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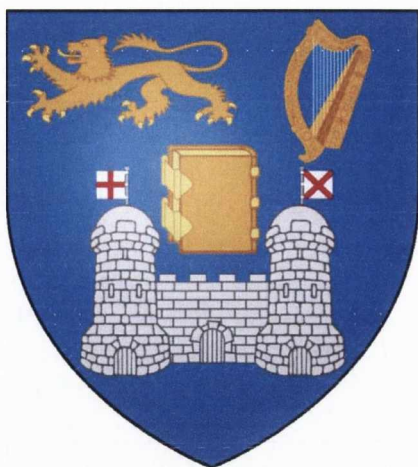
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TRINITY COLLEGE DUBLIN

**Formation of an ordered porous polymer microstructure
by water droplet templating**

A thesis presented to the University of Dublin,
Trinity College for the degree of Doctor of Philosophy

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June 30th, 2010.

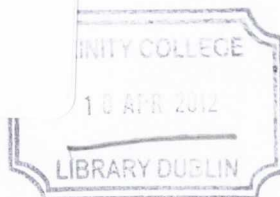
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Abstract

This thesis examines the complex system of competing mechanisms involved when evaporation of a polymer solution induces sufficient cooling to drive condensation of water droplets onto the solution surface, where they pack, order and are ultimately captured in a polymeric matrix as the solvent leaves. This use of rafts of water droplets to template a polymer solution leaves behind an ordered porous microstructured film of the polymer, upon evaporation of the water.

The dynamic mechanism, rather than studied as a whole, was broken down into an examination of (i) the equilibrium force balance of droplets on the solvent surface and (ii) the dynamical behaviour associated with solvent evaporation, water condensation and the evolution of polymer solution concentration.

The first section examines the interfacial energy balances that can ensure or prohibit stability of the water droplets at the solvent/air boundary. A theoretical model and a novel experimental approach are employed for a range of pure solvent systems. It is seen that standard techniques for defining a liquid lens is not sufficient to describe the water droplet stability observed at the interface, which leads to insights regarding the significant role of the three phase contact radius and its associated excess energy, the line tension.

The second section examines the highly dynamic mechanisms involved in the templating of water droplets, focusing on the controlled and systematic change in ambient flow and humidity conditions while analysing both the physical response of the droplets, through optical microscopy, and the resulting change in the solution through *in-situ* mass and temperature readings developed specifically for this task. Coupling this controlled formation with a precise analytical technique to examine the cross-sections leads to the means and understanding to control the internal microstructure through dynamic tuning of the mechanism, resulting in a broad range of previously unreported porous architectures using this technique.

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Abbreviations

AFM	Atomic Force Microscopy	PLA	Poly(D,L-lactic acid)
BF	Breath Figures	PMMA	Poly(methyl methacrylate)
BM	Bénard-Marangoni	PP	Polypropylene
Bo	Bond Number	PPE	Polyphenylene ether
CCD	Charge Coupled Device	PPO	Polyphenylene oxide
CSM	Continuous Stiffness Mode	PS	Polystyrene
DCM	Dichloromethane	PVC	Polyvinyl chloride
DCPS	Dicarboxy terminated polystyrene	RH	Relative Humidity
DI	De-ionised	rpm	Revolutions per minute
DOPE	Dioleoylphosphatidylethanolamine	SAM	Self-assembled monolayer
EDX	Energy-dispersive X-ray spectroscopy	SE1	Secondary electrons from primary electrons
FIB	Focused Ion Beam	SE2	Secondary electrons from backscattered electrons
HIM	Helium Ion Microscope	SEM	Scanning Electron Microscope
HKS	Hertz-Knudsen-Schrage	S-L-V	Solid-Liquid-Vapour
LCBC	Liquid-crystalline block copolymers	STM	Scanning Tunneling Microscope
L-L-V	Liquid-Liquid-Vapour	TEM	Transmission Electron Microscope
LMIS	Liquid metal ion source	Tg	Glass Transition Temperature
MEMS	Microelectromechanical systems	THF	Tetrahydrofuran
Mn	Number averaged molecular weight	VLE	Vapour Liquid Equilibrium
Mw	Weight averaged molecular weight		
PA			
PAA	Polyacrylic acid		
Paz	Poly(azobenzene-modified methacrylic acid)		
PE	Polyethylene		
PEO	Poly(ethylene oxide)		
PET	polyethyleneterephthalate		

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Chapter 1

Introduction

1.1 Project Introduction and Overview

With a rapidly increasing understanding of chemical and biological mechanisms of reaction and interaction, coupled with the extensive work examining the influences of and effects on functionally active interfaces, inevitably comes a desire to test and develop this knowledge through incorporation into synthetic, purpose-specific materials. While there is certainly a constant progression of scientific methods allowing access to visualisation and design of features of ever decreasing dimensions, the top-down development approach, which looks at direct material machining methods, is facing ever more stringent challenges. There are clear limitations when considering the formation of complex three-dimensional structures with patterned functionality that impose strict design criteria and require acceptance of significant energy related and monetary costs.

This situation has led to great interest in understanding and mimicking the self-organising mechanisms often observed in biological systems, for example the consumption of ATP coupled with pattern formation (1) and the dynamic nature of microtubule and actin polymers linked to the self-organisation of the cell cytoskeleton (2), but with the aim of a much broader technological application of the underlying principles.

Self-organisation is defined as the spontaneous creation of a globally coherent pattern out of local interactions (3). However, this behaviour is inextricably linked to open systems, far from thermodynamic equilibrium and with an external source of energy (4). The concept has a far reaching impact on society. Its roots are in the physical and biological sciences but self-organisation has also found applications in behavioural entomology (5), cybernetics and psychiatry (6).

The scientific study of self-organisation grew rapidly from the 1970's and has built a particularly close association with the development of polymer science. Again, due to the

observations in cell biology, it has long been recognised that polymers play a significant role in self-organisation and self-assembly designs. A polymer chain can be made of a number of smaller, chemically different blocks (known as block copolymers (BCP)), each with a different functionality and designed with specific, competing interactions in mind. Surface energy driven phase separations of BCPs can be exploited at a number of different length scales to give patterned and functional thin films (7), (8). Patterning and post-processing can lead to feature sizes on the order of the scale of a single polymer block, e.g. <10 nm. These patterns lead to differing etch rates and allow preferential removal of a polymer block, leaving a mask for further lithography. They can act as templates for nanomaterial growth, and have potential applications such as photonic crystals and waveguides, to name but a few areas of topical interest.

This thesis is focused on a self-organisation technique that occurs in a three component system, comprised of a homopolymer (α , ω -dicarboxy terminated linear atactic polystyrene, number averaged molecular weight 93.8×10^3 g/mol), a volatile organic solvent and water. This technique leads to an ordered polymeric microstructure, of the kind illustrated in Figure 1.1 with micron-scale pores supported by walls of nano-scale thin films at their thinnest points. Since the initial report of this technique in 1994 (9), often referred to as the Breath Figure Method (due to the vital role of water vapour condensation similar to that observed when breathing over a cold surface), there has been considerable interest in the porous microstructures that result from introducing water vapour over a polymer/solvent solution.

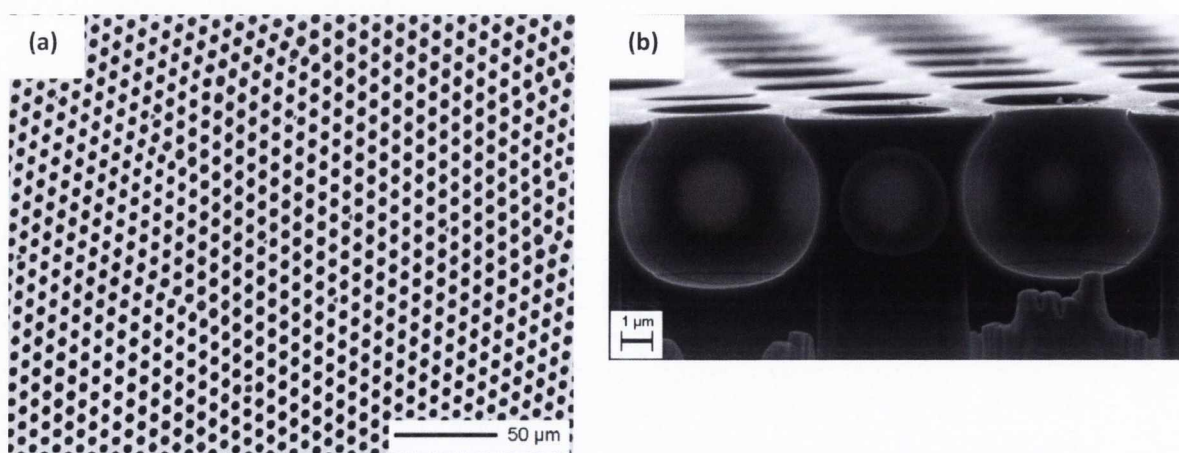


Figure 1.1: Scanning electron microscope image of an example film formed from dicarboxy-terminated polystyrene dropcast in chloroform. (a) A plan view of the self-organised polymer film showing an ordered microstructure due to water droplet templating. (b) A cross-section of a standard spherical pore architecture.

In brief, and with reference to Figure 1.2.1 in the next section, evaporative cooling at the polymer solution surface leads to water droplet condensation and ultimately, with the trapping of the water droplets by the polymer, imprinting their shape and leaving an ordered hexagonally packed porous microstructure. Although the actual pore growth mechanism is widely debated, the spherical microstructure is believed to be an intrinsic feature of this system, with only a few reports showing slight deviations without post-processing steps. Results found in the course of this thesis show this remarkable, one-step process to be in fact rich in flexibility with an untapped range of available microstructures that will broaden the scope of this material's applicability. As will be discussed in Section 6.1, there is great interest in this technique for the formation of biocompatible devices for a range of purposes, including cell signalling analysis and cell scaffold development for tissue engineering. The control of the microstructure along with the tunable nature of the material properties has also led to an interest in developing the technique to provide pharmaceutical delivery devices. Also, as will be mentioned in Section 1.2.6, this technique has been used to develop microlens arrays, superhydrophobic materials and growth templates for nanomaterials.

Alternative techniques exist to form micron scale porous polymer films, for example:

- (i) There is a wide range of techniques to use microspheres as a template in a polymer matrix before selectively removing them with solvent washing to leave the ordered, multi-layered structure (10). This technique however does not offer the same potential for the control of microstructure as water droplet templating, in terms of both the total porosity and the pore geometry, because of the limits placed by the solid template.
- (ii) Emulsion droplet templating also forms a three-dimensional porous solid through the formation and subsequent capture by a sol-gel process of the droplets. This is most applicable to inorganic rather than polymeric materials (10).
- (iii) Thermally induced phase separation can be used to form microporous polymer films by reducing the temperature of a homogeneous polymer solution until phase separation occurs, and upon freeze-drying and solvent removal, a porous sample remains (11). These are highly porous materials but do not possess an ordered structure.

The overall mechanism is deceptively complex and true to the earlier definition of self-organisation, it is formed in a highly non-equilibrium evaporation process. The approach taken in this thesis is to examine the complex mechanism by first breaking it into (i) a significantly

theoretical analysis of a quasi-equilibrium system where the positioning of the water droplet and its behaviour at the solvent/air interface can be explored, and (ii) a more experimental approach examining the highly dynamic behaviour of the solvent and water phase transitions. Prior to this, the introductory section will be completed with a more detailed overview of the method and an examination of the state-of-the-art in this water droplet templating technique.

1.2 Review of the Literature

1.2.1 Introduction

This chapter aims to communicate the current understanding from the literature, of the formation and control of porous polymer microstructures using the breath figure method. The initial explorations of condensate pattern formation on solid surfaces (12), (13) undoubtedly represent a milestone in the identification of some of the key phenomena involved.

However, it is a combination of the initial work examining the growth of condensate droplets (14) - (22) and the subsequent use of the droplets to template a polymer film (23) - (26) that really defines an emerging field of study and allows it to become a transferrable technology platform with a deeper understanding of the interplay of physical mechanisms and, ultimately, methods of control. Since these accounts were published there has been a rapid increase in interest with significant developments and further insights into the effects of complex mechanisms. The sizeable number of different accounts as well as the variety and even conflicting nature of the findings does not lend itself to a chronological review. The basic procedure, however, varies only slightly throughout most of the reports. To ensure clarity this review will summarise these key procedural steps. For each step, mechanisms described in the literature will be presented, highlighting where uncertainty remains or conflicting accounts exist. Following on from the formation mechanism, this chapter will also look at post-processing treatments currently being developed for this material, with future applications in mind.

The generic procedural steps into which the formation of ordered polymeric microstructures can be divided are listed below and illustrated in Figure 1.2.1:

1. *Polymer Solution Dosing*: A volatile organic solvent with dissolved polymeric material is dosed and spread over an uncontaminated substrate. (Figure 1.2.1-a)
2. *Solution Evaporation*: Removal of the solvent through natural or driven evaporation occurs with an associated cooling effect. (Figure 1.2.1-b)

3. *Water Condensation*: With the introduction of a humid atmosphere, the boundary layer at the solution/air interface is sufficiently loaded with water vapour so that the cooling in step 2 leads to super-saturation and condensation occurring from the vapour to the liquid phase. This results in water droplets at the solution/air interface that continue to grow with additional condensation. (Figure 1.2.1-c)
4. *Droplet Packing*: Due to non-coalescence phenomena and agitation of the surface induced by convection currents, the water droplets reach a minimum energy packing arrangement.
5. *Droplet Trapping*: The continued evaporation of the solvent ensures the droplets are caught in the increasingly entangled polymeric network. The polymer film is allowed to dry, removing any remaining solvent and water to reveal ordered arrays of pores in the film.
6. *Application Specific Treatments*: The material can be further functionalised or manipulated as required.

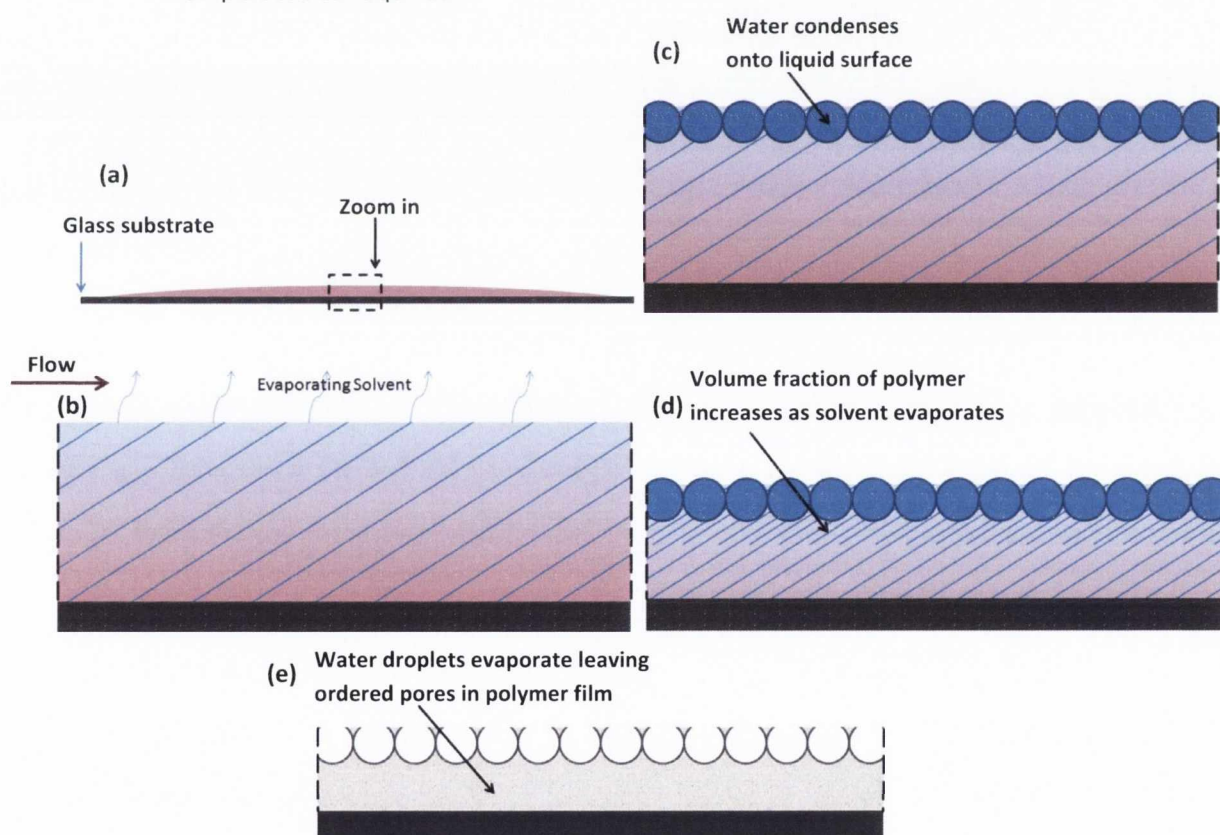


Figure 1.2.1: Mechanism of formation of ordered porous microstructure. (a) Solution dosed to flat, glass substrate, (b) A flow of humid air introduced across surface of evaporating polymer solution, (c) Evaporative cooling drives water condensation and surface tension driven convection. The water droplets continue to grow and pack closely, (d) Continued solvent evaporation increases volume fraction of polymer, (e) Evaporation of water droplets leaves behind porous microstructure.

These steps will now be examined more closely with reference to past studies before concluding with an overview of opportunities where further exploration and understanding is required or where current knowledge can be built upon.

1.2.2 Polymer Solution and Dosing

This section reviews the influence of polymer and solvent choice as understood from the literature. The volume and method of dosing are then considered, as well as the influence of the chosen substrates.

1.2.2.1 The Polymer

The founding work in this field is presented over three papers, in which many of the key principles relating to the choice of polymer are defined (23), (25), (26). These reports show that initially it was believed that star-like polystyrene based polymers are required to form porous films. The work by this group led to one of the proposed mechanisms regarding droplet non-coalescence, discussed further on in this section, suggesting that the precipitation of the polymer at the water/solvent interface is a key step in the system's stabilisation (26). This was concluded from an initial observation of large drops and their immediate coverage in a polymer "bag" upon entering an equivalent polymer solution. This was supported by X-ray scattering experiments, where a reduction in the characteristic length between the polymer block cores of the micellar aggregates was observed in the porous films, as compared with plain films prepared without the presence of water vapour. This reduction was related to the "precipitated-like" state of the polymer. Further work showed that linear polymers with specific functional groups, such as carboxylic acid or amino, could lead to micelle-like behaviour of polymers in solution and also give ordered arrays of pores. Polar-end groups were used to ensure polymer association in non-polar solvents. The required architecture or structure of the polymer when forming an ordered microstructure is a recurring subject in the literature. End-functionalised linear polymers have become popular for studies on such systems (27) - (32). However linear polystyrene, without additional functional groups, was unsuccessful in almost all studies unless mixed at a concentration below 25% _{w/w} with another polymer of the types mentioned previously.

A group of later studies (33) - (36) were key to understanding the role of the polymer architecture. Their results confirmed that comb and star polymers along with linear polymers with polar end groups all are likely to form a spherical shape in solution and lead to regular films. In confirmation of this, ester and carboxylic acid end group types were compared using light scattering. The esterification led to non-porous films while the carboxylic acid end group

gave ordered arrays. This was reflected in the spherical nature of observed micelles by light scattering in the carboxylic acid termination polymer only. It is this increase in chain density that they believe leads to a precipitation of the polymer at the water interface and a resultant stabilisation of the droplet until all the solvent has left. The formation of dense micelles with the aim of stabilizing the water droplets was also achieved using small molecule ionomers in solution (37) and polyion complexes (38), (39). The surfactant nature of the polymers was also the focus of many experiments and led to the work mentioned with amphiphilic polyion complexes (39), (40) and also the deliberate addition of surfactant polymers to stabilize a system (41). The two theories, the polymer precipitation “bagging” effect and surfactant stabilisation, are closely linked as the segment density is also influenced by the presence of functionalized end groups. Work showing the preferential presence of hydrophilic groups at the inside of the pores (36) support the theory that the hydrophilic ends, despite their relatively low concentration, are available to move to the interface.

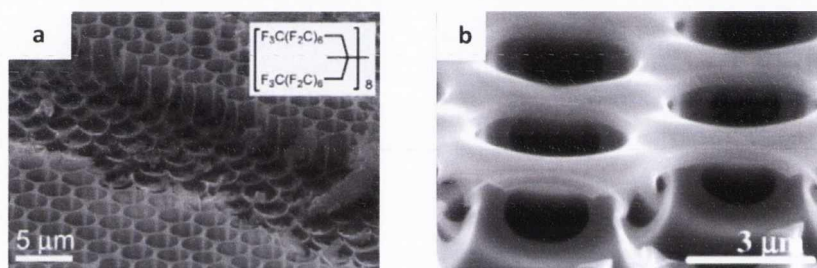


Figure 1.2.2: Scanning electron microscope images showing (a) an elongated porous structure attributed to the polymer used, perfluoroalkyl-functionalized G3 star polymer (42) and (b) interconnected pores in a regular honeycomb structure (43).

This is an important result as it allows feature specific functionalising of the ordered films. Surfactants can be deliberately added (41) to modify the microstructure of the pores, based on the assumption that it would upset the three phase force balance. Depending on the surfactant chosen, they reported a slight widening of the pore opening, a destabilising of the pores into a disordered multi-layered film, and a smooth polymer surface with irregular, widely spaced small indents. This is developed further (42) using a specifically designed series of star polymers, cited the tuning of hydrophilic/hydrophobic behaviour as the reason for modified and elongated pore morphology, as seen in Figure 1.2.2(a). The surface tension of the polymer solution is also believed to be one of the key reasons for droplet end-process coalescence (Figure 1.2.2 (b)) where the pores are interconnected (43) without losing the shape of the overall structure.

It should be noted that while unsuccessful results are reported from work with non-functionalised polystyrene and many of the groups above did not achieve ordered pores unless

including it only as a minority component in a blend, a number of groups (35), (38), (44) - (46) used this as a standard material for porous film formation, even though it conforms to neither of the discussed theories. Equally, it must be pointed out that other reports (47) show that rigid rod polymers, that are not expected to form star-like arrangements or micelles have also been used successfully. This topic is broached in the literature (36) and it is suggested that the range of polymers that can be used is very broad but that the process parameters that allow ordered film formation vary from the very broad and flexible for the micellar forming polymers to narrow and restricted for the non-functionalised polymers.

Use of amphiphilic block-co-polymers has been reported in many instances, for example (48), (49) and are explored as a route to control the pore opening size and spacing through changes in the hydrophilic or hydrophobic chain lengths, thus changing the droplet/solution interfacial tension (50). Over recent years, block-co-polymers and complexes targeting specific applications have been used to form the ordered microstructure. Some examples are detailed below and are illustrated in Figure 1.2.3:

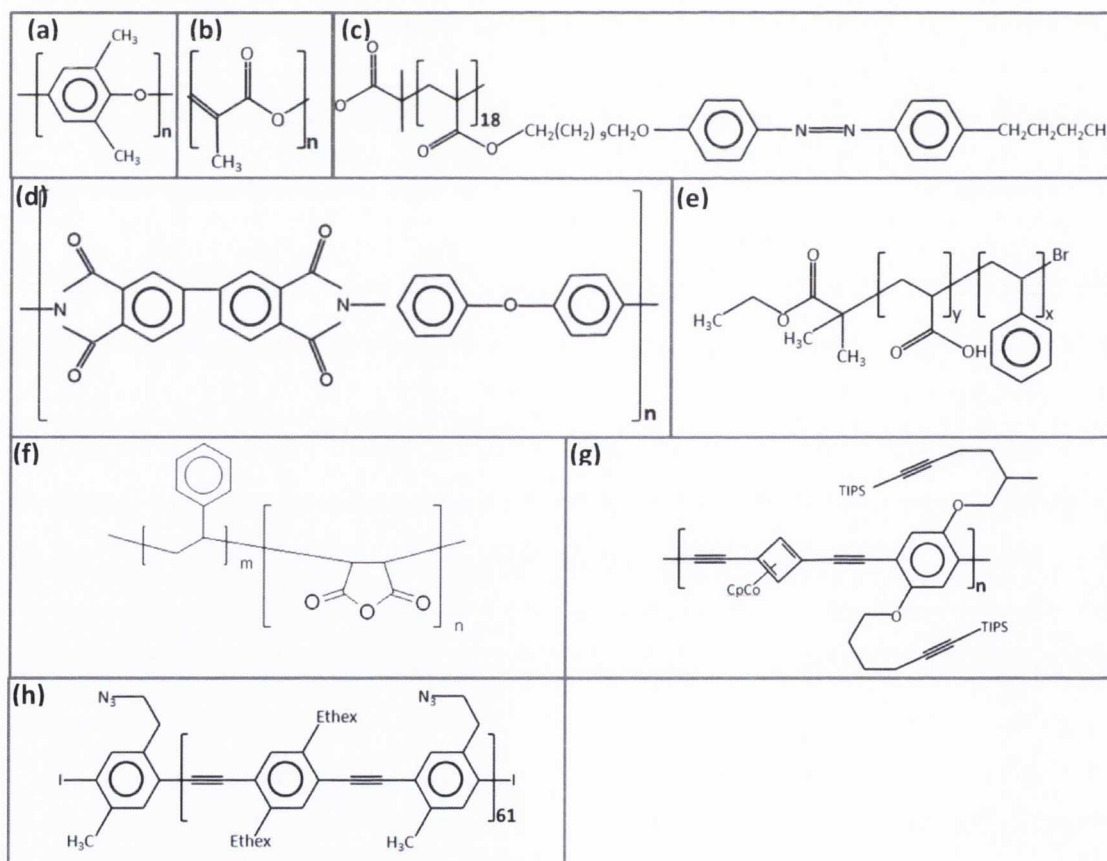


Figure 1.2.3: A range of polymers and complexes are used in the BF method, targeting specific applications. These include (a) Polyphenylene oxide, (b) Poly(D,L-lactic acid), (c) Poly(ethyleneoxide)-block-poly(azobenzene-modified methacrylic acid), (d) a polyimide, (e) Polystyrene-block-polyacrylic acid, (f) Poly(styrene-co-maleic anhydride), (g) Organometallic polyphenylene ether compound, (h) Poly(para-phenyleneethynylene) with photo responsive small molecules.

- (a) Polyphenylene oxide (PPO), a variety of high-performance thermo-plastic polymer (Figure 1.2.3(a)),
- (b) Poly(D,L-lactic acid) (PLA) in conjunction with a low concentration of stabilising dioleoylphosphatidylethanolamine (DOPE) as part of work to create biodegradable polyesters for biological applications (Figure 1.2.3(b)), (41), (51), (52).
- (c) An amphiphilic liquid-crystalline block copolymers (LCBC), poly(ethyleneoxide)-block-poly(azobenzene-modified methacrylic acid) (PEO-b-Paz), designed to improve flexibility (Figure 1.2.3(c)), (53).

A great deal of work has been carried out to explore the block-co-polymers that can possibly be used to enable cross linking and broaden the thermal and chemical environments to which these films can be exposed without damage. A range of successful candidates have been found, among which are a polyion complex of polyamic acids and dialkylammonium that can be pyrolysed to a polyimide (Figure 1.2.3(d)) (54), an amphiphilic diblock copolymer of polystyrene-block-polyacrylic acid (PS-b-PAA) (Figure 1.2.3(e)), (55), poly(styrene-co-maleic anhydride) (Figure 1.2.3(f)), (39) organometallic polyphenylene ether compounds (PPE) (Figure 1.2.3(g)), (56), photoresponsive small molecules and Poly(para-phenyleneethynylene) (Figure 1.2.3(h)), (57).

1.2.2.2 Polymer Molecular Weight

Few groups analyse the influence of polymer molecular weight. It was noted by Bolognesi *et al.* (31) noted from the three samples examined it was not a parameter of significant influence. A number of reports examined (23), (33)- (36), (58) the influence of molecular weight and found that the pore sizes decreased with an increase in molecular weight, as shown in Figure 1.2.4 (a). However, an increase in molecular weight, with an identical mass concentration meant that their molar volume had in fact decreased. It was this that Stenzel *et al.* (36) believed was the key factor in changing the time required for the polymer to stabilise the water droplets. With fewer polymeric chains, there is more time before the droplet is fixed in place and the droplet has a longer time to grow through continued condensation. When normalised for molar volume, only a very slight decrease in size occurred and they too agreed it was not a significant parameter in the control of pore sizes. However there is an influence reported regarding the pore regularity. Conflicting reports exist (59), (60), showing a decrease and increase respectively in pore size with increasing polymer molecular weight. Both reports show quite weak dependencies unless the molecular weight is raised far beyond 1000 kgmol^{-1} .

1.2.2.3 Polymer Concentration

Interestingly, as explored within this thesis, the solution must traverse a range of concentration regimes before it is finally entangled to a degree at which it is essentially fixed. However, despite the full range of concentrations experienced by the solution, the initial concentration remains a critical factor in designing the final porous film. It is an area with conflicting results. Reports show a steady increase in pore dimensions with initial concentration of solution (61), (62). However, alternative reports show a clear decrease in pore size with polymer concentration, as seen in Figure 1.2.4 (b) (36), (63) - (65). It is explained by Stenzel *et al.* (36) that this is due to an increased capacity to stabilise a larger surface area of water droplets before the precipitation of the polymer occurs. The increase in concentration is also noted to decrease the rate of evaporation, as dictated by Henry's Law, which may be responsible for lower cooling levels.

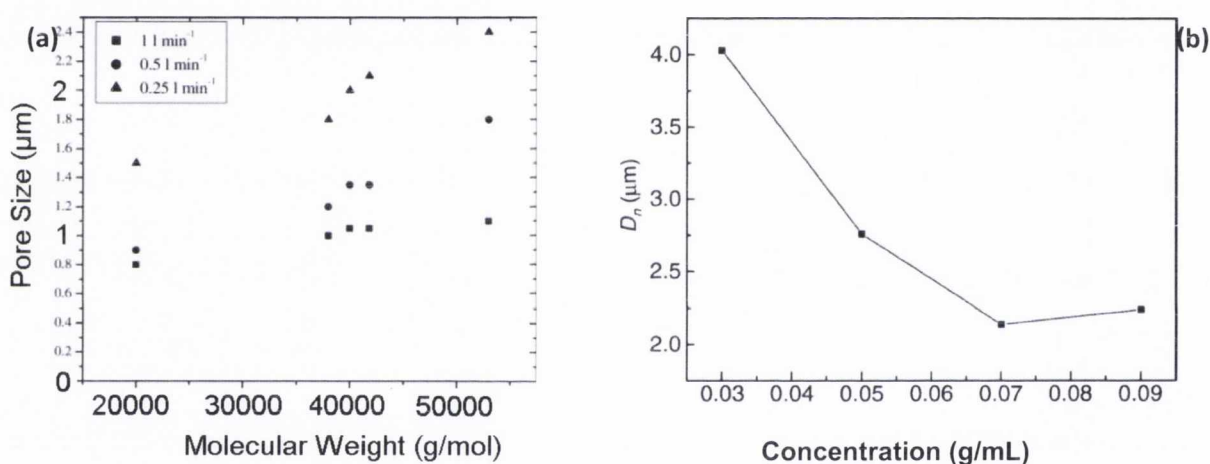


Figure 1.2.4: Example graphical representations from the literature of changes in pore size with polymer molecular weight and concentration. (a) A reported increase in the pore size with increasing molecular weight of a five-arm polystyrene star polymer with respect to the rate of the airflow (36), (b) A reported decrease of the pore size with increasing polymer concentration (64).

1.2.2.4 Solvent

The solvent in which the polymer is dissolved plays a crucial role in the process and this role will now be explored. There are far fewer solvents examined with this method than polymers. In fact only 11 have been identified from the past 16 years. The solvents used most often are chloroform, dichloromethane and carbon disulphide. Toluene, benzene and over recent years tetrahydrofuran are well-represented in the literature. Solvents such as carbon tetrachloride, dichloroethane, xylene (dimethylbenzene) and freon (trichlorotrifluoroethane) have been examined to a lesser extent.

The key requirements of the solvent are complete dissolution of the polymeric material and rapid evaporation with a sufficient latent heat of vaporisation such that evaporative cooling reduces the solution surface below the saturation temperature of the water vapour. Initially a non water-soluble solvent was thought to be required but the advent of THF in these studies showed that this is not the case as long as sufficient polymer is present to stabilise the water droplets before they dissolve into the solvent.

One of the most often referenced influences of the solvent is that its choice determines the likelihood of finding a multi-layered structure. A solvent that is less dense than water is expected to form a multi-layered microstructure (32), (49), (66). Alternatively, an approximate surface energy balance has been used to determine the stability of a water droplet at the solvent/air interface and from this it can be inferred when a multi-layered microstructure should be expected (31). The argument being, at these length scales, the bond number (Bo) is so small that gravitational effects on the drops should be minimal.

The non-polar nature of the solvent is recognised as an important feature, ensuring aggregation of the polar groups within the dissolved polymers. As discussed, this aggregation or pseudo star-polymer behaviour is believed by some to be responsible for ensuring sufficient precipitation of the polymer at the droplet interface and subsequent stability. The relationship between solvent volatility and film formation is examined in a later subsection when dealing specifically with the evaporation process.

1.2.2.5 Casting Volume

The polymer solution is drop-cast onto a flat substrate and it is this procedure that is one of the more significant variables across experimental arrangements. The dosed volumes range from a few microlitres (59) to a number of millilitres (67) depending on the study. Each experiment almost exclusively maintains the same volume to ensure repeatability. The groups that have monitored the effect of dosage volume have seen a steady increase in pore size with increasing droplet volume (68), (69). This is associated with an increased time required before evaporation is complete and so a lengthier period of condensation-driven droplet growth. It has been observed that an increase in dosage volume can detrimentally affect the ordered porous arrangement (35) and also encourage the change from mono- to multi-layered structures (37).

1.2.2.6 The Substrate

An uncontaminated, flat surface is most often used when dosing the polymer solution. It is a key component in the experimental set-up as it determines the spread of the solvent and in some cases the thermal gradients. Similarly to the solvent, this is a relatively overlooked element of the problem. Glass microscope slides and cover slips are the most commonly used substrates, with some studies examining silicon, mica, polyethylene (PE), polypropylene (PP), polyethyleneterephthalate (PET), polyvinyl chloride (PVC), poly(methyl methacrylate) (PMMA), chrome steel, and water. The substrates are occasionally temperature controlled (26), (35), (70), (71).

In most cases the influence of the various substrates was not commented upon. However, it was reported that (72) an improved ordering could be achieved with mica substrates when comparing identical conditions with silicon substrates. The belief is that in this case the wettability of mica provides the optimum solution spreading for their system. It was observed (37) that larger pores were formed when using PVC rather than PMMA substrates with an inferred relationship to the solution/substrate interfacial forces. Water has been used as a liquid substrate on a small number of occasions (68), (73). The most developed of these techniques (68) used the water temperature to control the interfacial energy with the spreading solution, thus controlling the spread and thickness. When liquid substrates are used, the improved spreading leads invariably to thinner films and in both papers the result is in fact an unsupported mesh rather than a standard porous film.

The thickness of a number of substrates has also been explored (71) showing that patterns only formed on chrome steel when the metal was below 100µm in thickness, while on PP, substrates of less than 150µm thickness are required. This is linked to the heat transfer behaviour of thicker substrates. For droplet templating to occur, the evaporation time is required to be much greater than the time required to reach a thermal equilibrium in the solution. It is believed that this is not the case with thicker substrates as the evaporative cooling is not compensated by an external heat flux due to the thermally conductive surface acting as a heat sink. This is not yet fully understood and not fully reconciled with the reported formation of droplet condensation upon external cooling of the substrate (74). Also, a decrease in pore size with an imposed temperature gradient increase of just a few degrees C suggests this is an area where further data is required (70).

