ω is the speed velocity, and η is the fluid viscosity. Meyerhofer identified two stages of spin coating. The early stage is the flow-dominated stage, the latter is evaporation-dominated, and the thin film thickness produced can be calculated using **Equation 2.3**. With this approach, Meyerhofer could predict the thickness of films using a positive-resist solute of Shipley AZ-1350 dissolved in methyl cellosolve acetate¹⁶ as presented in and predicted using **Equation 2.3** and his results are shown in **Figure 2.4**.

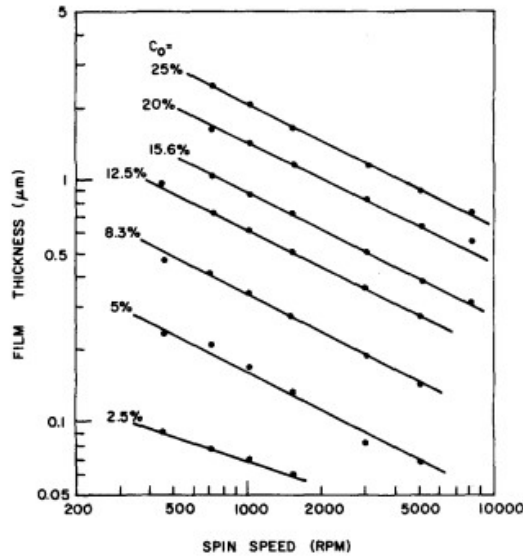


Figure 2.4 Measured film thicknesses as a function of spin speed (rpm) and solvent concentration¹⁶.

$$h_f = x \left[\frac{e}{2(1-x)k} \right]^{\frac{1}{3}} \quad [\text{Equation 2.3}]$$

Where h_f is the final thickness, e is the evaporation rate, x is the thickness change over time, and k is the fluid constant. Polymer film thickness have been measured for PS using the method developed by Hall *et al.*¹⁷.

2.1.3 Stability Analysis at Small Length Scales

Stability analysis is critical in maintaining good reproducibility of swelling in thin polymer films, especially at the nanoscale. Thin films are intrinsically unstable, and their physical characteristics can change significantly at reduced thicknesses^{18,19}. Decreasing the thickness of polymer thin films can lead to instabilities such as dewetting²⁰, elastic-contact²¹, and electro-hydrodynamic instabilities²². Additionally, thin films can exhibit stresses within their structure, whether in liquid form or containing polymeric material in a fluid phase. The Hamaker is derived from all the material constants of interacting media, which involves the refractive index and the dielectric constants, based on Lifshitz theory²³.

The relaxation time (**Equation 2.4**) can be derived from the Hamaker constants of interacting media which is measured by knowing the refractive indices and the dielectric constants of the media.

$$\frac{1}{\tau_r} = \left(\frac{h^3}{\eta}\right) \left[\gamma q^4 + \frac{3Aq^2}{6\pi h^4} \right] \quad [\text{Equation 2.4}]$$

Where A is a Hamaker constant (sum of all intermolecular interactions (dispersive, polar and hydrogen bonding), h is the film thickness, and the rest of the equation are arbitrary constants that fit experimental observations where γ is the surface tension and q is the wave of the instability. The Hamaker constant is a term that quantifies the sum of all intermolecular forces (C_{Tot}) between a material and its surroundings which is based on Lifshitz theory²³. The detailed explanation is reported by Israechvili *et al.*²⁴. The most important element of this equation relates to the relaxation time of the polymer, which is defined as the time taken for an instability to manifest itself and destroy the film. By

removing some of the constants, **Equation 2.5** can approximate the relaxation time at a specific thickness of the swollen film.

$$\frac{1}{\tau_r} \cong \left(\frac{h^3}{\eta} \right) \quad [\text{Equation 2.5}]$$

The relaxation time is inversely proportional to the thickness cubed and directly proportional to the viscosity of the swollen polymer film. Since the polymer film will be swollen, the thickness will increase with swelling ratio showing that the relaxation time will be low at large swelling ratios. C_{Tot} are weak intermolecular Van-der-Waal forces that are categorised into three different types: Keesom interactions (C_K), Debye interactions (C_D) and London Dispersion Forces (C_L) and have all been discussed by Israechvili²⁴.

Summarising these:

- Keesom interactions (C_K) depend on the interaction between two permanent dipoles on a surface. The force is mainly dependent on the dipole charge of both molecules.
- Debye (C_D) interactions are associated with the interaction of induction between a permanent dipole and an induced dipole. The force is dependent on the polarizability of one molecule that affects the dipole moment of the other.
- London dispersion forces (C_L) (van der Waals forces are a dispersion force) is caused by the fluctuations of charge between two molecules and is affected by the polarizability between the two molecules in addition to the excitation frequencies.

2.2 Solvent Absorption

The solvent vapour annealing (SVA) process is where the thin film is exposed to solvent vapour, increasing the overall volume of the polymer film. Solvent molecules diffuse into

the unaccompanied spaces in the polymer chain, increasing the thickness of the film perpendicular to the substrate *via* 1D swelling (**Figure 2.1**).

The standard method used to measure solvent absorption of thin films is reflectometry. This is where thin film thickness can be measured “in-situ” during the solvent vapour swelling process by comparing the refractive index of both the material and the solvent. The properties of the thin polymer film, such as thickness, refractive index and dielectric constant can impact the property of the wave²⁵, as shown in **Equation 2.6**.

$$\lambda = \frac{2nd}{i} \quad [\text{Equation 2.6}]$$

Where λ is the wavelength, n is the refractive index, d is the film thickness and i is an integer. The refractive index explicitly determines the amplitude of the oscillations for dielectric systems when there is no extinction coefficient (k) for dielectric material. Therefore, by analysing the period and amplitude of the oscillations, the reflectometer can determine the thickness and optical properties of the thin films, specifically for the characterisation of the thin films²⁶. The Lorentz-Lorenz rule of mixing²⁷ is used to compute the refractive index change of swollen polymer solutions, as shown in **Equation 2.7**.

$$\frac{n_{12}^2 - 1}{n_{12}^2 + 2} = \phi_1 \frac{n_1^2 - 1}{n_1^2 + 2} + \phi_2 \frac{n_2^2 - 1}{n_2^2 + 2} \quad [\text{Equation 2.7}]$$

Where ϕ_1 , ϕ_2 and n_1 , n_2 are the volume fractions and refractive indices of pure components 1 and 2, and the n_{12} is the refractive index of the swollen polymer.

The initial and swollen thickness of the polymer film is denoted as d_o and d_s , respectively and thus, the swelling ratio (SR) can be calculated using **Equation 2.8**. Initial thickness d_o is where only pure polymer is present ($\phi_{\text{solvent}} = 0$) and d_s is a mixture of polymer and solvent at different volume fractions ($\phi_{\text{solvent}} > 0$). The swelling ratio (SR) can be measured by calculating the volume difference between the solvent and the polymer film, as shown in **Equation 2.9**.

$$\frac{d_s}{d_o} = SR \quad [\text{Equation 2.8}]$$

$$SR = \frac{1}{\phi_{\text{polymer}}} = 1 - \frac{1}{\phi_{\text{solvent}}} \quad [\text{Equation 2.9}]$$

To understand the swelling dynamics of thin films, the physical and thermodynamic state of the polymer must be considered. In terms of sorption, this indicates that the penetrant will mix with the polymer and convert it to a rubber-like state. For rubbery polymers, the extent of dilation is limited by the saturation i.e., the solvent concentration during a swelling process. This can be measured by changing the saturation of solvent in a system.

2.2.1 Controlling Solvent Saturation

The Antoine equation can interpret the pressure where the solvent vapour is in thermodynamic equilibrium with its condensed state known as P_{sat} . The Antoine equation (a derivation of the Clausius-Clapeyron equation) allows the calculation of P_{sat} from constants A, B and C of the solvent at an absolute temperature, T. The saturation pressure of the solvent (P_{sat}) can be estimated from **Equation 2.10**.

$$\text{Log}_{10}(P_{\text{sat}}[\text{kPa}]) = A - \frac{B}{T[^\circ\text{C}] + C} \quad [\text{Equation 2.10}]$$

Antoine saturation curves are representations of the vapour-liquid equilibrium of a pure substance. The values used in the Antoine equation, are presented in **Table 2.1**.

Table 2.1 Antoine constants for the different swelling solvents.

	A	B	C	t _{Min} [°C]	t _{Max} [°C]	P _{sat} [mmHg]
Toluene	6.9509	1342.3	219.19	-27	111	6.2135E-32
Chloroform	6.9547	1171.0	226.23	-10	60	2318.9

The vapour pressure for chloroform is higher than toluene over the temperature range of 0 – 60 °C because of its higher volatility. Toluene has a much lower evaporation rate than chloroform, where toluene is 1.9 and chloroform is 8.8. The test solvents are compared to standard n-butyl acetate that has a vaporisation rate of 1²⁸. This indicates that the 2 solvents show a significant difference in their overall evaporative effects.

The Antoine equation can graphically represent the solvent's saturated pressure limits as a function of temperature, as shown in **Figure 2.5**.

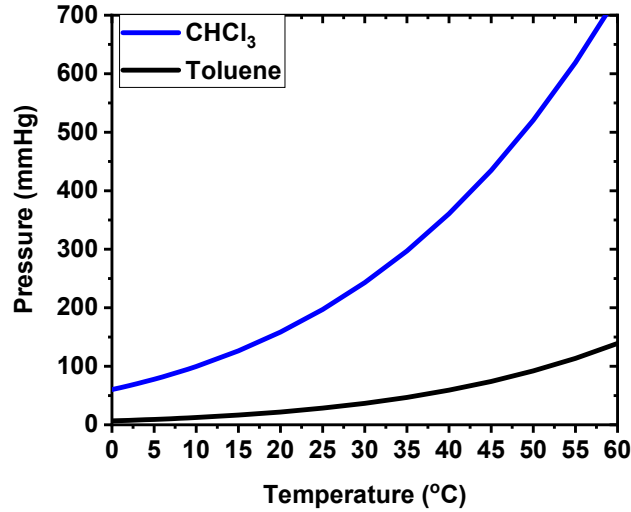


Figure 2.5 Saturation curves for chloroform (CHCl₃) and toluene (C₇H₈).

Saturation of solvents in the ambient, can be computed by calculating the vapour pressure (P) and saturated pressure (P_{sat}) at a given temperature, T as shown in **Equation 2.11**.

$$\frac{P}{P_{sat}} = \text{Saturation (\%)} \text{ at } T \text{ (}^{\circ}\text{C)} \quad [\text{Equation 2.11}]$$

By understanding the saturation of solvent vapour, the concentration of solvent in the thin films can be measured i.e., how many solvent molecules can occupy the free volume space in the polymer thin film.

2.2.2 Polymer-Solvent Interactions

The extent to which a polymer film and solvent will mix is governed by the molecular affinity between the two components and is indicated by the solvent parameters. The Hansen

solubility parameters (HSP)²⁹ for solvents considered here are presented in **Table 2.2**, and these values indicate the overall cohesive energies of specific fluids and solids.

Table 2.2 Hansen Solubility Parameters²⁹

	Dispersion (δd) (MPa^{1/2})	Polar (δp) (MPa^{1/2})	H-bonding (δh) (MPa^{1/2})
Styrene [1]	18.7	5.9	3.5
Chloroform [2]	17.8	3.1	5.7
Toluene [2]	18	1.4	2
THF [2]	16.8	5.7	8
Acetone [2]	15.5	10.4	7

When the polymer and solvent have similar solubility parameters, the polymer will dissolve in the solvent. There are three types of interactions accounted for by Hansen's approach, these are (1) dispersive (non-polar), (2) polar and (3) hydrogen bonding.

1. The dispersive forces are the collection of all the van der Waal forces in the material. These are denoted as the weakest forces and consist of Keesom, Debye and London dispersion forces, which occur as temporary attractive forces between atoms, as discussed in **Section 2.1.3**.
2. The polar contribution (also known as dipole-dipole) is attractive force between positively and negatively charged molecules.

- Hydrogen bonding is the final contribution and is considered the strongest of the intermolecular interactions. This is a particular type of dipole-dipole interaction, where attractive forces are generated from highly electronegative atoms such as N, O, and F and hydrogen atoms in the solid or molecule.

The sum of all the intermolecular forces determines the relationship between the polymer chains and solvent, ultimately determining the polymer's solubility for a given solvent²⁹. Values of the three Hansen parameters can be used as coordinates in 3D space with all HSP values, where the polymer has a specific interaction radius (R_0), as shown in **Figure 2.6**.

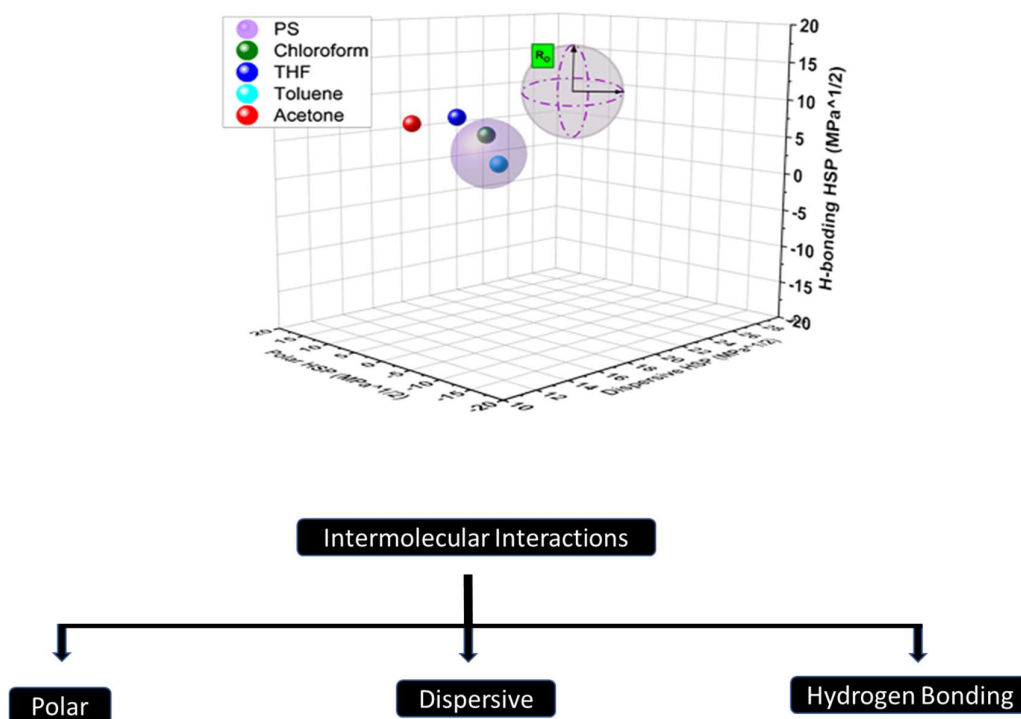


Figure 2.6 Hansen 3D-Space for PS and solvents.

The distance between a polymer and its respective solvent (R_a) can be measured by **Equation 2.12**.

$$(R_a)^2 = 4(\delta d_1 - \delta d_2)^2 + (\delta p_1 - \delta p_2)^2 + (\delta h_1 - \delta h_2)^2 \quad [\text{Equation 2.12}]$$

Combining the distance between molecules and the interaction radius, R_0 , the relative energy difference (RED) can be measured as shown in **Equation 2.13**.

$$RED = \frac{R_a}{R_0} \quad [\text{Equation 2.13}]$$

RED values identify the suitability of the solvent for different polymers. The criterion for RED is as follows:

1.) For RED < 1, the polymer will dissolve in the solvent.

RED = CHCl₃ /PS = 0.43 – YES

RED = Toluene /PS = 0.42 – YES

RED = THF/PS = 0.78 – YES

2.) For RED > 1, the polymer will not dissolve

RED = Acetone/PS = 1.17 – NO

Even though this is a useful technique for polymer-solvent dissolution and interaction, the HSP approach does not consider temperature. To account for temperature in polymer-solvent interactions, Flory-Huggins (FH) solution theory can be applied³⁰.

2.2.3 Flory-Huggins Solution Theory

By heating polymers above their melting point or dissolving them in a common solvent, better miscibility is achieved. This defines the free energy of mixing³¹. For rubbery polymer systems, Flory-Huggins solution theory³⁰ can predict the equilibrium penetrant fraction as a function of solvent penetrability and can describe specific interactions such as hydrogen bonding³². Flory-Huggin's solution theory describes the free energy of mixing (ΔG_{mix}) for polymer and solutes and is calculated using **Equation 2.14**.

$$\Delta G_{mix} = \Delta H - T\Delta S = RT[(x_1 \ln \phi_1 + x_2 \ln \phi_2) + N\phi_1\phi_2 \chi(T)] \quad [\text{Equation 2.14}]$$

Where ϕ_1 and ϕ_2 are volume fractions, $x_{1,2}$ are the mole fractions for the solvent and polymer respectively, and N is the total number of sites or segments. Furthermore, this equation relates to the well-known free energy of mixing equation where ΔH is the enthalpy of reaction ΔS is the entropy i.e. disorder in the system. Complete miscibility can be observed when $\Delta G_{mix} < 0$. **Equation 2.14** describes the mixing of polymer-solvent in respect to its entropic (ΔS) and enthalpic (ΔH) terms. The entropic elements describe the disorder of the polymer chains when mixing with the solvent. Enthalpy describes the energy change that occurs when mixing with the solvent. Differences in energy between the solvent and the polymer is denoted as χ and is known as the Flory-Huggins Interaction Parameter. In general, if the χ parameter is less than 1 the polymer will dissolve in the solvent which can then be considered as a “good” solvent. The interaction parameter is inversely dependent to temperature and increases with polymer concentration. **Equation 2.15** shows how to calculate the χ parameter for polymer-solvent mixing.

$$\chi_{12} = \alpha * \frac{V_1(4(\delta d_1 - \delta d_2)^2 + (\delta p_1 - \delta p_2)^2 + (\delta h_1 - \delta h_2)^2)}{RT} \quad [\text{Equation 2.15}]$$

Where the polymer denoted as [1] and solvent [2], mixing temperature denoted as T, R is the universal gas constant, V is molar volume of the solvent and α approximated as 1. Flory-Huggin's theory is a lattice-based equation of state (EoS) approach. It provides a description of the sorption behaviour of solvent and polymer when they are in a non-equilibrium state i.e., glassy/crystalline, and the penetrant can diffuse into the spaces unoccupied by the polymer. Polystyrene has been chosen to assess the swelling of a homopolymer film in two compatible solvents, chloroform ($\chi = 0.48$) and toluene ($\chi = 0.73$) as predicted by equation 2.15. An adaption of the Flory-Huggins equation can predict the swelling of polymer thin films at different solvent saturations (P/P_{sat}) by calculating φ_s , the solvent volume fraction which can be measured¹⁰. From interpreting the saturation, φ_s and knowing the Flory Huggins interaction parameter χ , and the degree of polymerisation, N, the impact of polymer-solvent swelling can be assessed using Equation 2.16.

$$\ln\left(\frac{P}{P_{\text{sat}}}\right) = \chi_{12}(1 - \varphi_s^2) + \ln \ln(\varphi_s) + (1 + N^{-1})(1 - \varphi_s) \quad [\text{Equation 2.16}]$$

For example, the theoretical Flory Huggin's swelling curve for linear PS (17k) (Figure 2.7) indicates that swelling of the film will increase to a swelling ratio of 2 at a saturation of 0.83 for both solvent systems.

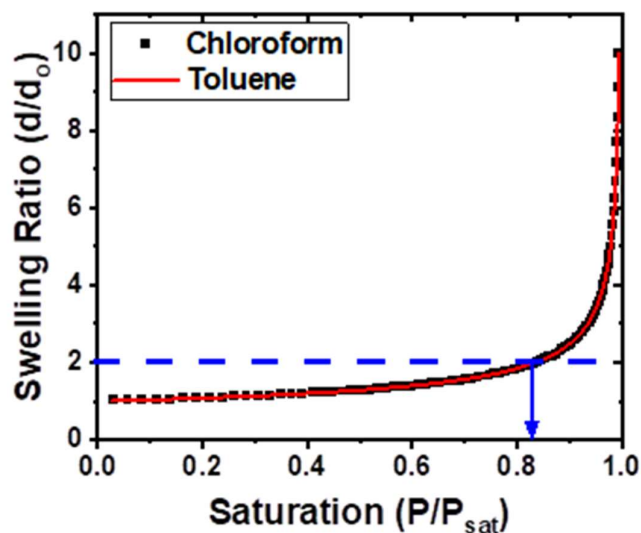


Figure 2.7 Theoretical swelling of linear 17k PS as predicted by Flory Huggins for solvents, chloroform (CHCl_3) and toluene (C_7H_8).

It is important to note that when P/P_{sat} has reached 1.0, the solvent will condense into a liquid as the actual vapour pressure is the same as the saturated pressure. This will cause the polymer film to dissolve into the liquid solvent and the thin film will become dewetted³³.

2.2.4 Diffusion

Diffusion is a process that occurs where there is physical mixing of substances (in this case, a solvent) and describes the natural movement of particles and can clearly be seen when molecules move from an area of high concentration to an area of low concentration and reach an equilibrium concentration. The results of diffusion can be readily seen and measured when unequal concentrations are mixed, but diffusion occurs even in fully equilibrated systems. The simplest model of diffusion follows Fick's Law of diffusion³⁴. Fickian behaviour involves the rate of diffusion is lower than the rate of relaxation of the polymer

where the flux (J) is proportional to the gradient in concentration (c) with diffusion coefficient (D) as a proportional constant as stated in **Equation 2.17**.

$$J = -D \frac{\partial c}{\partial x} \quad [\text{Equation 2.17}]$$

Fick's second law (**Equation 2.18**) describes how the concentration changes as a function of time by the change in flux in respect to position x; c_0 is the initial concentration of the film^{34,35}.

$$\frac{\partial c}{\partial t} = -\frac{\partial J}{\partial x} \quad 0 < x < l \quad [\text{Equation 2.18}]$$

Diffusion-dependent sorption can be divided into 3 regimes: Fickian diffusion, anomalous Fickian diffusion and Case II diffusion.

2.2.4.1 Fickian Diffusion

Fickian behaviour where the mass uptake is described as a function of the square root of time, where k is the constant diffusivity, and M_t is the mass uptake relation³⁵ as shown in **Equation 2.19**.

$$M_t = k \sqrt{t} \quad [\text{Equation 2.19}]$$

This can be seen where sorption equilibrium is achieved at a film surface. Fickian diffusion is always seen for rubbery polymers as the chains have high mobility. This will cause the

solvent diffusion rate to be slower than the polymer relaxation rate. Therefore, solvent uptake has relatively low characteristic diffusion times and solely depends on the diffusion process.

2.2.4.2 Anomalous Fickian Diffusion

Anomalous diffusion is where the relaxation time of the polymer has decreased significantly at $T < T_g$. As a result, the diffusion rate of the penetrant will be like the polymer relaxation rate. **Equation 2.20** describes the mass uptake of solvent.

$$M_t = kt^n \text{ where } \frac{1}{2} < n < 1 \quad [\text{Equation 2.20}]$$

The diffusion of the penetrant in the polymer is governed by both the diffusion rate and the relaxation rate of the polymer. This is referred to as Fickian Relaxation³⁶. Berens and Hopfenberg described a model in which the penetrant sorption into the dry polymer is dominated by a Fickian diffusion process, followed by a slower relaxation process³⁷.

2.2.4.3 Case II Diffusion

For a glassy polymer, the rate of diffusion is much higher than the rate of relaxation of the polymer and follows Case II diffusion. This is characterised by a rapid increase in solvent concentration in the swollen region and, thus, having a rapid solvent penetration between the swollen and dry inner core of the polymer film. As a result, the solvent front will rapidly advance at a constant rate, resulting in linear penetrant uptake with time, as shown in **Equation 2.21**.

$$M_t = kt \quad [\text{Equation 2.21}]$$

2.2.5 Glass Transition of Swollen Polystyrene Film

Polystyrene's bulk T_g value is measured at around 100 °C (373 K) in its dry bulk form i.e. no solvent is incorporated into the film. For a solvent-polymer system, the T_g can be measured using the Flory-Fox equation^{38,39} for a series of swollen polymer films, as shown in **Equation 2.22**.

$$\frac{1}{T_g} = \frac{\omega_1}{T_{g,1}} + \frac{\omega_2}{T_{g,2}} \quad [\text{Equation 2.22}]$$

Where T_g , $T_{g,1}$, $T_{g,2}$ is the glass transition for solvent-polymer at a specific weight fraction of pure polymer (ω_1), and pure solvent (ω_2) respectively. The threshold needed to become amorphous and mouldable can be measured and observed by knowing the glass transition of pure polymer. For example, polystyrene (PS) (T_g , 373 K)³⁸ solvent swelling can be calculated using toluene (T_g , 117 K)⁴⁰ and chloroform (T_g , 105.9 K)¹⁹ as swelling solvents. This gives insight into how the solvent concentration in the film influences the polymer's glass transition and decreases the polymer's volume fraction (ϕ_p) at different swelling ratios, as shown in **Figure 2.8**.

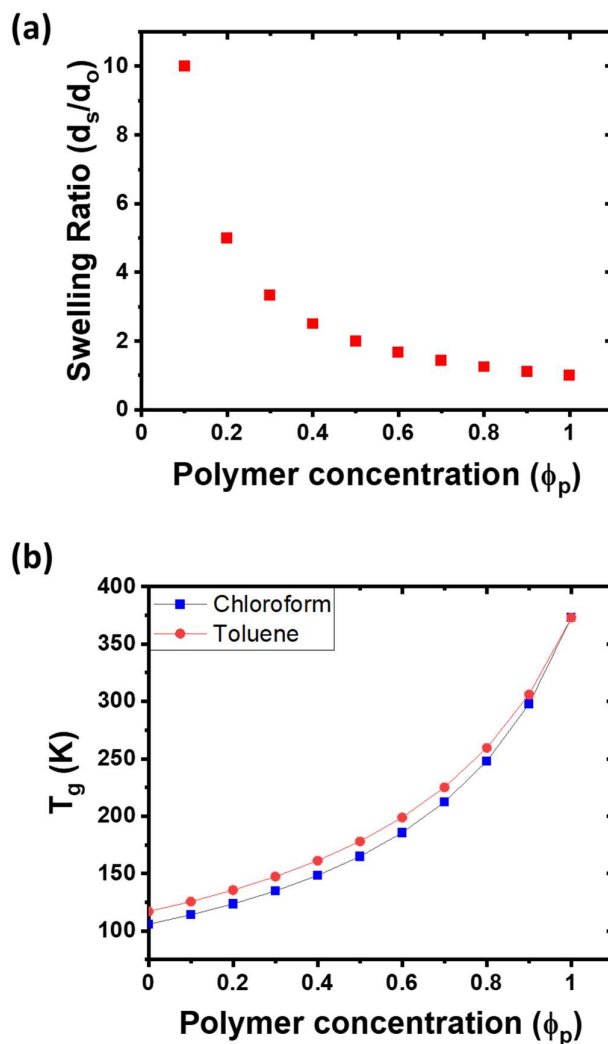


Figure 2.8 (a) Plots showing the polymer concentration in terms of swelling ratio (b) the effect of polymer concentration on the value of T_g for chloroform and toluene.

Solvent effects have a similar effect on polymer film mobility. By swelling the polymer film, the T_g value of the polymer can be reduced to values below room temperature, indicating that the polymer film will be swollen and mouldable at low swelling ratios at room temperature. From swelling the polymer with as low as 10%, solvent the polymer film becomes mobile as predicted by the Flory-Fox Equation⁴¹.

2.2.6 Nanoscale/Confinement Effects on T_g

Since the thin polymer films used in these swelling studies are at the nanoscale (a few 100 nm), the molecular mobility increases with decreasing thickness. Keddie *et al.*⁴² reported that the reduction in PS thin film thickness decreased the glass transition temperature and deviated from the expected value for bulk PS. This effect is not strongly molecular weight dependent but suggests that a liquid-like layer exists between the glassy layers when approaching values close to bulk T_g . A further investigation by Kawashima *et al.* reported the deviation of bulk T_g in films as thin as 20-30 nm using neutron reflectivity⁴³. In addition, they evaluated that the film's top layer was lower than bulk PS. Following Keddie's method, the impact of film thickness can be measured for a PS film thickness range from 50 – 500 nm series using **Equation 2.23**.

$$T_g(d) = T_g(\infty) \left[1 - \left(\frac{A}{d} \right)^\delta \right] \quad [\text{Equation 2.23}]$$

Where $T_g(d)$ and $T_g(\infty)$ are the glass transition temperature of the PS thin film with thickness d , and bulk PS, respectively. Keddie⁴² computed the characteristic length (A) for PS to be $A = (3.2 \pm 0.6 \text{ nm})$ and the exponent $\delta = 1.8 \pm 2$. It was noted that the characteristic length, A is not molecular weight dependent, and the equation is not associated with chain dimensions. Since T_g values were estimated for the swollen polymer films in **Section 2.2.5**, theoretical glass transition measurements are calculated at different film thicknesses using **Equation 2.23**.

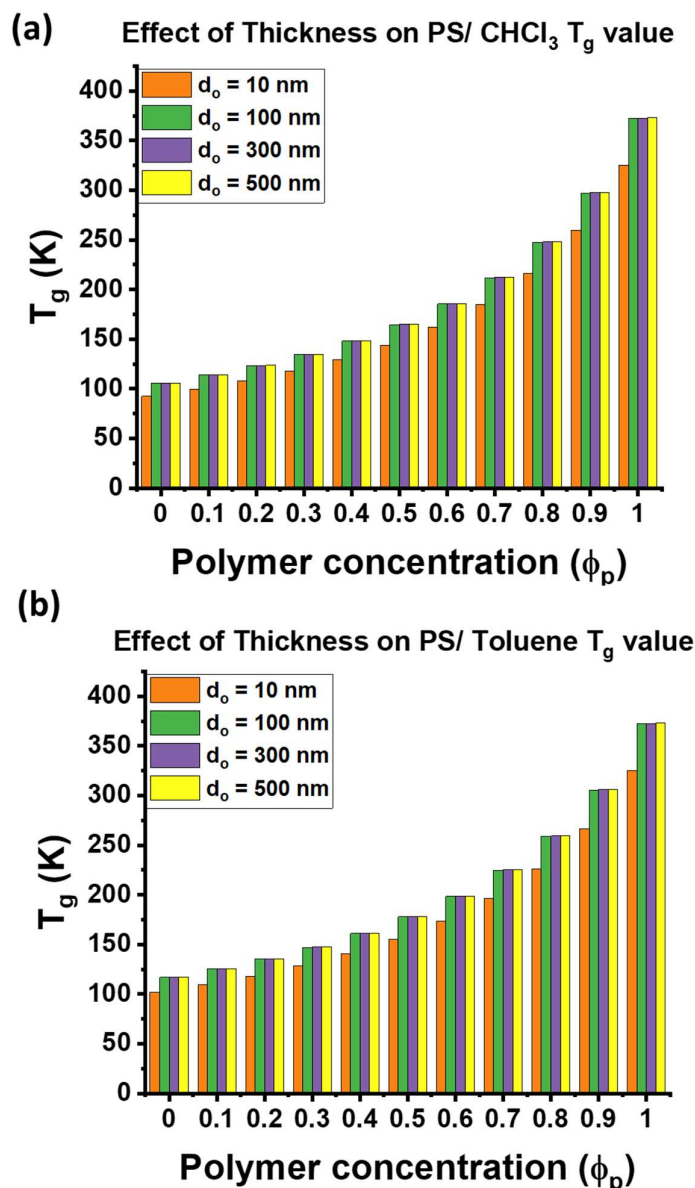


Figure 2.9 Comparison of T_g values for PS bulk PS thin film films at different thicknesses of 10,100, 300 and 500 nm for (a) PS/CHCl₃ and (b) PS/toluene.

Figure 2.9 shows that the change in thickness of the PS film shows very little/no change in the polymer film T_g values (< 2 °C in the difference). Once the solvent is incorporated into the films, there is a significant decrease in T_g for chloroform and toluene, respectively. This data shows that for film thicknesses above 100nm, there are only minor variances in T_g values for PS thin films, with deviations typically less than 2 °C.

2.3 Viscoelasticity of Polymer Solutions

Polymer swelling is a potential route for assembling and changing polymer film morphology by decreasing the viscosity of the polymer film and so increasing its mobility. This method has shown significant viability in patterning block-copolymer films producing feature sizes sub-25 nm^{44–46}. Here, we discuss the approach of plasticising a homopolymer film that can be templated by strictly controlling the swelling ratio. The polymer solution dynamics are factors that are critical for understanding polymer mobility for droplet templating. It has been reported that nucleation and growth of droplets can be enhanced on soft material when at the dew point⁴⁷. From this interpretation, the viscoelasticity of the film must be studied to identify whether specific polymer dynamics are required to deform the thin film and produce well-ordered porous arrays.

2.3.1 Rheological Analysis

Rheology is the science of deformation of a material and focuses on the viscosities of different fluids i.e the resistance of the fluid to deform and change its shape. Since water droplets will deform the film, it is essential to characterise and carry out theoretical analysis to understand the flow of swollen polymer films at high swelling ratios. Fluid rheologies are characterised by the shear stress and rate of a fluid. The shear rate is the velocity rate change when one layer of fluid passes over another adjacent layer. The shear stress is the force applied to the material and is calculated using **Equation 2.24**.

$$\tau = \frac{F}{A} \quad [\text{Equation 2.24}]$$

Where τ is the shear stress, F is the applied force, and A is the cross-sectional area of the fluid. From understanding the effects of shear stress on shear rate, solutions can be characterised with respect to their flow, as illustrated in **Figure 2.10**.

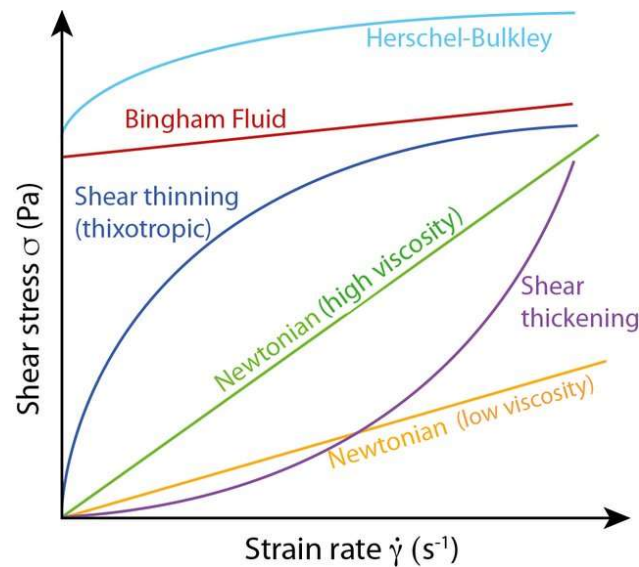


Figure 2.10 Fluid rheology characterised by shear rate and stresses⁴⁸.

These characteristics are:

1.) *Newtonian flow*

- a linear relationship between shear rate and flow i.e water

2.) *Shear Thinning*

- viscosity decreases with increasing shear stress i.e paint

3.) *Shear Thickening*

- viscosity increases with increasing shear stress i.e corn-starch/water mixture

4.) *Bingham Fluids*

- a rigid body at low shear stress and a viscous fluid at high e.g. toothpaste

5.) *Herschel- Bulkley*

- a complicated non-linear relationship between the shear stress and strain

In most polymeric systems, the fluid has shear-thinning properties i.e. the fluid's viscosity decreases with increasing shear stresses. Disentanglement of polymer chains is the cause of shear thinning. At low shear rates (also known as zero-shear viscosity), the viscosity will remain constant and only deviate at high shear rates.

2.3.2 Polymer Concentration and Molecular Weight

Random coils of polymer chains (composed of blobs (a “g” number of monomers)) can be used to explain the various types of solvent-polymer effects following De Gennes’ “blob” theory⁴⁹. The polymer coils (blobs) positional structure and interfacial morphology can be characterised for suitable solvents as a function of polymer concentration (ϕ_p), as illustrated in **Figure 2.11**.

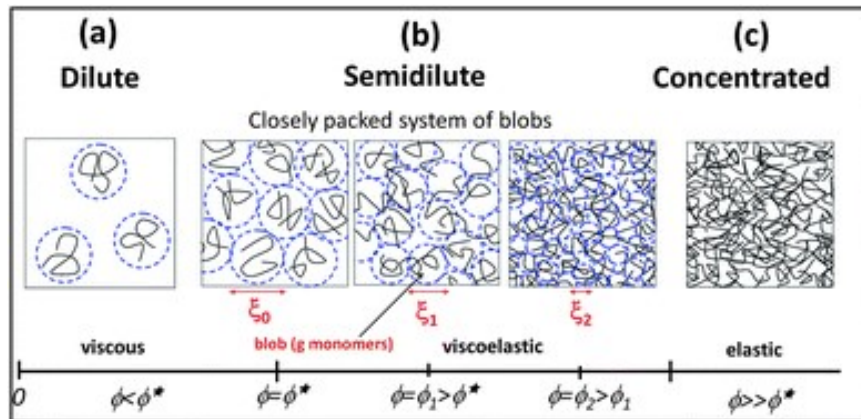


Figure 2.11 De Gennes’ Blob Analysis for Dilute and Concentrated Polymer Regimes⁴⁹.

In the dilute regime, the polymer is viscous at low concentrations ($\phi < \phi^*$) and the coils are separated from one another. At the semi-dilute regime, there is an overlap threshold ($\phi = \phi^*$), where polymer coils begin to overlap, resulting in close packing. Concerning the coil's size (ζ), there is a decreasing trend for the increase of polymer concentration. At large entanglements (concentrated), the coil size is negligible. The rheology of polymeric fluids can be categorised with respect to their concentration and molecular weight as proposed by Graessley *et al.*⁵⁰.

The regimes are broken down into 5 categories as shown in **Figure 2.12**.

- 1.) Dilute
- 2.) Concentrated, not entangled
- 3.) Semi-dilute, not entangled
- 4.) Semi-dilute, entangled
- 5.) Concentrated, entangled

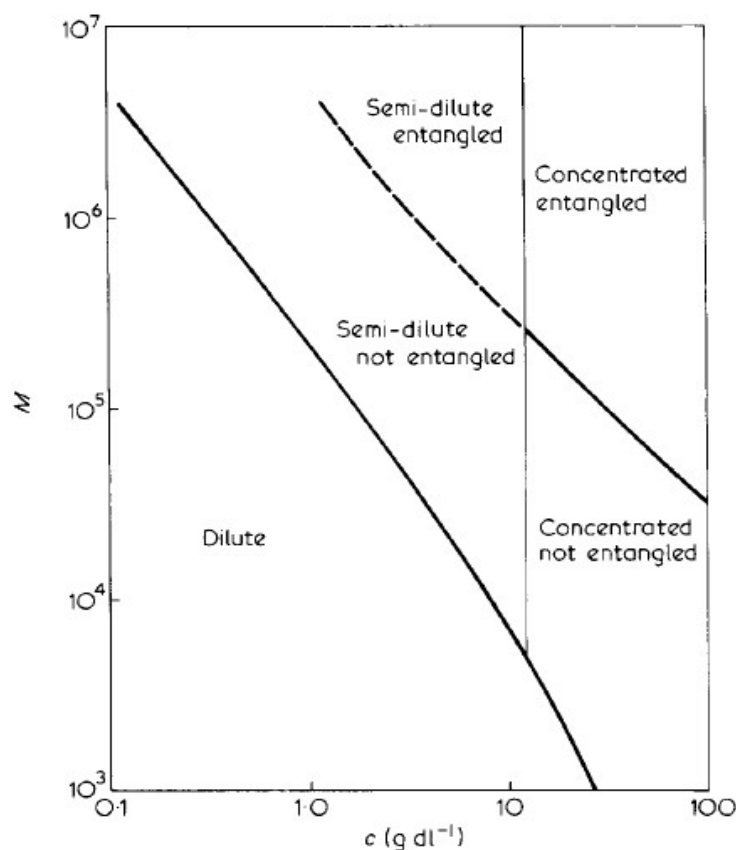


Figure 2.12 Concentration vs Molecular Weight – Polymer concentration regimes.⁵⁰

The critical molecular weight (M_c) is the specific molecular weight that causes reptation and entanglements in polymer solutions⁵¹. Reptation is defined as the entanglement of polymer chains in concentrated solutions and was first proposed by de Gennes in 1971⁵². Polymers with significantly low molecular weights should not entangle in the undiluted state as their zero-shear viscosity increases only slightly according to the principle of Bueche⁵³. Different models can represent the different regimes of polymer solution rheologies concerning the solvent quality effects and concentration of the polymer solution as illustrated in **Figure 2.13**⁵⁴.

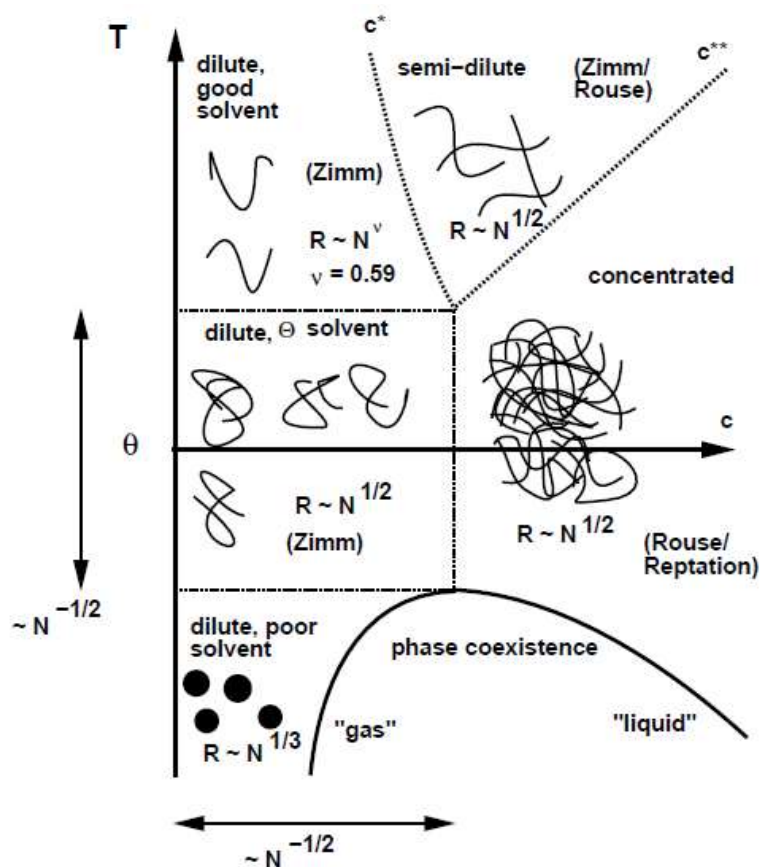


Figure 2.13 Illustration showing the various polymer-solvent interactions in respect to (C) concentration, (T) temperature and ($\sim N$) polymer chain length⁵⁴. Where R is the size of the chain (vector-vector), θ is a theta solvent, c^* and c^{**} is the critical entanglement and highly concentrated entanglement concentration respectively.

Burkhard also shows the various modes to identify the specific type of statistical systems in understanding rheology³⁸. Since the PS system is in the semi-dilute regime (swollen film), the Zimm model³⁹ can be used to obtain an approximation for the rheology of the swollen thin polymer film. This provides evidence that in a semi-dilute regime (using a suitable solvent) the solution follows Zimm/Rouse behaviour giving rise to **Equation 2.25**.

$$R \sim N^{\frac{1}{2}}$$

[Equation 2.25]

Where R is the generic soft matter size and N is the polymer chain length since there is an overlap between Rouse and Zimm behaviour.

2.3.3 Polystyrene Viscosities

Viscosities of solution can affect the breath figure method in a series of ways, as reported by Wong in 2006⁵⁵. It was reported that:

- 1.) In conventional BF methods, the viscosity of the polymer solution increases in time as the drop cast method evaporates solvent increasing polymer concentration and increasing the solution viscosity.
- 2.) An increase in the viscosity weakens the conventional forces in the solution and is not beneficial for packing the water droplets.
- 3.) Increasing the solution viscosity can hinder the growth of the water droplets at an earlier stage.
- 4.) The increasing viscosity of solution can impact the continuity of the water droplets sinking into the polymer solution

Since soft surfaces have long relaxation times, water droplets can form wetting ridges⁵⁶ as, shown in **Figure 2.14**.

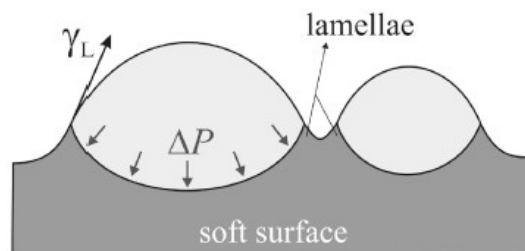


Figure 2.14 Schematic showing the wetting ridges that form by two droplets on deforming a soft surface. They prevent the liquid drops from coalescing/ merging.⁵⁶

Sokuler *et al.* describes that the Laplace pressure (ΔP) compresses the film, forming a wetting ridge that restricts the coalescence of droplets⁵⁶. By reducing the viscosity of the solution, these wetting ridges can decrease water droplet coalescent events by reducing friction. This friction is seen to increase with increased film viscosity.

Volatile PS solutions can be challenging to measure at room temperature due to rapid evaporation. Testing at low isobaric pressure would be needed to measure the solution's viscosity⁵⁷. Jarusuwannapoom *et al.* measured PS solution viscosities using a Brookfield DV-III programmable viscometer. The research aimed to electro-spin polystyrene fibres from a series of PS/ solvent solutions⁵⁸. PS molecular weights of 119 kg mol^{-1} with a polydispersity index (PDI) of 2.51 were used in this study. PS Concentrations used were 10, 20 and 30 % w/v, with viscosity measured in centipoise (cp) as presented in **Figure 2.15**.

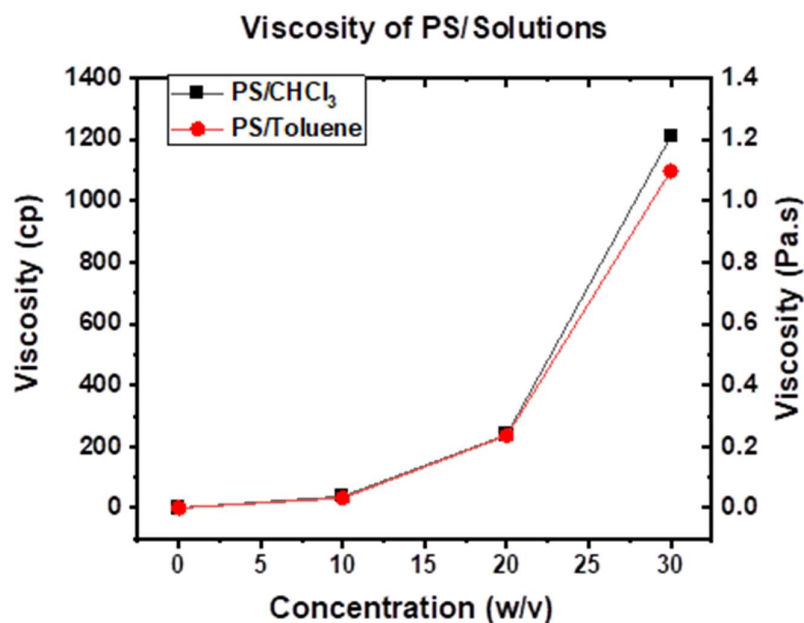


Figure 2.15 PS Solution dynamic viscosity.⁵⁸

The viscosity of both PS/toluene and PS/CHCl₃ show similar viscosities of up to 20 % w/v. There is a slight deviation in these values of above 30 % w/v. This indicates that both solvents follow a similar trend at these concentrations. The effect of molecular weight can also affect the viscosity of solutions, as discussed by Poh *et al.*⁵⁹. PS/toluene solution's zero-shear viscosities were measured to identify the effects of long chains in the polymeric solution. Molecular weights, ranging from 8.7×10^3 kg mol⁻¹ to 2.4×10^6 kg mol⁻¹ of polystyrene, change the solution's zero-shear viscosity, as presented in **Figure 2.16**, where the swelling ratio was extrapolated as a function of the concentration of the solution.

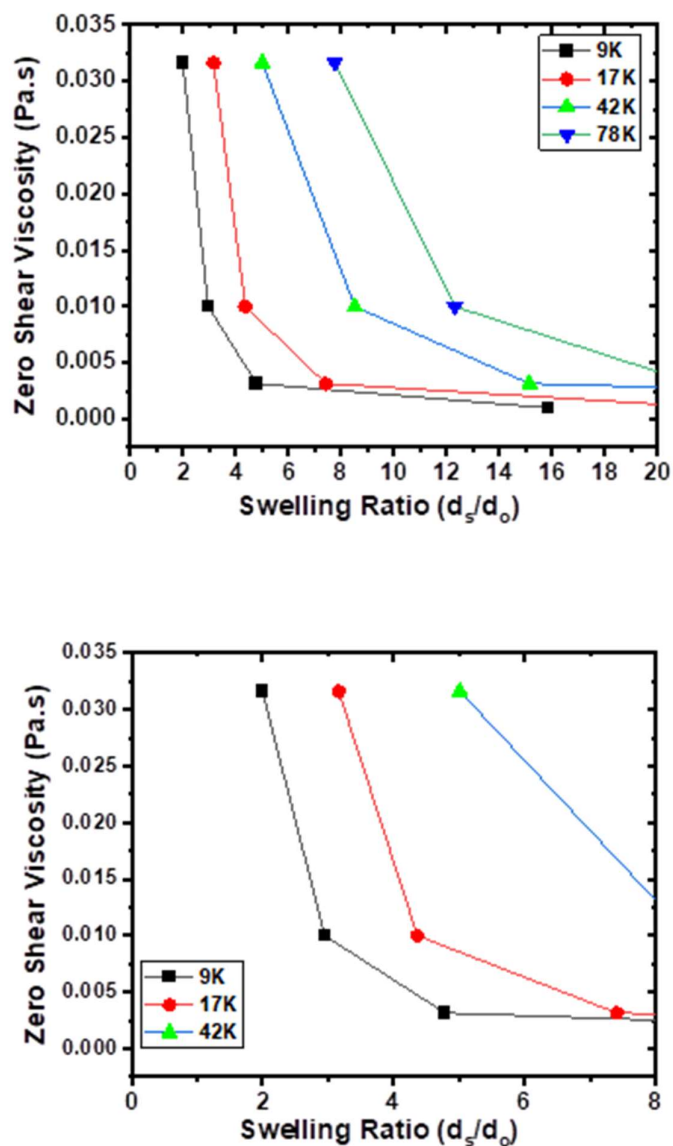


Figure 2.16 Poh's effects of PS molecular on the viscosity of PS/toluene solution⁵⁹.

Swelling ratio ranging from 0- 20 (top) and Swelling ratio ranging from 0- 8 (bottom).

The viscosity of PS/toluene solutions increases by increasing the polymer molecular weight. Since the 17 kg mol⁻¹ PS system is the primary molecular weight discussed in this thesis, the following swelling ratios achieve viscosities from 0 – 0.032 Pa s, as shown in **Table 2.3**.

Table 2.3 Viscosity measurements for PS/Toluene.⁵⁹

Mixture	PS/Toluene		
Swelling Ratio	3.16228	4.36516	7.4131
Viscosity (Pa s)	0.03162	0.01	0.00316

Due to the high evaporation rates of CHCl_3 , no literature values for highly concentrated PS solutions are present. Therefore, using the swelling ratio of polymer films is a more viable method to determine the optimal solvent penetration to deform and plasticise the film.

2.4 Droplet Shape and Wettability

2.4.1 Introduction to Wettability

The droplet shape and its morphology are critical to the breath figure (BF) process and have not been studied extensively for a swollen polymer film. By understanding and predicting the shape of droplets on the surface of swollen polymer films, further insight into how the droplet interacts with (i) the solvent, (ii) the polymer and (iii) the substrate can be obtained. Furthermore, by interpreting the surface energies and interfacial interactions between the 3 components in the system, the mechanism of the breath figure at the dew point of condensation can be assessed. Neumann-Young's equation is a valuable method for identifying the surface tension of materials using probe liquids with known surface energies⁶⁰. Surface tension is the main factor that affects the shape of droplets on a surface; however, when there are critically small length scales, gravitational forces are negligible and surface energies dominate. Young's equation can be used to discuss the energy differences of different substrates by using the Neumann triangle, where all forces are in equilibrium with one another, as shown in **Equation 2.26**.

$$\cos \theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} \quad [\text{Equation 2.26}]$$

Where γ_{SV} , γ_{SL} and γ_{LV} are the interfacial tensions between solid-vapour, solid-liquid, and liquid-vapour, respectively. This method is most useful for interpreting the spreading of water droplets and whether surfaces will be hydrophobic or hydrophilic if they are relatively flat. **Figure 2.17** illustrates how to measure the contact angle on flat surfaces following the Neumann rule where all forces are equal.

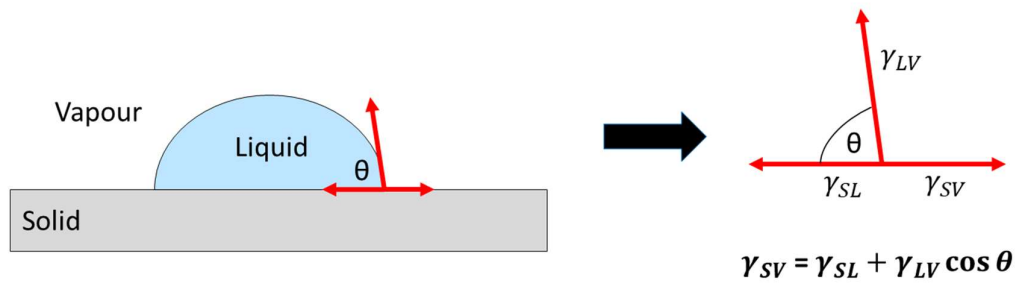


Figure 2.17 Neumann-Young's Approach.

Young's method assumes that the surface is entirely flat ($R = 1$) and can determine the surface energies of materials by measuring the contact angle of the probe droplet. The spreading behaviour of the droplet can, thus, identify the wetting properties of flat surfaces as shown in **Figure 2.18**, where the wetting of a surface is where the contact angle is less than 90° (**Equation 2.27**), and a non-wetting surface is more than 90° (**Equation 2.28**).

$$\gamma_{SV} > \gamma_{SL} \quad \theta < 90^\circ \text{ (Wetting)} \quad [\text{Equation 2.27}]$$

$$\gamma_{SV} < \gamma_{SL} \quad \theta > 90^\circ \text{ (Non - wetting)} \quad [\text{Equation 2.28}]$$

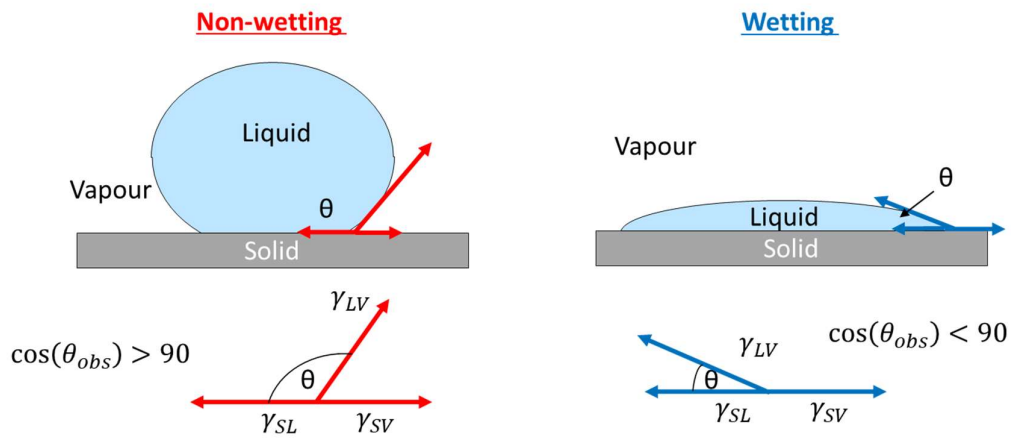


Figure 2.18 Schematic of spreading *via* the Young's equation.

2.4.2 Wenzel Equation

Young's measurement is an invaluable method for estimating the contact angle of smooth surfaces. However, in 1936 Wenzel proposed a method of measuring contact angles on rough surfaces⁶¹. However, in the real world, most substrate surfaces are not flat and roughness can affect the apparent contact angle. Therefore, roughness (R) is measured as presented in **Equation 2.29**.

$$R = \frac{Area}{Area_{flat}} > 1 \quad [\text{Equation 2.29}]$$

Where R is the roughness of the substrate, “Area” is the observed area including the roughness and “Area_{flat}” is the assumed area if the substrate has an R value of 1 (ultra-smooth). The substrate's R value can impact the surface contact angles as the probe liquid can occupy the valleys and troughs of the rough material in a non-wetting case, resulting in a higher observed contact angle than the real contact angle, as illustrated **Figure 2.19**.

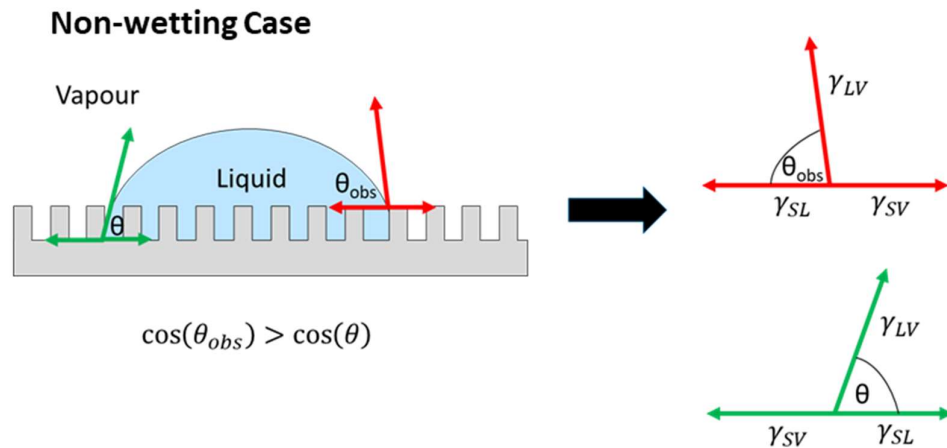


Figure 2.19 Schematic of Wenzel Roughness Affecting the Contact Angle for non-wetting cases.

For the wetting case, the water droplet fills the troughs and valleys, resulting in a lower observed contact angle, as presented in **Figure 2.20**.

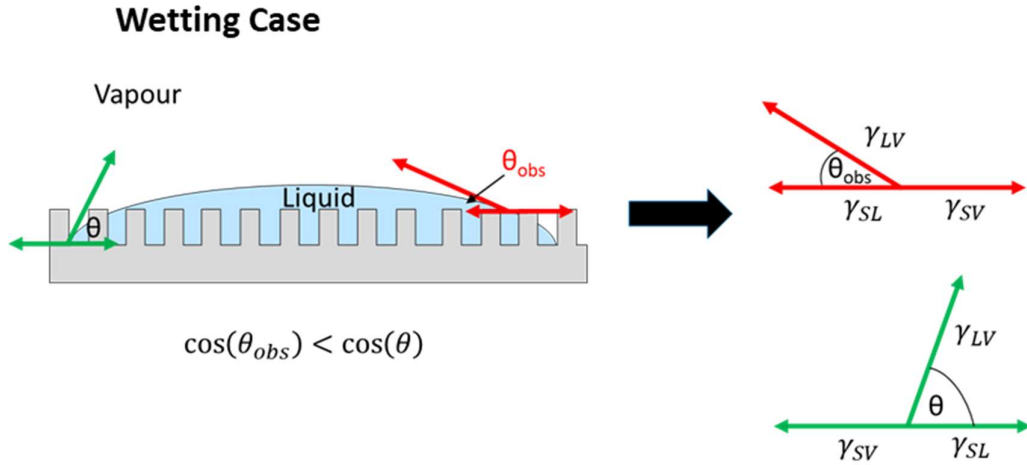


Figure 2.20 Schematic of Wenzel Roughness Affecting the Contact Angle for wetting cases.

In the wetting case, the observed contact angle is generally higher than the observed and for the non-wetting, the observed contact angle is less. Therefore, the Wenzel model can determine the roughness effect for each wetting criteria by computing the substrate roughness, R , as shown in **Equation 2.30**.

$$\cos \theta_{obs} = R \cos \theta \quad [\text{Equation 2.30}]$$

2.4.3 Cassie-Baxter Equation

In 1944, the Cassie-Baxter model was developed to interpret contact angles for porous, chemically heterogeneous surfaces or materials⁶². The liquid does not occupy the valleys

and troughs due to air gaps between the fluid and the substrate. Contact angles can be calculated using **Equation 2.31**.

$$\cos \theta_c = \sigma_1 \cos \theta_1 + \sigma_2 \cos \theta_2 \quad [\text{Equation 2.31}]$$

Where θ_c is the observed Cassie-Baxter contact angle, σ_1 and σ_2 are the fractional areas for the heterogeneous surface. Since the polymer film is homogenous i.e., only one polymer species present, the fractional area is $\sigma_2 = 1 - \sigma_1$. Since the aim is to template polymer films with droplets and produce porous materials, this equation will be used as a method to characterise the wettability of the templated porous films.

2.4.4 Water Saturation Theory and Analysis

Antoine saturation curves for water were investigated to identify the temperatures needed to induce condensation, where the water is at its dew point, i.e. condenses onto the thin film. The Antoine equation (**Equation 2.32**) is utilised to study the saturation limits for water at different temperatures.

$$\log_{10}(P_{sat}[kPa]) = A - \frac{B}{T[^\circ C] + C} \quad [\text{Equation 2.32}]$$

Where T is the absolute temperature and Antoine constants A, B and C are 8.071, 1730 and 233.4, respectively. This curve is useful in identifying the saturation pressure of water vapour when at equilibrium with its liquid state. Saturation pressure will change with increasing temperature, as stated by the Gas Laws⁶³. Saturated water conditions can thus be

driven by reducing the temperature of the material and allowing condensation of water at low temperatures. The proportionalities between the two temperatures in a system can identify where condensation and nucleation of water drops can occur from cooling to the critical dew point. Identification of the critical dew point can be measured by calculating the saturated pressure values of water at various temperature differences. This is defined as the point on the curve where the water can be converted from liquid to vapour at a specific temperature and pressure, as shown in **Equation 2.33**.

$$RH \% = \frac{Act VP}{P_{sat}} * 100\% \quad \text{[Equation 2.33]}$$

ActVP is defined as the actual vapour pressure, RH% is the relative humidity and P_{sat} is the saturated pressure measured by the Antoine equation at a specific temperature (**Equation 2.3**). **Table 2.4** shows the calculations for measuring the actual vapour pressure of water at specific temperatures and relative humidities using **Equation 2.33**.

Table 2.4 Calculations showing AcVP at different Temperatures.

Temperature (°C)	P_{sat} (kPa)	Act VP (kPa)		
		RH = 20%	RH = 50%	RH = 80%
5	0.87	0.17	0.43	0.69
10	1.22	0.24	0.61	0.98
15	1.70	0.34	0.85	1.36
20	2.33	0.47	1.16	1.86
25	3.16	0.63	1.58	2.53

A graphical representation of the change in actual vapour is shown in **Figure 2.21**.

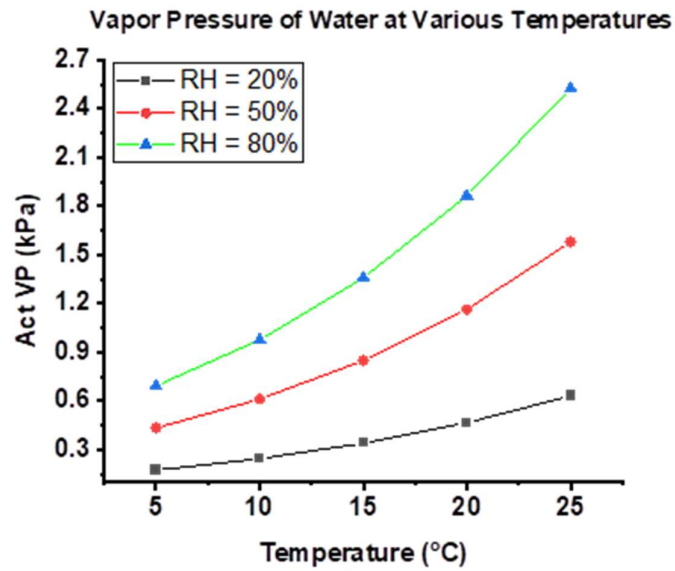


Figure 2.21 The effects of Temperature on the actual vapor pressure of water (ActVP). Predicted using Equation 2.33.

The determination of the critical dew point ($\text{Max } T_{\text{dew}}$) can be measured by measuring the actual vapour of water pressure in the system. The minimum temperature requirements needed to induce condensation are presented in **Figure 2.22**, where various RH values (20 %, 50 % and 80%) are assessed.