Non-planar substrates are also analysed briefly. Tilted samples have been observed to lead to higher energy packing densities (31). The potential to form breath figures across non planar substrates was recently explored by using an anthracene functional star polymer based on poly(methyl acrylate). The low glass transition temperature allowed it to be moulded to the contours in the substrate as seen in Figure 1.2.5.

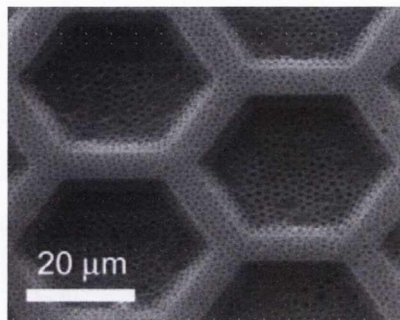


Figure 1.2.5: A scanning electron microscope image of a porous polymer film formed on a hexagonal transition electron microscope (TEM) grid. The polymer is an anthracene functionalised poly(methyl acrylate) star polymer, designed to allow non-planar breath figure formation, (233).

In most reports, the substrate is fixed and the humid atmosphere is either a calm static environment or alternatively delivered as part of a dynamic flow system. Alternatively, the substrate can be included as part of a spin coating mechanism to produce thinner films and more rapid evaporation (29). Ordered porous arrays still occur using this method.

This concludes the review of the initial procedure of dosing a polymer containing solution onto a substrate, the choices that this entails when designing an experiment and some of the trends identified to date regarding the different parameters. The next step to be examined is the solvent evaporation.

1.2.3 Solution Evaporation

The second step, the evaporation of the solvent, is closely linked to later sections covering vapour condensation and non-coalescence phenomena. For clarity this section will look solely at its effect on the surface temperature and the subsequent behaviour of the solution reported in the literature.

The evaporation of the solvent is a non-equilibrium process and in all experimental scenarios studied, the environment never approaches saturation. The drive to evaporate leads to cooling of the remaining bulk as the latent heat of vaporization removes significant energy from the system. Evaporation and the associated temperature change depend not only on the

intermolecular bonds of the solvent, that dictate its vapour pressure, but also on the energy input or the drive to evaporate.

The associated temperature drop is reported in a number of the key papers in the field with values between 25 and 30 degrees quoted as the absolute drop in temperature (32), (36). The evaporation is generally controlled through solvent choice or indirectly through modification of the air-flow (75). To date, there are no detailed reports regarding the effect of a change in airflow on the final film. In a step towards illustrating the air flow effect on solvent evaporation (76) a slight trend is reported showing increased rate of evaporation with increased air flow. It is noted that the unavoidable experimental noise inherent in the set-up obscures clear results. It is reported that the noise is due to the nature of the solvent drying and pinning process as well as differing initial drop-cast loads. Differing drop-cast loads often lead to varying thicknesses and the evaporation rate has indeed been linked to the thickness of the deposited solution (77).

It is reported that the change in volatility has a number of effects on the end result of porous structure. Firstly, lower volatility is reported to lead to larger end pore sizes. This is explained as an extended drying time leading to additional water condensation (78). Conversely, when the volatility is too low, no porous structures can form at all due to the minimal drive for the vapour to cool and condense at the solution/air interface (79). The volatility is also credited with ensuring ordered structure (80). This key report into the mechanism, often cited in the literature, illustrated the ordering mechanism observed in their work, shown in Figure 1.2.6. Convection currents, known as Marangoni convection, remove droplets from the surface and transport them to the edge of the evaporating solution, where they are packed and ordered. Marangoni convection is a circulatory current resulting from differences in surface tension within a liquid.

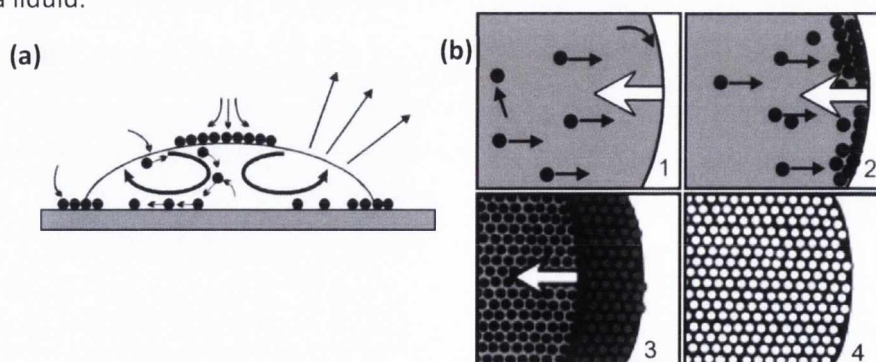


Figure 1.2.6: Illustration of the proposed mechanism of honeycomb structure formation (80) where (a) shows the side view of a dropcast polymer solution illustrating the influence of convection on the water droplets and (b) shows a plan view of the solvent drying and the packing of droplets from the edge back towards the rest of the film.

The difference in surface tension can be driven by variations in temperature, concentration of surfactants or electric fields (81). In this case it is suggested that due to a difference in temperature through solvent loss, the surface tension near the droplet surface is higher than that at the warmer base. This results in a tangential force, which if larger than the viscous forces takes the form of a convection current. These convection currents have been observed by other groups and analysed (82) with the specific application to porous polymer film formation. The conclusion here, based on the work by de Gennes (83), was that the influence of concentration gradients will dominate over temperature gradient-driven Bénard-Marangoni (BM) convection. While alternative methods exist in the literature for droplet formation and templating, it is generally agreed that these currents often exist and are observable in film formation. Their importance is still under scrutiny with regard to droplet ordering and packing as alternative driving forces such as capillary effects, steric repulsions and surface currents are also feasible factors. It should be noted here that an alternative mechanism for pore formation is found in the literature. It is postulated by Bormashenko *et al.* (84) that the pore formation is due to rapid solvent boiling. Rather than water droplets, it is the boiling of the solvent and resulting solvent vapour bubbles that they believe leads to the voids. The sample is dried with a relatively low humidity, fast jet of air while energy is supplied through a heat lamp. The samples and reported behaviours look extremely similar and so some results from this group are included in this review as it is likely that many of the same fundamental mechanisms are at work in both cases.

1.2.4 Condensation of Water

Once the solvent is dosed and evaporative cooling commences, introduction of water vapour to the system is believed by almost all groups to be the crucial step in the next stage of the formation mechanism. The balance of adsorption and re-evaporation of water molecules at the solution surface changes once the temperature of the solvent is reduced to the saturation temperature. The drive towards water condensation in this environment is significant and heterogeneous nucleation is believed the most likely form of its occurrence (85). As in any medium, this initially occurs rapidly in the form of vast numbers of small clusters. It is also reported from both theoretical and experimental results that these clusters grow, under fixed conditions, according to a predictable law, only deviating from the rate law upon coalescence with neighbouring droplets. This is true of both liquid and solid substrates. (15), (17), (19), (22). It is noted that for polymer containing systems, that the growth behaves as predicted for purely intrinsic growth, reflecting the non-coalescence behaviour discussed in more detail in a later section, 1.2.5 (22), (65), (86).

This continuous growth, in the presence of humid air, is believed to be the driving force behind the generally reported trend showing an increase in pore size with an increase in relative humidity or extended exposure to a constant level of supersaturation. This is believed to be due to the growth of the individual water droplets through continued condensation and has been quantified over a range of relative humidities by a number of authors (29), (35), (58), (63), (87)- (89). Two further points are notable from these results. Firstly, the scale of the change in pore size with humidity varies significantly across different reports and secondly, the errors and scatter at each point are very rarely reported but are known to be significant (31).

A detailed analysis regarding the minimum relative humidity required to form breath figures has not been attempted or compiled in the literature. However, it is found when reviewing all work with chloroform that reported minimum humidities where pores could form or form in an ordered manner reveals the “switch-on” humidity is approximately 50% (38), (69), (90). However, there are also other reports that provide values of 30%, 40% and 45% (64), (91), (92). The water soluble solvent, THF has a “switch on” humidity of approximately 40% (29), (53), (35) or 50% (52). However with the addition of water to this solvent it was reduced to 10-14% (29), (93). This complicates the analysis of humidity as the water within the THF is expected to evaporate and re-condense within the boundary layer. Maximum humidities are not generally discussed although it has been noted that extremely high humidities >85% often lead to droplet coalescence and poorly ordered resulting films. The presence of condensed water at the solvent/air interface is visible due to the scattering of light caused by the droplets. This haze is the breath figure formation on a liquid surface. Scattering of light caused by the final polymeric microstructure leads to the white colour observed in porous films, while non-porous films of the same material are transparent (90). These final, porous films are also observed to be iridescent, again due to the scattering and interference caused by the microstructure (40).

The combined parameters of solution concentration and humidity level of the environment are believed to be important. If the polymer concentration is too high, the droplets are not allowed to enter the interface due to the increased viscosity and the evaporative cooling is also adversely affected. If the concentration is too low, the water will not be stabilised by the polymer and an increase in coalescence results.

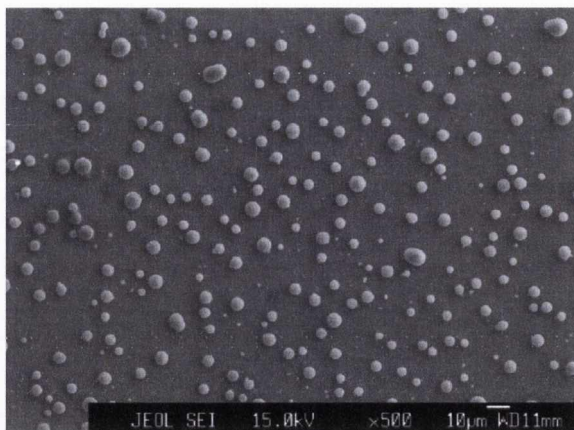


Figure 1.2.7: Scanning electron microscope image of a star-shaped poly(styrene-block-butadiene) four-arm copolymer with polybutadiene as the inner block, dropcast in toluene in a 98% molar percentage methanol in water vapour atmosphere. Known as the “reverse breath figure method”, this leads to spherical particle formation at the surface (94).

It is worth noting that a recent paper exhibited the successful introduction of a methanol vapour, rather than water vapour. This led to disordered microsphere patterns forming instead of pores (94). This inverse system is believed to be due to the high surface energy of the polymer solution compared with the condensing fluid leading to a reduction of the polymer surface area through microsphere formation, shown in Figure 1.2.7. This is an interesting area that has not yet been fully explored.

1.2.5 Droplet Packing

Once evaporative cooling and water droplet growth has occurred, the close packing of liquid droplets at a liquid/air interface becomes the central issue in successful breath figure templating. The reduction in droplet coalescence is influenced by choosing adequate drop volumes, concentrations, and humidities as mentioned previously. Looking at the phenomenon in more detail, the delayed coalescence is observed when droplets interact with a slow draining of the interstitial fluid, in this case the polymer/solvent solution (15) - (17), (22). A second method of non-coalescence referenced in this field (32) is thermocapillary motion of the water droplet, driving the neighbouring fluid to act as a lubricant (95). It has been reported that droplets can be kept apart by a film of evaporative vapour from a volatile solvent (96) as well as by air (97).

However, significantly delayed non-coalescence is only observed with the inclusion of an additional stabilising component. Polymers designed to adsorb or precipitate at the water/solvent interface are believed by most reports to be the reason this non-coalescence occurs, as pioneered by Pitois *et al.* (26).

It is presented in (26) and developed further in (40), (36) that non-coalescence through polymer stabilisation can occur through a number of means. Firstly, it could occur due to either the surface acting components adsorbing at the water interface, as discussed earlier, or secondly by polymer precipitation at the interface. In either case the polymer or the stabilising surfactant is assumed to lead to hard-sphere repulsion due to steric interactions between droplets. Thirdly, non surface-active polymers may lead to a similar effect when rapid evaporation reduces the time available for the droplets to coalesce, trapping the small droplets in the polymer, such as in reports where linear non-functionalised polystyrene is used (35), (38), (44) - (46). The presence of polymer at the droplet interface is supported by macroscale observations, where large submerged drops induce significant polymer precipitation and also large protruding droplets show polymer migration leading to a thin polymer film coating the surface of a water drop apparently without inhibiting further droplet growth. This appears to be transferrable to the micro droplet scenario, as seen by (26) and (98). Trapped pores appear to be covered with a thin film of polymer that either burst while drying or during later imaging by atomic force microscopy (99).

Stabilised droplets are observed in emulsions to still coalesce by a number of complex mechanisms over time and so limiting the drying time in the case of breath figures is also important to minimise the time where there is a risk of coalescence. Alternative views (32) based on optical microscopy observations, suggest a lubricating evaporative flow levitating the droplets, coupled with a surface tension induced thermocapillary convection in the water droplet is a more likely root of the non-coalescence.

The driving force behind the ordering of the droplets is also not completely decided. The surface deformability is suggested as the origin of an induced capillary force, leading to aggregating water droplets (16). An alternative view is that the combination of air currents at the solution/air interface and surface currents induced by convective flow in the solution lead to packing of the droplets (32). In this case a minimum energy packing arrangement is reached once non-coalescent behaviour continues to function.

The subsurface packing or multi-layered porous film observations were mentioned earlier when looking at the role of the solvent in determining their presence. An alternative "packing" approach is also put forward (32) based on both *in-situ* observation and final film structure. Following on from the thermocapillary convection argument for levitating, non-coalescing drops, upon collapse of this convection due to temperature equilibration, the droplets sink

allowing further droplets to nucleate, grow and order. The sinking water droplet is expected to act as a trail for the next set leading to the observed structures of multi-layered ordering pores.

1.2.6 Application Specific Treatments or Processes

A number of more recent papers have moved away from exploring the mechanistic aspects of the film formation and towards designing materials that are more applicable to specific problems. Some of the processes used and the related results are pictured in Figure 1.2.8 and summarised below:

- (a) The porous films are themselves used as moulds for PDMS stamp forming. The original sample is heated, stretched and then imprinted with PDMS to form microlens arrays (100).
- (b) Controlled shrinking of the porous films has also been used to alter or miniaturise the pores. The example shown has changed circular surface pores to elongated structures (101).
- (c) The breath figure technique can be used to create a thin mesh of nanocrystals, in this case Ag-CoO (102).
- (d) There is interest in the hydrophobic nature of the patterned film. This can be further enhanced, when there are interconnected pores, through peeling off the upper layer to reveal an array of pillars (43). This superhydrophobic surface has been modified further through electrolysis (103).
- (e) Hierarchical ordering has been developed, with one recent example a BCP phase separation within the internal pore structure (62).
- (f) Porous films, crosslinked to withstand high temperature, have been used as a substrate to add control to CVD growth of carbon nanotubes (104).

This section has summarised the important and most recent developments in the field of breath figure (or water droplet) templating of polymer films. It is clear from this review that it would be of great benefit to the field to improve the understanding of the formation mechanism of this technique and the extent to which microstructure can be controlled. There are a range of interdependent, complex mechanisms involved and so, firstly, the equilibrium force balance that allows the stable existence of water droplets at a solvent/air interface will be examined in Chapters 2 and 3.

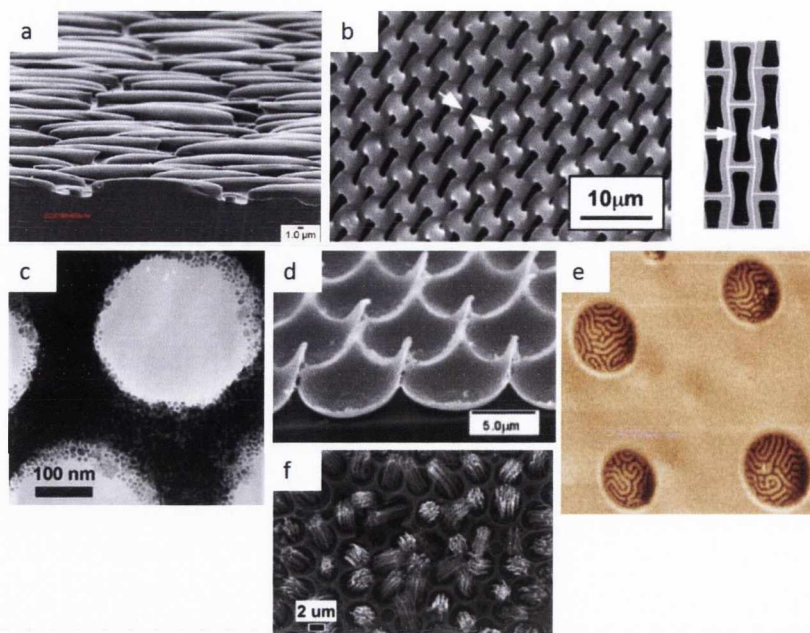


Figure 1.2.8: Examples from the literature that focus on application specific developments of the self organised polymer structures. (a) SEM image of a cross-section of an anamorphic microlens array film formed using the porous structures as a mold for a polycarbonate type copolymer containing PDMS(100), (b) SEM image and lattice model of a poly(buta-1,2-diene) structured film, formed by water templating and modified using a controlled film shrinking technique (177), (c) TEM image of a self-assembled Ag-CoO nanocrystal architecture formed using water droplet templating (102), (d) SEM image of silver pincushion structure formed by electroless deposition onto pillars formed from water droplet templating to give a superhydrophobic surface (103), (e) AFM image ($3\mu\text{m} \times 3\mu\text{m}$ scan) of internal structure of pores formed with water droplet templating and annealing technique using $\text{PS}_{5\text{F}_{21}}\text{-}b\text{-PS}_{31}\text{-}b\text{-PPEGMA}_{38}$ (62), (f) SEM image of carbon nanotubes forming circular pillars growing from the honeycomb microstructure made from polystyrene-*b*-poly(acrylic acid) diblock copolymer and ferrocene in a carbon disulphide solution (104).

Subsequently, in Chapters 4 and 5 the focus will shift to their understanding of dynamic behaviours involved in the self-organisation process. This will look at the role of the environmental conditions during the formation of a polymer microstructure and their effect on the solvent evaporation, solution temperature, water condensation and the evolution of polymer viscosity. Prior to this, Section 1.3 will detail the techniques, materials and software employed during the analysis.

1.3 Analysis Techniques and Materials

This section firstly describes the range of measurement and analysis techniques employed throughout this thesis. Each apparatus and technique will be introduced and the principles of its operation very briefly described. If sample preparation is known to be an influencing factor

for a particular technique, a detailed procedure for preparation is also included. This first part is divided between techniques which were developed and/or carried out by the author and techniques which were carried out by a third party. Secondly, a list is provided of the key chemicals used, their specifications and sources. Material properties are tabulated and included in Appendix 1.1.

1.3.1 Measurement and Analysis Techniques – Part 1

1.3.1.1 Upright Reflection Optical Microscopy

A range of upright reflection optical microscopes were employed (shown in Figure 1.3.2, with specifications in Table 1.3.1) for different analytical purposes throughout this thesis and are detailed in this sub-section. This is a basic analytical technique but one of the most commonly used in the literature for analysing porous polymer films both qualitatively and quantitatively. The samples were adhered to a glass substrate as part of the formation process and so were relatively flat, corresponding to the horizontal focal plane. The sample features, when viewed from above, are on the micron scale and within the resolution limits. However, an additional requirement for optical microscopy is that the samples must reflect a significant proportion of the incident light but the polymer samples are quite optically transparent. For this reason the results are split between bright-field reflection and dark-field reflection modes, as described below and illustrated in Figure 1.3.1 (105).

- (i) Bright field reflection is a standard technique, employing epi-illumination through the objective lens, uniformly illuminating and focusing on the sample. All reflected and scattered light returns back through the objective.
- (ii) Dark field microscopy is employed to improve contrast of the features with their surroundings or background. It differs from the bright field mode in that a hollow cone of light is instead produced, as shown in Figure 1.3.1, and this is focused on the sample from a highly oblique angle. This ensures that only light scattered by the sample returns through the objective and so features are clearly distinguished from a surrounding flat region.

Figure 1.3.2 shows the three optical microscope systems employed for the work reported in this thesis. Table 1.3.1 details the model and specifications of each microscope.

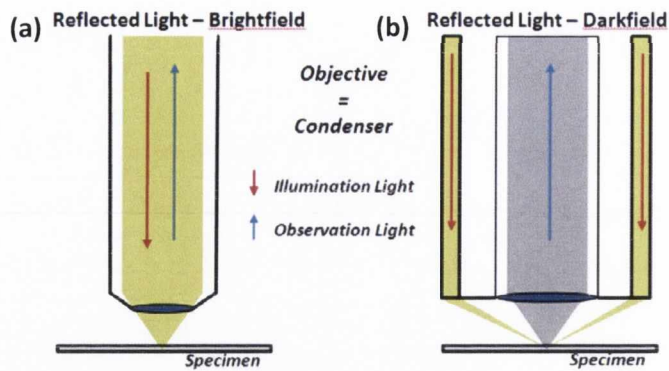


Figure 1.3.1: Illustration of the different paths of illumination and reflection used in the upright reflection microscopes for (a) brightfield mode and (b) darkfield mode of operation (105).

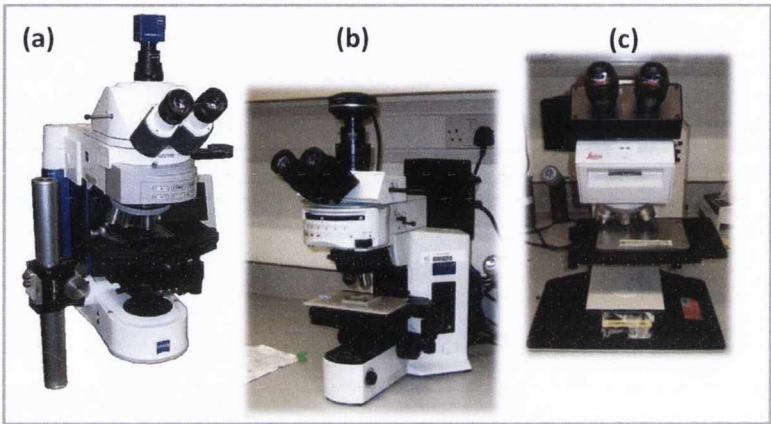


Figure 1.3.2: Photographs of the three different optical microscopes referred to within the reported work, namely (a) Zeiss Axiolmager X10, (b) Olympus BX51M, (c) Leica Microsystems DMR HC.

Microscope Name and Model	Olympus BX51M	Zeiss Axiolmager X10	Leica Microsystems DMR HC
Light Source	Mercury Burner	Mercury Burner	Unknown
Objectives	x5, x10, x20, x50, x100	x5, x10, x50	x5, x10, x20, x50, x100
CCD Camera	Olympus XM10	AxioCam ICc 1	None
- Resolution	1.4 megapixel	1.4 megapixel	N/A
Modes Used	Brightfield	Brightfield, Darkfield	Brightfield, Darkfield
Other Uses	1. Live Imaging of water droplet formation and ordering 2. Imaging manual dosing of nanolitre drops	1. Quantitative analysis of flat porous polymer films. 2. Qualitative analysis of film cross sections. 3. Extended focus imaging of indented films. 4. Imaging while manipulating microsphere positions on porous surface	Rapid, qualitative analysis of polymer film surface and internal microstructure

Table 1.3.1: Specifications of each optical microscope used and summary of key modes of use within this thesis.

Sample Preparation Procedures:

No preparation is required with optical microscopy when viewing a flat sample. The polymer films were formed on a flat glass surface, ideal for transferring to a microscope stage. Cross-sectional viewing was achieved using the breaking technique described in the upcoming electron microscopy section. The cross-section of interest was then placed in between two 5mm diameter glass slides, with the edge extending between them. This was mounted at 90° allowing imaging of the cross-section.

1.3.1.2 Scanning Electron Microscopy (SEM)

Scanning electron microscopy is the main tool used in this thesis to closely observe the polymer film microstructure and will be introduced briefly before listing the microscopes, specifications and sample preparation technique. The tools used for this thesis are detailed along with their specifications in Table 1.3.2.

Microscope Name and Model	Carl Zeiss SMT Ltd., EVO® Series SEM	Carl Zeiss SMT Ltd., ULTRA® Series SEM	FEI Strata Dual Beam FIB
Emission Type	Thermionic	Thermal field	Field
Magnification	7 - 1,000,000x	12 - 1,000,000x	Search Mode - Up to 500,000x Ultra High Resolution Mode - Up to 2,500,000x
Detectors Used	Everhart-Thornley SE2	EsB, InLens, Everhart-Thornley SE2	Everhart-Thornley SE2
Resolution	3nm at 30kV 10nm at 3kV	0.8nm at 15kV 1.6nm at 1kV	3nm - Electron Beam 7nm - Ion Beam

Table 1.3.2: Specifications of each scanning electron microscope used within this thesis.

This microscope emits and accelerates electrons from an electron gun, focuses and then raster scans them across a sample surface. The electron beam is created through either:

- (i) Thermionic emission, where a filament (tungsten or lanthanum hexaboride) is heated to the extent that electrons are freed and emitted;
- (ii) Field emission, where a sufficient electric field is applied to drive electrons out of a tungsten tip;
- (iii) Thermal field emission, which heats a Zirconium/Tungsten tip sufficiently to allow the diffusion of Zirconium Oxide to the end of the tip where field emission can be induced through an electric field.

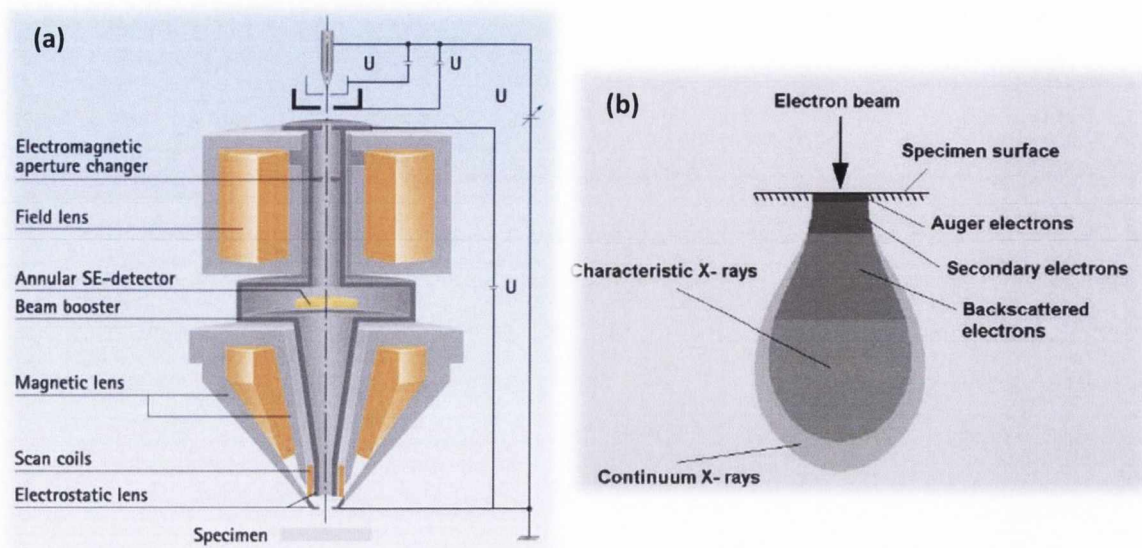


Figure 1.3.3: (a) Diagram of a column within a scanning electron microscope, highlighting the key components, (b) Interaction volume of an incident electron (106) beam during scanning electron microscopy.

The beam is focused using a series of electromagnetic lenses and scanned using the scan coils indicated in Figure 1.3.3(a). The electrons penetrate the sample surface and occupy a calculable interaction volume, as shown in Figure 1.3.3(b). A number of different effects may then occur. The incident electron can undergo sufficient scattering such that it nears an angle of 180° to its incident approach and leaves the sample. These are known as backscattered electrons and generally have energies between that of the incident beam and 50 eV (106). The yield depends significantly on the atomic number of the specimen (with higher atomic number elements leading to more significant scattering), thus allowing atomic number contrast imaging. Alternatively, the incident electrons can pass into the sample and undergo inelastic scattering with the atomic electrons. If sufficient energy is passed to these electrons they can overcome the local work function and escape as secondary electrons (SE1 type). SE2 secondary electrons can also be generated by inelastic scattering caused by backscattered electrons. Each type of secondary electron can be targeted by a specific detector, which then accelerates them towards a scintillator. The flashes of the scintillator are directed to a photomultiplier. The raster scanning of the beam allows an image to be rapidly constructed and interpreted by the attached computer. The SE1 type carries the high resolution data as they occur close to the sample interface. Finally, also indicated in Figure 1.3.3(b), X-Rays are emitted from the sample when the incident electron beam collides with and ejects a core electron from an atom. The decay of the atom to its ground state emits a characteristic signal, allowing spectra and

elemental analysis (107) using a technique known as energy-dispersive X-ray spectroscopy (EDX).

An SE2 detector collects secondary electrons and backscattered electrons, whereas an InLens detector can selectively collect only secondary electrons, thus improving the proportion of surface relevant information. A backscatter detector selectively collects the backscattered electrons, while a spectrometer analyses the emitted X-Rays. When working with electrically insulating polymer films, electron beam methods can not normally yield useful results as the incident beam energy builds up in the form of electrostatic charge on the sample and disrupts imaging. To avoid this, the sample of interest is coated in a thin layer of conductive material, as discussed later in this section.

Sample Preparation Procedures:

For optimum imaging of the polymer substrates, the following preparation technique was developed. The porous polymer film, attached to a glass substrate, was cut using a sharp blade wet with clean water. Alternatively a cut sample was dipped in clean water. The film then easily delaminated from the surface with minimum resulting mechanical effects such as cracking or stretching. The use of water has not shown any physical impact on the substrate when compared with a dry technique. The sample was laid upside down over two clean microscope cover slides, fitted approximately 1-2 mm apart over a clean, lint-free cloth. Clamping the film gently from above with two further clean glass slides, the sharp blade was brought down in a level manner to snap (rather than shear) the film. This led to reproducibly clean cross-sections. The pressure on the film from the slides has not shown any significant effect on the polymer film, other than at the edges where some deformation occurs and so these areas are avoided for future study.

To ensure charging does not affect electron beam imaging, the following procedure was developed. A metal disc was adhered to a stainless steel SEM pin-stub using a conductive silver paste. On evaporation of the paint's solvent, this led to a stiff bond. A disc of carbon based, electrically conductive, double-sided adhesive was attached to the disc. The polymer sample was carefully laid on the upper surface of this adhesive, with the edge of the polymer as close to the edge of the disc as possible, while still being supported by it. An illustration is supplied in Figure 1.3.4.

The adhesive disc was necessary as solvents from alternative fixing techniques may affect the film's microstructure. The edge furthest from the part of the sample of interest was then dabbed with a fine line of the same silver paste. This ensured a conductive path from the surface of the polymer to the conductive glue, which was well grounded to the SEM stub. This arrangement allowed for easy transfer of samples to a cross-section holder, as the metal disc could be removed from the stub using a sharp blade. Metal deposition coating is described later in this chapter and is the final step in preparing the sample.

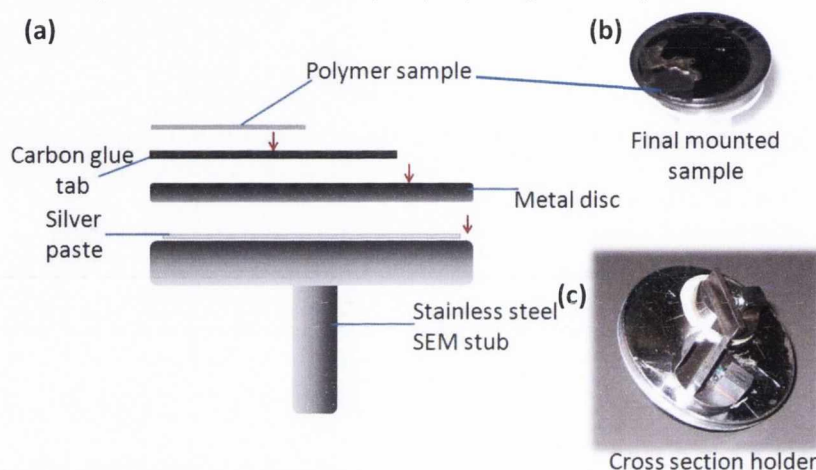


Figure 1.3.4: (a) Diagram of sample preparation for SEM analysis detailing the layers required to ensure a stable, conductive sample (b) Example of a prepared sample showing a polymer film coated in palladium attached to a metal disc using a carbon adhesive tab. The disk in turn is attached by conductive paint to the SEM stub, (c) An SEM stub with two cross-section holders attached for viewing the samples at 90° to the plane.

1.3.1.3 Focused Ion Beam (FIB)

A novel approach to cross-section analysis of the polymer microstructure was developed using the FEI Strata 235 Dual Beam focused ion beam microscope, shown in Figure 1.3.5(a). This tool houses a vertically mounted field emission scanning electron microscope and an ion beam column mounted at 52° with a tilt stage that can move accordingly to ensure a normal angle to the sample. A liquid metal ion source (LMIS) of Gallium positioned in the ion beam column also has an attached tungsten needle, which it wets when heated as shown in Figure 1.3.5(b). This forms a point ion source on application of an electric field (108). The ions are then accelerated to an energy of 30 keV and focused through electrostatic lenses to a beam diameter of approximately 10nm. Detectors can be chosen to pick up either the secondary ions or secondary electrons emitted to produce an image.

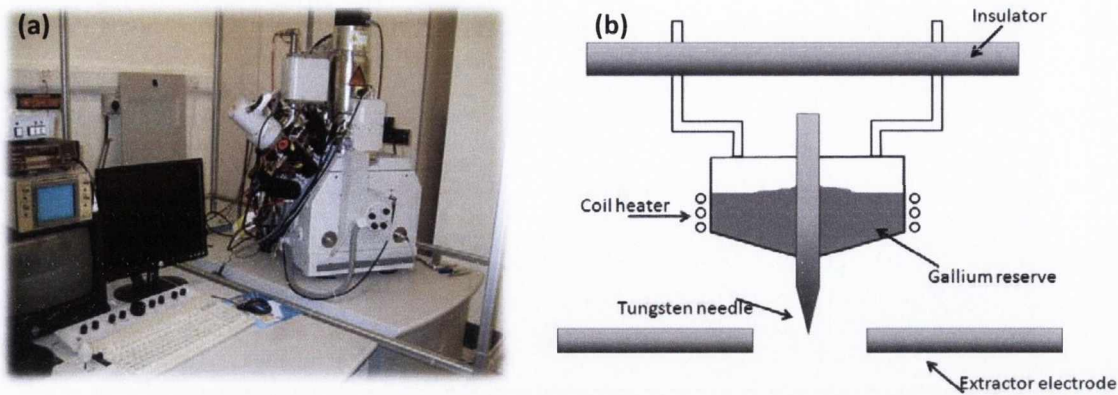


Figure 1.3.5: (a) Image of the FEI Strata 235 dual-beam microscope and work station (108) (b) Diagram of the gallium liquid ion source and housing, the tungsten tip and set up to eject ions towards the sample.

A LMIS of Gallium positioned in the ion beam column also has an attached tungsten needle, which it wets when heated as shown in Figure 1.3.5(b). This forms a point ion source on application of an electric field (108). The ions are then accelerated to an energy of 30 keV and focused through electrostatic lenses to a beam diameter of approximately 10 nm. Detectors can be chosen to pick up either the secondary ions or secondary electrons emitted to produce an image.

The incident beam of ions contains enough energy and mass that it can displace and eject atoms from the specimen, leading to highly controlled erosion or milling of the surface. Both the beam diameter and the range within the sample where the spreading energy has an impact are affected by the ion beam current. This is a key parameter in defining the resolution, quantity and rate of milling as well as controlling the amount of re-deposition of milled material.

Sample Preparation Procedures:

The polymer sample was prepared using the same method as described for the electron microscopy preparation and placed in the vacuum chamber of the FIB. The eucentric height and dual beam alignments were carefully set so that easy transition could occur between the horizontal electron beam imaging and the 52° tilted ion beam imaging and milling.

Due to the sensitivity of the polymer to the ion beam all alignment of beams greater than 30pA was carried out on a separate area from that used for analysis. This careful alignment ensured that using the electron beam alone, the sample could be positioned at the area to cross-section very accurately. A beam current of 30 pA or less (depending on the delicacy of the sample) was used to complete a rapid, low resolution scan of the area. Fine tuning of the

locations of the higher beam currents were carried out using this initial scan, aligning features around the area of interest with a reduced scan area.

It was found that the fine-polishing line-scan milling method must be used when removing areas of the polymer films. The standard FIB method of step milling through rapid raster scans did not lead to clean cross-sections and instead appeared to increase re-deposition of material inside the pores of interest. Working in from the edge of the polymer film, the fine polishing mill was carried out at high currents 1-3 nA initially. This was used to clear away the edges of the film and approach the pores of interest. The same fine polishing scan was then steadily used at decreasing currents as the beam gets closer to the pores of interest. For standard cross-section preparation this would normally be 300 pA, reducing to 100 pA and then 30 pA. For fine milling 1-10 pA milling was carried out. The key development of this technique that allowed accurate viewing of the pores was the careful low beam current milling used before the edge of the pore is milled. Milling into the pores at higher rates led to re-deposition that is clearly visible at the pore walls, thus obscuring the detailed microstructure. Also, it was found that the minimisation of the mill depth is important. Milling the porous walls removed a relatively small volume of polymer compared with the non-porous layer beneath. Extremely slow mills were also avoided as the slight drift in the soft sample over time led to poor control of the final cut.

1.3.1.4 Atomic Force Microscopy (AFM)

A Dimension 3100 atomic force microscope (AFM) was used during this study. As part of the analysis towards this thesis, AFM has been used occasionally to analyse the surface of polymer films. This is a surface probing technique that yields three-dimensional topographical information about the samples. As seen in Figure 1.3.6, a sharp probe at the end of a cantilever is used to probe the surface, positioned slightly above the interface using a piezocrystal. The probe, made from silicon nitride in our case, is line-scanned across the sample, each line undergoing a trace and re-trace scan. In contact mode the cantilever is deflected from a user-defined set point due to surface topography. This deflection is recorded by a laser beam, aligned to reflect off the back of the cantilever, onto the photodetector. The combination of signals from the four quadrants allows information about the vertical and torsional forces to be calculated and fed back to the AFM head Z-piezo to compensate for the height change and maintain the chosen tip-deflection. This forms a high resolution three dimensional image of the surface of the substrate. The AC mode (also referred to as Tapping Mode) oscillates the cantilever at its resonant frequency. The deflection of the laser mimics this oscillation and on

encountering a feature, both change accordingly. The feedback maintains the resonant frequency oscillation by moving the Z-piezo as before and mapping out the topography of the surface (109).

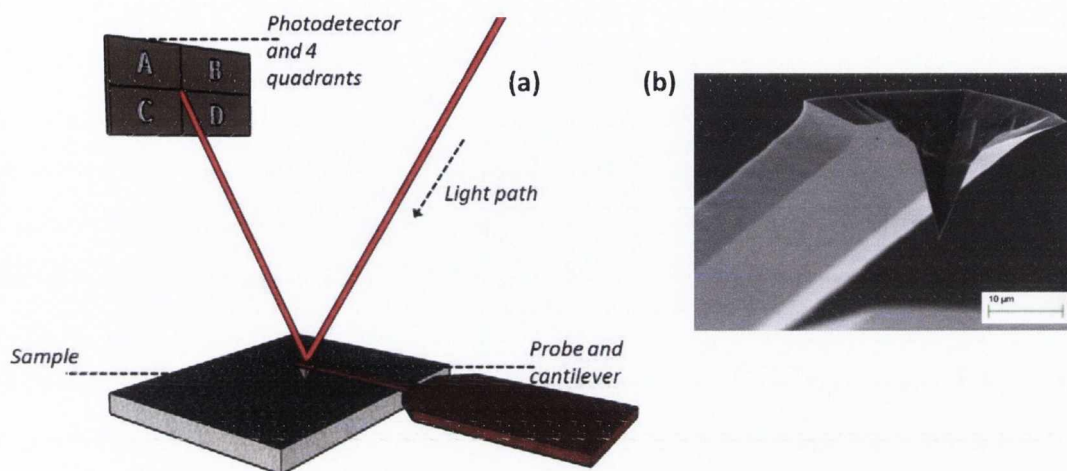


Figure 1.3.6: (a) Illustration of the principle of AFM showing the cantilever and probe, the laser and photodetector. As discussed in the text, a feedback exists between the photodetector signal and the piezo that controls the AFM tip motion. (b) SEM image of an AFM tip showing the sharp tip that contacts the surface of interest.

1.3.1.5 Sputter Coating

A Cressington Sputter Coater, Model 208HR was used to coat a thin layer of metal onto the polymer samples, providing the conductive surface required to allow high resolution electron beam imaging. The positive argon ion plasma is generated under a direct current potential between the substrate and the target. Similar to the ion beam milling principle, argon ions are now accelerated towards the metal target and displace metal atoms which are deposited on the samples.

Procedure:

The polymer samples were prepared on SEM stubs as described earlier. These fit into the stub holders in the Cressington chamber. The stage was tilted to approximately 45° to ensure an even coverage of the edges, where the bulk of analysis takes place. The stage was also set to rotate to ensure even coverage of all samples. The density of the material to be sputtered, the appropriate current and tooling factors were set, based on values provided by the tool owner. Standard procedures were followed to pump down the chamber to a vacuum below 0.01 mbar. The chamber was flushed through with Argon three to four times to ensure it was the main component present in the gas phase. Argon was leaked into the chamber at a pressure of

0.02 mbar before striking the plasma. As some metals have a thin oxide layer, the blanking disc was left closed for a short period to check if metal was deposited at the expected rate before proceeding with the coating. The quartz crystal monitor positioned in the chamber next to the stage was used in conjunction with the provided density and tooling factor to estimate the thickness of the resulting film. Once the procedure was complete the chamber was allowed to pump to the maximum vacuum value again while the target cools, at which point venting to nitrogen commenced. Conductive layers of silver, platinum/palladium alloys or pure palladium were used to coat polymer films and ensure imaging was possible by electron microscopy during this thesis. However, palladium was used for the majority of the time at a setting of 80mA and tooling factor of 1.4. The Cressington sputter coater was added to the equipment inventory during the course of the work for this thesis. It coincided with the move to higher resolution imaging. Prior to this, sputter deposition was carried out using an older tool but based on the same principles.

1.3.1.6 Oxygen Plasma Sample Cleaning

The Diener Pico Plasma Cleaner generates a plasma within a chamber from either oxygen or a mixture of oxygen and methane gases. Its main applications include removing resists in silicon processing, activation, cleaning and etching surfaces. For our purposes only oxygen is used. Our application in this case is purely to assist cleaning of the surface of a glass cover slip by ionising the supplied oxygen and allowing the ions and radicals to react with organic contaminants on the surface. This is a standard technique in SEM and STM chamber cleaning.

Procedure:

The glass substrates to be cleaned are very thin and light. To ensure they were not affected by the air flow in the chamber during the venting procedure they were mounted on heavier glass slides using a small piece of double sided vacuum compatible Kapton tape. They were attached only on the underside, to ensure the edges and upper face remains free of any trace amounts of adhesive.

These slides and their mounted glass substrates were positioned 2-3 cm from the outer edge of the internal plate. The position was not essential to the cleaning process but ensured reproducibility between samples. The standard operating procedure was then followed to pump the chamber to an operating pressure of 0.12 mbar before leaking in the oxygen. For this cleaning procedure an oxygen pressure of 0.25 mbar was used. This leaking was allowed to

continue for 2-3 minutes to ensure the chamber was almost free of nitrogen, which disrupted the efficiency of the oxygen plasma cleaning process. The plasma was struck and allowed to react with the samples for 6 minutes. 3 minutes was seen to be sufficient but a standard time of 6 minutes was used in case the initial plasma was not as pure as predicted. Once complete, the chamber was vented to nitrogen and the samples removed from the chamber and removed from their mounting using clean flat nose tweezers. A careful twisting motion removed the thin substrates without breaking. The samples were sealed in a pre-cleaned Fluoroware container until required. The tool was located in a Class 10,000 clean room and so removal and handling of the samples incorporated minimal contamination.

1.3.1.7 Nano Indenter

Nanoindentation was carried out using a MTS Nano Indenter XP. This tool was used to analyse the mechanical properties of the polymer films. A tip of well-defined nano or micron scale features was used for highly controlled indentation. This produced force-displacement curves for the material, used to calculate stiffness, hardness and elasticity values for the material as discussed in Chapter 6. Figure 1.3.7 shows an illustration of the key components of the indenter where an electric current running through a coil/magnet assembly induces a vertical movement with a force proportional to the current. This movement is registered to an accuracy shown in the specifications in Table 1.3.3, using a capacitance gauge which registers the relative movement of plates. The Continuous Stiffness Mode (CSM) oscillates the loading signal very slightly. The response can be interpreted to give continuous stiffness, hardness and elasticity measurements as the probe progresses through the film. This is essential for porous polymer films whose microstructure alters with distance from the surface.

Procedures:

The procedures and tips used for nanoindentation in this work are dealt with in Chapter 6 as they are an integral part of the experimental development. Sample preparation however is common across experiments. The polymer films were not removed from the thin glass coverslips upon which they are formed. This is due to the difficulty in re-attaching the sample without damaging its structure. The sample must be mounted on the metal stubs indicated in Figure 1.3.7. These were inserted and secured in the nanoindenter stage. It is essential in mechanical testing that the method of adhering the specimen to the stub does not interfere with the results. The stiffness value of the adhesive must be significantly higher than that of the material being tested. Normally samples were attached using a crystallising bonding agent.

The metal stub is heated to 130° Celsius at which temperature the glue stick can be applied to the surface.

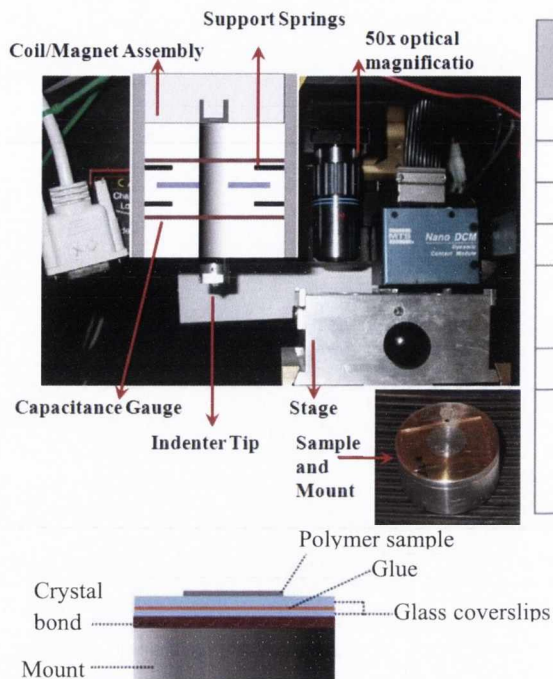


Figure 1.3.7: Combined image and diagram showing the key components of the nanoindenter and sample mounting. (Diagram of nanoindenter reproduced from MTS Nano Indenter XP User Manual)

MTS Nano Indenter System Specifications	
Displacement resolution	< 0.01 nm
Maximum indentation depth	> 500 μm
Load application	Coil / magnet assembly
Displacement measurement	Capacitance gauge
Maximum load capability	500 mN (50.8 g)
- with high load option	1 kg
Load resolution	50 nN (5.1 g)
Microscope	
Objective	x25 objective mag
Video Screen	x50 mag

Table 1.3.3: Specifications of nanoindentation device used within this thesis. (Table reproduced from MTS Nano Indenter XP User Manual)

The sample was attached to the stub and weighted to ensure a good bond while the glue was cooled slowly to ensure a stiff, crystallised bond. The polymer films could not be raised to such temperatures and so this method was used to attach a clean glass substrate. Once cooled a standard adhesive that sets at room temperature was used to attach the sample (a glass coverslip with attached polymer film) to the clean substrate. This is left to cure overnight. This glue crosslinks sufficiently that it is extremely stiff when compared with the sample and so allows relevant indentation results. Formation of the samples directly onto a pre-prepared stub and film was also used but due to the thermal conductivity of the stub, the pore formation mechanism was not representative of standard pores formed under those techniques. Once the sample was mounted and securely positioned in the stage, the alignment and indentation could commence. These procedures are discussed as part of Chapter 6.1.

1.3.1.8 Helium Ion Microscope

The Helium Ion microscope operates in a very similar manner to the scanning electron microscope however the secondary electrons are excited through probing with an incident

helium ion beam rather than an electron beam. This technique is to image samples with very low values of electrical conductivity, where high resolution and a large depth of focus are required. As shown in Figure 1.3.8, a helium gas is located in a cryogenic chamber where an ultra sharp tip is kept under a strong bias. The bias ensures ionisation at the tip, which can then be accelerated towards the specimen using similar lens systems as the focussed ion beam microscope discussed earlier.

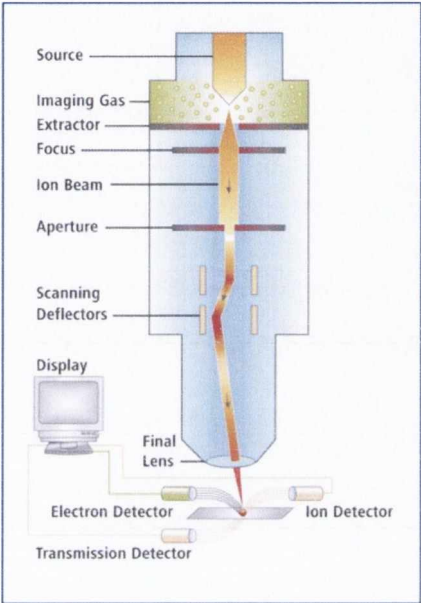


Figure 1.3.8: Diagram of a column within a scanning helium ion microscope, highlighting the key components (229).

Specification	Orion Plus
Resolution	$\leq 0.75\text{ nm}$
Accelerating Voltage	$\pm 30\text{ kV}$
Ion Beam	Range: 1fA - 100 pA
Ion source	Helium Gas Field Ion Source
Image Detectors	Everhart-Thornley, Microchannel Plate

Table 1.3.4: Specifications of the helium ion microscope used within this thesis.

The probe size and the interaction volume of the incident ion are smaller and narrower than electron beam methods, leading to surface sensitive images. An incident electron beam is used in conjunction with the helium ion beam to compensate for any build up of charge, thus removing the need for a conductive layer on an insulating sample. Sample preparation for the helium ion microscope is identical to that described for the electron microscope. The step involving application of a thin conductive coating can be omitted due to the charge compensation techniques available with this tool. Additional care is required during preparation to avoid all forms of contamination, to which this tool is especially sensitive.

1.3.2 Measurement and Analysis Techniques – Part 2

A number of tools operated by third parties were used during the work described within this thesis. They are as follows:

1.3.2.1 Combined AFM/ Raman Microscopy

Raman mapping measurements were collected at room temperature using RENISHAW in-Via Raman system coupled with CCD camera. An excitation laser source of wavelength 514 nm

was used with 2 mW power. A grating of 1800 lines/mm was used to provide a spectral resolution of approximately 1 cm⁻¹. Raman maps were taken with 1 second of exposure time, with one accumulation and the total number of points set at 60x60. The data was collected and analyzed with Wire 3.1 and NT-MDT Nova software.

AFM topographic images were collected in semi-contact mode with an NT-MDT inverted configuration system. Silicon tips with reflectance gold coated on the reverse side were used. These had a tip apex radius of 10 nm, a force of constant 2 N/m and a frequency of 170 kHz. The data was collected and analysed with NT-MDT Nova software.

1.3.2.2 Fluorescent and Confocal Microscopy

Fluorescent confocal microscopy discussed in conjunction with the collaboration in Section 6.2 was carried out using the Carl Zeiss Axiovert system and Zeiss LSM image software.

1.3.2.3 Eden250™ 3D Printing System

This high-resolution, three dimensional polymer printing system is used to produce the components for the experimental flow chamber detailed in Chapters 4 and 5. It has a printing resolution of: 42 µm in the X-axis, 84 µm in the Y-axis and 16 µm in the Z-axis.

1.3.3 In-situ Measurement Tools

This section lists the key tools shared across a number of experimental procedures detailed throughout this discourse. The make, model, usage and specifications are listed in Table 1.3.5.

Purpose of Tool	Measurent of Relative Humidity and Temperature of Chamber and Lab Environment	Evaporating Solution Temperature Measurement	Evaporating Solution Mass Loss Measurement
Make and Model No.	Rotronic HygroLog NT2-D	Home built thermocouple with National Instruments data logging system	Adventurer Pro MicroBalance
Key Details and Specifications	1. Operating Conditions: 0-100 %RH / -30 to 70 °C 2. Data Logging at 1 reading per 5 seconds. 3. Accuracy: +/- 1.5% RH, +/- 0.2 °C	1. OHAUS Precision fine wire thermocouples, CHAL-001 2. Fine thermocouples spot-welded to standard type K thermocouple and adapted BNC connection 3. National Instruments instrument box 4. National Instruments LabView Version 7	Readability: 0.0001g Output to computer: 1 reading every 1 second.

Table 1.3.5: Details regarding measurement of humidity, temperature and mass during the formation of porous structures.

1.3.4 Software for Data Analysis

Throughout this thesis, graphs of experimental data were plotted using Microsoft Excel and Mathematica Version 7.0, Wolfram Research Inc. Modelling the behaviour of water droplets at a solvent/air interface and the influence of line tension in Chapter 2 was carried out using Mathematica Version 7.0, Wolfram Research Inc.

Image analysis was carried out on both SEM and optical microscopy images using ImageJ (160), using either direct measurement techniques or a built-in particle analysis routine.

1.3.5 Materials

(a) Water

De-ionised and filtered water is used for breath figure formation. Ultra-pure MilliQ water is used for manual dosing experiments in Chapter 3.

(b) Polymer

The polymer used to study the formation of ordered microstructures through water droplet templating is detailed in Figure 1.3.9.

Name: α , ω Dicarboxy terminated Polystyrene (DCPS),

Description: $M_n = 93.8 \times 10^3$ g/mol, $M_w/M_n = 1.07$

Source: Polymer Source

CAS#: 9 003-53-6

The supplier's information, including size exclusion chromatography results, differential scanning calorimetry results and manufacturing process steps are included in Appendix 1.2.

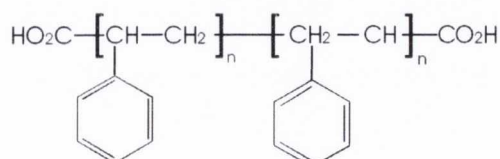


Figure 1.3.9: α , ω Dicarboxy-terminated Polystyrene (228)

(c) Solvent

The four solvents used as part of this thesis are chloroform, toluene, dichloromethane and butyl acetate. The grade, source and chemical structure are detailed in Figure 1.3.10. Key physical properties of these solvents, relevant to this thesis, are tabulated in Appendix 1.1.

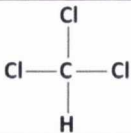
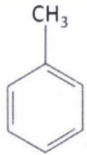
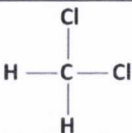
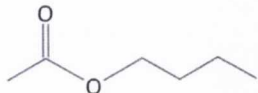
1. Chloroform for spectroscopy, Uvasol, ≥99% Merck	 <chem>ClC(Cl)(Cl)H</chem>
2. Toluene puriss., absolute, over molecular sieve (H ₂ O ≤0.005%), ≥99.7% (GC), Sigma Aldrich	 <chem>Cc1ccccc1</chem>
3. Dichloromethane, HPLC Grade, Sigma Aldrich	 <chem>ClC(Cl)H</chem>
4. Butyl Acetate anhydrous, ≥99%, Sigma Aldrich	 <chem>CC(=O)OCCCC</chem>

Figure 1.3.10: Details and chemical structure of solvents used throughout this thesis for the analysis of breath figure templating.

Chapter 1 has provided an overview of the field of using water droplets to template polymer materials and has detailed the tools and materials used to analyse this dynamic problem. Firstly, in Chapters 2 and 3, the aim is to understand the equilibrium force balance that allows the stable existence of water droplets at a solvent/air interface. This is approached through (i) extensive theoretical examination through the modelling of a pure three phase system using Mathematica software (Version 7.0, Wolfram Inc.) and (ii) experimental measurement of the droplets as they form and order at a pure solvent/air interface using optical microscopy. The role of the water, solvent and the polymer in breath figure templating are examined using this approach.

Secondly, in Chapters 4 and 5 the aim is to understand the dynamic behaviour involved in the self-organisation process. Specifically, the role of the environmental conditions during formation of a polymer microstructure are examined and their effect on the solvent evaporation, solution temperature, water condensation and the evolution of polymer viscosity are tracked or calculated. This is achieved using a range of flow chambers and formation techniques, with analysis of the samples using optical microscopy, focused ion beam milling and scanning electron microscopy. It would be of great benefit to the field to improve the understanding of the formation mechanisms present in this technique and the extent to which microstructure can be controlled. This approach aims to show that while the choice of the three phases will undoubtedly influence the final structure, tuning the formation conditions provides significantly more flexibility to the end result than previously reported in the literature.

Chapter 2

The Role of Interfacial Forces – Part 1

2.1 Introduction

As discussed in Section 1.3, water droplet templating is an intricate combination of both competing and interdependent events. It was also noted that the common approach of analysing this technique as one complete process has not to-date provided comprehensive understanding. To this end, the investigation is divided into two categories. The first considers only the situation where micron scale water droplets exist, interact and order at an air/liquid interface. This is analysed in this chapter, specifically from the viewpoint of fundamental interfacial interactions. The second grouping is concerned with the highly dynamic, non-equilibrium events that enable the existence of droplets at the interface, specifically environmental conditions, solvent evaporation and polymer entanglement effects, which are explored thoroughly in Chapters 4 and 5.

Both theoretical and experimental approaches are combined in this chapter to address the role of the system components, water, solvent, air and polymer. Of explicit interest is the role of each in determining if condensation takes the form of droplets, if droplets can locate at the solvent/air interface and if they can subsequently be used to form ordered polymeric microstructures. The aim of this section of work is to build an understanding of the competing interfacial forces to allow direct targeting of specific droplet shapes and hence internal polymeric microstructures. The focus of the theoretical and experimental work is on a polymer-free system to aid agreement between the two approaches. This is validated towards the end of this chapter, with the addition of polymer, showing that its role in defining the positioning of droplets at the interface is minimal.

As this chapter focuses on the effects of surface forces, the initial section will commence with an introduction to the origins of surface tension. This includes the specific concepts and representative equations that are employed directly during later hypotheses and model development while also providing a framework for the discussions that follow. The

fundamental concepts relating to three phase equilibrium will then be presented, highlighting the discord prevalent throughout literature on the topic. These concepts will then be applied directly to the stability of water droplets at a solvent/air interface. A combination of both modelling and experimental analysis of the three phase force balance will be presented and discussed in conjunction with related observations regarding non-coalescence and ordering phenomena. Finally a summary and discussion will highlight the key advances due to this analysis, the questions it has raised and the areas that require further development.

2.2 The Origins of Surface Tension

The concept of surface tension, γ , is often expressed as the force required when extending a surface by a unit length. Forces acting on the molecules in the bulk of the material in question are considered on average to be isotropic. This is contrasted by an unbalanced resolution of forces if the molecules are at an interface. The balance favours attraction into the bulk or conversely if the surface is to be extended, work is required to bring molecules from the bulk to the surface of the medium. With this in mind, rather than surface tension, the numerically equivalent term surface free energy is often employed with units of J/m^2 . A slight differentiation between the two terms is mentioned in Section 2.3.2. It can therefore be understood that to minimise surface energy, the molecules will try to retract into the bulk and minimise the surface area. The extension of the area requires work and as will now be discussed the origin and scale of this is related to the strength of the intermolecular attractions.

Intermolecular and interatomic forces can all be considered as purely classical attractions involving Coulomb's Law (110). They share an electrostatic origin but are characterised in many different ways, such as long or short range, Coulombic, hydrophobic or van der Waals interactions to name but a few. As in this chapter we are looking almost entirely at interfaces involving air, water and either non-polar or occasionally very weakly polar organic liquids the key interactions that need to be considered are van der Waals forces (111). These consist of three main contributions:

- (i) Keesom interactions, occurring between 2 permanent dipoles,
- (ii) Debye interactions, occurring between a permanent dipole and an induced dipole, and
- (iii) Dispersion interactions, which are attractive forces between two induced dipoles.

The discussion at the end of this chapter considers the possible role of a combination of these interactions but it should be noted that the intermolecular attractive forces in saturated hydrocarbons are essentially due to dispersion forces and so these alone will be considered initially (112). Interaction potentials are useful mathematical representations of the attractive forces that must be overcome to form new interfaces. These can be used to describe the van der Waals forces as a function of distance for two surfaces, as will be seen in Section 3.8. Using an approach from (111), the formation of two identical surfaces through overcoming these forces is described as Equation 2.1.

$$W = \frac{\pi C \rho^2}{12 D_0^2} = \frac{A}{12 \pi D_0^2} = 2\gamma \quad (2.1)$$

Where ρ is the number density of molecules (m^{-3}), C is the interaction constant (Jm^6), D_0 is the initial distance, usually taken as the interatomic spacing, W is the interaction function, and 'A' is the Hamaker constant, a measure of the interaction forces involved for the system.

By convention, when overcoming the interactions involved in just a single component, 1, 'W' is called work of cohesion, $2\gamma_{1/1}$. Work of adhesion is the term usually employed to describe the work required to separate two planes of differing materials (numbered 1 and 2) and the surface tension term above is modified to read $2\gamma_{1/2}$. This thesis focuses entirely on three phase systems and so the next section will look more closely at how the above principles are applied and modified to reflect such added complexity.

2.3 Three Phase Systems

It was noted in the Introduction, Section 1.2.1, that the templating mechanism relies on droplet formation and trapping at a solution/air interface that has been dosed onto a flat, uncontaminated substrate. The spreading of the solution on the substrate is a three phase problem, as too is the behaviour of water droplets at the solution/air interface. There now follows a brief introduction to the topic of three phase equilibrium, specifically as it occurs between (i) solid/liquid/air and (ii) liquid/liquid/air. This will contain the fundamental concepts that will be developed and modelled later in the chapter.

2.3.1 Solid-Liquid-Vapour (S-L-V) Systems

Using the interpretation from Section 2.2, stating that the work required to extend an interface is the work required to promote molecules from the bulk to the interface, the surface tension can then be understood as a force acting tangentially to the interface (113). For a three phase system such as a sessile drop, Figure 2.3.1 (a), these tangential force vectors can be pictorially represented. For the system to reduce its surface area, it will try to maximize the interfacial area with the lowest energy. The balance of the surface tension forces at equilibrium determines the shape of the droplet, with a characteristic contact angle, θ . At this point the three phase contact region experiences zero net force. If these forces are resolved with respect to the horizontal, it yields the Young Equation (2.2). This form of the Young equation allows wetting predictions based on surface energies or the exploration of surface energies from measuring contact angles of liquids on a solid surface.

$$\gamma_{1/2} - \gamma_{1/3} + \gamma_{2/3} \cos \theta = 0 \tag{2.2}$$

The situation where a solid surface is replaced by a liquid substrate is more complex and will be discussed in the following section.

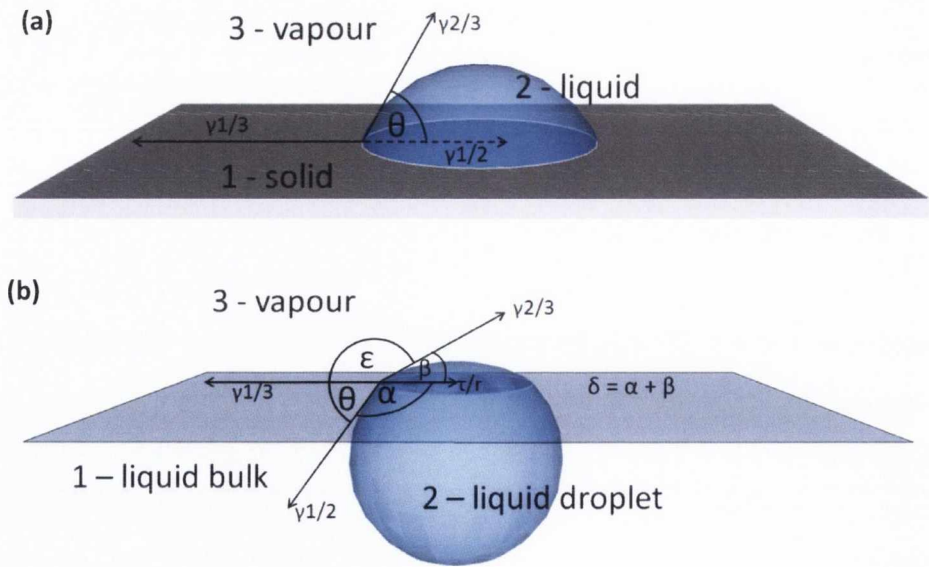


Figure 2.3.1: Illustration of the characteristic contact angles due to a balance of surface and interfacial tensions. (i) A sessile drop is shown sitting at a solid/air interface where the solid/droplet, solid/vapour and droplet/vapour surface energies are represented by $\gamma_{1/2}$, $\gamma_{1/3}$ and $\gamma_{2/3}$ respectively. The equilibrium contact angle is marked as θ . (ii) A liquid lens is shown at a liquid/air interface. The same notation is used but an additional term relating to the excess linear energy is included, τ/r .

2.3.2 Liquid-Liquid-Vapour (L-L-V) Systems

In the case of a solid interface, described above, there is an unbalanced vertical force component, $\gamma_{2/3} \sin \theta$, taking the form of a surface stress (113), (114) which is left unsatisfied unless the chosen material can yield and flow to balance it (115). The vertical force component is no longer “unsatisfied” when a droplet of one liquid phase rests on a second phase (known as a liquid lens) and so we observe two radii of curvature, one protruding from and the other submerged in the bulk liquid, as illustrated in Figure 2.3.1 (b).

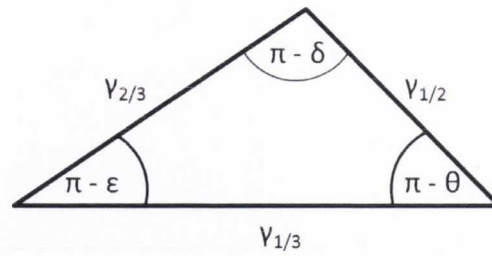
The angles, ε , θ & δ all sum to 2π and are characteristic of the particular system. Again, the balance of the interfacial tensions is such that the three phase contact region experiences zero net force. As discussed in Section 2.2, surface tension can be considered as the work required to increase the surface area of a body. It was noted by Gibbs (116) and further discussed by Rusanov (117) that this can occur by either stretching an existing surface or by creating a new surface and these definitions are used to divide between the mechanical force per unit of length and the energy required per unit of area. These may differ for a solid as the mechanical surface tension can be directional at a solid surface. The mechanical surface tension is designated by γ , while the thermodynamic term, surface energy, is designated by σ . However, importantly, the difference vanishes at isotropic open fluid surfaces when at equilibrium. So, while an additional contact angle is now involved, free liquid systems are more straightforward to interpret experimentally.

When examining the geometry associated with the surface tension vectors, illustrated in Figure 2.3.1 (b), it has been noted in a number of reviews of the subject, for example (118), (119) and (120) that the cosine of the contact angles are determined by the ratios of the interfacial tensions. For example the angle δ in Figure 2.3.1 (b) is represented by Equation 2.3.

$$\cos \delta = \frac{\gamma_{1/3}^2 - \gamma_{2/3}^2 - \gamma_{1/2}^2}{2 \cdot \gamma_{2/3} \cdot \gamma_{1/2}} \quad (2.3)$$

The mathematical procedure yielding this result can be used equivalently for the remaining two angles. As it is not detailed in full in the referenced documents, a derivation has been completed and placed in Appendix 2.1.

Leading directly from this approach, the three phase equilibrium is often presented as a force triangle, known as “Neumann’s Triangle” where the vectors representing surface tensions are the three components (120). For equilibrium to be satisfied, the sum of any two sides must not be greater than the third side. Figure 2.3.2 shows the proposed triangle and relationships with reference to angles defined in Figure 2.3.1 (b).



$$\gamma_{2/3} < \gamma_{1/2} + \gamma_{1/3} \quad (2.4)$$

$$\gamma_{1/3} < \gamma_{1/2} + \gamma_{2/3} \quad (2.5)$$

$$\gamma_{1/2} < \gamma_{2/3} + \gamma_{1/3} \quad (2.6)$$

Figure 2.3.2: Neumann's Triangle shows the relationship between the interfacial tensions and the supplements of the angles in a liquid lens at a liquid/air interface with reference to Figure 2.3.1 (b)[Figure based on (120)]. Equations 2.4-2.6 are rules that hold if an equilibrium lens is to form and are derived from the Neumann triangle.

Pictorially it is clear from Figure 2.3.2 that the triangle collapses at large enough values of $\gamma_{1/3}$. This can be interpreted as the three phase system reducing its overall surface energy by replacing the interface of high surface energy ($\gamma^{1/3}$) with a buffer zone, phase 2, which has low energies of interaction with the other two phases. In this case a stable lens can no longer be formed at the interface and its contact angle approaches π . When the relationships no longer hold then an equilibrium system cannot exist. Another method of presenting this principle is with equation 2.7. The resulting value 'S' must always be negative if a lens is to form. This comparison of surface tensions is called the 'Harkin Coefficient of Spreading' and gives an indication of the degree to which one phase spreads on the other (120).

$$S^{2,1/3} = \gamma^{1/3} - (\gamma^{2/3} + \gamma^{1/2}) \quad (2.7)$$

With a less negative coefficient of spreading in Equation 2.7, the liquid phase, 2, is more likely to spread on the liquid/vapour interface. A positive coefficient of spreading would suggest immediate formation of a spreading film (120).

Young's Equation and the equivalent Neumann's triangle are very useful for macro-scale predictions or measurements. However, micro-scale systems have an additional component to consider which will now be introduced.

2.4 Three Phase Interaction & Line Tension

2.4.1 Introduction to Line Tension

The region surrounding the three phase contact line is subject to an 'overlap' of intermolecular forces relating to each of the three phases. In this overlap region, known as the confluence

zone (indicated in Figure 2.4.1), the surface tension forces are no longer constant or represented by their bulk values. This is adjusted for in calculations with the introduction of a new value, the line tension. This allocates the complex modification of forces due to the three phase region to a single line where the phases meet. This was first commented on by Gibbs (121) when considering four or more homogeneous phases meeting about a line. Gibbs expected that improved “approximation in the theory of equilibrium and stability might be attained by taking special account, in our general equations of the lines in which surfaces of discontinuity meet. These lines might be treated in a manner entirely analogous to that in which we have treated surfaces of discontinuity.” He also noted the need to recognise a ‘linear tension’.