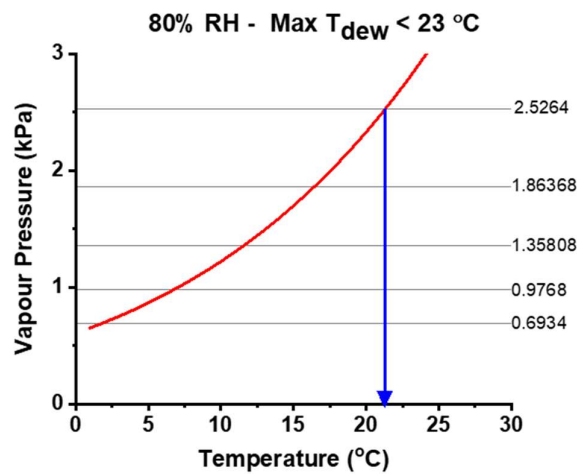
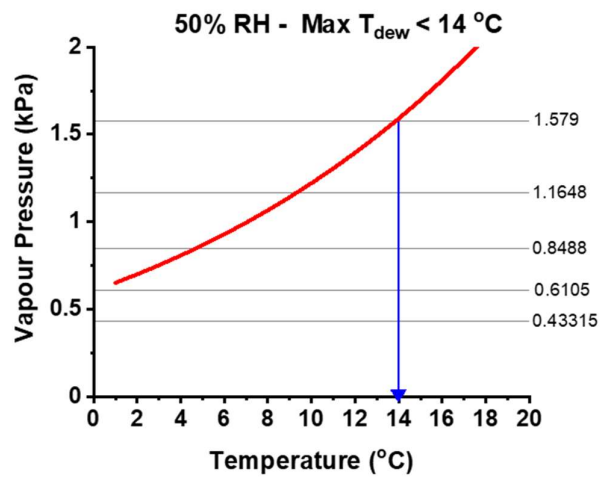
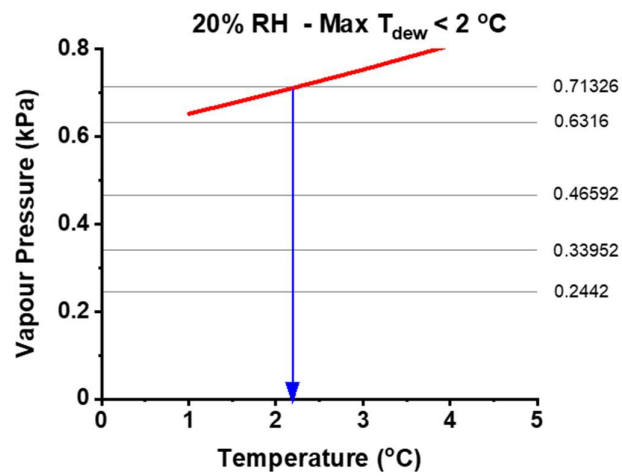


Figure 2.22 Condensation Limits at different vapour pressures and temperature.

The data shows that high RH% values are needed to induce condensation at temperatures close to the ambient. For example, 20, 50, and 80% RH require maximum dew temperatures (T_{dew}) of 2, 14, and 23 °C, respectively. This indicates that adequate RH values larger than 50 % are needed at 10 -15 °C.

2.5 Estimating Droplet Morphology

When explaining intricate systems where there are 2 solvents, unknown surface energies can be measured using the method proposed by van Oss, Chaudhury and Good (vOCG)⁶⁴. Here, a framework can be built by computing and identifying the surface tensions of media and their interfacial forces that act at SLV (solid-liquid-vapour) boundaries for numerous types of polymer-solvent systems.

The Lifshitz van der Waal (LW) forces and the acid-base contributions are calculated to measure the surface tensions of one phase. For any given phase, the polar contribution is measured in surface energies where the acid is the positive (+) and the base is the negative (-) component, as shown in **Equation 2.34**.

$$\gamma_1^{total} = \gamma_1^{LW} + 2\sqrt{\gamma_1^+ \gamma_1^-} \quad \text{[Equation 2.34]}$$

Where γ_1^{total} is the overall total surface energy, γ_1^{LW} is the Lifshitz surface energy and $\gamma_1^+ \gamma_1^-$ are the polar contributions from Lewis acid-base behaviour. Here, the charges in the acid-base component are 0, confirming that van der Waal forces dominate the surface tension of the fluid. The interfacial tensions between 2 phases can be measured by knowing the LW and acid-base terms of the 2 solvent systems. Here, the (1) polymer-solvent and (2) water interfacial forces are measured giving us a general estimate of the interfacial energies of the 2 condensed phases as shown in **Equation 2.35**.

$$\gamma_{12}^{total} = \gamma_1^{LW} + \gamma_2^{LW} - 2\sqrt{\gamma_1^{LW} \gamma_2^{LW}} + 2\sqrt{\gamma_1^+ \gamma_1^-} + 2\sqrt{\gamma_2^+ \gamma_2^-} - 2\sqrt{\gamma_1^+ \gamma_2^-} - 2\sqrt{\gamma_2^+ \gamma_1^-} \quad \text{[Equation 2.35]}$$

By following Preston *et al.*'s method⁶⁵ for investigating the effect of lubricant-infused surfaces (LIS), the effect of 3-phase interactions can be assessed. The criteria identified by Preston *et al.* are used as a method to interpret the interaction of water droplets on solvent-swollen polymer films.

2.5.1 Estimation of Wetting using Surface Energy Analysis

The surface energy, dispersive forces, and Lewis acid-base values of the material and solvents are presented in **Table 2.5**.

Table 2.5 Surface Energy Table of Solvents and Materials used.

Material/ Solvent	Dispersive (γ_{LW}) (mN m ⁻¹)	Lewis Acid (γ^+ / γ^-) (mN m ⁻¹)	Overall (mN m ⁻¹)
Water ⁶⁶	21.8	25.5 / 25.5	72.8
CHCl₃ ⁶⁷	27.2	3.8 / 0	27.2
Toluene ⁶⁸	28.5	0/0.72	28.5
Silicon with native oxide (SiO₂) ⁶⁹	38.6	4 / 34.0	61.9
Polystyrene (PS) ⁷⁰	41.9	0.08/0.15	41.9

Surface energies dictate the overall wettability of a substrate depending on its dispersive forces and acid-base interactions. Therefore, all surface energy data was taken from experimental contact angle data^{66–70}. Since silicon is the substrate of choice, its oxide will be considered the substrate material for assessing the interaction of solvents and water. This is because silicon can be easily oxidised to silica (SiO₂) in the presence of O₂⁷¹.

2.5.2 Three-Phase Systems

The solvent-water-silicon model is the simplest model for investigating the effects of water droplet morphologies on lubricated-infused chloroform silicon surfaces with a native oxide layer. CHCl_3 has little to no acid-base interaction, thus indicating that van der Waal forces dominate, giving an overall surface tension of 27.2 mN m^{-1} ⁶⁷. CHCl_3 /water has an interfacial tension of $\Delta\gamma_{dl} = 31.6 \text{ mN m}^{-1}$ for the two liquids calculated using **Equation 2.35**. Criteria 1 and 2 first investigate the effects of only the 2-liquid media, ignoring the substrate interactions from the model, as shown in **Figure 2.23**.

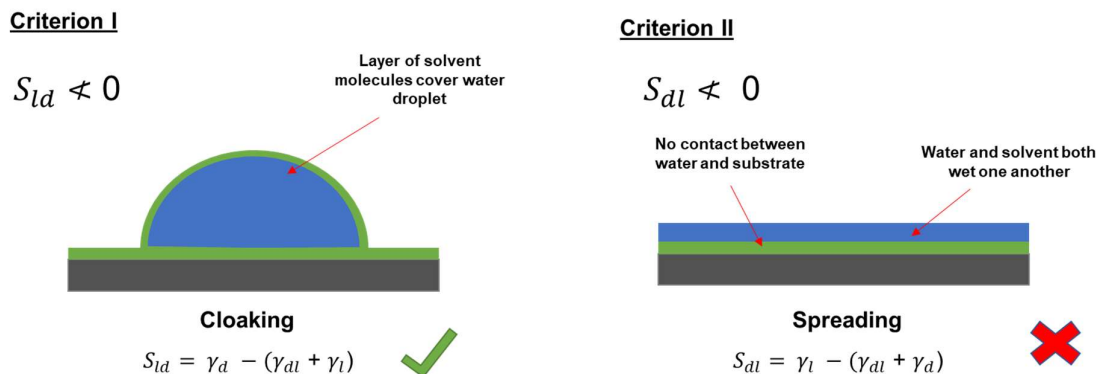


Figure 2.23 Schematics of criterion 1 and 2 illustrating the effects of $\text{H}_2\text{O}/\text{CHCl}_3$ interaction.

Criterion 1 ($S_{ld} \not\leq 0$) was calculated to be $14.0 \text{ mN m}^{-1} \not\leq 0$, indicating that the solvent will interact with the water droplets and the substrate surface, and mask the droplet from the vapour phase, thus, encapsulating the droplets. Criterion 2 ($S_{dl} \not\leq 0$) was calculated to be $-77.2 \text{ mN m}^{-1} < 0$; thus, criteria 2 can be rejected, indicating that the water will not produce a thin film on top of the chloroform surface and thus droplet beads will interact with the CHCl_3 , and minimal spread behaviour will occur. Both liquids are immiscible. Criteria 3 and 4 indicate how roughness can influence the interfacial energies at 3-phase contact lines, as illustrated in **Figure 2.24**.

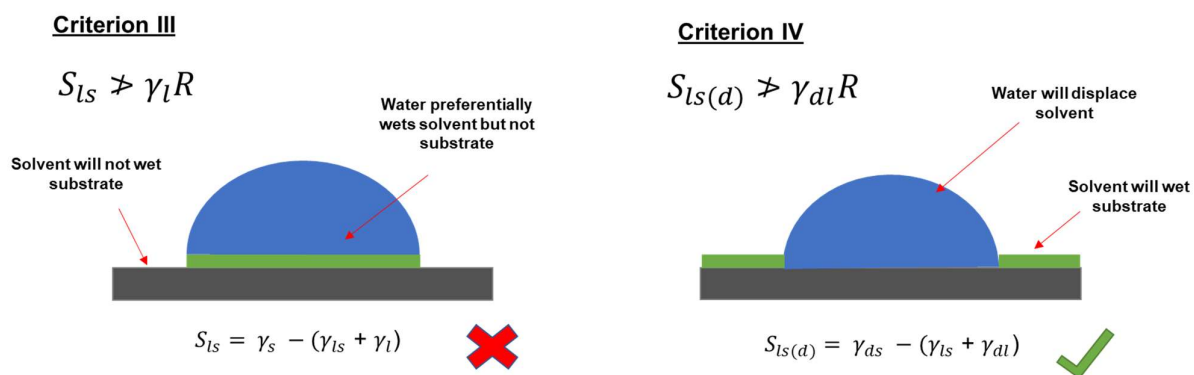


Figure 2.24 Schematics of criterion 3 and 4 illustrating the effect of H₂O/ CHCl₃ interaction.

In these conditions, the solvent-solid interfacial energies were calculated to be $\Delta\gamma_{ls}=1.59$ mN m⁻¹, indicating that the solvent will preferentially wet the silicon surface. When the water droplet-substrate interfacial energies are a negative value of $\Delta\gamma_{ds} = -2.37$ mN m⁻¹, there are strong acid-base interactions and high adsorption energies between the water and the SiOx surface. Upon observation of criterion 3, the silicon surface's roughness values range from 1-1.1 as it is generally flat, indicating that silica (SiO₂) will also be flat. Criterion 3 is as follows ($S_{ls} \not\geq -\gamma_l R$) establishing that the droplet will only wet the solvent film and not the substrate if the spread of solvent-liquid is not greater than the impact of roughness on $-\gamma_l$. S_{ls} is computed to be 33.1 mN m⁻¹, whereas $-\gamma_l R$ is evaluated to be -27.2 for a roughness value of $R = 1$. Since $S_{ls} > -\gamma_l R$, criterion 3 will be rejected, thus indicating that the droplet will want to wet the substrate preferentially. Criterion 4 illustrates the opposite effect: the droplet will displace the solvent and interact with the substrate surface. Criterion 4 is as follows ($S_{ls(d)} \not\geq -\gamma_{dl} R$) where $S_{ls(d)}$ is computed to be -35.6 mN m⁻¹ showing a strong spreading behaviour between the 3-phases. Since this value is very low and $-\gamma_{dl} R$ is computed to be -31.6 mN m⁻¹ for $R=1$, identifying that $S_{ls(d)} \not\geq -\gamma_{dl} R$ is accepted. Furthermore, analysis was carried out in the roughness range 1-1.1. A range of R from 1-1.1 was computed and confirmed which spreading will always dominate when on a silicon surface. A summary of the two spreading behaviour limits is shown in **Figure 2.25**.

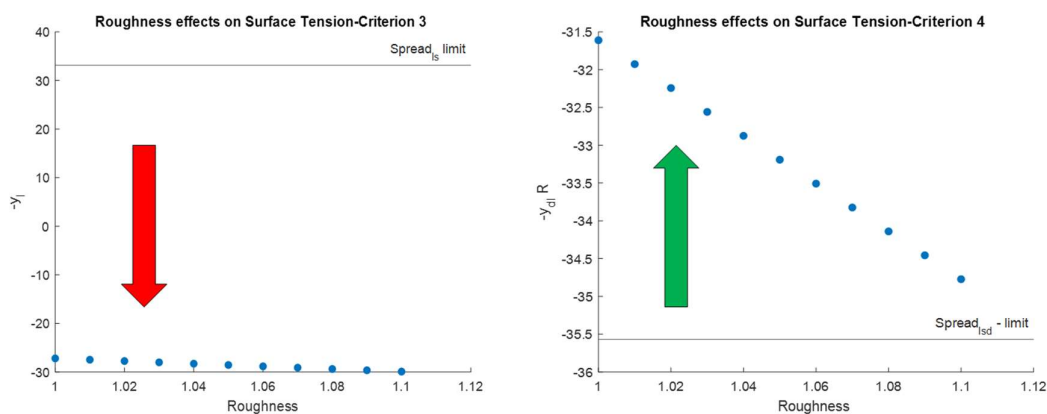


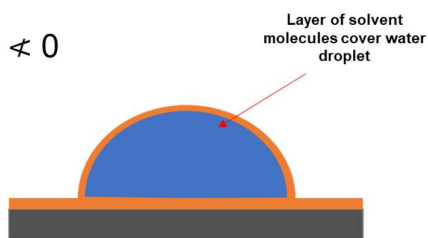
Figure 2.25 Graph illustrating (a) the spread limit and $-\gamma_l R$ showing the rejection of criterion 3 and (b) the spread limit and $-\gamma_{dl} R$ illustrating that criterion 4 is accepted for CHCl_3 , water and SiO_2 . All R-values of range from 1-1.1.

i Water/ Toluene/ SiO_2

The overall surface tension of toluene is 28.5 mN m^{-1} . From computing the 2 surface tensions of water and toluene, the water-toluene interface is calculated to be 42.9 mN m^{-1} . Criterion 1 describes that the solvent will cover the droplets resulting in a cloaking effect. Criterion 2 explains the opposite effects where a thin film of water spreads across the solvent and does not bead up into droplets. Both criteria are illustrated in **Figure 2.26**, where the water droplet sits on top of a toluene lubricated surface.

Criterion I

$$S_{ld} \not\leq 0$$



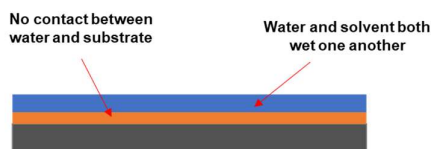
Cloaking

$$S_{ld} = \gamma_d - (\gamma_{dl} + \gamma_l)$$



Criterion II

$$S_{dl} \not\leq 0$$



Spreading

$$S_{dl} = \gamma_l - (\gamma_{dl} + \gamma_d)$$



Figure 2.26 Schematics of criterion 1 and 2 illustrating the effects of $\text{H}_2\text{O}/$ toluene interaction.

To fulfil these criteria, S_{ld} (spreading co-efficient of the droplet on a toluene lubricated surface) must not be less than 0. This is measured as 1.42 mN m^{-1} , indicating that $S_{ld} \neq 0$ shows that the droplet will be masked by the solvent and follows similar behaviour to the chloroform lubricated surface. Criteria 3 and 4 also show similar behaviour and are illustrated in **Figure 2.27**.

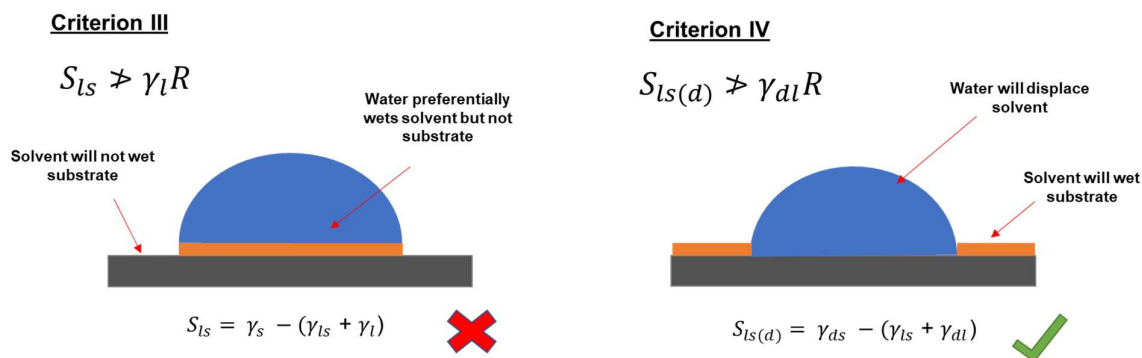


Figure 2.27 Schematics of criterion 3 and 4 illustrating the effect of PS/toluene interaction.

By measuring the effect of roughness of the silica surface, the water droplet will follow the same behaviour for toluene as it did for chloroform for a silicon native oxide surface with a surface energy of 41.9 mN m^{-1} , as shown in the graphs in **Figure 2.28**.

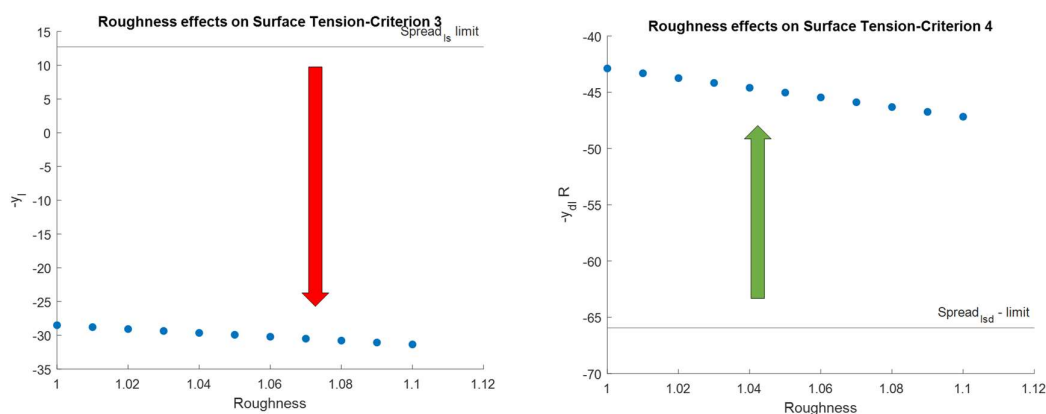


Figure 2.28 Graph illustrating (a) the spread limit and $-\gamma_l R$ showing the rejection of criterion 3 and (b) the spread limit and $-\gamma_{dl} R$ illustrating that criterion 4 is accepted for CHCl_3 , water and SiO_2 . All R-values of range from 1-1.1.

To summarise, this method gives us a useful indication of how the surface energies of 3-phase systems can be predicted for solvent-water-substrate surfaces. In the next section, polymer properties will be discussed, showing how this technique can be further adapted to polymer melts and how they interact with droplets in an SLV system.

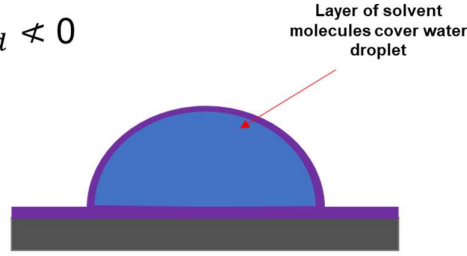
ii PS/ Water/ SiO_2

The polymer of interest in this study is polystyrene (PS), an aromatic, hydrophobic polymer. From the initial observation of this polymer system (p), the polymer's hydrophobic properties will influence the droplet shape and morphology of the droplet shape^{72,73}.

Dispersive forces dominate the surface tension of PS as it has little to no polar interactions due to the bulky phenyl groups in the polymer chains giving an overall surface energy of 41.9 mN m^{-1} ⁷⁰. Therefore, criteria 1 and 2 are rejected for a PS/ H_2O / SiO_2 , as shown in **Figure 2.29**.

Criterion I

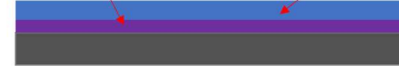
$$S_{ld} \neq 0$$

**Cloaking**

$$S_{ld} = \gamma_d - (\gamma_{dl} + \gamma_l)$$

**Criterion II**

$$S_{dl} \neq 0$$

No contact between
water and substrateWater and solvent both
wet one another**Spreading**

$$S_{dl} = \gamma_l - (\gamma_{dl} + \gamma_d)$$

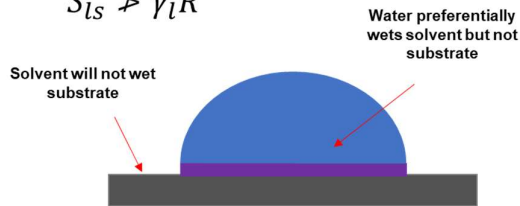


Figure 2.29 Schematics of criterion 1 and 2 illustrating the effects of H₂O/ PS interaction.

The polymer, PS will not interact with the water droplets (d). S_{ld} and S_{dl} are computed to be -17.0 mN m^{-1} and -78.4 mN m^{-1} , suggesting that the polymer will not interact with the water droplets since both $S_{ld}/S_{dl} < 0$. This is understandable as the polymer-water surface tension, $\Delta\gamma_{dp} = 47.7 \text{ mN m}^{-1}$, is high due to the polymer not wanting to interact with either the water or the hydrophilic surface. This results in the displacement of PS, resulting in the formation of porous, thin films as described in criterion 4, where the water will interact with the substrate surface as shown in **Figure 2.30**.

Criterion III

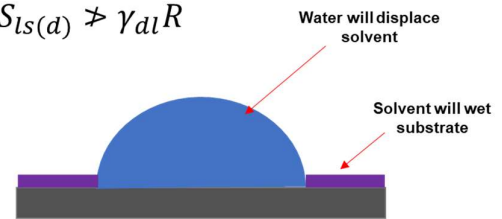
$$S_{ls} \neq \gamma_l R$$



$$S_{ls} = \gamma_s - (\gamma_{ls} + \gamma_l)$$

**Criterion IV**

$$S_{ls(d)} \neq \gamma_{dl} R$$



$$S_{ls(d)} = \gamma_{ds} - (\gamma_{ls} + \gamma_{dl})$$



Figure 2.30 Schematics of criterion 3 and 4 illustrating the effects of H₂O/ PS interaction.

To understand the influence of the substrate, criteria 3 and 4 can identify the water droplet morphology on a polymer melt. The same method in the previous section is applied where the criterion is accepted if the spread is not larger than the impact of roughness on the polymer surface tension calculated at $\gamma_p = -42.1 \text{ mN m}^{-1}$ for $R = 1$ and $S_{ls} = 1.04 \text{ mN m}^{-1}$. Since $S_{ls} > -\gamma_l R$ criterion 3 is rejected, indicating that the water droplet will only preferentially wet the hydrophobic polymer film. Furthermore, analysis was carried out for roughness 1-1.1 and all R-values were rejected. In contrast, criterion 4 was accepted due to the repulsive nature of PS and water. This criterion identifies that the water droplet will displace the polymer melt to interact with the substrate surface. Since the water has a great affinity for SiO_2 , it is evident that criterion 4 is the most predictable. A summary of the two criteria is illustrated in **Figure 2.31**, showing the limits on which criteria will occur.

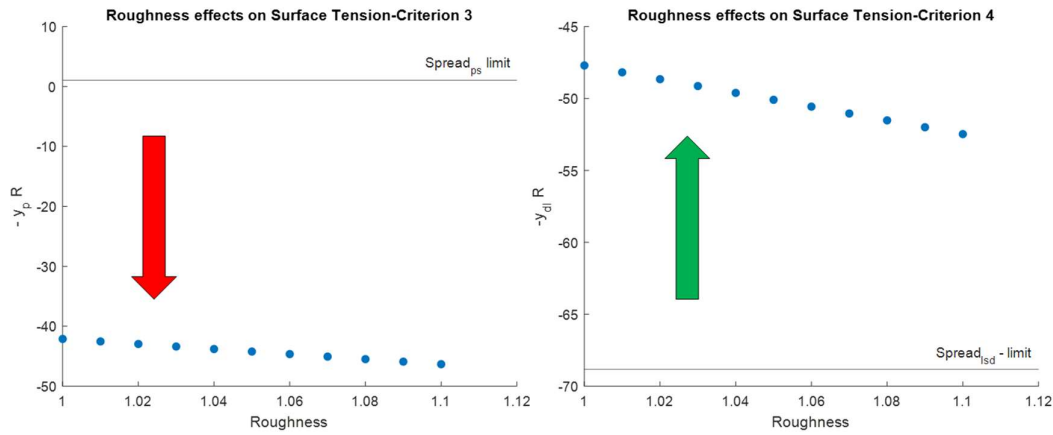


Figure 2.31 Graph illustrating (a) the spread limit and $-\gamma_p R$ showing the rejecting of criterion 3 (b) the spread limit and $-\gamma_p R$ to allow indicating that criterion 4 is accepted for PS, water and SiO_2 . All R values of range from 1-1.1.

Since PS and CHCl₃ have both shown evidence that both cases favour criterion 4, the droplet templating of a CHCl₃ swollen PS film will be displaced by the water droplet if it has enough mobility to move.

2.5.3 Elimination of Dewetting

For most systems, because of surface energy differences, coherent polymer films at substrates are thermodynamically less stable and represent the presence of kinetic barriers where phase separation or dewetting of the polymer occurs. Dewetting of polymer thin films has been characterised as a viscoelastic problem where the nucleation of holes can accelerate the destruction of thin films^{74–78}. Viscoelastic analysis of dewetting polymers has been studied thermally by producing a polymer melt at high annealing temperatures (above T_g) on flat substrates such as silicon⁷⁸. Suppressing polymer film dewetting on arbitrary substrates is a key motivation for developing advanced polymer processing techniques such as polymer metal infiltration⁷⁹ and producing well-controlled breath figures *via* droplet templating⁸⁰. The controlling parameter for film dewetting is the spreading coefficient, presented in **Equation 2.36**.

$$S = \gamma_{lv}(\cos \theta_e + 1) \quad \text{[Equation 2.36]}$$

Where γ_{lv} is the surface tension of the solution and θ_e is the contact angle of the solution droplet in contact with the supporting substrate and the solution's vapour. The solution film is intrinsically stable in the complete wetting regime ($S > 0$). In the partial wetting regime ($S < 0$), a critically unstable film thickness exists. The capillary length (κ^{-1}) and critical film thickness (e_c) can be estimated using **Equation 2.37** and **Equation 2.38**, respectively⁸¹.

$$\kappa^{-1} = \sqrt{\frac{\gamma}{\rho g}} \quad [\text{Equation 2.37}]$$

$$e_c = 2\kappa^{-1} \sin\left(\frac{\theta_e}{2}\right) \quad [\text{Equation 2.38}]$$

Where γ is the surface tension, ρ is the density and g is the gravitational constant. With $\kappa^{-1} \approx 1.6$ mm, an estimated value of $e_c \approx 195$ μm is calculated. This implies that the PS films are intrinsically unstable for a wide range of film thicknesses from micro to nanoscale.

PS droplets formed via a thermal dewetting process on clean hydroxylated SiO_x wafers exhibit a contact angle, measured by AFM, to be $\sim 7^\circ$ ⁸². The polymer and the surface's interaction are either affected by physisorption or chemisorption. Physisorption is considered a reversible process where unstable bonds are formed by weak van der Waal's forces⁸³. PS-OH has amphiphilic properties resulting in the hydroxyl groups favouring the SiO_x surface that has good adsorption with silanols⁸⁴. Chemisorption is where there is a strong bond between the substrate and the polymer that is either covalent or ionic, resulting in it being “chemically” bound to the substrate⁸⁵. A covalent bond is formed via a dehydration reaction where the PS-OH and silicon hydroxyl can bond together to form an epoxide⁷¹. This reaction binds the polymer to the substrate surface at the terminal end. It forms a brush-like structure, where the polymer is vertically aligned perpendicular to the substrate, as shown in **Figure 2.32**.

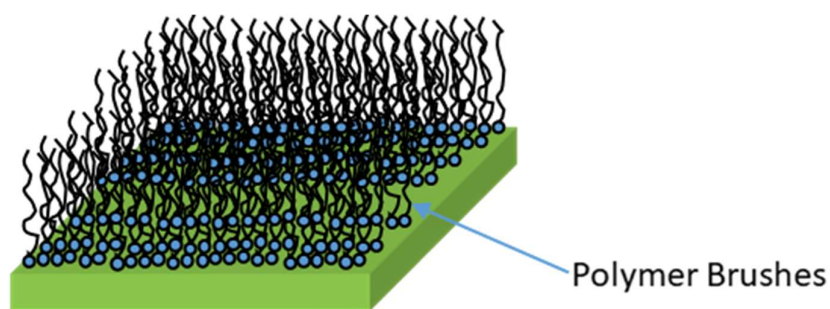


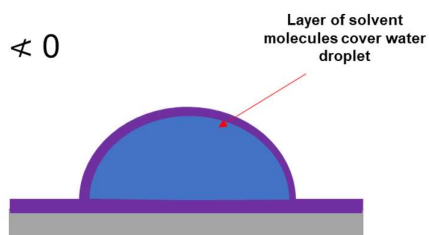
Figure 2.32 Illustration of polymer brushes bound to the substrate.

Several researchers have reported that tethering a brush to the surface can change the properties and stabilise the films sitting atop a brush of a similar chemical nature^{77,86,87}. When untethered chains are placed atop a well-defined tethered polymer, the brush and polymer can interpenetrate and influence the dynamics of the untethered polymer melt⁸⁸. Uger *et al.* concluded that the tethered chains not only slow down the brush dynamics but can also slow down the surface layers on top of the brush allowing for a more robust polymer film⁸⁸. The molecular weight of the brush is critical in stabilising the homopolymer in a viscous state. Sharma *et al.* identified that the critical molecular weight for auto-dewetting of a homopolymer on a brush is approximately $N_H > 0.5N_B$, where N is the polymerisation index for the homopolymer and the brush, respectively⁷⁷. Therefore, we propose that adding a brush to the substrate should improve the polymer swelling process and eliminate issues such as dewetting.

By carrying out the same procedure outlined in **Section 2.5.2**, the effect of the polymer brush acting as a substrate can be assessed. The analysis concludes that no criteria can be rejected, thus identifying a new method for understanding the impact of the substrate on the solvent swollen thin films. **Figure 2.33** illustrates that the water droplets will not interact with the surface of the substrate that has been modified with a PS brush.

Criterion I

$$S_{ld} \neq 0$$



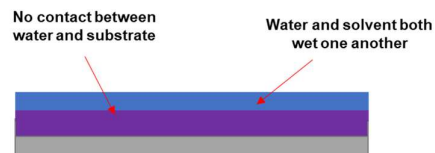
Cloaking

$$S_{ld} = \gamma_d - (\gamma_{dl} + \gamma_l)$$



Criterion II

$$S_{dl} \neq 0$$



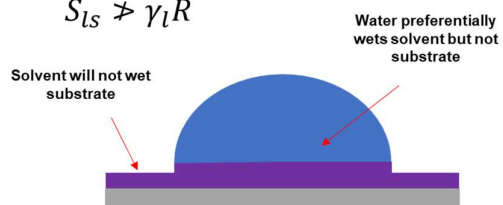
Spreading

$$S_{dl} = \gamma_l - (\gamma_{dl} + \gamma_d)$$



Criterion III

$$S_{ls} \neq \gamma_l R$$

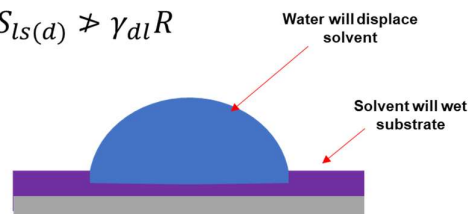


$$S_{ls} = \gamma_s - (\gamma_{ls} + \gamma_l)$$



Criterion IV

$$S_{ls(d)} \neq \gamma_{dl} R$$



$$S_{ls(d)} = \gamma_{ds} - (\gamma_{ls} + \gamma_{dl})$$



Figure 2.33 Graph illustrating the impact of water droplet templating on a PS brush annealed to a silicon wafer.

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Chapter 3

Sample Preparation and Characterisation Studies

3.1 Materials

3.1.1 Homopolymers

Atactic polystyrene (PS) (P40440-S) (Polydispersity Index (PDI): 1.03) was purchased from Polymer Source and used without further purification. The polymers have a corresponding glass transition temperature (T_g) of 99.68 °C and 105.08 °C for molecular weights of $17 \times 10^3 \text{ g mol}^{-1}$ and $42 \times 10^3 \text{ g mol}^{-1}$ (described as PS 17K and PS 42K) respectively. Differential scanning calorimetry (DSC) thermograms for each polymer are presented in the Appendix section.

3.1.2 Functionalised Polymers

Atactic polystyrene, hydroxyl-terminated (PS-OH): 6 kg mol^{-1} (P11116-SOH) (PDI:1.05), 10 kg mol^{-1} (P18787-SOH) (PDI :1.09) were purchased from Polymer Source and used without further purification. The polymers have a corresponding T_g of 95 °C.

3.1.3 Solvents

IPA (70%, HPLC grade) and acetone (99.9% HPLC grade) were the chosen cleaning solvents for substrate preparation. Polymers were dissolved using anhydrous toluene (anhydrous 99.8 %), THF (anhydrous 99.8 %), chloroform (anhydrous 99.8 %), and acetone (HPLC Grade 99.9%). toluene (anhydrous, Grade 99.9%), chloroform (HPLC Grade 99.9%) and anhydrous ethanol (anhydrous 99.8%). Chloroform (HPLC Grade 99.9%) and toluene

(HPLC Grade 99.9%) were the chosen swelling solvents. All solvents were purchased from Merck and used as received.

3.2 Sample Preparation

3.2.1 Homopolymer (PS) Thin Film Preparation

PS (P40440-S)¹ was dissolved in various solvents (toluene, THF, chloroform (CHCl₃), acetone) and stirred overnight to yield various w/w. % polymer solutions as shown in **Table 3.1**.

Table 3.1 Concentration and Spin-coating Conditions.

Solvent	Polymer (w/w.%)	Spin Speed (RPM)
Anhydrous toluene	2, 4, 5	500, 1000
Chloroform	2	1000
Acetone	2	1000
THF	2	1000

Silicon wafers (Intel, mechanical grade) were cleaved into 2 x 2 cm squares then placed in a vial (10 mL) filled with acetone and sonicated for 20 mins. After sonication the silicon was removed from the acetone, dried with a dry nitrogen stream, placed in a vial filled with IPA and sonicated for 20 minutes. After 20 minutes had elapsed the wafers were dried with a dry nitrogen stream. Homopolymer solutions were spin-coated² onto the clean silicon wafers at different velocities (500 rpm, 1000 rpm) to yield different film thicknesses.

The thickness control of PS thin films was measured for various concentrations of PS/toluene solutions. The thicknesses of films can be reduced by either (i) increasing spin speed velocity or (ii) reducing concentration as shown in **Figure 3.1**.

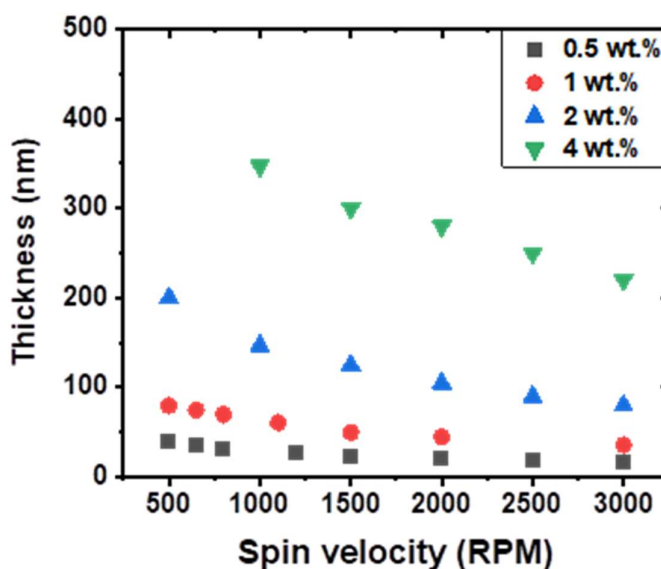


Figure 3.1 Experimental film thickness measurements for PS/toluene spin-coated solutions by Hall *et al.*².

3.2.2 Brush Fabrication

The brush synthesis was carried out following Lundy *et al.*'s method^{3,4}, as shown in **Figure 3.2**.

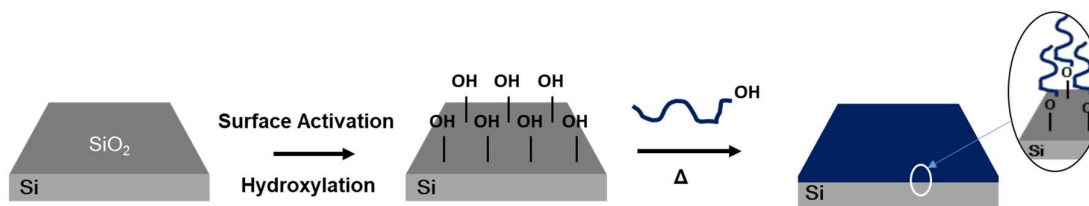


Figure 3.2 Schematic of the thermal annealing process to produce a thin polymer brush using the “grafting to” process.

Silicon wafers (Intel, prime grade) were cleaved into 2 x 2 cm squares, then placed in a vial filled with acetone and sonicated for 20 minutes. After sonication, the silicon was removed from the acetone, dried with a dry nitrogen stream, placed in a vial filled with IPA and sonicated for 20 minutes. After 20 minutes had elapsed, the wafers were dried with a dry nitrogen stream. The silicon surfaces were cleaned and hydroxyl-functionalised using an oxygen plasma treatment (Diener, Zepto One) for 5 minutes (40 kHz, 50 W). PS-OH was dissolved in anhydrous toluene as described by stirring overnight to yield a 0.6 w/w.% and 0.2 w/w.% for PS 6K and PS 10K, respectively. The solutions were spin-coated at 3000 RPM to yield thicknesses <10 nm. Samples were then thermally annealed for 1 minute at the required temperature of 190 °C. Concentration and annealing conditions are summarised in **Table 3.2**.

Table 3.2 Concentration and Annealing Conditions for PS Brushes.

Polymer	Solvent	Concentration used (w/w.%)	Annealing (°C)
PS-OH (6K)	Anhydrous toluene	0.6	190
PS-OH (10K)	Anhydrous toluene	0.2	190

Figure 3.3 illustrates the thermal annealing mechanism for brush formation. The binding of the polymer chains to the substrate occurs *via* a condensation reaction^{3,4}.

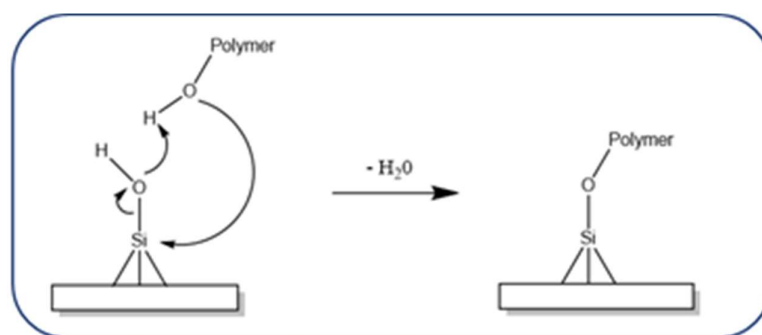


Figure 3.3 Mechanism of the condensation reaction to graft polymer to the silicon substrate.

The functionalised wafers were placed in a vial (10 mL) filled with anhydrous toluene and sonicated for 20 minutes. The wafers were removed, and the same washing procedure was carried out twice, using fresh toluene for each wash. After sonication, the silicon was removed from the acetone, dried with a dry nitrogen stream, and placed in a sealed sample holder. Lundy *et al.* reported a brush thickness of 3.4 nm for 6 kg mol⁻¹ PS-OH⁴. This was measured using TEM and is reported in the supplementary section of the paper.

3.2.3 Stacked Architecture using PS and PS brush

PS (P40440-S) was dissolved in toluene and stirred overnight Homopolymer solutions were spin-coated² onto the prepared brushes (3.2.2) at different velocities (500 rpm, 1000 rpm) to yield different film thicknesses. This produced a polymer stacked architecture, as illustrated in **Figure 3.4**.

Table 3.3 Concentration and Annealing Conditions for PS Brushes.

Brush surface	Concentration of homopolymer (w/w.%)	Spin velocity (RPM)
PS-OH (6K)	2, 4, 5	1000
PS-OH (10K)	2, 4, 5	1000

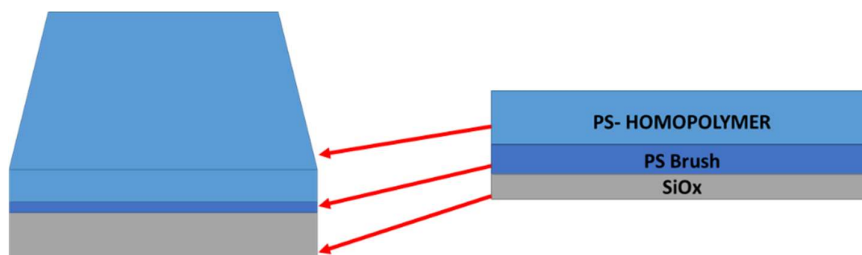


Figure 3.4 Stacked Architecture of the PS Brush-Homopolymer bi-layer.

3.3 Solvent Vapour Breath Figure (SVBF) Procedure

The swelling procedure for the Solvent Vapour Breath Figure method was carried out as follows:

1. All software packages (Filmetrics, Matlab) were set up on the computer prior to experimentation and were ready to run as soon as all apparatus was set up, and the right conditions were met. The setup for the software is discussed in presented in **Chapter 4** in the Appendix section.
2. The reflectometer was standardised using a reflectance standard of Si (<100>) purchased from Filmetrics followed by a background scan. Initial film thicknesses were measured using the F3 reflectometer using a recipe where the refractive index (n) of PS = 1.45 was used. Caution was taken to prevent the reflectometer from over-saturation.
3. Samples were placed in the middle of the copper stage above the reflectometer probe (F3-CS), which was mounted directly above the viewport of the SVA chamber. The chamber was purged with N_2 for 5 minutes to remove any excess solvent from previous experiments.
4. Once the chamber had been successfully vented, the N_2 flow was directed to the di-bubbler setup. The solvent bubbler temperature (T_{bub}) was reduced by evaporative cooling and maintained at a lower temperature than the ambient *via* PID control. Flow rates were fine-tuned using the flow metres upstream, and both solvent systems were vented to ambient prior to thickness measurements.

5. Initial thicknesses were measured at 5-second intervals (a count) at a stage temperature (T_{stage}) of 15-20 °C (depending on the temperature of T_{bub}). Average initial thicknesses and standard deviations were recorded.
6. After 10 counts (50 seconds), the solvent was directed to the chamber to initiate the swelling process. Usually, the T_{stage} was kept 1 °C above T_{bub} to prevent solvent condensation.
7. Once the polymer swelling was maintained at a specific swelling, the water was incorporated into the chamber at specific times of 250 seconds, 500 seconds, and 750 seconds.
8. Next, the initiation of polymer de-swelling *via* heating was performed to remove any trapped excess solvent. Once the condensation time was complete, both the solvent and water lines were vented, followed by an increase of T_{stage} to 20-25 °C for 20 counts (100 seconds).
9. All real-time software measurements were saved, and the sample was removed from the chamber. Samples were stored and sealed in the sample holder to eliminate any risk of contamination.

3.4 Characterisation

3.4.1 Atomic Force Microscopy

Atomic force microscopy (AFM) measurements were taken using a Park Systems XE7⁵ system in non-contact mode with silicon cantilevers (PPP-NCHR, Nanosensors, USA) with a force constant of 42 N m^{-1} . Atomic Force Microscopy⁶ (AFM) is a surface probe technique that yields 3-dimensional topographies for non-conductive samples such as polymer thin films. A sharp tip with a tip radius curvature of $< 10 \text{ nm}$ is used to probe the sample. Non-contact mode (NCM) is one of the main imaging tools used to analyse surface morphology. This mode utilizes an oscillating cantilever close to sample's surface without touching it. An image is captured due to the attractive forces between the tip and the sample that cause the cantilever to oscillate. The setup for the AFM is shown in **Figure 3.5**.

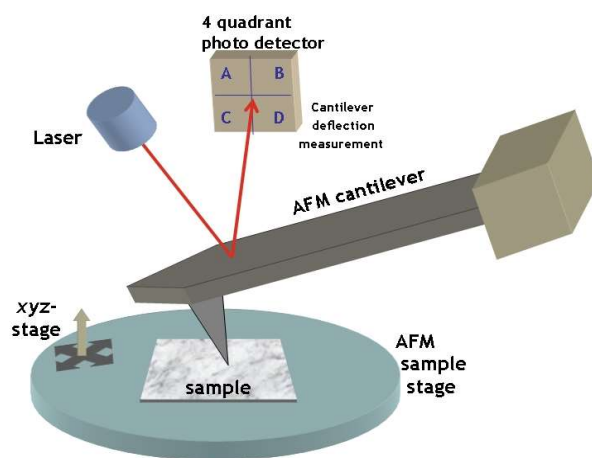


Figure 3.5 Atomic Force Microscopy (AFM) setup.

3.4.2 Scanning Electron Microscopy

Scanning electron microscopy⁷ (SEM) is a characterisation technique where micro and nanostructures can be observed using a focused beam of electrons interacting with the sample surface. When the electron beam penetrates the sample, scattering events occur. Numerous types of events can occur depending on the angle of emission of the electron beam as shown in **Figure 3.6**. This is known as the interaction volume⁸.

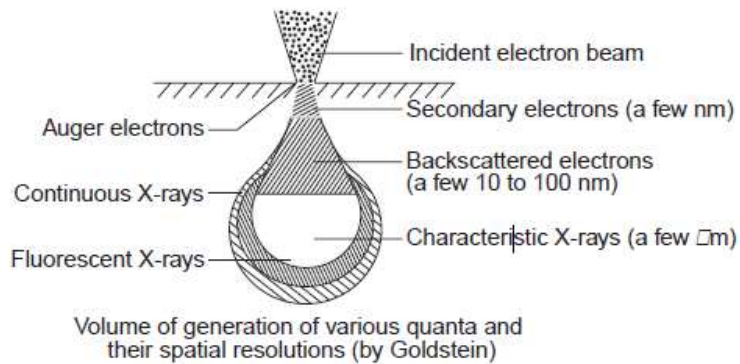


Figure 3.6 The interaction volume of a specimen⁹.

The incident electron can scatter at 180 degrees resulting in a back-scattering event which has an energy of $\sim 50 \text{ eV}$ ¹⁰. The incident electron can pass through the sample and undergo inelastic scattering. If sufficient energy passes through the sample, the electrons can overcome the work function and convert into secondary electrons (SE_2 type). The SE_2 detector produces an image through scattering events which targets the SE_2 secondary electrons. SE_1 type electrons have higher resolution as these are at a closer proximity to the sample and are detected by the In-lens detector. If the electrons are at a high accelerating voltage (kV), they can damage the sample surface. This is known as sample charging.

SEM measurements were performed using a Carl Zeiss Ultra using an SE_2 detector at an accelerating voltage of 2kV to prevent sample charging. For imaging at an angle, samples

were cleaved in the centre using a pliers and mounted on 90-degree sample holders as shown in **Figure 3.7**.

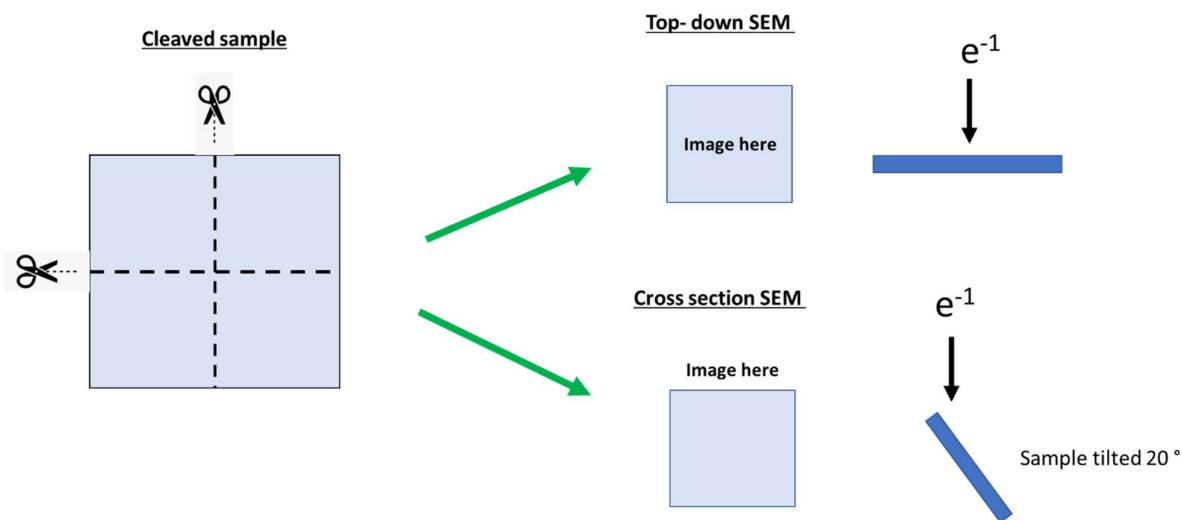


Figure 3.7 Procedure to follow for (i) top-down and (ii) cross section imaging.

For top-down imaging no tilt was required, and a standard specimen stub was used. For cross section the sample was mounted on a 90° sample holder purchased by Ted Pella and the sample stage was tilted 20°.

3.4.3 Focused Ion Beam

Focus ion beam (FIB) (AURIGA) was a method adapted to observe the cross section of a single pore and analyse the morphology of the droplet on the substrate. This technique can mill the sample surface using heavy ions such as Ga^{+} . This technique can be coupled with SEM to acquire 3-dimensional morphologies¹¹.

FIB milling was performed at 30 kV from 600 pA, 240 pA to 120 pA, at a tilt angle of 54 °. The sample was imaged at a tilt angle of 36 ° and a 5 mm working distance was used. A low accelerating voltage of 2kV and a 30-micron aperture was applied to prevent charging.

3.4.4 Optical Imaging

The Olympus BX51 optical microscope was used to analyse the images. The images were captured using an AxioCam ERc 5s. All optical images were imported to ImageJ¹² and processed to determine pore size and polymer coverage of the thin film samples adapted and further refined from a method carried out by Murphy for characterising the porosity of PMMA membranes¹³.

Table 3.4 Pixel Analysis.

Magnification	Pixels /μm
5X	0.89
10X	1.78
50X	8.88

All image post-processing was carried out using ImageJ software¹² (Version 1.46r). This software was used to analyse the feret diameter, pore homogeneity and coverage.

3.4.5 Contact Angle Goniometry

Contact angle (CA) goniometry¹⁴ is a quantitative technique used to measure the wettability of surfaces. The shape of the solvent drop is determined by the surface tension of the liquid and the surface interface, as discussed in **Section 2.5**. Dynamic CA measurements were recorded for each sample using a high-speed camera (Nikon, 60 Hz sampling rate) to capture advancing CAs using water as a probe liquid. Liquids were dispensed at a flow rate of 6 nLs⁻¹ using a 35-gauge needle with a droplet volume of 60 – 90 nL. The setup for the goniometer is shown in **Figure 3.8**. This was a non-commercial instrument built at Trinity college. The goniometer setup was calibrated using a known sample standard before measuring. Usually,

a clean silicon surface with a contact angle of approximately 20-30 ° was used to calibrate the setup.

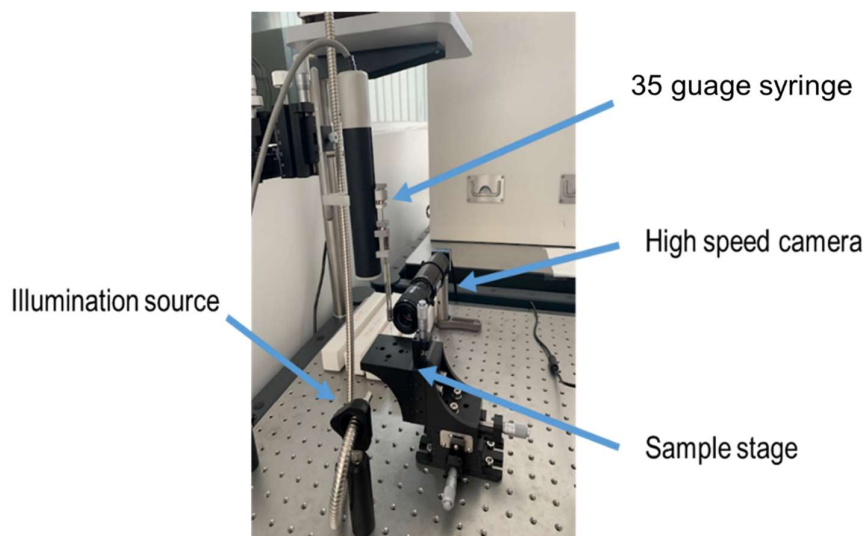


Figure 3.8 Goniometer contact angle setup.

3.4.6 Reflectometry

Reflectometry¹⁵ was the method chosen to analyse the swelling dynamics of the polymer film in-situ during experimentation. Filmetrics F3-CS reflectometer with a UV-vis light source (380–1050 nm) was mounted on top of the quartz viewport to monitor the film thickness, as shown in **Figure 3.9**.

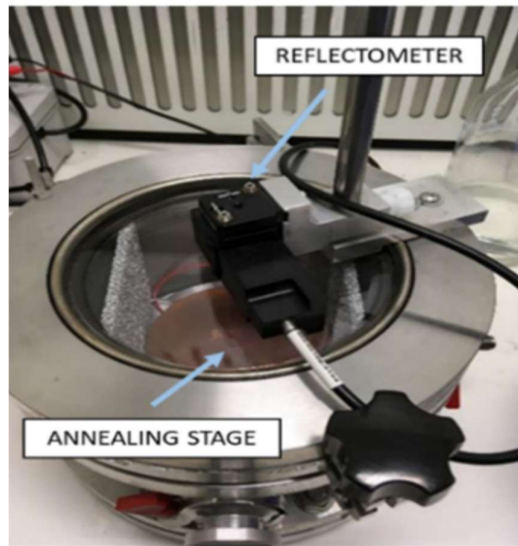


Figure 3.9 F3-CS reflectometer mounted directly above the viewport of the stainless steel SVA chamber.

The thin film characteristics are measured via the reflection or transmission of light through the sample and then analysed over a range of wavelengths. The F20 system takes thickness measurements every 5 seconds during each swelling experiment. Since light has wavelike properties, the reflection can be in or out of phase because of thin film interference as shown in 3.1:

$$\lambda = \frac{2nd}{i} \quad [\text{Equation 3.1}]$$

Where λ is the wavelength, n is the refractive index, d is the film thickness and i is an integer. If the reflections are in phase, the wavelength of light will oscillate. The amplitude of oscillations is related to the refractive index and the extinction coefficient of the sample to be tested. The more oscillations that occur on the software, the thicker the sample will be. The system is calibrated using a standard Si (100) surface from “Filmetrics”. Firstly, the reflectance of the standard is taken followed by a background scan to remove any noise when

taking measurements. The oscillations shown in **Figure 3.10** identify the reflectance of the sample material at different wavelengths.

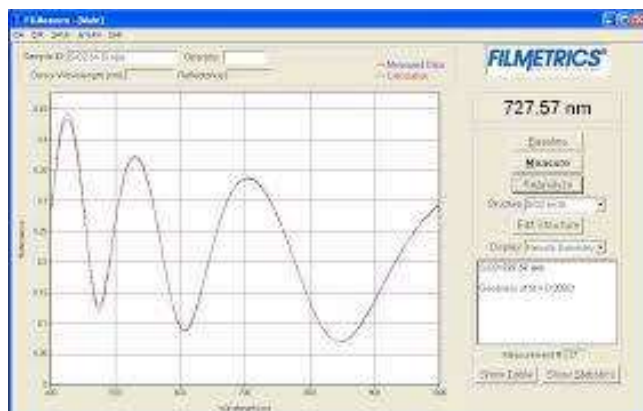


Figure 3.10 – Screenshot of Filmetrics software showing the various oscillations of reflection of a sample.

To interpret the swelling effect of solvents, the initial and swollen thickness of the polymer film is denoted as d_o and d_s , respectively, and the swelling ratio (SR) can be measured as shown in **Figure 3.11**.

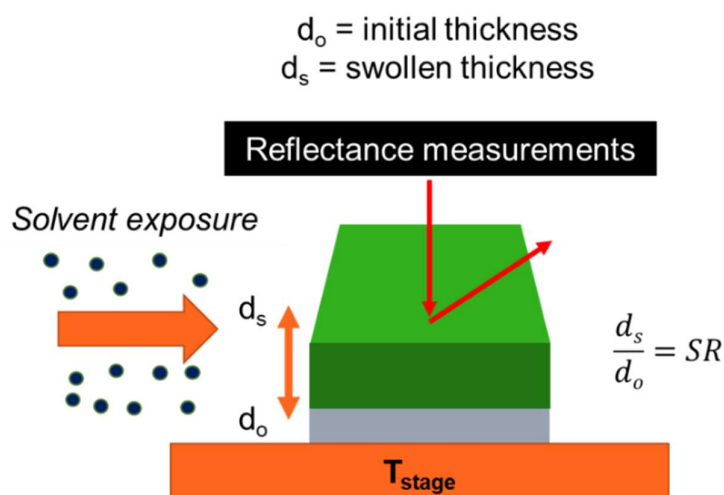


Figure 3.11 A schematic showing the swelling of the thin film when exposed to solvent vapour. Reflectance measurements are taken directly in the centre of the thin film and monitored during the entire swelling process.

Since the polymer film is swollen by the solvent, the refractive index will change for thickness, d_s . The Lorentz-Lorenz rule of mixing is used to compute the refractive index change as shown previously in **Section 2.2**¹⁶. The refractive indices of pure solvent and polymer are shown in **Table 3.5**. This will be discussed in further detail in **Chapter 4**.

Table 3.5 Optical Properties of Material and Solvent.

Component	Refractive Index Value @ 600nm
Polystyrene ¹⁷	1.59 ± 0.001
Chloroform ¹⁸	1.44 ± 0.001
Toluene ¹⁹	1.50 ± 0.001

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Chapter 4

Construction of a Solvent Vapour Breath

Figure Rig

4.1 Introduction

4.1.1 Solvent Vapour Annealing (SVA)

A specialised stainless steel annealing chamber was constructed by Lundy *et al.* in 2018 to accelerate the diffusion rate of THF for the self-assembly of a high χ (chi) block-copolymer, PS-*b*-P₄VP (polystyrene-*block*-poly-4-vinylpyridine) ($\chi_{\text{PS-P4VP}} = 0.524$). Self-assembly of block-copolymers is driven when the χ value is usually low ($\chi < 0.5$)¹, however, with dynamic solvent vapour, current static annealing limitations can be overcome². A stream of inert N₂ carrier gas is incorporated into a bubbler filled with THF, and the vapour proceeds to the SVA chamber. The saturation of the solvent can be controlled by the difference of temperature in the bubbler (T_{bub}) and the copper stage (T_{stage}). THF has good compatibility for the P4VP ($\chi = 0.086$) and less so for the PS ($\chi = 0.414$), as reported by Lundy *et al.* ². This approach demonstrated adequate reproducibility for high- χ BCP films over a large scale without any defects arising from polymer dewetting as the solvent saturation is kept below 1 ($S < 1$).

The low diffusivity of PS-*b*-P₄VP, associated with the long annealing time of 4h *via* the static method, was reduced to 15-30 minutes using the dynamic solvent vapour annealing approach. Furthermore, this dynamic SVA process can also be scaled to a 4" wafer, which allows this polymer rig to be suitable for upscaling the process for device fabrication; long-range ordering can be seen as shown in **Figure 4.1**.

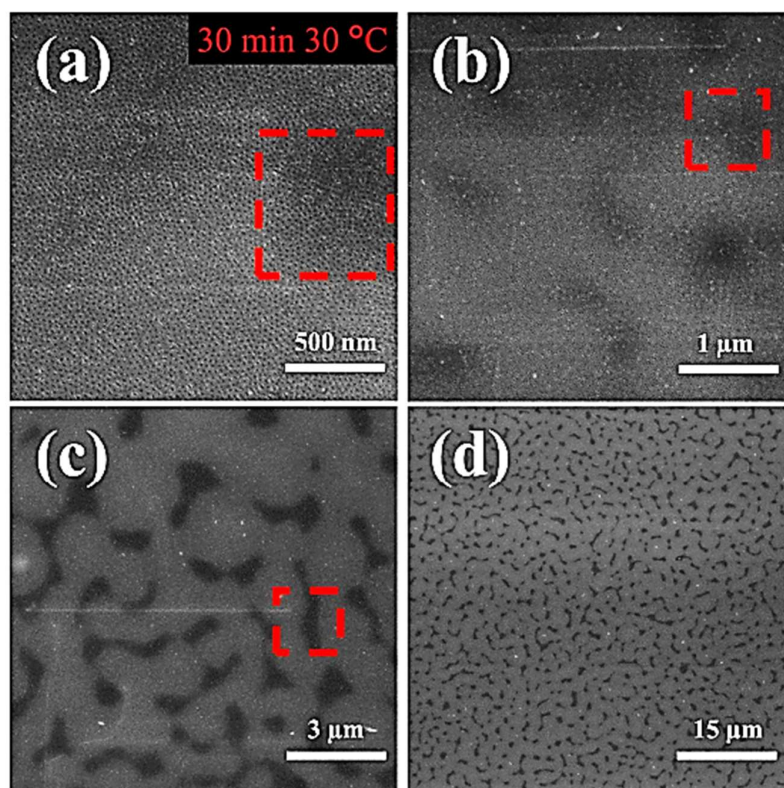


Figure 4.1 SEM micrographs (a) – (d) show the long-range ordering of PS-b-P4VP film annealed at 30 °C for 30 minutes with no dewetting present. (a) shows cylindrical ordering with a patterned dark region (red inset) present and is seen at lower magnifications (b), (c) and (d). Taken with permission from Lundy *et al.* ²

Following this study, the use of the SVA chamber shows great potential in creating highly viscous films that can be easily deformed and produce patterns over long ranges. Previous investigations have shown that soft materials can increase the nucleation of water droplets on surfaces³. Since the previous setup can swell polymer films to high swelling ratios while maintaining their structural integrity, a new droplet templating method can be studied. There are advantages such as the risk of solvent pooling can be prevented by controlling the saturation of the solvent *via* temperature control and eliminating issues with polymer

dewetting that have been seen in many static approaches where the saturation of solvent is less controlled.

4.1.2 Previous Setup

Lundy's chamber consists of a stainless-steel ISO straight connector part with a 4 x KF fitting located at 90° intervals machined around the chamber with a $V_c = 1.94$ L, as presented in **Figure 4.2**. Two Swagelok feedthroughs were used as gas inlets and outlets, and a 9-pin D sub-connector can transmit power to the resistance temperature detector (RTD) probe embedded inside the copper stage. A proportional integral derivative (PID) feedback loop effectively controls the saturation in the chamber using an ATEC 302 controller connected to a thermoelectric cooling (TEC) unit. A quick-access door with a glass viewport (Kodial), for film thickness measurements, is located at the top of the chamber, where an F3 series reflectometer is fitted.

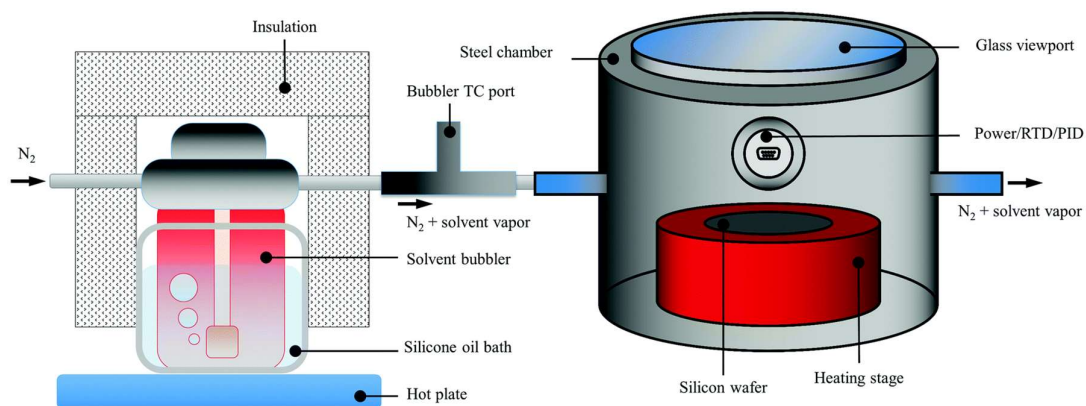


Figure 4.2. A schematic of the solvent vapour annealing chamber as constructed by Lundy *et al.*²

To acquire temperature readings, a 3-wire RTD probe (Omega, OD = 1.5 mm, Tolerance AA, ± 0.01 °C) is embedded inside the copper stage. The setup for the stage heating is

presented in **Figure 4.3**. Although Lundy discussed the use of the chamber and its electronics for promoting cooling in his thesis⁴, this new and effective electronic and hardware setup has not been published⁵ or discussed in detail. Therefore, the complex electronic setup will be discussed in detail in **Section 4.2.2.2**. Lundy's previous method⁶ did not allow cooling of the copper stage and the use of a flexible polyimide heater between the copper stage and the Polyether-ether-ketone (PEEK) holder, as shown in **Figure 4.3**.