Depending on the three phase system, distribution of forces will be quite unique and depend on the associated long and short distance forces (e.g. van der Waals, electrostatic, solvation and steric forces (111)). This ‘real’ system can, as suggested by (121) and described in reviews on the topic (120), (122), (123), be described by a simple idealised model where the varying forces across the film surface are not included, but are attributed to a dividing line of three phase contact instead. As suggested by Gibbs, equating the real and idealised systems yields an expression for the linear tension.

This tension is in essence a one-dimensional equivalent to surface tension. Similar to section 2.3.2 it can be viewed with a mechanical (τ) or energetic description (κ). τ , as shown in Figure 2.3.1 (b) is a single component acting transversely in the force balance, whereas κ is interpreted as the work of formation of a new line per unit length. Also the three dimensional Laplace pressure, where the difference in pressure is due to the surface curvature, has a two dimensional equivalent pressure within the three phase contact region that is related to the curvature (or inverse of the radius) of the three phase contact line, as derived in Appendix 2.2. However, if an open fluid at equilibrium can be assumed, the mechanical and energetic values are equivalent.

In the literature it is almost entirely accepted now that line tension can have either a negative or positive value. This opinion was put forward by Gibbs (121) for “a line in which three surfaces of discontinuity are regarded as meeting” and is supported by a number of discussions and theoretical arguments (120), (122), (124) - (127). However there are counter arguments, if fewer in number (128), (129). Experimental work has yielded both positive (130) - (133) and negative (134) - (140) values for line tension. These can be described respectively

as a drive to expand or drive to retract the three-phase interface line. However, the scale of the line tension still remains unclear. While theoretical estimates based on a method introduced in the next section yield values on the order of 10^{-11} N, experimental values range between positive and negative values on the order of 10^{-6} N to 10^{-11} N. It has been noted that the wide range of values has in some cases been due to the chosen experimental technique or a product of the sensitivity of line tension values to the system geometry (141) as well as issues such as contamination, surface roughness and surface heterogeneity (134). It has been noted that where agreement is close, it is due to the author ensuring a close link between the experimental geometry and the model chosen (123).

The scale and sign of the line tension is still a matter of debate. In some reports, such as Binks (167), it is not required at all to account for stability or micron scale particles at a fluid/fluid interface. However, when they take it into account, it is calculated to affect the stability of the particle. Line tension is always found to exhibit values that suggest a very minor role when compared with surface tension. It is only expected to significantly contribute to the mechanical equilibrium of microscopic and sub-microscopic systems, such as those found in highly disperse and colloidal systems (141). This has led to a surge of interest from those involved in microfluidics, condenser design, froth flotation, emulsion science, and cell adhesion, to name but a few. The appropriate methods of analysis and measurement and even the relative influence of line tension are still areas of uncertainty and debate. The key points regarding the incorporation of line tension into a system model will now highlighted.

2.4.2 Theoretical Approaches to Defining Line Tension

There are a number of reports detailing complex theoretical approaches to defining and quantifying line tension for individual systems. They have been classified clearly by (123) as falling into either “local” or “non-local” approaches. The local approach is best understood from Figure 2.4.1, based on a method, notably used by Rowlinson *et al.* (120) and Qu *et al.* (129) among others.

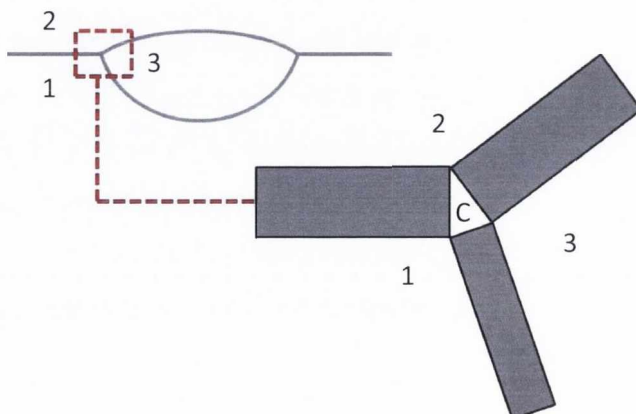


Figure 2.4.1: Phases 1,2 and 3 are assumed to meet at an intersection known as the confluence zone, labelled C, where each phase can influence the other two. For example, a water drop(3) could rest at a solvent (1), air(2) interface.

It is assumed that there is a triangular confluence zone and that it is in this interfacial region that the three phases interact. Interactions between phases outside this zone due to long range forces are assumed to be insignificant. “Non-local” approaches such as applied by Solomentsev *et al.* (127) and Rusanov (117) take into account the long range forces from outside the triangle indicated in Figure 2.4.1, due to interactions between interfaces. Complexity arises with either approach as a density profile is required for the confluence zone, which can only be estimated using for example mean field theory. The final result is extremely dependent on the choice of mean field (120), (123), (141). Theoretical techniques will not be examined in detail but these ideas will be raised within the discussion section, so it is important to note the two different approaches.

2.4.3 Experimental Approaches to Defining Line Tension of S-L-V Systems

Line tension is a challenging parameter to measure and because of this many different approaches have been reported. Initial techniques looked at soap films or membrane formation between two bubbles (142) - (144), the study of bubbles on and in liquid films (138), and the rupture of pendant drops using micron scale spherical particles (145). However the prevalent experimental method for estimating line tension is now through the study of particle or fluid contact angles when at a liquid/air interface (130), (131), (134), (146) - (152). However, while the principle is similar, with a three phase contact formed in a controlled manner and the equilibrium contact angle examined, the geometries of the apparatus and interactions are often quite different. The measurement of line tension appears in the literature using a wide range of materials and geometries. While some techniques will be referred to in this chapter, the studies looking at individual droplets of liquid will be most relevant. It has been noted by Babak (141) that an accurate analysis maintains consistency between the geometry of the system and the theoretical analysis. The work looking at S-L-V systems is not fully applicable, because as mentioned in Section 2.3.2, there is an additional term of surface stress due to unresolved vertical forces that we do not see in our system. However as the bulk of work looking at individual droplets was carried out this way it is a useful source of experimental findings that must then be carefully interpreted for the L-L-V scenario.

As mentioned, the most often applied technique is the recording of the change in contact angle with droplet size. For S-L-V systems such as Figure 2.3.1 (a), where the Young equation is normally applicable, an inclusion of a line tension term, τ , leads to a change in the balance in surface energies. Once this is assumed to be stable and so all vectors sum to zero, the same

derivation that leads to Equation 2.2 can be updated to give the modified Young Equation, as seen in Equation 2.8:

$$\gamma^{1/2} - \gamma^{1/3} + \gamma^{2/3} \cos\theta + \frac{\tau}{r} = 0 \quad (2.8)$$

The additional term due to the line tension, $\frac{\tau}{r}$, scales with the radius of curvature of the three phase contact line, r . This allows a weak interfacial force to still have a significant effect once features reach the micron and sub-micron lengthscale. An example of the change in contact angle observed in an experiment is reproduced in Figure 2.4.2 from (152).

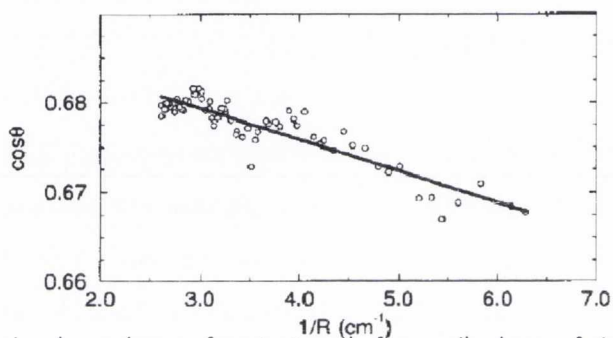


Figure 2.4.2: Drop size dependence of contact angle for sessile drops of cis-decalin on a self-assembled monolayer of long-chain alkanethiols on a gold surface with a linear fit (152).

In this and many other papers, it is realised that line tension is one of the possible causes of this change in contact angle. The effect of line tension is hypothesised to be especially pronounced in wetting/drying transitions (153), so many experiments target the low contact angle lens (130), (131). These are also far easier to measure using interference techniques. Unfortunately due to inherent surface roughness, contamination and heterogeneities these results are often questionable. While they are inherently more difficult to measure, this is one of the reasons for interest in liquid droplets resting on a second liquid phase. Such a liquid lens avoids all of the problems mentioned above and so the next section will briefly introduce this approach.

2.4.4 Approaches to Defining Line Tension of L-L-V systems

Liquid lenses at a liquid/air interface are much closer to the system of interest in this thesis. The Neumann triangle, discussed earlier, can be modified to include a line tension term (154). Known as the Neumann Quadrilateral, the imbalance in the triangle is offset by a new and final side, designated as the line tension vector. Alternatively, through resolving the forces for systems such as in Figure 2.3.1 (b), where a liquid droplet sits at a liquid/air interface, we get the following expression with an included term for line tension (155):

$$\gamma^{1/2} \cos\alpha - \gamma^{1/3} + \gamma^{2/3} \cos\beta + \frac{\tau}{r} = 0 \quad (2.9)$$

The three phase contact term, $\frac{\tau}{r}$, is present because the line tension is a two dimensional force acting over the entirety of the contact line. To project this onto the same plane as the surface tensions when resolving the force balance, the line tension per unit of curvature is required. As curvature is described as r^{-1} this leads to a $\frac{\tau}{r}$ term. As shown in Appendix 2.2, this is also equivalent to a two dimensional Laplace pressure.

This first section of Chapter 2 covered the key relevant principles in intermolecular forces and their manifestation as surface energies and tensions, providing a basis from which the relationships in the remainder of the chapter will be derived. As stated in Section 2.1 one proposition of the thesis is that the understanding of breath figures would benefit from analysing the conditions at which a water droplet can be positioned at a liquid/air interface. In porous polymer film formation, the droplets are known to form and order while all phases are still fluid and from the resulting open pores it is clear that by the end of the process they exist at the solution/air interface. Observation and quantification of these events with different systems would be a major step towards their understanding.

With this in mind, Section 2.4 will look at the development and application of the principles discussed in the introduction regarding capillarity and three phase equilibrium. Firstly, looking solely at a pure solvent/polymer free scenario, the relationships will be stated that relate to a system of water droplets at a solvent/air interface, taking note of the assumptions involved. Secondly, a simple model will be introduced incorporating these relationships and the behaviour of the three phase equilibrium will be analysed for a number of solvents and scenarios. Results will be discussed both in terms of trends arising from the theoretical analysis and also in terms of trends that can feasibly be tested.

Section 2.5 of this chapter aims to test these trends by a series of experiments. Finally the assumption that our findings can then be applied to a polymer containing system will also be tested.

2.5 Theoretical Analysis of Three Phase Equilibrium Systems

2.5.1 Introducing Key Mathematical Relationships

As noted in Section 2.4.1 the energetic and force balance approaches to balancing interfacial energies are interchangeable for an open fluid system, such as the one studied as part of this thesis (138). As the system is trying to minimise its surface area, it will need to maximise the

interfacial area with the lowest energy. This section uses an approach derived in detail by Pujado & Scriven (155) and then adopted by other groups active in the analysis of liquid lenses (118), (136), (139), (147). This balance of the interfacial forces, with reference to Figure 2.5.1, examines the wettability of a liquid droplet in the bulk of a second liquid.

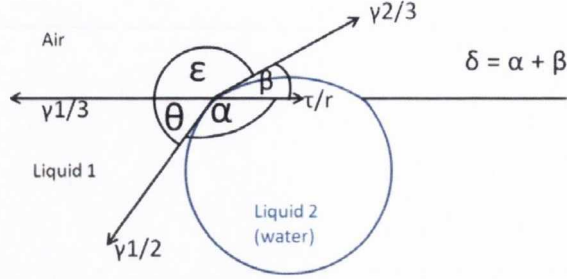


Figure 2.5.1: Two dimensional representation of Figure 2.3.1(ii) showing the forces acting on a droplet at a solvent/air interface.

If a lens can form at the interface, the level of projection into each phase is determined by the relative wettability. This leads to an equilibrium shape made up of two spherical caps, as seen in Figure 2.5.1, which when resolved with respect to horizontal forces yield the following relationships for the angles of the droplet:

$$\alpha = \text{ArcCos} \left[\frac{r(\gamma_{12}^2 - \gamma_{23}^2 + (\gamma_{13} - \frac{\tau}{r})^2)}{2\gamma_{12}(\gamma_{13} \cdot r - \tau)} \right], \quad \beta = \text{ArcCos} \left[\frac{r(\gamma_{23}^2 - \gamma_{12}^2 + (\gamma_{13} - \frac{\tau}{r})^2)}{2\gamma_{23}(\gamma_{13} \cdot r - \tau)} \right] \quad (2.10), (2.11)$$

Where γ_{23} , γ_{12} , γ_{13} are the surface tensions of the air/water, solvent/water and air/solvent interfaces respectively. τ is the line tension and r is the radius of the three phase contact region of the droplet. If in these equations the line tension is allowed to reach zero, then the remaining relationships are those found when considering the Young equation and Neumann triangle (118), (119).

Further useful relationships, developed in the same works, follow geometrically:

$$\text{Volume of lower section of droplet:} \quad V = \frac{\pi r^3}{3 \sin^3 \alpha} [\cos^3 \alpha - 3 \cos \alpha + 2] \quad (2.12)$$

$$\text{Volume of upper section of droplet:} \quad V = \frac{\pi r^3}{3 \sin^3 \beta} [\cos^3 \beta - 3 \cos \beta + 2] \quad (2.13)$$

These relationships are all that is required to analyse and predict the behaviour of a pure three phase liquid-liquid-vapour system. However, to legitimately apply this model, the following must be assumed:

1. The surfaces are free from any adsorbed monolayers or wetting films.
2. The solvent surface is planar up to the droplet interface.

3. Gravity does not have any significant effect on the droplets. This was tested by looking at the capillary length, as defined by Adamson *et al.* (113),

$$a = \sqrt{\left(\frac{\gamma}{\Delta\rho \cdot g}\right)} \quad (2.14)$$

Where γ is the surface tension, $\Delta\rho$ is the difference in density between the droplet in question and its surroundings, g is the acceleration due to gravity. For a droplet of water in air the resultant capillary length is 2.7 mm and the smallest capillary length for solvents used in this thesis is 2.4 mm. The largest of the drops analysed was approximately 0.4 mm in diameter but the bulk of analysis was carried out on drops in the tens of micrometers scale.

4. Bulk surface tensions are independent of drop size for the scale of drops examined.
5. The system is at chemical and thermal equilibrium.
6. The surface tensions of the pure solvents used in this chapter do not stray significantly from literature values, used throughout. This was minimised by using high quality chemicals used only for this work, taking care to avoid contamination.

With this approach, the potential for water lenses to form an equilibrium lens at a solvent/air interface can be examined. Further to this, an analysis to understand the stability of a lens at the interface must be carried out. To do this the change in Gibbs free energy of a droplet is examined, illustrating the energy required to eliminate a droplet from the bulk solvent and create a re-shaped droplet at the interface:

$$\Delta G = \gamma_{12} \left(\frac{2\pi r^2}{1+\cos\alpha} \right) + \gamma_{23} \left(\frac{2\pi r^2}{1+\cos\beta} \right) + 2\pi r \tau - (\pi r^2) \cdot \gamma_{13} - \frac{3}{R} (V_\alpha + V_\beta) \cdot \gamma_{12} \quad (2.15)$$

Where V_α represents the volume of the submerged section of the droplet and V_β represents the volume of the protruding section of the droplet. These relationships, along with Harkin's spreading coefficient and Neumann's triangle as introduced in section 2.3.2, will be used to explore the theoretically predicted behaviour of the volatile solvent systems used in water droplet templating techniques. The influence of line tension, droplet volume, three phase contact radius and surface tensions will now be presented with a discussion after each key result. A final summary will then tie in the key findings of this work.

2.5.2 Results of Theoretical Examination

2.5.2.1 Potential for Lens Formation or Spreading

As remarked earlier, based on the Neumann triangle, the coefficient of spreading gives an indication of the degree to which one phase spreads on the other. As shown in Table 2.5.1, a

number of different solvents used with the BF Method were examined using the Harkin Coefficient of Spreading (Equation 2.7) and it was noted that all of the solvents gave large, negative results. Such values suggest the poor wettability of the water phase on the chosen solvents. The water phase is, as expected, minimising its area with the highest surface tension. While this corresponds to the formation of a lens with a very small drive to spread, the scale of the results suggest that the lenses may not be stable at the interface. Examining the systems with equation 2.7, it is shown in Table 2.5.2 that Neumann’s Triangle in fact predicts that only one of these systems, carbon disulphide, can allow a stable lens to form at the solvent/air interface. Examining a range of other solvents used in literature for water droplet templating, they too are almost entirely predicted not to form stable lenses at the solvent/air interface.

Solvent	Spreading Coefficient	Neumann Triangle Inequality Rule
Chloroform	-73.8	$\gamma_{23} \not< \gamma_{12} + \gamma_{13}$
Toluene	-80.8	$\gamma_{23} \not< \gamma_{12} + \gamma_{13}$
Butyl Acetate	-62.2	$\gamma_{23} \not< \gamma_{12} + \gamma_{13}$
Carbon Disulphide	-87.8	$\gamma_{23} < \gamma_{12} + \gamma_{13}$

Table 2.5.1: Harkin’s spreading coefficient for four solvents based on a water lens at a solvent/air interface, and the status of the inequality rule from the Neumann Triangle that states the largest surface tension of the three components must not be greater than the sum of the other two for an equilibrium liquid lens system to form. Values calculated using Equation 2.7.

2.5.2.2 Limitation to Stable Size of Three Phase Interface

Once line tension is included in the force balance, Equations 2.10 and 2.11 can be developed further to give:

$$-1 \leq \cos\alpha \leq 1 \tag{2.16}$$

$$-1 \leq \cos\beta \leq 1 \tag{2.17}$$

Setting Equations 2.16 and 2.17 to $|\cos\alpha| = 1$ and $|\cos\alpha| = 1$, and substituting into Equations 2.10 and 2.11, yields expressions for two distinct critical radii, Equations 2.18 and 2.19. From these we can infer that the liquid droplet can only be present at the surface for a specific range of radii that depend on the surface and line tensions involved. These two expressions yield four values in terms of τ . These two groupings are shown in Table 2.5.1 and are applicable to either positive or negative line tensions.

$$R_{critical} = \frac{\tau}{\gamma_{13} \pm (\gamma_{23} + \gamma_{12})} , R_{critical} = \frac{\tau}{\gamma_{13} \pm (\gamma_{23} - \gamma_{12})} \tag{2.18),(2.19}$$

Solvent	Critical Radii (positive line tension)	Critical Radii (negative line tension)
Chloroform	$7.83\tau \leq R_c \leq 13.93\tau$	$-13.55\tau \leq R_c \leq -56.18\tau$
Toluene	$7.31\tau \leq R_c \leq 15.43\tau$	$-12.38\tau \leq R_c \leq -113.64\tau$
Butyl Acetate	$8.90\tau \leq R_c \leq 11.99\tau$	$-16.08\tau \leq R_c \leq -30.12\tau$
Carbon Disulphide	$6.56\tau \leq R_c \leq 17.30\tau$	$-11.39\tau \leq R_c \leq 147.1\tau$

Table 2.5.2: Range of stable three phase contact radii defined for each solvent system and dependent only on the value of the line tension associated with the three-phase confluence zone.

2.5.2.3 Line Tension, Droplet Shape and Stability

Including a line tension term, $\frac{\tau}{r}$, in the modified equation as seen in the force balance in Figure 2.5.1 and the updated Neumann Quadrilateral discussed in Section 2.4.4, takes into account the short and long range intermolecular forces at work when three phases come into close proximity. At decreasing droplet radii this balancing term will have an increasing effect. To see how this affects the stability of the droplets and to examine the feasibility of different signs for line tension for the system of interest to this thesis, Equations 2.10 and 2.11 are applied to a range of three different line tensions for a system of water droplets at the chloroform/air interface. The values of line tension ($\tau = |50|, |100|, |150| \text{ nN}$) are examined as they are on the scale of other experimental values in the literature.

Plots of the droplet contact angles of water droplets at a chloroform/air interface (as defined in Figure 2.3.1 (b)) against calculated three phase contact radii are presented in Figure 2.5.2 based on Equations 2.10 and 2.11. From these graphical representations it appears positive line tension is not a feasible solution. The reasons, in conjunction with the graphical results for chloroform in Figure 2.5.2, are as follows:

- (i) A positive line tension yields an initial angle of 180° for the part of the droplet both above and below the interface. This means the liquid droplet will protrude out of and into the interface, with infinitely large radii of curvature. The emerging part of the drop only deviates slightly from this angle for the entire range of feasible three phase contact radii. As the droplet grows, it is then rejected from the solvent and a droplet with a very high contact angle is formed above the liquid surface. This seems a highly unlikely configuration.
- (ii) At no stage does the drop have a vanishing volume. The droplet must appear at a finite value rather than grow through condensation. This is difficult to reconcile with the idea of condensation fuelled droplet growth at the interface.

As mentioned in Section 2.5.2.2 it can be seen that solutions only exist within a specific range of three phase contact radii for each chosen value of τ . Examining the equivalent representation for negative line tension in Figure 2.5.2, it can be seen that maximum and minimum stable radii are again predicted and this time the droplets can evolve from a flat raft with no contact angle above or below the interface. The evolution of the droplet shape with volume appears more reasonable and is represented in Figure 2.5.3. In later sections, specific values for line tension will be estimated but initially, a value of -40 nN is used based on a quick estimate from a standard pore opening size and approximate contact angle, thus allowing a clearer visualisation shown in Figure 2.5.3. It can be seen that at extremely small volumes, the water droplet is predicted to form a small flat lens. With an increase in volume, this extends into each phase. As the volume increases further the droplet approaches a submerged contact angle of 180° at which point it can no longer be considered stable at the interface.

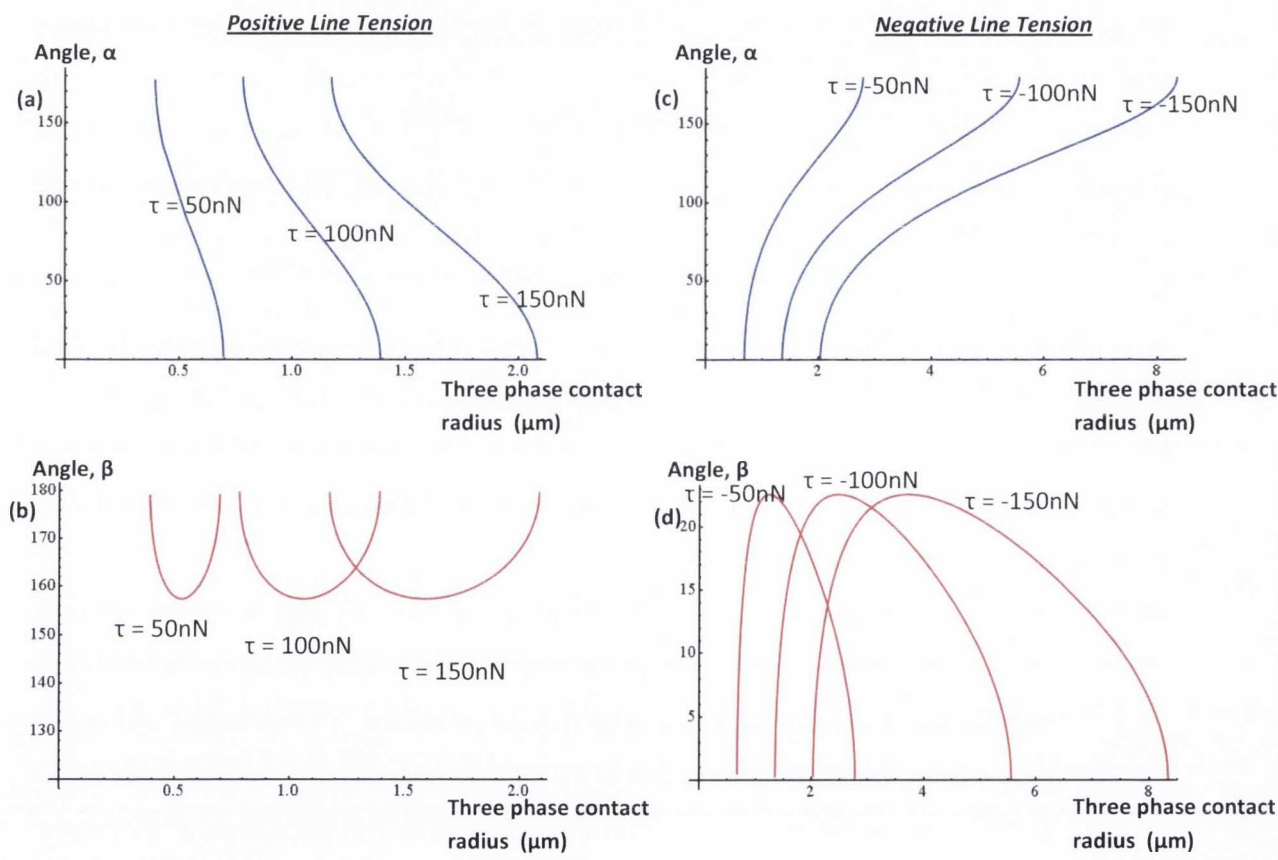


Figure 2.5.2: For a water droplet at a chloroform/air interface, the submerged droplet angle, α , and protruding angle, β , from Figure 2.5.1, are predicted as the three phase contact radius increases. These predictions are represented graphically using Mathematica for three example positive line tensions (a)-(b) and for three example negative line tensions (c)-(d).

If however a solvent is chosen that obeys the Neumann Triangle inequalities, then no upper limit is found and the droplet contact angle asymptotes to a finite value.

Figure 2.5.3 is not correct in its scaling across droplets due to the size range involved. However it consists of the correct angles in each case to aid the understanding of predicted droplet shape. It is noted that for other solvents, while the scale and range of three phase contact areas that form stable droplets differ, the trend of droplet shape evolution with size carries over.

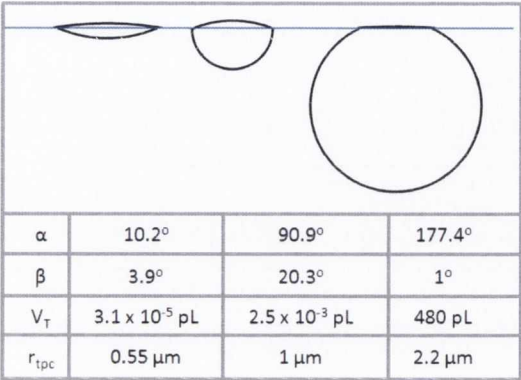


Figure 2.5.3: Using a constant value of -40nN as an example line tension, this is a representation of predicted droplet shapes and their angles, as defined by Figure 2.5.1, based on three different droplet volumes. With each volume, the three phase contact radius and contact angles were calculated using Equations 2.10, 2.11, 2.12, 2.13.

Using Mathematica, Equations 2.10, 2.11, 2.12 and 2.13 were used to calculate the three phase contact radius and contact angles α and β with increasing total droplet volume. Once a volume is reached that is similar to a pore formed with the BF method, it is expected that the contact angles predicted will also be close to those normally observed because the value for line tension used was estimated using such a pore. However, from this analysis, as shown in Figure 2.5.4(a), when comparing three solvents, butyl acetate, chloroform and toluene, the initial increase in both of the contact angles occurs while the droplet volume is very small indeed. As the droplet increases in size, it rapidly approaches higher submerged contact angles (α). It then responds slowly to the growth of the droplet volume, increasing steadily towards 180°.

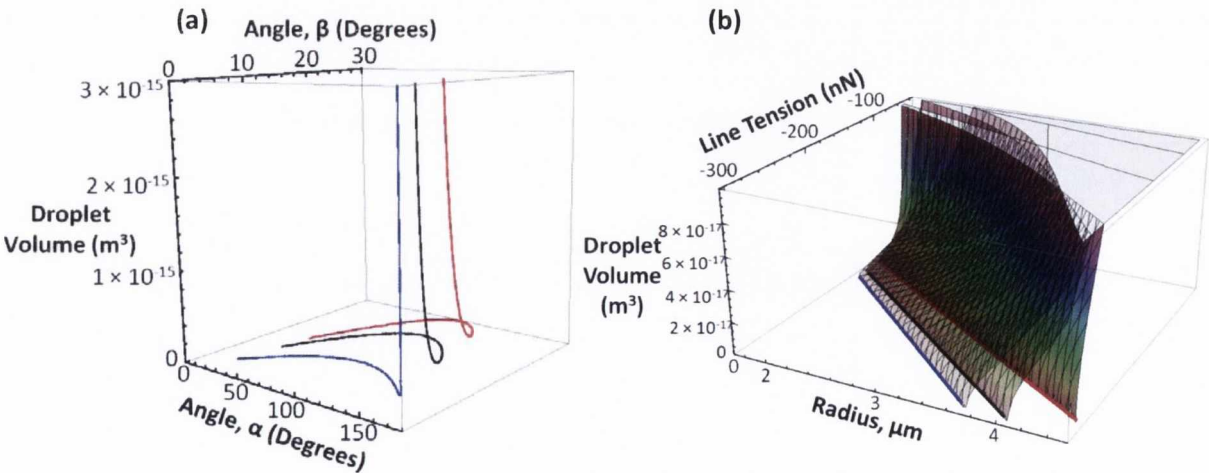


Figure 2.5.4: (a) Using a constant value of -40nN as an example line tension, this is a representation of predicted changes in the angles α and β as shown in Figure 2.5.1 with increasing droplet volume for solvents butyl acetate (blue), chloroform (black) and toluene (red) (b) Graphical representation of calculated relationship between the three phase contact radius, line tension and the droplet volume for the same three solvents labelled at the base of each curve by the same colour coding.

It can be seen in Figure 2.5.4 (b) that for a chosen value of line tension, as the droplet volume increases, the rate of increase in the three phase contact radius also changes. This is affected by line tension and also significantly by interfacial tensions as can be seen from a comparison of different solvents. The spread of this initial and end radii is also affected significantly by the interfacial energies. In all cases, as the droplet grows, the rate of increase of the three phase contact radius is reduced. At increasing sizes, the three phase contact radius becomes less and less sensitive to the change in volume. This is an important point to consider when thinking later about the homogeneity of droplet sizes when forming breath figures.

2.5.2.4 Relationship between three phase contact radius and line tension

To illustrate the relationship between line tension and the three phase contact radius, an approach similar to Aveyard & Clint 1997 is used (136). These two properties are plotted against the contact angles formed by a droplet of water at a chloroform/air interface in Figure 2.5.5 (a). Taking any fixed value for line tension, a graph of the form Figure 2.5.5(b) can be extracted showing that, depending on the line tension, a broader or narrower range of stable radii are available over which we see the full range of contact angles. Equally if the radius is fixed then, as in Figure 2.5.5 (c), we can see which feasible line tensions give a droplet of the radii and contact angles observed. As the line tension values become larger (or more negative), the “collar” of line tension (153) can be understood to be forcibly widened or loosened and so the contact angles progressively decrease.

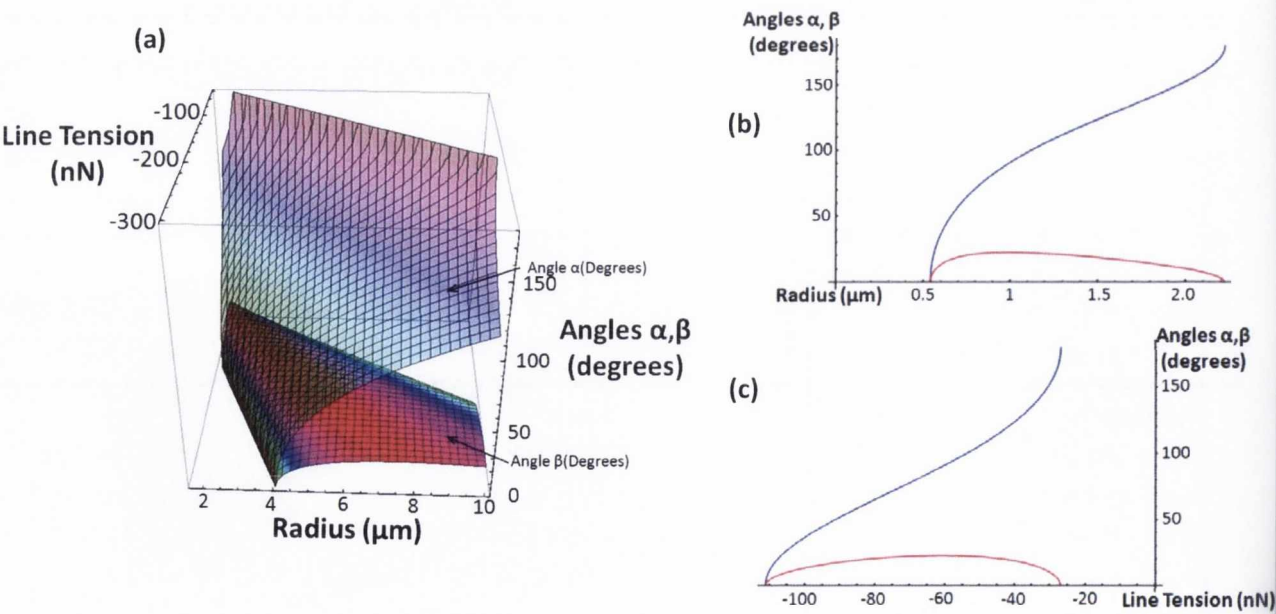


Figure 2.5.5: Based on the mathematical description of the system in Section 2.5.1 of a water droplet at a chloroform/air interface, (a) shows the angles α and β as dictated by the stable three phase radius and line tension, (b) shows a two-dimensional extract from (a) at a fixed line tension and (c) shows a two-dimensional extract from (a) at a fixed three phase contact radius.

These graphs examine the system without regard to the volume. It is also useful to consider a fixed volume droplet in a system of known surface tensions. The total volume is a function of line tension and three phase contact radius only. If the volume is set then there is only one degree of freedom and only one further parameter is required before the entire system is defined. This can be either the three phase contact radius or the line tension.

For a set volume, in this case 0.015pL, a line tension is chosen and an iteration technique run in Mathematica (156) to solve the relationship for the three phase contact radius, the local contact angles and subsequently the change in Gibbs free energy as defined by Equation 2.15. This is completed for a range of line tensions resulting in Figure 2.5.6. Again chloroform was used as the bulk solvent. Figure 2.5.6 shows that in fact due to the slightly higher surface energy of solvent/water compared with solvent/air and coupled with the work required to overcome the negative line tension, a droplet is at a higher energy state when completely submerged than when at the interface. However, once a stabilising line tension decreases in magnitude, this changes and the droplet decreases its energy by submerging in the solvent bulk. The energy difference is quite large and ensures that similar to solid spherical particles (148), liquid droplets can also be trapped at the interface with little regard for thermal influences.

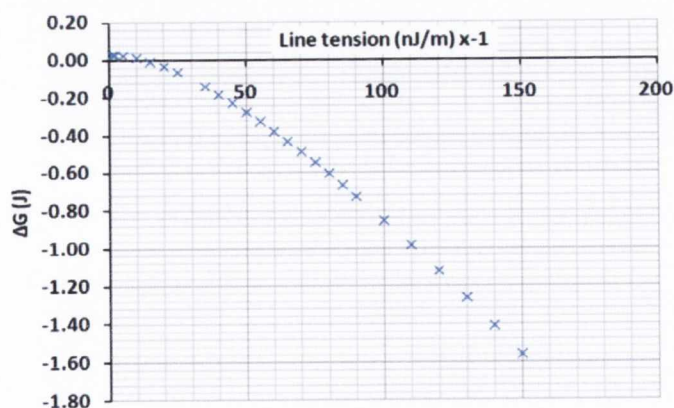


Figure 2.5.6: For a fixed droplet volume of 0.015pL, the change in Gibbs free energy when a water droplet moves from the chloroform/air interface to the bulk solvent is calculated using equation 2.15, with a negative value signifying a higher energy level in the bulk. This figure examines this value for a range of line tensions.

An alternative method, holds the line tension constant, for example in this case -100 nN and allows the volume to vary, solving in each case for the equilibrium position of the droplet. From this position, the change in Gibbs Free Energy is again calculated and it can be seen from Figure 2.5.7 that at very small droplet volumes there is a negative value, which reaches a maximum as the droplet grows. However, larger droplets reach a transition to a positive change in energy and are unstable at the interface. In work by Binks (167), where line tension

is not invoked, the particles considered were shown to have maximum stability at $\alpha = \beta = 90^\circ$. In the case of our fluid lenses, with two radii of curvature, this result is not expected. It is found that the maximum negative value of Gibbs free energy in Figure 2.5.7 occurs with contact angles $\alpha = 122^\circ$ and $\beta = 19^\circ$. Without accounting for line tension, a stable lens is still not formed using this theoretical approach.

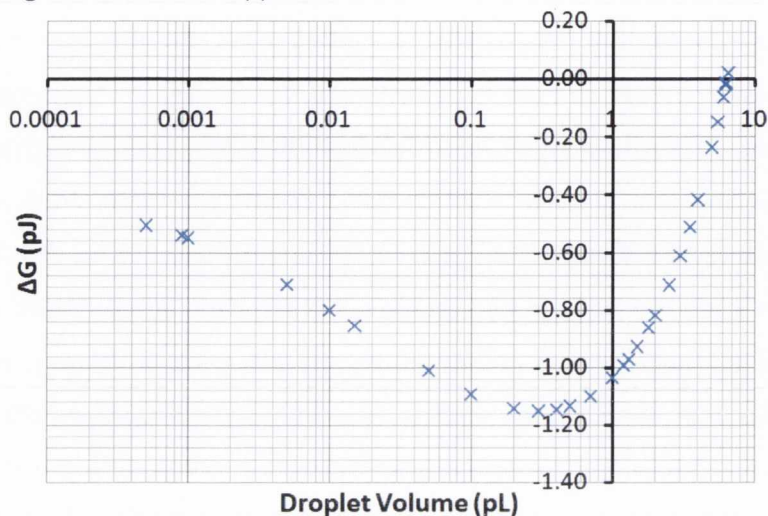


Figure 2.5.7: With a constant line tension of -100 nJ/m , the change in Gibbs Free Energy is calculated at increasing volumes of the water droplet at a chloroform/air interface. The graph shows that with increasing droplet volumes, a maximum stability is reached before a rapid change towards an unstable scenario.

Turbulence and hydrodynamic forces are noted as potentially supplying enough energy to remove droplets of this scale from the interfaces (148). In the work of this thesis, it will be shown that the most likely source of such a force is the surface tension driven convection currents observed during solvent evaporation.

2.5.3 Discussion

This purely theoretical approach has given many insights into the predicted behaviour of our three phase systems. With the assumptions included in Section 2.5.1, the presence of a negative linear excess energy is required to form drops that are stable at the solvent/air interface for a specific range of three phase contact radii. This is true of most solvents used for the formation of porous polymer films by droplet templating. This suggests that the role of line tension may be a very important aspect to consider when trying to understand the mechanism of formation. Although, in theory, a positive or negative line tension can stabilise the droplets, it is believed to be negative due to the arguably unreasonable and unobserved solutions to the positive line tension results for these solvents. The range of line tensions that correspond to standard observed contact angles, reported later in Chapter 3, are of the correct order as discussed in literature. With this simple model, we can see the conditions for which the

droplets are stable at the surface. It is also noted that as they grow in volume, assuming a fixed line tension, their three phase contact radii rapidly begin to asymptote, which may go some way towards accounting for the homogeneous three phase contact regions observed in the formation of porous microstructures. Also, the range of stable three phase contact radii varies significantly with the solvent chosen. This suggests that improved control over droplet size and shape could be achieved through component choice and improved control of droplet growth. This initial model allows a complete examination of droplet stability, shape and position at the interface once the surface tensions are known. To develop this further it must be tested against experimental results and reconciled with any differences. The standard approach for observing the manifestation of a line tension is to observe the change in contact angle with the change in the length scale of the three phase contact. This is normally achieved through dosing of different sized droplets. The next chapter looks at a novel experimental approach under development with the aim of recording the droplet shape and volume *in-situ*.

Chapter 3

The Role of Interfacial Forces – Part 2

3.1 Introduction to the Experimental Analysis of Three Phase Equilibrium Systems

There are few reports focusing on surface tensions, line tensions and the detailed behaviour of water droplets for the systems required in the formation and capture of breath figures in polymer films (157,158). There are also only a few studies in the field of line tension analysis looking at the scale of droplets discussed in this thesis or using the selected organic solvents. It is hoped any experimental advances would be beneficial to both fields and would allow an improved insight into the stability of droplets at these interfaces.

Also, as the polymer solution changes in concentration during the evaporation process, experimentation is necessary to begin to understand how this will influence the surface tension balance and specifically if the assumption is justified that analysis of pure solvent systems can be translated to polymer solutions.

This chapter will detail the experimental techniques and associated procedures to explore the phenomena of water droplet formation at a liquid/air interface and the balance of surface tensions and line tension. Both manual dosing of water droplets and condensation from vapour are used to study the stability and contact angles of the droplets at the surface. The results and validation are presented before proceeding to a final overall discussion that will incorporate the findings from both the theoretical aspects in Chapter 2 and the experimental approach detailed in this chapter.

3.2 Experimental Set-up and Description

The behaviour of water drops on solvent surfaces was observed using the Olympus optical microscope detailed in Section 1.3.1.1. Three configurations of this experiment were

developed. The first two aim to controllably form water drops at a solvent/air interface through water vapour condensation while allowing clear imaging of the droplet dimensions. They differ in their method of introduction of a humid vapour flow and also the thickness of the solvent layer being studied. These were developed as different solvents different solvents required different conditions to ensure stable, repeatable results. The third configuration is a manual dosing system that delivers nanolitre scale water droplets to the solvent/air interface. This allows observation of droplet stability as well as measurement of droplet size and geometry. This separate system aims to show if the method of introduction of water to the interface is important.

The three configurations or apparatus will now be detailed separately before discussing the humid flow delivery, image recording, analysis and substrate cleaning protocols, which are shared across the methods.

3.2.1 Method 1

The first method consists of a glass well (Figure 3.2.1(e)), approximately 5 mm deep, formed by adhering a thin section of glass tube to an inverted chambered Lab-Tek, thickness 0, cover slip with adhesive. This adhesive is cured at 110° to ensure stability. The chamber is filled with ice and inverted onto a spill tray, also half filled with ice. The aim is to maintain a chilled solvent to induce water condensation while reducing solvent evaporation and convection currents. The tray is initially placed directly onto the microscope stage. A more recent development places the glass well inside a chamber shown in Figure 3.2.1(f). The chamber was constructed in an attempt to reduce the disturbance to the surface from a direct flow of air. This experiment was carried out on a lab bench with a portable extractor/filter positioned to remove the solvent vapours. Due to the cooling of the substrate, condensation rapidly forms on the glass before solvent dosing can occur. To delay this, dry nitrogen is guided to flow over the substrate until dosing occurs. The timer is started when the humidity/temperature recordings commence. The time is noted when the solution of interest is dosed into the well using a micropipette and a pre-prepared pipette tip, formed in a hook to allow an angled dose. The solution surface is then observed using the microscope and droplet images are recorded, noting times where relevant. It is observed that, using toluene, most of the solvent remained at the end and very little in fact evaporates.

3.2.2 Method 2

The second configuration, shown in Figure 3.2.1 (c) uses a purpose built flow chamber, designed using SolidWorks and constructed using the 3D printer noted in Section 1.3.2.3. There is an inlet in the chamber for the humid flow of nitrogen, which passes over the substrate and a slim humidity probe before exiting at the far end. A microscope coverslip, approximately 100 μ m thick, cleaned as per the protocol discussed in Section 3.2.4 is placed on two glass slides to reduce the distance to the lens and allow focus to be achieved. A Rotronics humidity and temperature probe (as detailed in Section 1.3.3) is inserted into the side of this chamber and records conditions at the location of the drop-cast solvent at intervals of 5 seconds. Once the glass substrate is in place, dry nitrogen flows across the sample to avoid water condensation.

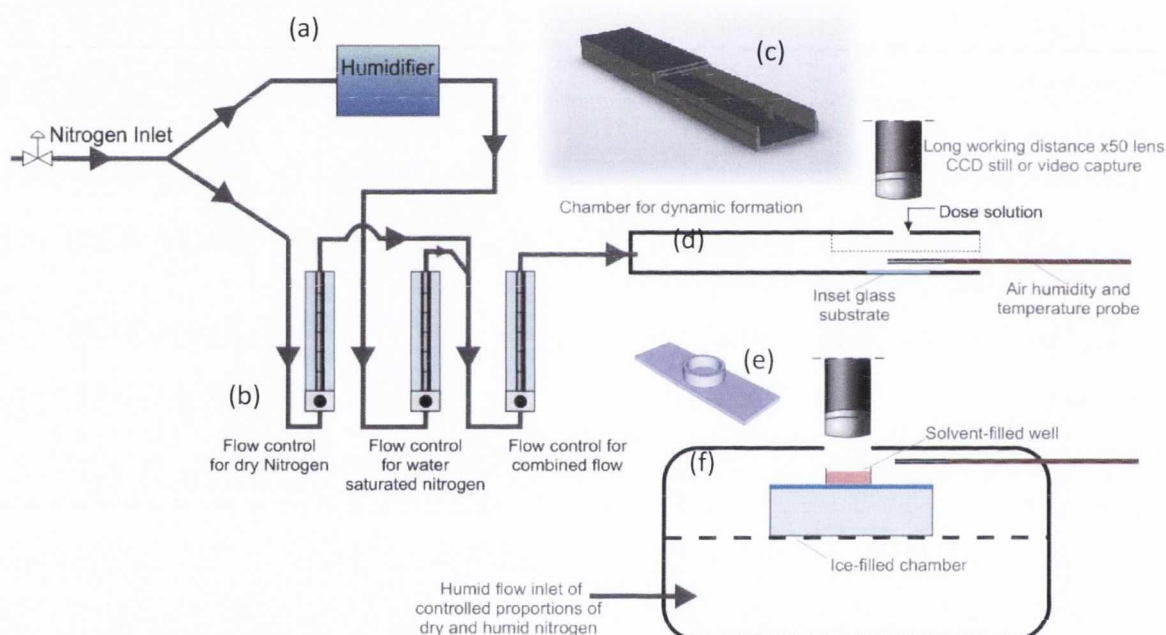


Figure 3.2.1: Apparatus for the delivery and observation of water condensate at a liquid/air interface to allow droplet contact angle measurement. (a) Humidifies a flow of nitrogen, (b) controls the level of humidity delivered, (c) is a model of the flow chamber indicated as (d), which also contains the glass substrate and dropcast solvent. (e) Shows an illustration of the glass well used in the apparatus (f) shown here as an equivalent set-up using a humidity chamber.

This is the latest point at which the humidity and temperature measurements can commence. There is a small port positioned directly above the sample. Using pre-prepared hooked micropipette tips, solvent is dosed using a micropipette through this port. Subsequently this port also allows direct observation using long working distance lenses. The time of dosing is recorded as is any time when the humid flow is switched on or off during the process. This is to allow later correlation with recorded humidity. Where relevant, the dose volume will be stated in the results section. Normally a dose volume of 60 – 100 μ L is used. The above method is

used for toluene as slow evaporation provides sufficient cooling to induce condensation at very high humidities (>80%). With other solvents either slow evaporation does not induce sufficient cooling to encourage water condensation or alternatively rapid evaporation leads to total solvent loss within too short a period and induces strong convection currents. To avoid these problems, the chamber and solution are chilled in ice before each experiment as are the glass slides supporting the substrate. The chamber is then mounted for the duration of the experiment on a flat surface of ice under the entire length of the chamber. Due to heat loss to the environment remaining quite constant, this maintained the glass coverslip at 12-13°C for the duration of an experiment. The solvent in question is also pre-chilled to approximately 5°C in the chemical fridge just before use. When cooling is applied it is essential to ensure the substrate is only exposed to dry nitrogen prior to solvent dosing, to ensure water contamination is avoided. Dosing and recording of parameters are as stated previously.

3.2.3 Method 3

The additional changes required for the third experimental configuration is shown in Figure 3.2.2. A fine glass capillary is formed into an ultra-sharp tip using a Narishige PC-10 vertical heating/pulling system. The final diameter is reproducibly less than 500 nm. Using a tweezers, the undeformed end of the long glass tip is then fed into capillary tubing and sealed using an additional overlaid heat sensitive shrink-film and heat gun. The far end of the tubing is connected to a 1 mL syringe, filled with Nanopure (Thermo Scientific) de-ionised water. The glass tip is secured to a thin cylindrical metal mount and attached to the Kleindiek MM3A-EM (159) nanomanipulator shown in Figure 3.2.2. Prior to use, the tips were flushed through with the Nanopure deionised water. The combination of a micromanipulator with an ultrafine tip allows for careful positioning and dosing of very small quantities of fluid.

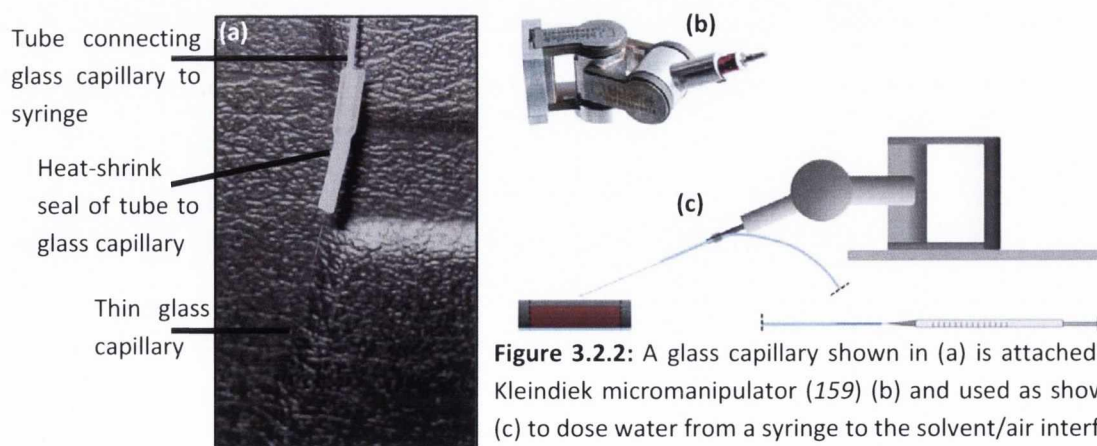


Figure 3.2.2: A glass capillary shown in (a) is attached to a Kleindiek micromanipulator (159) (b) and used as shown in (c) to dose water from a syringe to the solvent/air interface.

Work examining the stability of the droplets in the solution was carried out in a deep solvent. This was constructed using a thick glass coverslip attached using an adhesive to a high quality

stainless steel gasket to form a chamber. These were both cleaned using the same technique as the highly cleaned glass substrates discussed in Section 3.2.4. The substrate is positioned on a chilled, flat base in the same manner as the flow experiment and placed on the microscope stage. This is mounted on the ice bed to ensure cooling. The solvent is also cooled in the chemical fridge as before. As this experiment is carried out in air, conditions are recorded only for the lab environment. The solvent is dosed into the chamber until almost full and the glass tip positioned close to the surface. Using low magnification (x5), the tip is controlled using the Kleindiek manipulator to be slightly above the plane of focus, with the solvent/air interface just at or slightly below the plane of focus. A droplet, shown later in the results section in Figure 3.3.1, forms at the end of the tip or gathers slightly back from the end of the tip and can be dosed to the solvent pool by running the tip into and out of the solvent surface. The tip is then moved away at high speed to allow a change to higher magnification lens (x50) to study the droplet. The deep pool is important as it can be clearly seen when a droplet remains at the surface or when it slowly sinks.

Due to the associated reduction in hydrodynamic forces in thinner layers of liquid, all of the contact angle measurements are carried out by dosing onto a coverslip in the chilled flow chamber as described previously rather than using the same deep pool of solvent. However, the chamber lid is removed for the duration of the experiments to allow access to the manipulator. In these experiments a much finer control is required with the manipulator as the layer of liquid is necessarily very thin. The focal plane is set at the surface of the liquid. The glass tip is brought slowly closer to the liquid and monitored under the microscope. At the point where the solvent surface snaps to contact with the glass tip a droplet is ejected from the tip using the syringe and then the tip is slowly retracted. The tip is then rapidly moved away. A low magnification (x5) is used to centre the drop in the screen. As this experiment is under atmospheric conditions, the dosing and recording times are not recorded.

3.2.4 Shared Features Across Three Methods

All of the configurations of the experiment share the following common factors:

- (i) Humid flow

The humid flow is delivered, as indicated in Figure 3.2.1 (b). The source of dry, filtered nitrogen is split into two streams. The first is directed to a flow meter and controller, the second towards a wash bottle containing de-ionised and filtered water at 60°C (Figure 3.2.1(a)). This saturated flow is piped through a flow meter, combined with the dry flow and passed through one more meter. For the experiment using the glass well, the flow was either piped slowly into

the larger chamber or gently through a spreading nozzle and across the surface. For the bulk of experiments, when using the flow chamber, the stream is split into two parallel entry ports and into one end of the chamber. The controlled combination of initial, dry and saturated flows of nitrogen coupled with the rapid chamber humidity feedback allows precise control over the delivered humid airflow. For each experimental run, the ambient and system temperature and humidity were recorded using a Rotronics hygrometer (Section 1.3.3). The flow rate was maintained at 1 – 1.5 Lmin⁻¹.

(ii) Cleaning protocol

The glass well used in the initial experiments was cleaned with soapy water and then repeated cleaning in acetone, propan-2-one and DI water with high pressure nitrogen used to dry the substrate. Microscope coverslips were most often used as the substrate. Two cleaning procedures were used. Fresh coverslips are rinsed in acetone, propan-2-one and then sonicated for three minutes in propan-2-one followed by high pressure nitrogen drying. The first two sets of results using one solvent were completed using this technique. It was noted however that results differed when switching to a new batch of coverslips. The AFM showed these to have significant deposits of an unknown material prior to cleaning compared with the older batch and a more rigorous cleaning method was employed. The microscope coverslips are first cleaned with warm soapy water using lint free cloth, rinsed with Nanopure deionised water and blow dried with nitrogen. They then undergo a 10 minute sonication in acetone followed by rinsing in water and blow drying again. Next they are subjected to 10 minutes sonication in methanol followed by rinsing with Nanopure (Thermo Scientific) water and blow drying in nitrogen. While an acid treatment is often used in literature, it also can provide other sources of potential contamination and significantly roughens the surface. Instead, to ensure any trace amounts of organic contaminants are removed the coverslips are then placed in an oxygen plasma using the asher noted in Section 1.3.1.6. The oxygen plasma ensures organic substances are broken down and reacted. Contact angle measurements show that this cleaning process has a significant effect leading to almost complete spreading of water. Experiments showed this process ensures the results observed previously are reproduced. The relevant cleaning process will be referenced when reporting results.

(iii) Image Recording and Analysis

Images are captured using the CCD camera, detailed in Table 1.3.1 for the Olympus BX51M microscope. Calibration was carried out for this microscope using an AFM calibration grid. The microscope views the droplets from above, as indicated in Fig. 3.2.3 (a). When focusing close

to the centre of a droplet, the submerged radius (r_{sub}) is quite clear, with the outer edge of the dark, sharp black line taken to be the outer edge of the droplet as seen in Figure 3.2.3(b). This is discussed in more detail with the validation in Section 3.8.1. Re-focusing towards the top of the droplet reveals a dark circle at the solvent surface. This is understood to be the portion of the droplet emerging from the solvent and the associated three phase contact line and is also shown in Figure 3.2.3(b). From this the three phase contact radius is measured (r_{tpc}). Calibrating the microscope with an AFM calibration grid, the CCD images captured can be used with image analysis software, ImageJ (160), to extract the measurements required. Where the contrast is sufficient a threshold is applied, converting the selected image to a binary format. The outer and three phase contact diameters are detected using a built-in particle counting technique. Where the contrast is not sufficient, which is true for most cases, manual measurements are taken instead. Two circles are fitted to each droplet, showing the outer diameter and three phase contact diameter. Errors are discussed in the validation section, 3.8.1. The relationship in Equation 3.1 is a simple geometric equation that allows the contact angle to be calculated.

$$\sin \theta = \frac{r_{tpc}}{r_{sub}} \quad (3.1)$$

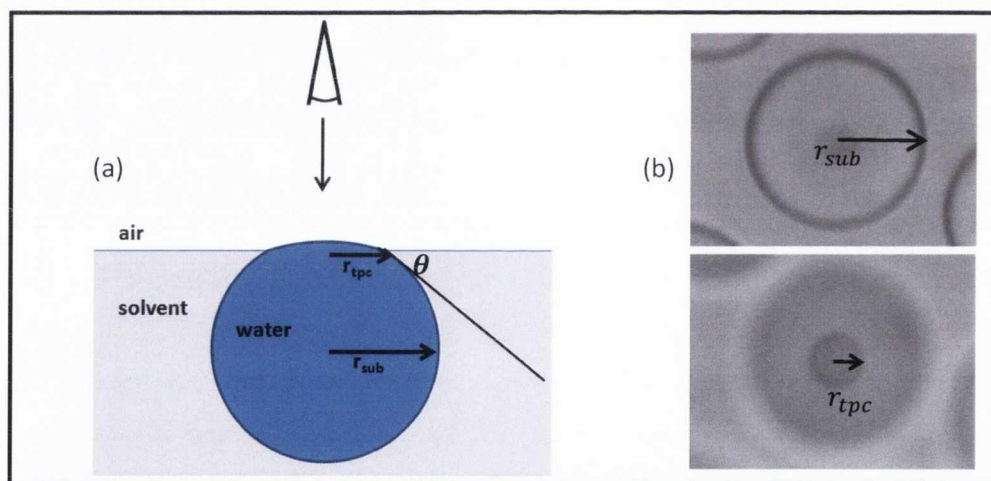


Figure 3.2.3: (a) Illustrates the positioning of a water droplet at a solvent/air interface and indicates the key geometrical measurements, the radius of curvature of the submerged droplet (r_{sub}), the radius of the three phase contact region (r_{tpc}) and the contact angle, θ . (b) Shows a pair of images taken of a water droplet at a butyl acetate/air interface, with optical microscopy. This technique allows focusing on and measurement of both r_{sub} and r_{tpc} .

3.2.5 Method Precedence

The approach described in Sections 3.2.1 - 3.2.4 was developed after the initial observation during a droplet tracking experiment that the three phase contact radius and submerged droplet radius could be identified. No previous reports have been found in the literature using such a technique for micron scale liquid droplet analysis. However, a number of reports take

advantage of similar observations and are summarised here to show where an overlap exists with existing techniques and where a new approach was required. Additionally, as part of the method validation, the level of errors and potential issues with employing this method are presented in Section 3.8.1.

The first key report found dated back to 1979 (161) where the group was looking at the change in wetting angles of glass microspheres with different levels of surfactants. The method observed the glass particles, using an inverted optical microscope, when they were trapped at the end of pendant drops of water. According to the authors, when a three phase contact is formed (Figure 3.2.4(a)) reproduced from (161), the part of the spherical particle that projects from the liquid strongly scatters light reflected from it, resulting in a black disc corresponding to the wetting perimeter with a central bright spot also observed (Figure 3.2.4(b)). The white “ghost” ring is the outline of the submerged droplet. With the combination of refractive indices used in this paper the authors state that the white ring represents 89% of the true diameter of the microsphere, going on to estimate the contact angle by:

$$\sin \theta = \frac{r_{tpc}}{r_{sub}} = 0.89 \frac{r_{tpc}}{r_{app}} \quad (3.2)$$

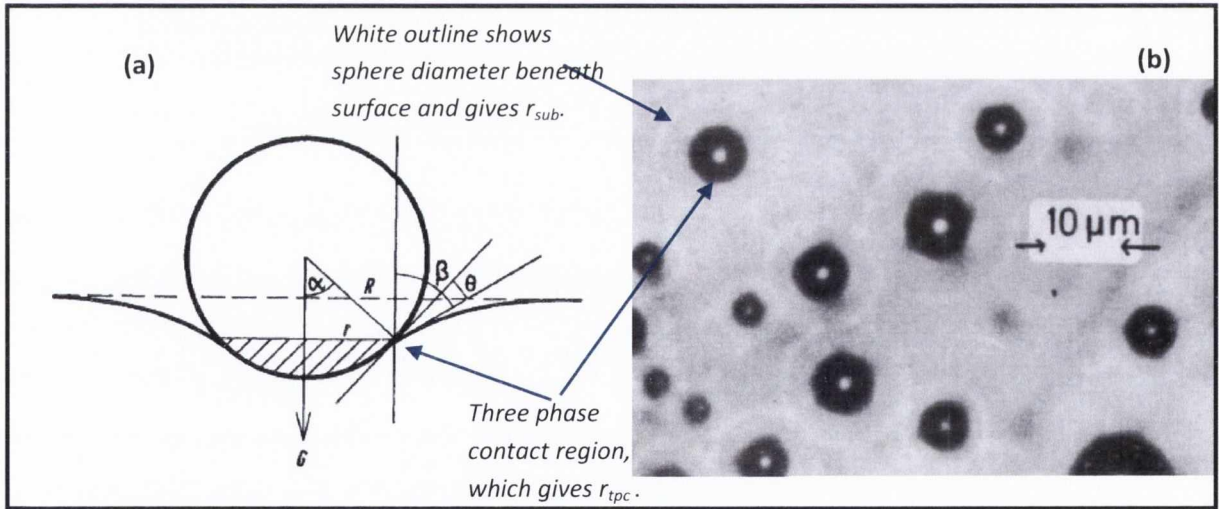


Figure 3.2.4: Reproduced from (161), the earliest example found of an optical microscopy technique used to measure the contact angle of spherical particles at an air/liquid interface. In this method the inverted imaging of glass spheres as they protrude through the liquid pendent drop allows measurement of the three phase contact radius and total submerged radius.

The authors use this technique to estimate line tension (approx. 10^{-11} N). Each of their subsequent papers includes an examination of the equilibrium receding contact angle of spherical particles with the electrolyte (162) - (164) using the same technique but with the estimate for the contact angle without the correction factor as shown earlier in Equation 3.1.

This technique and its results are referenced and used by (123), (165) - (167). The key argument against the validity of the results using this technique is that the heterogeneity of the glass spheres due to non-uniform adsorption of organic molecules over the surface will impact the wetting. This was noted by (149), pointing towards the non-circular perimeters in Figure 3.2.4(b) as evidence of this occurrence. Additional citations (146), (168), (169) also report the results or incorporate their line tension theory. Additional reports exist in the literature that also use the optical contrast at the three phase contact radius as a source of measurements (170) - (172). From the literature search, the methodology of measuring the contact angles through direct observation has some valid precedence. The dark circle seems to occur either due to light scattering or destructive interference depending on the system explored. It is important to note that our contact angles are in the region where geometrical constraints will not occur and as our system is entirely fluid there are not expected to be heterogeneities on the surface to affect wetting.

3.3 Results - Stability of Water at Solvent/Air Interface

This experiment was carried out with the aim of clarifying if a small droplet of water can indeed be stable when dosed to a solvent/air interface, when descriptions such as Neumann's Triangle and the Young Equation predict that it is not and to begin to understand if the mechanism of formation of porous microstructures is somehow responsible for the unexpected stability i.e. if nucleation and slow steady droplet growth due to condensation and coalescence events is different in effect or behaviour to dosing a single full size droplet suddenly to the interface. The experimental results reported in this section were all carried out as described in Method 3, Section 3.2.3 using water droplets dosed onto butyl acetate under atmospheric conditions, which were quite constant at approximately 25% relative humidity, 21.5° Celsius and a pressure of 1.027bar. The apparatus described, including the optical microscope, was positioned in a fume hood. This may have contributed to some level of uncontrolled air flow at the solvent/air interface. Four observed results were identified when exploring this dosing mechanism and are illustrated in the sections of still images taken from recording the dosing process that are shown in Figure 3.3.1 and 3.6.

3.3.1 Stable Lenses

The first observation is that the droplets of water can often be observed as stable lenses at the solvent/air interface. As shown in Figure 3.3.1(a), directly after dosing, the clear silhouette of

the droplet is observed and remains in focus at the surface until moving out of range of the CCD recording. Occasionally, later in the experiment, droplets are observed to pass back into range of the camera and while they cannot be identified with earlier images, it does signify this is not just a short term stability. Apart from the clear silhouette remaining in focus, almost all of the droplets remaining at the interface develop a bright spot in the middle only. This spot is believed to signify that three phase contact is established. Under low magnification and inaccurate focus, it was noted that the image captured by the CCD did not reflect an accurate contrast of the three phase contact when compared to viewing through the objective lens, which appeared darker. Also, at this x5 magnification, it is not possible to tell if the spot is adequately in focus and represents a dimensionally accurate three phase contact. Later experiments look at this in more detail.

3.3.2 Sinking Droplets

The second observation is that droplet sinking also often occurs using this dosing method, as shown in Figure 3.3.1(b). Once dosed to the interface, a clear silhouette of the droplet is initially observed. This then steadily becomes more blurred as it sinks and drops out of focus. Initial experiments showed it is more likely for the droplet to remain at the interface if the tip was gently dropped down vertically to the liquid as opposed to inserting it at an angle. This was the method used in Figure 3.3.1. Further exploration showed that the vigorous nature of the dosing, which relied on solvent/tip contact to occur also affects the stability. Subsequently more gentle approaches and retractions are used but these still lead to a mix of stable and unstable droplets.

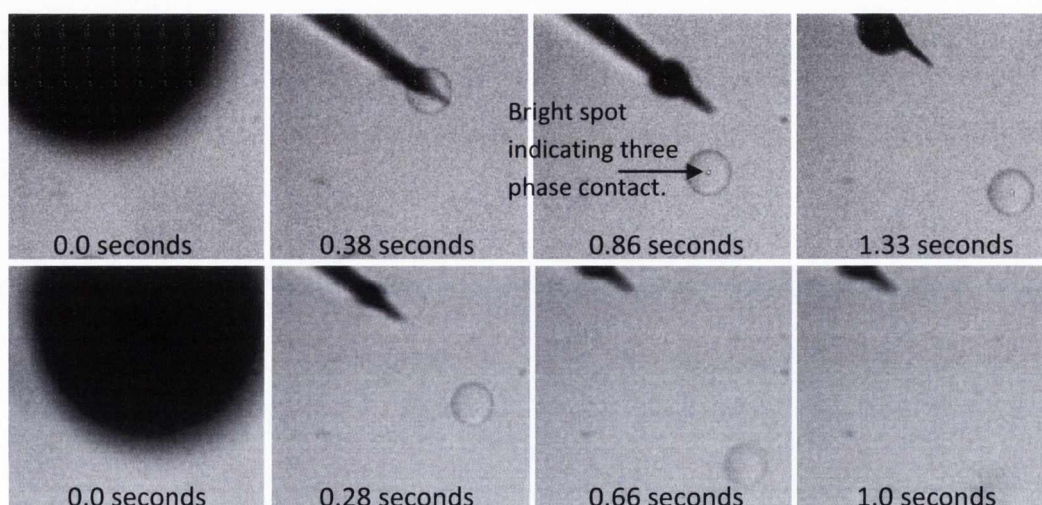


Figure 3.3.1: Optical microscopy images of a water droplet dosed through a glass capillary onto a butyl acetate solution. Images in row (a) show a droplet remaining at the solvent/air interface while images in row (b) shows a droplet sinking soon after dosing.

3.3.3 Rising Droplets

Using a tip movement speed that was part way between the vigorous and more gentle approaches that led to the images in Figure 3.3.1(a) and (b) respectively, a sequence of drops are formed over a two minute period. Droplets are seen to mimic the behaviour of Figure 3.3.1(a) and (b) with some drops sinking and others remaining at the interface. A third behaviour is also observed. On a number of occasions, illustrated in Figure 3.3.2(a), droplets are clearly visible but have not formed a three phase contact region. Normally, this leads to the droplet sinking but instead, after a time, some droplets develop the three phase contact point recognised by the central bright circle and remain stable at the interface.

3.3.4 Destabilising and Sinking Droplets

Generally, once a three phase contact has been formed the droplet remains at the surface and just disappears out of view of the CCD recording, possibly reappearing later due to the Brownian motion. However, on a number of occasions the droplet was disturbed and as a result submerged completely. This occurred most often when the dosing action of the tip catches an earlier drop, adds additional volume and then retracts. Figure 3.3.2(b) shows a different classification of disturbance, where two stable drops meet, coalesce and subsequently become unstable at the interface and descend into the solvent bulk. It should be mentioned that meeting and coalescing of droplets was a one-off occurrence but the immediate response to this event is worth illustrating.

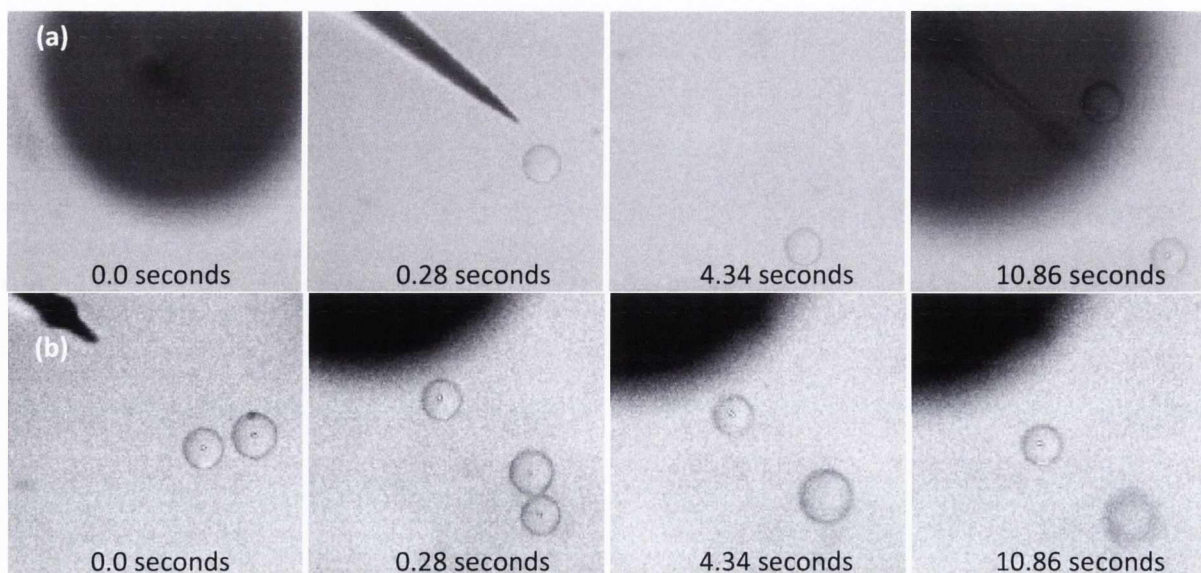


Figure 3.3.2: Optical microscopy images of a water droplet dosed through a glass capillary onto a butyl acetate solution. Images in row (a) show the droplet remaining at the interface but only developing a clear three-phase contact region after 11 seconds. Images in row (b) show a coalescent event lead to a droplet sinking out of the focal plane.