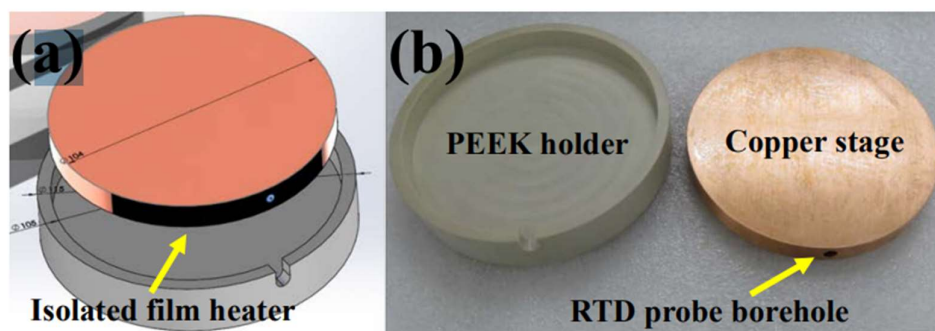


Figure 4.3 Copper stage with a PEEK holder. Taken directly from reference.²

The arrangement ensure that the heating element is isolated from the swelling solvent, ensuring that it is protected during the annealing process. PEEK was viable and suitable material with a good rigid structure, favourable insulating properties, and high chemical resistance to aggressive solvents. A 2.5 mm borehole was fabricated on the side of the copper stage to improve the temperature readout by the probe. Computer-aided designs (CAD) show the probe's location and are presented in this chapter's supplementary section.

4.1.3 Solvent Vapour Breath Figure Setup (SVBF)

The SVA chamber was chosen as a strategy to improve thin film swelling. This new method is a reverse of the BF methods discussed previously^{7,8} where the polymer film is produced first and subsequent treatments can create micro-features *via* droplet templating. This approach is a possible profitable bottom-up technique for rapidly producing microporous templates. In addition, SVBF provides a new understanding on how porous structure can be formed and will be assessed as a suitable method for structuring thin polymer films.

The procedural steps are as follows:

1. Thin polymeric films with coherent thicknesses can be produced on flat, clean substrates *via* the spin coating method. All polymer film thicknesses can be modified by changing the concentration of the solution or the spin speed.
2. Polymer films will be swollen with suitable swelling solvents to plasticise the film and make it mouldable by the water droplets. In a viscous-like state, the polymer chains will be able to move within the polymer-solvent solution effectively reducing the T_g of the thin film to room temperature⁹. Rapid swelling of films can occur whilst keeping the saturation below 1 ($S < 1$).
3. The use of reflectometry is applied to observe the swelling dynamics^{2,5} of the thin films pre-condensation and is a robust method in probing and characterising the effect of homopolymer-solvent swelling. Furthermore, humidity probes can measure the RH% in the chamber and gives a good indication of the temperatures needed to induce condensation using the Antoine equation, where P_{sat} can be measured for water¹⁰.

4. The effect of water on the SVBF templating process can be monitored by reducing the T_{stage} to temperatures below the dew point. By controlling the RH% conditions and temperature (T_{stage}), water droplet templating can be induced on the swollen polymer films at different viscosities by controlling the swelling ratio (SR). The water droplets can deform the swollen films, and when they reach a critical size, they can pack and form ordered pores, as discussed in Zhang's review¹¹.

5. Temperature and saturation control can provide a method to replicate the breath figure process *in-situ*. Volatile solvents are usually used to reduce the temperature of the polymer solution¹², therefore chloroform is the primary swelling solvent of interest. By strictly refining the temperature between the bubblers (T_{bub}) and stage (T_{stage}), better control of pore formation can be measured.

4.2 SVBF Construction and Apparatus

Regarding the previous setup as presented in **Figure 4.2**, the system is not adequate or effective as a Breath Figure (BF) rig, as only one streamline is present. Therefore, new rig modifications are needed to create a breath figure-controlled apparatus. The new rig design, shown in **Figure 4.4**, involves the addition of new piping setups, flow controls, and *in-situ* humidity measurements as well as improved heating and cooling of the sample and gases.

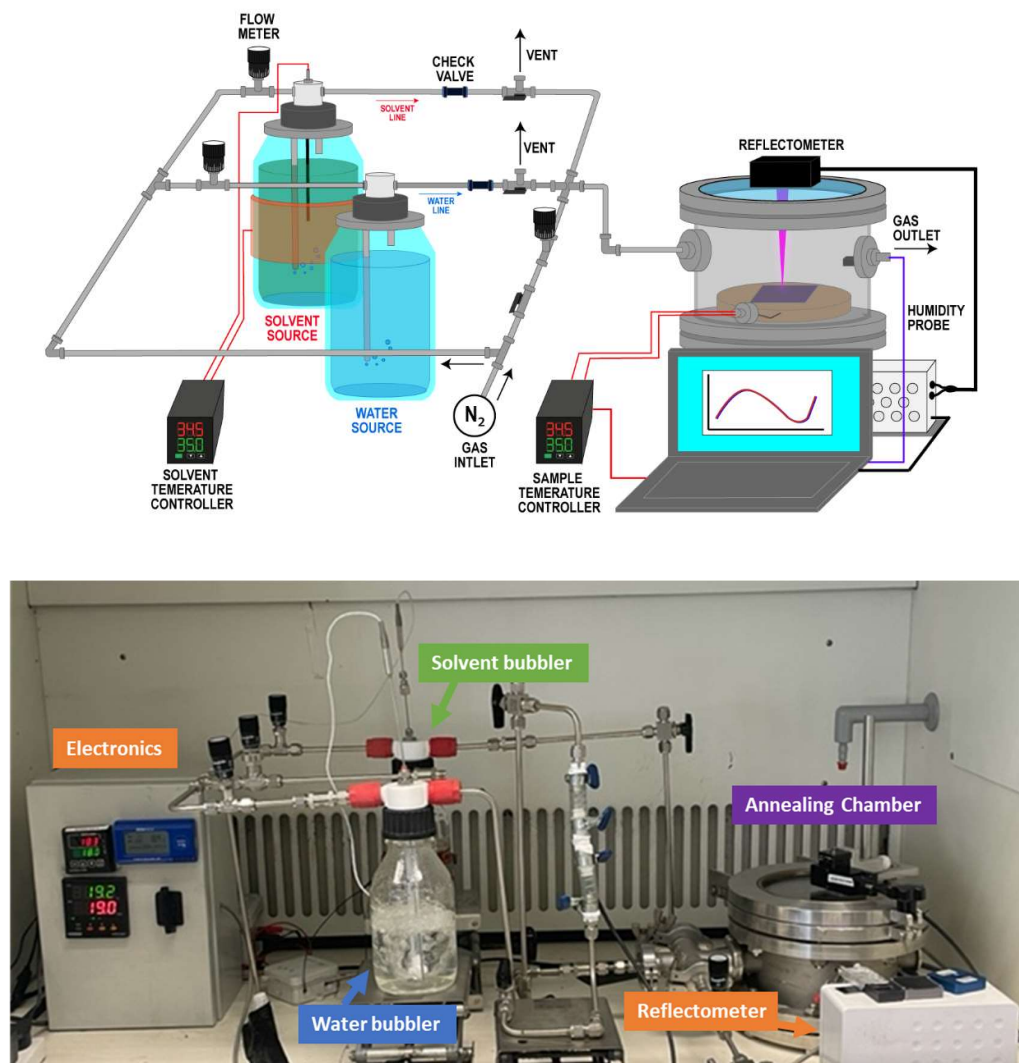


Figure 4.4. The modified SVA chamber setup with (Top) schematic of the setup and (Bottom) Overall image of the setup

There were several factors and controls to consider prior to the upgrades. The objectives are as follows:

- 1.) The addition of a secondary flow line consisting of a second bubbler setup connected to the same N₂ stream.
- 2.) Construction of flow control valves to both piping setups to properly balance and regulate the water/solvent vapour ratio entry into the chamber and eliminate suck-back issues.
- 3.) Temperature control improvements in the solvent bubbler using a heating jacket.
- 4.) The use of relative humidity probes downstream from the water bubbler and inside the SVA chamber can monitor the change in RH% values in real-time.

4.2.1 Plumbing Setup and Apparatus

A new piping apparatus was constructed with the aim to allow the current N₂ source to carry both solvent and water from each bubbler setup, as shown in **Figure 4.5**.

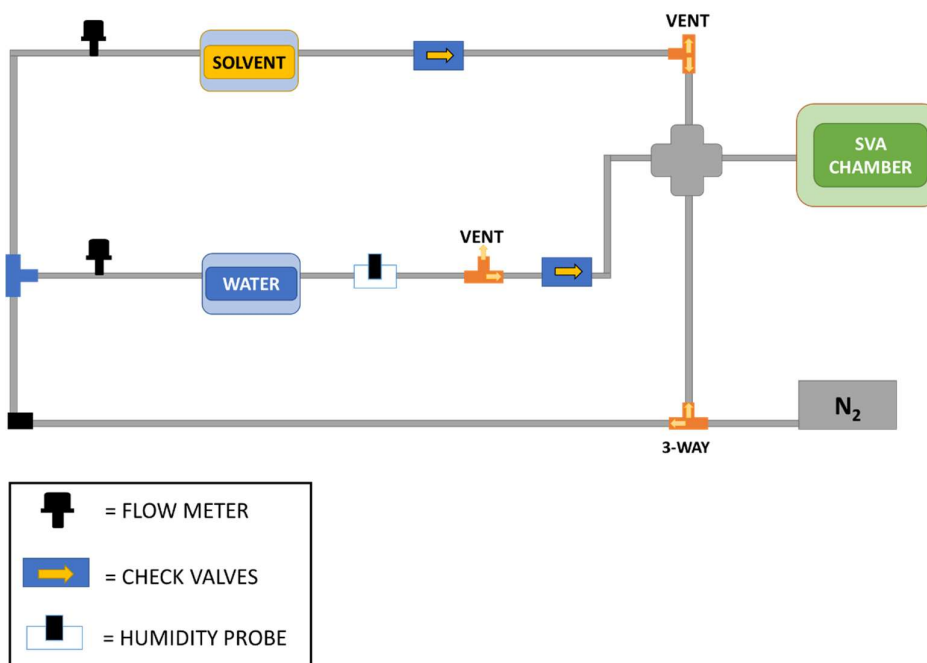
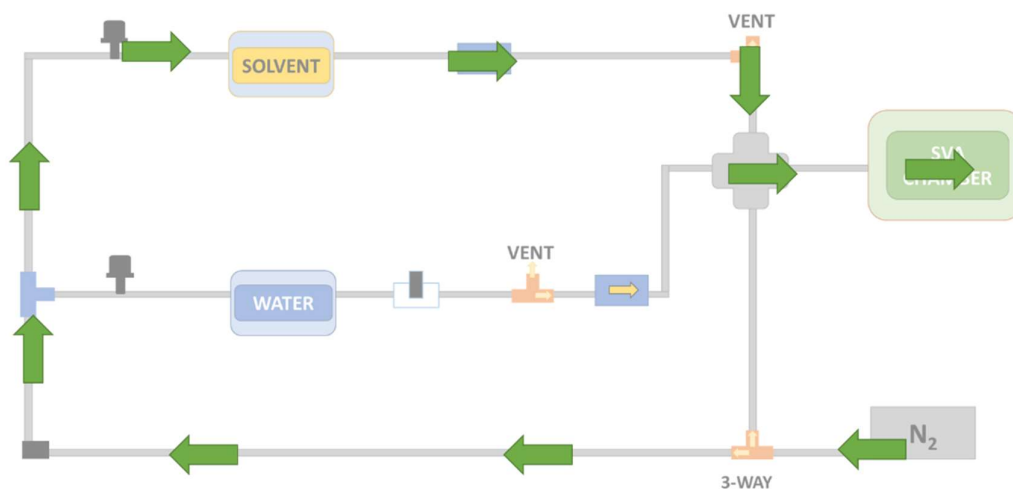


Figure 4.5. Piping apparatus for the solvent and water line

The piping for both the solvent and water consisted of stainless steel and was purchased from Swagelok with an outer diameter (OD) of 6 mm with a wall thickness of 1.5 mm. The maximum working pressure of 74.53 MPa¹³ was calculated which are adequate for the flow rates required for the swelling process.. The ball valves function (3-way, SS-42GS6MM, Swagelok) in controlling the direction of vapour flows in the piping setup as, illustrated in **Figure 4.6**.

SOLVENT LINE ON



WATER LINE ON

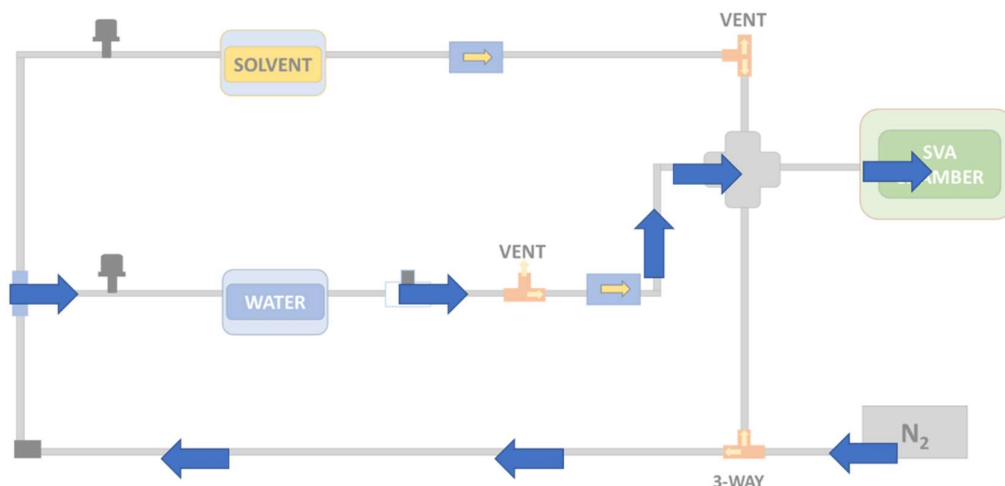


Figure 4.6. The direction of vapour flows in the two solvent lines

Venting lines are positioned directly after each bubbler using 3-way ball valves (SS-42GS6MM). These valves aim to expel solvent vapours into the atmosphere until correct conditions have been met, prior to polymer swelling. Flow controllers (SS-SS6MM, $C_v = 0.004$) used in the setup were purchased from Swagelok and were constructed into the piping design to control solvent:water ratios. Flow coefficients (C_v) can regulate the amount of N_2

flow into the bubbler apparatus by changing the number of turns on the Vernier handle and controlling the valve's opening, as presented in **Figure 4.7**.

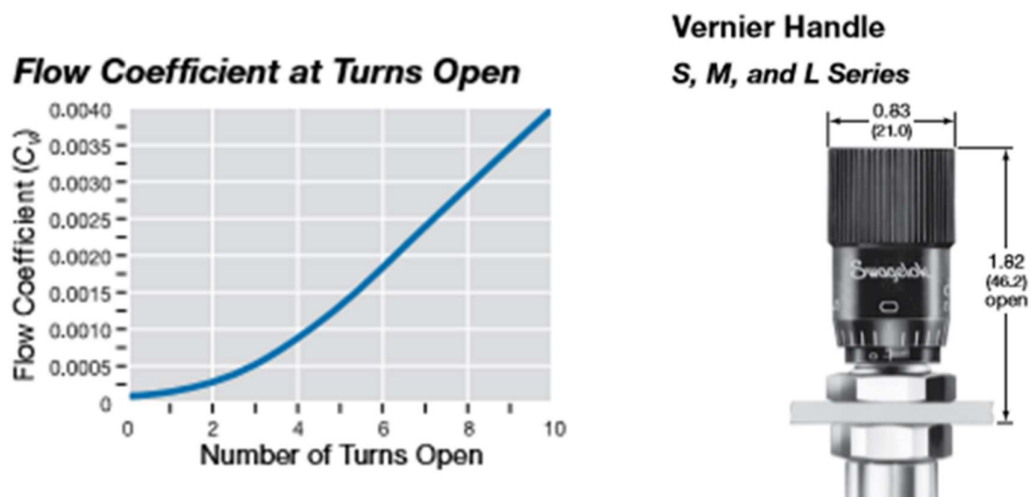


Figure 4.7. Flow metering valves used (SS-SS6MM) and image taken from Swagelok manual. Flow rate restricted to a Max C_v value of 0.004.

Flow rates and the ratio of solvent:water in the chamber can be controlled by increasing or decreasing the opening of the valves in each of these piping setups. Issues with suck-back were encountered, resulting in piping contamination due to regarding the difference in resistance between the two lines. In order to remove this problem, the flow meters (SS-SS6MM) were added to balance vapour flow using high pressures upstream (~ 3 bar). Check valves purchased from Swagelok (SS-6C-MM) were added to both bubbler lines to remove the risk of solvent/water contamination by making the flow uni-directional. The issue with suck-back was removed by pushing the vapour directly to the chamber. polytetrafluoroethylene (PTFE) O-rings were needed for the solvent line setup, as the polymer needs to be resistant to volatile organic vapours such as chloroform, THF and toluene. The chemical stability of the PTFE allows the rig to be multi-functional and versatile when investigating different swelling solvents in future projects.

4.2.2 Temperature Controls and Electronics

4.2.2.1 Solvent Bubbler Controls

Controlling the temperature of the solvent bubbler is vital for maintaining consistent temperatures in each of the swelling experiments. A PID controlled unit (Watlow 965) with a 3-wire RTD probe (Omega, OD = 1.5 mm, Tolerance AA, ± 0.01 °C) is positioned inside the solvent bubbler and sealed from the ambient using a reducing union (S100-1-2, 1.5 mm Tube OD x 6 mm, Male NPT) purchased from Swagelok. The setup of the solvent bubbler is shown in **Figure 4.8**.

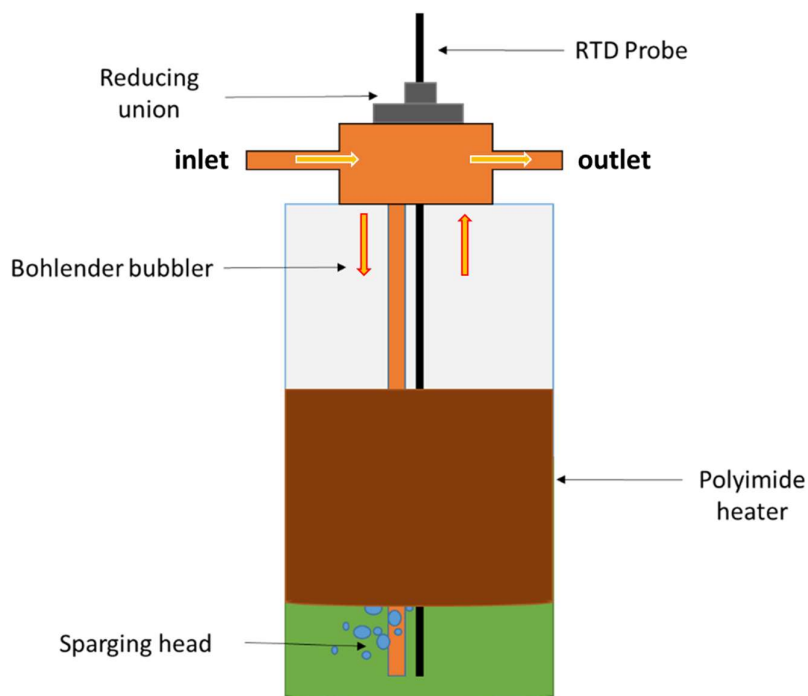


Figure 4.8 Solvent bubbler setup. Integration of RTD probe inside the solvent bubbler to measure the internal temperature of solvent in the bubbler setup.

The heating element consists of a flexible polyimide film heater purchased from Omega (KHA-110/10, 100 W, and 115 VAC). Sufficient heating can be supplied to the solvent bubbler, where the heater is connected to a solid-state relay unit that acts as an on/off switch to control the temperature. PID is a control loop mechanism where an error value, $e(t)$ is

continuously measured between the setpoint (SP) and actual point (AP) of a process parameter, in this case, temperature. The overall control function, $u(t)$, can dictate temperature control by changing the proportional (K_p), integral (K_i), and derivative errors (K_d), as shown in **Equation 4.1**. Multiple resources on how PID feedback loops work are highlighted in Borase *et al.*¹⁴.

$$u(t) = K_p e(t) + K_i \int_0^t e(\tau) d\tau + K_d \frac{de(t)}{dt} \quad [\text{Equation 4.1}]$$

The PID control unit was auto-tuned at temperatures below 20 °C. The wiring diagram for the heating setup is shown in **Figure 4.9**.

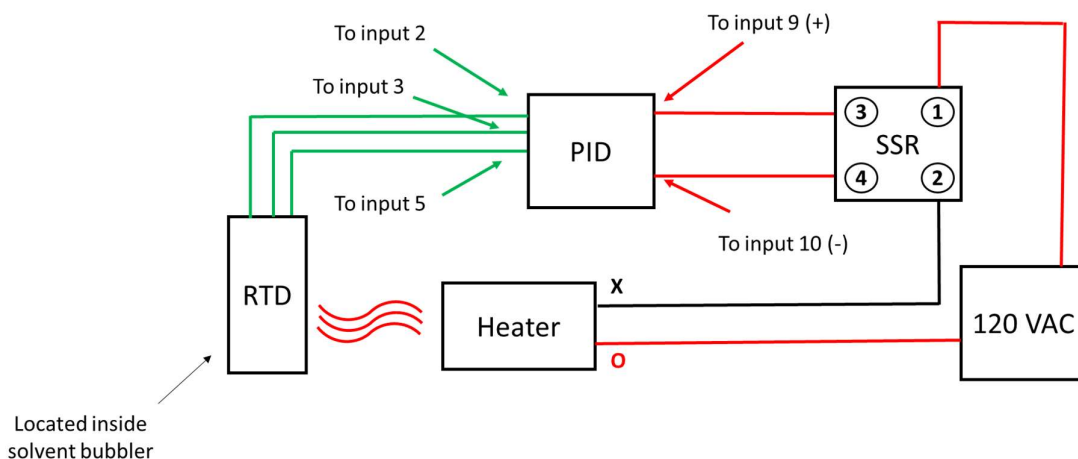


Figure 4.9 Wiring diagram of the PID-controlled solvent bubbler setup.

4.2.2.2 Stage Temperature Controls

The addition of a TEC unit to the SVA chamber provides a method to heat or cool the stage temperature through PID control (**Equation 4.1**). Samples are placed on a copper (Cu) stage with a thermal conductivity of 394 W m⁻¹ K⁻¹.

A 3 wired RTD (Pt100) sensor measures the temperature of the stage. The increase in temperature of a metal is directly proportional to the increase in the resistance, where Pt has a resistance of $0\ \Omega$ at $100\ ^\circ\text{C}$. The probe has an outer diameter (OD) of 1.5 mm and is in the centre of the annealing stage, directly below where the samples are positioned, as presented in **Figure 4.10**.

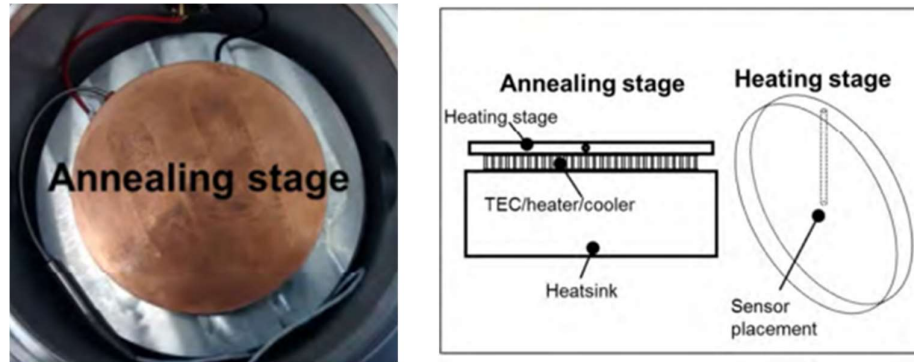


Figure 4.10 Image (left) and CAD design (right) of the annealing stage and the RTD sensor location. Images are reproduced from Lundy *et al.*⁴.

A more sophisticated electronic setup is required for stage cooling. In this wiring setup, the polarity (direction) of the current is controlled using a H-bridge (FTX100, CTech). The control of polarity either heats or cools the Peltier (TEC) module (134.4 W, 14.3 A, 62 mm x 62 mm, Radionics) positioned underneath the copper stage. In addition, a sophisticated PID (ATEC302, CTech) is used that controls the temperature. The complete wiring setup for the stage temperature controls is shown in **Figure 4.11**.

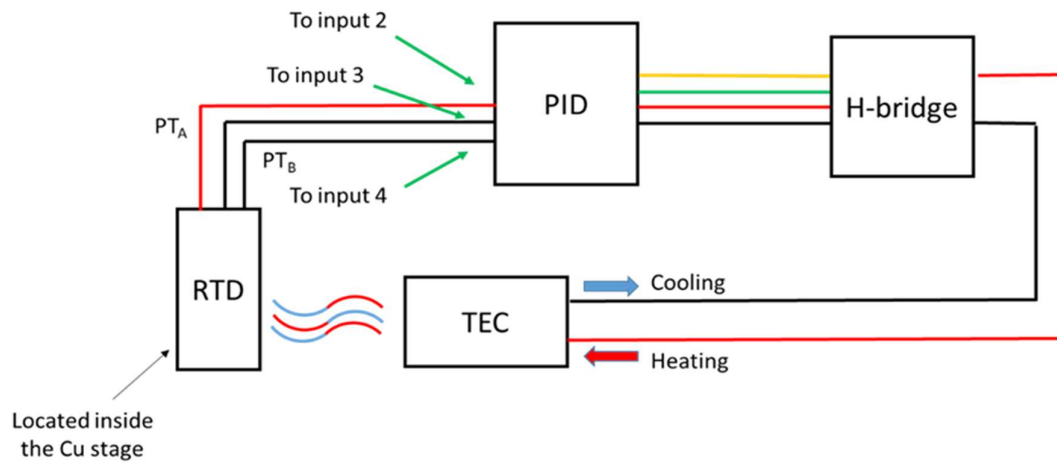


Figure 4.11 Wiring diagram for the stage temperature control setup

Figure 4.12 shows the type of PID controller used and an image showing the wiring setup for the H-bridge and power supply unit.

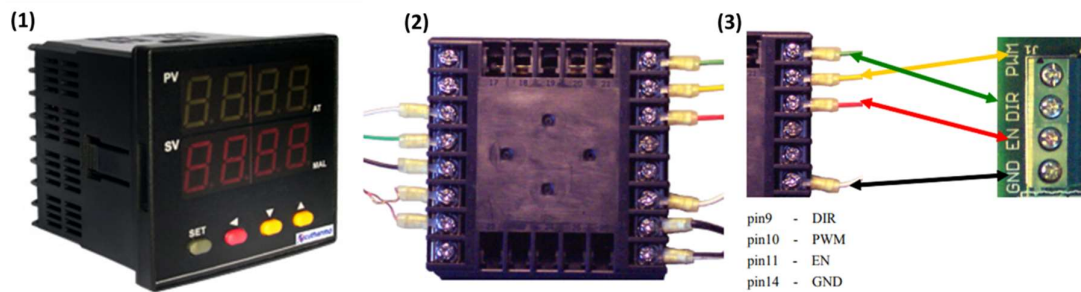


Figure 4.12 (1) The front of the ATEC302 that reads the setpoint and actual temperature (2) the back of the PID showing the wiring connections for PSU and the H-bridge (3) The wiring diagram for the ATEC and the H-bridge. Wiring is green, yellow, red, and black for DIR, PWM, EN and GND, respectively.

The H-bridge amplifier (FTX-100, **Figure 4.13**) controls the direction and power of the electrical current. The DC voltage is 7V, the maximum current is 6A, and the maximum power output is 42 watts.



Figure 4.13 The H-bridge (FTX100) is connected to the PSU and PID controller.

A thermoelectric cooler (TEC) system is used to heat or cool the copper stage by either absorbing or rejecting heat. The TEC material is usually ceramic and consists of semi-conductors that follow the Peltier effect, as shown in **Figure 4.14**.

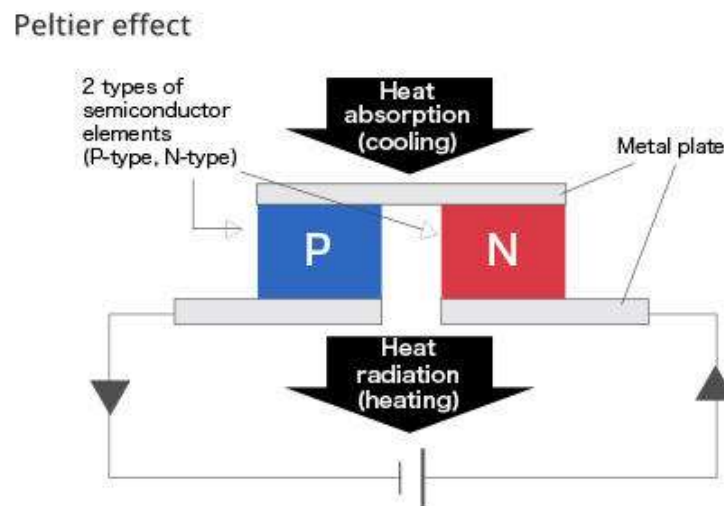


Figure 4.14 Schematic of the Peltier Effect.

This process involves the cooling of one side, resulting in the heating of the other side, when an electric current flows in a circuit consisting of different semiconductors¹⁵ such as p-type and n-type silicon, as shown in **Figure 4.15**.

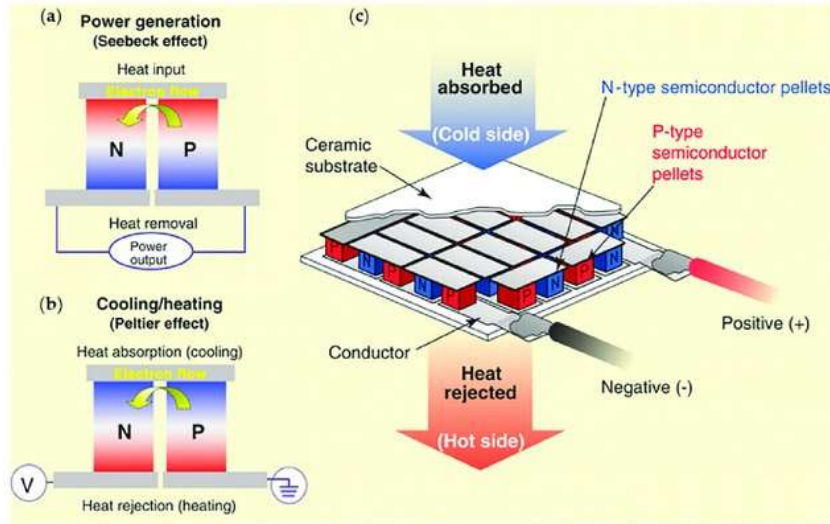


Figure 4.15 The Peltier Effect resulting in the heating and cooling of the TEC.¹⁵

From the addition of the TEC module to the SVA design, better control can be achieved at lower temperatures *via the Peltier effect*¹⁶. This is critically important for the breath figure templating as low temperatures are needed¹⁷ to promote condensation at temperatures below room temperature. The following section will discuss the detection of relative humidity (RH%), water vapour saturation, and vapour pressure using humidity probes.

4.2.3 Humidity Controls

Humidity probes were fitted into the water line to measure the real-time humidity values in the piping setup and the chamber. By adding humidity probes, the aim is to:

1. Rationalise an understanding of the role of relative humidity (RH%) and dew point temperature to initiate the condensation process inside the SVA chamber.
2. Interpret and compare the effects of mixing solvent and water vapour pressures in the SVA chamber.
3. Maintain temperatures at the dew point during the swelling process and monitor the changes of RH% at different temperatures of T_{stage} .

4.2.3.1 Humidity Probes

Relative humidity probes (Farnell, Amphenol Advanced Sensors, T9602 Humidity and Temperature Probe) were connected to an Arduino board run using a Matlab script shown in the appendix section of this chapter. Temperatures and relative humidity (RH%) can be measured by calculating the voltage change using **Equations 4.2** and **4.3**. Data can be acquired by measuring the metal oxide's electrical capacitance change. In 2008, nanostructured sensors using TiO_2 were used to improve the adsorption and desorption and thus the capacitance response¹⁸.

From knowing the resistance of the temperature/ humidity sensors, the voltage can be measured.

$$V_{out} = V_{in} * \left(\frac{R_2}{R_1 + R_2} \right) \quad [\text{Equation 4.2}]$$

The Steinhart- Hart equation can then be used to identify the temperature of the humidity probes.

$$\frac{1}{T} = A + B \ln R + C(\ln R)^3 \quad [\text{Equation 4.3}]$$

Where T is the temperature, R is the resistance in Ohms and A, B and C are Steinhart-Hart coefficients for the thermistor. The thermistor used is the Telaire T9602 type. A Matlab script was created in Nokia Bell labs to measure the temperature and relative humidity and is shown in the Appendix.

Humidity probes were inserted immediately after the mixer (RH₁) and inside the stainless-steel chamber (RH₂). Changes in relative humidity throughout the piping setup and inside the chamber were recording using the probes. Usually, RH₁ values are measured to be > 80%, and upon removal of the mixer, values of > 90% can be achieved. A humidity chamber was fabricated and added to the water line, as shown in **Figure 4.16**.

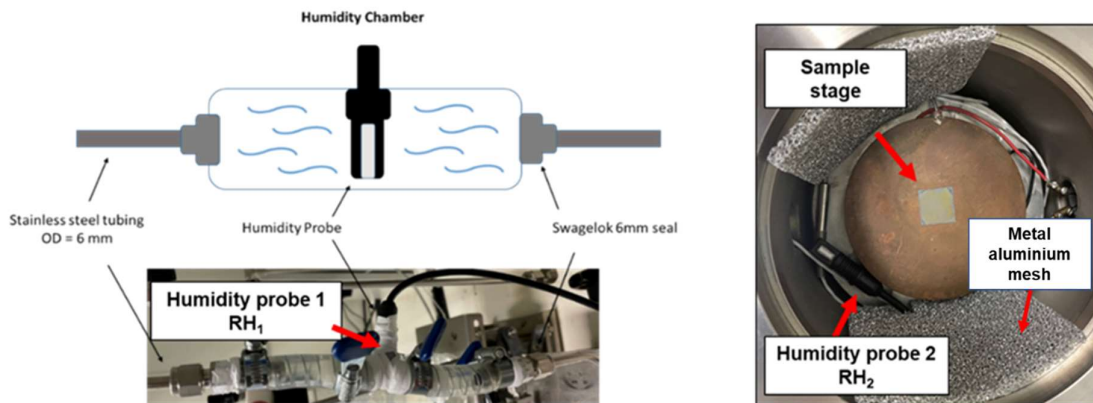


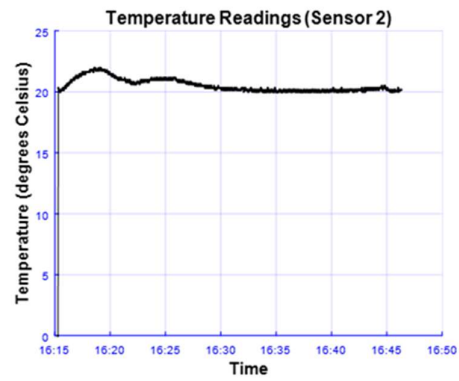
Figure 4.16. Schematic of the humidity chamber downstream from the water bubbler (left). Humidity probe located inside the chamber next to a metal aluminium mesh.

A small orifice was cut into the plastic that acts as a humidity chamber and sealed from the ambient. Swagelok fittings were attached to each end of the humidity chamber to produce a tight seal from the ambient. Probe 2 was placed inside the humidity chamber and was located at the base where minimal solvent interaction will occur with the probe. The solvent is distributed evenly using an aluminium metal mesh to disperse the solvent molecules. This prevents solvent pooling.

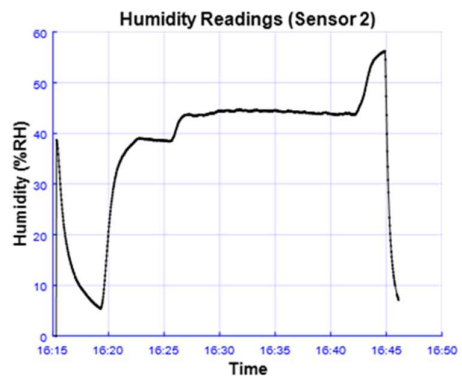
4.2.3.2 Software

The humidity probes were run on three different scripts using the same MATLAB programme. The script that acquires the data is described in the appendix section of this chapter. Raw data extracted from the probe is shown in **Figure 4.17**.

(i)



(ii)



(iii)

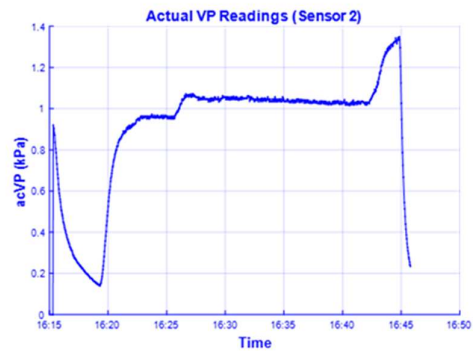


Figure 4.17. Real-time probe raw data scripts recorded and measured using Matlab software.

(i) Temperature (T) vs. Time

(ii) Relative Humidity (RH %) vs. Time

(iii) Actual Vapour Pressure (AcVP) vs. Time

AcVP stands for the actual vapour pressure of the water vapour and can be measured using **Equation 4.4** by calculating the saturated water vapour pressure (P_{sat}) at a given temperature (T).

$$Actual VP = P_{sat} * RH\% \quad [Equation 4.4]$$

The actual vapour pressure of the water is more useful than RH% at a given temperature, and the relative humidity can change with ambient conditions. Therefore, by measuring ActVP, condensation limits at different temperatures can be acquired. Time-temperature analysis can be recorded using the ATEC302 controller software and can log the temperature data using a USB port (Prolific). This can be used to modify the variables (proportion band, integration, and derivative value), but most importantly, can change the set point temperature of T_{stage} during experimentation. The ATEC software panel is shown in **Figure 4.18**.

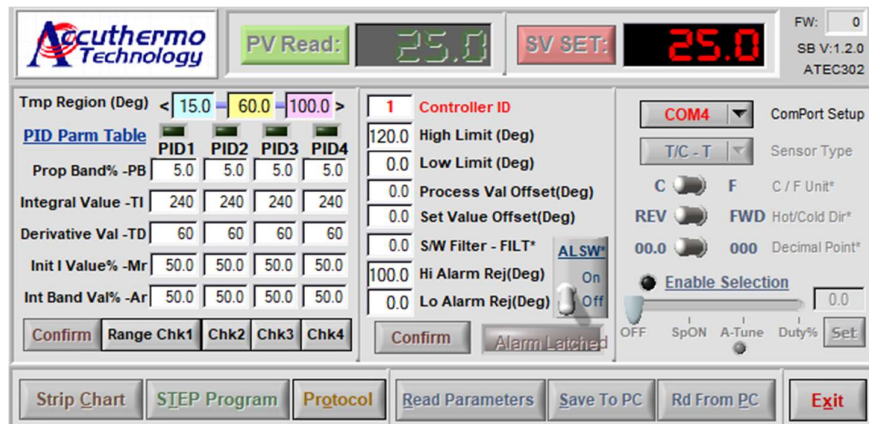


Figure 4.18 Accuthermo ATEC302 software for controlling temperature via USB connection.

By interpreting T_{stage} and the vapour pressure of water at a specific point in time, the condensation process can be controlled by decreasing the temperature of the stage to a

saturation value larger than 1. Increasing the precision of thin film swelling *via* temperature control is a robust method that can be adapted to the SVBF method. Furthermore, quick evidence of many variables such as flow rate, temperature or solvent concentration can be easily changed as polymer swelling can be very sensitive to temperature changes and the condensation effects.

4.2.4 Reflectometry Setup and Procedure

Reflectometry was the method chosen to analyse the swelling dynamics of the polymer film *in-situ* during experimentation. Since the polymer film is swollen by the solvent, the refractive index will change for thickness, d_s , as previously discussed in **Section 2.2**¹⁹. The Lorentz-Lorenz rule of mixing is used to compute the refractive index change. The refractive indices of pure solvent and polymer are shown in **Table 4.1**.

Table 4.1. Optical Properties of Material and Solvent

Component	Refractive Index Value @ 600nm
Polystyrene ²⁰	1.59 ± 0.001
Chloroform ²¹	1.44 ± 0.001
Toluene ²²	1.50 ± 0.001

The effective refractive index, n_{12} shows slight changes in the reflective properties of the PS thin film as shown when swollen in the swelling solvents, CHCl_3 and toluene. The ϕ_p values of 0.5 (SR = 2), 0.33 (SR = 3), 0.25 (SR = 4), 0.2 (SR = 5) and 0.17 (SR = 6) were assessed to show the change in n as shown in **Figure 4.21**.

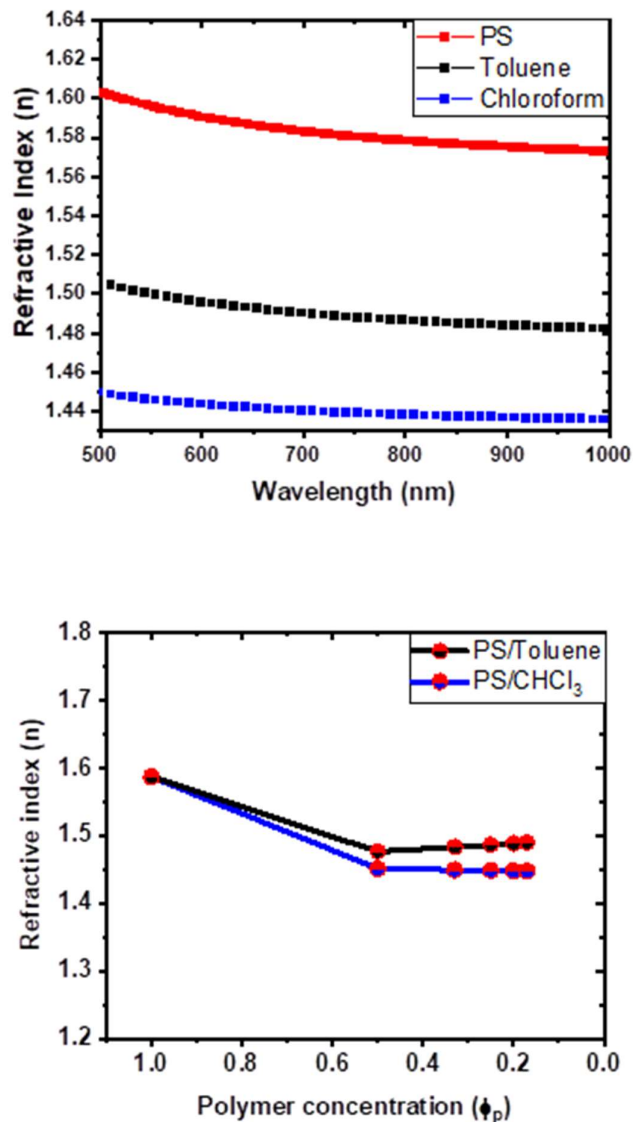


Figure 4.21. (Top) Pure toluene and CHCl₃ refractive indices over a wavelength range of 500 -1050 nm. (Bottom) Change in refractive index for swollen PS thin film at polymer concentrations (ϕ_p); 0.5 (SR = 2), 0.33 (SR = 3), 0.25 (SR = 4), 0.2 (SR = 5) and 0.17 (SR = 6).

Since the values of n only change at approx. ~ 0.1 , there should be no significant effects on the reflectometer signal when these values are inputted into the Filmetrics software; however, the goodness of fit will still be assessed. This method gives us an accurate

representation of how the sample's reflectance can change during the swelling process; however, the roughness of the sample can also impact the reflectance of the signal²³. Since water droplet templating produces porous media, the goodness of fit (GOF) acquired by the reflectometer can drop to 0. Exposure of the bare SiO_x surface ($n = 1.4580$ at 600 nm)²⁴ can impact the change in the PS film's reflectivity and result in acquiring an invalid representation of film thickness. Therefore, subsequent analysis and characterisation of the film after swelling should be carried out.

All calibrations were carried out prior swelling.

- RTD probe calibrations were carried out using 2 RTD probes at a set temperature. If the 2 probes were both measuring a consistent temperature of ± 0.5 °C, the system is calibrated.
- The humidity probes were calibrated using boiling water in a beaker. If the probes show high RH% values for each measurement, the system is adequately calibrated. Further analysis was carried out by changing the flow rate of water in the chamber.
- The reflectometer was calibrated using a standard SiO_x purchased by Filmetrics at a known thickness. This was used to identify that the reflectometer was giving accurate values. The oxide thickness was usually 3100 Å thick.
- Gas flows were not measured as the rig did not have the suitable apparatus to measure flow rates. The ratio of solvent: water was measured. This is discussed in detail in Chapter 5.

4.3 Conclusion

In conclusion, to this section, the adapted rig now has the functionality to produce breath figures. This involved multiple modifications to the current SVA setup by creating a di-solvent vapour system that can plasticise polymer films and condense water onto the swollen film by strictly controlling the temperature of T_{stage} . The addition of probes to the setup provides the rig user with a method to quantify the dew point and temperatures needed to induce condensation. Furthermore, implementing a Matlab script to set up better data acquisition and humidity control, can automate the process for future studies. Furthermore, the use of flow valves in the setup can control the swelling rate of thin polymer films, and the kinetics of thin-film swelling can be assessed.

However, several issues were noted after the construction that could easily be remedied with upgrades:

- **Use of temperature control in the water bubbler.** The water bubbler setup could be better controlled using another PID setup, as the bubbler temperature remained at ambient temperature. By maintaining the water at a specific temperature, experiments are kept constant and will not rely solely on the ambient temperature of the room.
- **Use of heated piping.** By heating the piping setup, the issue with condensation on the pipes could be avoided. This allows the temperature of both the solvent and water bubblers to be heated reducing the time needed to reach adequate saturation values in the chamber. Furthermore, the temperature of the stage could be kept at higher temperatures and faster condensation would be possible.

- **More precise control of flow rates.** Flow rate analysis was a challenge for both piping setups as (1) the organic solvents were not compatible with many types of flow metres and (2) the cost would greatly increase, as highly specific flow metres would be required.
- **Greater control of stage temperature.** The temperature of the stage solely relies on the feedback loop of the PID controller that has specific parameters that controls the heating and cooling. Further optimisation could be carried out to improve the ramp of heating and cooling in an aim to get to set point temperatures at quicker time intervals.
- **Automation.** The rig has the capacity to be automated however, due to time restraints and lack of expertise in this field, it was not possible. By automating the polymer swelling and controlling condensation using computer programming, would be an ideal method for acquiring data and achieving better control.

Following on from this, optimisation, control, and parameter requirements will be discussed in the next chapter. SVBF requires specific parameters for breath figure to occur for linear PS systems²⁵. Since temperature effects and flow rate measurements can be modified, the SVBF method will be carried out on thin PS films in the aim to produce microporous thin films following this novel method and design.

4.4 References

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Chapter 5

Optimisation of Solvent Swelling and Condensation to Create Porous Polystyrene Thin Films

5.1 Introduction

PS is a low-cost polymer with high spin-coating thickness uniformity¹, process stability, and functions as a dry etch negative resist². PS film swelling can be monitored by *in-situ* reflectometry. As discussed in **Chapter 2**, the polymer film exposed to solvent vapour can become mouldable and can be structured by condensing water droplets. Conceptually, this process avoids the challenges associated with complex heat/mass transfer dynamics by strictly controlling the film's swelling and templating in a stepwise manner through temperature and vapour flow control. Furthermore, this approach facilitates understanding the role of thermodynamics and wetting interactions³ on water droplet templating and interprets the effects of polymer swelling on the production of BF patterned films. Using these concepts, a fast, fully automated, low-cost, and scalable method for producing microporous polymer resists can be produced and function as pattern-transfer templates for lithographic applications can be developed.

Innovative processing capabilities to produce new bottom-up templates are in high demand because of top-down costs and manufacturing process limitations for large volume production⁴. BF type methods require specially designed and constructed polymeric systems with well-designed process controls, especially regarding the control of humidity levels. Humidity is the main factor that affects porosity, density, and size. This chapter assesses the

use of solvent swelling and the mixing of 2 different vapour flows to create microporous polymer films. By strictly controlling the temperature and flow rate, each parameter involved within the BF process can be fine-tuned, such as thin film swelling, solvent concentration, and water vapour saturation.

5.2 Polymer of Interest

The polymer system that has been specifically chosen for breath figure optimisation is the atactic homopolymer, polystyrene (PS). Polystyrene is polymer with repeating aromatic styrene units. Since the polymer is atactic, the phenyl groups are (structurally) randomly distributed along the polymer chain and is amorphous. It is usually synthesised *via* free radical chemistry. Polymer source reports that the polymerisation is usually carried out in THF solution at a low temperature of $-78\text{ }^{\circ}\text{C}$ ⁵, as shown in **Figure 5.1**.

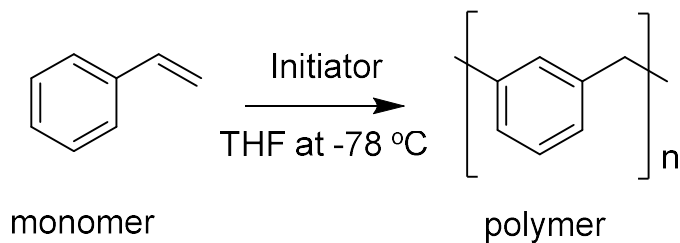


Figure 5.1 Anionic polymerisation of styrene as reported by Polymer Source for P40440S⁵.

PS was chosen as a viable polymer as a considerable amount of research has been previously outlined and is an ideal candidate for producing breath figures due to its swelling characteristics, as shown in numerous studies^{6–10}. However, strict control is needed for dynamic approaches^{11–15}. The polymer has a glass transition temperature (T_g) of $100\text{ }^{\circ}\text{C}$ and a melting point (T_m) of $270\text{ }^{\circ}\text{C}$. Polystyrene is one of the most used plastics worldwide and is easily accessible for synthesis. Polystyrene thin films are ideal electrical insulators¹⁶ and

have excellent optical clarity¹⁷ regarding their amorphous nature. Additionally and of particular importance, it can function as a negative resist for electron beam lithography¹⁸ due to having good chemical resistance to acids and bases. Furthermore, the templates can be easily removed using organic solvents such as toluene and THF, post-treatment. Zeyu *et al.* used polystyrene spheres to create nanostructures to improve solar panel reflectance by enhancing the light trapping¹⁹ by using the spheres as templates for creating “back reflectors” after Ag sputtering.

5.3 Optimising PS Thin Film Uniformity

5.3.1 Polymer Solvent Choice

The spin-coating method was adopted as the first approach in up-scaling the BF process to produce thin films of a similar thickness. Polymer solutions were spin-coated onto clean silicon wafers at different velocities and polymer concentrations, yielding various thicknesses following the Hall *et al.* method¹ for a selection of different solvents. The choice of spin-coating solvent is critical in forming films of uniform thicknesses on the SiO₂ surface with respect to the solvent physical properties (**Table 5.1**), such as volatility, wettability, and polymer-solvent interactions.

Table 5.1 Material Physical Properties.

Solvents/Materials	Molar Mass (g mol ⁻¹)	Density (g cm ⁻³)	Vapour Pressure (20°C, kPa)	Enthalpy of vaporisation (kJ mol ⁻¹ at 298.15K)
Toluene (PhCH ₃)	92	0.866	3.786	38.1 ± 0.11
Tetrahydrofuran (C ₄ H ₈ O)	72.11	0.889	19.792	32.9
Acetone (CH ₃) ₂ O	58.08	0.7845	24.571	29.7 ± 0.004
Chloroform (CHCl ₃)	119	1.49	21.086	31.20 ± 0.08
Styrene (C ₈ H ₈)	104.15	-	-	-

The studied solvents are as follows: toluene, tetrahydrofuran (THF), acetone and chloroform (CHCl_3). Solvents with high evaporation are needed to produce good thickness distribution on flat substrates²⁰. The solvents with the highest vapour pressures at room temperature are THF (19.8 kPa), chloroform (CHCl_3) (21.1 kPa) and acetone (24.6 kPa) in increasing order. Toluene was shown to be the least volatile (3.79 kPa). Wettability of the substrate to the solvent must also be accounted for. Toluene has a computed static contact angle of 3° for SiO_2 (**Figure 5.2**)²¹.



Figure 5.2 Toluene static contact angle on SiO_x .²¹

Unfortunately, other solvents such as THF, chloroform, acetone were challenging to measure contact angles with respect to their high volatility.

5.3.2 Substrate Analysis

The substrate used in this project is Intel grade Si wafer with an orientation of $\langle 100 \rangle$. This Si wafer is undoped, has a thickness of 650 μm , and is single side polished. For a 10 x 10 μm scanned region, root-mean-squared roughness ($\text{RMS} = 0.243 \text{ nm}$) was measured by Atomic Force Microscopy (AFM) (**Figure 5.3**).

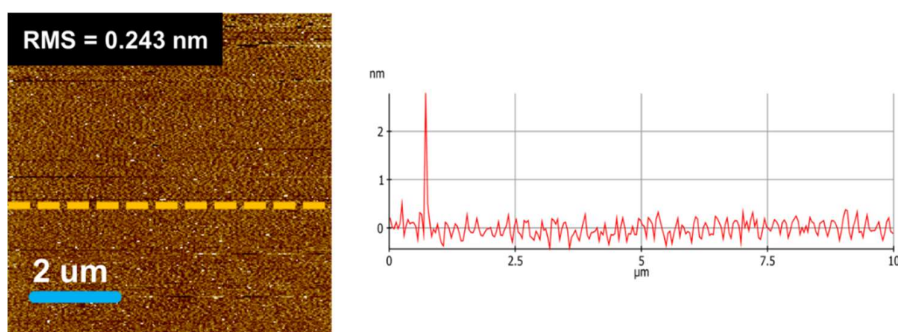


Figure 5.3 AFM image (10 x 10 μm) of an ultra-smooth SiO₂ substrate surface with a graphical representation of z- height.

A native SiO₂ is generally exposed to the substrate's surface as Si readily oxidises in ambient conditions. This causes the substrate to be hydrophilic and has a water contact angle of 20.7° for an ultra-clean silicon surface at room temperature²². Since the contact angle is low, the water will spread readily across the substrate and will have a low surface tension on a high energy SiO₂ surface that was measured to be 280 mJ m⁻². Oxygen plasma treatment has also been shown to decrease the water contact angle of the substrate, as shown in

Figure 5.4.

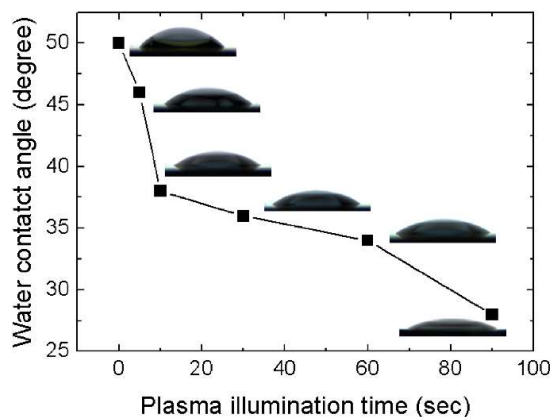


Figure 5.4 The change in water contact angle in respect to plasma illumination time.

Substrate cleanliness effects the overall static contact angle of the SiO₂ surface²³.

Reproduced from cited source.

Kim *et al.* reported that plasma treatment removed impurities such as physisorbed species and volatile organic contaminants that can affect the contact angle²³. This occurs by bombarding the substrate surface with ionised gas resulted in removing any foreign particles from the surface. Oxygen plasma can also hydroxylate the silicon surface thus activating the surface for subsequent chemical reactions.

Previous studies have shown that any solvent with hydrophilic end groups have good wetting properties on a silica surface²⁴. The 2 types of favourable solvents for a silica surface are (a) polar protic solvents that have polar OH groups and (b) dipolar aprotic solvents that have a large dipole moment within the molecule and possess no OH groups.

The types of suitable solvents for silica are shown in **Figure 5.5**.

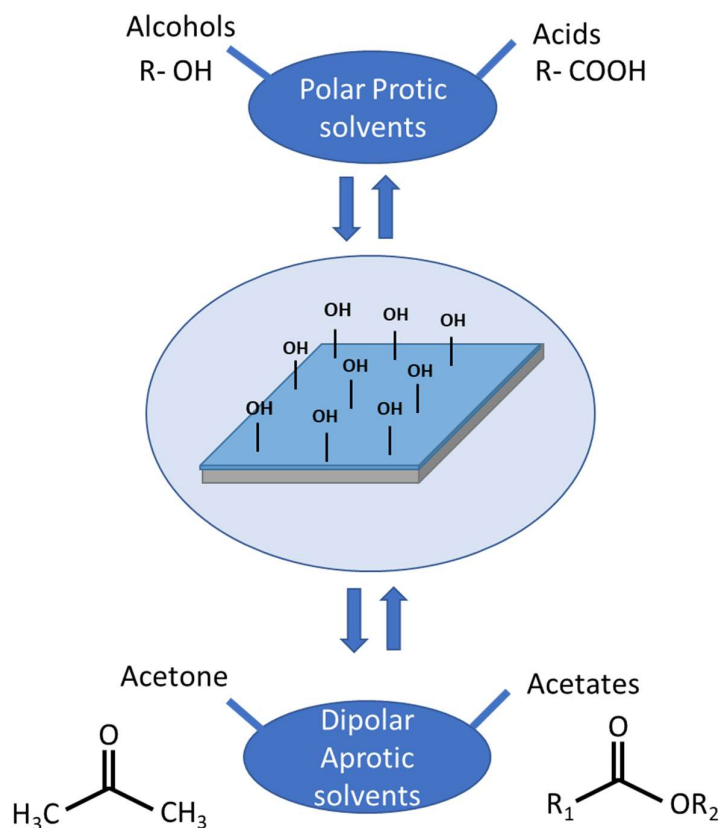


Figure 5.5 Types of solvents that have favourable interaction with a silica surface.

5.3.3 Thin Film Quality Study

Different types of colours can be generated by modifying the thickness of the thin film. This is phenomena occurs as result of thin film interference²⁵. The PS/toluene, PS/THF and PS/CHCl₃ thin films generated blue, orange-purple, and green respectively as shown in **Figure 5.6**. There was no clear film colour for the PS/acetone solution.

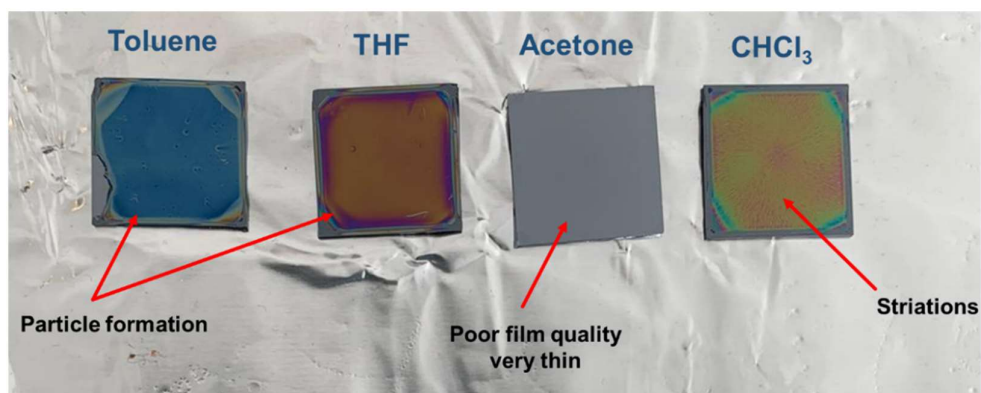


Figure 5.6 Types of solvents that have favourable interaction with a silica surface.

The thickness of the film can be measured following **Equation 5.1**.

$$2nd \cos \beta = \left(m - \frac{1}{2}\right) \lambda_r \quad \text{Equation 5.1}$$

Where n is the refractive index, d is the film thickness and β is the angle in the film calculated by knowing the incident angle α , using Snell's law²⁶. From knowing the wavelength order (m) and the maximum wavelength λ_r , the thickness of the film can be measured. All the thickness measurements were recorded using the reflectometer.

PS-solvent solutions (2 w/w. %) were spin-coated at 1000 rpm and the film quality was compared. Initial thicknesses (d_0) of samples were measured as 123 ± 3 , 228 ± 3 and $363 \pm$

13 nm for toluene, THF and CHCl_3 , respectively. The acetone-polymer solution was unsuccessful as only polymer agglomerations could be seen on the silicon wafer.

The samples were analysed in more detail using AFM (Atomic Force Microscopy) to interpret the effects of the polymer-solvent dynamics (**Figure 5.7**). The PS-toluene ($d_o = 123 \pm 3$ nm) solution formed agglomerates on the surface, were 20 nm in height. Even though satisfactory polymer-solvent interaction was calculated ($\chi = 0.73$), suggesting good solubility for this solvent system²⁷, the agglomerates could perhaps be external contaminants from the environment.

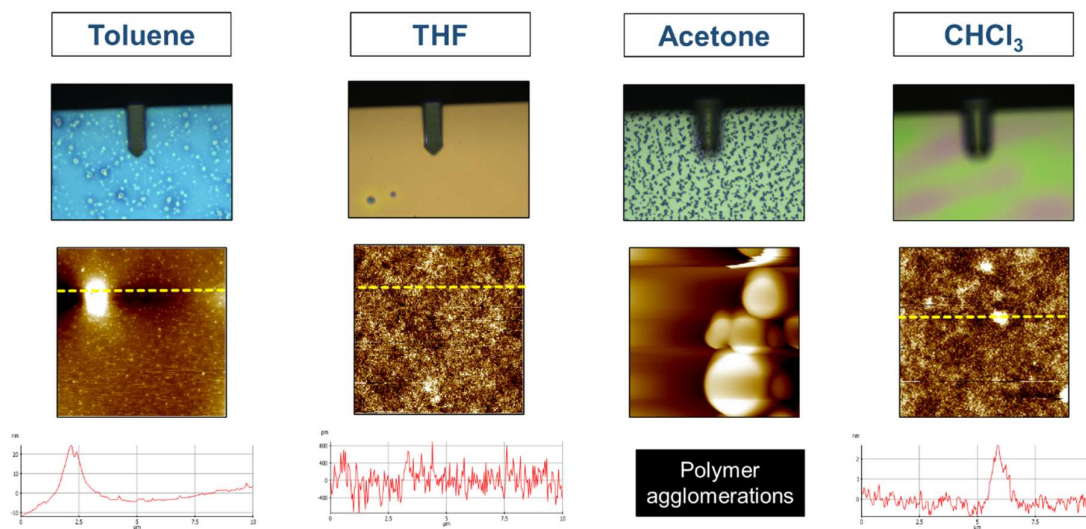


Figure 5.7 Optical images and AFM images and height profiles (10 x 10 μm).

The PS-THF ($d_o = 228 \pm 3$ nm) solution shows much better thin film uniformity and smoothness in the order of picometres can be seen. THF has similar compatibility to toluene ($\chi = 0.77$). It was suggested that THF might have a better affinity to the SiO_2 wafer than toluene due to its anhydride moiety, which gives the solvent hydrophilic interaction with the substrate surface.

If the polymer chain has good interaction with both solvent and polymer a uniform film can be produced. Surprisingly, acetone was the worst solvent of all those studied as no coverage of polymer film can be seen throughout the entire sample, even though it is a good dipolar protic solvent. Since there is poor monomer-solvent interaction and quick evaporation rates, large micron size agglomerations of polymer can be seen. Acetone was not investigated any further.

The PS-CHCl₃ ($d_o = 363 \pm 13$ nm) solution showed striations/ streaks across the entire film i.e., the polymer film had poor thickness distribution. Even though the solution has a $\chi = 0.48$, the volatility of the solvent affected the uniformity of the polymer film. THF was the best solvent for the spin-coating method. However, the film was too thick at this w/w.%. A lower w/w % of THF generated similar comets (particle contaminants) in the PS film. Therefore, toluene was used as the spin-coater solvent for the duration of the project. Toluene was an adequate solvent for spin-coating PS and PS brushes by filtering the solution with a 0.2 μm PTFE filter. The large impurities seen without filtering were removed. This approach improved polymer films and the quality is shown in **Figure 5.8**

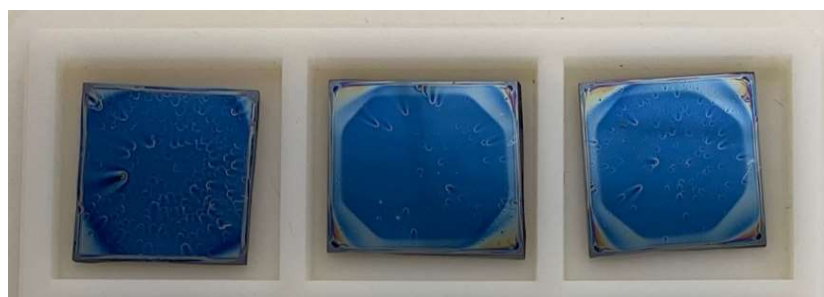


Figure 5.8 Image of 100 nm Polystyrene (PS) thin films on native silicon substrate.