3.3.5 Results – Summary

These experiments show conclusively that water is stable at the solvent/air interface in the form of small spherical droplets. The adherence to the solvent/air interface is quite strong once made and rarely lost unless physically disturbed. The water does not appear to be ejected into the solution or onto its surface. It appears to cling to the glass tip due to its wetting properties and only to jump to the solvent phase on contact. The rate of withdrawal of the tip from the solvent appears to have an effect on the stability of the droplet. Slower injection leads to a lower likelihood of attachment of the drop to the solvent/air interface, as does approaching the surface vertically rather than entering it diagonally. It is interesting that when the droplets do not adhere to the water/air interface, water sinks. Gravity is not expected to play a significant role at these length scales as mentioned earlier but there are expected to be strong convection currents due to temperature variation within the solution due to cooling at the base and walls and these may have an effect. In the next section, a more sensitive method that can accurately measure the contact angle is applied to allow measurement in the change in Gibbs Free Energy. However, if the droplets energetically favour the solvent/air interface then a physical disturbance, which can move the droplet out of the region of influence of the interface, would be required to induce sinking. This distance is expected to be in the order of 100 nm, where the expected van der Waals interaction ends.

3.4 Contact Angle Measurements on Manually Dosed Droplets

The novel approach developed to dose and measure small droplet contact angles was discussed in detail in Sections 3.2.3 and 3.2.4. The analysis of recorded droplet images allows identification of the three phase contact radius (r_{tpc}) and the outer diameter and hence submerged droplet radius (r_{sub}). The contact angle can then be calculated using Equation 3.1. This configuration combining a chilled substrate, improved avoidance of external air movement and a thinner fluid layer has been found to reduce surface and bulk currents in the solvent significantly. The solvent is allowed to spread on a glass coverslip and so the thickness is only a few hundred micrometres. The coverslip is within the flow chamber and although the lid is removed to allow access for the manipulator, the sidewalls offer some protection from the air flow in the lab. This ensures the droplets are moving at relatively low velocities and can be tracked and captured by CCD imaging. Careful droplet tracking while controlling the fine focus allows the outer diameter and three phase contact area to be imaged. Examples of

obtained images are shown in Figure 3.4.1. Often, at high magnification, the droplets are larger than the field of view and so a number of images are taken and image analysis takes each into account when measuring the relevant dimensions. Butyl acetate is again used as the solvent to (i) allow comparison with the results in the previous section, (ii) provide continuity with the section regarding breath figure formation and (iii) to ensure minimum evaporation during the course of the experiment.

3.4.1 Results

This method uses a very delicate dosing to ensure the droplet does not adhere directly to the glass surface below the interface. If dosed with sufficient care, droplets are stable at the solvent/air interface. Once formed only two behaviours are noted.

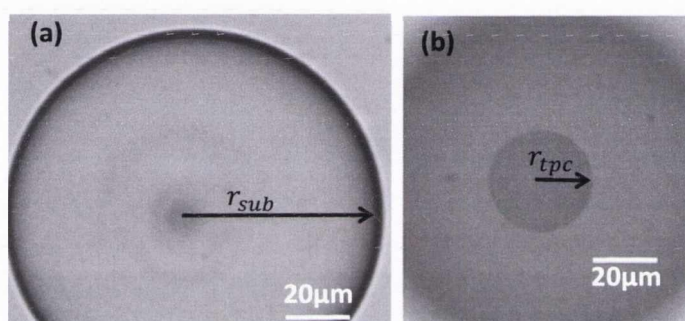


Figure 3.4.1: Optical microscopy image of a manually dosed water droplet on butyl acetate. Using a x50 magnification, (a) shows the outer diameter of the droplet in focus and (b) shows the three phase contact radius in focus.

Either the droplet (i) remains at the solvent/air interface, in which case it moves in a random motion at increasing velocities due to a decrease in size from evaporation, or alternatively (ii) it destabilises and spreads on the glass surface below the interface. This latter situation is difficult to avoid when the solvent layer is thinning from evaporation and when the droplet sizes are very large. The depth of the droplet approaches the depth of the film and hydrophilic interactions ensure attraction and wetting of submerged glass surface. The hydrophilic nature of the glass substrate is clear from the near perfect wetting exhibited in the contact angle measurements of water on clean substrates in Appendix 3.1.

Once the droplet is formed and present at the interface, it is noted that the size begins to decrease slowly over time. The low relative humidity, 25%, ensures a slow drive towards droplet evaporation. Droplets are observed for their lifetime and it is seen that the droplet reduces in size, down to the micron scale. Cooling of the experimental system appears reduce this effect and while the droplet is not at perfect equilibrium, evaporation is slow. This

evaporation of droplets while present at the interface is extremely important, as discussed later in Section 5.7.3. It shows both a dynamic control of the droplet size and also the ability of a droplet to grow and shrink rapidly through the mass transfer that can occur at the comparatively small three phase contact region. The evaporating droplets do not appear to have different contact angles to condensing droplets but a larger sample size may help confirm this. Each droplet tracking video is analysed and the behaviour of the system contact angle with three phase contact radius is recorded in Figure 3.4.2. The error bars are based on the uncertainty in the image edges of both the internal and external diameter.

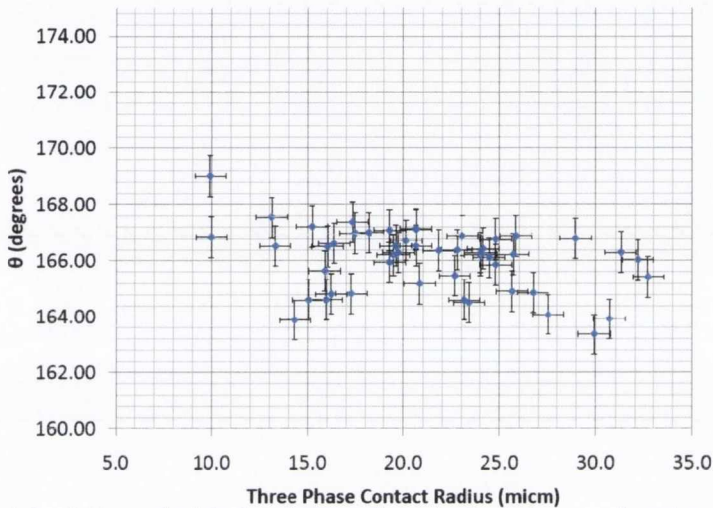


Figure 3.4.2: A plot of the calculated submerged contact angle, α , of water droplets at a butyl acetate/air interface against the observed three phase contact radius.

Notably this shows there is no observed change in contact angle with lens size. The average contact angle over the range is 166.0° with a standard deviation of 1.1° . Any trend must be quite subtle and within the level of the errors and noise. With this in mind, Figure 3.4.3 was prepared to compare the actual contact angles with those predicted by the modified Young equation. To do this, an average line tension value, 7.14×10^{-7} N, was used. This was calculated using Equation 2.9, the measured three phase contact radii and the values for the surface and interfacial tensions for water and butyl acetate.

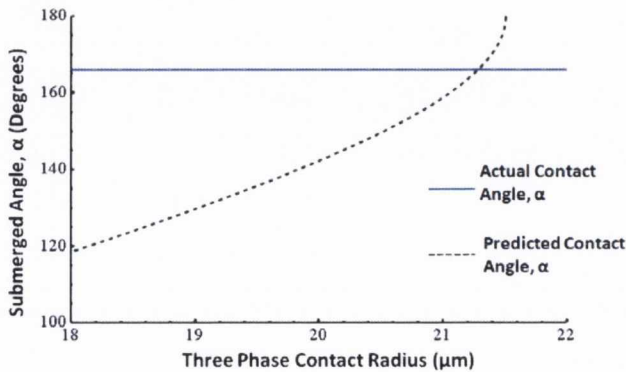


Figure 3.4.3: Predicted and measured trends are compared for water droplet submerged contact angles, α , over a range of three phase contact radii with butyl acetate as the bulk liquid phase.

It is clear that to maintain a constant contact angle with a term allowing for the excess energy at the three phase contact line, this value cannot be fixed as is normally assumed and must in fact scale with the lens size. This is seen in Figure 3.4.4. when comparing the volume of the submerged section of the droplet, found using Equation 2.12, with the line tension, calculated using Equation 2.10. This graph includes results when looking at condensation dosing of water as well, but these will be discussed in detail in the next section.

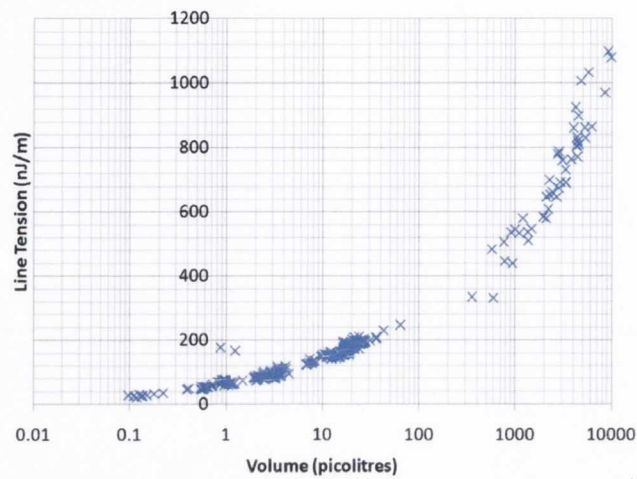


Figure 3.4.4: A plot of the calculated line tensions for water at a butyl acetate/air interface based on optical microscopy measurements against total water droplet volume.

Figure 3.4.5 shows the associated change in Gibbs Free Energy of a droplet moving from the bulk to the surface, both for changes in three phase contact radius and droplet volume. This uses a line tension value calculated using Equation 2.9 and shows that unlike Figure 2.5.7, there does not appear to be a minimum value for Gibbs Free Energy and the droplets appear only to increase in stability with increased volume. This contradicts the standard assumption that the line tension has a fixed value, the implications of which will be raised again in Section 3.6 with regard to the discussion of line tension.

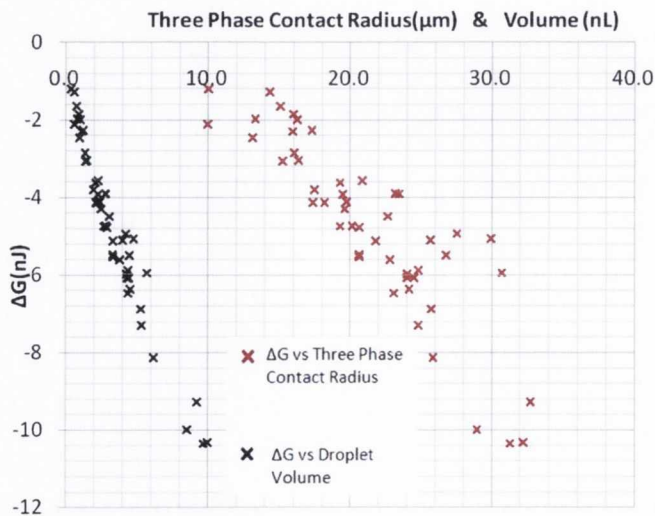


Figure 3.4.5: The change in Gibbs free with droplet volume (black) and three phase contact radius (red) calculated using equation 2.12 for measurements taken using optical microscopy of water droplets at an air/butyl acetate interface.

3.4.2 Summary of Results

A novel dosing system has been constructed to provide droplets of nanolitre scale to the surface of a bulk solvent with accurate control over position and force of dosing. The droplets examined ranged in size from approximately 20 to 60 μm in diameter, as seen in Figure 3.4.2. The dosing technique was adapted to form either droplets stable at the interface or droplets that immediately submerged. It was noted that the droplets were indeed stable at the interface as is reinforced by the large negative values calculated for Gibbs Free Energy. It was also noted that no significant change in contact angle with lens size is observed. This will be discussed at the end of Chapter 3. It is well known that mechanical and hydrodynamic forces can disrupt this stability and indeed this is the case here, with droplets sinking once detached from the surface. Most importantly, it was shown that stability is not a product of the technique used to introduce water to the interface as will highlighted in the next section where condensation is used to form lenses.

3.5 Dosing droplets by Condensation – Breath Figures

The method used to analyse nanolitre scale droplets, detailed in Method 2, Section 3.2.2, was applied to smaller droplets grown through condensation of water vapour onto the solvent surface. As described in Section 3.2.3, this necessarily required modification of the apparatus. As this approach is not well documented or developed, it was not clear what accuracy or sensitivity we could expect. With condensation dosing, the droplets can be significantly smaller but also critically far more numerous. This increased the number of data points considerably, which has strengthened confidence in the results. As mentioned in the process description, we found that repeatable results required a combination of two focused images, one at the surface and a second to capture the internal diameter of the droplet. However, as one focuses through a droplet different optical effects are observed. It is therefore important to state the assumptions we made to take direct measurements and also the evidence used to form them.

3.5.1 Analysis of Optical Features and Errors

Firstly, the three phase contact region is believed to be the dark region at the centre of the droplet (161). Also, from focusing it is noted that they are the features closest to the microscope lens and so the feature at the solvent surface. The errors involved in the measurement of the three phase contact radius are examined using butyl acetate as the

solvent. The values vary from 0.98% of the radius value for extremely large drops to 5.7% of the radius value for smaller droplets. This will increase further with decreases in drop volume due to the resolution of the camera and the stability of the droplets. The measurement of the diameter is limited not only by the manual focus but also by the pixilation of the image. We looked at the region of ambiguity in each image and measured the maximum and minimum interpretable drop sizes in a selection of 20 droplets from different experimental runs.

This cannot translate to an impact on the accuracy of contact angle results without determining the uncertainty of the outer diameter. The outer diameter of the droplets is subject to more severe optical effects that need to be examined. While we do not see the same scale of the “ghost” rings at the droplet diameter observed in (161), there are white bands surrounding the darker circumference of the droplets. These will now be discussed with reference to two different sample sets, firstly with a system of water droplets on butyl acetate as shown in Figure 3.5.1 and secondly with a system of water droplets on chloroform as shown in Figure 3.5.2.

Starting with the samples formed with butyl acetate as the solvent, when focusing on the three phase contact radius of the water droplet (a), the area of white “haze” is quite large, however, focusing to the maximum droplet diameter it can be seen that while a white band exists at the edge of each droplet, they have been observed to overlap partially, (b), or completely, (c), leading to the darker edges touching.

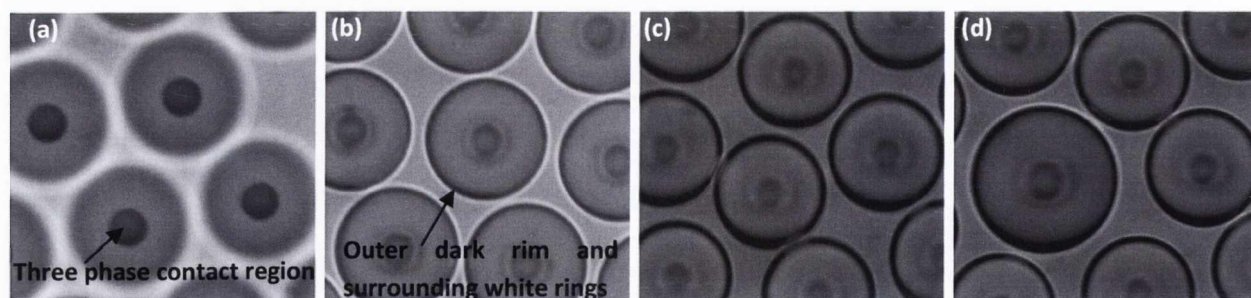


Figure 3.5.1: Optical microscopy images showing (a) the three phase contact region, (b) the outer diameter of water droplets on a butyl acetate surface and a surrounding white ring. A coalescence event for two water droplets is recorded in (c) and (d) .

Looking at water droplets formed on a chloroform interface with the same approach shows a similar picture. (a) – (c) in Figure 3.5.2 show that the ordering and packing appears to occur with the edges of this white band interacting. Upon close packing however, this is not the case as seen in (d)-(f), where many contacts occur between the darker edges. Larger droplets are also clearly captured with either a slight gap with white rings or touching with an interruption to the white rings. Examples from these two solvents suggest that while the origin of the white

band is not clear, it seems highly unlikely that it signifies the location of the edge of a droplet. The interactions between droplets linked to these white bands appear to occur when the surface is loosely packed. This suggests the bright band could perhaps originate from interference from non-planar three phase contact leading to a slight meniscus.

As a result of this, the measurements taken were exclusively at the edge of the outer dark rim, observable only when focusing down through the droplet to the widest point. The error in measurement is taken in a similar way as before and using butyl acetate varies from 0.27% of the radius value for extremely large drops to 6.7% of the radius value for smaller droplets. At the worst case, combining the errors of both measurements, the error in measurement of contact angle for smaller droplets is ± 1.1 deg in this case. This is expected to decrease for larger droplets due to the resolution of the microscope, and indeed was seen earlier to be ± 0.36 degrees. Small droplets are therefore expected to have much larger errors associated with them due to the method of measurement.

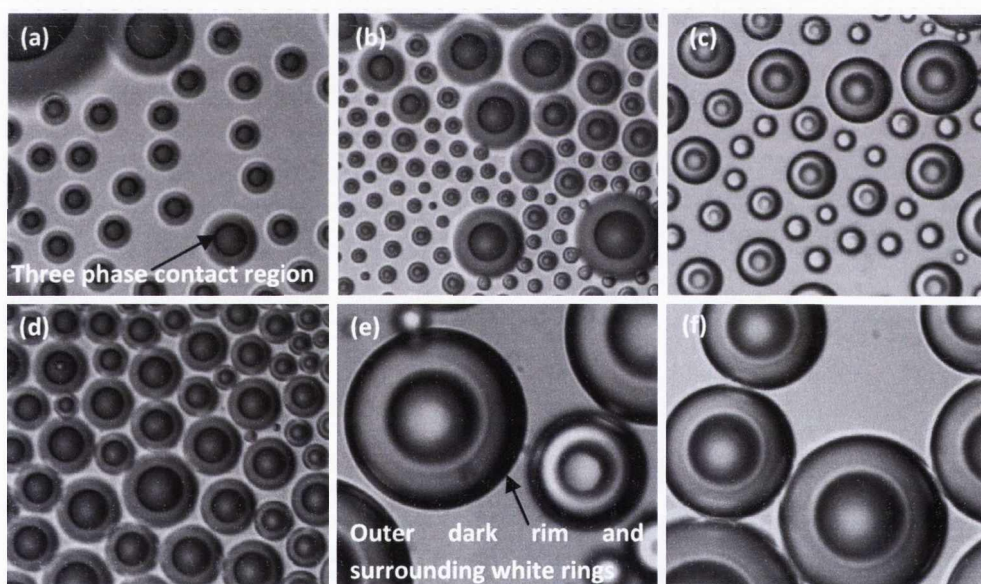


Figure 3.5.2: (a)-(f) Optical microscopy images at x50 magnification of the three phase contact region and outer diameters of water droplets at a chloroform/air interface.

3.5.2 Errors in Humidity

This method, which relies upon airflow to deliver the moisture, can lead to poor imaging due to energy delivered to the droplets from the air stream. To overcome this, most videos are recorded with the flow turned off for some duration. This allowed clear imaging of the droplets at the expense of a fluctuating humidity. To see if this has a significant impact two separate runs of butyl acetate were recorded and frames were identified where the humidity was at a maximum and minimum for that sample. The droplets in these frames are compared for contact angles and found not to be significantly different for a humidity change of 20%.

3.5.3 Results – Pure solvents

The method of condensation dosing and optical observation is still under development but from the analysis of errors, well enough defined to compare contact angles of different solvents. The three solvents used were chloroform, toluene and butyl acetate. Chloroform and toluene were chosen due to their relevance in the field of water droplet templating studies. Butyl acetate was chosen due to its relatively low vapour pressure, low water solubility, relatively low polarity and low toxicity. The resulting contact angles are shown in Table 3.5.1, with the pore sizes and data scatter illustrated in Figure 3.5.3. The line tension is calculated for each droplet using Equation 2.10 and divided by the three phase contact radius of the droplet as a normalisation procedure. This normalised line tension is seen to scale inversely with the solvent/air and solvent/water surface tensions, showing that for low surface tension systems a larger line tension force is required to maintain a droplet at the interface. These results showing a constant contact angle echo those of section 3.4.1. It is important to note that the calculated values for line tension are on the upper scale of those reported in the literature. Also, the key predicted observation of droplet size dependence of contact angles has not been recorded. This will be discussed further in Section 3.6.2.

Solvent	$\gamma_{\text{Solvent/Air}}$ (J/m ²)	$\gamma_{\text{Solvent/Water}}$ (N/m)	Contact Angle, α (Degrees)	Normalised Line Tension, τ_n (J/m ²) $\times 10^4$
Chloroform	0.027	0.028	146.9 $\pm$ 3.5	-33.4 $\pm$ 1.5
Toluene	0.028	0.036	169.9 $\pm$ 2.4	-14.8 $\pm$ 0.3
Butyl Acetate	0.0251	0.0145	161.7 $\pm$ 2.8	-53.8 $\pm$ 0.5

Table 3.5.1: Surface tensions, average contact angles and normalised line tension for water droplets on chloroform, toluene and butyl acetate.

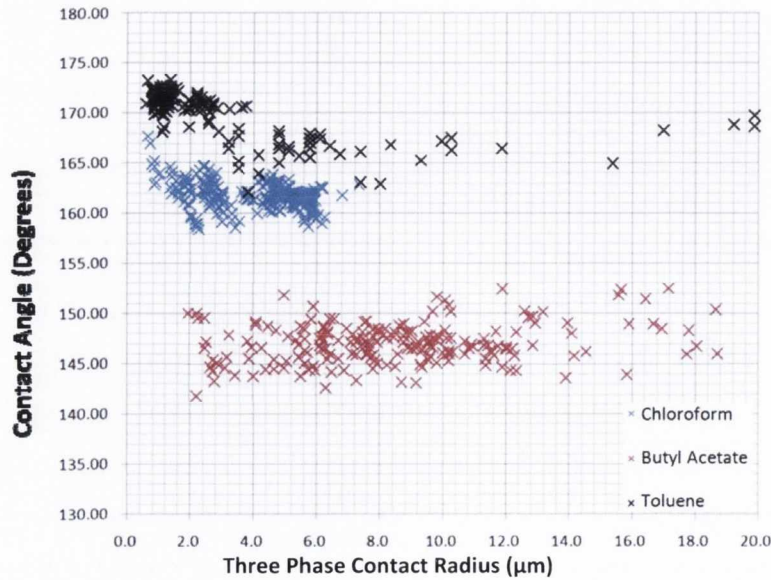


Figure 3.5.3: Plot of the calculated submerged contact angle, α , of water droplets on chloroform, butyl acetate and toluene plotted against the measured three phase contact radius.

3.5.4 Results – Polymer/Solvent Solutions

Two solutions were prepared with dicarboxy-terminated polystyrene (DCPS) in first chloroform then toluene. 3% by mass DCPS in chloroform was used, as is the standard concentration used throughout chapter 4. An equivalent molar concentration was calculated and used for the toluene sample. If equivalent mass concentrations were used, it would lead to a significant change in molar concentration of polymer due to the very different densities involved. Further details of the results will be in Chapter 5, when examining the control of process dynamics and their resultant control on pore morphology. The contact angles found are detailed in Table 3.5.2.

Solvent	Contact Angle, α (Degrees)
Chloroform	146.9 ± 3.5
with DCPS	142.7 ± 2.7
Toluene	169.9 ± 2.4
with DCPS	167.0 ± 1.5

Table 3.5.2: Comparison of calculated values of the submerged contact angle, α , of water droplets on pure solvent with those on polymer solutions of the same solvent.

While only a slight drop in average contact angle is seen, they are borderline in their significance due to the errors involved. Interestingly, there does seem to be a slight trend in contact angle with the three phase contact radius when looking at the chloroform/DCPS solution, as shown in Figure 3.5.4. At these length scales, errors of 5 degrees are feasible but as these are based on the final image analysis detection it would be a more random error that would not lead to a trend.

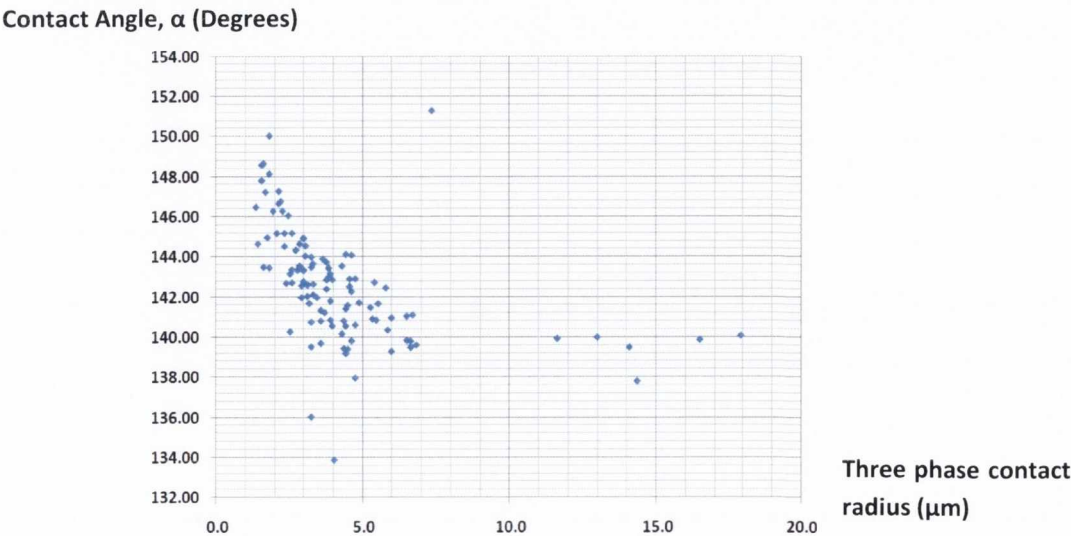


Figure 3.5.4: Plot of the calculated submerged contact angle, α , of water droplets on chloroform/DCPS solution against the measured three phase contact radius. This shows a slight trend in contact angle with droplet size near the resolution of the current set-up.

3.5.5 Results – Additional Observations

3.5.5.1 Droplet Coalescence

Using Method 2, Section 3.2.2, it was also noted that close packed droplets of water in chloroform are not very stable against coalescence. The overall drop size increases due to both intrinsic and coalescent growth. As a result, chloroform samples were noted to have a wide range of droplet sizes as reflected in Figure 3.5.5. Also in this figure a series of rapid coalescent events are indicated.

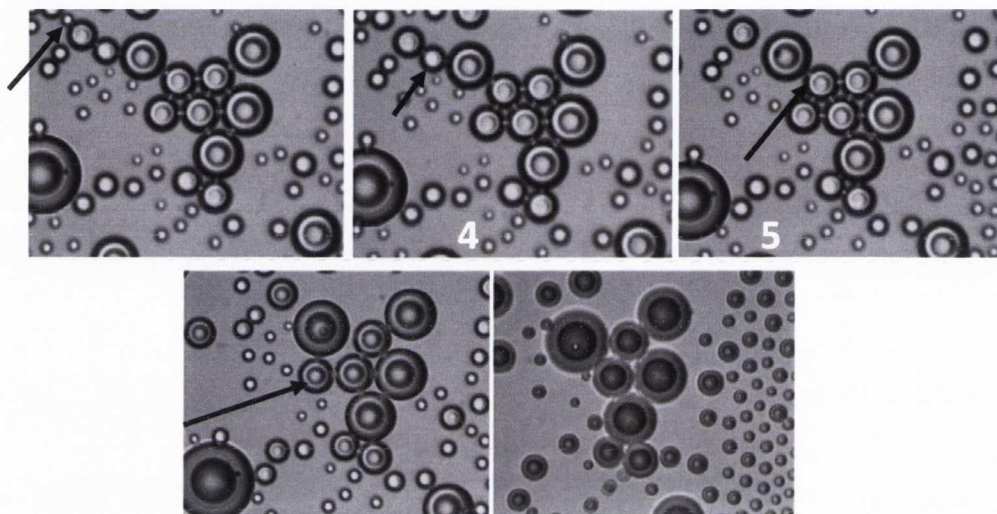


Figure 3.5.5: Optical microscopy images of water droplets on a chloroform surface. Coalescence events are observed and the droplet about to be engulfed is indicated with a black arrow.

Also, it was noted that when working with chloroform, significant currents were observable in the solvent. These could be seen because of the large quantities of very small droplets that were trapped and circulated within them. Only very large droplets could be clearly seen as these remained at the solvent/air interface.

3.5.5.2 Addition of polymer

Qualitatively, once polymer is added to chloroform, the instances of coalescence appear to drastically decrease. Events still occur but rarely. There are also fewer extremely large pores, that grew due to coalescence.

Toluene shows a similar but even more dramatic trend. Comparing only the experiments using the same dosing technique as with butyl acetate and chloroform (Method 2, Section 3.2.2), coalescence dominates droplet interactions. This leads to sparse coverage of widely varying droplet size. Interestingly, although of poor quality due to the speed of movement, initial droplet formation was captured with toluene and it is seen that the droplets initially form as isolated and non-interacting entities. Once their coverage increases they start to coalesce and

this leads to the non-homogeneity of droplet size. Again, adding polymer to the system reduces this to the stage where ordered droplets of small homogeneous size are formed in rafts across the surface, as seen in Figure 3.5.6.

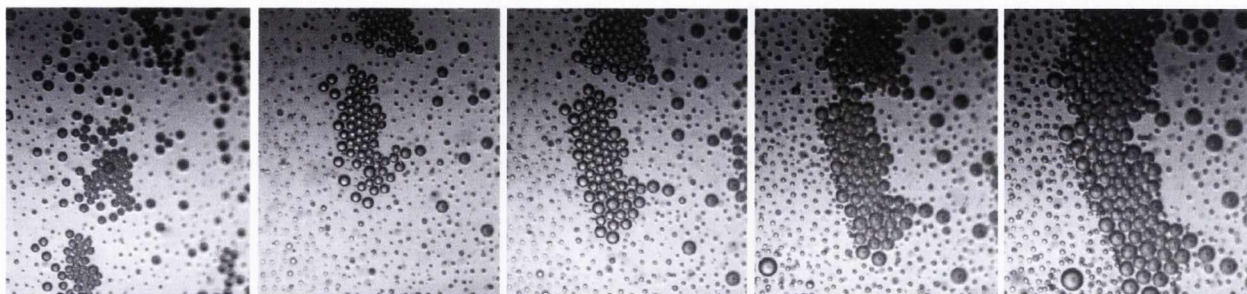


Figure 3.5.6: A sequence of images taken with optical microscopy show rafts of water droplets ordering and growing on a toluene/DCPS polymer solution.

Butyl acetate is the clear exception to the above observations in that water droplets in this medium are extremely stable against coalescence as seen in Figure 3.5.1(d). Coalescence is observed on rare occasions but generally the droplets remained relatively monodisperse in size and isolated throughout the duration of the experiment. Droplet interaction, packing and flow are observed with virtually no coalescence occurring. In fact, there are occasions when the dark rims on the outer parts of the droplet images touch. In general, the repulsion appears to occur without physical contact, which may explain the lack of coalescence. It is conjectured that the white bands that surround the droplet images are optical effects from non-planar menisci that lead to a long range repulsion. This is an extremely important observation as this solvent is not used in Breath Figures but offers the opportunity of reducing the quantity of defects due to the freedom to pack over long periods and its stability.

3.6 Summary and Discussion

3.6.1 Key points

This novel method for contact angle measurement was examined thoroughly in terms of the errors and the artefacts to show that it can be used to yield contact angle results. This was required as it is not yet a method prevalent in the literature. Alternative methods did not allow analysis of such high contact angles and did not offer a solution to measuring large quantities of micron scale droplets. Errors are very low for the majority of results but can increase significantly with very small droplet measurements. This can be improved upon by switching to a more advanced image analysis software.

Exploring as wide a range of droplet size as was feasible with the current set-up yielded no trends in contact angle with the size of the droplet. The constant value for the normalized line tension, shown in Figure 3.6.1 for three different solvents, infers that the line tension term must scale with the length of the radius. Another interpretation is that a constant force is acting in the balance shown in Figure 2.5.1 and the implications of this will be discussed shortly. This is specific to each solvent as each had its characteristic contact angle.

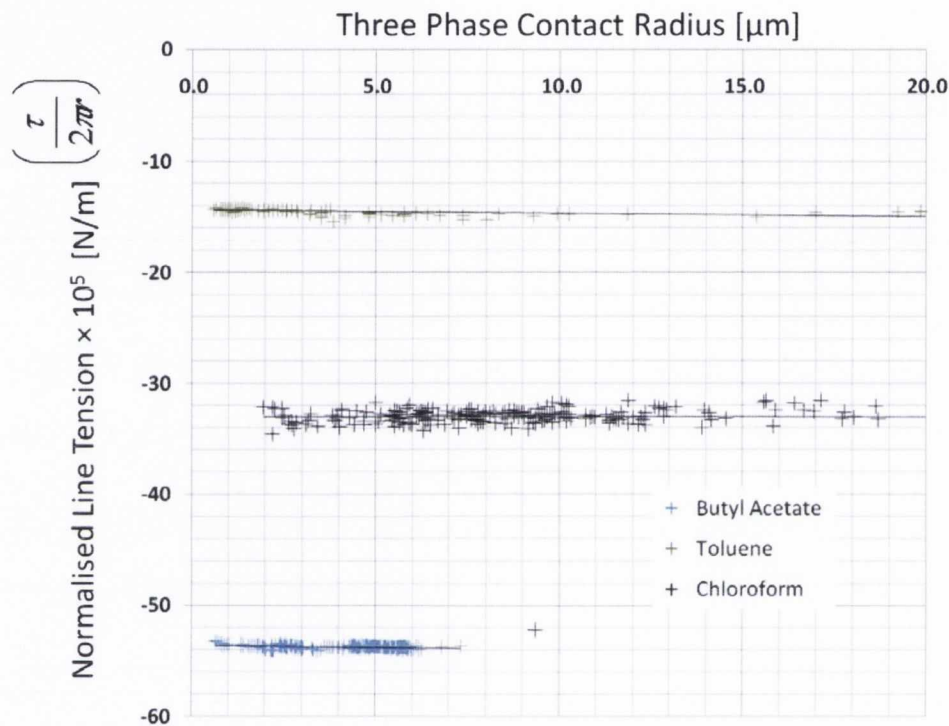


Figure 3.6.1: Normalised line tension is calculated by dividing the calculated line tension from optical measurements of water droplets at a solvent/air interface by the circumference of the three phase contact radius. It can be seen that this is essentially constant for the measured values.

It was shown that water droplets are stable at the solvent/air interface by manual and condensation growth, thus showing that an additional interaction is definitely required for the Neumann relation to explain the results. As shown in Appendix 3.2, it is unlikely the temperature dependence of surface tension or the curvature effect on surface tension are responsible for this phenomenon.

Interestingly, the contact angle of the water droplet at the solvent/air interface is shown to change very little with addition of a significant quantity of polymer. With an interfacial acting polymer, the balance of surface tensions is expected to change significantly. For this reason, the surface tension of the pure polymer, DCPS, was measured using the sessile drop technique

summarised in Appendix 3.3. A value of 0.022 N/m was found, which compares well with the only other reported value found in the literature, 0.027N/m (31). It is hypothesised that with the surface tension being quite close to that of the solvent, its effect on the contact angle may be reduced. However this validates the initial assumption that a model, once finalised, for pure solvents will be applicable to the polymer system to the benefit of controlling the water droplets for use as a template.

The reasons for the constant contact angle when clarified, will have a significant impact on the understanding of water droplet stability and templating and so a number of reasons for this behaviour will now be suggested.

3.6.2 Examining the Constant Contact Angle

It is possible that assumption 1, Section 2.5.1, is invalid and that the surfaces are not free from adsorbed layers. It is possible that water vapour will adsorb to some extent on the solvent surface while it is under the conditions required for condensation to occur. However, this is not expected to have a significant impact on the surface energy. If, on the other hand, a Gibbs layer of solvent migrates and adsorbs onto the water droplet/air interface, this is expected to decrease the surface energy of the water significantly. Equally, if the water droplet reaches a saturated chemical equilibrium with the solvent, a lower surface energy generally results. For example water saturated with chloroform is reported to have a surface energy of approximately 0.064 J/m². However, even at these low values, the surface tension balance alone is not sufficient to explain the contact angles observed. While the necessary line tension term would be a factor of 10 smaller, it is still a significant factor in the force balance.

As it appears that line tension is likely to be important in this system and yet the contact angle is not changing with droplet volume as predicted, it was considered whether the line tension value in fact held a constant value. The possibility of line tension being a function of the three phase contact radius and contact angle has argued in the literature in terms of sessile drops by (122), (151), (173) with the basic explanation that the relative inclination of the phases determines the extent of the molecular interaction, which in turn is responsible for defining line tension (122).

Experimentally, a dependence of line tension on droplet size and contact angle has also been noted for liquid lenses but is still yet to be fully defined (174), (175). The droplet/surface

interaction angles examined within this thesis have not been directly considered and will now be briefly examined.

Based on the theory in Section 2.1, it was examined if a change in the curvature of a spherical drop could be expected to lead to a change in the strength of interaction with a surface. The Derjaguin approximation is a mathematical approach developed to estimate the interaction (either repulsive or attractive) between two spherical particles (111). It can be adapted to also show the interactions between a spherical particle and a flat surface, which leads to Equation 3.8:

$$W(D) = - \frac{4\pi^2 C \rho^2 R}{(n-2)(n-3)(n-4)(n-5)D^{n-5}} \quad (3.8)$$

Where $W(D)$ is the net interaction energy at a distance D . R is the radius of the spherical particle, n = number of interactions, C is a constant, ρ is the number density of molecules in the spherical particle. As shown in Figure 3.6.2 (a), we can consider a spherical droplet of water approaching the air/solvent interface and consider the interaction force. Figure 3.6.2 (b) illustrates that when at the interface, the region where the three phases interact and exert an influence over each other is confined to a wedge. This circular wedge is also the region responsible for the deviations from bulk values of surface tension, referred to in Section 2.4.1 as the confluence zone. With an increase in the droplet radius, it can be seen from Equation 3.8, that the interaction is expected to increase in strength with the radius of the droplet. This can be understood by considering at high submerged contact angles, the wedge region will increase in volume as the droplet grows. This may be responsible for an increase in interaction strength with the radius of the droplet.

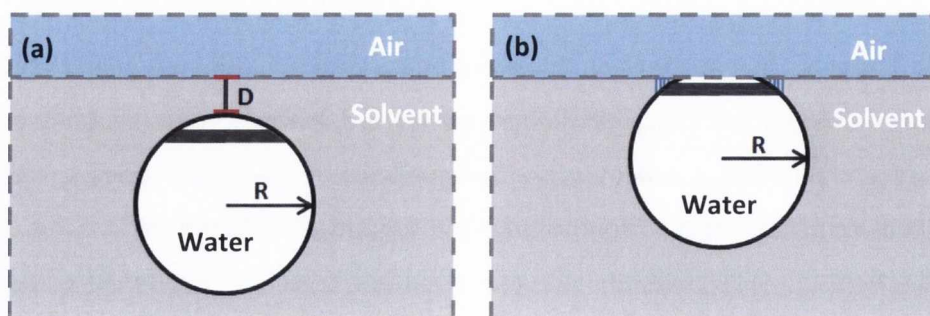


Figure 3.6.2: (a) A spherical particle approaching an interface has similar geometries and interactions as (b) a droplet of water at an interface.

This region of interest is similar to the non-local confluence zone discussed in Section 2.4.2 and so these models should be consulted for ways to deal with the interacting geometries appropriately.

There is one further explanation as to why the constant contact angle may be observed, despite the expectation that a significant line tension value is present. The optical measurement technique assumes that two spherical caps meet at the three phase interaction line. However, as this is an all-fluid system, this may not necessarily be true. It is feasible that the effect of the three phase line tension is isolated to the region very close to the solvent/air interface while the rest of the submerged section of the droplet is only affected by the two phase interaction between the solvent and the water. A change in contact angle below the diffraction limit of light will not be observable in the optical microscope.

It is quite likely that the effect of the three phase contact region, approximated by the line tension, is affected by an adsorbed layer of solvent at the water/air interface. Coupled with the predicted increase in the effect of this three phase region with an increase in droplet radius, it is believed that line tension values are most likely smaller than calculated within this chapter and not fixed. An examination of adsorbed surface layers and their effect on surface tension for the materials in this chapter should be carried out. More accurate measurements will also be required to observe minor changes in contact angle, which would currently be obscured even if present.

3.7 Next Steps

- Experiments are planned to look at the change in the surface tensions with (i) saturation of water with solvent, (ii) formation of a Gibbs layer of solvent on water and (iii) formation of a Gibbs layer of water on chloroform.
- The next stage of experiments will require improved temperature control to ensure minimal convection currents. This is hoped to allow clearer imaging of smaller droplets. Coupled with improved image analysis software, it is important to view the smaller scale drops accurately.
- The model will need to be adjusted with respect to changes in interaction due to the change in contact angle.

- Contact angles of the droplets need to be examined at the sub-micron scale. One potential method is the formation of polymer films using these droplets as templates and using focused ion beam milling to examine the resulting contact angles.

This work gave significant insight into the action of water droplets at a fluid/air interface. Techniques for manual and condensation dosing of micron-scale water droplets were developed that allow stable tracking and measurement. A novel technique for contact angle measurement of the droplets was presented that allows large quantities of data to be collected. These experiments showed the minimal role of the polymer in the ability of water to form a stable droplet at the solution/air interface during the breath figure process. Values for line tension were calculated that led to these observations but may need to be adjusted to include the presence of a Gibbs layer at the droplet/air interface. Results confirmed that the polymer solution requires almost identical line tensions and acts only as a means of trapping the water droplets, rather than having an impact on the stable contact angles at the interface. The following two chapters will look at the use of these droplets as templates for a polymer film in a non-equilibrium, dynamic environment. It is hoped that the coupling of the two approaches will lead to advances in the understanding of the overall mechanism.

Chapter 4

Breath Figure Templating – Part 1: Microstructure Formation and Control

4.1 Introduction

Chapters 2 and 3 examined the fundamental effects and influences of micron scale water droplets existing, interacting and ordering at an air/liquid interface. This was approximated as an equilibrium problem and analysed with regard to interfacial interactions. Chapter 4 is concerned with the highly dynamic, non-equilibrium events that enable the existence of these droplets at the interface. The work presented here describes the experiments carried out, while attempting to identify the key parameters that affect the formation and morphology of ordered microporous polymer films by water droplet templating. The chapter focuses on the effect of influencing parameters on both the pore opening, as is the standard approach throughout the literature, and also on the internal microstructure, which is analysed using a novel technique developed as part of this work and is rarely detailed in the literature. This will be followed in Chapter 5 by experimental and theoretical analysis of the system in an attempt to quantify the changing physical properties that are driving the behaviour identified in this chapter.

The first section will detail the experimental techniques and procedures used to form and analyse the porous polymer films. The formation techniques are grouped into the earlier static methods using a calm humid environment, as often found throughout the literature, and the more recent development of a dynamic, humid air flow technique. The latter represents the source of the bulk of results due to its improved repeatability, control and parameter measurement. However some results will be presented using the earlier technique due to the importance, even if of a more qualitative nature, of the behaviours observed.

4.2 Experimental Apparatus and Procedures

This section provides details of sample preparation for the methods detailed in Chapters 4 and 5. Each section of results and discussion will reference the appropriate technique and state any variations as required.

4.2.1 Polymer Solution Preparation

A new glass vial is used for each solution. This is flushed with high pressure nitrogen to remove any dust. Each vial is labelled with the sample code, concentration, chemical name and hazard symbol. The vial is placed on a mass balance. The target mass of polymer is weighed into the vial using clean tweezers. The required mass of chloroform is then added to the vial. This is added in the fume hood, sealed and then transferred to the balance to check the weight. Once the mass of chloroform is slightly in excess of the target, the solution is mixed manually for one minute. When making solutions with a high concentration of polymer or if using a batch of densely packed polymer, the solution is subjected to sonication mixing for a few minutes to aid dissolving. The lid is opened and the inside of the vial is checked to ensure no polymer remains on the walls. Some small amount of evaporation is then allowed over time to bring the solution to the correct concentration. The solution is sealed and allowed to sit until all air bubbles induced in the mixing have disappeared. Before use, the solution is checked visually to ensure no obvious contamination or insoluble materials are present.

4.2.2 Solution Dosing

The polymer solution is dosed using a micropipette. When using a chamber with a static humid environment, a range of volumes is used and is detailed when appropriate in the text. The flow technique uses a standard volume of 60 μL per sample due to the size of the glass substrate. Each apparatus that was designed as part of this thesis has a port to allow dosing while at the required humidity. A fresh tip is used for each sample. A steady flow of solution is used when dosing, neither applying enough force to create a fast jet nor so little as to give drop-wise addition. Reproducibility of spread is examined later in this chapter.

4.2.3 Water Vapour Supply

Water vapour is obtained by bubbling dry nitrogen through a Dreshel flask of 90 mL warm water and its headspace. A water temperature of 55-60°C is maintained using a hot plate. The volume of water ensures that no water is flushed through the inlet to the formation chamber. The gas flow is also kept as low as possible for the same reason.

4.2.4 Substrate Preparation

Initial work, using the static environment formation detailed in section 4.2.5, was carried out using plain glass microscope slides for the substrate. These were replaced upon moving to spin-coating and flow methods. In the reported work, unless stated otherwise, the substrates are 22 mm x 22 mm glass, super clean cover slips from VWR International, supplied in a dust resistant packaging. These are approximately 100 μm thick. For almost the entirety of results reported in Chapters 4 and 5 these substrates are sonicated in clean propan-2-ol and dried with a high pressure nitrogen gun before use. Very early work with these substrates did not add this extra cleaning step, however, a fresh slide was used each time. The substrate is only handled near the edges using a clean, flat-nosed tweezers or held briefly by the edges using clean gloves to avoid contamination.

4.2.5 Initial Experimental Techniques

Section 4.3 describes insights from the early stages of the project when the apparatus was being developed. The methods referenced in this section are outlined below with reference to an associated illustration of the apparatus in Figure 4.2.1.

In the apparatus (a) – (e) presented in Figure 4.2.1, a humid environment is provided by leaking a low flow of nitrogen into a Dreschel flask of warm water and piping the outlet stream of vapour-entrained nitrogen into the chamber. Flow control is minimal but the flow is maintained at a low level to try and keep the chamber as calm an environment as possible. The relative humidity is measured using a small, stand-alone hygrometer (THpen thermo-hygrometer 8708) and recorded manually from a digital readout at regular, timed intervals. The chamber is a desiccator with a chemically resistant base and lid. The base can be levelled and this is checked before each experimental run. Apparatus (f) uses a higher flow of nitrogen and so half the amount of water is added to the Dreschel flask to avoid transfer of liquid water directly to the desiccator.

Procedures

- (a) The first basic experiment involved placing a microscope slide in the chamber, dosing the polymer solution, closing the lid and increasing the humidity to the desired value. The process is timed from the point of dosing and the humidity recorded manually.
- (b) The system was modified to allow dosing directly into a humid environment and avoid humidity fluctuation.

- (c) A spin coater was constructed and inserted into the chamber. The speed is set before each experimental run by adjusting the attached variable resistor and measuring the rotations with a tachometer. This allows spin coating to occur at a known and fixed humidity. Dosing and spin time are recorded.
- (d) An inverted sample is formed using the same technique as (a). However, the sample is dosed onto a slide attached to a stand that can then be quickly inverted and sealed in the chamber.
- (e) To avoid the uncertainty in humidity and humidity ramping when employing the inverted technique, a motorised rapid sample flipping device was constructed and installed in the chamber. The sample is formed as in experiment (b). Once the dosing has occurred an external switch is closed and the motor flips the sample 180°.
- (f) A rudimentary flow set-up was assembled. A glass chamber was constructed, using a standard adhesive for glassware. The chamber is approximately 10 mm high and 26 mm wide for the flow experiments. The diagram shows a similar set-up where the height was increased to allow an inverted and upright sample to be formed simultaneously.

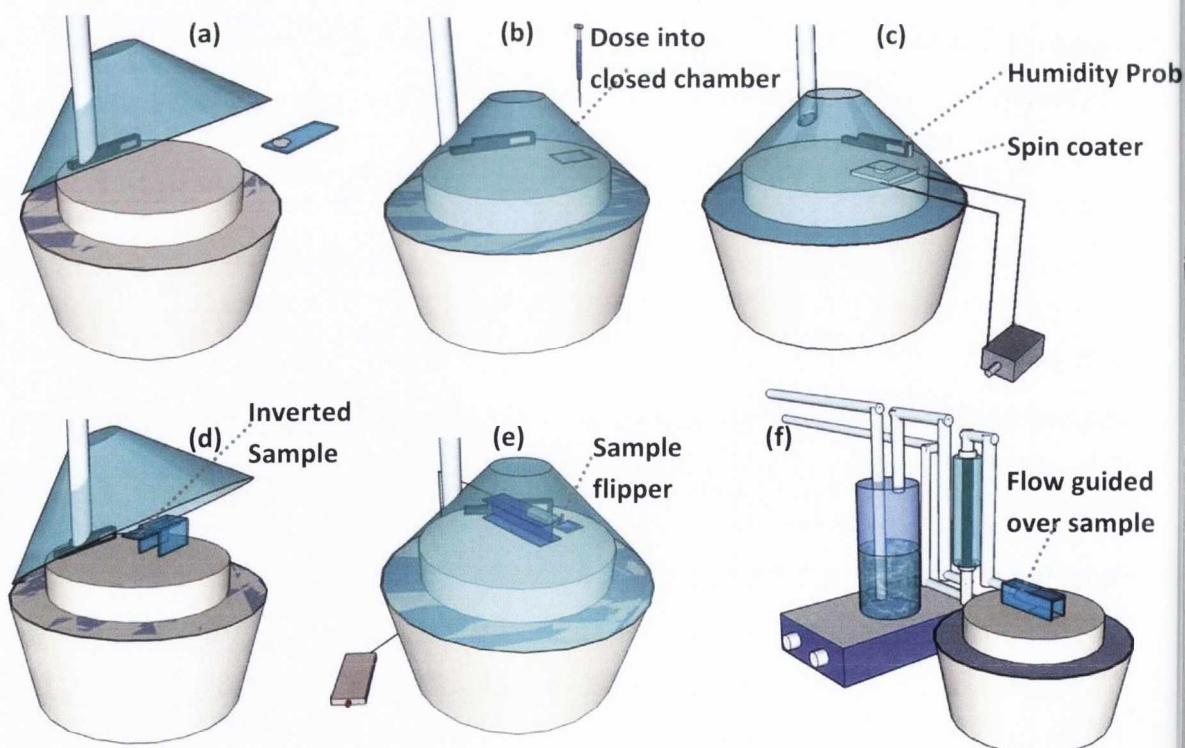


Figure 4.2.1: Illustration of six different apparatus during development stage of project, referenced throughout Chapter 4. (a) - (b) involve microstructure formation by drop-casting in a static humid environment. (c) involves spin coating in a humid environment. (d) - (e) use an inverted sample holder and (f) introduces a flow of vapour to the drop-cast sample.

4.2.6 Dynamic Flow Technique

As will be discussed in Section 4.3, the initial findings using the methods in (a) – (e) show advantages in pursuing a methodology with a flow of humid air rather than a static environment but the apparatus needed to be refined to allow improved humidity and flow control.

The following descriptions refer to the apparatus developed to incorporate these improvements, illustrated in Figure 4.2.2 (a) and (b). A solid, flat stainless steel base is used to provide stability to the apparatus. Four bars with screw threads are fastened into this base to support the chamber by means of a Perspex platform. This platform material provides the necessary thermal insulation, as discussed later in this chapter. The platform can be easily levelled, with height adjustment at each corner and has three mini spirit levels to aid accurate adjustment. Two further bars are attached to the base to allow retort stand clamps to be added for positioning the inlet tubing and humidity probes in a stable manner.

Two different chambers are used with this apparatus. The first is made from three pieces of cut and smoothed glass and is used for the experiments where a rapid change in humidity is required. The top of the chamber and the two walls are clamped together, using a foam sealant to ensure minimal leakage from the system. This three sided chamber is placed onto the base, where Parafilm M and a Teflon tape are used to improve the sealing of small gaps. A weight is added to the top of the chamber to ensure stability. The chamber is approximately 10 mm high and 26 mm wide. A dosing port is drilled in the roof of the chamber. The chamber is separated, cleaned and re-assembled before each set of experiments.

The second chamber is formed from a plastic material, designed in SolidWorks printed using the 3D polymer printer listed in Section 1.3.2.3. The internal dimensions of the two chambers are the same and the sample is 130 mm from the inlet in both cases. The chamber has a lid and dosing port that fit together to give a flat internal surface and minimal flow disruption. Some hygroscopic nature has been observed in this material which prevents rapid humidity changes.

The humidifier of Figure 4.2.2 consists of 90 ml of de-ionised water, heated to 55-60°C in a Dreschel flask. A single nitrogen inlet is split into two streams, one is sent to the Dreschel flask to entrain water and the other remains a dry nitrogen flow. Each flow has its own flow controller and an additional in-line on/off valve. The humid flow controller is treated as a flow

meter and remains open. Through control of the total flow and the dry flow, the total and proportional division of flow is achieved (for example closing the flow controller to a 50% setting diverts 50% of the total flow to the humidifier). The final flow is split just before delivery to the chamber, using two tubes to spread the flow. These tubes are fitted using a plug and sealed at the entrance to the chamber. The slim hygrometer probe detailed in Section 1.3.3 is inserted into the end of the chamber and fitted parallel to the sample drop point. Independent control of flow rate and humidity is possible and measured by the final combined final flow meter and the hygroscope probe.

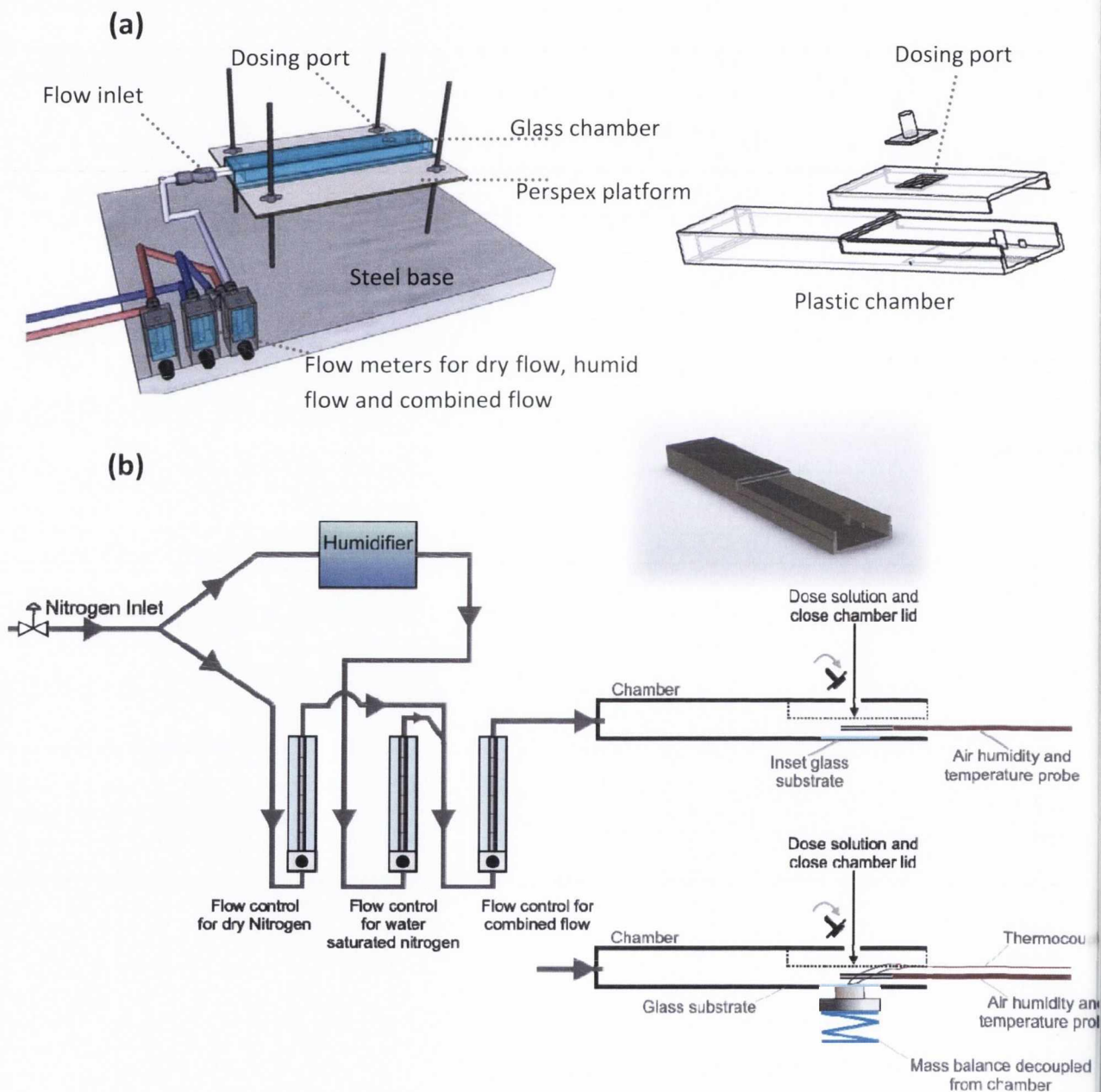


Figure 4.2.2: A flow chamber set-up is illustrated in (a) showing both the glass and plastic chambers. The ability to control the delivered flow rate and relative humidity is illustrated in the process diagram (b) along with further details as to the placement of the substrate and measurement probes.

Once the apparatus is set up as described, there are four standard operations that are referenced in Chapters 4 and 5 and the procedures are detailed below.

4.2.6.1 Standard, Steady Flow Experiment

1. A clean glass substrate is placed in the chamber, under the dosing port. The plastic chamber has a depression approximately the size and depth of a single coverslip to avoid flow disruption.
2. The relative adjustment of the dry and wet flow controllers is set, to ensure a steady, targeted flow rate is achieved at the desired humidity.
3. The stop watch and the ambient humidity measurements are started simultaneously. The chamber hygrometer readings commence 5 seconds later.
4. 60 μL of the polymer solution is dosed and the dosing port is closed.
5. At 6-8 minutes (depending on sample), all flows are stopped and the sample removed.

4.2.6.2 Modulated Flow Experiment

1. A clean glass substrate is positioned under the dosing port as before.
2. The flow to the humidifier is shut off using the flow controller and also the line's on/off valve.
3. The desired dry flow flow rate, usually 5 Lmin^{-1} , is set.
4. The stop watch and the ambient humidity measurements are started simultaneously. The internal humidity readings are started 5 seconds later.
5. 60 μL of the polymer solution is dosed and the dosing port sealed. The time is noted.
6. At 30-45 seconds, the overall flow rate is reduced to the desired level, the flow controller valve and the on/off valve on the humid line are opened and the valve for the dry air is closed. The same overall flow rate continues but is directed entirely through the humidifier, providing a rapid increase in the chamber humidity.
7. When nearing the desired humidity level, the flow control valve for the dry-air line is re-opened to a set value decided before the experiment and then a fine adjust can be made to achieve the desired humidity.
8. If a 3 stage modulation is required then a dry flow is re-instated at the desired time to complete the experiment.
9. At 8 minutes from the time of dosing, all flows are stopped and the sample is removed.

4.2.6.3 Temperature Measurement

An apparatus and procedure is required to measure the solution temperature during formation. A type K thermocouple, shown in Figure 4.2.3, is fit into either chamber as required

and carefully positioned so that the curved junction makes contact with the sample coverslip (shown using Figure 4.2.3(a)). The thermocouple is calibrated, as shown in Appendix 4.1.

The polymer film formation process can then be carried out as described but with an additional time check when the thermocouple recording is commence

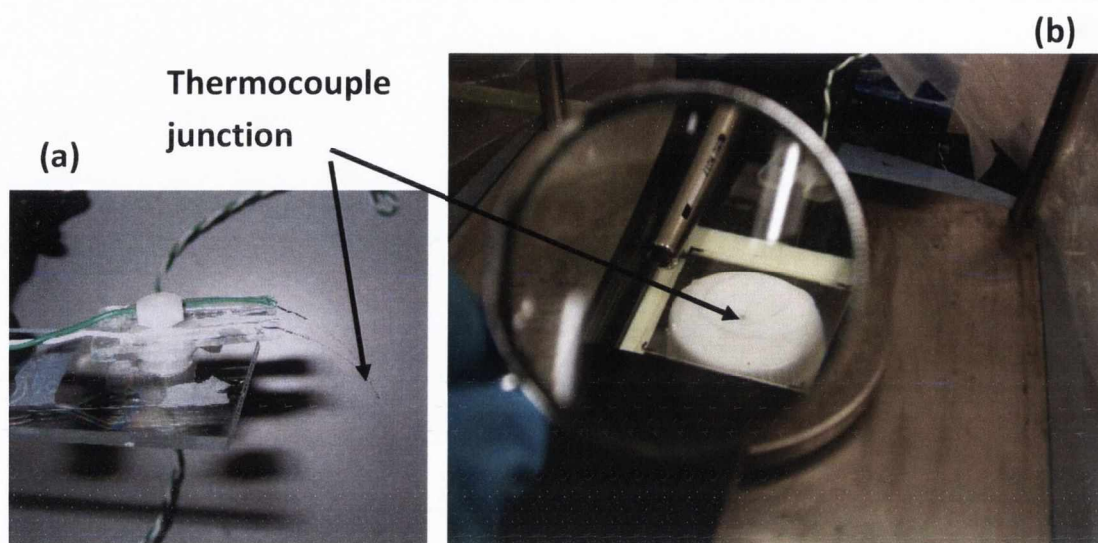


Figure 4.2.3: A thermocouple is used to monitor the temperature of the evaporating polymer solution. (a) Shows a Type K thermocouple fixed in a glass fork and attached to a glass coverslip using PTFE screw/nut to avoid degradation from the harsh solvent environment. (b) View of thermocouple in contact with a formed polymer film.

4.2.6.4 Mass Measurement

The rate of evaporation *in-situ* is required to aid insights into the mechanism. The following set-up was designed accordingly.

The glass chamber has been modified and a new plastic chamber produced to allow the insertion of a substrate from below, with the substrate directly coupled to the mass balance as shown in Figure 4.2.4 (a) and (b). The dashed lines of Figure 4.2.4 (a) indicate a large plastic covering to shield the balance while in the fume hood and avoid flow disruption. The height and level of the chamber is adjusted to ensure a flow as close to standard techniques as possible. Before an experimental run the flow of nitrogen is tested at the targeted flow rate to ensure its effect on the mass reading is avoided (or for very high flow rates, recorded to allow a correction value). An additional time marker is noted for the start of mass recording via a laptop connected to the balance.

4.2.6.5 Combined Measurement

As seen in Figure 4.2.2 (b) and Figure 4.2.4 both temperature and mass measurements can be combined. The procedure used is the same as detailed for the dynamic flow technique with the aim of recording *in-situ* measurements of evaporation.

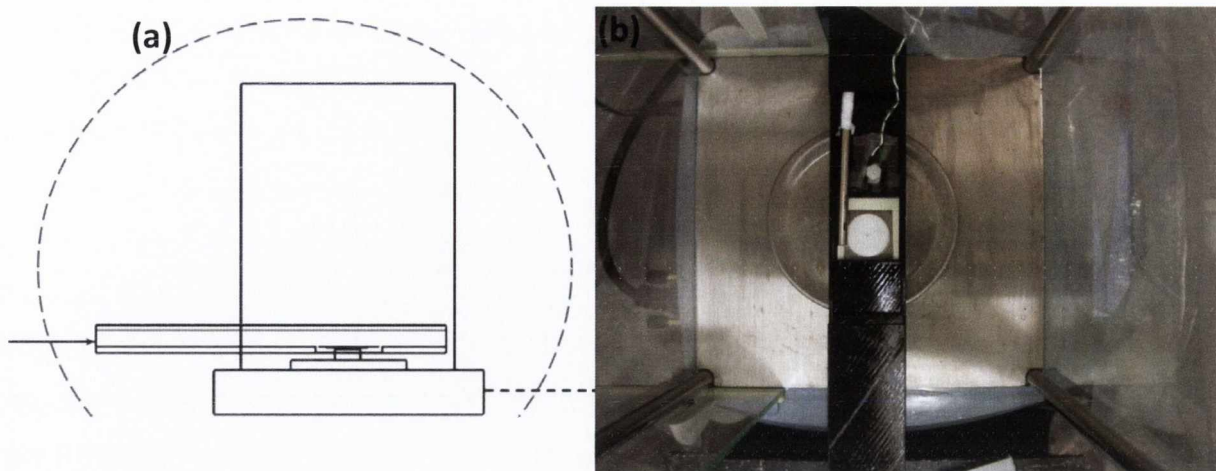


Figure 4.2.4: (a) Diagram showing the mass balance / flow chamber arrangement with the sample protruding into the flow chamber from the balance without contacting the edges. A plan view is provided in (b).

4.3 Static Environment - Experiment Description and Results

A number of experiments from the initial work in a static humid environment aided in understanding the challenges faced in the design of experimental techniques reported in the literature. The following four sub-sections detail several of the critical parameters that need to be controlled. Each section comments on the capabilities provided by prior methods and the motivation for the new approach developed in this thesis.

4.3.1 Humidity Control

A static humid environment appears ideal for analysing the environmental effects on the mechanism of formation but a number of issues were identified through experiment. As shown in Figure 4.2.2, the relative humidity is provided by a stream of nitrogen passing through a container of warm water and the humidity level is modified through fine adjustment of the flow of nitrogen, as is often the case in the literature. When the entering flow is kept purposefully low to avoid turbulent currents within the chamber, any deliberate change in humidity is very slow to manifest. Increasing this flow is expected to lead to an unpredictable, turbulent internal environment. For this reason, the static method, while stable within its narrow set of conditions, is not deemed suitable for an exploration of a wide range of the system parameters as it compromises the reproducibility and ease of interpretation of results. These internal flow effects along with the inherent control signal lag are believed to be key contributors in the difficulties obtaining reproducible results with this method.

4.3.2 Dosing and Spreading of Polymer Solution

The dose volume of polymer solution used in the literature typically varies from a few microlitres to a few millilitres. Early work in the static environment found that the relatively large volumes, approximately 500 μL , often led to erratic spreading and evaporation behaviour across the glass substrate. The spread of the solution seems to be an important factor, with different levels of ordering achieved for similar volumes of solution, if they are spread differently. In general, an improved spreading was observed to aid the ordering of the pores. To examine the influence of spreading more closely, the spin-coating apparatus, shown in Section 4.2.2, was constructed. The increased spreading was observed to lead to excellent ordering and much smaller pores, of less than 1 micron in diameter. These small pores were formed in highly ordered arrays using an optimum spin speed of 980 rpm for 2 seconds before leaving the spread film in a static humid environment to complete the drying process. Smaller pores (700-800 nm) were formed using a spin speed of 2000 rpm for the same duration. Unfortunately the coverage of pores was very low, as was the quality of ordering, with most of the sample remaining non-porous and transparent. This method was not adopted as a standard technique for this dissertation as intuitively any variation in spin speed changes the relative air motion and drying behaviour of the sample at the same time as altering its thickness. Such inseparable parameters increase the complexity of the interpretation of results.

A standard drop-casting technique was decided upon, using a fixed volume of 60 μL . This delivers sample sizes that are manageable using all the identified analytical techniques, while ensuring the solution does not approach the edge of the substrate but still spreads significantly and does not form a concave lens. As it is commented upon in the literature that the thickness of solution dosed can have an effect on the final film (68), (69), an analysis was carried out to evaluate the error involved in this system. Twenty samples were completed, dosing the chloroform solution with 3.5%_{w/w} DCPS onto glass substrates, each according to the method in in Section 4.2.6.2. Using a flow technique, an initial fast flow, followed by a steady slow, flow was implemented as part of this experimental run. Each of the twenty samples were photographed and measured. The mass of the deposited film was recorded and a pseudo density calculated to represent a value for spreading. From Table 4.3.1, it can be seen that the mass of solution dosed is not highly reproducible. However, when the total average mass of the films formed is compared with the average area covered, the final spread of film in mg/cm^2 has a standard deviation of 7.5%.

	Area of film (cm ²)	Mass of dose (mg)	Mass of film (mg)	Spread (mg/cm ²)
Average	0.99	83.7	2.6	2.6
Std. Dev.	0.06	2.3	0.2	0.2
% Dev.	6.5	2.8	9.1	7.5

Table 4.3.1: From analysis of 20 samples, the average area, dose size, film mass and spread are calculated along with the standard deviation and percentage deviation. This shows the errors involved in the drop-casting technique.

Throughout the course of this work, erroneous doses, both high and low, have been discounted due to undocumented potential volume effects.

4.3.3 Substrate material

Due to the nature of the solvents used in this study, glass was deemed a compatible substrate. The material beneath the substrate also affects the system due to the large surface interaction. Using the static method, it is noted that this substrate supporting layer must be made from a thermally insulating material. Samples dosed onto glass slides attached to a metal base or to the thermally conducting surface of a Peltier element are found to be significantly and detrimentally affected, making it very difficult to form a porous system. This was examined further with the spin-coating technique, where a similar observation is made with porous films forming across the substrate apart from the centre of the sample where the slide is fixed from beneath by a metal stub to the magnetic holder. A crude test was carried out with the underside of a glass slide coated in two strips of insulating material, with the middle attached to a wide strip of copper, leading to a metal stub. A clear trend can be observed in the sample, where the pores form in a much greater number and density in the area adjacent to the insulating material.

To maximise the range of achievable conditions and the responsiveness of the system without sacrificing knowledge of the flow direction it was decided to move permanently to a dynamic flow technique, as detailed in Section 4.2.6. Apparatus shown in Figure 4.2.1 (f) was an intermediary developmental step and similarly to the static technique only a few of the key observations will be commented upon throughout this thesis. It was decided to use a smooth, flat plastic base to ensure there were no thermal paths that could interact with the thin glass substrate. A standard drop-casting technique was decided upon using a fixed volume of 60 µL. No additional spreading was applied when dosing the solution.

4.3.4 Influence on Microstructure using Static Environment

The static environment, including the spin coating technique, consistently led to spherical or slightly ellipsoidal pores. These were mostly found as a monolayer of pores open to the solution/air interface. Multi-layers were not formed using chloroform, despite predictions to the contrary based on surface tension arguments (31). In an attempt to see if the buoyancy argument mentioned in Section 1.2.2.4, may indeed be critical in restricting detachment of the droplets from the interface, an inverted set-up and procedure, Section 4.1(d), was used. This did not lead to foam-like multi-layer structures but instead gave elongated cylinders, similar to those discussed later in Section 4.4.6 and shown here in Figure 4.3.1. To avoid the uncontrolled nature of the procedure, which used external dosing and flipping with subsequent introduction to the humidity chamber, a device was constructed to allow the sample to be rotated 180° through a remote switch, Section 4.1(e). Once the dosing and inversion was contained within the system this showed a significant decrease in the elongation of the pores. Two conclusions followed from this work, firstly, it could be confirmed that buoyancy of the droplets in the surrounding bulk liquid did not play a role in positioning of the droplets at the interface. Secondly, it was subsequently hypothesised that rather than inversion promoting the formation of cylindrical pores, it was instead most likely the pre-treatment through exposure to a different air flow and humidity at the initial drying stage that somehow led to this destabilising of the droplets.