A reduction in crystallites can be seen; however, they were removed during the solvent swelling process and did not impact the droplet templating process when characterising the films.

5.4 Solvent Swelling Studies

As previously discussed, the swelling of thin films was achieved by exposing the film to solvent vapour. The solvent molecules can enter the dynamic pore system within the polymer matrix. The molecules diffuse through the film, increasing the volume of the overall film following *Fick's Law of diffusion*²⁸, where the diffusion rate is lower than the polymer chain's relaxation rate. The following section discusses the effect of swelling polymer films in different solvents compatible with PS.

5.4.1 Chloroform (CHCl₃) Swelling

Chloroform (CHCl₃) has been identified as a good swelling solvent for linear PS because of suitable polymer-solvent interaction ($\chi = 0.48$). Furthermore, numerous BF studies use CHCl₃ as the solvent with respect to its high volatility, which can rapidly reduce the temperature of the polymer-solvent solution^{29–32}. 17 kg mol⁻¹ (17K) polystyrene films (127 ± 3 nm) were spin-coated onto silicon wafers and swollen at different CHCl₃ saturations to identify the optimum solvent uptake before the polymer film dewets at a specific molecular weight of 17K. Dewetting³³ can occur at high saturations ($S > 1$) as the solvent condenses, destroying the polymer film³⁴. This is where the polymer film begins to destabilise, and holes appear within the polymer film. This was not effective for templating thin films, as the pattern will not be produced during the templating process. Therefore, careful attention to temperature and solvent vapour pressure is needed. A temperature of $T_{\text{bub}} = 20\text{ }^{\circ}\text{C}$ was maintained *via* PID control for each experiment. The T_{stage} value was decreased to reduce the vapour pressure of the solvent in the chamber resulting in changing the solvent saturation conditions in the chamber. Stage temperatures recorded for each solvent saturation are shown in **Table 5.2**, with additional data showing the swelling efficacy of the chloroform

solvent at the P/P_{sat} values ($P/P_{\text{sat}} = S$). The swelling experiments are graphically shown in **Figure 5.9**.

Table 5.2 CHCl₃ Swelling Analysis at $T_{\text{bub}} = 20 \pm 0.15$ °C.

P/P_{sat}	T_{stage} (°C)	ΔT (°C)	Swelling Factor (d/d_0)	Solvent Uptake (ϕ_s)
0.7 ± 0.0019	26.6 ± 0.15	6.6	1.298	0.23
0.8 ± 0.0021	24.3 ± 0.15	4.3	1.370	0.27
0.9 ± 0.0023	22.4 ± 0.15	2.4	1.429	0.3
1.0 ± 0.0025	20.7 ± 0.15	0.7	*DW	*DW

*DW – Dewetted

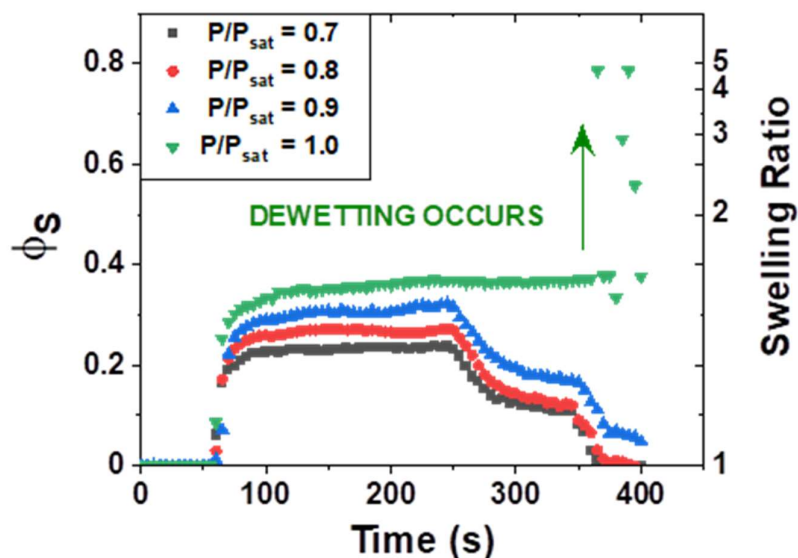


Figure 5.9 In situ reflectometry measurements monitoring the swelling of linear PS.

Saturation effects were fine-tuned by modifying T_{stage} with an offset value of $+ 0.7$ °C for each temperature recorded for chloroform as shown in **Table 5.2**. The propagation error (i.e. error of uncertainty) was used to calculate the uncertainty of saturation measurements for both temperature probes with tolerance of ± 0.15 . The partial derivatives for the Antoine equation for CHCl₃ were $A = 6.95465$, $B = 1170.966$ and $C = 226.232$. Changing the saturation (P/P_{sat}) of the solvent in the chamber can impact the penetration of solvent into the PS film by keeping the temperature of the solvent bubbler constant (20 ± 0.5 °C) while

modifying T_{stage} . The highest T_{stage} temperature (26.6 °C) resulted in the lowest swelling ratio of 1.2, equivalent to a ϕ_s value of 0.16, identifying that 16% of solvent was incorporated into the polymer film matrix. Low stage temperature (20.7 °C) results in the highest swelling ratio of 1.8, followed by dewetting. The rapid jump in thickness at ~ 380 seconds, formed agglomerates of polymer and the exposure of the bare silicon surface caused reflectometer errors to occur. In addition to this, since P/P_{sat} was at the saturated temperature ($S > 1$), the solvent caused the film to rupture and dissolved into polymer agglomerates on the surface. Film dewetting resulted in defects which caused irregular porosity in the thin films. The rapid removal of solvent at 250 seconds for each experiment was carried out by heating T_{stage} to 20 °C, followed by an N_2 purge. Post-swelling optical images are presented in **Figure 5.10**.

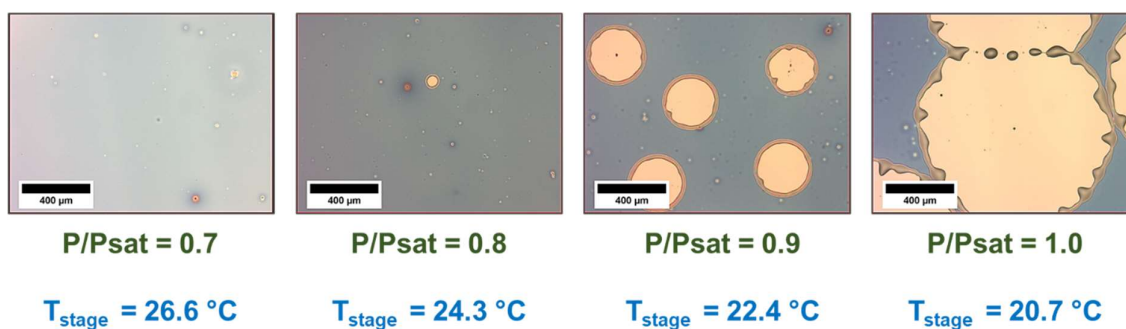


Figure 5.10 Optical images of post-swelling 100 nm 17 kg mol⁻¹ PS films on native Si surface.

The most successful swelling was $P/P_{\text{sat}} = 0.8$. A swelling ratio of 1.4 was recorded, acquiring an estimated ϕ_s value of 0.3 ($SR \sim 1.4$), indicating that the polymer film was reasonably swollen for the entire swelling process. An increase in saturation caused the entire polymer film to degrade. High chloroform saturations were unsuitable for swelling linear PS (17K) as it resulted in dissolving the thin film as shown in **Figure 5.11**.

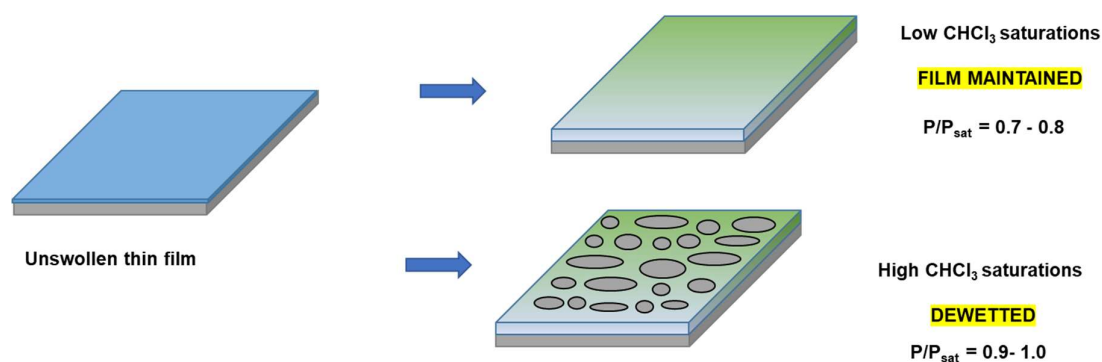


Figure 5.11 The effects of dewetting at different saturations.

5.4.2 Toluene Swelling

Another solvent under investigation was toluene, which also was reported as a good swelling solvent for linear PS, having suitable polymer-solvent interaction $\chi = 0.73$. BF studies using toluene have also been reported elsewhere^{31,35}. However, toluene is less volatile³⁶ than CHCl_3 , so more energy (higher temperatures) would be needed to vaporise the solvent. Therefore, higher ΔT values were needed compared to CHCl_3 as the temperature changes must be much higher to increase the saturation of toluene in comparison to CHCl_3 as previously discussed in 5.4.1

A similar swelling procedure as discussed in 5.4.1 was carried out; however, HPLC grade toluene was used as the swelling solvent. Toluene swelling contrasted with chloroform as better swelling stability can be seen for all experiments. The temperature of the solvent bubbler was kept constant (20 ± 0.5 °C) while modifying T_{stage} with an offset value of + 0.7 °C for each temperature recorded for toluene as shown in

Table 5.3. Propagation errors were also used to calculate the uncertainty of saturation measurements. The uncertainties were measured by calculating the partial derivatives of the

Antoine equation and inputting the values of $A = 6.95087$, $B = 1342.31$ and $C = 219.187$, respectively. Reflectometry swelling analysis is shown in **Figure 5.12**

Table 5.3 Toluene Swelling Analysis at $T_{\text{bub}} = 20 \pm 0.15$ °C.

P/P_{sat}	T_{stage} (°C)	ΔT (°C)	Swelling Factor (d/d_0)	Solvent Uptake (ϕ_s)
0.7 ± 0.0021	27.5 ± 0.15	7.5	1.23	0.19
0.8 ± 0.0024	24.9 ± 0.15	4.9	1.32	0.25
0.9 ± 0.0027	22.7 ± 0.15	2.7	1.71	0.42
1.0 ± 0.0029	20.7 ± 0.15	0.7	1.78	0.44

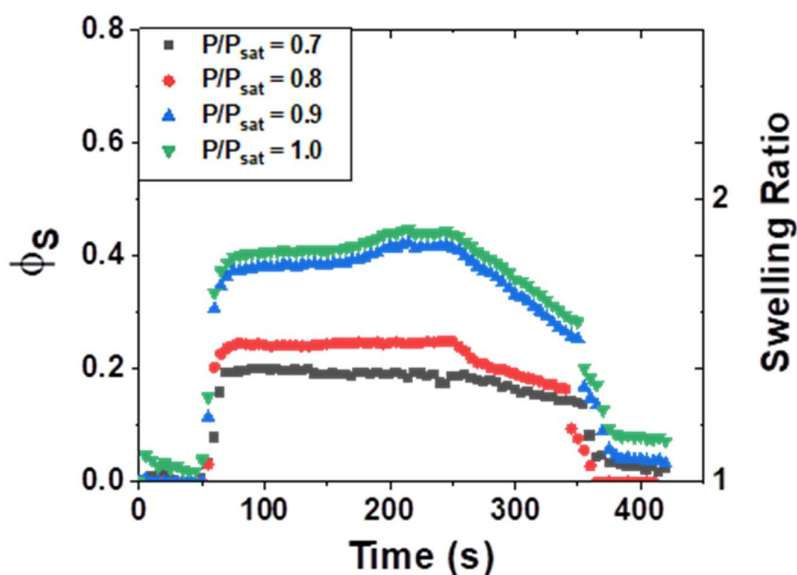


Figure 5.12 In situ reflectometry measurements monitoring the swelling of PS 17K on native silicon substrate in different saturations of toluene vapour.

The highest T_{stage} temperature (27.5 ± 0.15 °C) resulted in the lowest swelling ratio of 1.2, equivalent to a ϕ_s value of 0.18, indicating that 18% of solvent had been incorporated into the polymer film matrix. Conversely, low stage temperatures (20.7 ± 0.15 °C) result in the highest saturation where the solvent can begin to condense onto the film. This results in the highest swelling ratio of 2, where $\phi_s = 0.5$ indicates the film had 50% solvent uptake and no

dewetting was detected by the reflectometer. The solvent was vented at 250 seconds and the film was heated to 30 ± 0.15 °C to drive off any excess solvent in the film.

The swelling data shows lots of promise for toluene swelling the polymer film to higher swelling ratios compared to CHCl_3 . To better understand the film stability, post-swelling optical images were taken to identify the film's quality, as shown in **Figure 5.13**.

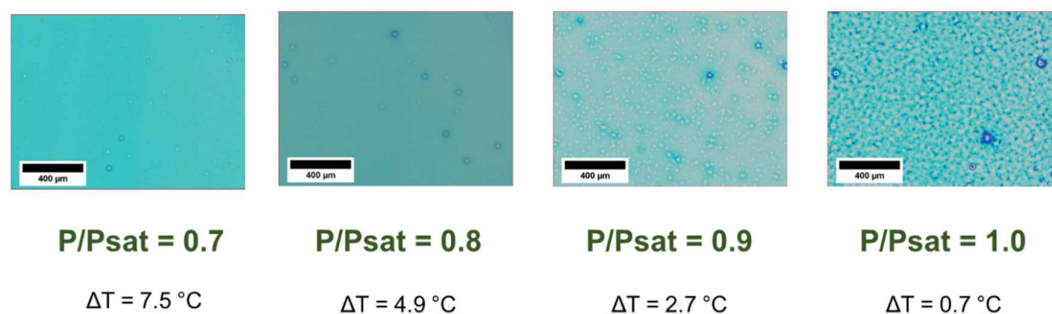


Figure 5.13 Optical post-swelling images of PS 17K swollen in toluene at various saturations; 0.7, 0.8, 0.9, 1.0.

Optical measurements showed minimal dewetting at all saturations and the film quality remained intact. There were minor pockets of dewetting observed at saturations of 0.9 and 1.0; however, the film was not dewetted in contrast to CHCl_3 (**Figure 5.10**). This was not surprising, as the solvent would begin to dewet the film at these saturations as shown previously in **Figure 5.11**. An unusual feature can be seen at $P/P_{\text{sat}} = 1.0$, where a contrast of colour in the film from film dewetting occurred in various regions generating different thicknesses across the entire film. AFM analysis was carried out to observe these dewetting regions showing increased trough depth at higher saturations, as presented in **Figure 5.14**.

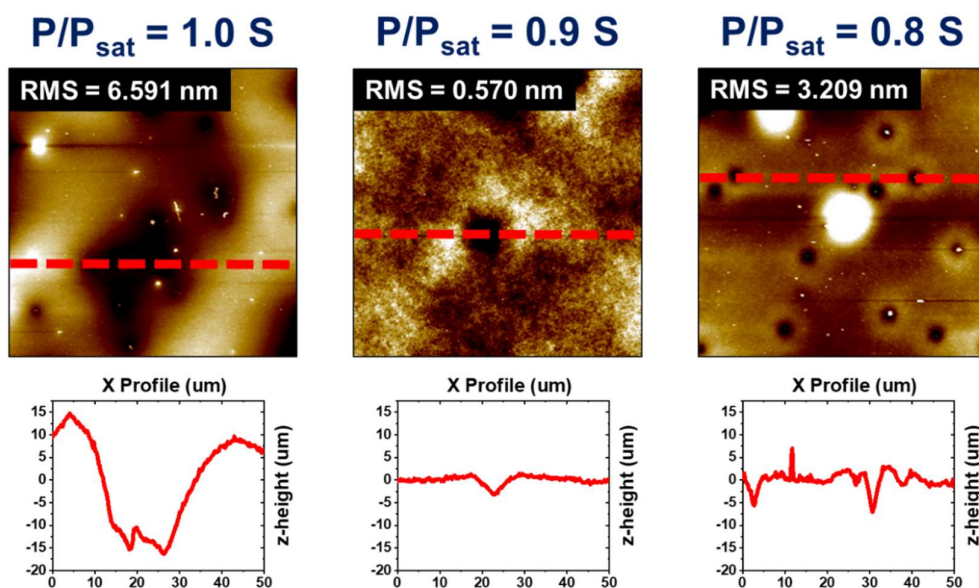


Figure 5.14 AFM post-swelling images (50 x 50 μm) of PS 17K swollen in toluene at various saturations; 1.0, 0.9 and 0.8.

There was a significant difference between $P/P_{\text{sat}} = 0.9$ and $P/P_{\text{sat}} = 1.0$ as the polymer dewetted by increasing the saturation. Although there is a higher RMS for $P/P_{\text{sat}} = 1.0$, this additional dewetting resulted in a higher RMS value. The agglomeration of the polymer was measured with a z-height of 12 nm.

5.5 Uncontrolled Static Condensation Procedure

Firstly, a quick investigation was carried out to identify if high relative humidity (RH %) can be achieved by adding vials of de-ionised water into the SVA chamber. This experiment was carried out prior to further rig modifications. The setup for the uncontrolled experiment is shown in **Figure 5.15**.

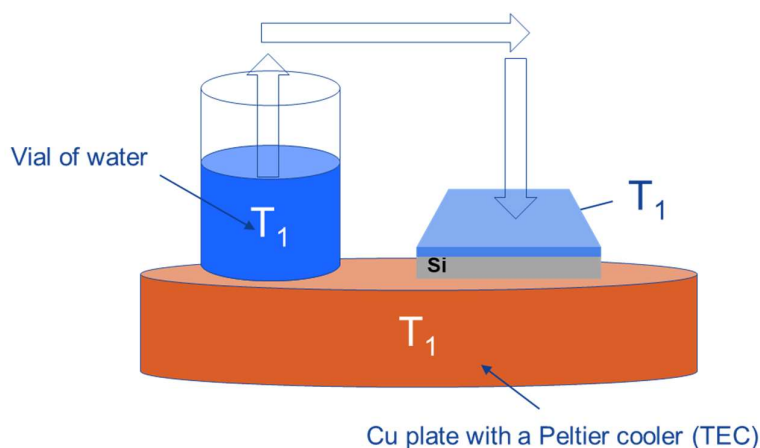


Figure 5.15 Schematic and setup for the static water droplet templating approach.

Since both the water and the sample were placed on T_{stage} , the temperature of the water and the sample would be a similar temperature; thus, it would be impossible to induce condensation as conditions of $\Delta T = 0$. Additionally, since there is a considerable distance between both the sample and the water, the water must be heated to vapour to reach the sample. Evaporation of the water must be achieved to carry the water vapour to the sample. Since the thermoelectric cooling (TEC) setup cannot heat/cool or achieve large ΔT values in short ranges, the current setup is not suitable for the static approach.

Vials of water (2 x 30 ml) were heated at 100 °C on a hot plate and immediately placed on the stage and the vapour pressure of the solvent was recorded at an ambient temperature of 17 °C. The quick decay of RH % in the chamber identified that there would not be enough

time for the vapour to condense onto the thin film as the actual vapour pressure of the solvent was too low to induce condensation at standard temperature and pressure (STP). An exponential decay of 70% - 0% occurred in less than 30 minutes as shown in **Figure 5.16**.

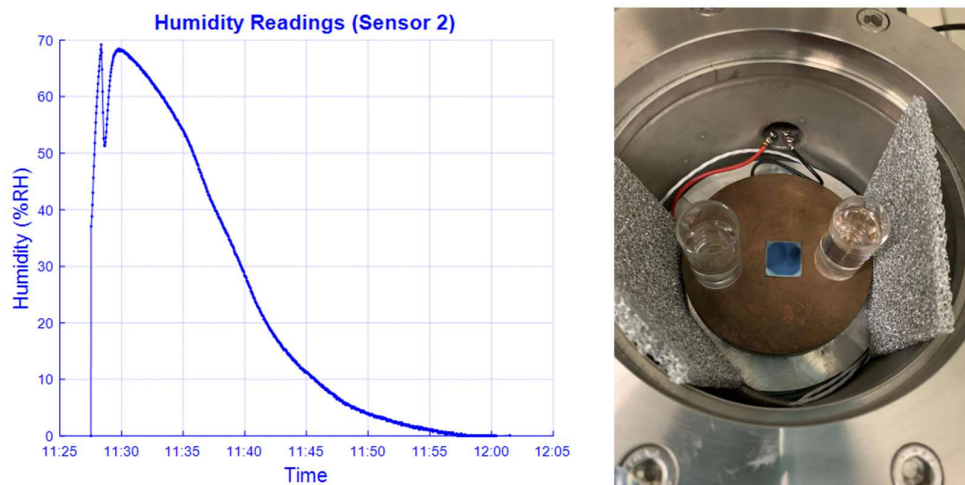


Figure 5.16 (a) Decay of RH% monitored inside the SVA chamber at T = 17 °C.

Low sub-ambient temperatures ($< 0\text{ }^{\circ}\text{C}$) were required to allow for nucleation events of droplet formation. This experiment concluded that numerous problems were encountered with this approach and further rig construction and optimisation were needed.

- 1.) The water must be carried to the sample via a different approach. For example, a dynamic approach would be more applicable for droplet templating as N_2 carrier gas can carry the water to the sample and have enough kinetic energy to drive the water to condense onto the sample.
- 2.) The control of temperatures between the water and sample must be isolated from one another, as the TEC heating unit cannot have high ΔT values in close proximities. However,

by creating a second bubbling unit, N₂ can carry the water vapour to the SVA chamber by constructing a secondary plumbing system, as discussed in **Chapter 4**.

3.) The relative humidity must be maintained at values approx. 60 % and higher throughout the entire swelling process to work at room temperature. The droplet templating method can occur over longer time intervals by maintaining good RH% values by continuously adding water vapour to the chamber. Decreasing T_{stage} can induce condensation and can be controlled by maintaining lower values of the water T_{bub} .

5.6 Flow Rate Measurements using a Rotameter

A rotameter was located upstream from the water bubbler to calculate the water flow rate in the humidity line, as shown in **Figure 5.17**.

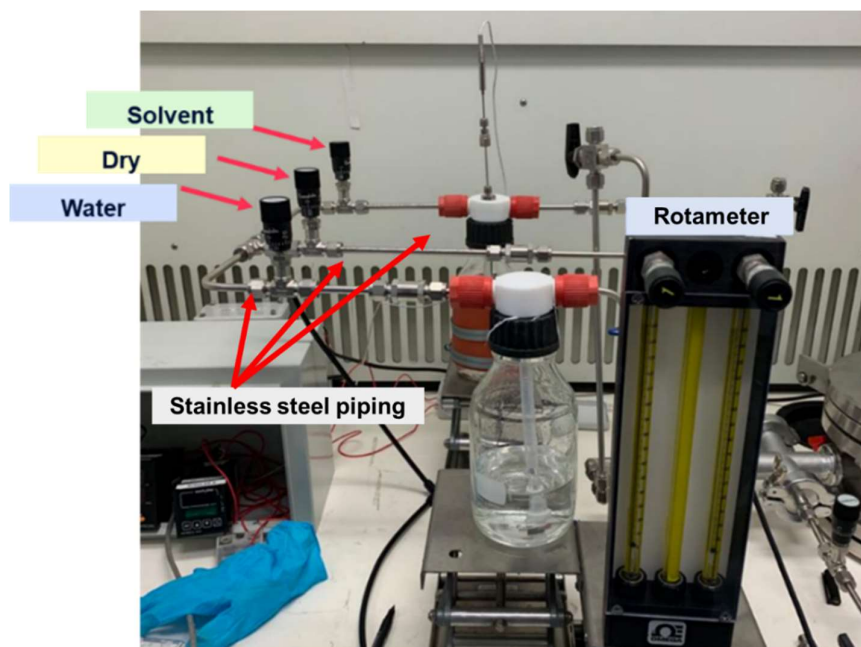


Figure 5.17. Construction of a mixer to the SVA setup.

Relative humidity (RH%) calibrations were carried out at different flow coefficient (C_v). Valves were constructed upstream from the 2-bubbler setups. The opening and closing of the ball valves control the amount of N_2 flow that enters the bubbler set up at a specific rate. The flow rates were then measured using the mixer setup and were constructed upstream from the bubbler, as previously discussed in **Chapter 4**. The maximum flow rate that can be read from the rotameter was 850 cubic centimetres per minute (cc/min). However, when a pressure of 3 bar was applied to the mixer, it could not read the flow rate when the flow coefficient value was $C_v > 0.000125$. Therefore, there is a limitation to using the mixer at high pressures, which resulted in a drop in RH% values at both probes. Both measurements of probes 1 and 2 are shown in **Figure 5.18**.

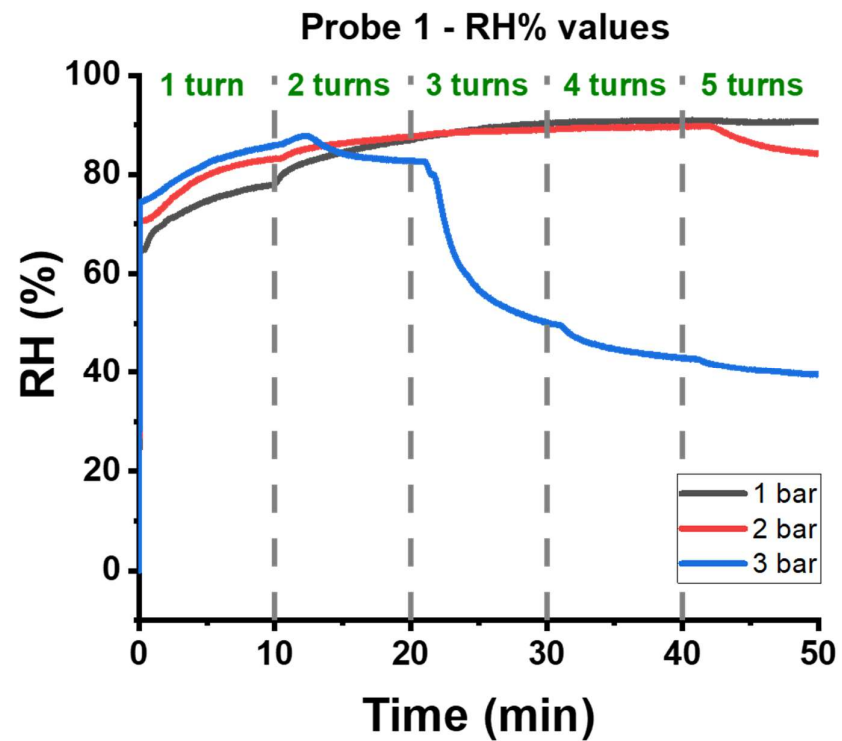
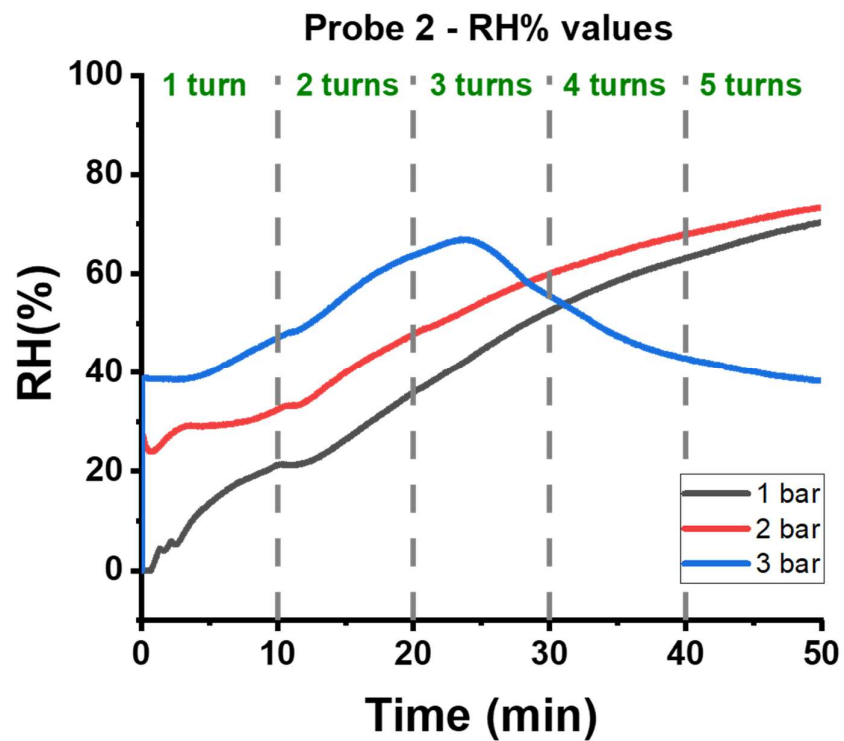


Figure 5.18. Humidity analysis for changing the flow rate of gas by changing the C_v value (flow coefficient).

There was a drop in RH. % values in both probe 1 and 2 after 3 turns ($C_v = 0.005$). Note 0.000125 equates to 1 turn. From firstly understanding the effect of CV on flow rate, optimisation was carried out to identify the conditions needed to improve the flow rate and reduce the time scale to approach adequate RH % values (80%). This was considered a challenge as the maximum flow rate of the mixer could only yield a value of 850 cc/min taking an average of 22 minutes to fill $V_c = 1.94$ L (reported by Lundy) with a mixture of the carrier gas and water. All measurements were recorded at 22 °C and all data is shown in **Figure 5.19**.

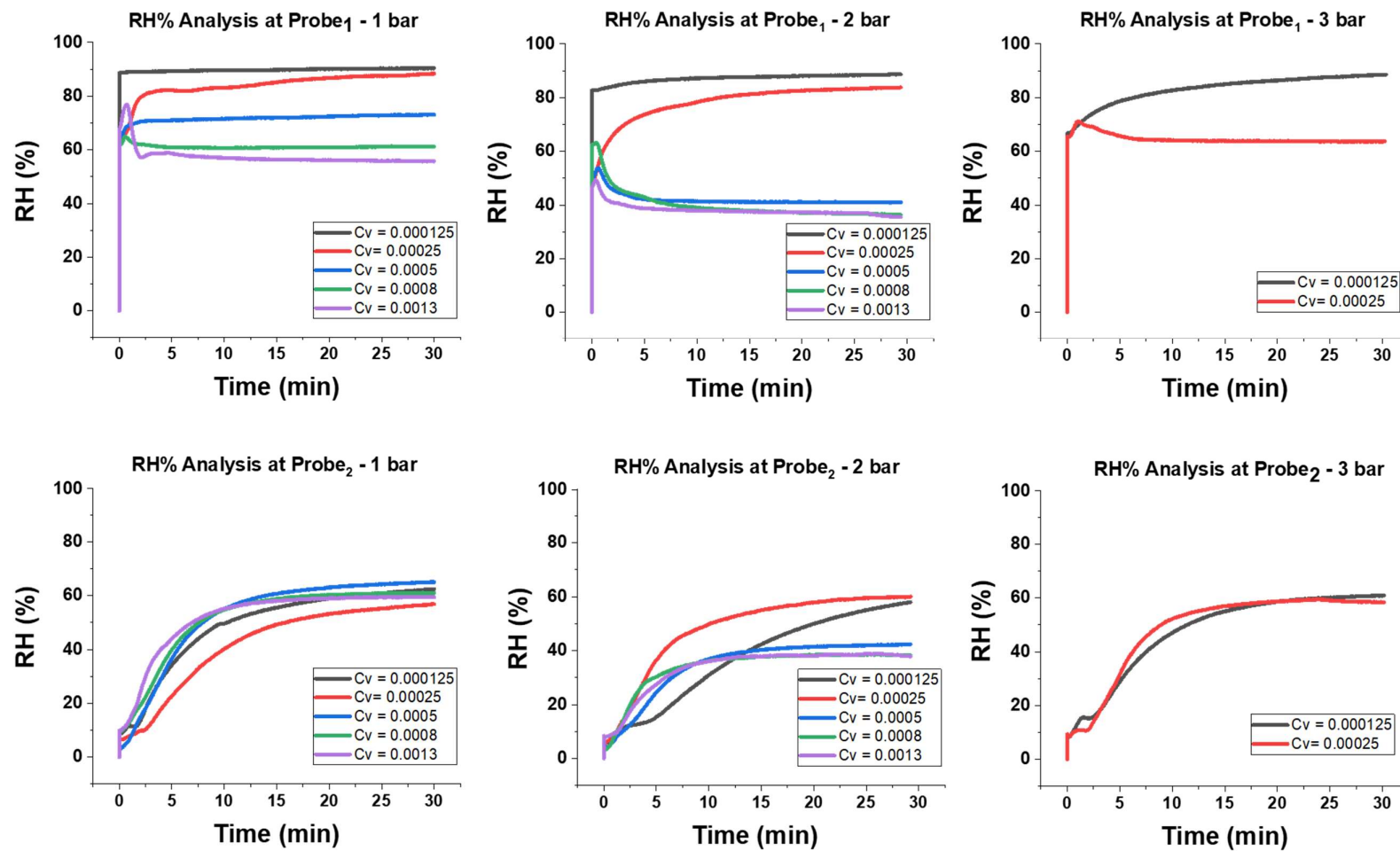


Figure 5.19. Optimisation of RH% from changing the Cv value and pressure.

- At 1 bar, the RH values ranged from 60-90%, depending on the C_V value of the flow valves. The highest RH recorded at this pressure was 90% for a C_V value of 0.000125, equivalent to 1 turn on the flow valve. However, at probe 2 (located in the chamber), the RH% values plateaued at 50-60% and it took approx. 20 minutes to reach these values.
- At 2 bar, RH values have a significant deviation (40 - 85 %) and there was a significant drop in RH at higher C_V values. This was because the vapour was restricted from the flow valves in the mixer a, thus saturating it at high N_2 pressures. Unsatisfying values of < 60 % RH were recorded, thus indicating that the higher pressure from the cylinder will decrease the water vapour saturation.
- At 3 bar, the same issue arised and the RH values max at 60%. Only 2 C_V values were investigated ($C_V = 0.000125$, $C_V = 0.00025$) as these showed the most promise. Both showed very high RH% values at probe 1. However, these were greatly reduced at probe 2 and plateaued at 60% after 10 minutes.

From analysing the temperature of probe 1 and 2 there was considerable loss of heat caused by the condensation of water in the pipes upstream from the chamber. This may have influenced the amount of water vapour entering the chamber throughout the experiment. As a result of these deductions, water bubbler heating was carried out to increase the saturation of water in the chamber Unfortunately, the mixer was not viable to work at room temperature as the vapour pressure was too low. The addition of extra resistances to the setup resulted in water vapour pressures maxing at RH % values of 60% at a temperature

of 22 °C ($P_{\text{sat}} = 2.64 \text{ kPa}$), indicating that a $T = < 15 \text{ °C}$ was needed to induce condensation at a vapour pressure of 1.58 kPa as shown in **Figure 5.20**.

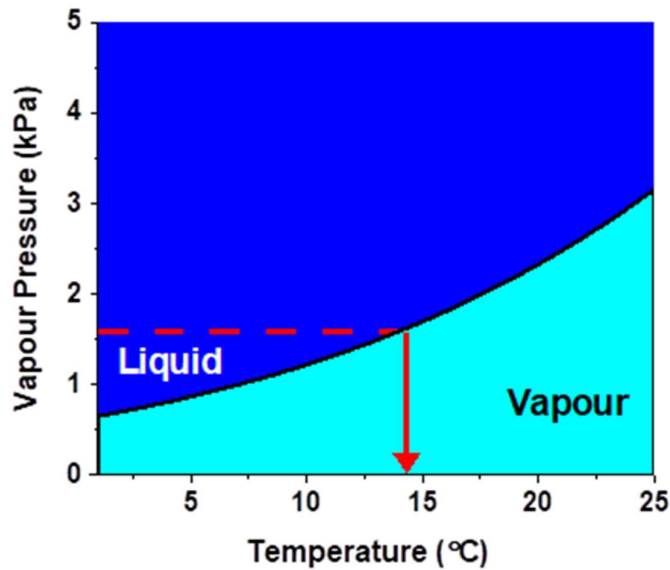


Figure 5.20 Saturation limit for 60% RH ($T_{\text{sat}} < 15 \text{ °C}$) where $P_{\text{sat}} = 1.58 \text{ kPa}$.

5.6.1 Bubbler Temperature Effects on Water Saturation

The temperature of the bubbler (T_{bub}) can be altered to increase the saturation of water in the chamber. By increasing ΔT , the saturation inside the stage can be increased. From heating the bubbler to 30 °C, both temperatures recorded between probe 1 (upstream from the mixer) and probe 2 (located in the chamber) were similar to one another ($\Delta T = 0$) at a flow coefficient of 0.0013 C_v (5 turns). Loss of heat occurred in the piping and mixer upstream from probe 1, resulting in both probes approaching ambient temperatures. Both real-time temperature and RH % probe measurements using the Matlab script (**Figure 5.21**) displayed similar temperature readings for both probes. Further experimental analysis was carried out where the hot plate was set to 100 °C and at a C_v , a value of 0.0013 (5 turns) was measured. The data is shown in **Figure 5.22**.

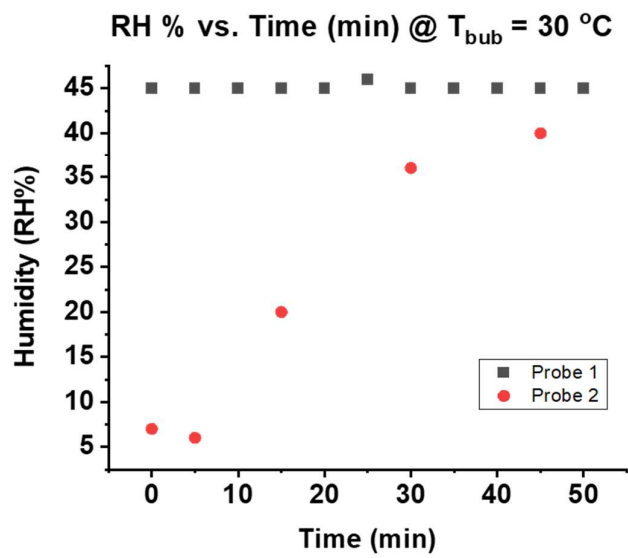
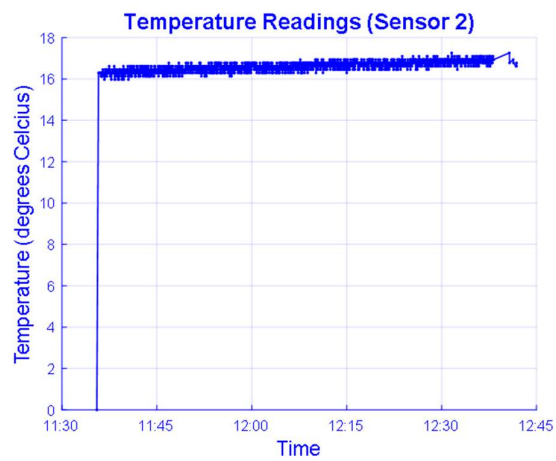
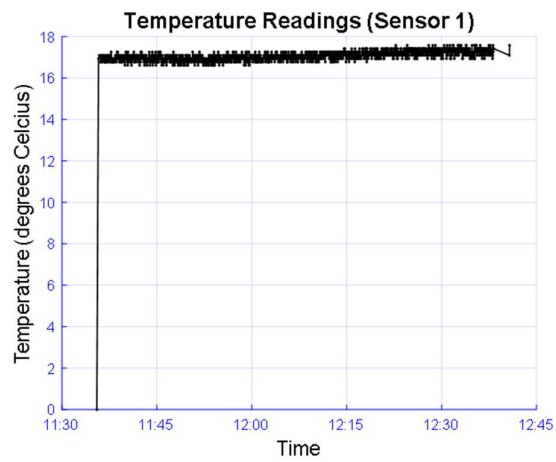


Figure 5.21 Temperature readings from probe 1 and probe 2 and the relative humidity measured at both probes at 30 °C.

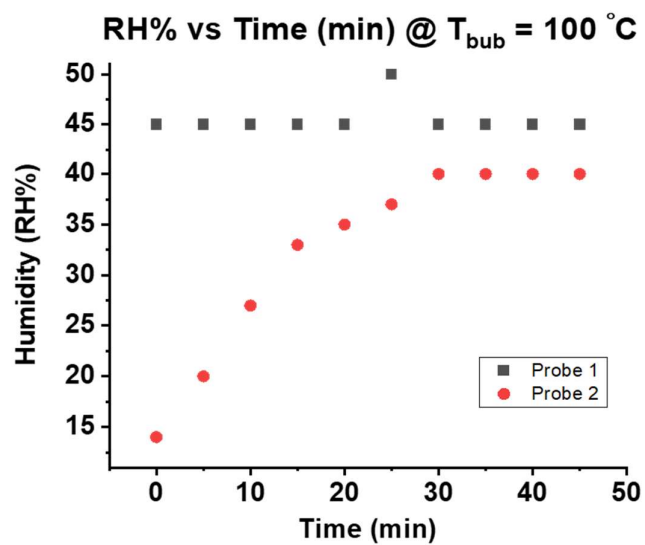
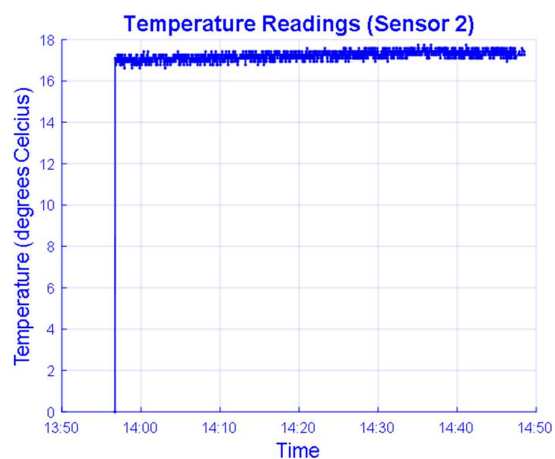
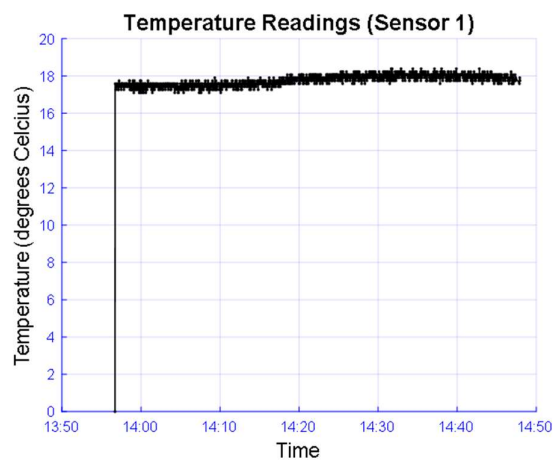


Figure 5.22. Temperature readings from probe 1 and probe 2 and the relative humidity measured at both probes at 100 °C.

When measuring the RH% values at both probe 1 and 2, it is evident that probe 2 was reaching a similar RH% value to probe 1; however, it takes a very long time (> 50 min) and would require very low T_{stage} values of < 4 °C where $P_{\text{sat}} = 0.89$ kPa. In addition, both the temperature recorded at the probes showed no impact in increasing the water saturation in the chamber. As a result, the mixer was removed from the piping setup as it was causing too many issues in maintaining adequate RH% values and the time taken to reach these values was too long (> 50 min). Furthermore, it is not viable to heat the water bubbler above ambient temperature as condensation in the piping setup will occur.

5.7 Removal of the Rotameter

Upon removing the rotameter, a significant difference in RH % values in the chamber using the same flow rate of 0.0013 CV were observed, indicating that the mixer was the main problem. At 10 minutes, the RH% at probe 2 increases from 0-60 %, showing significant improvements in water flow rate by removing the mixer (**Figure 5.23**).

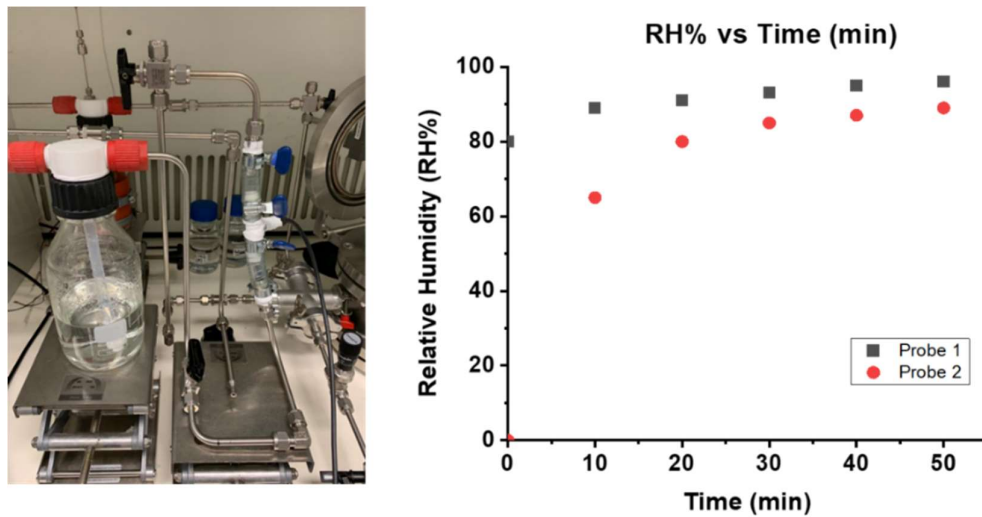


Figure 5.23 Removal of mixer improves the relative humidity and the flow rate of water vapour.

Since 80% RH value was achieved at $T = 23\text{ }^{\circ}\text{C}$ equivalent to $P_{\text{sat}} = 2.25\text{ kPa}$. Water condensation can occur at a minimum temperature of $19\text{ }^{\circ}\text{C}$ since the RH% has been greatly increased, as shown in **Figure 5.24**.

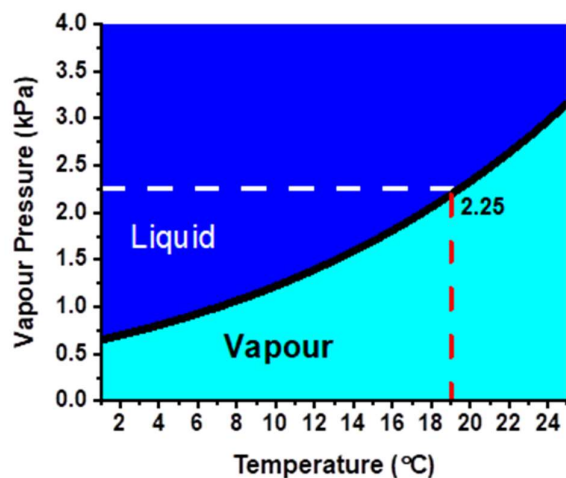


Figure 5.24 Saturation curve predicting condensation at 19 °C at 80% RH.

5.8 Condensing onto the Substrate

A condensation test was carried out to identify and visualise the role of temperature in the condensation process. A clean silicon wafer was added to the chamber. The stage temperature (T_{stage}) was reduced in increments of 2 °C to determine when condensation would begin to occur on the silicon wafer. The experimental data is illustrated in **Figure 5.25**, where condensation was initiated at approx. ~10 minutes at $T_{\text{stage}} = 12$ °C.

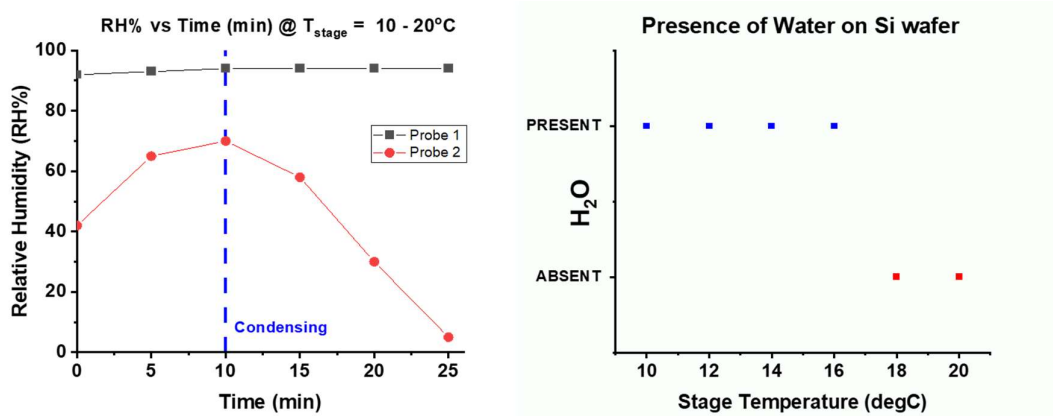


Figure 5.25 Real time data showing the impact of reducing T_{stage} on the RH% in the chamber and the presence of water seen on Si wafers at different temperatures of

T_{stage} .

From decreasing the T_{stage} , a decrease in RH % was observed. This is because there is less water vapour in the air, which indicates that the vapour will convert to liquid under saturated conditions, i.e., condensation was occurring. Evidence of water droplets was measured by reflecting the light of the reflectometer on the silicon wafer. Images were then taken to identify where water condensation would begin to form on the silicon wafer. T_{stage} values as low as 16 °C allowed condensation to occur, as shown in **Figure 5.26**.

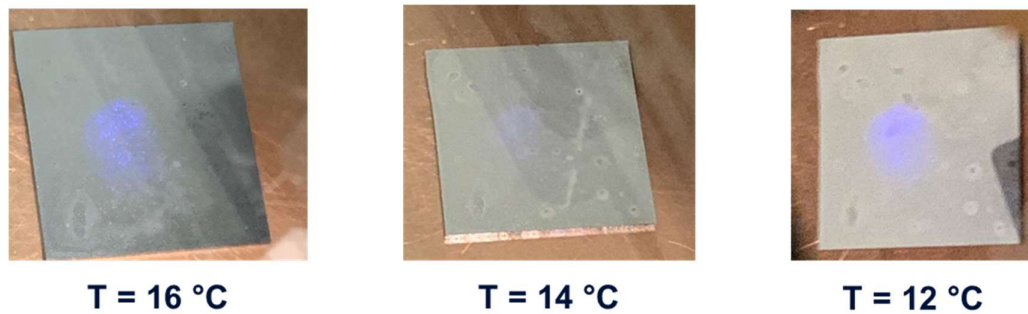


Figure 5.26 Images of water condensation occurring on at various T_{stage} values.

5.9 Flow Rate Ratios

The solvent to water ratio was controlled by changing the flow rate of solvent and water using the flow metres constructed upstream from the two-bubbler apparatus.

5.9.1 Controlling Condensation at $T_{\text{stage}} = 5\text{ }^{\circ}\text{C}$

3 different ratios of water: CHCl_3 (1:1, 2:1, 1:2) were investigated to identify the optimal swelling and water vapour pressure needed to droplet template a plasticised polymer film at $10\text{ }^{\circ}\text{C}$ using CHCl_3 swelling solvent. Flow coefficients were recorded and are displayed in **Table 5.4**.

Table 5.4 Flow rate values using the Vernier handle.

Ratio (H_2O : CHCl_3)	H_2O flow coefficient	CHCl_3 flow coefficient
1:1	5 turns (0.0013 Cv)	5 turns (0.0013 Cv)
2:1	10 turns (0.004 Cv)	5 turns (0.0013 Cv)
1:2	5 turns (0.0013 Cv)	10 turns (0.004 Cv)

All polymer film initial thicknesses were measured at approximately 130 nm for 50 seconds, followed by the immediate exposure of the water: solvent mixture into the SVA chamber. All experimental data is shown in **Figure 5.27**, where solvent T_{bub} was kept at $20\text{ }^{\circ}\text{C}$ and pressure maintained at 2 bar.

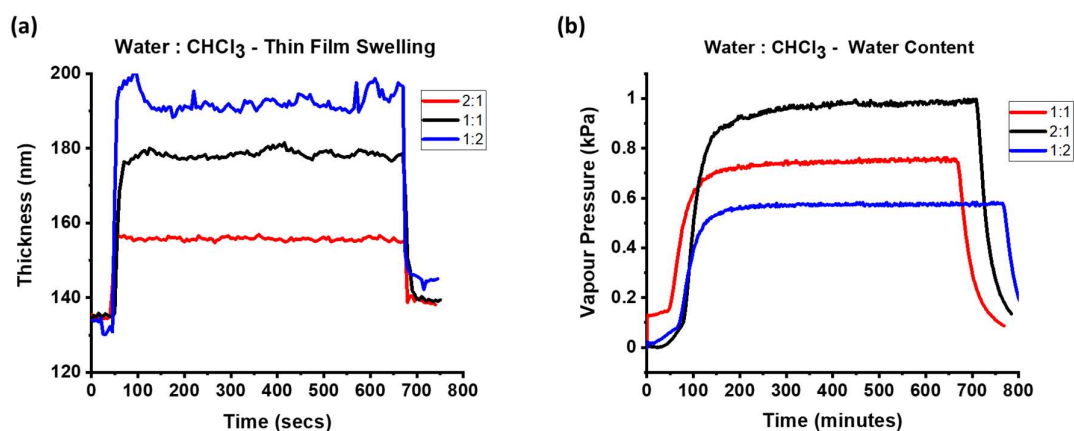


Figure 5.27 (a) Thicknesses measurements of H₂O : CHCl₃ thin film swelling measured by reflectometry and (b) vapour pressure measurements calculated by Probe 2 inside the SVA chamber at T_{stage} = 10 °C for the same experiment.

In **Figure 5.27 (a)** there was a contrast in swelling for all different ratios. This is because the water acts as a diluent for the CHCl₃ reducing the swelling ratio of the thin film. The swelling ratio remains consistent for all swelling experiments and thickness was recorded for 750 seconds (~12 min). The swelling ratios recorded for 1:1, 2:1 and 1:2 was 1.35, 1.15 and 1.49, respectively. No dewetting was observed for any of the swelling experiments. In **Figure 5.27 (b)**, the vapour pressures were recorded to identify if condensation can occur at T_{stage} = 10 °C. Similarly, the solvent influences the water vapour pressure as it also acts as a diluent and results in much lower vapour pressures (kPa). As expected, the highest vapour pressure was recorded at a ratio (water: CHCl₃) of 2:1 as the water vapour flow was double the solvent. Even though the water vapour pressure was high, it still did not meet the criteria to condense onto the thin film below the T_{sat} value, which was recorded to be ~ 1.2 kPa. The maximum swelling ratios (a) and optimal vapour pressures were recorded and illustrated in **Figure 5.28**.

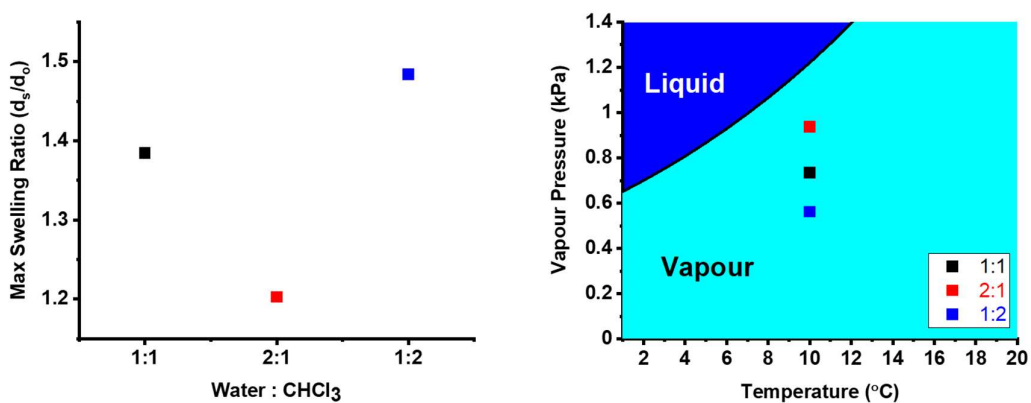


Figure 5.28 (a) Maximum swelling ratio recorded at 1:1, 1:2, 2:1 for $\text{H}_2\text{O} : \text{CHCl}_3$ (b) Vapour pressure analysis at the same ratio. All experiments carried out at $T_{\text{stage}} = 10^{\circ}\text{C}$.

The experimental analysis has shown that it will be impossible to template for any ratios at $T_{\text{stage}} = 10^{\circ}\text{C}$. Therefore, the stage must be reduced to a lower temperature to promote the condensation of water. In addition, strict monitoring of solvent penetration and swelling ratio should be recorded. At the highest saturation, dewetting of the polymer film can occur, as previously discussed. Post-swelling optical images are displayed in **Figure 5.29**.

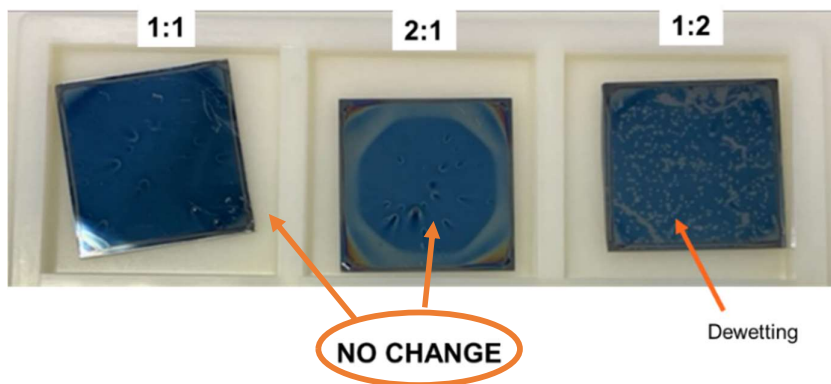


Figure 5.29 Image of the PS 17k thin films in silicon wafers post-swelling at water: CHCl_3 ratio of 1:1, 2:2 and 1:2 at $T_{\text{stage}} = 10^{\circ}\text{C}$.

No droplet templating can be seen in any of the films and dewetting occurred for 1:2. Following these observations, the experiment was replicated at a lower temperature where $T_{\text{stage}} = 5\text{ }^{\circ}\text{C}$.

5.9.2 Controlling Condensation at $T_{\text{stage}} = 5\text{ }^{\circ}\text{C}$

The reduction of stage temperature is the ideal solution for promoting condensation. At lower temperatures, the vapour pressure needed was lowered. The same experiment discussed in 4.9.1 was conducted at $T_{\text{stage}} = 5\text{ }^{\circ}\text{C}$. The reflectometer monitored average thicknesses for the entire experiment for ratios 2:1 and 1:1; however, dewetting can be seen for 1:2, where the solvent concentration was double the water, as shown in **Figure 5.30**.

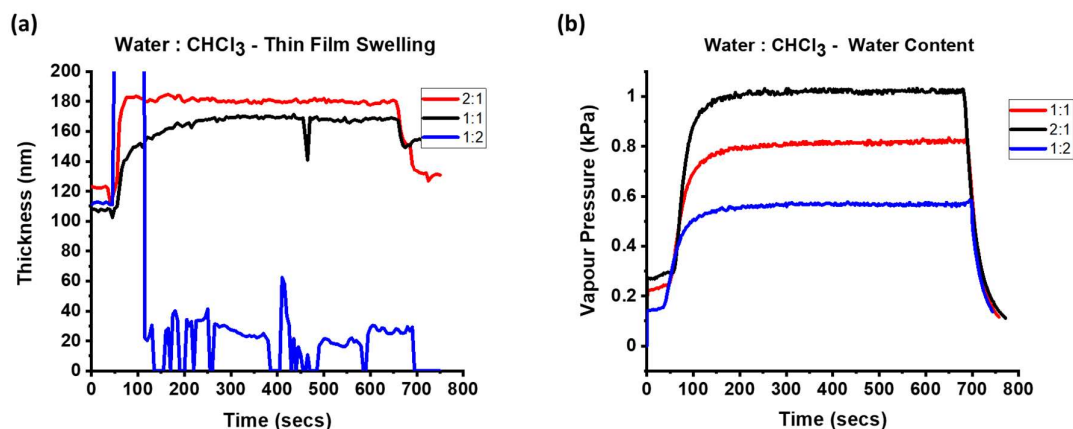


Figure 5.30 (a) Thicknesses measurements of $\text{H}_2\text{O} : \text{CHCl}_3$ thin film swelling measured by reflectometry and (b) vapour pressure measurements calculated by Probe 2 inside the SVA chamber at $T_{\text{stage}} = 5\text{ }^{\circ}\text{C}$ for the same experiment.

For 1:2, the solvent concentration was double the water, resulting in a dramatic drop in thickness as the solvent completely dissolved the polymer, showing large fluctuations in thickness, lower than the film's initial thickness (d_0). The water vapour pressure was similar to the previous experiment and the T_{stage} did not seem to play a dramatic role in changing

the vapour pressure of the water. Regarding the swelling ratio, 1:1 and 2:1 show a similar swelling ratio of ~ 1.5 . For a ratio of 1:2, the polymer film dewetted as the SR increased to 6.5, rapidly which resulted in immediate dewetting as the reflectometer signal failed. Therefore, an inaccurate SR for the film was measured since the polymer film was dissolved by the solvent. Vapour pressure analysis identifies that only the 2:1 ratio can meet the criteria to droplet template as it was above the threshold needed to condense. A swelling ratio of 1.5 can be achieved while maintaining a water vapour pressure of 1.0 kPa in the SVA chamber resulting in a maximum swelling ratio and vapour pressures were recorded and are shown in **Figure 5.31**.

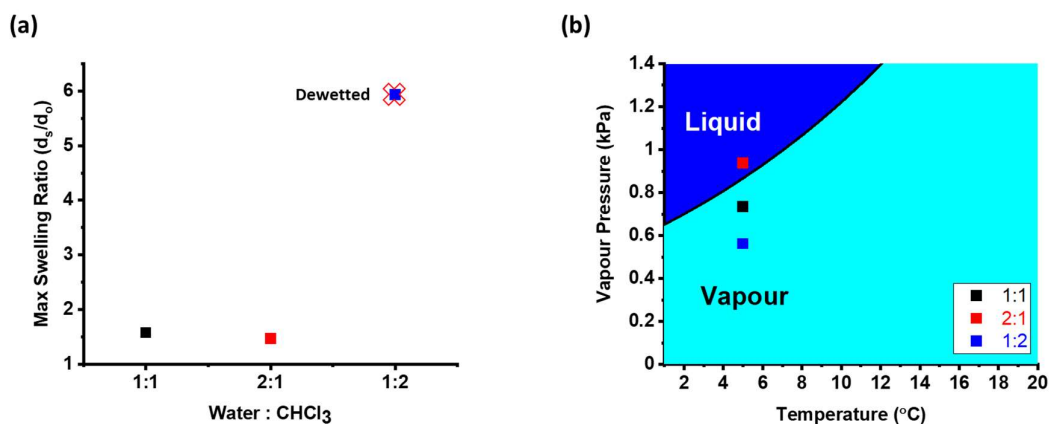


Figure 5.31 (a) Maximum swelling ratio recorded at 1:1, 1:2, 2:1 for Water: CHCl_3
(b) Vapour pressure analysis at the same ratio. All experiments carried out at $T_{\text{stage}} = 5^{\circ}\text{C}$.

Optical images were taken to identify the quality of the film after the swelling, droplet templating was observed for 2:1 as expected as the polymer was at an effective swollen state and the vapour pressure was above the condensation limit where $P_{\text{sat}} = 0.866$ kPa at a $T_{\text{stage}} = 5^{\circ}\text{C}$. Therefore this investigation concludes that a ratio of 2:1 is the most suitable

water:CHCl₃ ratio to droplet template and adequately swell the film as 1:1 cannot meet P_{sat} conditions and 1:2 dewets the film as shown in **Figure 5.32**.

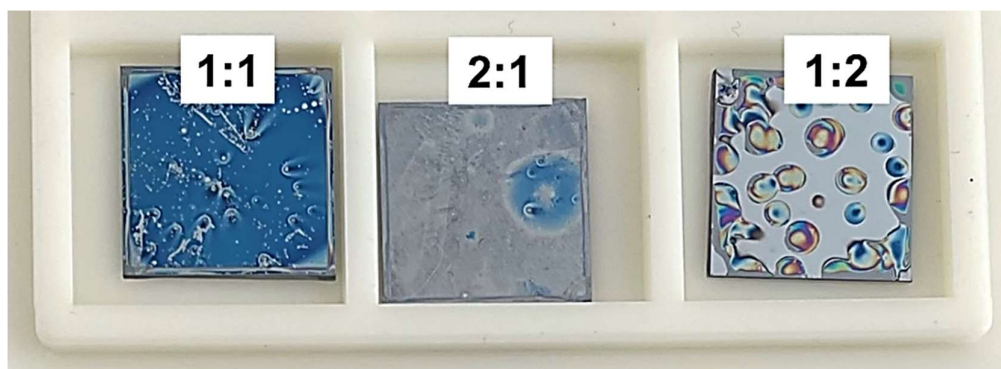


Figure 5.32 Image of the PS 17k thin films in silicon wafers post-swelling at CHCl₃:
water ratio of 1:1, 2:1 and 1:2 at $T_{\text{stage}} = 5\text{ }^{\circ}\text{C}$.

5.10 Impact of Vapour Flow on Film Swelling

The solvent's role is to plasticise the polymer film, making it templatable by reducing its viscosity. Water vapour pressure controls the size of the water droplets impacting the pore morphology. T_{stage} has a binary effect between these two parameters where the reduction of temperature drives the swelling process and the condensation events. Since there are two flow effects present, both vapour systems and the exposure times need to be studied and assessed. A summary of the process is shown in **Figure 5.33**.

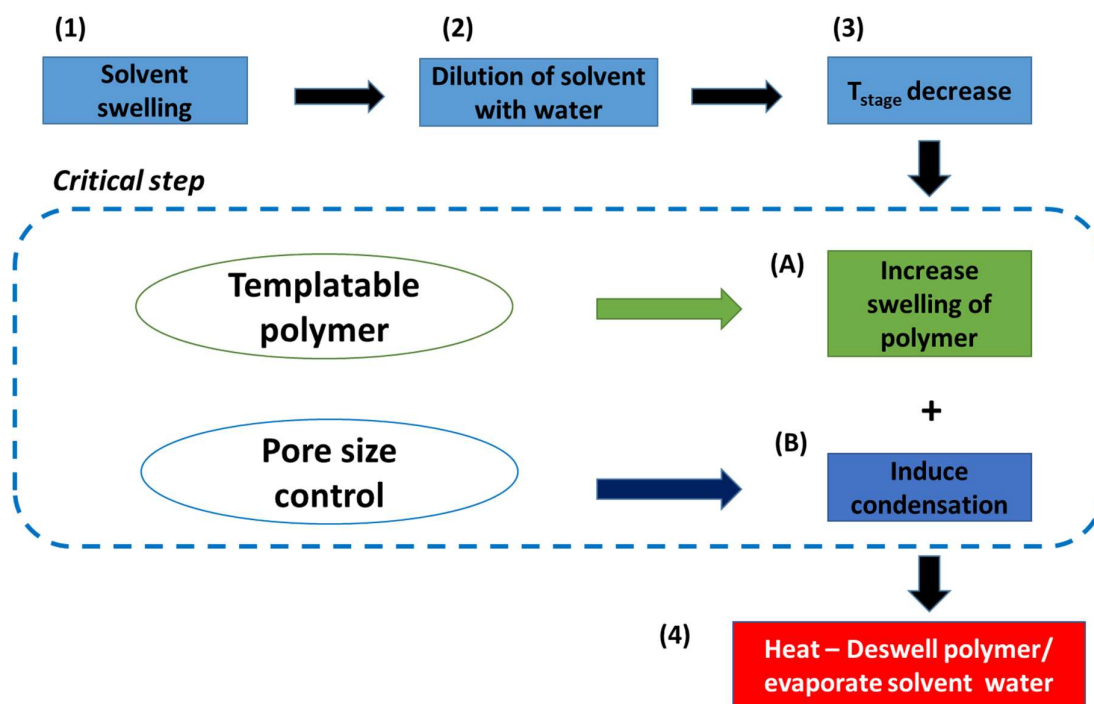


Figure 5.33 A schematic of the water droplet templating approach.

5.10.1 Polymer Swelling followed by Condensation

The polymer film must become mouldable when the water is added to the chamber to induce condensation onto the swollen film. The next section will discuss different methods and systematic processes for creating microporous films. The polymer system studied is PS 17 K swollen in CHCl_3 . All polymer film thicknesses were recorded at approximately 100 - 120 nm. The approach to follow is demonstrated in **Figure 5.34**.

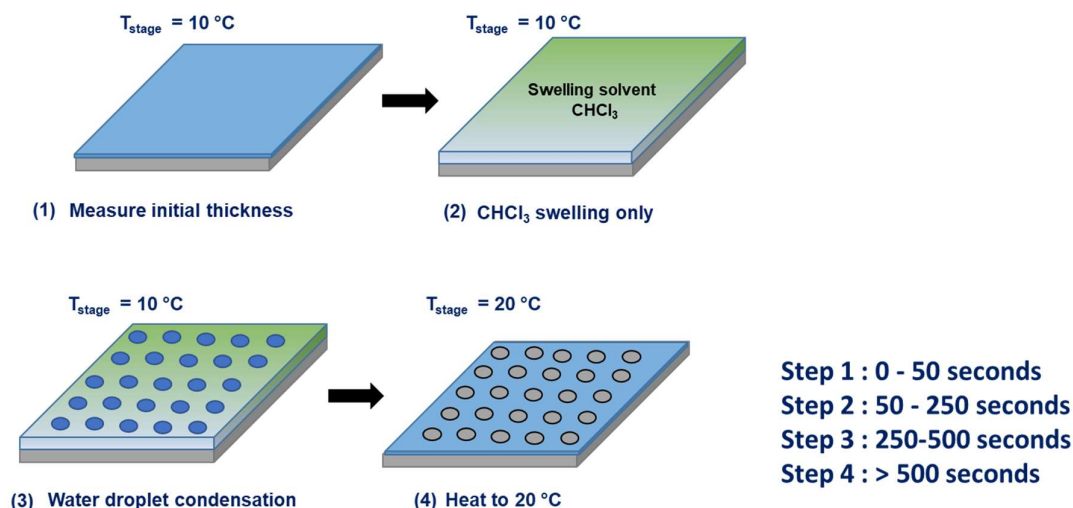


Figure 5.34. Process for swelling PS with CHCl_3 swelling followed by droplet condensation. All solvents removed by heating.

Step 1: Initial film thickness measurements

Step 2: PS thin film swollen in CHCl_3 at $T_{\text{stage}} = 10^\circ\text{C}$

Step 3: Water incorporated into the chamber at $T_{\text{stage}} = 10^\circ\text{C}$. Solvent vented.

Step 4: Water driven off *via* heating $T_{\text{stage}} = 20^\circ\text{C}$.

Figure 5.35 shows *in-situ* analysis of what occurs when $T_{\text{bub}} = 16^\circ\text{C}$, acquiring a $\Delta T = 6^\circ\text{C}$ between the solvent and the bubbler, where $S < 1$.

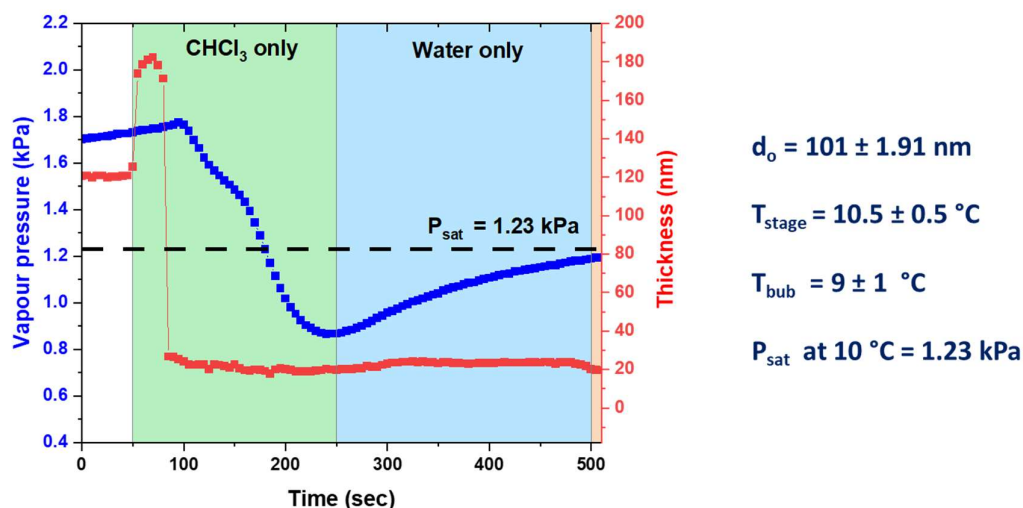


Figure 5.35. Reflectometry analysis and water vapour pressure measurements of PS swollen in CHCl_3 followed by water condensation. No mixing of solvents. All solvents removed by heating.

Before solvent entry into the chamber, the water vapour pressure remained constant (~ 1.3 kPa) above the limit for condensing onto the polymer film at 250 seconds. There was no entry of solvent into the chamber. The saturation pressure of water, $P_{\text{sat}} = 1.23$, was measured at probe 2 (located inside the chamber) reading where $T_{\text{probe}} = 23$ °C. Water condensation can be induced onto the film at this temperature where $T_{\text{stage}} = 10$ °C. After 50 seconds, the vapour pressure of the water was 1.3 kPa. Once only pure solvent was added to the chamber, there was a rapid increase in thickness ($\phi_s = 0.35/\text{SR} = 1.5$) followed by an immediate drop caused by rapid film dewetting at $T_{\text{bub}} = 16$ °C ($\Delta T = 6$ °C). The increase in ΔT was the main reason for dewetting, as S value > 1 causes the pooling of solvent during the swelling process ($S = \sim 1.3$).

Optical images were taken post-swelling showing an “orange peel”^{37,38} dewetting effect where the polymer film immobilises itself from the surface forming an orange-peel like structure. The dewetting of the films is shown in **Figure 5.36**, where TL, TR, BL, and BR

are top left, top right, bottom left and bottom right areas across the entire surface, respectively.

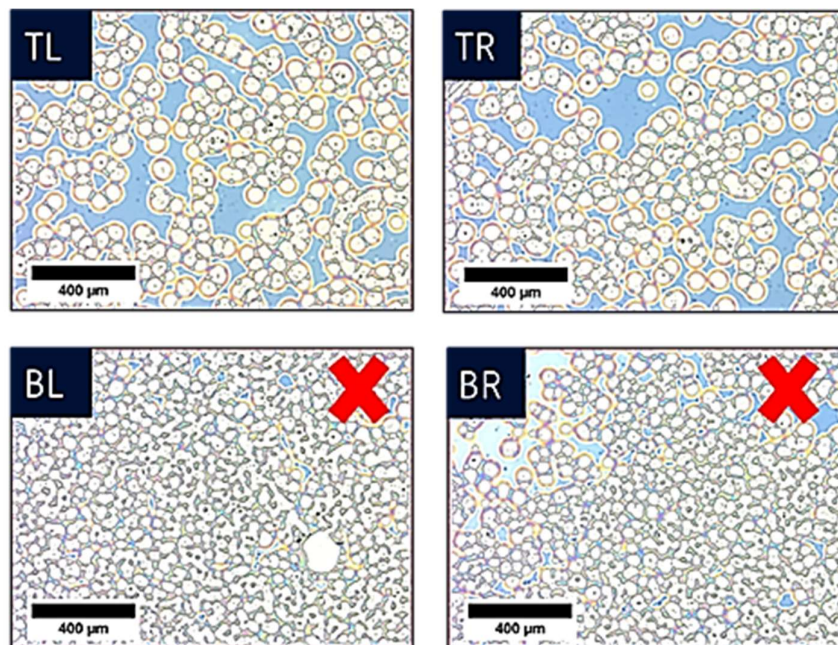


Figure 5.36 Post-swelling optical images of PS 17K (120 nm) on native silicon after CHCl_3 swelling followed by condensation.

PSD (Pore-size diameter) measurements were taken using ImageJ software (method explained in **Section 3.5.4**) acquiring an average pore size of 50-60 μm in diameter.

Since $\Delta T = 6^\circ\text{C}$ was very high and caused immediate dewetting, lower ΔT values between solvent and bubbler were observed to identify if higher T_{stage} values can promote condensation. The same swelling experiment was carried out as previous; however, T_{bub} was reduced to 9.3°C ($\Delta T = 1.2^\circ\text{C}$) and the ratio of 1:1 solvent: water was introduced as illustrated in **Figure 5.37**. The experimental process is shown in **Figure 5.38**

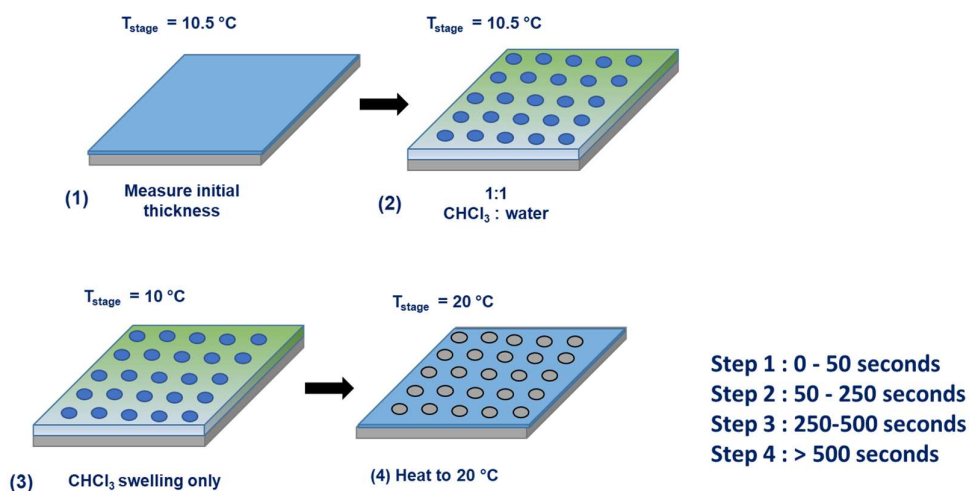


Figure 5.37. Process for swelling of PS in 1:1 (H₂O: CHCl₃) swelling followed by solvent swelling.

Step 1: Initial film thickness measurements

Step 2: PS thin film swollen in H₂O: CHCl₃ in a 1:1 ratio at $T_{\text{stage}} = 10.5\text{ }^{\circ}\text{C}$.

Step 3: CHCl₃ incorporated into the chamber at $T_{\text{stage}} = 10.5\text{ }^{\circ}\text{C}$. Water vented.

Step 4: Solvent driven off *via* heating $T_{\text{stage}} = 20\text{ }^{\circ}\text{C}$

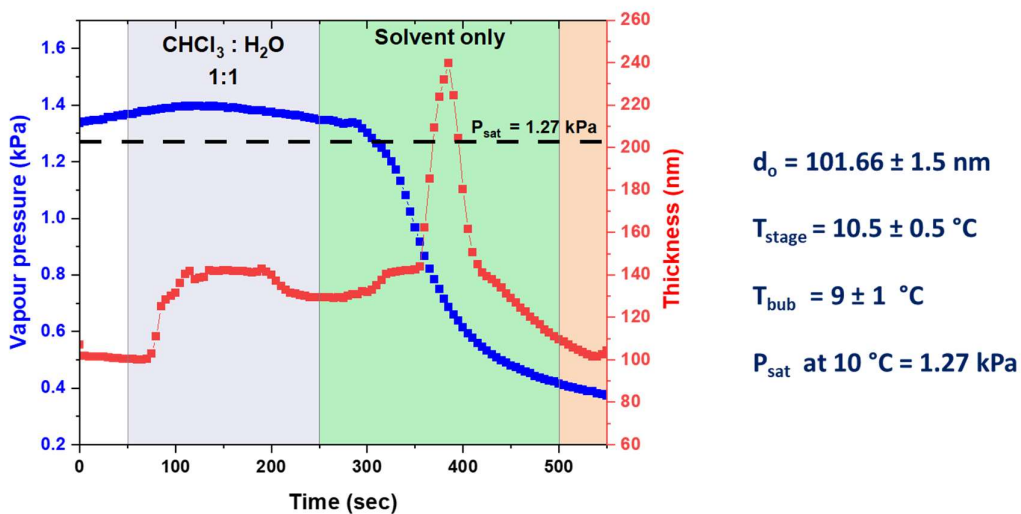


Figure 5.38 Reflectometry analysis and water vapour pressure measurements of PS swollen in 1: 1 (H₂O: CHCl₃) followed by solvent swelling and heating. All solvents removed by heating.

The effect of water in the chamber was investigated. A mix of water and solvent was added to the chamber to increase the water vapour pressure, followed by immediate exposure to only solvent after 250 seconds. At the beginning of the experiment, the water vapour pressure remained constant (~ 1.3 kPa) above the limit for condensing onto the polymer film. The saturation pressure of water, $P_{\text{sat}} = 1.27$, was measured at probe 2, located inside the chamber, reading as $T_{\text{probe}} = 20$ °C. Water condensation can be induced onto the film at $T_{\text{stage}} = 10.5$ °C as it is above the saturated pressure limit $P_{\text{sat}} = 1.27$ kPa. After 250 seconds, the water was vented, and only pure solvent enters the chamber resulting in an increase in thickness ($\phi_s = 0.35$ / $\text{SR} = 1.5$) $\Delta T = 1.2$ °C) where $T_{\text{bub}} = 9.3$ °C ($\Delta T = 1.2$ °C). Since $T_{\text{bub}} < T_{\text{stage}}$, the solvent saturation was less than 1 ($S < 1$) in this case, indicating that the solvent will not condense onto the polymer film. Better swelling stability can be seen in this experiment compared to the dewetting observed previously (**Figure 5.36**). Optical images were taken post-swelling indicated better porosity formation, as shown in **Figure 5.39**.

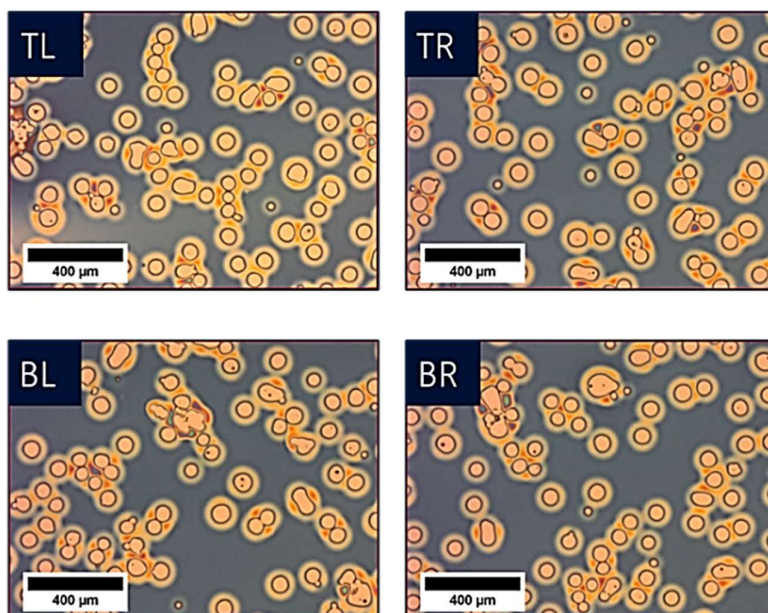


Figure 5.39 Post swelling optical images of PS 17K (100 nm) on native silicon after swelling in a ratio of 1:1 (H_2O : CHCl_3) followed by CHCl_3 swelling only.

The films show no evidence of ordering. PSD measurements using ImageJ estimated pore sizes of approx. 50-60 μm in diameter. Since the pores are similar in size, circular in shape and consistent throughout the entire sample, it can be assumed that the water has templated the plasticised polymer film. The sensitivity of the polymer to CHCl_3 solvent was interpreted as necessary for maintaining the film stability. Since the temperature of the stage must be below the dew point, it may be first suitable to increase the relative humidity in the chamber before solvent exposure.

5.10.2 Condensation followed by Polymer Swelling

Since solvent alone causes the polymer film to dewet at high ΔT values, the introduction of water followed by solvent may be a more viable option. Therefore, temperature studies were carried out where the film was exposed to water vapour at a high RH value, followed by solvent addition. Here, the swelling of PS films ($\sim 120\text{ nm}$) in chloroform vapour at various humidities is outlined in **Figure 5.40**.

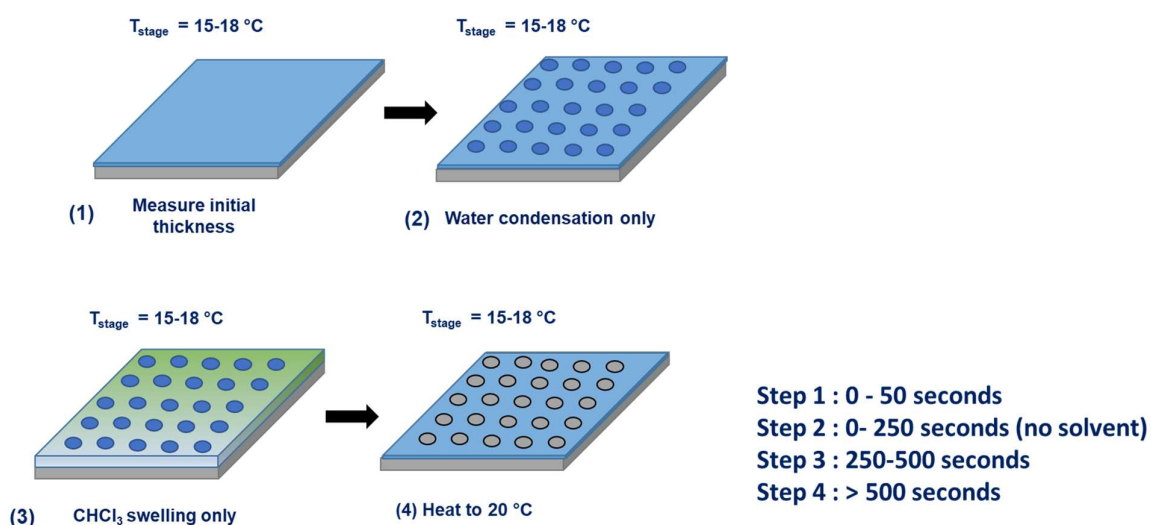


Figure 5.40. Process for condensing water on to PS followed by CHCl_3 swelling. All solvents removed by heating.

Step 1: Initial film thickness measurements

Step 2: Water condensed on to PS film at different T_{stage} values (15 – 18 °C)

Step 3: CHCl_3 incorporated into the chamber. Water vented.

Step 4: Solvent driven off *via* heating where $T_{\text{stage}} = 20$ °C.

In situ thickness measurements were taken for 600 seconds (10 minutes) where firstly, water vapour entered the chamber from 0 - 250 seconds, followed by CHCl_3 vapour from 250- 500 seconds. The procedure is presented in **Figure 5.41**.

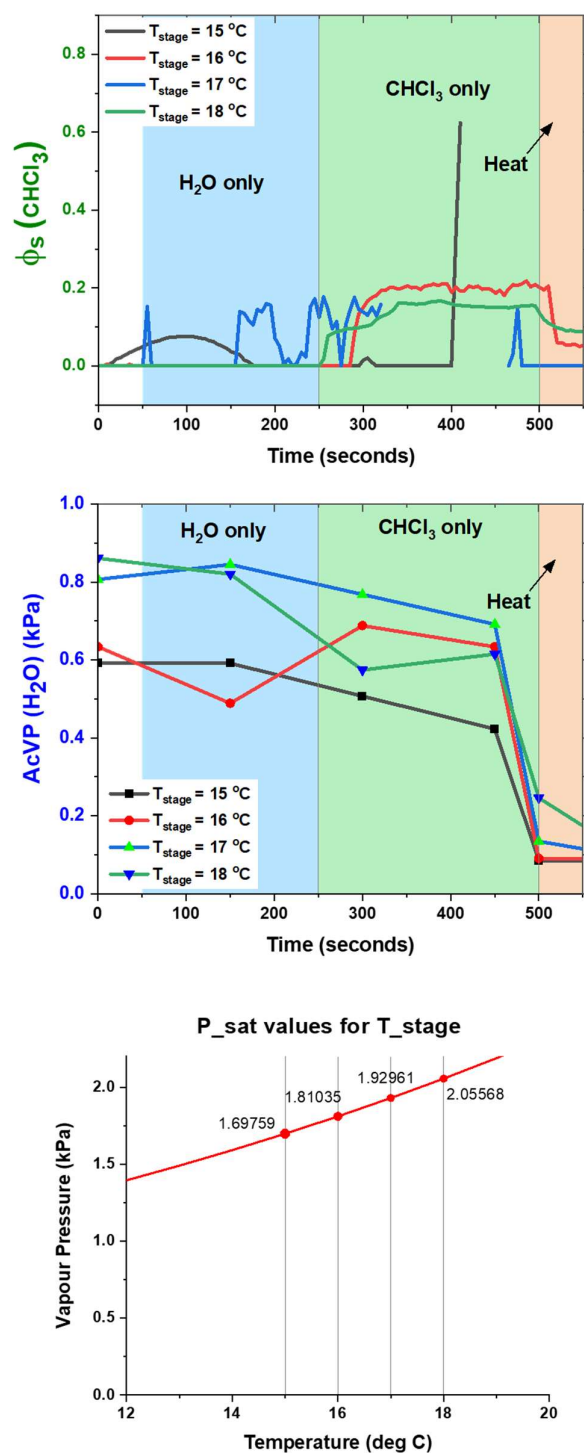


Figure 5.41 Polystyrene/CHCl₃ in situ analysis at temperatures, 15 °C, 16 °C, 17 °C, 18 °C. Real time (a) ϕ_s analysis measured using the F3 reflectometer after 250 seconds (b) Water vapour pressure measured using a humidity probe located inside the chamber from 0 – 600 seconds and (c) Calculated P_{sat} measurements to interpret minimal vapour pressures needed to condense on to the film.

The thickness was not recorded between 0-250 seconds as a reflectometer error occurs when water condenses onto the surface. These thickness measurements were considered experimental artefacts as the contribution of water to the polymer film changes the refractive index of PS, which is $n = 1.45$ thus changing the reflectance characteristic of the PS film. After 250 seconds, the solvent was incorporated into the chamber and the water was kept flowing. Low relative humidity was recorded as the flow rates were 1:1 ratio (the mixer was also present). Once the solvent entered the SVA chamber, a significant decrease in relative humidity was observed for all experiments. The solvent T_{bub} was maintained at 20 °C for all experiments. The temperature of the stage was maintained at set temperatures of 15 °C, 16 °C, 17 °C and 18 °C, as shown in **Figure 5.42**.

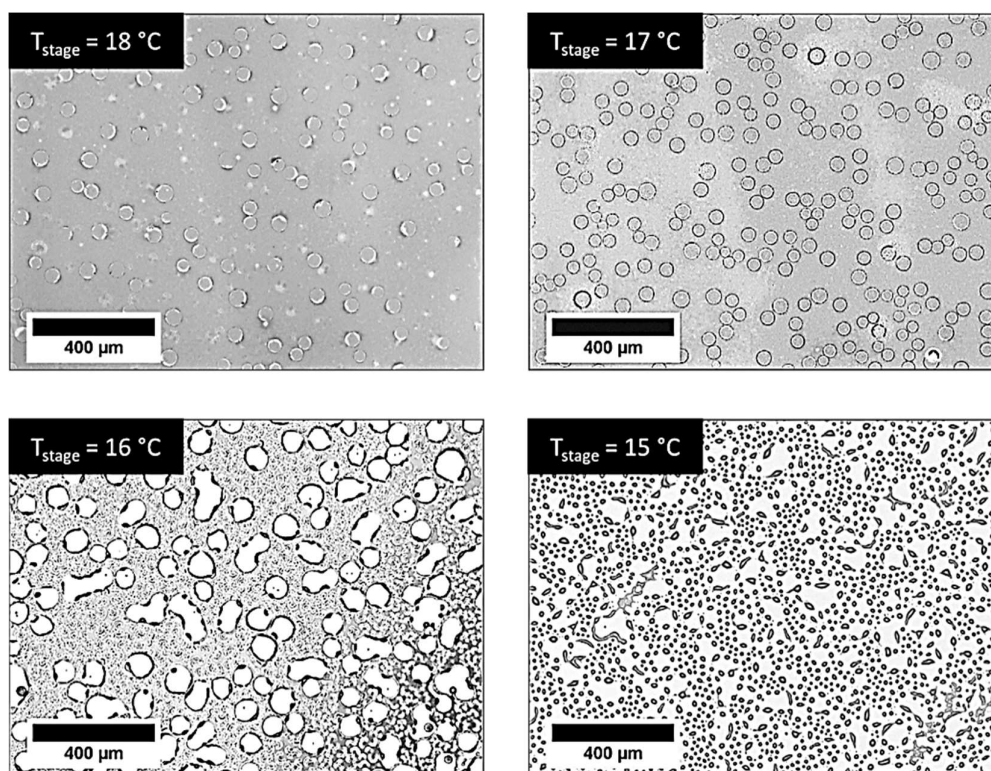


Figure 5.42 Post swelling optical images of PS 17K (100 nm) on native silicon.

Samples were firstly droplet templated followed by polymer swelling in CHCl_3 . T_{stage} values of 15 – 18 °C were investigated.

At 15 °C, the entire polymer film completely dewetted as the CHCl_3 saturation was too high at this temperature. The water: solvent ratio of 1:1 caused the film to rapidly dewet due to the large temperature difference ($\Delta T = 5\text{ }^\circ\text{C}$). At 16 °C, no porosity can be seen; however, there is evidence of dewetting and unusual noodle dewetting structures were positioned close to the large dewetting spots. A magnified image of the polymer film quality can be seen in **Figure 5.43**, indicating the temperature and flow rate will still cause polymer film destruction at a low value of $\phi_s = 0.2$ where $\Delta T = 4\text{ }^\circ\text{C}$.

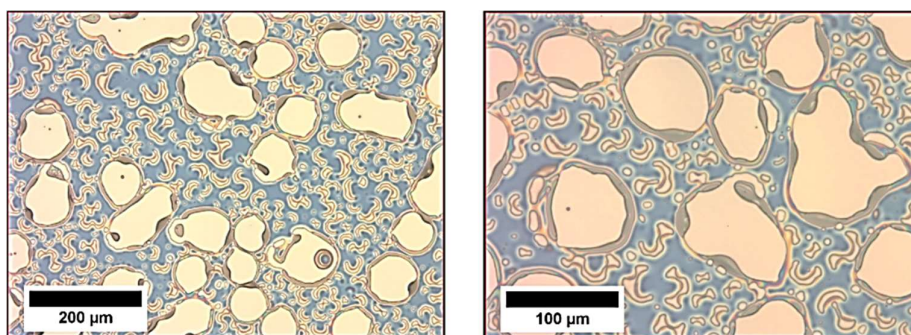


Figure 5.43 Post-swelling optical images of PS 17K swollen in CHCl_3 at $T_{\text{stage}} = 16\text{ }^\circ\text{C}$.

Dewetting can be seen throughout the entire sample.

By increasing the temperature to 17 °C ($\Delta T = 4\text{ }^\circ\text{C}$), an unusual observation is seen where polymer dewetting has occurred and accelerated, resulting in ring-like patterns forming within the PS film and the nucleation of film breaking up around these pores. As a result, the random circular arrays of rings were produced where the water droplets resided, as presented in **Figure 5.44**.

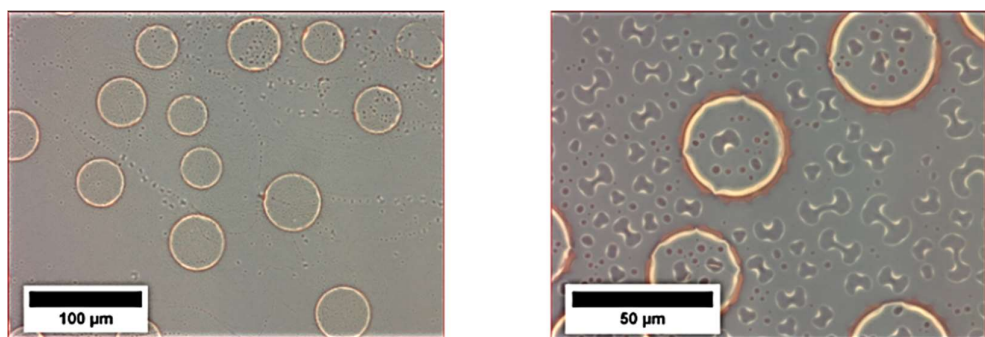


Figure 5.44 Dewetting rings of PS 17K. Films were exposed to water first followed by CHCl_3 swelling at $T_{\text{stage}} = 17^\circ\text{C}$.

Since no pore formation was seen *via* this method, a higher SR of polymer is needed for the water droplets to displace the thin film. Dilution of solvent at lower temperatures of T_{stage} can maintain a higher swelling ratio while also keeping the vapour pressure of water at a sufficient saturation.

5.11 Dilution Effect

A modified procedure was needed since the 5.2.6.2 method was ineffective in producing ordered porous material using separate vapour flows. The dilution effect of water and solvent swelling was assessed and is shown in **Figure 5.45**.

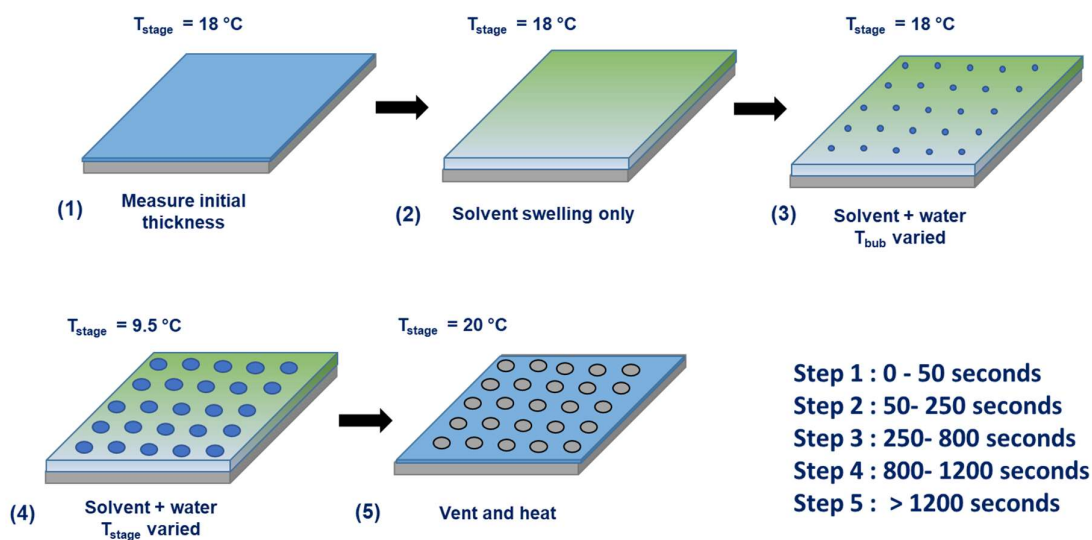


Figure 5.45. Process for creating microporous films. The film is swollen in solvent first followed by the addition of water in a 2:1 ($\text{H}_2\text{O} : \text{CHCl}_3$) ratio. Bubbler and stage modified to control droplet templating. All solvent removed by heating.

Step 1: Initial film thickness measurements

Step 2: CHCl_3 incorporated into the chamber only where $T_{\text{stage}} = 18\text{ }^{\circ}\text{C}$.

Step 3: PS thin film swollen in $\text{H}_2\text{O} : \text{CHCl}_3$ in a 2:1 ratio at $T_{\text{stage}} = 18\text{ }^{\circ}\text{C}$. T_{bub} modified to increase solvent saturation in chamber.

Step 4: T_{stage} modified promote water condensation on to the PS film at $T_{\text{stage}} = 9.5\text{ }^{\circ}\text{C}$.

Step 5: Solvent driven off *via* heating where $T_{\text{stage}} = 20\text{ }^{\circ}\text{C}$.

This method was the most suitable for monitoring the droplet templating process, as fewer reflectometry errors could be seen. The swelling dilution process is shown in **Figure 5.46**.

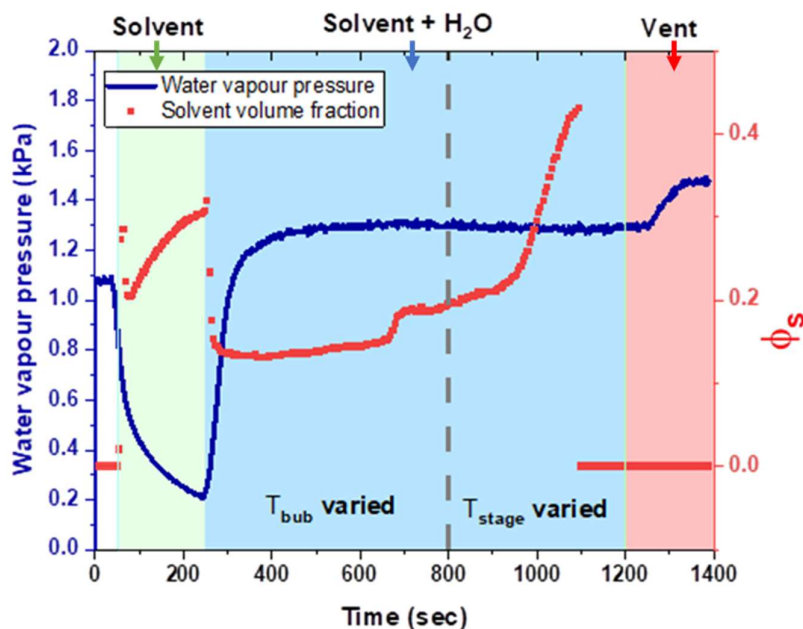


Figure 5.46 Reflectometry Analysis (red) and water vapour pressure (blue) for the dilution process. A flow rate of a 2:1 ($\text{H}_2\text{O} : \text{CHCl}_3$) ratio water was used.

The method presented in **Figure 5.46** is much more viable than all other swelling discussed in 5.2.6.2. This method allows us to track the initial swelling of the polymer film at a specific flow rate. Since only solvent was present in the chamber, the vapour pressure of water dramatically decreased. Once the film became swollen ($\phi_s = 0.3$), water vapour was added to the chamber to increase the water's vapour pressure but decreased the solvent penetration ($\phi_s = 0.18$). Since the ratio of water: solvent was 2:1, the swelling ratio was considerably lower. The most critical step was the condensation control by decreasing T_{stage} . As a result, the polymer film was swollen at lower temperatures while maintaining high water vapour pressures (kPa). The stage temperature was reduced to $11\text{ }^\circ\text{C} - 9.5\text{ }^\circ\text{C}$, where $T_{\text{sat}} = 11\text{ }^\circ\text{C}$ was measured at $P_{\text{sat}} = 1.3\text{ kPa}$ as shown in **Figure 5.47**.

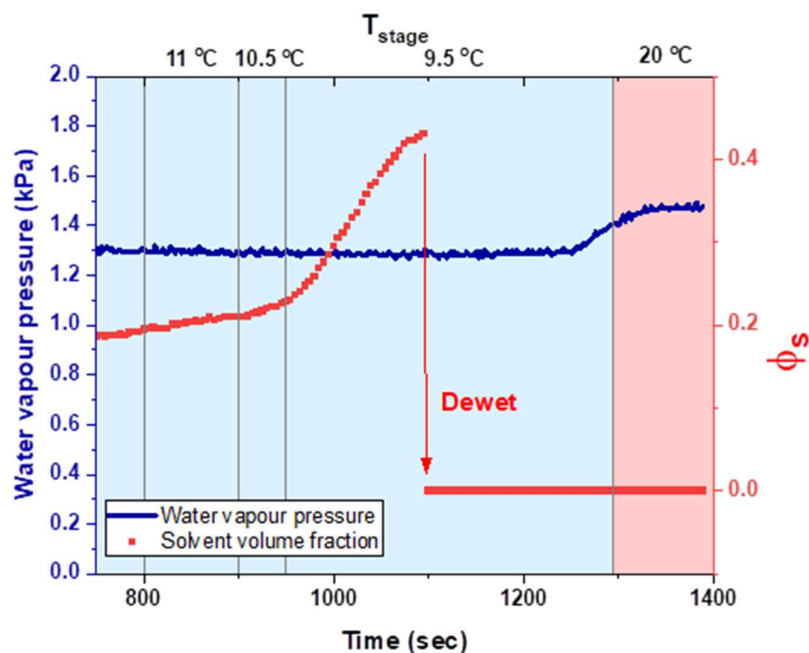


Figure 5.47 Reflectometry Analysis with a ratio of water: solvent (2:1). Reduction of $T_{\text{stage}} = 9.5 \text{ °C}$ allows for droplet templating to occur.

Evidence from this work shows that the film can be droplet templated once the vapour pressure surpasses the saturation limit. A vapour pressure of 1.3 kPa was measured and would require a temperature of $>11 \text{ °C}$ to induce condensation, as presented in **Figure 5.48**.

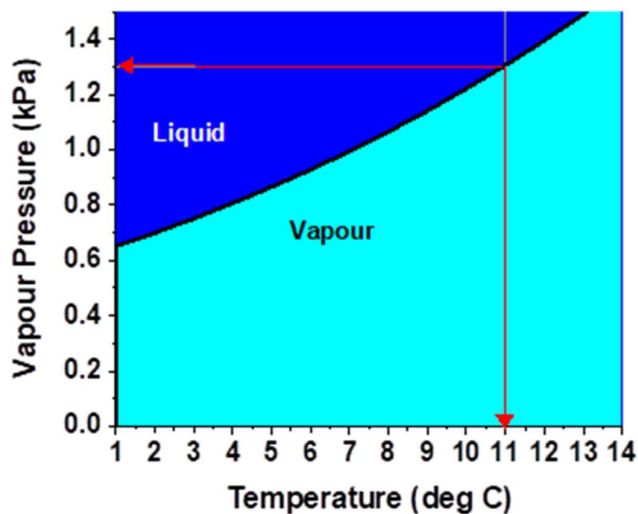


Figure 5.48 Critical vapour pressure needed to induce condensation at 1.3 kPa.

When looking at the post swelling analysis, better droplet templating can be observed across the entire sample, as presented in **Figure 5.49**.

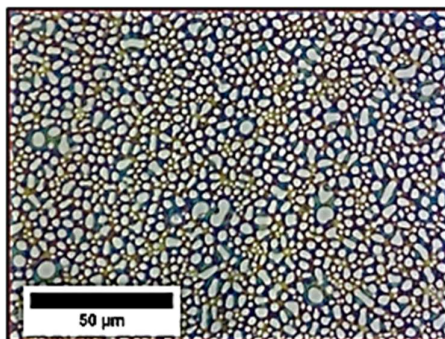


Figure 5.49 Optical image of the PS (17k) 100 nm after post-swelling procedure.

The images indicate that the substrate has been exposed at the surface and further characterisation was carried out by atomic force microscopy. A root mean square (RMS) roughness of 129.52 nm with a max z-value height of 187 nm and a trench depth of 360 nm indicated that the water droplets entirely displaced the polymer film as the initial film thickness d_0 was measured as 100 nm as shown in **Figure 5.50**. Therefore, this method was adopted as the main swelling procedure used for the rest of the project as it has shown optimal results in templating viscoelastic PS films with water.

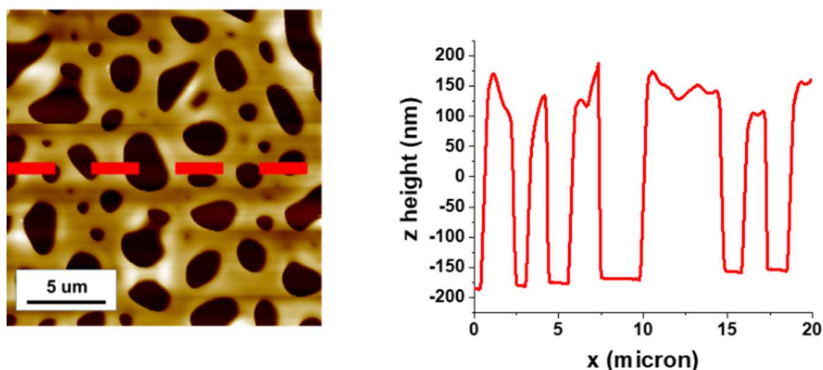


Figure 5.50 AFM Pore depth analysis of PS 17k (100 nm) (20 x 20 μm) after post-swelling procedure.

5.12 Conclusion

In conclusion, numerous investigations were carried out to identify if the SVA chamber can be used as droplet templating equipment to produce microporous media *via* a breath figure type method. Although strict conditions must be met, this process shows excellent potential for upscaling polymer film droplet templating by increasing the patterning density across samples as large as 2 x 2 cm. In summary, several deductions have been made.

- The polymer-solvent compatibility is vital for showing good swelling efficacy. At high saturations, dewetting can occur. Therefore, the saturation must always be less than 1 ($P/P_{\text{sat}} = S < 1$).
- The control of temperature in the solvent bubbler and stage is essential for maintaining the solvent saturation in the chamber. Furthermore, the stage temperature also impacts the role of condensation during the droplet templating process.
- A ratio of 2:1 ($\text{H}_2\text{O} : \text{CHCl}_3$) will be adopted for all droplet templating studies, as it achieved the optimal conditions for swelling and droplet templating. The temperature of the stage must be lower than 10 °C. The vapour pressure cannot increase higher than 1.0 kPa at these flow rate ratios.
- The dilution effect is the most promising method for producing porous films as the solvent initiates the film's swelling followed by the addition of water at an earlier stage. Therefore, by controlling the rate of swelling and condensation of the films, the issue of dewetting can be reduced, and condensation can be better controlled by mixing two solvents vapour flows as discussed in **Section 5.10.3**.

Understanding the effects of water-solvent vapour swelling and condensation aims to create a fast, fully automated, low-cost, and scalable method for producing microporous polymer films.

5.13 References

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Chapter 6

Pore Size Control and In-depth Characterisation of Porous Polystyrene Films

6.1 Introduction

Thin polymer films offer a unique way to create functional templates for pattern transfer and have become of considerable interest in nanotechnology and nanomanufacturing¹⁻⁵. However, polymer film dewetting⁶ is a common problem in many industrial surface coating techniques, resulting in irregular porosity throughout, delamination and cracking of samples.

Dewetting is defined as the breakup of thin films resulting in the nucleation of holes that can lead to the destruction of the surface coating on the substrate surface⁷⁻⁹. Understanding and manipulating this process is relevant to the nanotechnology industry as these processes are more likely to occur at nanometre scales. Dewetting of thin films, especially polymers, have been characterised as a viscoelastic problem where the nucleation of holes can accelerate the destruction of the film. This chapter effectively investigates a form of controlled dewetting and analyses a droplet templating method as a route to expose the silicon surface and order the shape of the pores *via* the SVBF droplet templating process.

6.2 Thin Film Analysis

Thin films of various thicknesses of the atactic homopolymer PS were produced using concentrations of 2, 4 and 5 w/w % of 17 kg mol⁻¹ PS/toluene solution and deposited onto substrates at 500 and 1,000 rpm. **Figure 6.1** illustrates the thickness of the thin films after

spin coating that were measured using the F3 CS Filmetrics reflectometer. The thickness of polymer films is dictated by the polymer solution viscosity, which is altered by increasing the polymer concentration. **Table 6.1** shows a summary of the spin coating parameters.

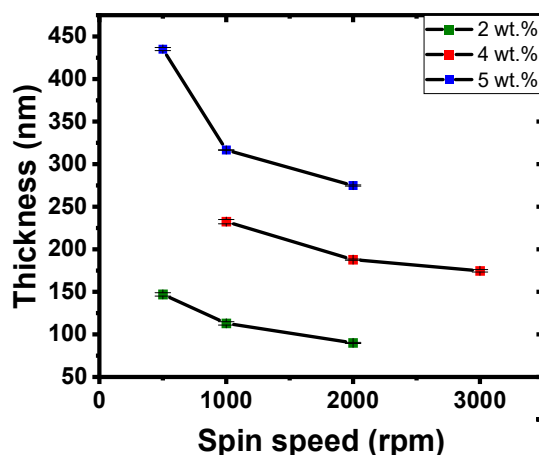


Figure 6.1 Thickness of PS (17K) thin films after spin-coating concentrations (2,4 and 5 wt.%) of PS/Toluene solutions at different spin velocities (RPM).

Table 6.1 Spin-coating Parameters for PS 17k /Toluene Films.

Thickness (d _o) (nm)	Polymer concentration (w/w.%)	Spin Velocity (RPM)
100 nm	2	1000
200 nm	4	1000
300 nm	5	1000
400 nm	5	500

PS thin films averaging 100, 200, 300, and 400 nm were used. The selection of different thicknesses required adjusting the spin speeds, and concentration. The colours of the thin films after spin coating, as described above, are shown in **Figure 6.2**.

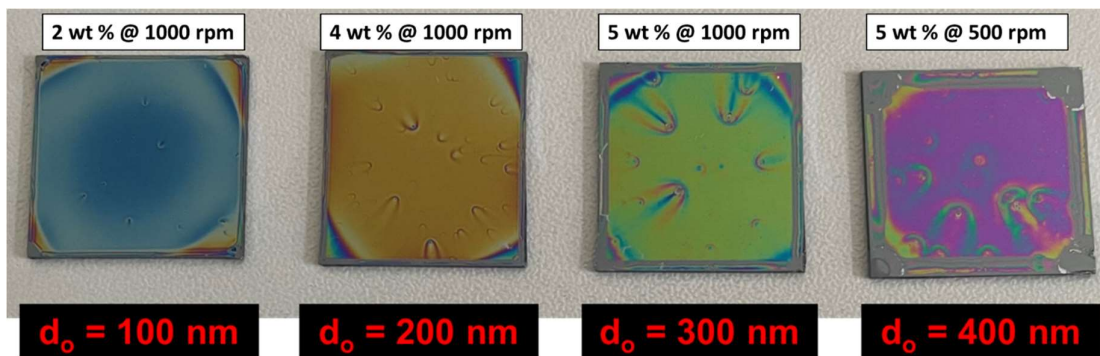


Figure 6.2 PS/Toluene spin coated on to silicon wafer at different concentrations and spin speeds. Thicknesses of 100, 200, 300 and 400 nm achieved using 2, 4 and 5 wt.% solutions.

6.3 Solvent Swelling and Condensation

All swelling/ condensation experiments were conducted *via* the dilution method (Section 5.13), using chloroform as the solvent. Figure 6.3 presents the swelling of chloroform (CHCl_3) on the PS thin films before water condensation by reducing the stage temperature (T_{stage}) to the dew point.

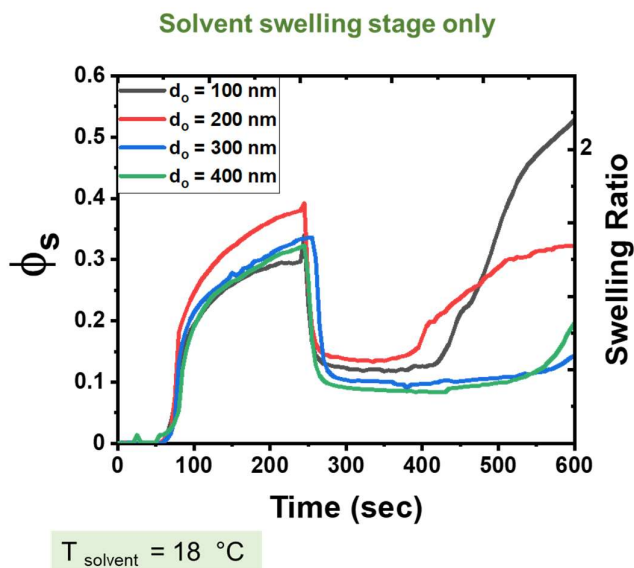


Figure 6.3 (a) The thin film swelling effects of PS (17K) in CHCl_3 and $\text{CHCl}_3/\text{H}_2\text{O}$ at 250 seconds *via* the dilution method. After 500 seconds, the water vapour pressure AcVP is at $T_{\text{dew}} = 6.5^\circ\text{C}$.

The solvent swelling stage only shows the solvent's effect on the PS thin films, between 0-250 seconds. A significant drop in ϕ_s at 250 seconds which indicated the addition of water to the chamber, thus, diluting the organic solvent (CHCl_3), in the vapour phase and a reduction in swelling was seen. The overall swelling plot of the experiment is shown in **Figure 6.4**, where the solvent bubbler (T_{bub}) remains at 18°C , T_{stage} was maintained at 19°C (white region) and reduced to 6.5°C to induce condensation of water (blue region). After 500 seconds, T_{stage} was heated to 20°C (red region).

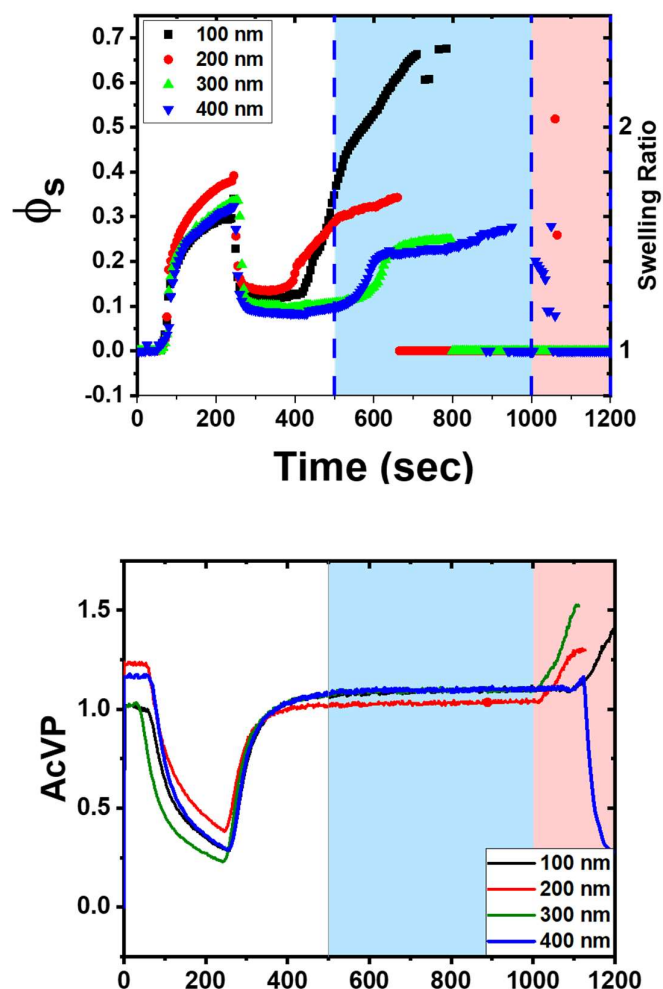


Figure 6.4 (Top) The thin film swelling effects of PS (17K) in $\text{CHCl}_3/\text{H}_2\text{O}$ vapour. The condensation time was at 500 seconds (blue shaded region) and the method adapted was the *dilution method*. **(Bottom)** The change in water vapour pressure in respect to time. At 500 seconds, the water vapour pressure was maintained at 1 kPa where $T_{\text{stage}} = 6.5^\circ\text{C}$.

The swelling effect of the polymer (prior to water addition) resulted in solvent incorporation of an approximate value of $\phi_s = 0.3\text{-}0.4$, thus indicating that a volume of 30- 40 % of chloroform was present in the thin film. However, once the water entered the chamber, the ϕ_s value dropped to 10-20 %. The reduction of the stage temperature (T_{stage}) caused a rapid

increase in polymer swelling as solvent saturation increased; however, it did not reach the condensation limit until the vapour pressure reached 1 kPa. The water saturation increased and condensed onto the surface at $T_{\text{dew}} = 6.5\text{ }^{\circ}\text{C}$ as calculated using the Antoine equation and is graphically presented in **Figure 6.5**.

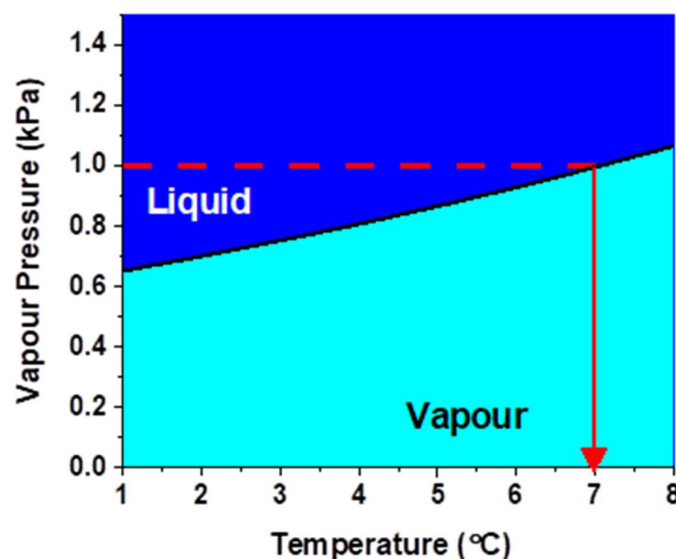


Figure 6.5 Condensation limit to allow condensation to occur. Predicted as $< 7\text{ }^{\circ}\text{C}$.

It is important to note that it takes 100 seconds to reach the dew point. Therefore, the stage was reduced to a set point at approximately 350 seconds to allow the temperature to reduce from 18°C to the T_{dew} of $6.5\text{ }^{\circ}\text{C}$ at 500 seconds. The vapour pressure was maintained and measured using the humidity probe inside the chamber. The probe measured a vapour pressure of 1 kPa at 500 seconds, which is adequate for condensing on to the film. A rapid increase in surface roughness can be seen when the water templates the polymer film at these temperatures.

6.4 Pore Characterisation of Porous PS Thin Films

Optical images were taken immediately after the swelling to understand the morphology of the films. Optical images of the porous films after the SVBF method are shown in **Figure 6.6**.

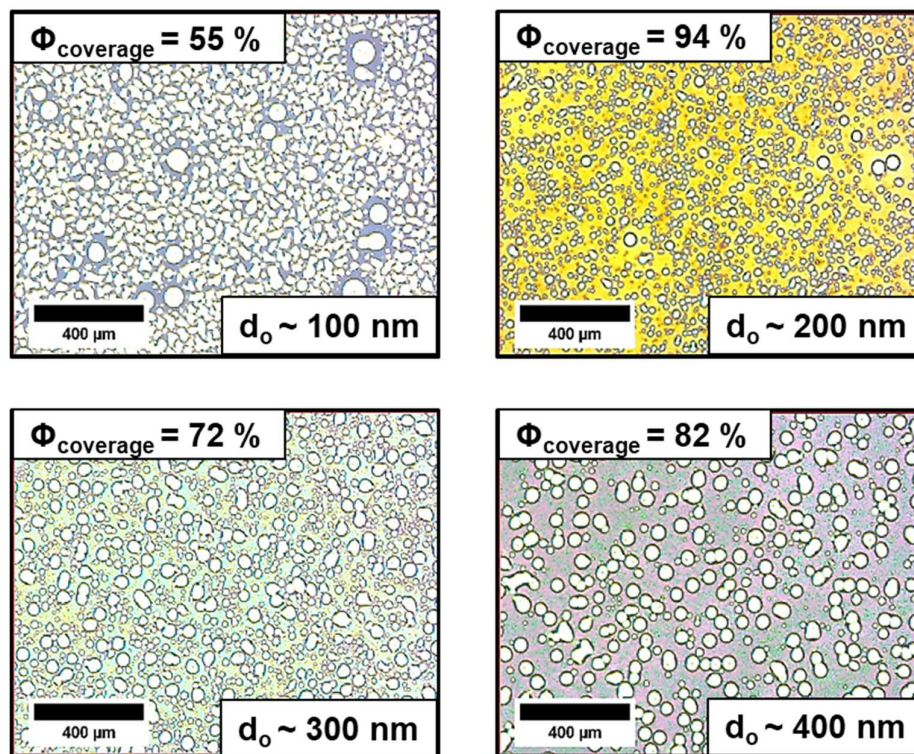


Figure 6.6 (a) Optical Images of post swelling of PS 17K thin film on a silicon wafer at 500 seconds of condensation. Initial thicknesses (d_o) were recorded at 100 nm, 200 nm, 300 nm and 400 nm with Φ_{coverage} = polymer coverage (%).

Polymer coverage (i.e % area covered by the polymer) was measured using ImageJ software and was calculated using **Equation 6.1**. Polymer coverage (Φ_{coverage}) values are 55 %, 94 %, 72 % and 82 % for the 100, 200, 300 and 400 nm respectively. From using ImageJ software, the overall area for a 5x image is calculated to be ($1549 \mu\text{m} \times 1164 \mu\text{m} = 1,804,311 \mu\text{m}^2 = \sim 180 \text{ cm}^2$) where 1 pixel = $0.888 \mu\text{m}$. Please see appendix (A.1).

$$\Phi_{coverage} = \frac{\text{Polymer Area Coverage}}{\text{Total Image Area}} \#[\text{Equation 6.1}]$$

The ImageJ software can filter the porosity generated by the water droplets by filtering 0.8-1 circularity, where n is the number of pores. Circularity refers to the shapes deemed circular within the ImageJ software package and can effectively identify where the water droplets templated the thin films. SEM images were used to determine the films' porosity by increasing each image's contrast and silicon exposure, indicating that the droplet had fully penetrated the thin film. Top-down SEM images (**Figure 6.7**) show a better resolution of pore morphology and how the circularity increases at higher thicknesses.

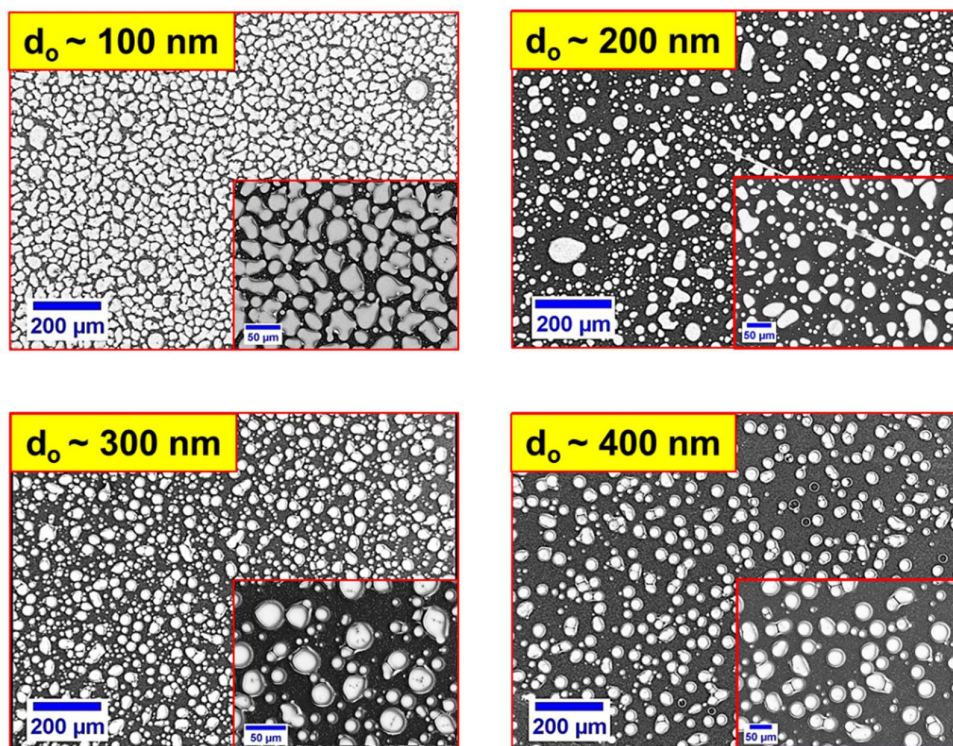


Figure 6.7 Top down SEM analysis of atactic PS (17K) at different thicknesses where the condensation time is 500 seconds. Accelerating voltage at 2kV.

Measurements such as the Feret diameter (d_f) (average measurement along a specified direction, from one end to another), pore area and pore coverage were recorded at a circularity between 0-1 as presented in **Figure 6.8** where bright the bright areas show the exposed silicon surface. The tables of analysis for all of **Chapter 6** can be found in the **Appendix Section**.

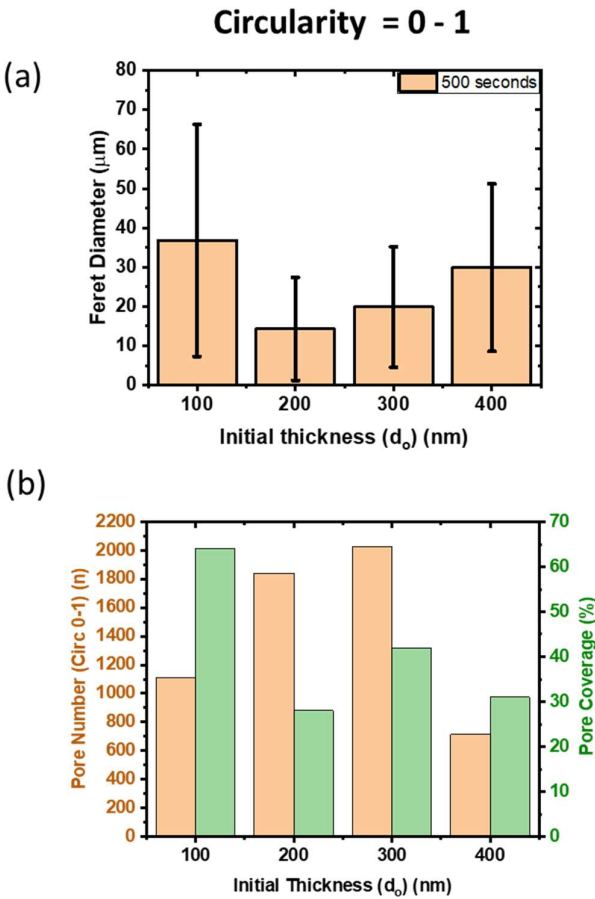


Figure 6.8 (a) Measurements of pore diameters and (b) pore number and coverage for PS films ($d_0 = 100 - 400$ nm) at 500 seconds condensation. Data is filtered with circularity 0-1.

The 100 nm film demonstrated the highest pore coverage (64 %), and considerable evidence of dewetting can be seen in **Figure 6.7**. Coalescent events have occurred, resulting in an average pore diameter of $36.8 \pm 29.5 \mu\text{m}$ and $n = 1111$ (pore number). The 200 nm film produced the lowest pore coverage (28 %) and showed minimal dewetting. Less coalescent

events have occurred, resulting in the lowest average pore diameter of $14.3 \pm 13.1 \mu\text{m}$ with $n = 1842$ pores. The 300 nm and 400 nm thin films have 42 % and 31 % pore coverage, with average pore diameters of $19.9 \pm 15.3 \mu\text{m}$ and 29.9 ± 21.3 , respectively. By filtering 0.8-1 circularity, dewetting or coalescent events can be omitted, and the pores templated can be assessed, identifying the efficacy of droplet templating (**Figure 6.9**).

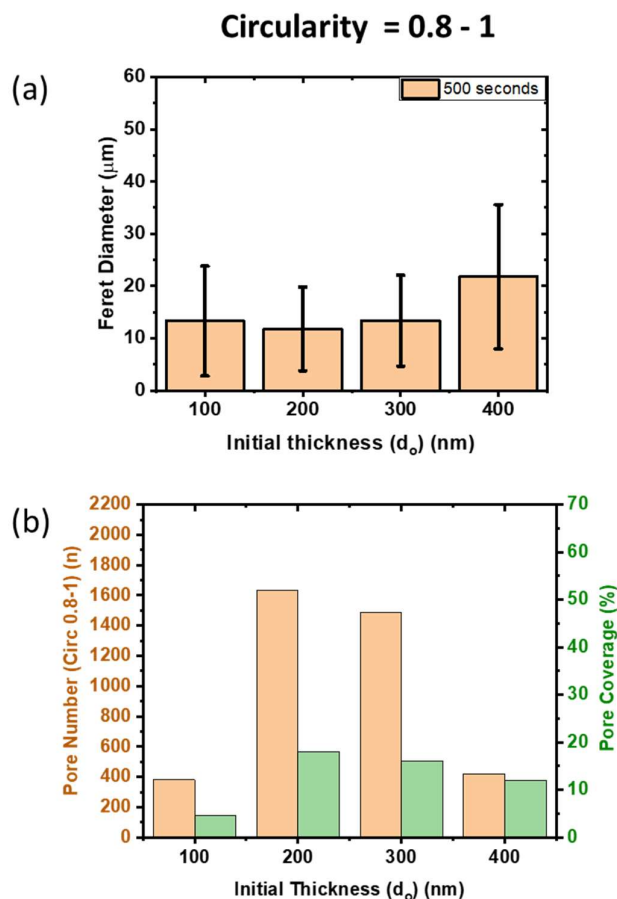


Figure 6.9 (a) Measurements of pore diameters and (b) pore number and coverage (%) for PS films ($d_0 = 100 - 400 \text{ nm}$) at 500 seconds condensation. Data is filtered with circularity 0.8-1.

Templating efficacy was measured following **Equation 6.2** and data is shown in **Table 6.2**.

$$\text{Pore Templating Efficacy} = \frac{\text{Circular Pores}}{\text{Overall Pores}} \quad \text{Equation 6.2}$$

Table 6.2 Droplet Templating Efficacy for PS (17k) 100-400 nm at 500 seconds of condensation. Green cells highlighted show optimal templating.

Initial Thickness (d ₀)	Templating Efficacy (%) (No. Circular pores / No. All pores *100 %)
100 nm	34.3
200 nm	88.5
300 nm	73.3
400 nm	59.1

The 100 nm film has a circular pore diameter (i.e. the film templated by the droplets) value of $13.3 \pm 10.5 \mu\text{m}$ with $n=381$ pores of this size detected. The circular and overall pore coverage are 4.6% and 64 %, indicating that most of the film has been subjected to dewetting. The 200 nm film has a smaller circular pore diameter of $11.8 \pm 8 \mu\text{m}$ with $n = 1631$ pores of this size detected. However, circular pore coverage is 18 %, indicating that only 10 % of the area of the film was subjected to coalescence and dewetting resulting in effective droplet templating (88.5 %). The 300 nm thin film produced an average circular pore diameter of $13.4 \pm 8.7 \mu\text{m}$ with $n=1,484$ pores of this size detected. The circular pore coverage and overall pore coverage are 16% and 42%, respectively, with an efficacy of 73.3 %. This also shows good templating in similarity to the 200nm thin film. The 400 nm films have the largest pore diameter of $21.8 \pm 13.8 \mu\text{m}$ with $n = 422$, and minor dewetting can be seen. Circular pore coverage and overall coverage were measured as 12 and 31 %, respectively, with an efficacy of 67.1 %. Pore size distributions for all thicknesses show a significant non-symmetric right skew in the data between $500 - 2000 \mu\text{m}^2$ for all thicknesses studied. This indicates that there is a larger ratio of smaller pores to larger pores.

Please see appendix A.9. A “rim effect” was observed for all pore structures in the SEM cross-sectional images as shown in **Figure 6.10**. This was due to the film delaminating off the silicon surface.

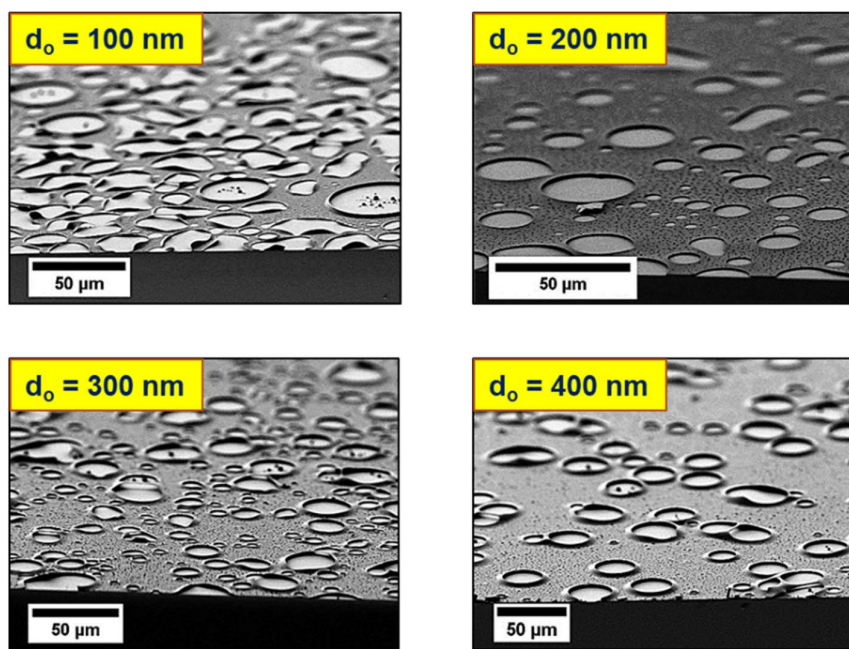


Figure 6.10 Cross-sections (tilt at 20°) and pore depth analysis for each of the different polymer thicknesses, $d_o = 100 \text{ nm}$, $d_o = 200 \text{ nm}$, $d_o = 300 \text{ nm}$, $d_o = 400 \text{ nm}$.

All SEM cross-sectional images show exposure of the silicon surface with unordered porosity seen throughout the thin films. Additionally, atomic force microscopy (AFM) measurements were carried out to measure and quantify the pore depth (**Figure 6.11**)

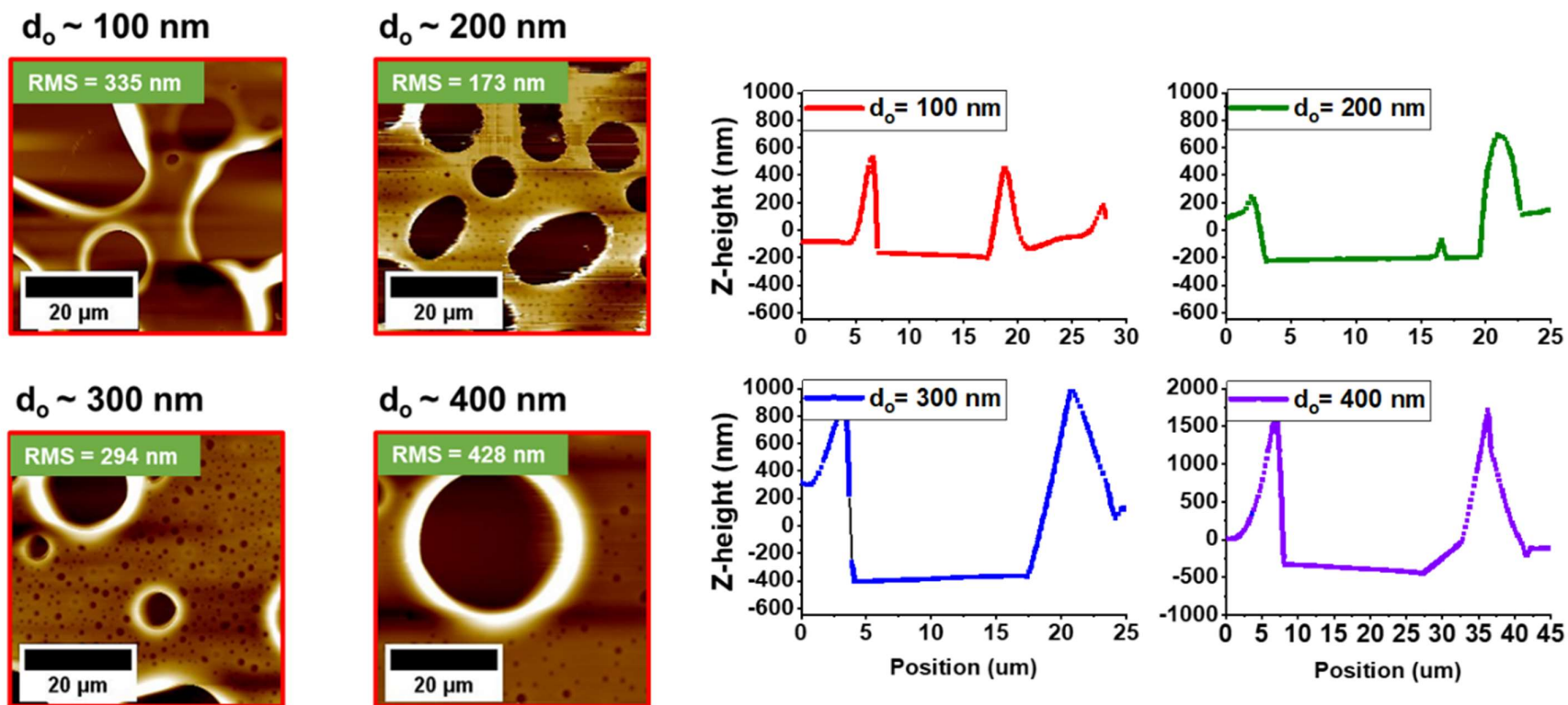


Figure 6.11 AFM topography (50 x 50 μ m) of pore types from 100-400 nm with pore depth profiles measured using XEI software (right).

Root mean squared (RMS) roughness values of 335, 173, 224, and 372 nm were measured for the 100, 200, 300 and 400 nm thin films, respectively. All pores have a penetration depth approximate to the initial thickness of the film, assuming there are no rims present. Surprisingly, the 100 nm has a significantly RMS value of 335 nm, indicating the effect of dewetting^{7,9} on the polymer film at the saturations of both water and solvent. Furthermore, by carrying out pore depth analysis, all values show that no polymer remains in any of the pores, and the rim heights of each pore differ at each thickness. Due to the increase in rim heights and polymer film breakup, contrasting heights of approximately 500, 600, 1000, and 1800 nm were measured for 100, 200, 300 and 400 nm, respectively. The ratio of pore height to initial thickness shows a decreasing trend for 100-300 nm films; however, the 400 nm is an outlier for having a relatively large rim height. These are 1:5, 1: 3, 3:8 and 4: 15 for 100, 200, 300, and 400 nm, respectively. AFM images in **Figure 6.12** show the contrast in pore height for each measured sample using an RGB (Red- Green- Blue) coloured system.

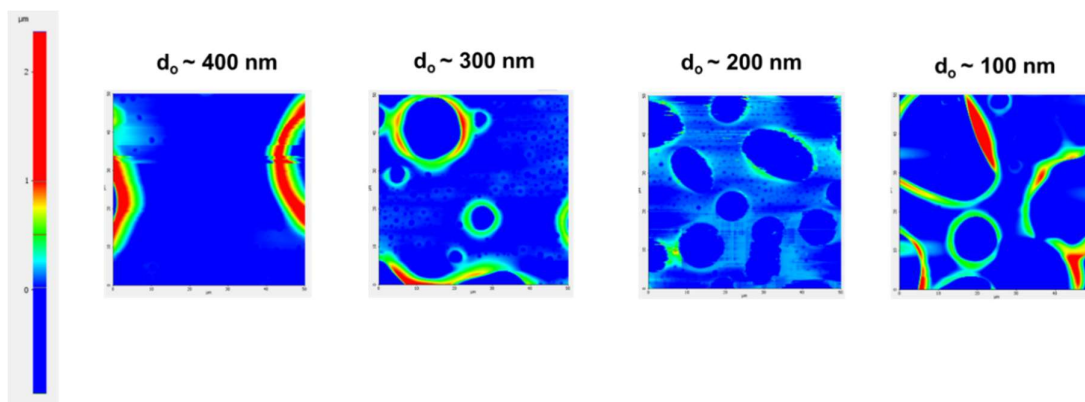


Figure 6.12 AFM Images showing various rim pore heights by changing the AFM image to RGB style.

AFM RGB-type images show the droplet effects on the pore rim height in the PS films. 400 nm and 100 nm generate rim heights as high as $2\mu\text{m}$ (2000 nm), which is significantly higher than the initial thickness of the films by order of magnitude. These trends show the

complexity of the system where pore size is determined by the interactions with the surface transport of the film during the templating and the size of the water droplets concerning initial film thickness. The droplet drives the system towards wetting stabilisation¹⁰ but does not completely wet the surface due to the low contact angle of solvent¹¹ and spread miscibility of the polymer as the film de-swells, as discussed previously in **Chapter 2**.

Figure 6.13 illustrates the effects of the water during the swelling condensation process where (A) a rim is formed by polymer displacement, (B) high slopes are caused due to high contact angle between water and PS and (C) the surface wetting reduces the contact angle at the water-substrate interface.

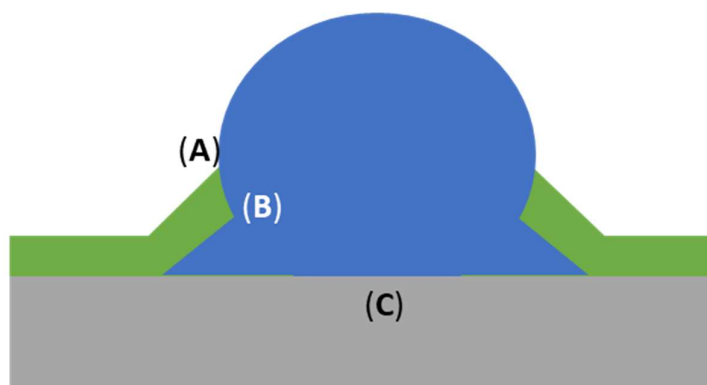


Figure 6.13 A graphic showing the effect of the water droplet on the swollen thin film on the silicon substrate. (A) Well formed rim by polymer displacement and low attachment. (B) High slope of side wall because of high contact angle. (C) Surface wetting causes shape at substrate.

Cross-section analysis using Focused Ion Beam (FIB) identifies the interaction of the substrate with the water droplets by observing the contact angle once the water droplet has been removed as shown in **Figure 6.14**. Milling was performed on single pores in the 400 nm and 100 nm films. The pore shape shows a low contact angle close to the silicon substrate

($\sim 55^\circ$), indicating that the water ingressed underneath the polymer and wetted larger areas of the silicon surface and displaced the polymer film from the substrate for all films (100, 200, 300, and 400 nm).

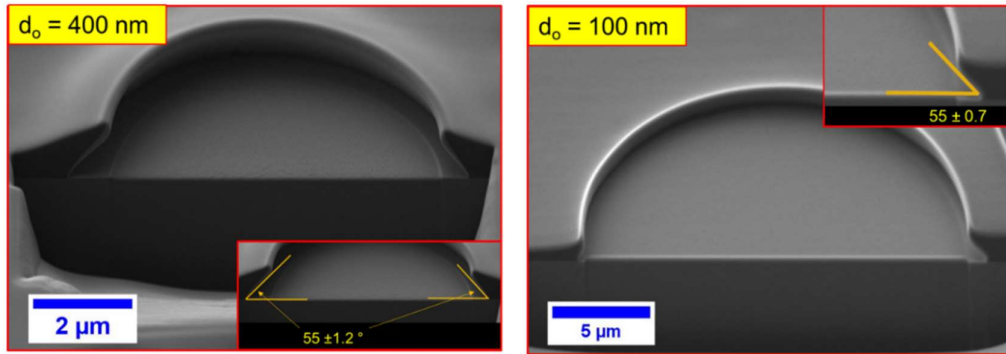


Figure 6.14 Cross section-FIB of the PS thin film at $d_o = 400$ nm and $d_o = 100$ nm. Tilt angle correction at 36° measuring a contact angle of 55° .

Once the temperature in the chamber increased, the water evaporated, thus being removed from the silicon surface. The polymer's hydrophobic properties do not want to interact with the water molecules and result in the formation of a rim (**Figure 6.15**).

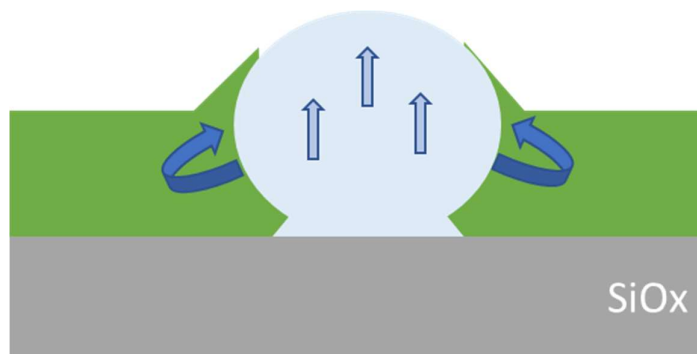


Figure 6.15 Formation of rim after removal of water droplet.

Preliminary data show the mechanisms of how the swollen polymer and water interact with each other and the displacement of the film has been discussed in detail in **Chapter 2**¹¹. By changing the initial thickness of the film, different pore sizes and rim heights can be produced upon removal of the droplets. Porosity increases at higher thicknesses in addition to rim heights; however, if the film is too thin, delamination will occur when exposed to a swelling solvent^{12,13}.

6.4.1 Effects of Condensation Time on Pore Uniformity

be swollen following the previous procedure; however, condensation times will be assessed. As seen previously, the swelling effects are similar, indicating that the incorporation of solvent via saturation results in a similar swelling effect ($\phi_s = 0.3 - 0.4$) for each of the thicknesses studied, as shown in **Figure 6.16**.

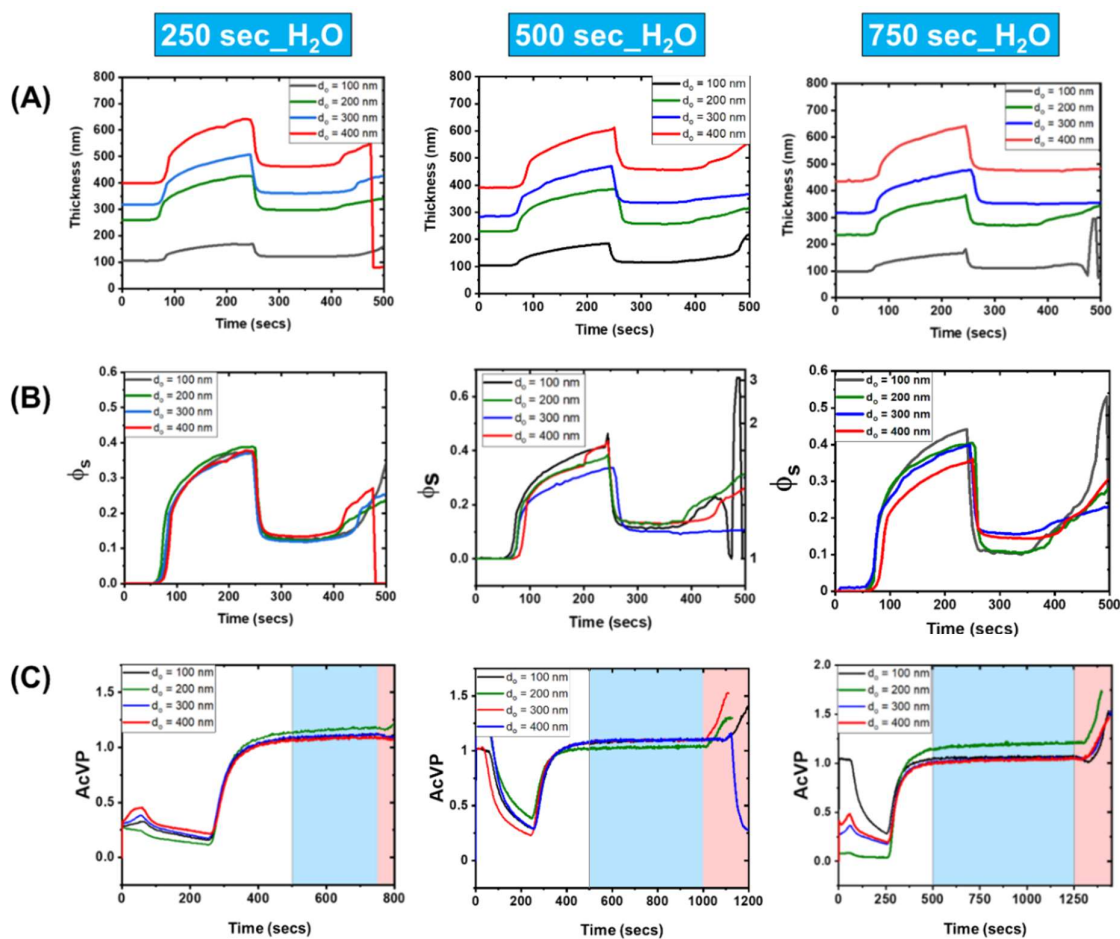


Figure 6.16 (A) Thickness measurements of PS swollen films in CHCl₃ vapour from 0-250 seconds and CHCl₃/H₂O vapour from 250 – 500 seconds (B) Solvent volume fraction measurements in CHCl₃ vapour only from 0-250 seconds and CHCl₃/H₂O vapour from 250 – 500 seconds (C) Actual vapour pressure (ActVP) measurements for all experiments, condensation times (blue region @ 250, 500 and 750 seconds). Addition of water vapour at 250 seconds for each experiment. T_{stage} at 6.5 °C at 500 seconds.

At approximately 400 s, all thin films swell due to the reduction in T_{stage} to T_{dew} . The 100 nm films increased the highest relative to the other three thicknesses studied. This indicated that thinner films have more instability with respect to having less mass transport limitations^{14,15}.

SEM characterisation (**Figure 6.17**) shows polymer dewetting at the longest condensation time (750 seconds). As expected, initial observation of the post-swelling SEM images suggests that the 100 nm thin films dewetted as predicted from the swelling analysis and the thicker films formed polymer agglomerates on the surface of the substrate.

Large deviations in pore size can be seen across all thin films thus both types of porosities need to be assessed. ImageJ analysis was carried out to identify the effect of droplet templating on all thin films, by carrying out the same procedure as discussed in **Section 6.2**, where condensation time is the variable.

PS Thin Films

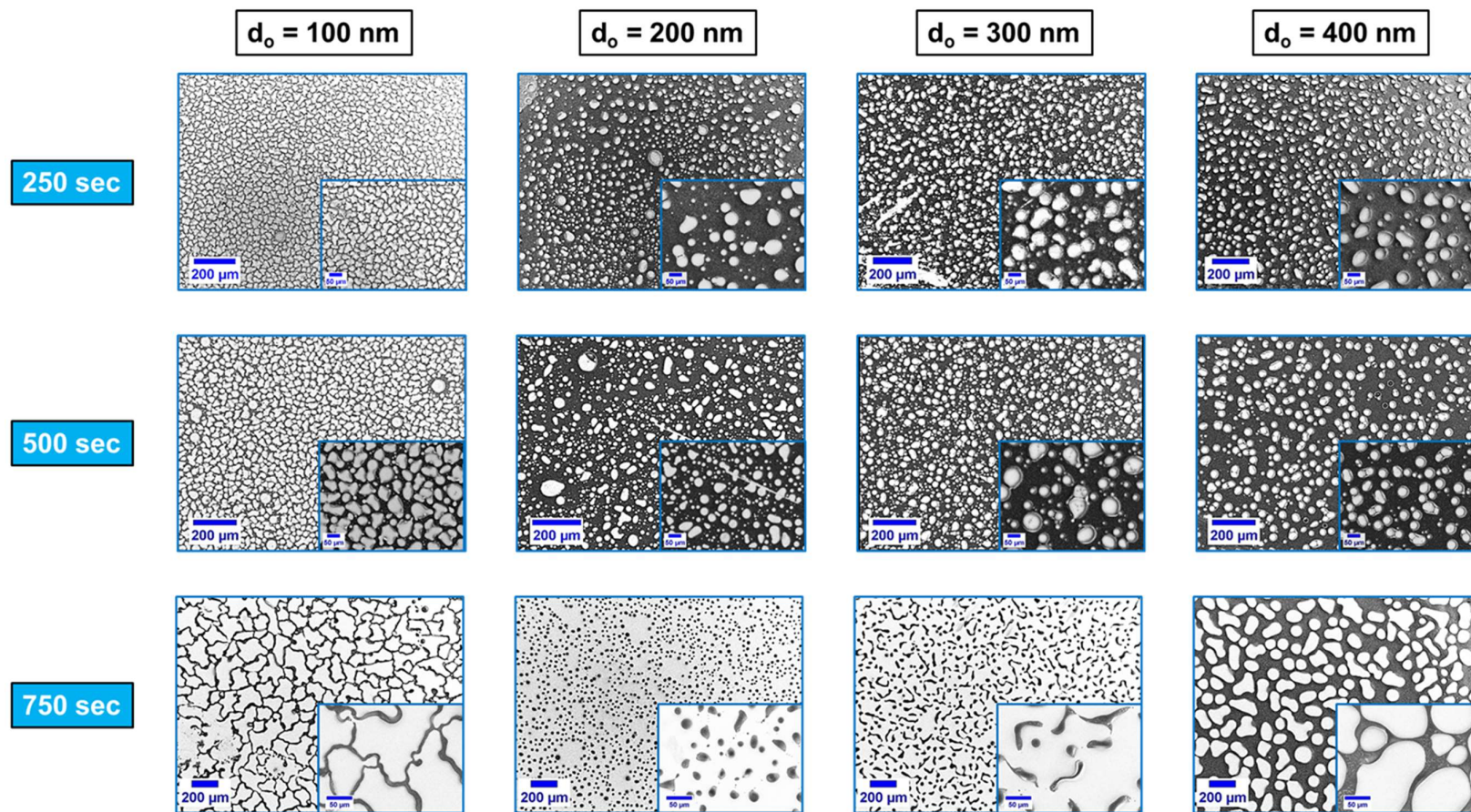


Figure 6.17 Top down SEM images of PS (17K) at 100–400 nm respectively at 250, 500 and 750 seconds of condensation, respectively.

Imaging carried out using SE₂ detector at an accelerating voltage of 2 kV.

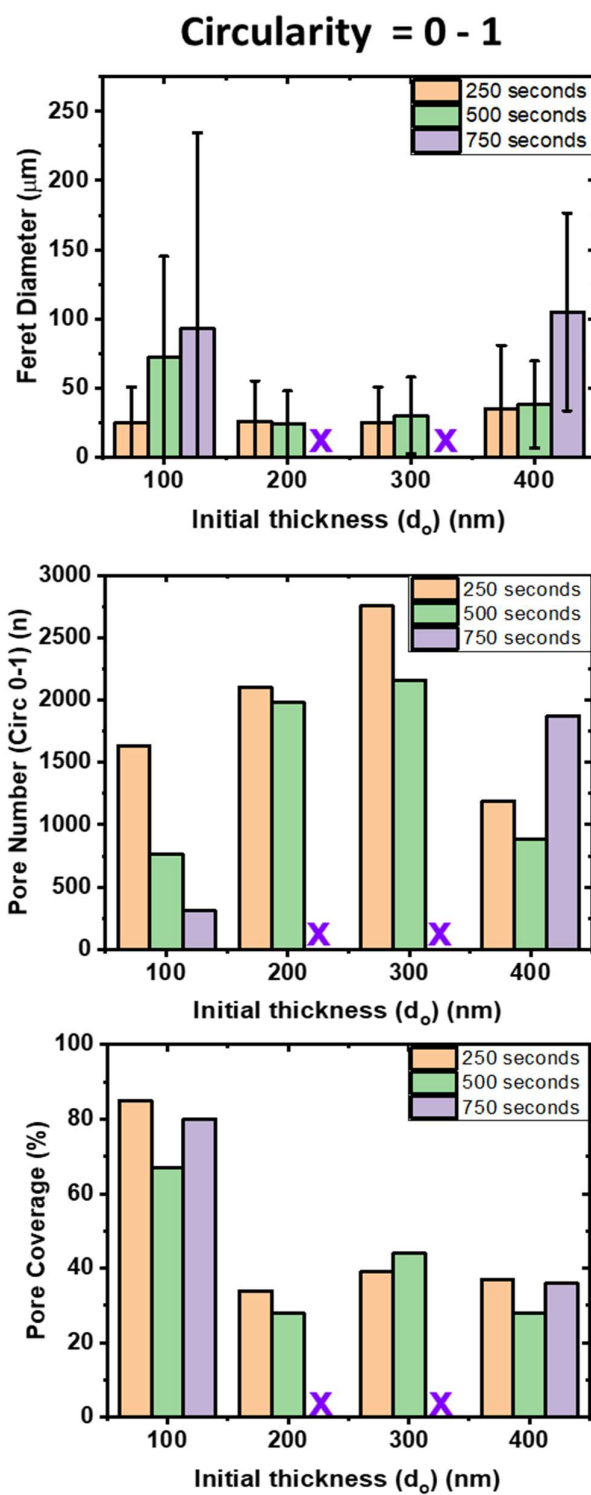


Figure 6.18 (a) Measurements of pore diameters and (b) pore number and coverage (%) for PS films ($d_0 = 100 - 400$ nm) at 250, 500 and 750 seconds condensation. Data is filtered with a circularity of 0-1.

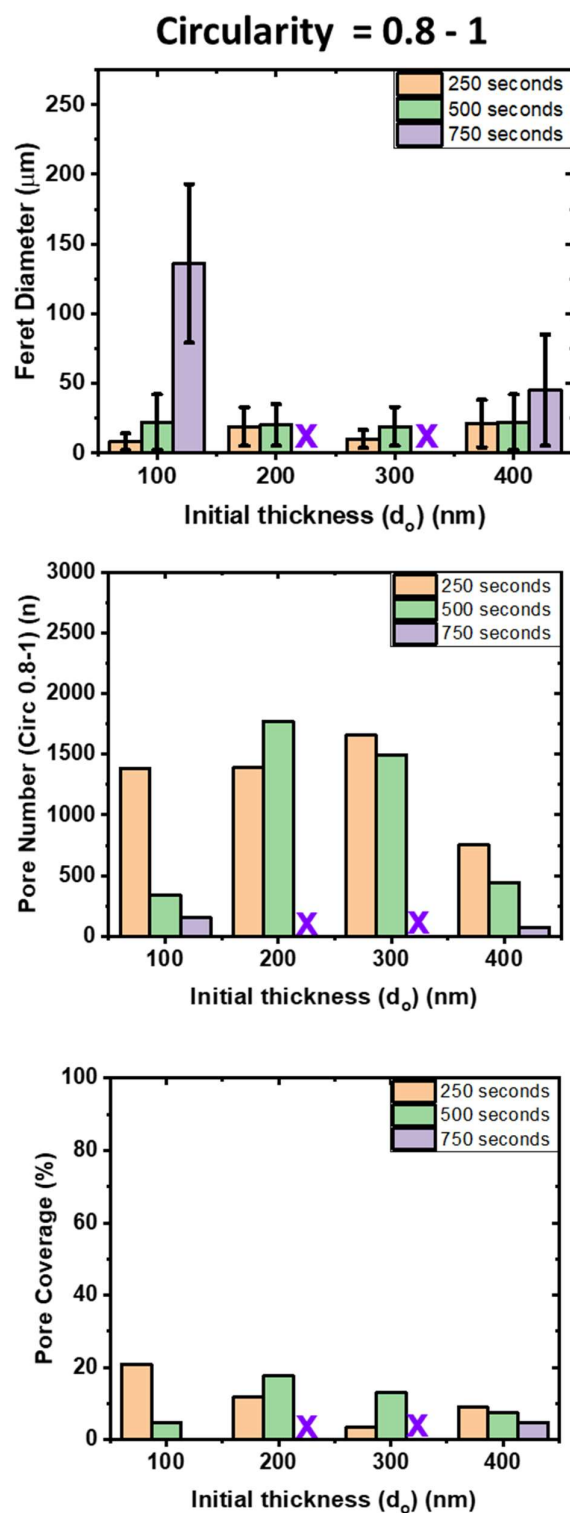


Figure 6.19 (a) Measurements of pore diameters and (b) pore number and coverage (%) for PS films ($d_o = 100 - 400$ nm) at 250, 500 and 750 seconds condensation. Data is filtered with a circularity of 0.8-1.

Templating efficacy (%) is shown in **Table 6.3** for all thicknesses and condensation times.

Table 6.3. Droplet Templating Efficacy for PS (100 -400 nm) films at different condensation times. Green cells highlighted show optimal templating.

Initial Thickness (d ₀) (nm)	Templating Efficacy (%) (No. Circular pores / No. All pores *100 %)		
	250 s	500 s	750 s
100	84	44	51
200	66	89	0
300	60	69	0
400	63	51	4

At a condensation time of 250 s, dewetting was at its lowest and pore diameters ranging from **0 - 80 μm** were observed with a range of **2 -38 μm** for circular pores. Total pore coverage (85 %) and circular pore coverage (21 %) were the highest for the 100 nm. Efficacy values of 84, 66, 60 and 63 % were calculated for the 100, 200, 300 and 400 nm, respectively.

At a condensation time of 500 s, there is an increase in pore diameter standard deviation with respect to increasing coalescent events and solvent dewetting. Pore diameters ranging from **0 - 150 μm** were observed, with a range of **2-40 μm** for circular pores. The most effective film templated at 500 s was the 200 nm with a low total pore coverage of (28 %) and high circular pore coverage of 17.8 %. Efficacy values of 44, 89, 69 and 51 % were calculated for the 100, 200, 300 and 400 nm, respectively. Circular pore sizes remain similar for 250 seconds and 500 seconds, indicating that droplets follow a similar distribution before coalescence occurs.

At a condensation time of 750 s, the 200 and 300 nm films dewetted. Overall pore diameter deviations increase, increasing the pore diameter range **(0- 240 μm)**. Circular pore sizes significantly reduce, indicating that coalescence¹⁶ and dewetting⁶ are the main factors that expose the silicon surface at this condensation time. Efficacy values of 51 % and 4 % were recorded for 100 and 400 nm, respectively.

In summary, it is challenging to improve the ordering of the thin film using the PS homopolymer film alone. Condensation times can impact pore size; however, minor increases can be seen and dewetting is prevalent for all thicknesses.

6.5 Functionalising the PS Films (PS-COOH)

6.5.1 Introduction

Thin films of a functionalised PS were studied as an additional method to improve the ordering of pores by increasing the amphiphilic properties of the polymer chain at a molecular weight of 16.5 kg mol^{-1} (similar to PS as discussed in **Section 6.3**). It is expected that by increasing hydrophilicity problems with dewetting may be mitigated^{17,18}. This would allow for verification of the model. It was reported that adding hydrophilic groups to the polystyrene chain could improve the ordering of the droplets via drop cast methods¹⁸. This work looks at extending the work by Zhu *et al.* and carrying out the solvent vapour breath figure method on a functionalised PS thin film. Dicarboxy-terminated Poly (styrene) (PS-COOH, P3949, Polymer Source) was used where the carboxylic acid functional group is attached to the α and ω position of the polymer as shown in **Figure 6.20**.

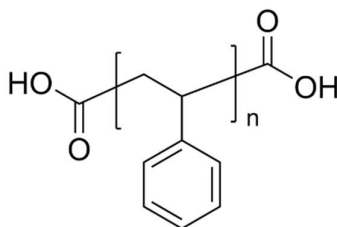


Figure 6.20 Chemical structure of Carboxy-terminated Poly(styrene).

A solution of PS-COOH generated thicknesses of 147 ± 2 , 113 ± 2 and 90 ± 0.7 nm using a 2 wt.% solution of PS-COOH/toluene at 1000, 2000 and 3000 rpm, respectively. **Figure 6.21** shows the thickness of the thin films after spin coating and was measured using the F3 CS Filmetrics reflectometer.

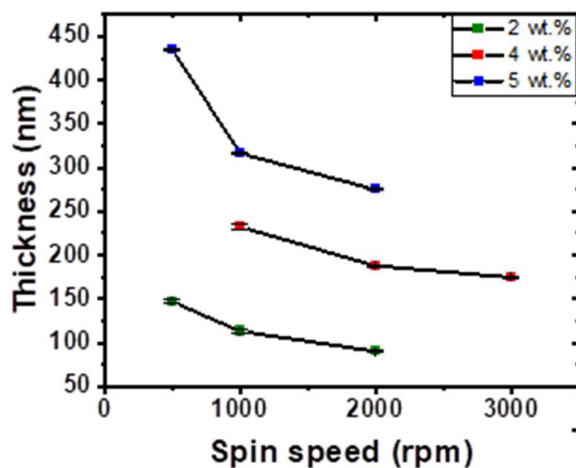


Figure 6.21 Thickness of PS-COOH (16.5 K) thin films at different concentrations (2, 4 5 w/w %) and different spin velocities (RPM).

6.5.2 PS-COOH Swelling Analysis at Low Water Vapour Pressure

Thin films were swollen in CHCl_3 following the process outlined in section 6.2. The temperature of the bubbler was changed for each experiment as the T_{ambient} was recorded as 17.3 °C; however, this was not considered a large issue as the swelling effect relies on the saturation of solvent in respect to ΔT between solvent bubbler and stage. **Figure 6.22** illustrates both experiments carried out where condensation was carried out for (i) 250 seconds and (ii) 500 seconds. The blue shaded region is the time of condensation, and the red shaded region is where T_{stage} is heated at 20 °C removing solvent from the films.

Solvent swelling stage only – 0- 500 seconds

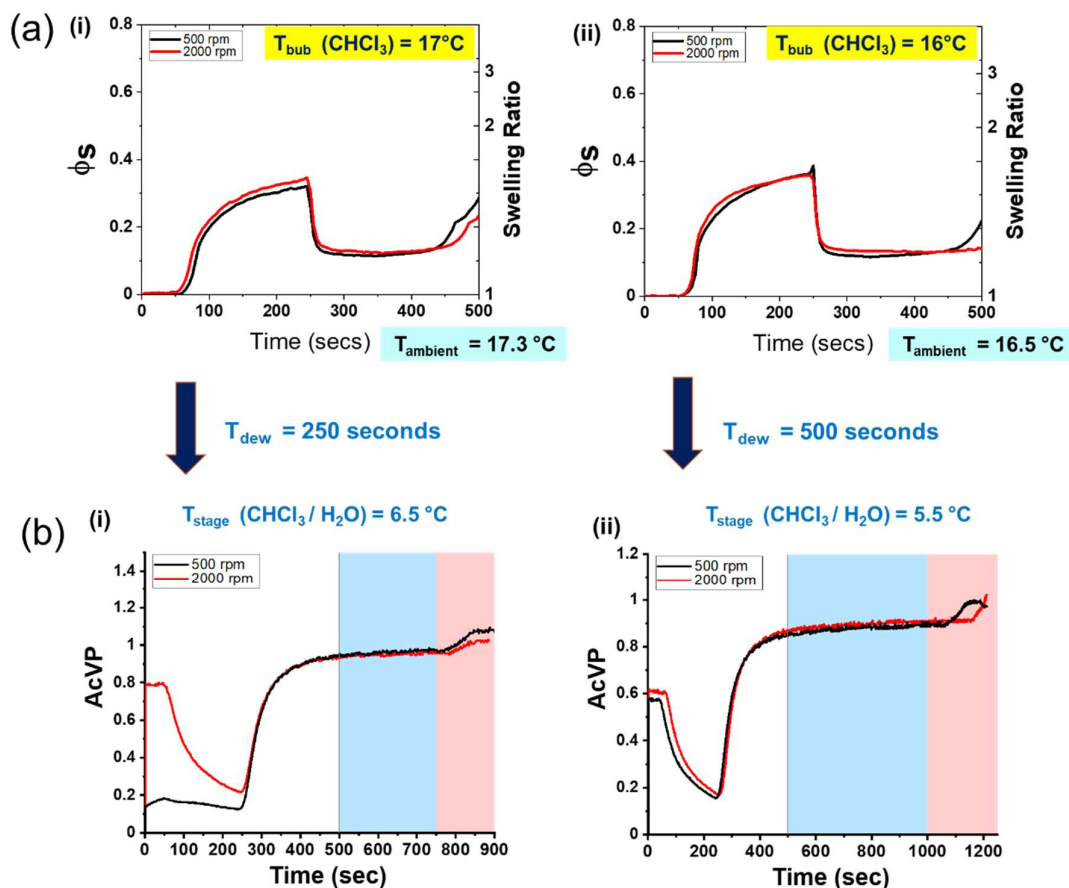


Figure 6.22 (a) The swelling effect of the polymer *via* solvent incorporation (ϕ_s) for 500 seconds at the beginning of the experiments (i) and (ii). **(b)** The water vapour pressure (AcVP) analysis for experiments (i) and (ii) with a ΔT value of $11.5^\circ C$ for T_{stage} and T_{bub} . Condensation occurs at 250 seconds and 500 seconds for (i) and (ii), respectively.

In respect to the swelling analysis, the PS-COOH thin films followed similar swelling effects comparable to the PS resulting in a ϕ_s value of 0.3. Condensation occurred at a ΔT of $11.5^\circ C$ where the condensation times were at 250 seconds and 500 seconds ($P_{dew} = 0.9$ kPa / $T_{dew} = 5.5^\circ C$). Top-down SEM analysis showed a large contrast in porosity in comparison to the PS films as a result of having hydrophilic end groups (**Figure 6.22**).

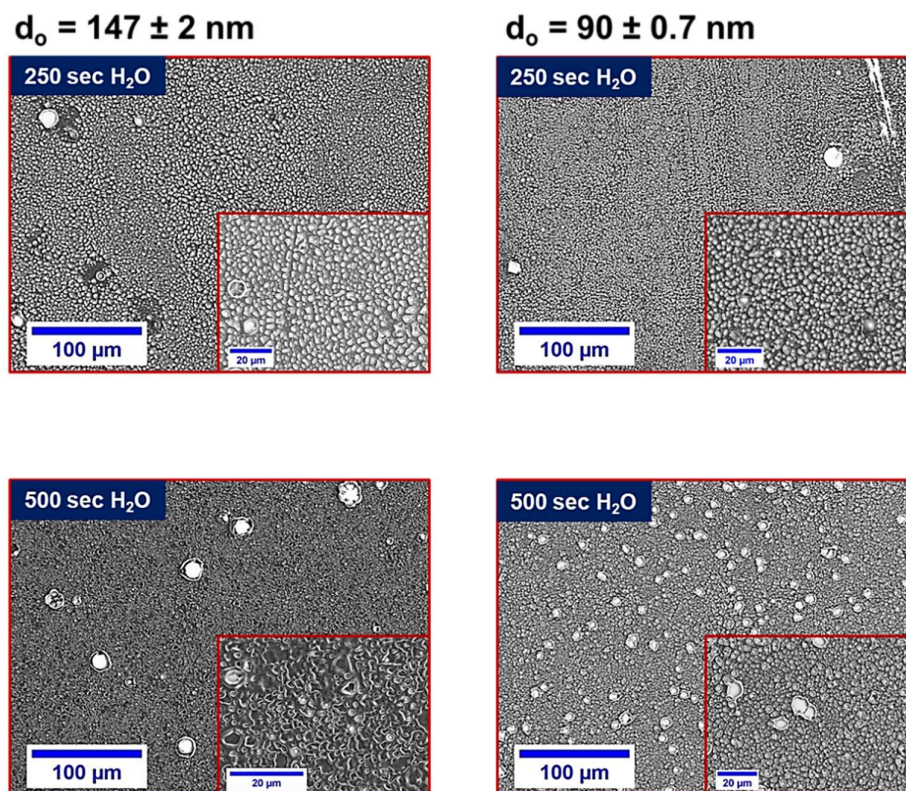


Figure 6.23 Top down SEM analysis of PS-COOH (16.5 K) with different thicknesses of 147 nm and 90 nm at water condensation times of 250 sec and 500 sec. Accelerating voltage at 2kV.

AFM characterisation (**Figure 6.24**) of the thin PS-COOH films presented much smaller pores compared to the PS samples at lower water vapour pressures. This might suggest that the size of pores is determined by the wetting phenomena^{10,19,20} as well as other factors. RMS values for the 250 sec and 500 sec were 77, 112, 65, and 120 nm for the 90 nm and 147 nm thin films, respectively

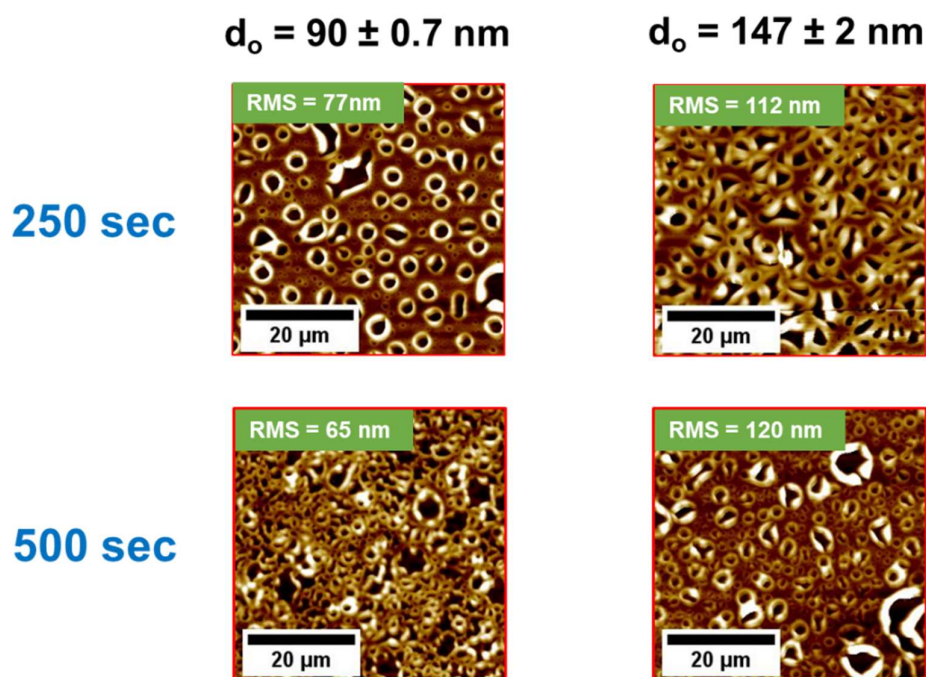


Figure 6.24 AFM Images (50 x 50 μm) for the PS-COOH (16.5 K) films with an initial thickness of 147 ± 2 nm and 90 ± 0.7 for 250 seconds of condensation.

Pore sizes were measured using ImageJ software as the SEM images were challenging to measure due to the unusual pore geometries. In addition, no filter was attached for the porosity in the AFM images. **Table 6.14** presents the data for the AFM images and indicates that longer condensation times reduce the size of the pores that are close to being microporous (Feret diameter (d_f) < 50 nm).

Table 6.4 Pore Analysis for PS-COOH (AFM).

Thickness (d_o) (nm)	Pore Size (Feret Diameter d_f) (μm)	
	250 s	500 s
90	2.3 ± 1.6	1.3 ± 1.6
147	0.7 ± 0.4	0.8 ± 0.7

When observing the films by cross-section SEM, it appears that the 500 seconds have reduced the size of the pores (**Figure 6.25**). This may have occurred due to an Ostwald ripening effect^{21,22}, in which the larger droplets are more energetically favoured than the smaller ones causing in-homogeneity over time as observed in micro and nano-emulsions²¹. Ostwald ripening is where smaller pores will emerge first as it is more thermodynamically stable to create numerous small pores than ones that are larger.

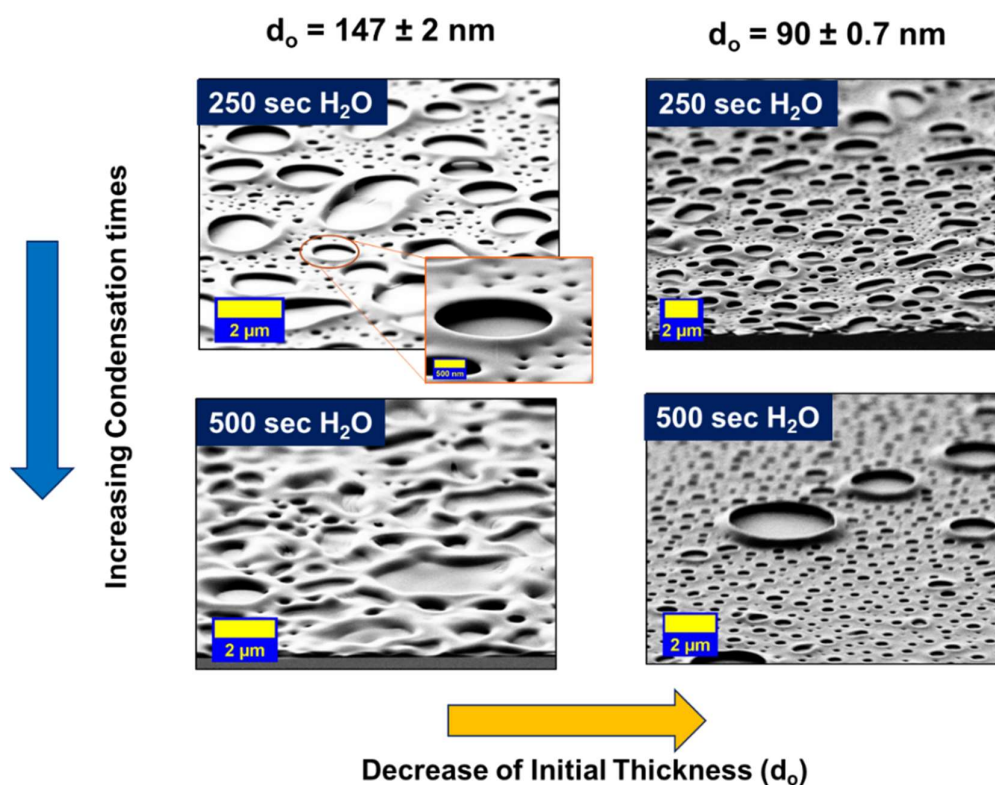


Figure 6.25 SEM Cross-sections for PS-COOH (16.5 K) with different thicknesses and water condensation times. Accelerating voltage at 2kV.

The contrasting behaviour between the PS-COOH and PS identifies the significant impact on the functional groups to improve the templating. Since the carboxyl group is polar, it favours interaction with the water droplets and stabilises them at an earlier stage resulting in smaller pore sizes^{18,23}. It is evident that functionalising the PS chain is the best route in

improving the ordering of the thin films and does not destabilise them. Compared to the PS, no delamination was reduced, and there was no change in the sidewall angle close to the silicon surface.

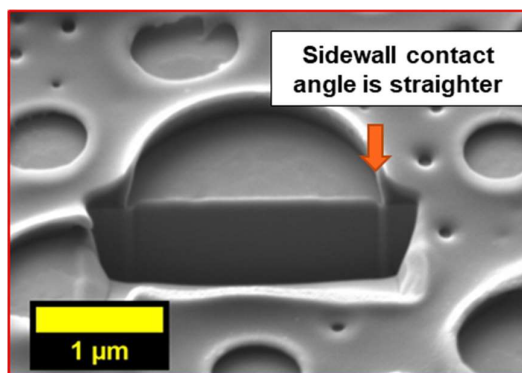


Figure 6.26 FIB/SEM Cross-sections at 1 μm for PS-COOH (16.5 K) at an initial thickness of 100 nm and a water condensation time of 250 seconds. Accelerating voltage at 2kV.

As previously seen, the thin films for PS automatically dewetted at thicknesses < 100 nm, however, for the PS-COOH very little/ no dewetting can be seen.

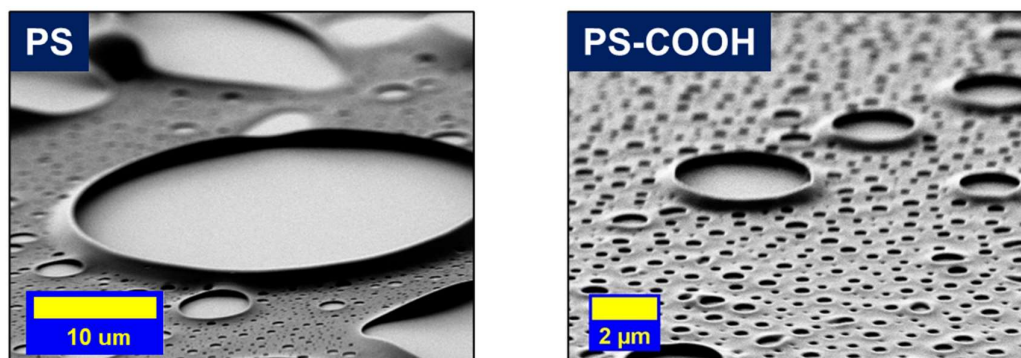


Figure 6.27 SEM Cross-sections for PS 17K (100 nm) and PS-COOH 16.5 K(90 nm) at 500 seconds of condensation. Imaging acquired using a SE_2 detector at an accelerating voltage of 2 kV and a tilt angle of 20° .

By increasing the water vapour pressure in the chamber, solvent driven dewetting and an increase in droplet templating can occur at these thicknesses by increasing the rate of swelling of polymer ($\phi_s = 0.5$ for experiment 1 to $\phi_s = 0.7$ for experiment 2) where there is a significant difference in pore formation as shown in **Figure 6.28**.

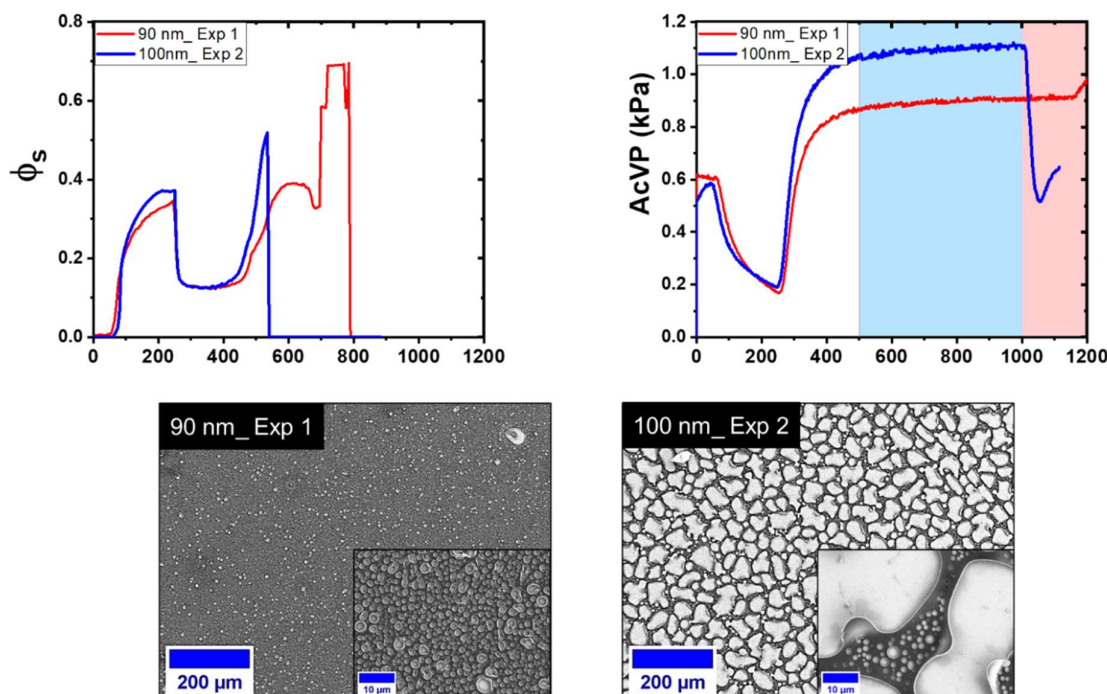


Figure 6.28 Swelling analysis of PS 16.5 K(~100 nm) in CHCl_3 , at different water vapour pressures (Experiment 1 is at a lower vapour pressure than Experiment 2) and at the same condensation temperature ($T_{\text{stage}} = 6.5\text{ }^{\circ}\text{C}$).

The first experiment demonstrated little to no pore formation; however, the second generated large porous areas in the polymer thin film at a thickness of 100 nm. This is due to the change in water vapour pressure. Once the water vapour pressure reaches 1kPa, the film can be templated by the droplets. No pore formation will occur if it does not reach the condensation threshold, as predicted by the Antoine equation²⁴.

6.5.3 Condensation Effects of PS-COOH (100 – 400 nm)

In this section, the effect of condensation time on PS-COOH templating will be discussed.

Figure 6.29 displays the experimental swelling procedure, indicating similar swelling effects and water vapour pressures for thicknesses of 100, 200, 300, and 400 nm at condensation times of 250, 500 and 750 s.

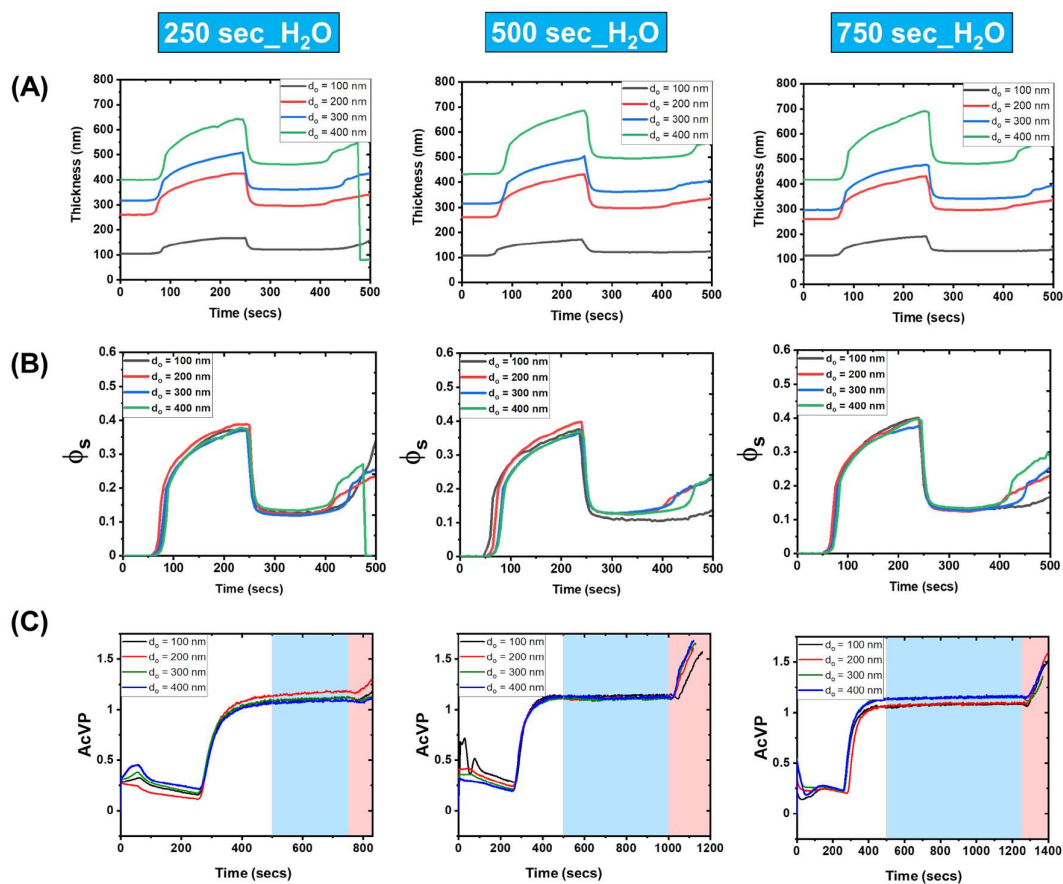


Figure 6.29 (A) Thickness measurements of PS-COOH swollen films in CHCl_3 vapour from 0-250 seconds and $\text{CHCl}_3/\text{H}_2\text{O}$ vapour from 250 – 500 seconds (B) Solvent volume fraction measurements in CHCl_3 vapour only from 0-250 seconds and $\text{CHCl}_3/\text{H}_2\text{O}$ vapour from 250 – 500 seconds (C) Actual vapour pressure (ActVP) measurements for all experiments, condensation times (blue region @ 250, 500 and 750 seconds). Addition of water vapour at 250 seconds for each sample. T_{stage} at 6.5 °C at 500 seconds.

All experimental parameters followed the same trends for each of the swelling procedures reported previously in **Section 6.1**. Solvent incorporation of $\phi_s = 0.3 - 0.4$ was recorded for all swelling experiments from 0- 250 seconds, followed by a significant drop to $\phi_s = 0.2$. All vapour pressures were recorded at approximately 1 kPa indicating that condensation will occur at 6.5 °C as shown previously in **Figure 6.5**.

Post-swelling SEM images are shown in **Figure 6.30** for the thicknesses recorded. From initial observation of the images, an increase in pore size can be seen by increasing condensation time and unusual black structures start to emerge at higher thicknesses.

PS-COOH Thin Films

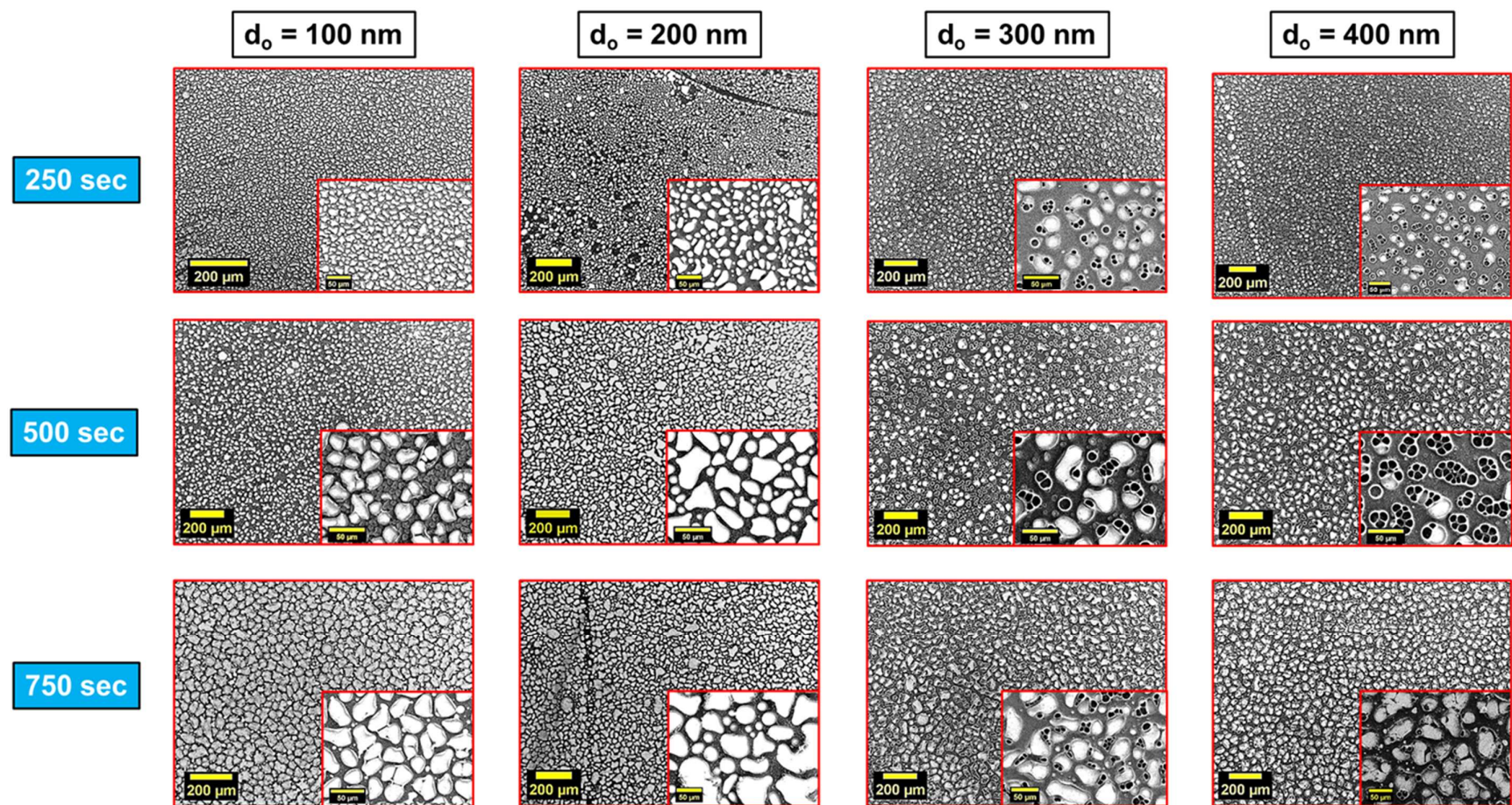


Figure 6.30 Top-down SEM images of PS-COOH (17K) at different thicknesses and water condensation times. Imaging carried out using SE₂ detector at an accelerating voltage of 2 kV.

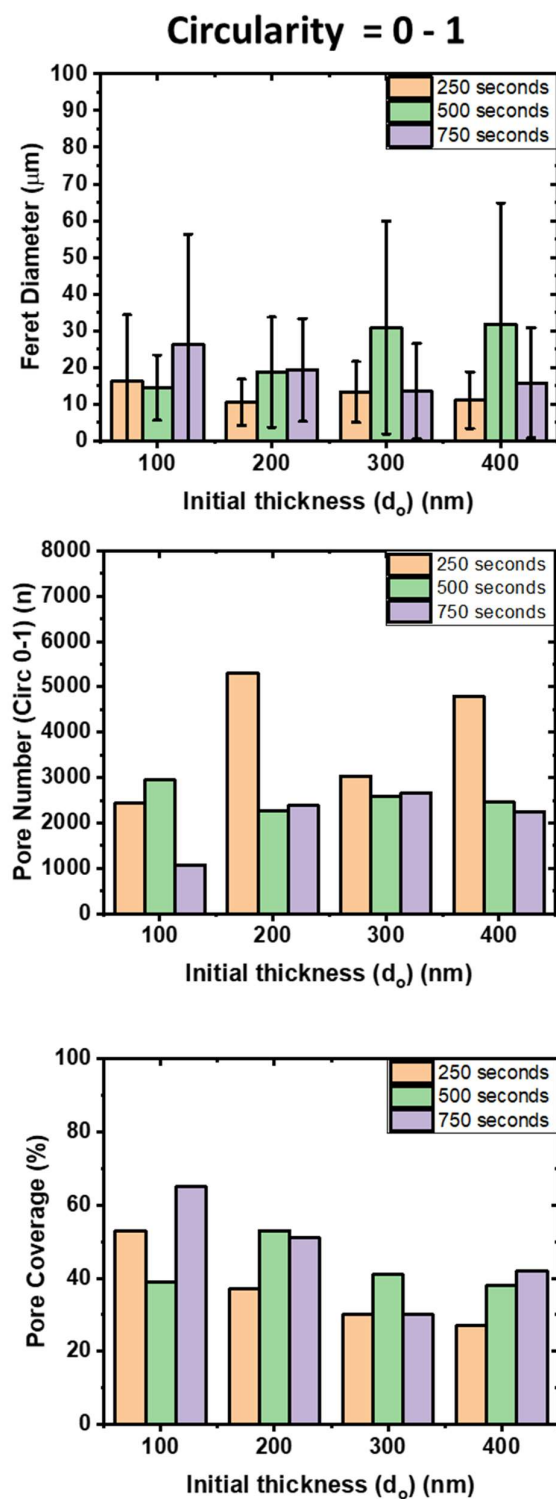


Figure 6.31 (a) Measurements of pore diameters and (b) pore number and coverage for PS-COOH films ($d_0 = 100 - 400$ nm) at 250, 500 and 750 seconds condensation.

Data is filtered with a circularity of 0-1.

Circularity = 0.8 - 1

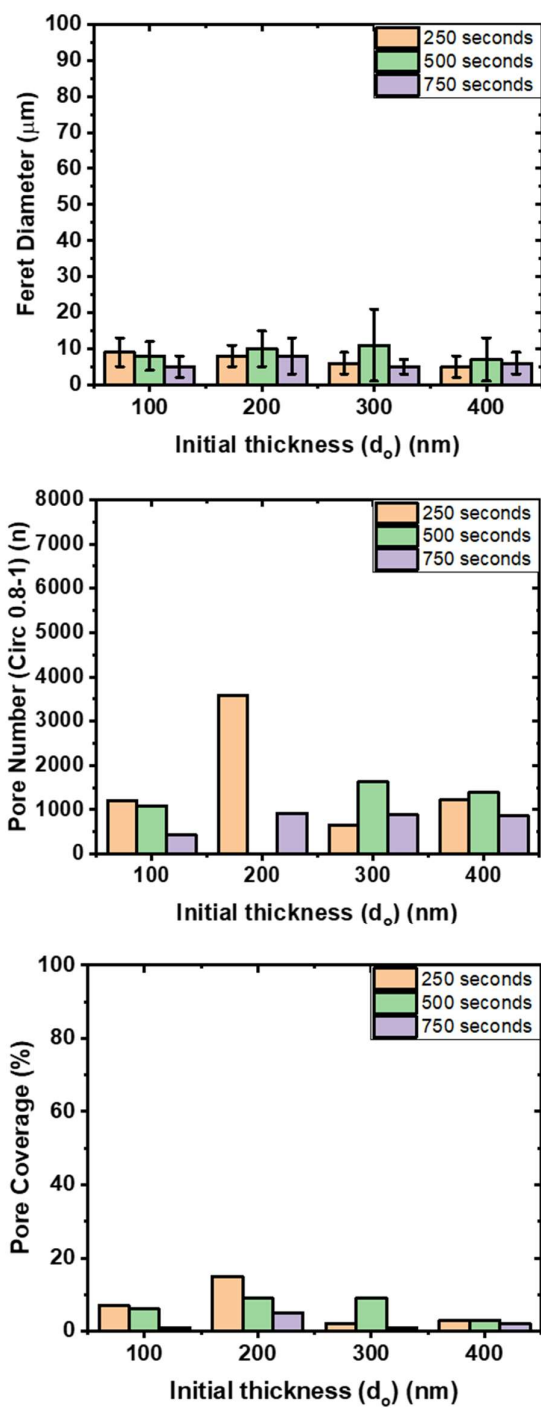


Figure 6.32 (a) Measurements of pore diameters and (b) pore number and coverage for PS-COOH films ($d_o = 100 - 400$ nm) at 250, 500 and 750 seconds condensation.

Data is filtered with a circularity of 0.8-1.

Table 6.5 shows the efficacy of droplet templating for all thin films at different condensation times.

Table 6.5 Droplet Templating Efficacy for PS-COOH (100 - 400 nm) films at different condensation times. All circularity < 80 %.

Initial Thickness (d ₀) (nm)	Templating Efficacy (%) (No. Circular pores / No. All pores *100 %)		
	250 sec	500 sec	750 sec
100	50	37	40
200	68	51	39
300	22	28	33
400	25	27	39

At a condensation time of 250 s, dewetting was at its lowest and pore diameters ranging from **0 - 70 µm** were observed with a range of **2 -38 µm** for circular pores. The most effective templated film was 200 nm with a total pore coverage of 37 % and circular pore coverage of 15 %. At this condensation time, the efficacy values of 50, 68, 22 and 25 % were calculated for the 100, 200, 300 and 400 nm.

At a condensation time of 500 s, there is an increase in pore diameter standard deviation concerning an increase in coalescent events and polymer dewetting, as discussed previously in **Section 6.3**. Pore diameters ranging from **6- 42 µm** were observed, with a range of **1-21 µm** for circular pores. The most effective film templated at 500 s was the 200 nm with a total pore coverage of 53 % and circular pore coverage of 9 %. Efficacy values of 37, 51, 28 and 27 % were calculated for the 100, 200, 300 and 400 nm, respectively. Circular pore sizes

remain similar for 250 seconds and 500 seconds, indicating that droplets follow a similar distribution before coalescence occurs. Dewetting is more prevalent when exposing the film to solvent over extended periods.

At a condensation time of 750 s, the pore sizes increase for all film thicknesses, and no polymer agglomerations can be seen (**Figure 6.30**). Pore diameters ranging from **0-60 μm** were observed with a range of **2- 13 μm** for circular pores. Circular pore sizes significantly reduce, indicating that coalescence¹⁶ and dewetting⁶ are the primary factors that expose the silicon surface at these condensation times. Efficacy values of 51 % and 4 % were recorded for 100 and 400 nm, respectively. The most effective film templated at 500 s was the 100 nm with a total pore coverage of 65 % and circular pore coverage of 1 %. Although the pore coverage looks minimal (specifically for circular), the number of overall pores and circular pores is 1080 and 436. Since size is a limiting factor on the pore area distribution, the test would be considered invalid and should not solely just rely on the ImageJ software. Efficacy values of 37, 51, 28 and 27 % were calculated for the 100, 200, 300 and 400 nm, respectively.

Pore area distribution histograms show a right skew in all of the data sets (**Appendix Figure 6.53**); however, the 500 seconds identify optimal homogenous porosity where 100, 200, 300, and 400 nm thick films have a tight distribution at 0-100 μm^2 indicating a frequency of 60 % for 100 nm and 90 %, for the 200-400 nm thicknesses. Interestingly, for the 400 nm sample, the distribution gets tighter at higher condensations as the polymer maintains the pore shape by interacting with the hydrophilic end groups of the PS chain.

It is apparent from **Figure 6.31** that by increasing the condensation time of water in the chamber increases the standard deviation of pore diameter for all film thicknesses. When the time was increased to 750 s, the pore area increased due to polymer dewetting⁸ and

coalescence, that have a negative influence on the thin film quality and the templating efficacy. Furthermore, coalescence events can occur more rapidly as the water droplet grows, decreasing the distance between neighbouring droplets²⁵.

Although the films are porous in appearance, the unstable nature of polystyrene on a silicon wafer⁸ results in the delamination of the polymer at lower thicknesses. Furthermore, there are dark areas on the surface of the film, indicating a different swelling effect (due to the carboxyl groups in the PS chain^{17,18}) in comparison to the linear atactic PS (17K) where repulsive forces dominate. A different pore structure was observed for PS-COOH at higher thicknesses. Cross-section SEM observed the black features at high magnifications and was imaged at a 20° tilt (Figure 6.33).

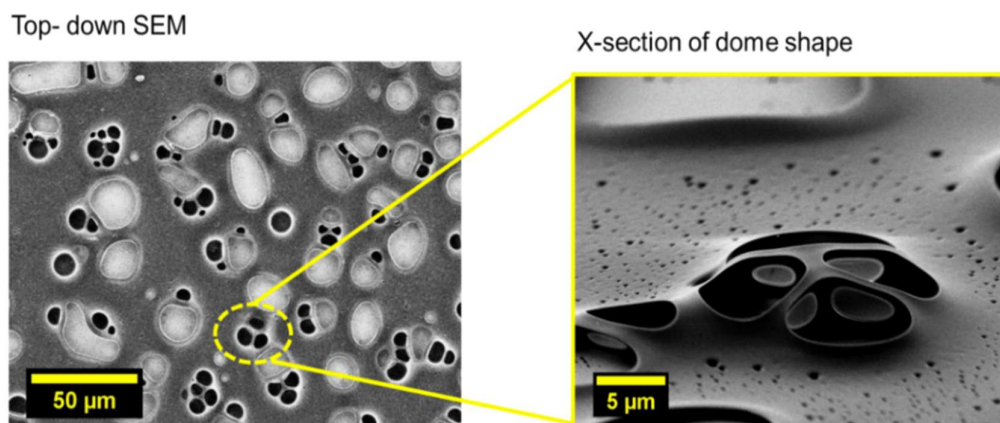


Figure 6.33 Top down SEM SEM images of PS-COOH (17K) and cross-sectional SEM image(tilt angle = 20 °) at 400 nm showing the encapsulation of droplet morphology. Condensation time at 250 seconds. Imaging carried out using SE₂ detector at an accelerating voltage of 2 kV.

By increasing thickness, the pore formation becomes more pronounced, where the droplets are encapsulated by the thin film creating a “dome shape”. This looks similar to a pre-breath figure formation²⁶ ; however, this type has never been observed in the literature. It was

postulated that the polymer at higher thickness moulds around the droplets, resulting in a more pronounced 3-D-like structure. Cross-sectional (**Figure 6.34**) analysis of the films (100- 400 nm) differs significantly from another when decreasing thickness and the different pores are observed only at 400 nm. Delamination effects can be seen for the 100-200 nm, and the film is kept intact for the 300-400 nm films.

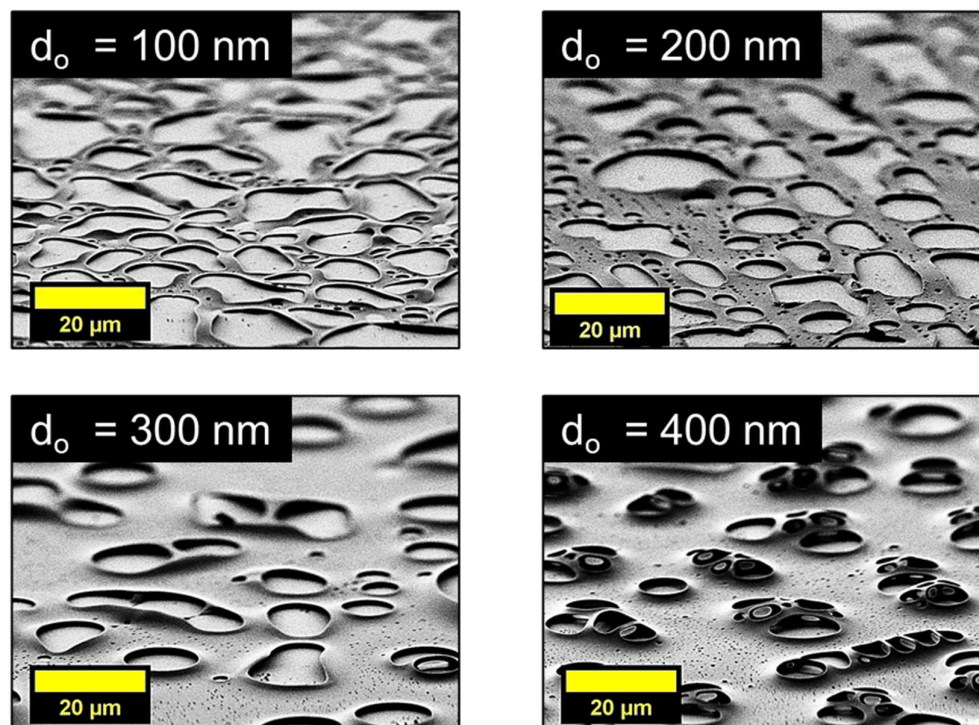


Figure 6.34 Cross section SEM images of PS-COOH (17K) (tilt angle = 20 °) at 100-400 nm at a condensation time of 250 seconds. Imaging carried out using SE₂ detector at an accelerating voltage of 2 kV.

Figure 6.35 illustrates the effects of water during the swelling condensation process where (A) a rim or dome shape is formed with respect to the affinity of the PS-OOH groups in the chain (B) low slopes are seen at the sidewall as a result of having a high contact angle

between water and PS²⁰ and (C) the surface wetting¹⁰ reduces the contact angle at the water-substrate interface.

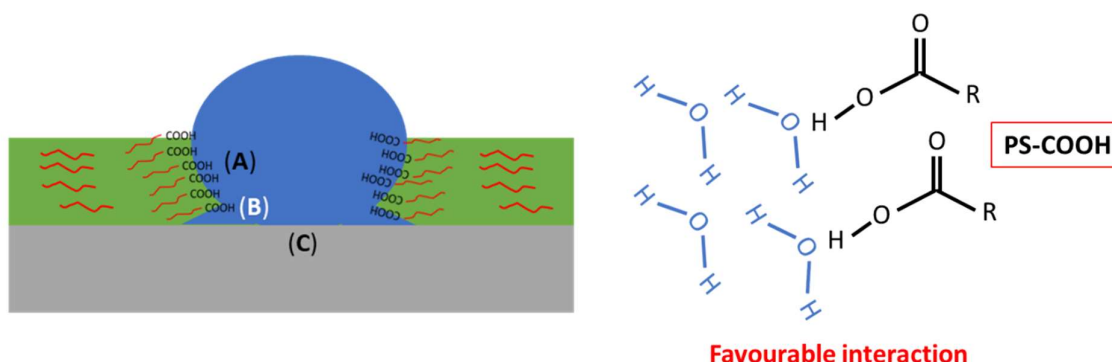


Figure 6.35 A graphic showing the effect of the water droplet on the swollen thin film on the silicon substrate. (A) A structured dome is produced due to favourable polymer interaction. (B) The low sidewall slope is with respect to a low contact angle between the water and the substrate. (C) Surface wetting is less pronounced at the substrate, and a deeper trough is produced due to the polymer enveloping the droplet morphology.

It is clear the polymer envelopes the droplet shape when it evaporates from the surface *via* heating as shown in **Figure 6.36**.

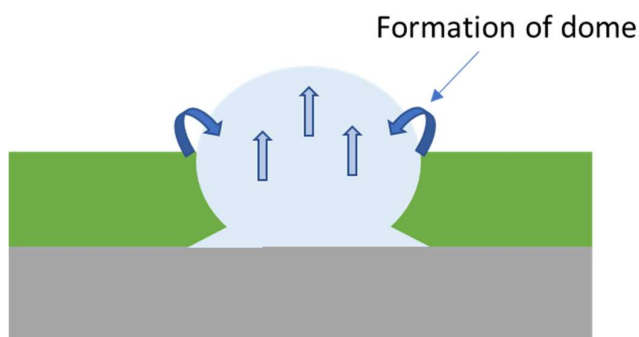


Figure 6.36 Graphic showing the formation of the dome after removal of droplet.

In summary, the PS-COOH interacts with the water droplets when adding functional groups to the polymer. As a result, PS-COOH formed a new type of pore geometry on the surface

with respect to having hydrophilic end groups, and the PS only produces one type of pore geometry. **Figure 6.37** illustrates the differences between the two polymeric films, where the PS (17 kg mol^{-1} , $d_o = 400 \text{ nm}$) exposes the silicon wafer and creates a circular porous structure. In contrast, the PS-COOH (16.5 kg mol^{-1} , $d_o = 400 \text{ nm}$) produces 3-D porous structures.

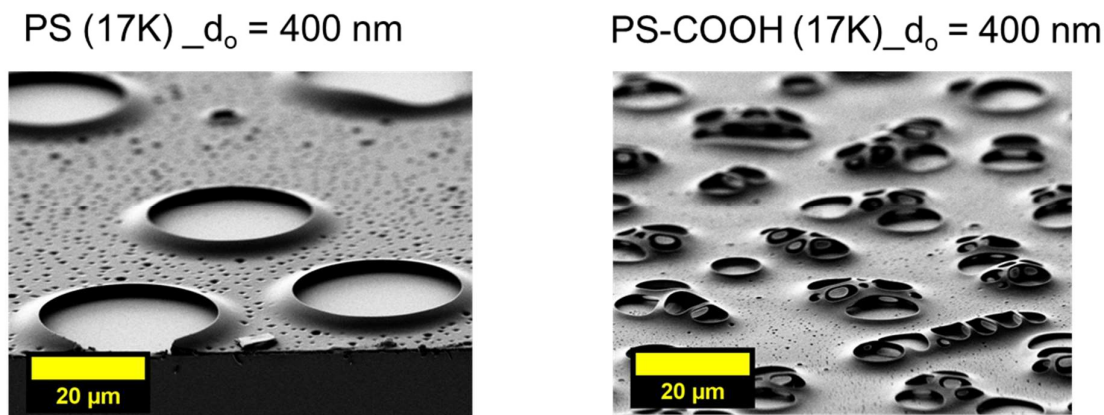


Figure 6.37 SEM Images of PS (17K) and PS-COOH (17K) at 500 seconds of condensation. Initial thickness of both films is 400 nm. Imaging carried out using SE₂ detector at an accelerating voltage of 2 kV.

Concerning templating efficacy, surprisingly, the PS-COOH was not effective in exposing the silicon surface as the films have an affinity to the water, thus obscuring the substrate. A maximum value of 68 % was recorded for the PS-COOH; however, the PS was 85-90 % effective. Although PS is a better polymer for acting as a template, the increase in condensation time still affects both polymer types, and dewetting and coalescence have not been prevented. A possible method to stop dewetting from occurring will be discussed in **Section 6.6**.

6.6 Substrate Modification with a PS Brush

6.6.1 Introduction

Several strategies can be implemented to improve the wetting of polymers on an unstable substrate (i.e surfaces that energetically favour de-wetting). For example, PS is intrinsically unstable on a silicon surface⁸; however, modification to the substrate can improve the stability of the thin film²⁷. The polymer-surface interactions are either by physisorption or by chemisorption. Physisorption is a reversible process where weak Van-der-Waal's forces form unstable bonds. For example, PS-OH has amphiphilic properties resulting in the hydroxyl groups favouring the SiO_x surface by having good adsorption properties with silanols²⁸. Chemisorption is where a strong bond is formed between the substrate and the polymer, which is either covalent or ionic, thus binding the polymer to the substrate²⁹. For example, a condensation reaction can produce an epoxide and thus bind to the substrate changing the wettability³⁰.

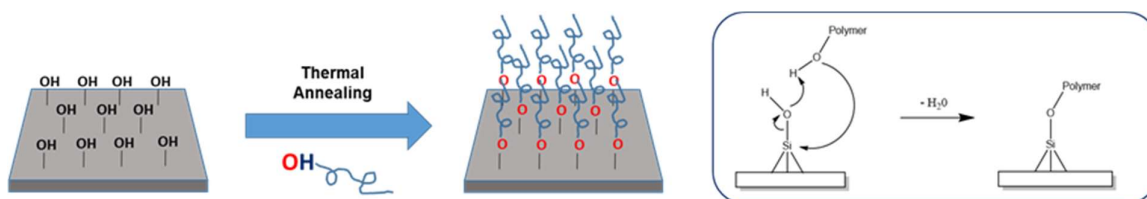


Figure 6.38 Thermal annealing of a brush to a SiO_x substrate via dehydration reaction.

Several researchers have reported that tethering a brush (a polymer chain) to the surface can change the properties and stabilise the films sitting atop a brush of a similar chemical nature^{27,31,32}. When untethered chains are placed atop a well-defined tethered polymer, the brush and polymer can interpenetrate and influence the dynamics of the untethered polymer melt³³. Uger *et al.* discussed that the tethered chains not only slow down the dewetting

dynamics but can also slow down the dewetting of surface layers atop of the brush allowing for a more robust polymer film and partially eliminating the issues involved with dewetting³³. The molecular weight of the brush is critical in stabilising the homopolymer in a viscous state. Sharma *et al.* identified that the critical molecular weight for auto-dewetting of a homopolymer on a brush is approximately $N_H > 0.5N_B$ where N is the polymerisation index for the homopolymer and the brush respectively²⁷.

Here, the stability of swollen polymers at a similar swelling ratio (SR) of solvent is assessed. The silicon surface is functionalised with a PS brush to modify the wettability and interaction between of the PS and solvent and substrate. This was previously discussed in **Chapter 2 (Section 2.5.3)**.

6.6.2 Brush Characterisation

Polymer brush films were synthesised as outlined in **Chapter 4**. Using a 0.6 w/w. % solution of PS-OH produced approximately a polymer brush thickness of ~ 6 nm as reported by Lundy *et al.*³. Adequate polymer bonding was confirmed by measuring the water contact angle of 89 ± 2 and $90 \pm 1.9^\circ$, and RMS values of 0.328 and 0.167 nm were measured for the PS 6K and PS 10K brush films, respectively (**Figure 6.39**).

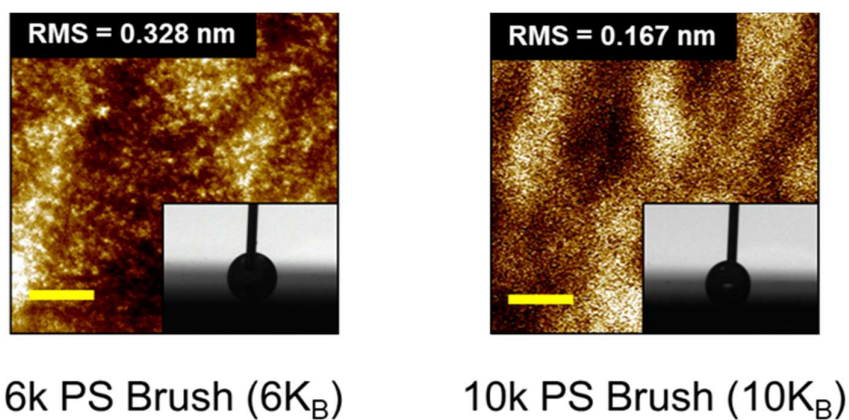


Figure 6.39 AFM Images of PS Brushes Post Annealing with inset water contact angle. Conditions are as follows ; 190 °C, 5 min, 3x toluene washes for both PS 6K_B and PS 10K_B.

There was a very little change in sample thicknesses when the homopolymer was spin-coated (at 2 w/w. %) onto the brush substrate at 1000 rpm, as presented in **Figure 6.40**.

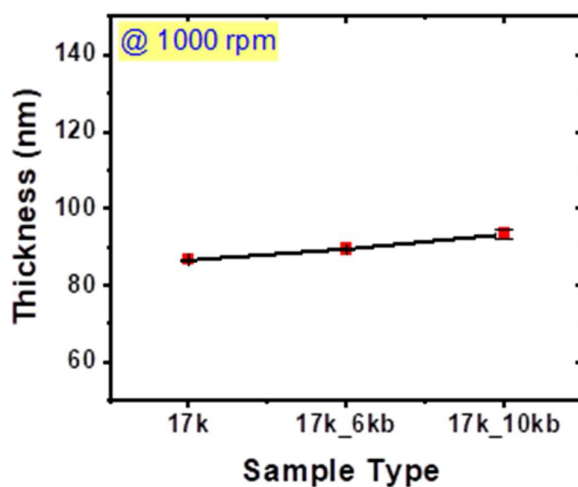


Figure 6.40 Thickness produced after spin coating homopolymer (PS 17K) on to the PS 6K_B and PS 10K_B Brushes

The homopolymer (17K PS) was spin-coated onto the respective brushes at different spin speeds and solutions, as shown in **Table 6.6**.

Table 6.6 Concentration and Annealing Conditions for PS Brushes.

Film thickness on brush (nm)	Concentration of homopolymer (w/w.%)	Spin velocity (RPM)
100	2	1000
200	4	1000
300	5	1000
400	5	500

The SVBF process was carried out where the solvent bubbler (T_{bub}) was maintained at 18 °C and T_{stage} at 6.5 °C. Condensation was carried out for 500 s, then the solvent was vented, and the stage temperature (T_{stage}) was heated to 20 °C to remove excess solvent from the film.

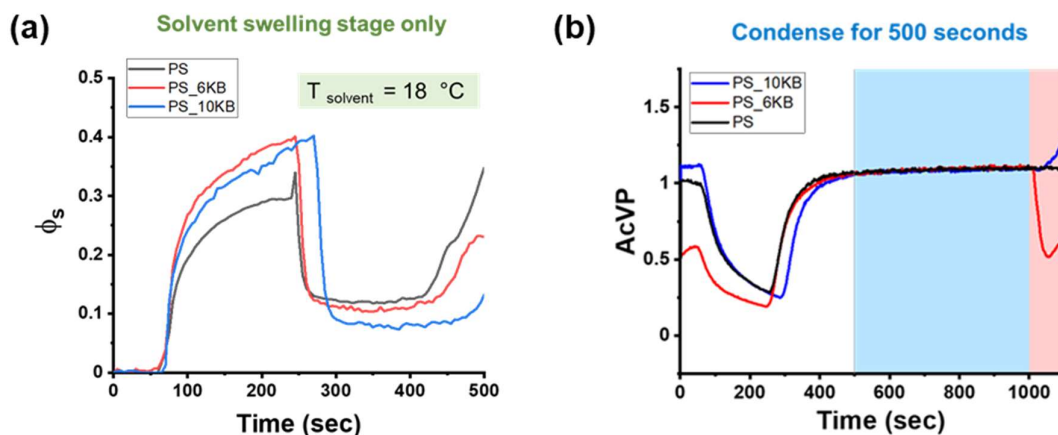


Figure 6.41 (a) Solvent swelling with CHCl_3 from 0- 500 sec where CHCl_3 added at 50 sec and water at 250 sec. Ratio of $\text{H}_2\text{O} : \text{CHCl}_3$ at 2: 1 . (b) Actual water vapour analysis for PS, PS 6KB and PS 10KB. $T_{\text{Stage}} = 6.5^\circ\text{C}$ at dew point.

At 250 s, the solvent fraction differed for each of homopolymer on brushes ($\phi_S = 0.3$, $\phi_S = 0.4$ and $\phi_S = 0.4$ for PS, PS-6K_B and PS-10K_B respectively). Better stability can be seen for the brushes as they can absorb more solvent, as shown in **Figure 6.41**. When water is added to the chamber, all solvent incorporation is reduced to $\phi_S = 0.1$. Upon cooling T_{stage} to 6.5 °C, the homopolymer increases rapidly; however, the brushes maintain the swelling of the film. Post swelling optical images are shown in **Figure 6.42**.

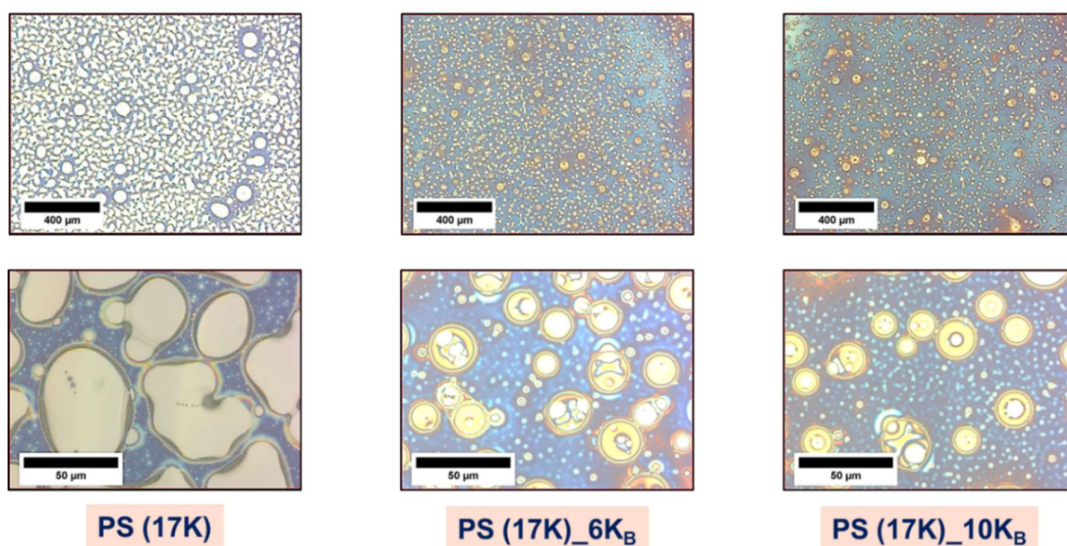


Figure 6.42 Optical images of the PS , PS on a 6k brush and PS on a 10k brush at 250 seconds of condensation.

Preliminary analysis shows that the thin films remain intact when brushes are annealed to the surface of the silicon wafer. Polymer coverage of 44 %, 79 % and 88 % for PS (no brush), PS 6k and PS 10k when analysing the images at low magnification (scale bar = 400 μm) in **Figure 6.42**. FIB milling indicated that the pore geometry (**Figure 6.43**) differed significantly from PS on a silicon surface, as the higher contact angle (150 °) indicated that the water is interacting with a hydrophobic surface³⁴.

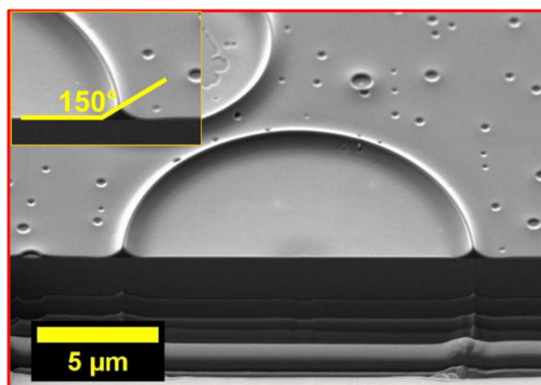


Figure 6.43 Cross section FIB/SEM of the PS thin film (100 nm) on 6k brush.

Measured contact angle of approximately 150 °at a 36° tilt correction. The substrate was milled in a stepwise manner to observe the thickness of the film.

Figure 6.44 illustrates the effects of the water during the swelling condensation process where there is (A) no rim/ dome formation occurs as the homopolymer remains intact and wets the substrate (brush), (B) high slope of sidewalls because of high contact angle of water with PS and, (C) minimal surface wetting due to hydrophobic interaction between water and polymer brush surface³⁵.

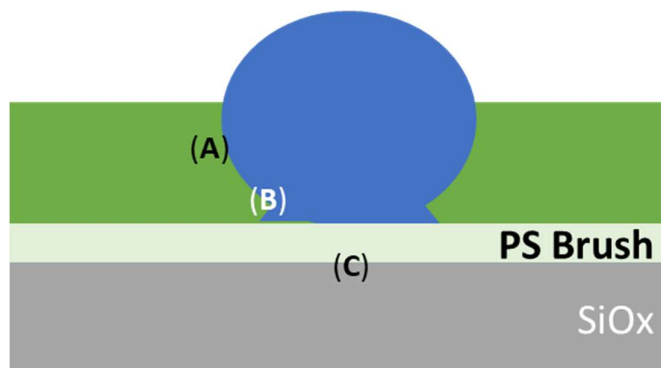


Figure 6.44 Graphic showing the effect of the water droplet on the swollen thin film on the silicon substrate. (A) No rim formation as homopolymer remains intact as a result of the brush. (B) A high slope of sidewalls forms due to the high contact angle of water with PS homopolymer. (C) Minimal surface wetting due to hydrophobic interaction between water and polymer brush surface.

After removing the water droplets, a larger contact angle was seen (**Figure 6.43**), indicating that the water is not spreading onto the substrate as it has poor interaction with the PS brush. Furthermore, since a brush of a similar type is substituted for the solvent, the homopolymer will wet the hydrophobic surface (**Figure 6.45**), thus eliminating the issues of dewetting as seen in **Section 6.1** (Homopolymer PS swelling).

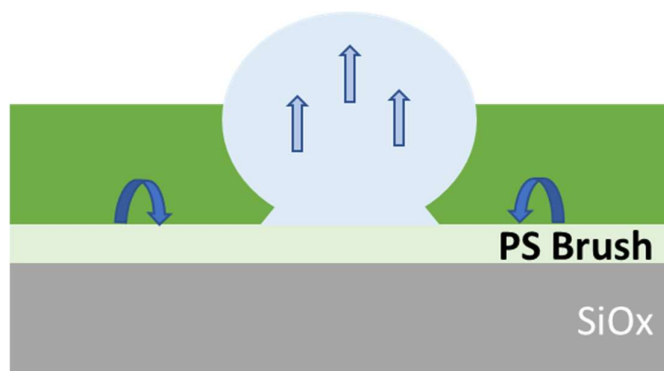


Figure 6.45 Graphic showing the interaction between the homopolymer and the brush once the droplet has been removed.

In summary, the brush improved the stability of the homopolymer during the solvent swelling, and dewetting was significantly reduced for the 100 nm thin films.

6.6.3 Effect of homopolymer thickness on 6k PS brushes

Here, thin films ranging from 100-400 nm were swollen following the previous procedure and the impact of condensation time was assessed. As seen previously, the swelling effects were similar, indicating that the incorporation of solvent via saturation resulted in a similar swelling effect ($\phi_s = 0.3 - 0.4$) for each of the thicknesses studied, as shown in **Figure 6.46**.

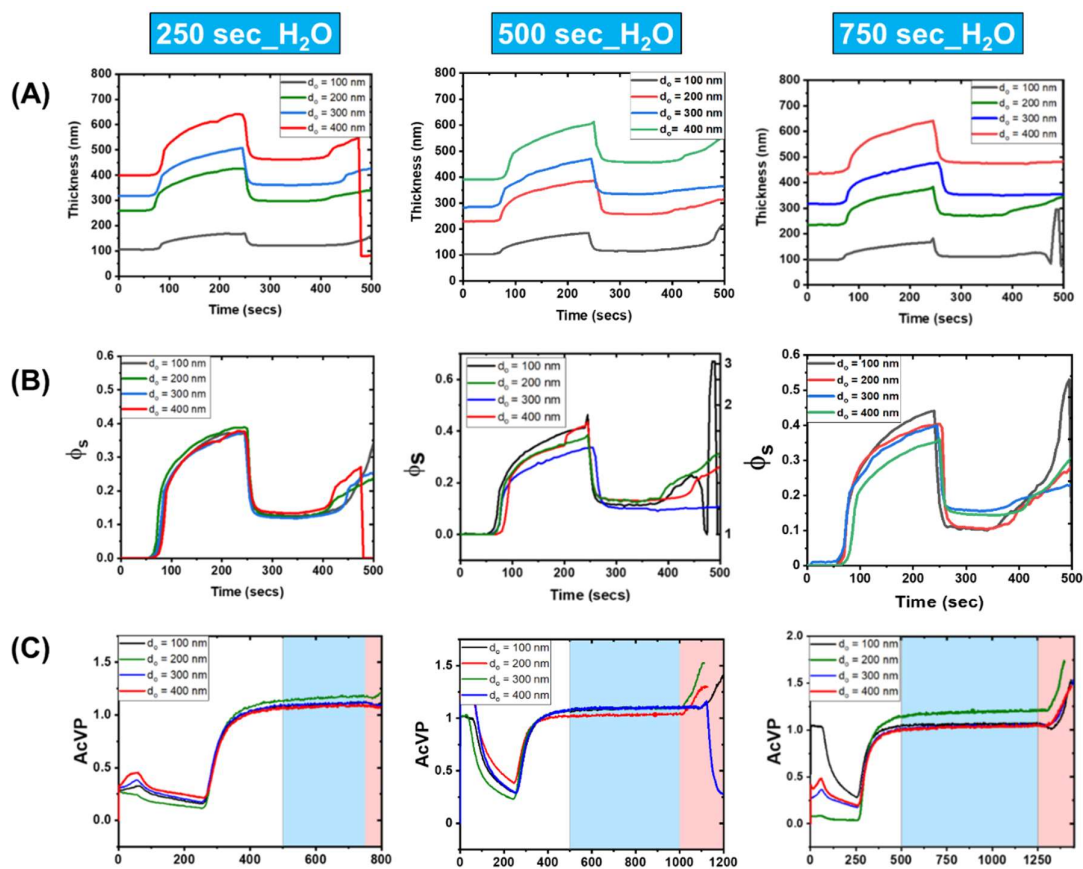


Figure 6.46 (A) Thickness measurements of swollen PS films on 6k PS brush in CHCl_3 vapour from -0-250 seconds (B) Solvent volume fraction measurements in CHCl_3 vapour only from 0-250 seconds (C) Actual vapour pressure measurements for all experiments, condensation times (250, 500 and 750 seconds). Addition of water vapour at 250 seconds for each sample. T_{stage} at 6.5 °C at 500 seconds.

All vapour pressures were at approximately 1 kPa at a stage temperature of 6.5 °C to induce condensation. SEM analysis was carried out post-swelling to analyse the effect of a 6k brush on the stability of the thin films (**Figure 6.47**) and all pore analysis is detailed for total porosity (**Figure 6.48**) and circular porosity (**Figure 6.49**).

PS Thin Films on 6K PS Brush

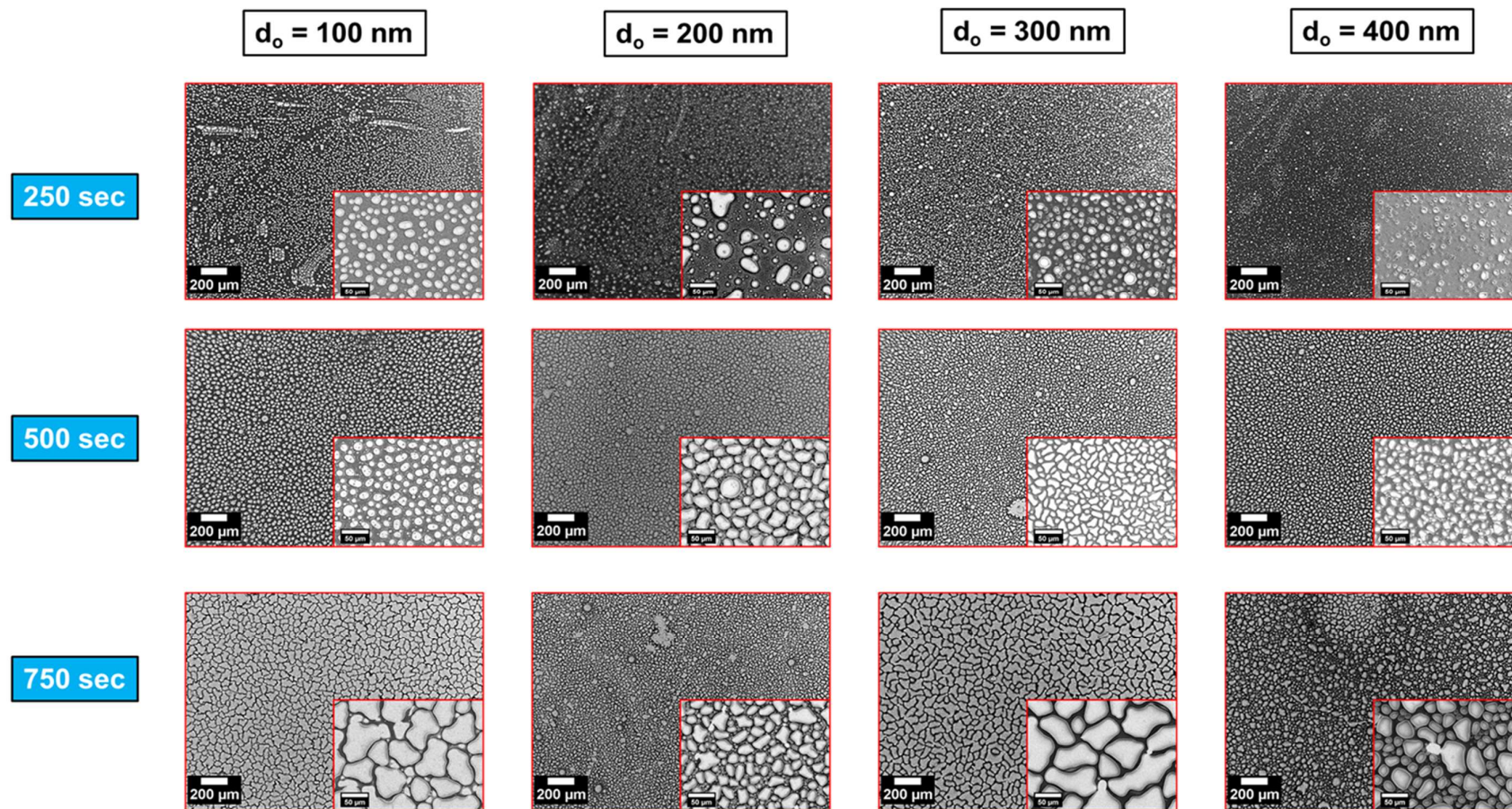


Figure 6.47 Top-down SEM images of PS homopolymer (17K) on 6K PS brush at different thicknesses and water condensation times.

Imaging carried out using SE₂ detector at an accelerating voltage of 2 kV.

Circularity = 0 - 1

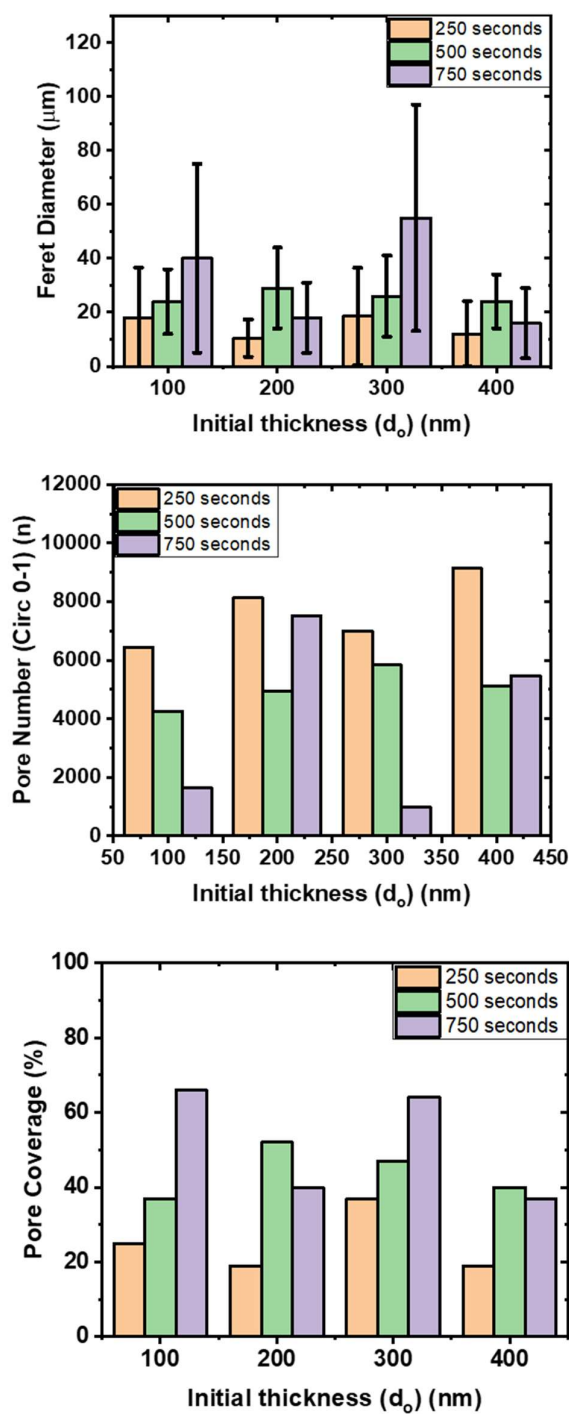


Figure 6.48 (a) Measurements of pore diameters and (b) pore number and coverage for PS (17K) films on 6K PS brush ($d_o = 100 - 400$ nm) at 250, 500 and 750 seconds condensation. Data is filtered with a circularity of 0-1.

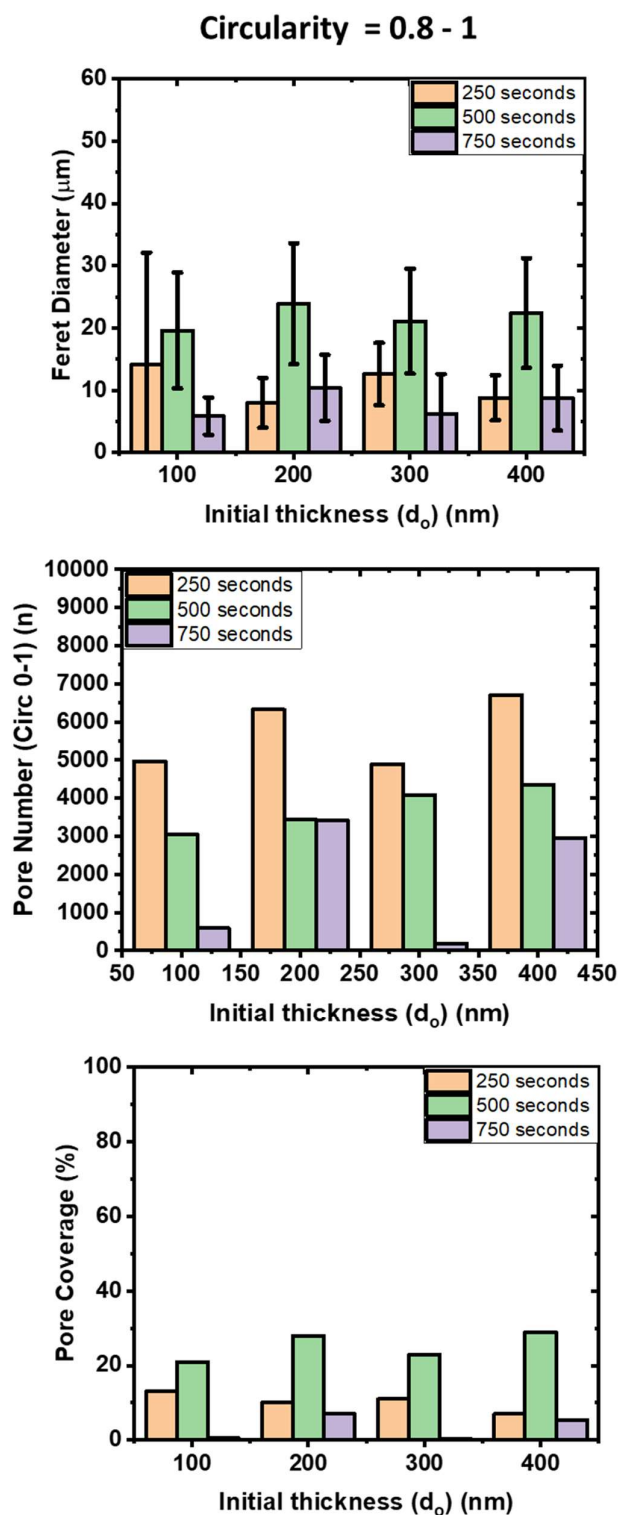


Figure 6.49 (a) Measurements of pore diameters and (b) pore number and coverage for PS (17K) films on 6K PS brush ($d_o = 100 - 400$ nm) at 250, 500 and 750 seconds condensation. Data is filtered with a circularity of 0.8-1.

Templating efficacy (%) is shown in **Table 6.7** for all thicknesses and condensation times.

Table 6.7 Droplet Templating Efficacy for PS on PS 6k brush (100 -400 nm) films at different condensation times. Green cells highlighted show optimal templating.

Initial Thickness (d ₀) (nm)	Templating Efficacy (%) (No. Circular pores / No. All pores *100 %)		
	250 sec	500 sec	750 sec
100	77	72	36
200	78	70	45
300	70	70	20
400	77	72	36

At a condensation time of 250 s, dewetting was at its lowest and pore diameters ranging from **0 – 37 µm** were observed with a range of **0-32 µm** for circular pores. The most effective templated film at this condensation time was 200 nm, with a total pore coverage of 19 % and circular pore coverage of 10 %. Efficacy values of 77, 78, 70 and 77 % were calculated for the 100, 200, 300 and 400 nm at this condensation time, respectively. These were the highest average efficacy values recorded (75.5 %) in a set. The brush has reduced dewetting effect across all 4 film thicknesses, especially for the 100 nm films that increased from 44 to 72 %.

At a condensation time of 500 s, there is an increase in pore diameter standard deviation; however, it remains constant for all films. Pore diameters ranging from **14-44 µm** were observed with a range of **13-34 µm** for circular pores. All pore sizes were in a tighter distribution at this condensation time in comparison to the other two. The most effective film

templated at 500 s was the 100 and 400 nm with a total pore coverage of 37 and 47 % and circular pore coverage of 21 and 29 %, respectively. Efficacy values of 72, 70, 70 and 72 % were calculated for the 100, 200, 300 and 400 nm, respectively. Dewetting has been significantly reduced.

At a condensation time of 750 s, the pore sizes increase for all film thicknesses, and no polymer agglomerations can be seen in comparison to PS on silicon (**Section 6.1**). Pore diameters ranging from **3-75 μm** were observed, with a range of **2- 15 μm** for circular pores. The most effective film templated at a condensation time of 750 s was 200 nm with a total pore coverage of 40 and a circular pore coverage of 7 %. Efficacy values of 36, 45, 20 and 36 % were calculated for the 100, 200, 300 and 400 nm, respectively. Although the films still have low efficacy values, dewetting and polymer agglomeration have been reduced, whereas coalescent events²⁵ of water droplets are still prevalent. Droplet templating efficacy range from 20-45 % by adding a brush to the surface where, in contrast, PS had an efficacy of 0-50 % for the 100 and 400 nm thin films only. This indicates that the effective templating has improved using the PS brush as it is in a tighter range.

It is postulated that the pore openings may enlarge due to two different mechanisms. For the “hydrophilic case “, coalescent events occur as the distance between the neighbouring droplets is near one another at the substrate surface. As discussed in **Section 1.1**, the spreading effect of water indicates how the delamination of PS occurs for a homopolymer on a silicon surface, as it is unstable⁸. The hydrophobic case of dewetting may occur because of the decreasing distances between droplet to droplet, leading to coalescence³⁶ at the polymer film interface when a brush is on the substrate surface, resulting in high contact angles. Voids can form once the merged droplets are removed, which results in a more

extensive porous network throughout the polymer thin film. **Figure 6.50** illustrates both cases.

Hydrophilic Case – PS on SiOx



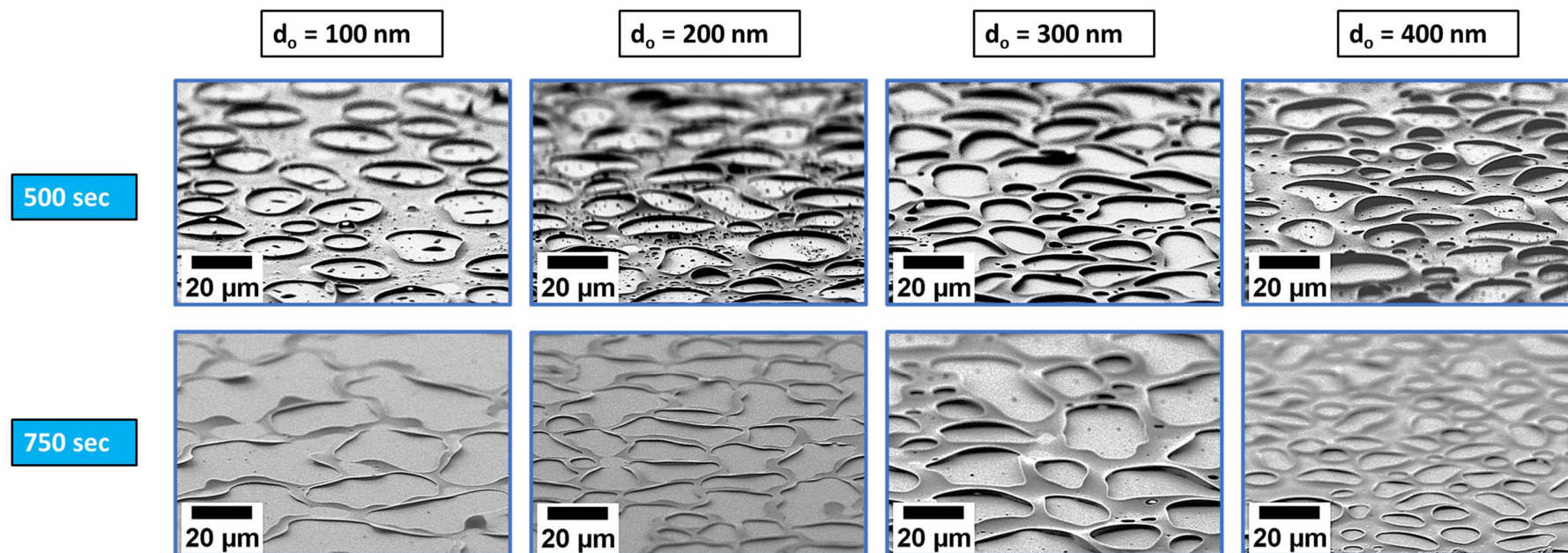
Hydrophobic Case - PS on brush



Figure 6.50 Effect of water droplet interaction during a coalescent event¹⁶

Cross-section analysis was also carried out to interpret the thin film's post-swelling as presented **Figure 6.51**. The SEM images show porosity throughout each sample and how the pore sizes significantly increase from 500 – 750 seconds of condensation.

In summary, the issue with dewetting has been significantly reduced. Condensation times can impact pore size; however, minor increases in pore sizes are seen when the film is thicker. Standard deviations in diameter remain at the highest for the condensation times at 750 seconds.



6.51 SEM cross section of PS thin films on a 6K PS brush ($d_o = 100, 200, 300$ and 400 nm) at 500 seconds and 750 seconds of condensation. All films remain intact, and no agglomerations can be seen for any of the studied thin films. Imaging carried out using SE₂ detector at an accelerating voltage of 2 kV.

6.7 Conclusion

In conclusion, the SVBF method has shown great promise in controlling the pore size of thin polymer films through either solvent-induced dewetting or water droplet templating. The key points of this chapter are as follows.

- Linear polystyrene is a challenging polymer to control pore size and retain order for each type of thickness studied. Although the polymer's hydrophobic properties pose an issue in retaining homogenous porosity, exposing the silicon substrate is vital and can be achieved following the dilution method. Solvent and water were incorporated into the chamber at a specific ratio of 2:1 (water: solvent) to swell the film and droplet template when the temperature was reduced to 6.5 °C. The most effective film templated was 200 nm at a condensation time of 500 seconds, with an efficacy value of 89 %.
- Di-carboxylated polystyrene (PS-COOH) improved the interaction of the polymer with the droplets; however, the substrate was not exposed, and dome-like shapes were produced post-SVBF process. The morphology of the patterned films were significantly different to PS, especially at higher thicknesses. PS-COOH had the lowest droplet templating efficacy, with respect to the polymer encapsulating the droplet and masking the silicon surface. The most effective film templated was 200 nm at a condensation time of 250 seconds, with an efficacy value of 68 %.
- Functionalising the silicon surface with a polymer brush (PS) has been shown to reduce the effects of dewetting, thus improving templating efficacy. Although the films had reduced circularity at longer condensation times, the film remains intact in

all cases. The most effective film that was templated was 200 nm at a condensation time of 250 seconds, with an efficacy value of 78 %.

- The use of ImageJ software has been an effective method in characterising the porous, thin films with respect to diameter, pore area distributions, filtering pore type and using statistics to develop a new method to assess the porous, thin films *via* the SVBF method.
- Finally, this chapter has delved into a novel process of producing porous, thin films, using the mechanics of thin film swelling and condensation. This method has never been studied before and is in its preliminary stages. A wide range of polymers, solvents and other factors can be added to the process to improve the droplet stability while exposing the silicon substrate.

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Chapter 7

Conclusion and Future Work

7.1 Final Conclusions

The work described quantitatively demonstrated that it is possible to use the SVBF approach to scale the porosity of thin films. Different experimental techniques can lead to variations in porosity size, density, and morphology. Statistical methods have been adapted using software packages (ImageJ) to interpret the films post-swelling and acquire evidence on the efficacy of the templating.

Chapter 2 focused on the theoretical observations of droplet templating thin films with water droplets. The findings, through theory, generated interest in using a hybrid-BF approach as a tool for bottom-up lithography¹, by exposing the substrate and creating porous thin films *via* a green approach, using small volumes of organic solvents and water droplets. Using theoretical models to interpret the effects of 3-phase systems² provided information on whether droplet templating thin polystyrene films is possible at small length scales, on the orders of nanometres. This approach is plausible for all different types of polymeric-solvent interactions.

Chapter 4 discussed the construction of a novel rig that can be used as an additional method to up-scale current breath figures³. The rig was modified using a current solvent vapour annealing setup that had the functionality to produce nanofeatures *via* block-copolymer self-assembly⁴. The use of solvent vapour swelling effectively reduces the quantities of solvent used as the solvent bubbler only needed to be changed after 4 or 5 hours of use. The rig has

the functionality to decrease cost and time in producing templates and is a viable tool for creating micropatterns and nanopatterns rapidly.

Chapter 5 described the optimisation of vapour pressure, temperature, and templating techniques to create a suitable environment to produce microporous media. Solvent-driven swelling alone can cause the polymer films to dewet⁵ rapidly if saturation values are more than 1 ($S > 1$). Water droplet templating will only occur if the stage temperature is at the critical dew point of 6.5 °C, where the actual vapour pressure of water is 1 kPa. When mixing solvents, it is critical that the polymer is significantly swollen to become mobile, and the water is at a high vapour pressure. If the stage temperature is too low, solvent-driven dewetting and coalescence of droplets can occur. Flow rate ratios of 2:1 (water: solvent) were chosen to create porous films, where the water usually reaches 0.3 – 1 kPa over 250 seconds. The *dilution method* was chosen as the ideal templating method as (1) the thin film swelling can be assessed before water incorporation, and (2) the dew point can be easily identified and controlled.

Chapter 6 presented methods on how to create homogenous porosity by changing variables such as (1) the thin film thickness, (2) condensation times, (3) polymer type and (4) substrate. Polystyrene (17 kg mol^{-1}) was shown to dewet rapidly at high condensation times (750 s) and its porosity was not ordered. The pore size was directly proportional, and an increasing trend was observed by increasing the condensation time. Since the polymer is hydrophobic, it will have a repulsive effect on the water and form a rim at higher thicknesses. Functionalising the polystyrene chain with carboxyl groups lead to better interaction with the water droplets, as proposed by Zhu *et al.*⁶. Efficacy in templating was significantly reduced when functionalising the polymer, as the film did not expose the substrate at higher thicknesses. Adding a polymer brush to the substrate reduced the solvent-driven dewetting

of PS. Homogenous porosity significantly increased for all films using the polymer brush and exposure to the silicon substrate was achieved.

In general, the thin films produced during the work carried out for this thesis set a baseline for future work and represent a starting point for carrying out the SVBF approach on different types of polymer thin films. PS was the polymer chosen as the ideal candidate for assessing the applicability of the process; however, more complex structures like block-copolymers, star polymers and branched polymers may lead to better ordering and homogenous porosity as outlined by Zhang *et al.*⁷. However, considerable work could still be done to improve the PS thin films and make them more viable as an industry standard. For example, the rig design could be further optimised with better temperature controls and automation to improve its templating ability. In addition, controlling the temperature of the water bubbler and automating the swelling process using a feedback loop between the stage temperature and the reflectometer will allow for better control and reproducibility.

7.2 Future Work

7.2.1 Pattern Transfer

From the data gathered and the methodologies developed for the work presented, the following steps would be to use the porous, thin films as lithography templates. The micropatterned media can be produced by either adding a new material (*material deposition*) or removing selective regions of the substrate (*substrate etch*).

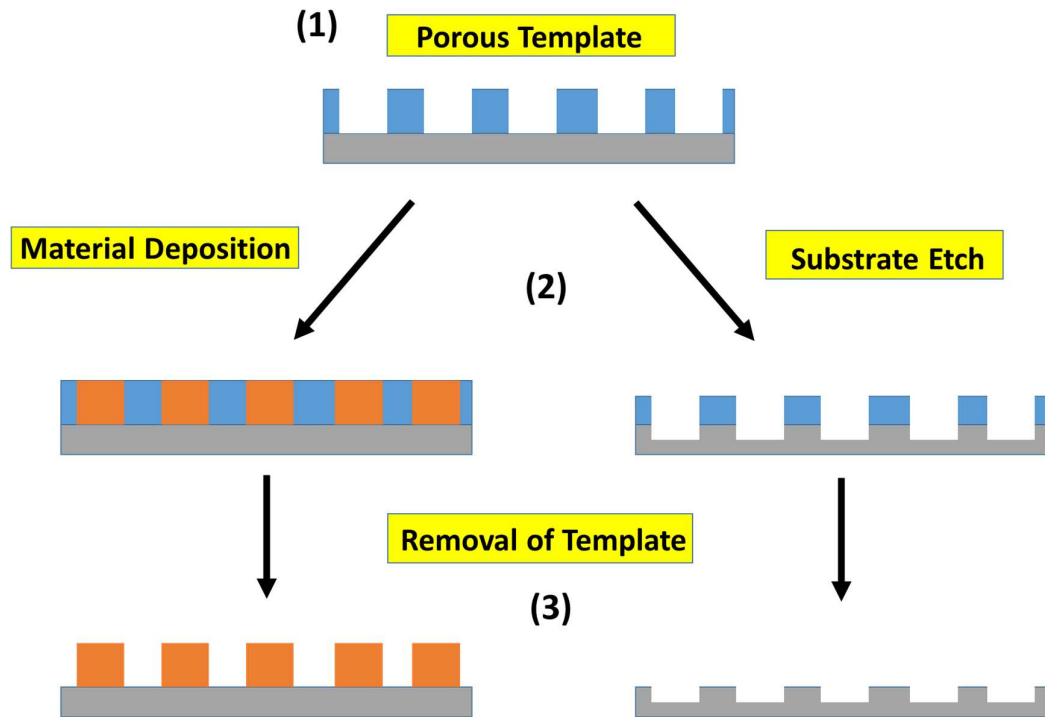


Figure 7.1 Fabrication steps to pattern transfer the substrate.

Techniques adapted to deposit material onto the substrate could be physical vapour deposition (PVD)⁸, chemical vapour deposition (CVD) and electrodeposition (ED). PVD is a coating process that deposits films from a condensed matter source *via* the gas phase to the surface to be coated. The method is known as “sputtering” and is widely used in battery

research and manufacturing⁸. CVD relies on chemical interaction with a volatile precursor that reacts and decomposes onto the substrate surface⁹. This process is often used in semiconductors to produce coherent thin films, particularly for graphene^{10–12}. ED requires that the substrate must be conductive to be templatable¹³. Changing the substrate to a conductive material (such as copper) makes electrodeposition of material into porous regions possible.

Substrate etching is a method where the substrate material can be removed *via* a dry or wet etch. Deep reactive ion etching (DRIE) is a plasma-based etching process that produces deep holes and trenches in silicon wafers¹⁴. Etched silicon is of significant interest in producing micro-electro-mechanical systems (MEMS) and silicon capacitors¹⁵. Using the SVBF templates as negative resists can create microporous silicon wafers by high-resolution electron beam lithography¹⁶. Wet etching is carried out using highly reactive acids such as HF¹⁷; however, the polymer films may be removed as it is prone to remove the polystyrene thin films, as described by Wang *et al*¹⁸.

Finally, hierarchical patterns are possible by combining the production of breath figures with current block-copolymer self-assembly (BCPSA) methods¹⁹. The creation of pores can create a hard mask allowing for hierarchical patterns. For example, nanopatterns can be produced in micro-regions on the substrate surface. PS-*b*-P4VP can be used as a polymer template to produce metal nanodots following solvent vapour annealing methods^{5,20–22} and metal infiltration^{4,23}. This can be combined with a porous PS hard mask to produce ceria dots in micro-regions, as shown in **Figure 7.2**.

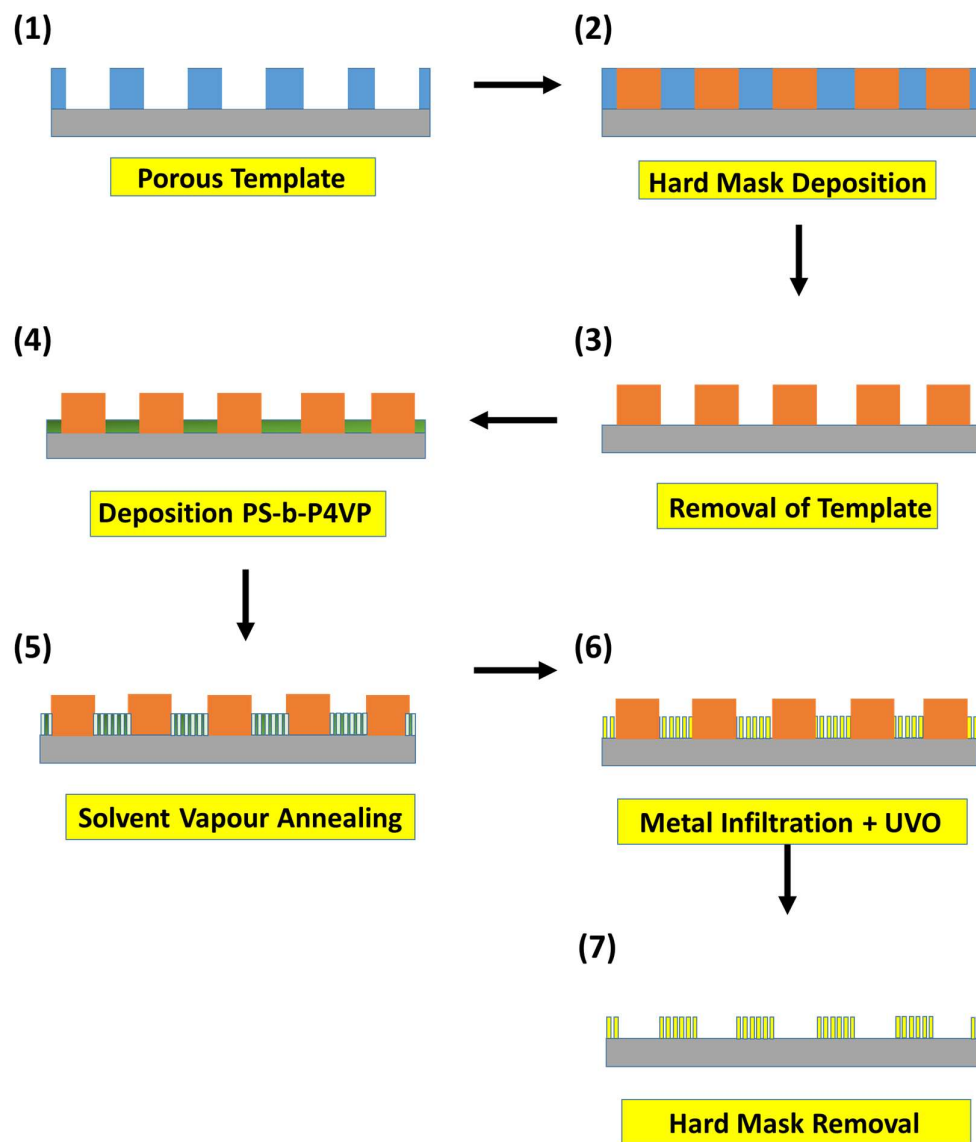


Figure 7.2 Fabrication steps to produce block nanopatterns in micro-regions.

The fabrication steps are as follows.

- 1.) Create a porous template *via* the SVBF method
- 2.) Addition of a hard mask. The hard mask of choice is iron oxide (Fe_2O_3).
- 3.) Removal of porous template produces Fe micropillars.
- 4.) Deposition of PS-b-P4VP by spin coating
- 5.) Solvent vapour annealing of PS-b-P4VP using CHCl_3 to produce dots.

6.) Metal infiltration will be carried out *via* spin-coating $\text{Ce (III).NO}_3.6\text{H}_2\text{O}$ ethanolic solution. The metal is selective for P4VP, and UV-ozone can oxidise the metal to remove PS and oxidise the metal salt precursor to CeO_2 as shown in **Figure 7.3**.

7.) The hard mask can be removed using concentrated citric acid. This creates CeO_2 nanodots in selective micro-regions.

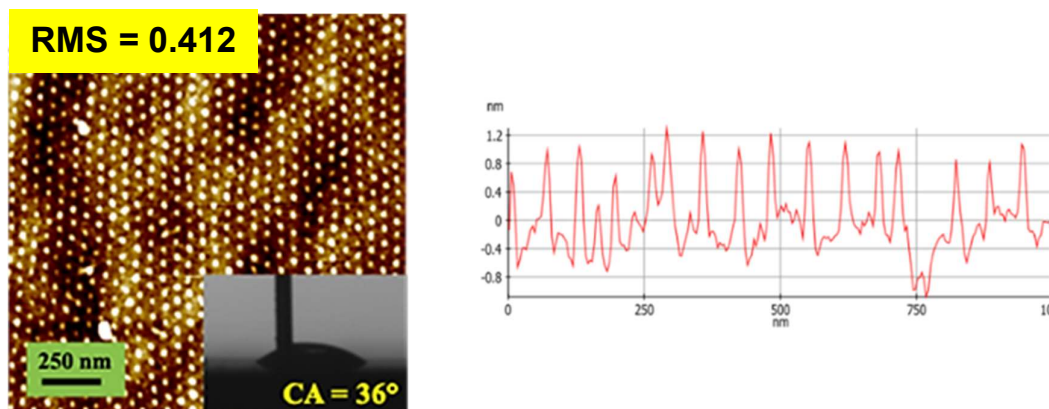


Figure 7.3 1 x 1 μm AFM image with water contact angle inset and a height profile of CeO_2 dots. RMS value of 0.412 nm and the surface is hydrophilic (CA = 36 °).

Lanthanide coatings such as ceria can be used in nanoelectronic applications for solar applications^{24,25}, photocatalysis^{26,27} and can act as a superhydrophobic coating²⁸. Furthermore, the addition of specified regions of superhydrophobicity and hydrophilicity can be used to improve the cooling of electronics²⁹, create heat sinks³⁰ and evaporative heat transfers system *via* droplet spreading and removal³¹.

7.2.2 Toluene as a Swelling Solvent

Toluene was also shown to have good interaction with polystyrene (PS) and acts similarly to chloroform with respect to polymer-solvent interactions having a χ value of 0.73, identifying it as a suitable solvent for swelling PS. Therefore, a preliminary swelling study was carried out using toluene, detailed in **Figure 7.4**.

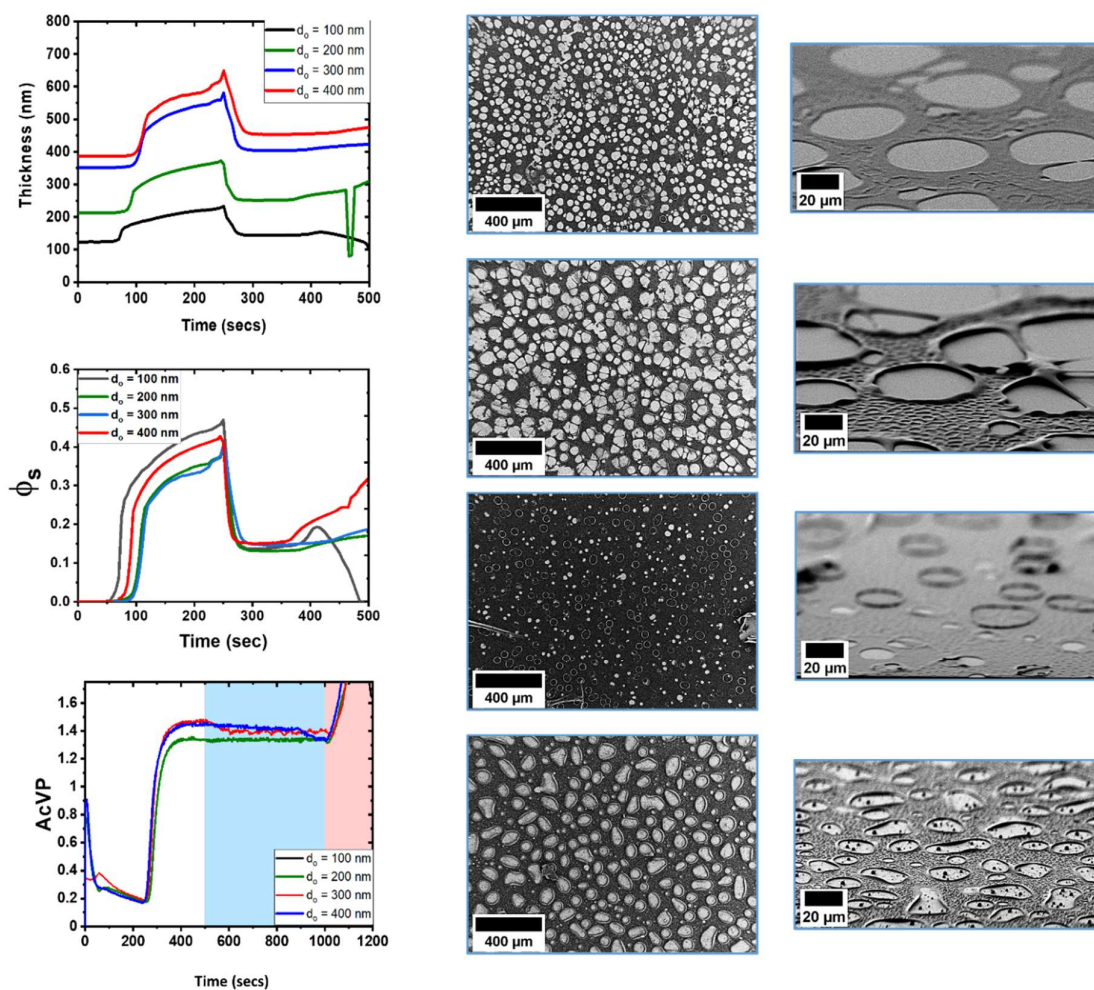


Figure 7.4 SVBF method using toluene as a swelling solvent. Films were swollen in toluene vapour for 0-250 seconds and water was added at 50 seconds. T_{stage} kept at 6.5 $^{\circ}\text{C}$ and actual vapour pressure measured at 1.2-1.4 kPa. Condensation time = 500 seconds.

The temperature of the stage (T_{stage}) was kept 1 °C higher during the solvent swelling stage. This is because toluene has a much lower evaporation rate than chloroform, resulting in the bubbler's temperature (T_{bub}) taking time to reach the required temperature of 20 °C. Similar swelling effects can be seen for the thicknesses (100 – 400 nm) and a ϕ_s value of 0.3-0.4 was acquired.

The SEM images show porosity across all thin films, except for the 300 nm where ring-type structures have formed. This could be due to the 300 nm having the lowest ϕ_s value and should be repeated. Toluene is a challenge to use as a solvent with respect to having a lower vapour pressure. Better thermal controls may be needed when working with less volatile solvents. An additional future study would be to assess different homopolymer types such as PMMA³², PEO³³ and PVP³⁴ which have demonstrated good templating ability in the drop cast approach.

7.2.3 SVBF Method using Thick Films

Even though this research project aimed to expose the silicon surface, the rig could also be used as a method to create breath figures using thicker films. Breath figure pore morphologies are produced when drop-casting polymeric solutions on to substrates, and the thickness for most BF arrays have been reported in micron⁷. Using the SVBF method, pore formation could also be possible by swelling the thick film in suitable solvent and condensing droplets into the swollen matrix. A quick study was carried out to identify if this would be possible to template thick films following the SVBF approach, as shown in Figure 7.5.

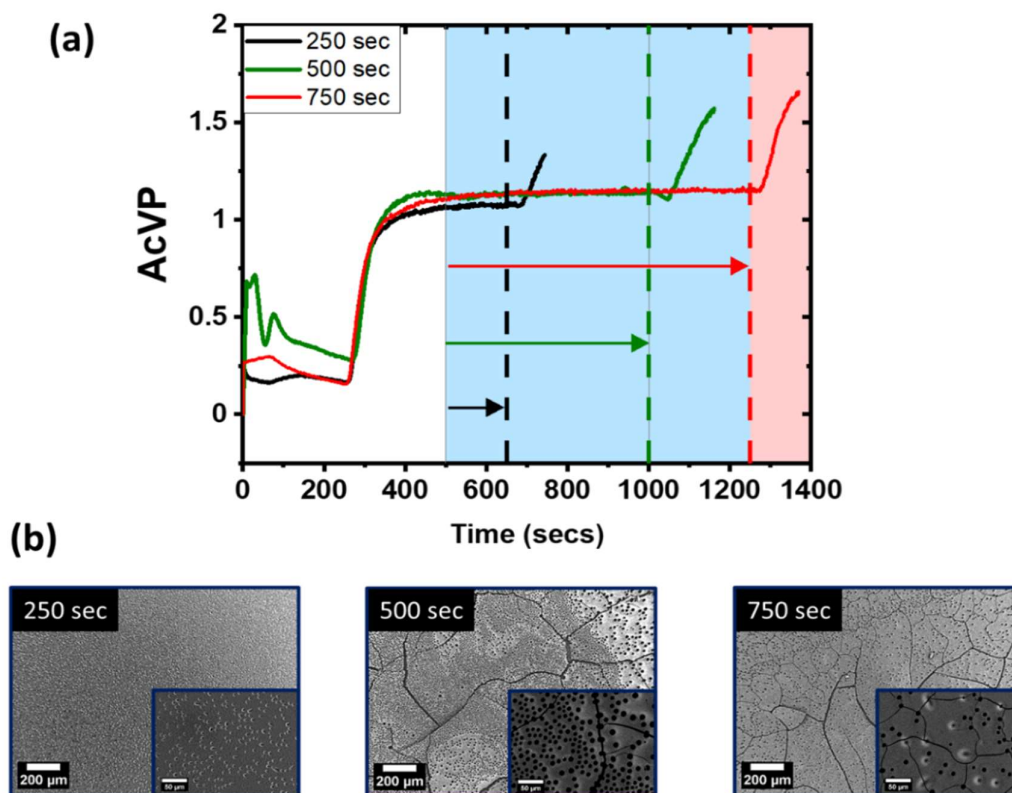


Figure 7.5 (a) Actual vapour pressure of water measurements over time. CHCl_3 entered the chamber at 0-250 seconds followed by water. Condensation times of 250 s, 500 s and 750 s were assessed. (b) Top-down SEM images of PS (17K) show porosity within the thin film and cracking is also observed.

Here, the same approach was carried out where chloroform (CHCl_3) was incorporated into the chamber, followed by water and the temperature of the stage was reduced. The thick films were produced by spin coating a 5 wt. % PS toluene solution at 200 rpm. Unfortunately, since the film was too rough, swelling measurements could not be acquired by the reflectometer (15 nm – 70 μm) as the reflectance of the light was affected³⁵. Instead, actual vapour measurements of 1 kPa were measured and the condensation times were varied. Porosity can be seen in all thin films indicating that the solvent can make the polymer film elastic and the droplets can deform it. Further characterisation by SEM cross-section indicated that the droplets had fully penetrated the films at 500 and 750 seconds.

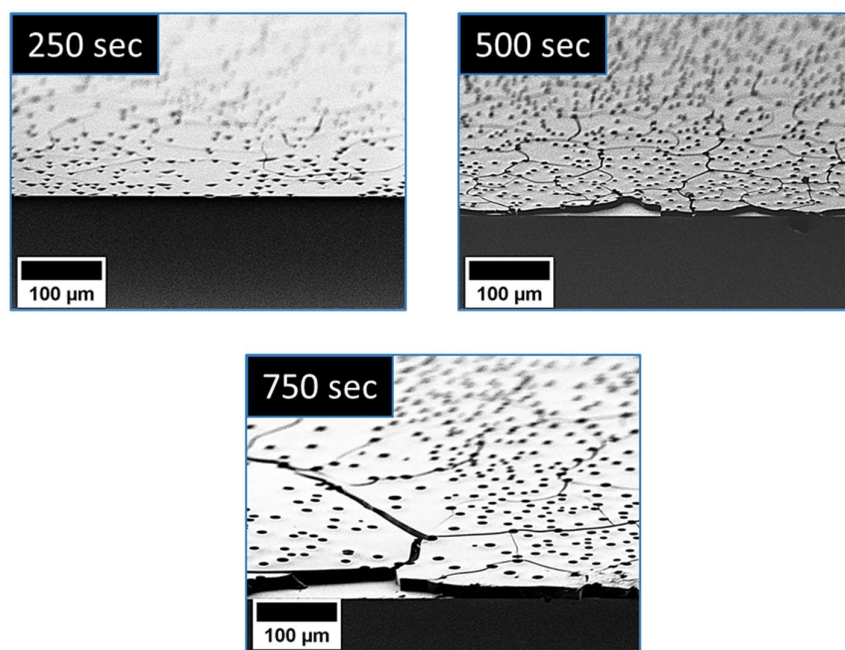


Figure 7.6 Cross section SEM images of PS (thick films) at 250, 500 and 750 seconds.

To conclude, the SVBF approach is a versatile process that can be adapted to numerous polymeric-solvent systems. Even though the SVBF approach is in its infancy phase, preliminary results have shown to be promising, and this thesis provides an overview of how the process can be applied to the industry.

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Appendix

A.1 Image J analysis

SEM and optical images were imported to ImageJ¹² and processed to determine pore size and polymer coverage of the thin film samples following Murphy *et al.*¹³ method. If optical images were used, the estimated pixel measurements (**Table 3.4**) were applied to Step 2. A scale bar was added to the SEM images by measuring the scale per pixel using the following commands.

1. Click the *Draw Straight Line* icon in the ImageJ tray: draw a straight line over the existing scale bar in the imported image.
2. *Analyze > Set Scale*: set the known distance to the scale to *Microns*, ensure *Global* is ticked, and click *OK*.

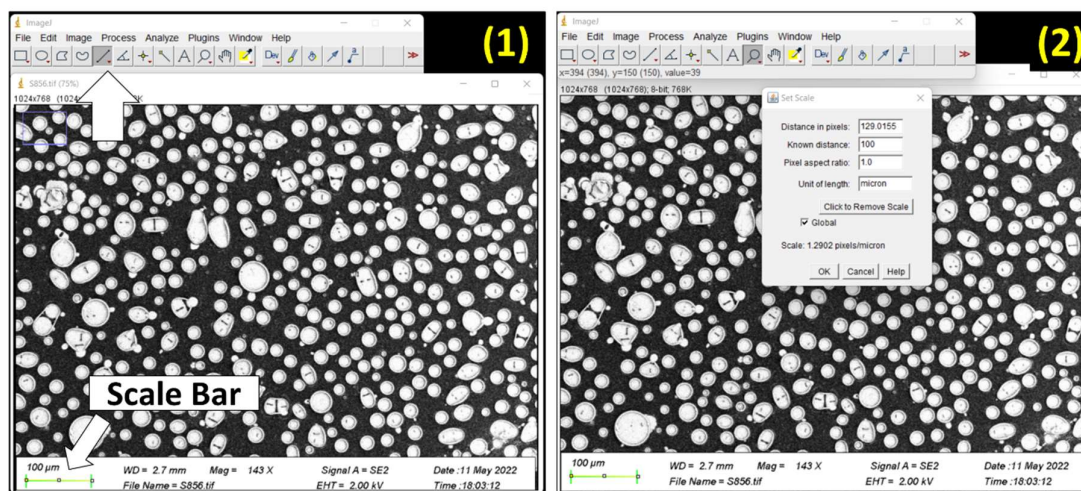


Figure A.1 Stepwise commands implemented in setting a global scale for image analysis using ImageJ. Scale set to 1.29 pixels/um.

Following the global assignment of the scale, plain images of the thin film images are imported to ImageJ and taken through the following set of commands to determine the polymer coverage.

1. *Process>Sharpen.*
2. *Image>Adjust>Threshold:* the threshold is altered in the dialogue box to fill all the pores in red. Once all pores are adequately filled, *Apply* is clicked.
3. *Image>Type>32 bit.*
4. *Process>Binary>Fill Holes and De-speckle*
5. *Analyze>Analyze Particles:* set *Size (Microns²)* to 5-Infinity to omit any minor pixel errors, set *Circularity* to 0-1, set *Show* to Outlines, tick *Display results*, and click *OK*.
6. The data was then exported to Microsoft Excel.
7. The total area is determined from the X and Y coordinates calculated by ImageJ and displayed in the processed image.
8. The pore area is estimated by subtracting the pore coverage from the overall area.
The pore coverage (%) is estimated by dividing the total area by the pore area.

The plain images are imported to ImageJ for pore measurements and taken through the following steps to determine feret diameter and pore area.

1. *Process>Sharpen.*
2. *Image>Adjust>Threshold:* the threshold is altered in the dialogue box so that all pores are filled in red, once all pores are adequately filled *Apply* is clicked.
3. *Image>Type>32 bit.*
4. *Process>Binary>Fill Holes and De-speckle*

5. *Analyze>Analyze Particles*: set *Size (Microns²)* to 5-Infinity, set *Circularity* to 0-1, set *Show* to Nothing, tick *Display results*, and click *OK*.
6. The data are then exported to Microsoft Excel.
7. The data are treated and grouped in Origin and histograms are produced. Bin size is set to 100 and plotted from 0-500 μm^2 .

The steps above are detailed in **Figure A.2** to illustrate how pores are measured using the ImageJ software.

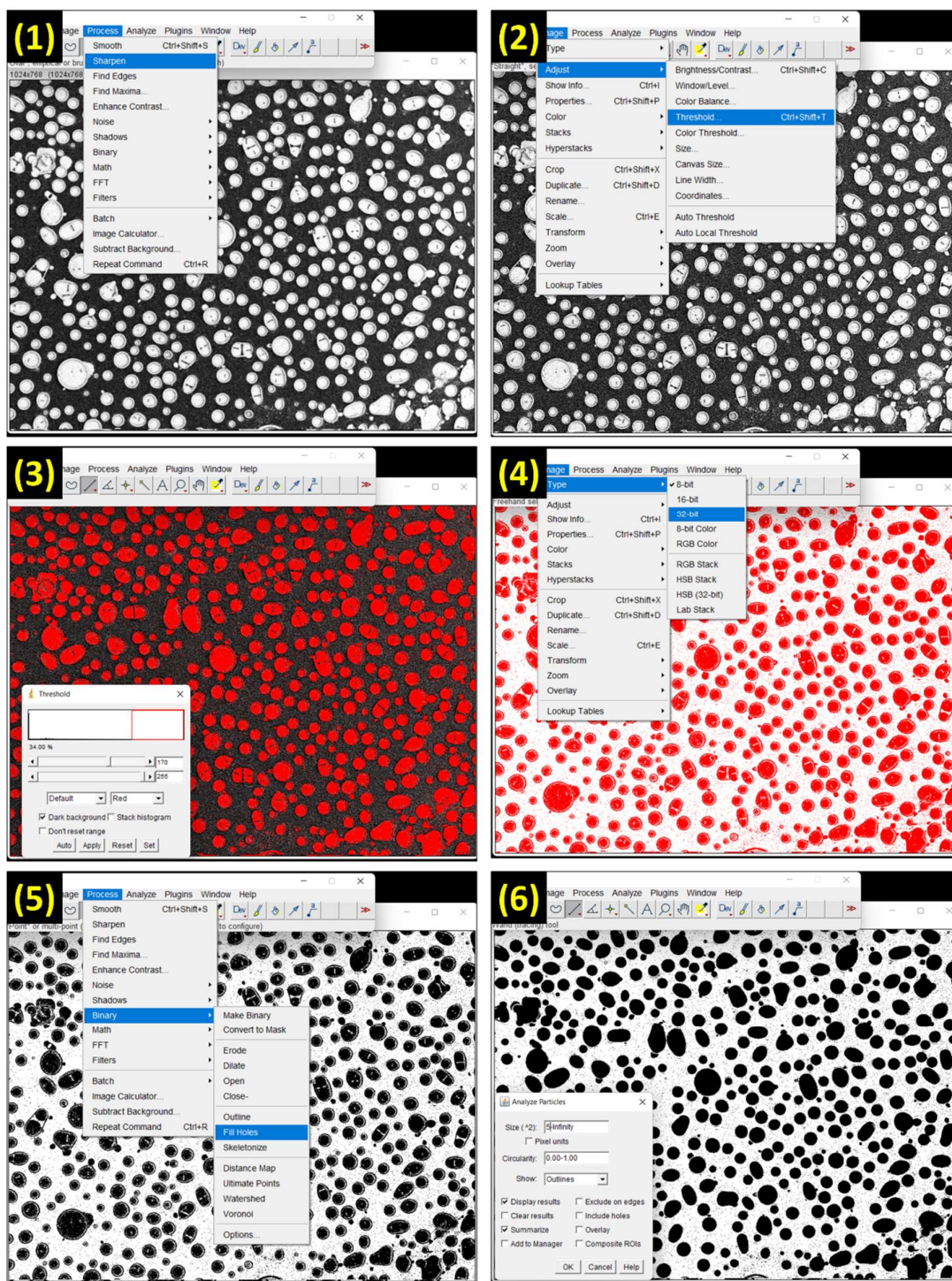


Figure A.2 Stepwise commands implemented in measuring pore diameter and coverage using ImageJ. Scale set to 1.29 pixels/um.

Figure A.3 shows the pore pattern produced after the steps discussed previously.

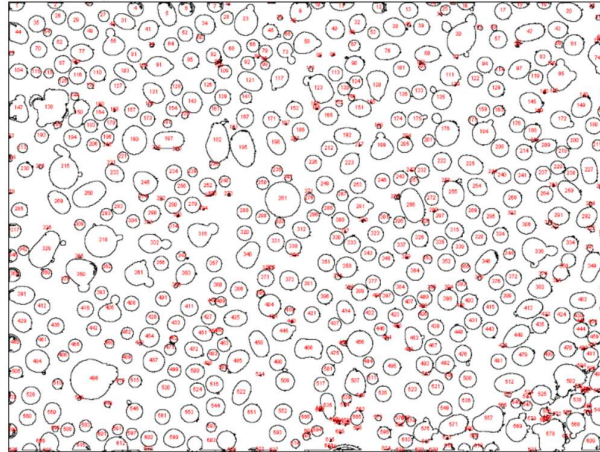


Figure A.3 Outline of pores after following the procedure detailed in Figure 3.13

A.2 CAD Design for the copper plate setup

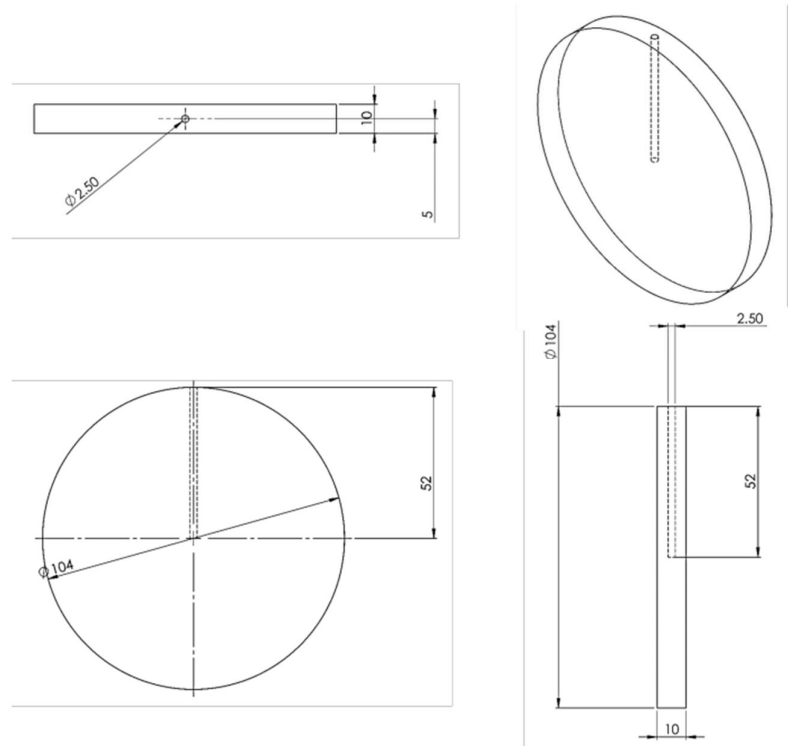


Figure A.4 Orthographic and isometric CAD drawings of a copper plate to be used as the annealing stage. Taken directly from reference.²

A.3 Addition of Multitube Rotameter to SVBF Setup

The mixer located upstream was added to the setup to calculate the flow rate of the water in the humidity line. Relative humidity (RH%) calibrations were carried out at different C_v values to interpret the flow rates measured by the mixer. This C_v controls the concentration of N_2 flow that enters the bubbler setups. Changing the number of turns on the flow metre and leaving the mixer valve fully provides a method for estimating the flow rate, as shown in **Figure A.5**.

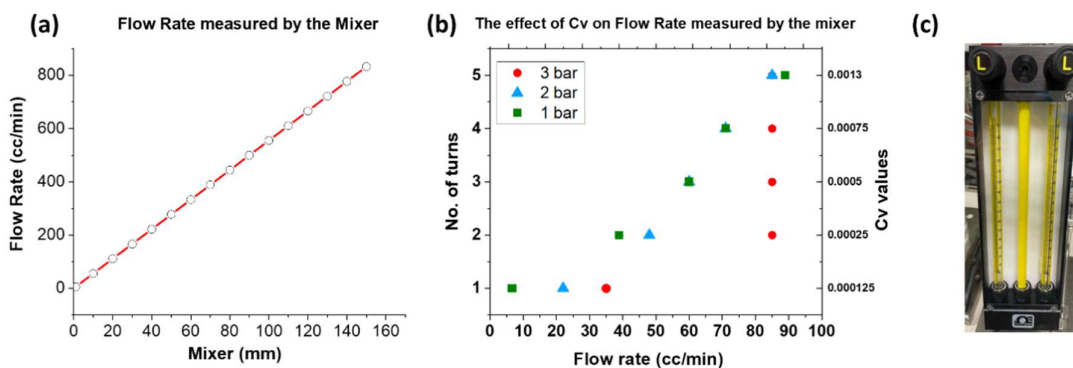


Figure A.5 (a) Flow rates measured from the mixer, (b) The effect of changing C_v and pressure affects the flow rate of the water vapour, (c) Image of the mixer (Omega, multitube rotameter) located downstream from the bubbler setup.

The mixer was shown to be highly ineffective in improving the flow rates of the solvent and seemed to restrict the changes in RH% values. This was removed from the setup as it did not benefit the SVBF method. However, it was a valuable method for identifying the flow rates measured at different pressures and C_v values.

A.4 Steps for Calibrating the Reflectometer

Please see below the steps taken to calibrate the F3 series reflectometer. This process was carried out prior to each experiment.

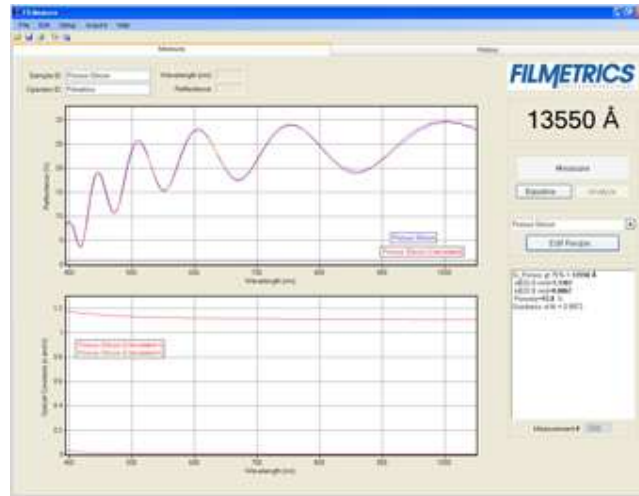


Figure A.6 Filmetrics Software

- 1) The Filmetrics software was set up as shown in **Figure A.6**.
- 2) Integration time was modified to prevent signal saturation. Reflectance values above 3200 % are sufficient.
- 3) Reflectance measurement of the untreated thin film sample is measured.
- 4) The reflectance of the reference Si <100> is recorded
- 5) A blank signal is measured i.e., no reflectance should reach the reflectometer.
- 6) Measurement of initial thickness d_0 recorded for 10 counts i.e. 50 seconds (1 count = 5-second interval)
- 7) The swelling procedure is carried out, ensuring that the thickness is measured throughout the entire experiment with a satisfactory GOF.

A.5 Matlab Scripts

The script for measuring the RH% values is shown below. This was run using a Matlab script and an Arduino board.

```
a = Arduino;

time = now;    % initialisation of variables ;
humiditysens2 = 0;
tempsens2 = 0;
acvp2 = 0;

A= 8.07131;
B= 1730.63;
C= 233.426;

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%% FIGURE 2
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

%TEMPERATURE

figureHandletempsens2 = figure('NumberTitle','off',...
    'Name','Temperature Readings',...
    'Color',[1 1 1],'Visible','off'); % pulling the figure out - creating a figure with
conditions

% Set axes
axesHandle = axes('Parent',figureHandletempsens2,...
    'YGrid','on',...
    'YColor',[0 0 1],... % blue
    'XGrid','on',...
    'XColor',[0 0 1],... % blue
    'Color',[1 1 1]); % setting up axs
hold on;

plotHandletempsens2 =
plot(axesHandle,time,tempsens2,'Marker','.', 'LineWidth',1,'Color',[0 0 0]);
xlim(axesHandle,[min(time) max(time+0.0001)]);
% plotting data

% Create xlabel
xlabel('Time','FontWeight','bold','FontSize',14,'Color',[0 0 0]);
% Create ylabel
ylabel('Temperature (degrees Celsius)','FontWeight','bold','FontSize',14,'Color',[0 0
0]);
% Create title
title('Temperature Readings (Sensor 2)','FontSize',15,'Color',[0 0 0]);
```

```

hold on;

%HUMIDITY

figureHandlehumsens2 = figure('NumberTitle','off',...
    'Name','Humidity Readings',...
    'Color',[1 1 1],'Visible','off');
% Set axes
axesHandle = axes('Parent',figureHandlehumsens2,...
    'YGrid','on',...
    'YColor',[0 0 1],...
    'XGrid','on',...
    'XColor',[0 0 1],...
    'Color',[1 1 1]);
hold on;
plotHandlehumsens2 =
plot(axesHandle,time,humiditysens2,'Marker','.', 'LineWidth',1,'Color',[0 0 0]);
xlim(axesHandle,[min(time) max(time+0.0001)]);
% Create xlabel
xlabel('Time','FontWeight','bold','FontSize',14,'Color',[0 0 0]);
% Create ylabel
ylabel('Humidity (%RH)','FontWeight','bold','FontSize',14,'Color',[0 0 0]);
% Create title
title('Humidity Readings (Sensor 2)','FontSize',15,'Color',[0 0 0])
hold on;

%VAPOUR PRESSURE (KPA)

figureHandleacVP2 = figure('NumberTitle','off',...
    'Name','AcVP Readings',...
    'Color',[1 1 1],'Visible','off');
% Set axes
axesHandle = axes('Parent',figureHandleacVP2,...
    'YGrid','on',...
    'YColor',[0 0 1],...
    'XGrid','on',...
    'XColor',[0 0 1],...
    'Color',[1 1 1]);
hold on;
plotHandleacVP2 = plot(axesHandle,time,acvp2,'Marker','.', 'LineWidth',1,'Color',[0
0 1]);
xlim(axesHandle,[min(time) max(time+0.0001)]);
% Create xlabel
xlabel('Time','FontWeight','bold','FontSize',14,'Color',[0 0 1]);
% Create ylabel
ylabel('acVP (kPa) ','FontWeight','bold','FontSize',14,'Color',[0 0 1]);
% Create title
title('Actual VP Readings (Sensor 2)','FontSize',15,'Color',[0 0 1]);

```

```

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
READ DATA
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

```

```

stoptime = '23:59';
timeInterval = 2;
count = 2;

```

```

while ~isequal(datestr(now,'HH:MM'),stoptime)           %datestr
    time(count) = datenum(clock);

```

```

    %plot sensor 2A

```

```

    %temp

```

```

    tempsens2(count) = (((readVoltage(a,'A2'))/5)-0.2424)*165
    set(plotHandletempsens2,'YData',tempsens2,'XData',time);
    set(figureHandletempsens2,'Visible','on');

```

```

    %humidity

```

```

    humiditysens2(count) = ((readVoltage(a,'A3'))/5)*100;
    set(plotHandlehumsens2,'YData',humiditysens2,'XData',time);
    set(figureHandlehumsens2,'Visible','on');
    datetick('x','HH:MM');

```

```

    %acvp measurement

```

```

    t = [tempsens2];
    AN2 = A -(B./(t+C))
    P_SAT_mmHg = 10.^(AN2) %mmHg
    P_SAT_kPa = P_SAT_mmHg/7.501 %kPa
    h = [humiditysens2];
    acvp2 =(h.*P_SAT_kPa)./100
    set(plotHandleacVP2,'YData',acvp2,'XData',time);
    set(figureHandleacVP2,'Visible','on');
    datetick('x','HH:MM');

```

```

pause(timeInterval);
count = count + 1;
end

```

```

%% TYPE CLEAR IN COMMAND WINDOW TO RESET %%

```

A.6 Calculating the saturation of water at a specific temperature

A = ?

```

B = ?
C = ?          %% vp in mmHg and temp in deg C

t = ??? ;
AN = A -(B./(t+C))
P_SAT_mmHg = 10.^(AN) %mmHg
P_SAT_kPa = P_SAT_mmHg/7.501 %kPa

%%%%%%%%%%%%%%

% Psat_kPa_2 = 1.3 % kPa
% P_SAT_mmHg_2 = Psat_kPa_2*7.5002 % mmHg
%
% T2 = (B/(A- log10(P_SAT_mmHg_2))-C)

```

A.7 Suck-back Validation

A miscibility test was carried out to measure the amount of a solvent that could potentially contaminate the water bubbler. This was important to validate a problem with suck-back that could potentially damage the valve apparatus, especially in the water line where no chemical-resistant valves were used. Solvent contamination was identified early in the project when no valves were present. A quick test with IPA and water in separate bubblers confirmed that two immiscible phases of organic solvent and water could be seen when emptying the water bubbler. Identification of immiscibility of the two liquids, suck-back was occurring and was detected in the lines as shown in **Figure A.7**.

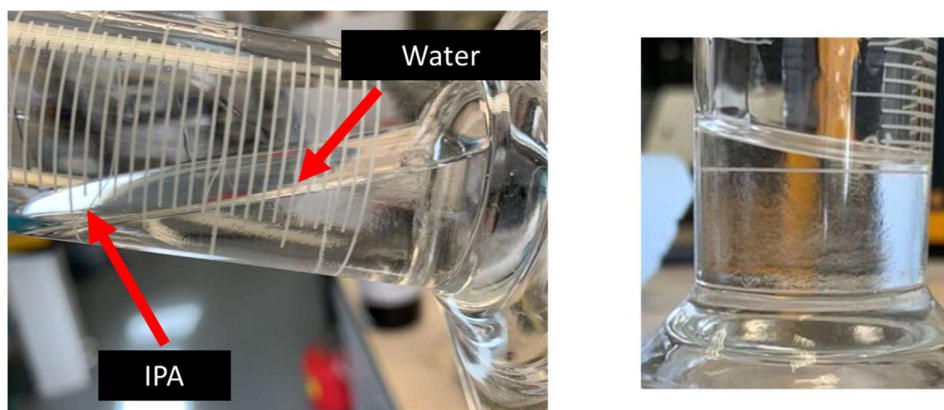


Figure A.7 Testing for suck-back using a probe solvent of IPA.

For the first test, the mixer was absent from the apparatus to identify if it was causing the suck-back problem. Next, different flow rates and the constant pressure of 2 bar were applied to the lines for 5 minutes to identify if specific flow rates could cause suck-back in the lines. This test identified no problems with suck-back, indicating that the mixer was not the issue and its resistances did not impact the apparatus. For the second test, the mixer was added back to the apparatus generating more resistances in the water line. This identified that neither mixer nor flow rates were the issues. The check-valves and flow metres

removed the suck-back problem investigated at the preliminary stages of the project. All the above tests are reported in **Table A.1** and **Table A2**.

Table A.1 Suck-back validation without mixer.

System setup	Flow coefficient	Suck back visible
All on	0.0005 Cv	NO
H ₂ O Bubbler only	0.0015 Cv	NO
Solvent Bubbler only	0.0015 Cv	NO
Dry N ₂ only	0.0015 Cv	NO
Solvent bub fully on	0.004 Cv	NO
All fully open	0.004 Cv	NO
Water turned off	0	NO
Water turned on and 2 lines off	0.004 Cv	NO
All turned off cylinder	0	NO

Table A.2 Suck-back validation with mixer

System setup	Flow coefficient	Suck back visible
All on	0.004 Cv	NO
H ₂ O Bubbler only	0.004 Cv	NO
Solvent Bubbler only	0.0015 Cv	NO
Dry N ₂ only	0.004 Cv	NO
Reduction of flow at mixer (H ₂ O)	0.004 Cv	NO

Water turned on and 2 lines off	0.004 Cv	NO
All turned off from cylinder	0	NO

A.8 Saturation Error Analysis

Antoine Equation

$$p = A - \frac{B}{C + T}$$

Antoine Constants

Chloroform

A	B	C
6.95465	1170.966	226.232

Toluene

A	B	C
6.95087	1342.31	219.187

Partial Derivatives from the Antoine Equation (Calculated using Wolfram Alpha³⁹)

- For x

$$\frac{\partial p}{\partial x} = \frac{10^{a-b/(c+x)}}{10^{a-b/(c+y)}} = \frac{b10^{\frac{b}{c+y}-\frac{b}{c+x}}}{(c+x)^2}$$

- For y

$$\frac{\partial p}{\partial y} = \frac{10^{a-b/(c+x)}}{10^{a-b/(c+y)}} = \frac{b10^{\frac{b}{c+y}-\frac{b}{c+x}}}{(c+y)^2}$$

Where $x = \text{Temperature (Probe 1)}$

$y = \text{Temperature (Probe 2)}$

- Uncertainty

- Recorded at a tolerance of 0.15 for each temperature probe.

$$\left(\sqrt{\frac{\partial p}{\partial x} * 0.15} \right)^2 + \left(\sqrt{\frac{\partial p}{\partial y} * 0.15} \right)^2 = \text{Uncertainty}$$

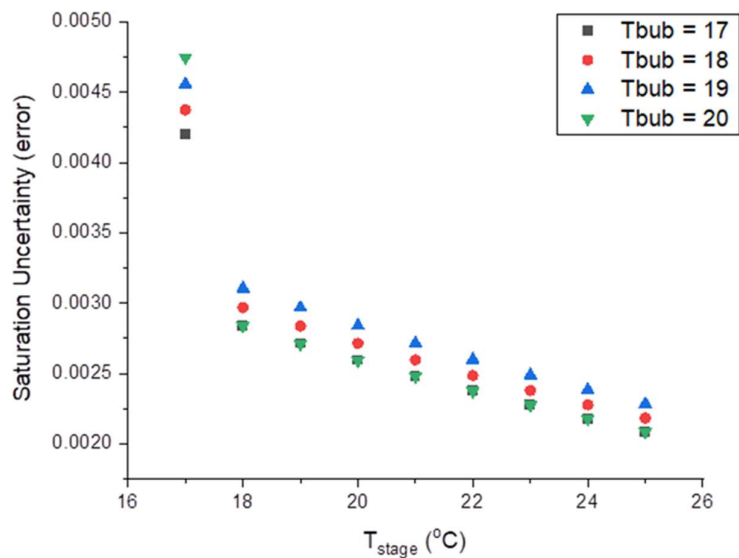


Figure A.8 Uncertainty measurements for chloroform at $T_{\text{stage}} = 16 - 26$ °C.

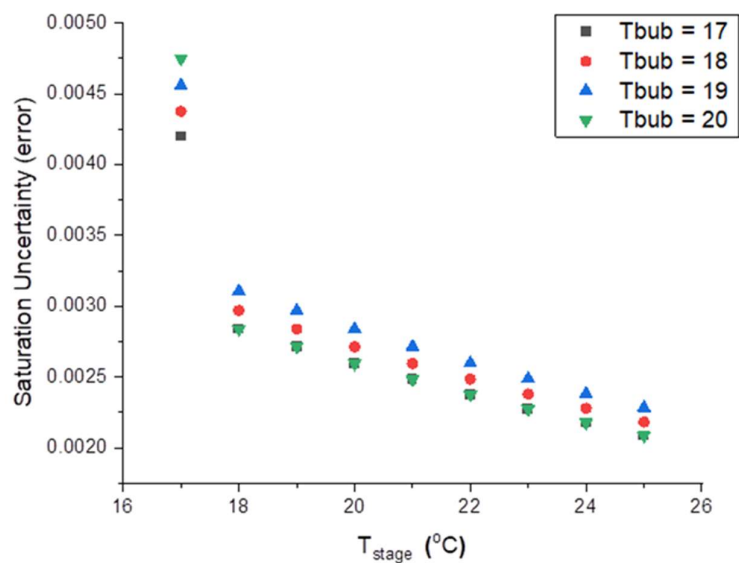


Figure A.9 Uncertainty measurements for toluene at $T_{\text{stage}} = 16 - 26$ °C.

A.9 Data Analysis for PS

Table A.3 Porosity Data (*Circularity 0-1*) for PS (17k) 100-400 nm at 500 seconds condensation

Thickness (d_0) - Homopolymer	Pore diameter (μm)	Pore Area (μm^2)	Pore Number (Area = 1329 x 997 μm^2)	Pore Coverage (%)
100 nm	36.8 ± 29.5	730 ± 882	1111	64
200 nm	14.3 ± 13.1	170 ± 313	1842	28
300 nm	19.9 ± 15.3	284 ± 397	2024	42
400 nm	29.9 ± 21.3	630 ± 732	714	31

Table A.4 Porosity Data (*Circularity 0.8-1*) for PS (17k) 100-400 nm at 500 seconds of condensation

Initial Thickness (d_0)	Pore diameter (d_f) (μm)	Pore Area (μm^2)	Pore Number (Area = 1329 x 997 μm^2)	Pore Coverage (%)
100 nm	13.3 ± 10.5	160 ± 284	381	4.6
200 nm	11.8 ± 8	117 ± 179	1631	18
300 nm	13.4 ± 8.7	143 ± 205	1484	16
400 nm	21.8 ± 13.8	403 ± 411	422	12

Table A.5 Droplet Templating Efficacy for PS (17k) 100-400 nm at 500 seconds of condensation.

Initial Thickness (d _o)	Templating Efficacy (%) (No. Circular pores / No. All pores *100 %)
100 nm	34.3
200 nm	88.5
300 nm	73.3
400 nm	59.1

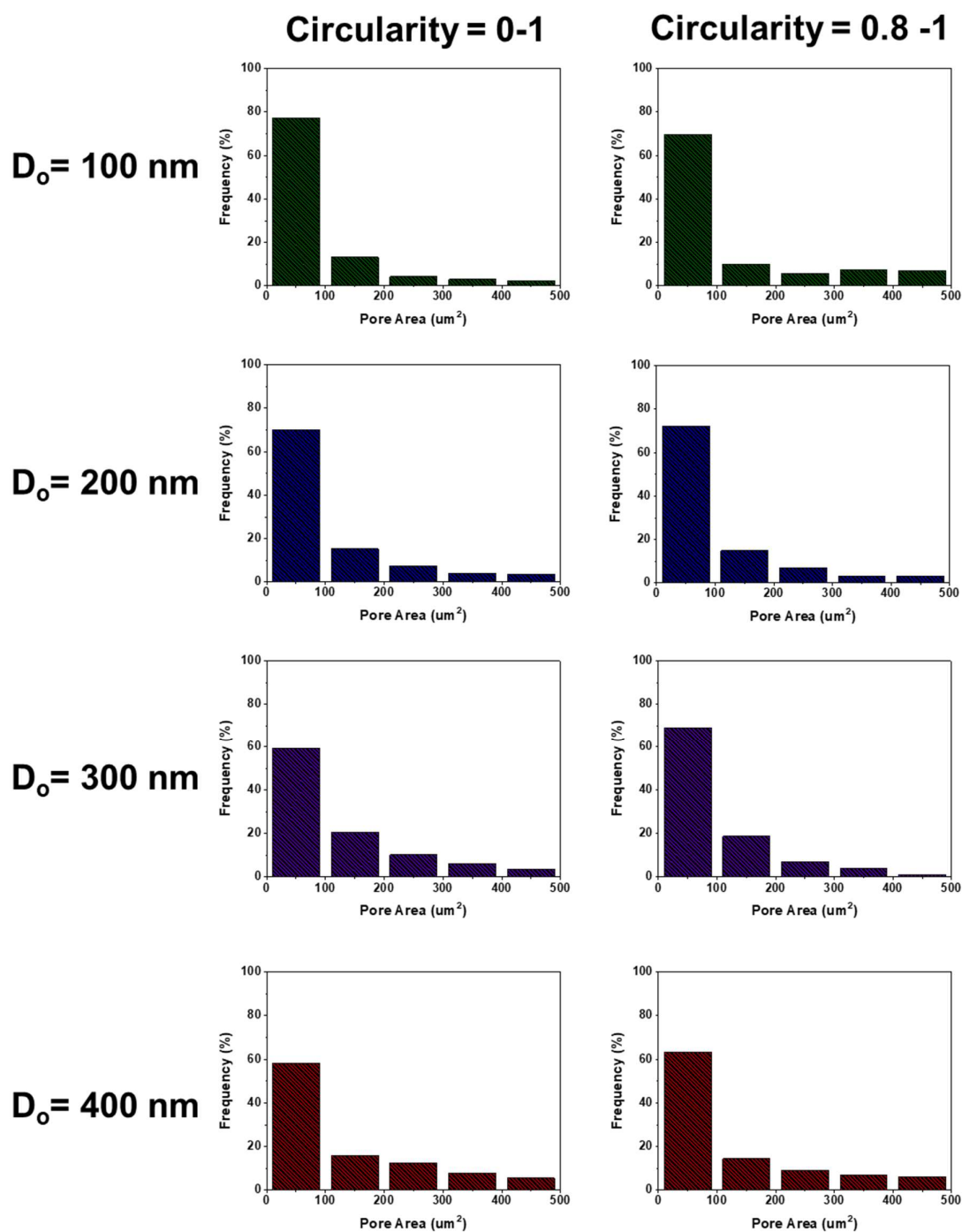


Figure A.10 Pore Area Distributions for $d_o = 100\text{-}400$ nm thin films with circularity filtered to 0-1 and 0.8-1 respectively. Condensation time for the was 500 seconds.

Table A.6 Porosity Data (*Circularity 0-1*) for PS (17k) 100-400 nm at 250, 500 and 750 seconds of condensation

Initial Thickness (d _o) (nm)	Pore diameter (d _f) (um)		
	250 sec	500 sec	750 sec
100	25 ± 25.6	72 ± 73.2	93 ± 141.5
200	26 ± 29.1	24 ± 23.9	0
300	25 ± 25.7	30 ± 27.7	0
400	35 ± 45.8	38 ± 31.5	105 ± 71.5

Initial Thickness (d _o) (nm)	Pore number (n)		
	250 sec	500 sec	750 sec
100	1636	767	310
200	2104	1983	DEWETTED
300	2755	2160	DEWETTED
400	1190	884	1872

Initial Thickness (d _o) (nm)	Pore Coverage (%)		
	250 sec	500 sec	750 sec
100	85	67	80
200	34	28	DEWETTED
300	39	44	DEWETTED
400	37	28	36

Table A.7 Porosity Data (*Circularity 0.8-1*) for PS (17k) 100-400 nm at 250, 500 and 750 seconds of condensation

Initial Thickness (d ₀) (nm)	Pore diameter (d _f) (um)		
	250 sec	500 sec	750 sec
100	8 ± 6	22 ± 20	136 ± 57
200	19 ± 14	20 ± 15	N/A
300	10 ± 6.5	19 ± 14	N/A
400	21 ± 17	22 ± 20	45 ± 40

Initial Thickness (d ₀) (nm)	Pore number		
	250 sec	500 sec	750 sec
100	1381	337	157
200	1388	1772	0
300	1659	1493	0
400	752	446	74

Initial Thickness (d ₀) (nm)	Pore Coverage (%)		
	250 sec	500 sec	750 sec
100	21.0	4.70	0.23
200	12	17.8	0
300	3.5	13	0
400	9.0	7.5	4.8

Table A.8 Droplet Templating Efficacy for PS (17k) 100-400 nm at 250, 500 and 750 seconds of condensation

Initial Thickness (d _o) (nm)	Templating Efficacy (%) (No. Circular pores / No. All pores *100 %)		
	250 sec	500 sec	750 sec
100	84.4	43.9	50.6
200	66.0	89.4	0
300	60.2	69.1	0
400	63.2	50.5	4.0

A.10 Data Analysis for PS-COOH (250, 500, 750 sec)

Table A.9 Porosity Data (*Circularity 0-1*) for PS-COOH (17k) AFM Image analysis

Initial Thickness of Film (d ₀) (nm)	Pore Size (Ferret Diameter d _f) (μm)	
	250 sec	500 sec
90 nm	2.3 ± 1.6	1.3 ± 1.6
147 nm	0.7 ± 0.4	0.8 ± 0.7

Table A.10 Porosity Data (*Circularity 0-1*) for PS-COOH (17k) 100-400 nm at 250, 500 and 750 seconds of condensation

Initial Thickness (d ₀) (nm)	Pore diameter (d _f) (μm)		
	250 sec	500 sec	750 sec
100	16.3 ± 18	14.5 ± 8.9	26.3 ± 30
200	10.5 ± 6.3	18.7 ± 15	19.3 ± 14
300	13.3 ± 8.3	26.6 ± 16	13.5 ± 13
400	11.1 ± 7.7	24.0 ± 11	15.8 ± 15

Initial Thickness (d ₀) (nm)	Pore number (n)		
	250 sec	500 sec	750 sec
100	2434	2941	1080
200	5307	2266	2379
300	3038	5830	2661
400	4790	5134	2254

Initial Thickness (d_o) (nm)	Pore Coverage (%)		
	250 sec	500 sec	750 sec
100	53	39	65
200	37	53	51
300	30	47	30
400	27	41	42

Table A.11 Porosity Data (*Circularity 0.8-1*) for PS-COOH (17k) 100-400 nm at 250, 500 and 750 seconds of condensation

Initial Thickness (d_o) (nm)	Pore diameter (d_f) (um)		
	250 sec	500 sec	750 sec
100	9 ± 4	8 ± 4	5 ± 3
200	8 ± 3	10 ± 5	8 ± 5
300	6 ± 3	11 ± 10	5 ± 2
400	5 ± 3	7 ± 6	6 ± 3

Initial Thickness (d_o) (nm)	Pore number (n)		
	250 sec	500 sec	750 sec
100	1214	1096	436
200	3591	1145	920
300	655	1632	883
400	1218	1387	869

Initial Thickness (d_o) (nm)	Pore Coverage (%)		
	250 sec	500 sec	750 sec
100	7	6	1
200	15	9	5
300	2	9	1
400	3	3	2

Table A.12 Droplet Templating Efficacy for PS-COOH (17k) 100-400 nm at 250, 500 and 750 seconds of condensation

Initial Thickness (d _o) (nm)	Templating Efficacy (%) (No. Circular pores / No. All pores *100 %)		
	250 sec	500 sec	750 sec
100	50	37	40
200	68	51	39
300	22	28	33
400	25	27	39

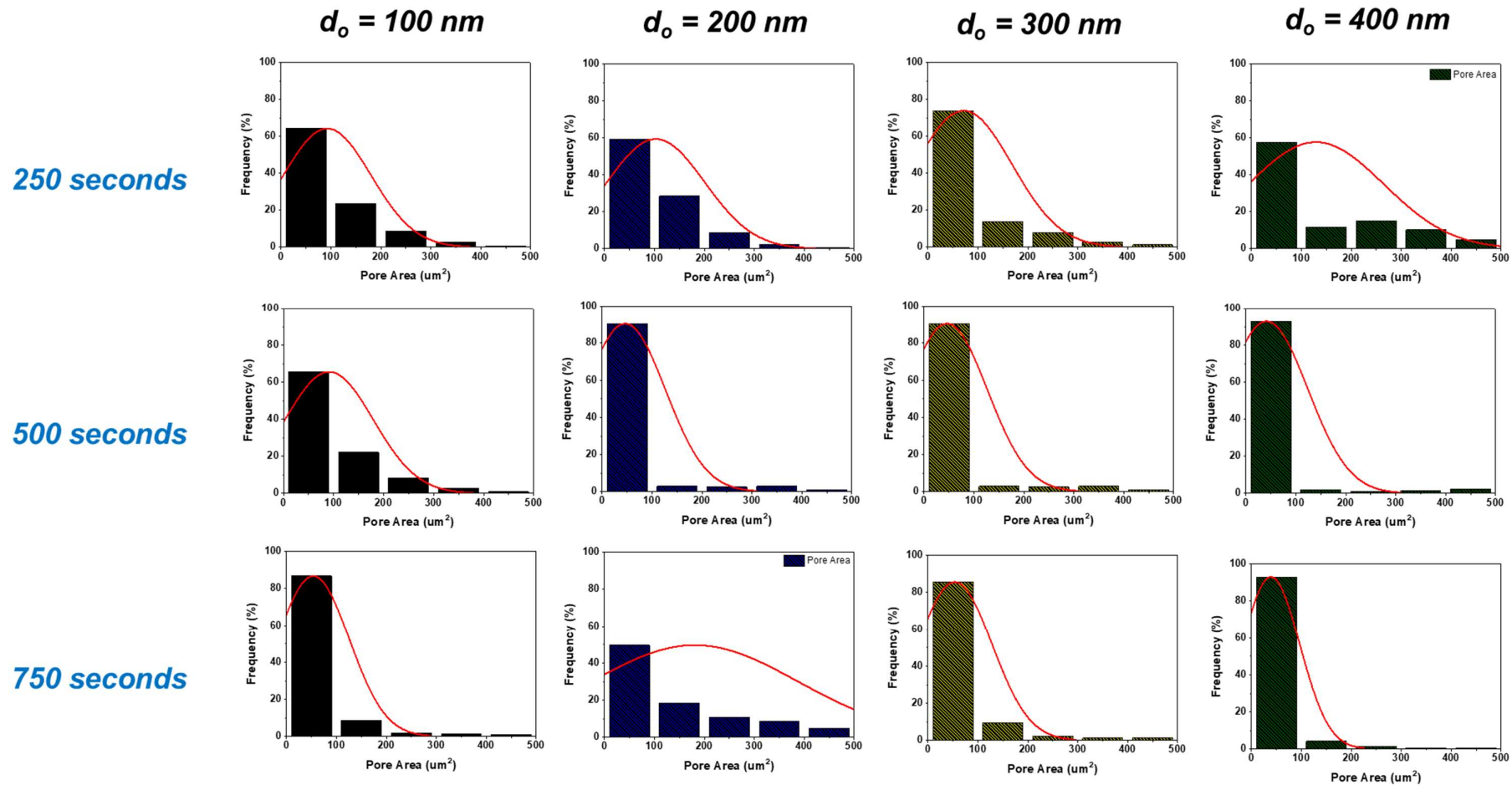


Figure A.11 Pore Area Distributions for the thin films 100-400 nm at condensation times of 250 sec, 500 sec and 750 sec. Pores were filtered using ImageJ from 0.8-1 circularity in the software. Total image area = $1735 \times 1301\ \mu\text{m}^2$

A.11 Data Analysis for PS Homopolymer on Brush (100- 400 nm)

Table A.13 Porosity Data calculated using ImageJ (*Circularity 0-1*) for PS 17K) films on 6K brush (100 -400 nm) at different condensation times.

Initial Thickness (d _o) (nm)	Pore diameter (d _f) (um)		
	250 sec	500 sec	750 sec
100	18.1 ± 18.5	24 ± 12	40 ± 35
200	10.4 ± 6.95	29 ± 15	18 ± 13
300	18.5 ± 18	26 ± 15	55 ± 42
400	12.07 ± 12	24 ± 10	16 ± 13

Initial Thickness (d _o) (nm)	Pore number		
	250 sec	500 sec	750 sec
100	6445	4261	1633
200	8129	4929	7532
300	7005	5830	966
400	9137	5134	5477

Initial Thickness (d _o) (nm)	Pore Coverage (%)		
	250 sec	500 sec	750 sec
100	25	37	66
200	19	52	40
300	37	47	64
400	19	40	37

Table A.14 Porosity Data calculated using ImageJ (*Circularity 0.8-1*) for PS 17K) films on 6K brush (100 -400 nm) at different condensation times.

Initial Thickness (d _o) (nm)	Pore diameter (d _f) (um)		
	250 sec	500 sec	750 sec
100	14.1 ± 18	19.6 ± 9.3	5.85 ± 3.0
200	7.99 ± 4.0	23.91 ± 9.7	10.4 ± 5.3
300	12.6 ± 5.5	21.1 ± 8.4	6.21 ± 6.4
400	8.90 ± 3.6	22.4 ± 8.8	8.74 ± 5.2

Initial Thickness (d _o) (nm)	Pore number (n)		
	250 sec	500 sec	750 sec
100	4964	3061	588
200	6323	3444	3414
300	4897	4082	193
400	6707	4360	2955

Initial Thickness (d _o) (nm)	Pore Coverage (%)		
	250 sec	500 sec	750 sec
100	13	21	0.5
200	10	28	7
300	11	23	0.3
400	7	29	5.5

Table A.15 Droplet Templating Efficacy for PS (17k) on PS 6K brush . Thicknesses of 100-400 nm at 250, 500 and 750 seconds of condensation.

Initial Thickness (d _o) (nm)	Templating Efficacy (%) (No. Circular pores / No. All pores *100 %)		
	250 sec	500 sec	750 sec
100	77	72	36
200	78	70	45
300	70	70	20
400	77	72	36

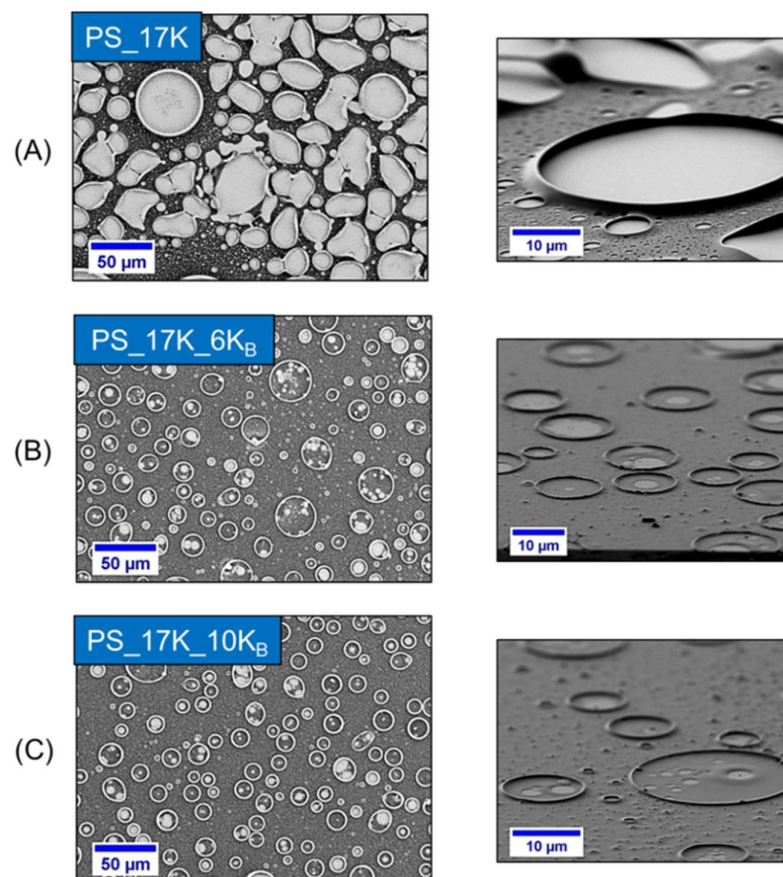


Figure A.12 SEM Top down images and x-sections at a tilt of 20 °. Condensation time was 250 seconds.

A.12 References

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