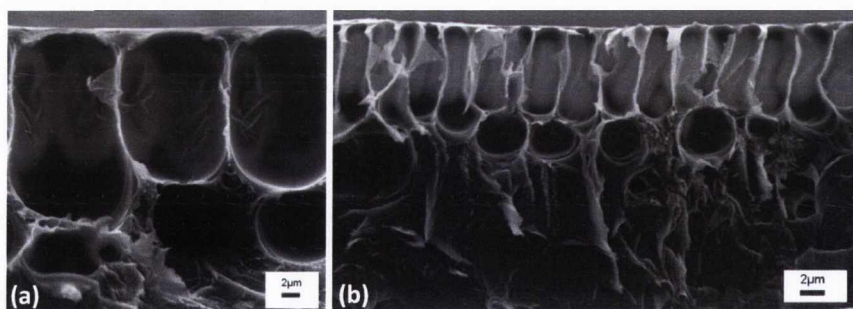


Figure 4.3.1: Cross-sectional views of the porous polymer films using SEM. (a) shows a sample made using the method illustrated in Figure 4.2.1(b) using 4% DCPS in chloroform, a 370µL dose and 65-70% RH. (b) shows a sample made using the inverted method illustrated in Figure 4.2.1(d) using 4% DCPS in chloroform, 60µL dose and 65% RH.

A crude flow technique, Figure 4.2.1(f), showed that with substrates at both orientation elongation and destabilising of droplets could be achieved without inverting the sample. These observations gave a critical, if very qualitative, insight into the potential modification of the microstructure through understanding and controlling the solution evaporation and polymer entanglement processes over the duration of the pore development. As discussed in Section 1.2 the solution evaporation controls the surface temperature and therefore must directly control the ability of the water to condense. A dynamic tuning of this water condensation

through solvent evaporation control would provide a new control technique and further understanding of the system. Before experiments involving the control of these parameters and the development of a controlled, dynamic flow technique are presented, the influence of the relative humidity, air flow rate and solution concentration are examined for this mechanism.

4.4 Dynamic Flow Method

As seen in Figure 4.2.1 and the description of the results, the low level of control over such a dynamic system only lends itself to purely qualitative results. However, these initial results gave sufficient insight regarding the manipulation of pore microstructure that a system with finer control was constructed to allow greater access to different microporous architectures and an improved understanding of the system. The method described in Section 4.2.6 was developed and the following section details the examination of the phase space of conditions and the quantitative and qualitative results.

4.4.1 Influence of the Environmental Conditions on Pore Formation

As discussed in Chapter 1 Section 2, the quantity of water vapour available to condense in the environment adjacent to the solution/air interface is identified as one of the most important parameters to control when forming ordered arrays of pores by the method of water droplet templating. The effect of relative humidity has been explored by every group involved in the field but to very different degrees of precision. Despite this attention, there are still some key questions that need to be tackled by experimental technique to enable an understanding of not just the effect of a change in relative humidity on the observable pore opening, but also the influence of the flow rate by which it is delivered and the influence on the three dimensional microstructure. Apart from reporting the direct, observable changes brought about by careful manipulation of the humidity level, it is also desirable to design experiments that may lead to further insights into the mechanism of action of the environmental conditions surrounding the evaporating solution. In this section, results are presented for experiments that vary both the flow rate and the relative humidity to see if such insights can be revealed.

The first insight targeted was raised in Section 1.2.4. A minimum humidity boundary is believed to exist for this process to occur and is rarely reported with any detailed analysis. The definition for the critical humidity in the literature is either the level below which no pores are

observed, or below which ordering of pores does not occur. The different experimental techniques, materials and definitions do not allow a review document to define any trends for this important parameter. In this section, the onset of critical humidity is defined as the lowest humidity at which any sign of arrays of pores occurs in the resulting film. As it defines a limiting factor below which no porous film can form, it was decided to explore this region of the formation phase space. The presence or pores is straightforward to confirm visually due to the inherent diffraction of light.

4.5 Experimental Details and Results

4.5.1 The Influence of Inlet Flow Humidity

All of the following experiments, unless expressly stated, used solutions of 3.00%_{w/w} DCPS in 97.00%_{w/w} chloroform. The experimental set-up and cleaning procedures are detailed in the apparatus and procedures Section 4.2.5.

4.5.1.2 Examination of the Critical Onset Humidity

Using a constant flow technique also detailed in that section, a series of samples was prepared at decreasing levels of relative humidity. As mentioned in Section 1.2.4, an area of closely packed pores in a polymer film is indicated by its white or iridescent appearance due to the scattering of light it causes. The absence of pores leads only to transparent films. The decrease in humidity was continued until a transition occurred from a white porous sample to a completely transparent non-porous sample. This was initially carried out using a step decrease in humidity of 5%. As stated earlier, the lowest humidity found where pores occur is the critical humidity. This was carried out at a low flow rate and then repeated for nine further flow rates from 0.5 Lmin⁻¹ to 5 Lmin⁻¹. Based on the dimensions of the chamber this is equivalent to a velocity range from 0.035 m/s to 0.352 m/s. The relative humidity is monitored and recorded during each run. With careful operation, the chamber can be maintained quite accurately at a chosen relative humidity value. To confirm the results found and reduce the error in identifying the critical humidity below the 5% relative humidity mark, a second series of samples was created. Using the initial set as a guideline it was feasible to set the humidity half way between the humidity that led to a transparent sample and the critical humidity. This is a very narrow range for humidity control but it led to a more accurate representation of the change in the critical humidity level with flow rate, as seen in Figure 4.4.1. This figure also shows the induced change of the onset critical humidity with a change in flow rate, e.g.

changing from approximately 48% at 0.5 Lmin⁻¹ to 35% at 3 Lmin⁻¹. This data set reports a clear decrease in the critical humidity level with the increase in flow rate until the trend begins to level out to a minimum at higher flow rates. The implications of this finding will be revisited in the discussion section towards the end of this chapter.

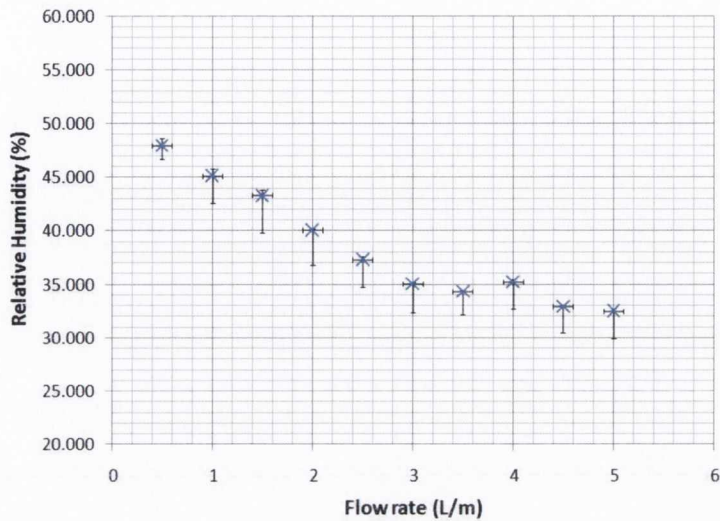


Figure 4.4.1: The observed critical or onset humidity level for pore formation is shown for a range of nitrogen/water vapour flow rates through the chamber. This set of data used a polymer solution consisting of 3% DCPS in chloroform.

The critical humidity was also found, using the same method, for solutions of dichloromethane and toluene for a flow rate of 1 Lmin⁻¹ and is reported in Figure 4.4.2. Each solution was made up to an equivalent molar concentration to that of the chloroform/polymer solution. The three critical humidity levels are quite different for each solvent, covering a range of 30% to 80% relative humidity. The physical drivers of this change will be looked at again in Chapter 5 however it is noted here that the critical humidity levels of the three solvents plot linearly with the boiling point and latent heat of vaporisation, while the vapour pressure value is approximated very well by a power law curve.

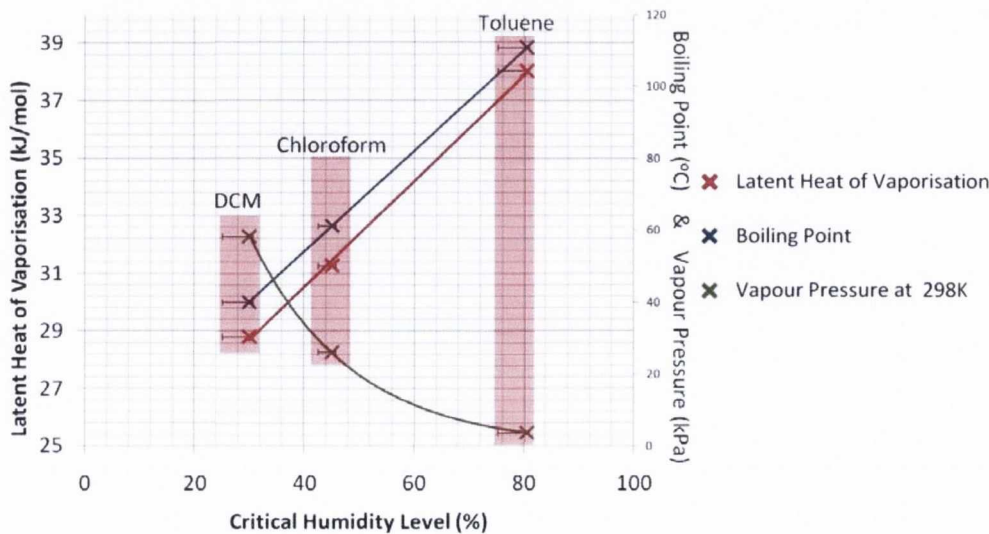


Figure 4.4.2: The relationship between critical or onset humidity and the physical properties of the solvent are examined. The theoretical values of latent heat of vaporisation, boiling point and vapour pressure of the solvents are plotted against the onset humidity value found experimentally.

4.5.1.3 Influence of Flow Humidity on Pore Size

Most reports studying the influences of formation show an increase in pore opening size with increasing relative humidity. This analysis is most often completed using a small number of pores from each sample, and the standard deviation, errors and distribution are rarely reported. While porous films are often locally homogeneous in size, this is not the case across the sample. This experiment was thought important enough to carry out as part of this thesis because of the insight it may give into the interplay between the coupled mechanisms of solvent drying and water condensation. Also, it was thought that the existing measurements from the literature could be improved upon by averaging over a large number of pores (approximately 2-10,000 pores for each data point depending on the sample). Each sample is formed using the apparatus and procedure described in Section 4.2.5 at a fixed flowrate. Lmin^{-1}

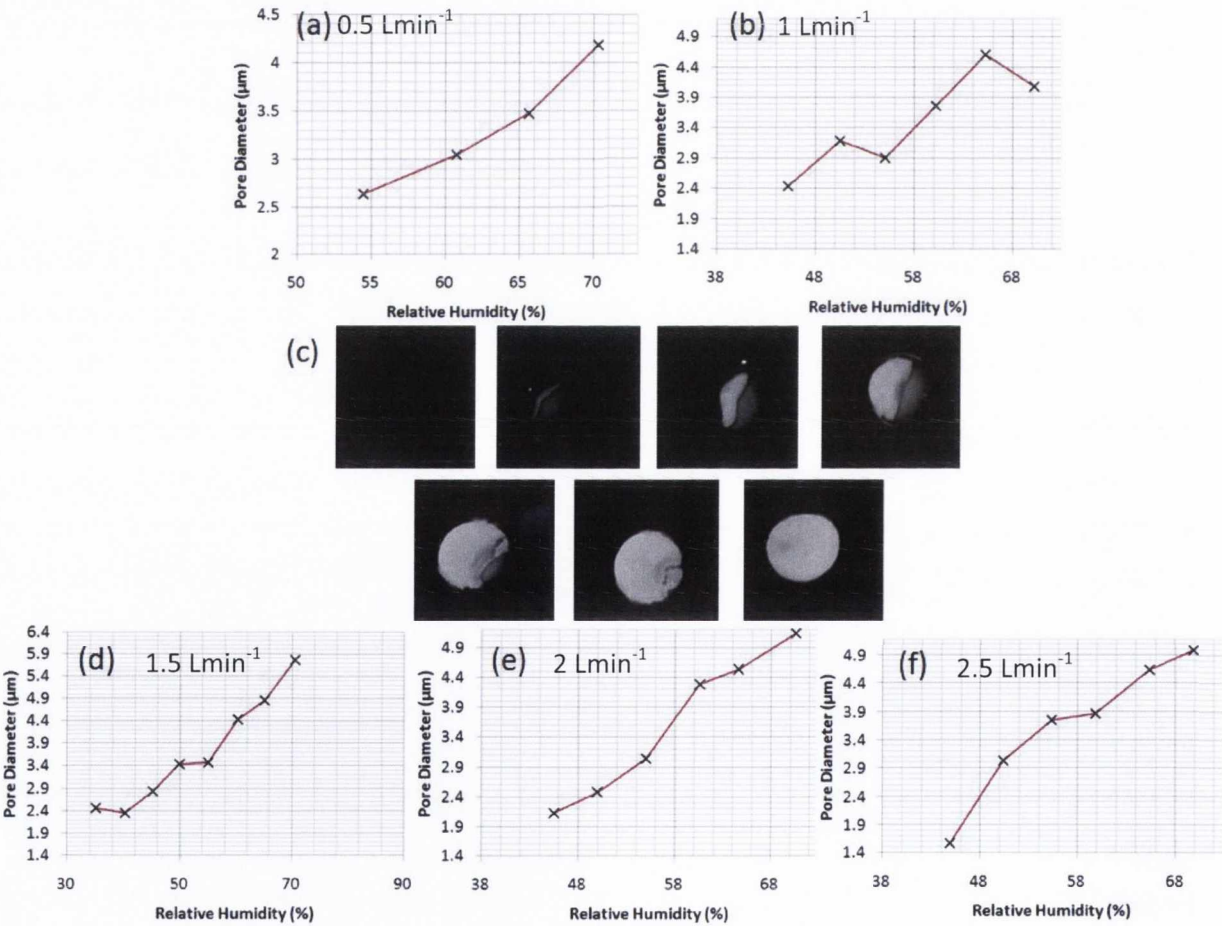


Figure 4.5.1: Referring to samples made with a 3%_{w/w} solution of DCPS in chloroform, the graphs show the change in pore diameter measured by optical microscopy at different values of relative humidity for (a) 0.5 Lmin^{-1} , (b) 1 Lmin^{-1} , (d) 1.5 Lmin^{-1} , (e) 2 Lmin^{-1} , (f) 2.5 Lmin^{-1} . The red lines in each plot are only present as a visual aid and do not represent a fit (c) Shows samples formed during preparation samples at 1 Lmin^{-1} (b), with pores being observed wherever a white surface appeared.

Once formed, images of the sample were captured using the Carl Zeiss microscope and CCD camera described in Section 2.1. “Loading effects” are observed, as seen in Figure 4.5.1 (c), where the pore formation occurs at the side of the sample closest to the inlet. This is believed to be the section of the film that experiences the measured conditions. A combination of a drop in humidity across the sample and transport of solvent vapour across the sample may be responsible for the changes noted in many samples. For this reason, measurements and cross-sections are only taken from the half of the sample closest to the flow inlet, where they are seen to be most constant. A sequence of images was taken by sweeping in a raster scan fashion across the sample, stopping randomly to record an image. This is carried out until the sample area is covered. This can take 10-20 images. This technique was used to avoid the pitfall of recording images only of the standard, ordered arrays, which would unrealistically avoid the areas of coalescence. The images were analysed using ImageJ (160) with a particle analysis routine. The output was then filtered to exclude artefacts and provide an average pore size, standard deviation and standard error. The pore sizes were imported into Mathematica (156) to allow the production of a pore size distribution histogram. Figure 4.5.1(c) shows the series of samples relating to the points in Figure 4.5.1 (b) at a flow rate of 1 Lmin^{-1} . It can be seen that the porous area increases in size with the increase in humidity, starting from the leading edge where the flow is coming from. All five of the flow rates examined show a trend of increasing pore size with humidity. The standard deviations have been omitted in these graphs but will be looked at in Figure 4.5.2. It should also be noted that the standard errors are very small, mainly due to the significant number of pores counted during this process.

Looking at a fixed flow rate of 1 Lmin^{-1} , samples were formed using two alternative solvents, dichloromethane and toluene. As seen earlier, dichloromethane can form pores at a lower relative humidity than chloroform, while toluene requires much higher relative humidity for the mechanism to function. Staying at least an additional 5% above the critical humidity values, samples were formed using DCM at 35%, 50% and 81% relative humidity and toluene at 85% and 95% relative humidity. In Figure 4.5.2 the standard deviation rather than the standard error has been included as the vertical error bar. A linear trend results, showing a consistent change in pore size with humidity, independent of the chosen solvent. The widening of the vertical error bars signifies non-homogeneity of pore size, which in this case mainly stems from the coalescence of the water droplets, which become more prevalent at high relative humidity. For each solvent, the standard deviation values widen as the humidity is increased from the critical value.

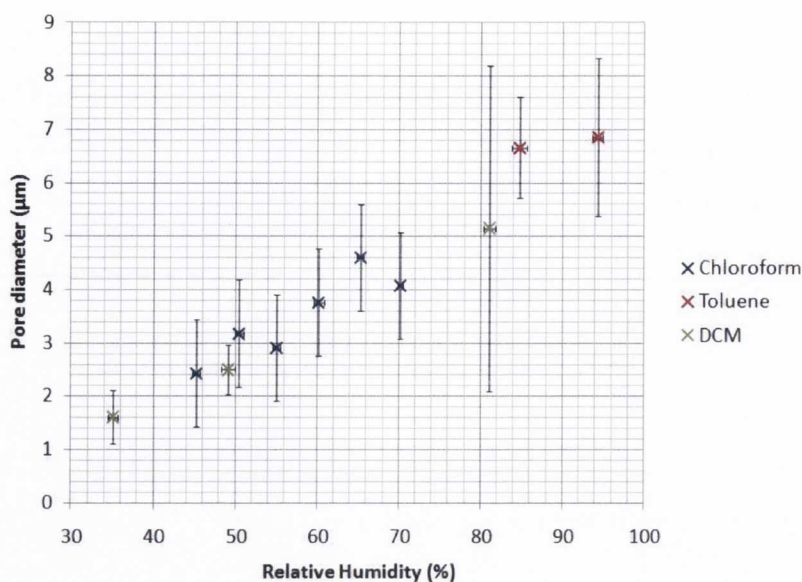


Figure 4.5.2: Pore size measurements using optical microscopy are detailed for three different solvents, dichloromethane, toluene and chloroform. All samples are formed with a 1 Lmin^{-1} humid flow, with a solution of 3%w/w DCPS in chloroform or equivalent molar concentration of dichloromethane or toluene. A linear increase in the pore size with relative humidity is observed across the three solvents.

A look at pore size distribution histograms shows a wider distribution of pores sizes frequently occurs at higher values of humidity and often a bi-dispersity of pore size is observed, as shown in Figure 4.5.3.

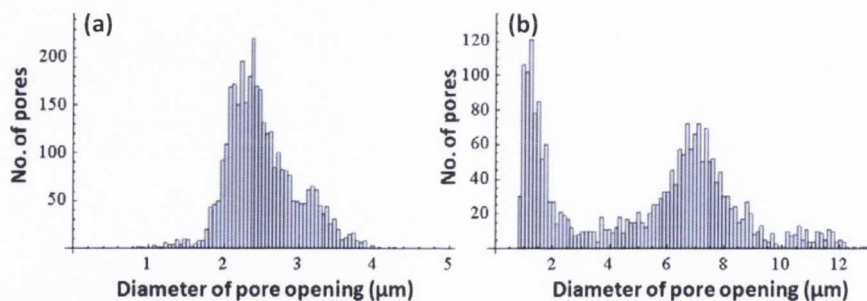


Figure 4.5.3: These two plots show pore opening size distributions, measured using optical microscopy and calculated with Mathematica, for samples prepared using a solution of DCPS in dichloromethane and a flow of nitrogen and water vapour of 1 Lmin^{-1} . The relative humidity is set at (a) 45% RH and (b) 80%

If the pore sizes, close to the critical humidity, are included in the plot of humidity against pore opening diameter, then it is found that the trend often breaks down. The pores at, or very close to, their respective critical humidity values are often found to be larger than predicted, as shown in Figure 4.5.4 for three of the flow rates studied. They are in general poorly ordered and the pore openings mono-disperse in size. Apart from the unexpectedly high pore opening diameter, two further points of interest are noted regarding the samples formed at very low relative humidity. Firstly, these samples display significantly more iridescent behaviour when observed under daylight than those formed at higher humidities. Secondly, observation of the

pores using optical microscopy is much more difficult than with samples formed at higher humidity. The image contrast is significantly reduced and while pores can still be observed, the ability to focus and record an image are impaired. Both observations suggest a change in the porous microstructure and this will be examined in Section 4.5.1.3.

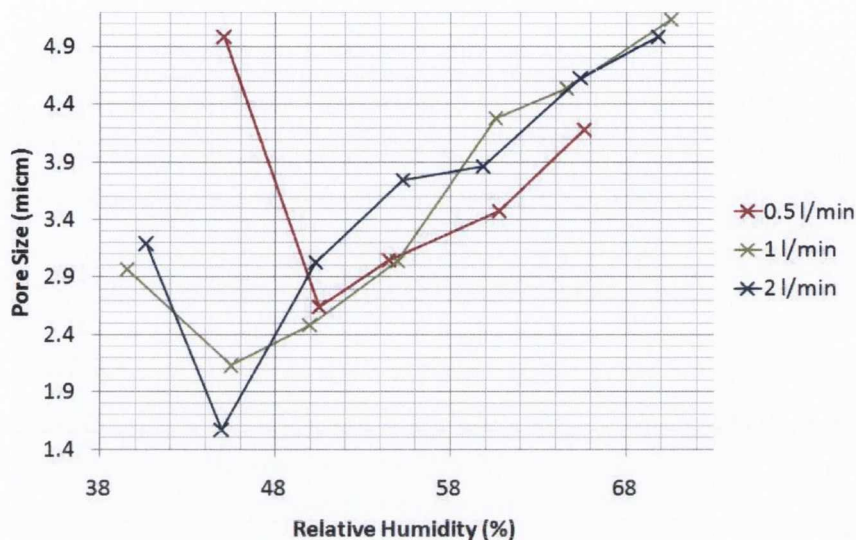


Figure 4.5.4: This graph shows the change in pore opening size with humidity for samples made with a solution of 3%_{w/w} DCPS in chloroform and a flow of humid nitrogen of 0.5 Lmin⁻¹ (red), 1 Lmin⁻¹ (green) and 2 Lmin⁻¹ (blue). The deviation from the trend close to the critical humidity value is also shown. The lines between the points are only to aid visualisation and are not representative of a fit.

4.5.1.3 Influence of Humidity on Pore Microstructure

The subsurface structure of the films is not reported or examined in detail in the literature. Simple adjustments to the formation, such as changing the humidity level, have significant effects that aid in the understanding of the mechanism. The development of focused ion beam milling of porous polymer structures, as described in Section 2.3, allows the preparation of very clean cross-sections. This technique was used to look at samples very close to the critical humidity level for a range of flow rates. The critical onset humidity occurs very close to the point where the vapour-liquid equilibrium of water is at equilibrium between evaporating and condensing but is favouring condensation for enough of the duration that pores can be formed. Analysis pores formed at these critical humidity levels reveals a highly unusual shallow, flat-based pore microstructure. The depth of these pores is also affected to some extent by the loading phenomenon noted earlier. The leading edge (or front end) of the sample has the deepest of the pores. These are still very shallow and as with the standard approach, this is the common region of measurement to ensure reasonable comparison across samples. These rapidly transition to steadily more shallow pores until a non-porous

transparent film remains, reflected in the transition from porous to non-porous film in Figure 4.5.1 (c). The shallow pores, as illustrated in Figure 4.5.5, appear to have a pronounced lip surrounding the opening and protrude slightly from the surface.

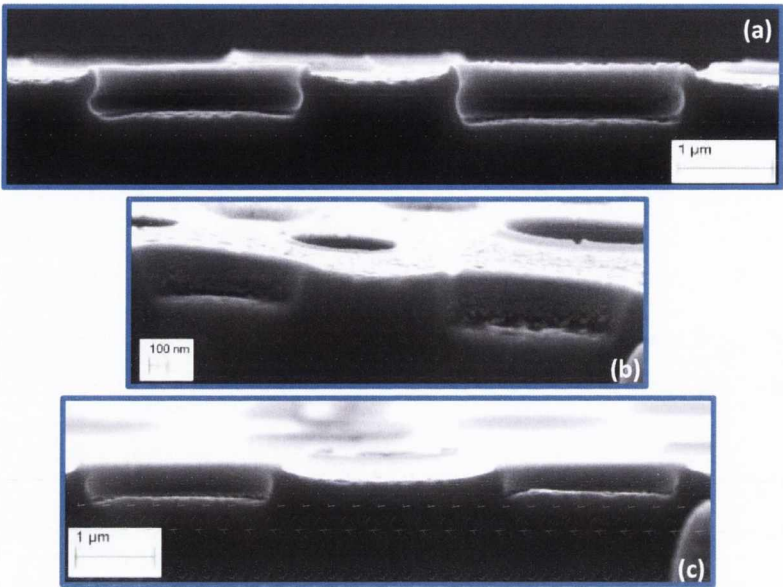


Figure 4.5.5: Images taken using SEM following ion beam milling of the polymer film to create cross-sections. Samples made with a solution of 3%_{w/w} DCPS in chloroform with a flow of humid nitrogen of (a) 45% RH at 1 Lmin⁻¹, (b) 32% RH at 5 Lmin⁻¹ and (c) 37.5% RH at 2.5 Lmin⁻¹. These images show the unusual, shallow, flat-based porous structures found at the critical humidity levels.

When the humidity is increased slightly above the critical humidity, there is an improvement in ordering and the pores become slightly deeper but still retain their shallow, flat based nature. It is observed that at slightly higher humidity levels still, the standard ordered spherical imprints are left in the polymer film. At much higher relative humidity, coalescence and poor ordering dominate. Figure 4.5.6 illustrates the differing behaviours.

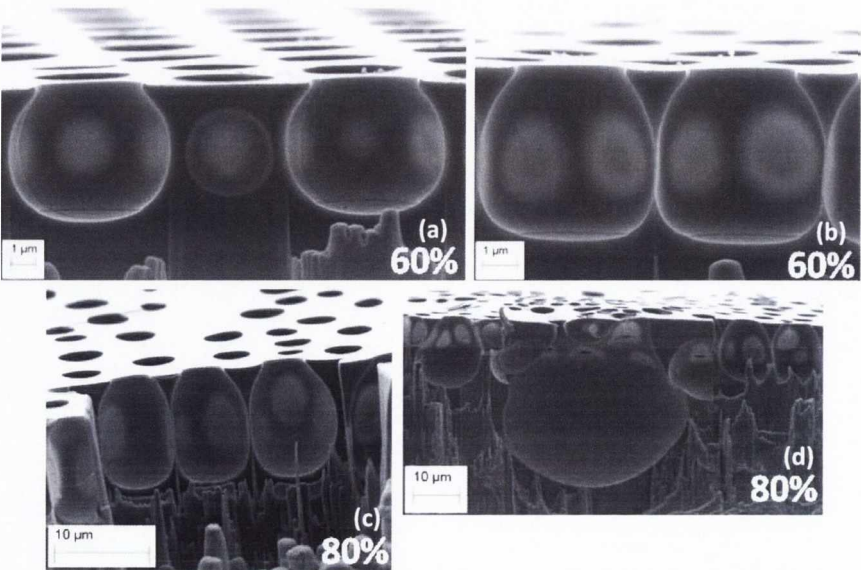


Figure 4.5.6: Images taken using SEM following ion beam milling of the polymer film to create cross-sections. Samples made with a solution of 3%_{w/w} DCPS in chloroform with the following conditions, (a) 60% RH at 1 Lmin⁻¹, (b) 60% RH at 1 Lmin⁻¹ but at different location to (a), (c) 80% RH at 1 Lmin⁻¹, (d) 80% RH at 1 Lmin⁻¹ but at different location.

These results will be interpreted when a closer look at the mechanism of formation of shallow pores is carried out in Section 4.5.3. This will incorporate findings from a number of sections including the next, which examines the effect of the initial solution concentration on the final microstructure.

4.5.2 The Effect of Polymer Concentration

While considering the dynamic controls of solvent evaporation and water condensation, it is important to look at the effect of the change in polymer concentration in the initial solution. As a change in concentration can significantly affect the rate of evaporation of the carrier solvent, there may be an influence over droplet growth. During the evaporation process of the polymer solution, examined in more detail in Chapter 5, the concentration of polymer rapidly increases. As mentioned in the Introduction chapter, it has been reported on a number of occasions (36), (63), (64), (92) that the initial drop-cast concentration has a measurable effect on the final pore opening dimensions. Initial work under the static humid conditions showed a linear increase in the thickness of the non-porous section of the film with an increase in polymer concentration. This is partly due to the increased quantity of polymer but also due to the rapid increase in viscosity of these solutions with every step increase in concentration and their combined influences on spreading. The following experiments were carried out using the controlled flow technique with the aim of examining the influence of the concentration on the microstructure of the films. Solutions were made up at 3, 3.5, 4, 4.5, 5, 5.5, 6, 6.5, 7, 7.5 and 8% w/w of DCPS in chloroform. Each solution was used to form samples at 70% and 80% relative humidity. All samples were formed at a constant flow rate of 1 $Lmin^{-1}$. The samples were all observed in both plan view and cross-sectional view using optical microscopy. Focused ion beam milling and scanning electron beam microscopy were then used to reveal the internal microstructure.

4.5.2.1 Influence of Polymer Solution Concentration on Pore Size and Order

Contrary to the literature, a clear trend of decreasing pore size was not observed, despite the significant increase in polymer concentration. As shown earlier in Figure 4.5.2, at 70% relative humidity and 1 $Lmin^{-1}$, a 3% w/w polymer solution leads to approximately 4-5 μm diameter pores. It is found that increasing the polymer concentration of the cast solution to 5% w/w decreases the average pore opening size to 2.6 μm , with a standard deviation of 0.7 μm . However, at 8% w/w the distribution of pore sizes is extremely large and so the trend breaks down when looking at average values. Pores in one area, closer to the leading edge than the centre of the sample, are found to have an average diameter of 2.3 μm , which is at least

consistent with a decreasing pore size. However, further in towards the centre of the sample, significant coalescence and much wider pore openings determine that the average pore dimension is above that of the 5%_{w/w} solution and so no definite conclusion can be reached.

The level of ordering observed in this series of samples varies significantly with concentration. The lowest concentrations have relatively good ordering, but this steadily deteriorates with an increase in concentration. The most coalescence and worst ordering occurred in the sample of 4.5%_{w/w}. However, unexpectedly, the ordering began to improve steadily again from 4.5 – 8%_{w/w} concentration, despite optical examination showing significant subsurface growth and change.

It was also noted that for 7.5 and 8%_{w/w} polymer concentration, the mechanism of formation began to break down. During the formation of the porous film, the evaporation of the solution was drastically disrupted. The initial evaporation and breath figure formation occurred as usual. The solution at the edge of the drop-cast area and its immediate vicinity dried to give a porous film. The large, enclosed area was clearly not drying as quickly as the remainder of the film. A polymer film had formed at the solution/air interface and beneath this there was a thick layer of trapped solvent, leading to a blister-like formation, which very slowly diffused out to give the final film. This disruption to the formation process left behind a central section of the film with an iridescent appearance. This porous region was difficult to observe with optical microscopy as the contrast was significantly reduced, similar to the observation in Section 4.5.1.2. The microstructure of the these pores is shown in Figure 4.5.7 (b).

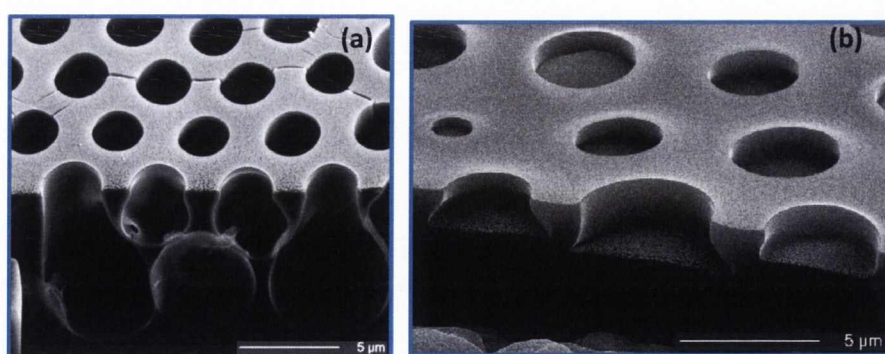


Figure 4.5.7: Images taken using SEM following ion beam milling of the polymer film to create cross-sections. Samples made with a solution of 8%_{w/w} DCPS in chloroform. Image (a) shows the pore openings do not dictate the interior microstructure, image (b) is taken where the formation process breaks down, near the centre of the sample and flat-based pores with quite straight sides result.

4.5.2.2 Influence of polymer solution concentration on microstructure

A number of trends are revealed once the internal microstructure is determined. Firstly, as seen in Figure 4.5.7(a) despite the existence of relatively well ordered pore openings at the

film/air interface it is clear that this homogeneity is not reflected by the underlying microstructure. Secondly, flat-bottomed pores are observed in the areas where the mechanism was seen to break down, as shown in Figure 4.5.7(b). The shape and depth of these pores differ, as will be detailed next, but a common flat base persisted.

The following is a summary of the changes in internal microstructures as a function of concentration, starting with the 70% RH samples. From 8% to 7% polymer concentration, conical-flask like pores are observed having a narrowing neck and wide, flat base, as shown in Figure 4.5.8 1(a) and 2(a). These are observed throughout the sample. From 7% to 6% concentration these features decrease in prominence and more and more round-bottom pores are seen. From 5.5% to 4.5% concentration, pores similar in shape to pendant drops occur, having a spherical base but a narrowing neck, Figure 4.5.8 3(a). Significant amounts of coalescence also occur. From 4% to 3% the standard spherical pores are observed.

Moving to the 80% relative humidity, the presence of conical-flask like behaviour was noted for the highest concentration only, when using the optical microscope to view the entire sample cross-section. However this sample has significantly lower levels of its occurrence and the microstructure is in general more inclined to “wine—bottling”. This instability, normally seen in foams (176), is coupled with an increase in round-bottom pores and is prevalent in this and the 7.5% sample. An example from the 8% concentration sample is shown in Figure 4.5.8, 1(b). The previously mentioned flat based pores also exist at this humidity where the solvent trapping occurred during the sample formation. From 7% to 5% similar microstructures are observed, as seen in Figure 4.5.8 2(b). Near the front end of the sample the features are very deep elongated pores and often appear as if they are widening in the middle and in most cases are not very straight. These give way further into the sample to pores that are still non-spherical, generally broadening beneath the surface to form wine bottle or ellipsoidal shapes. These features are interspersed with large cavernous coalescence. While these remarks are also true of 4.5%, it is the concentration that displayed the longest and thinnest pores near the front end of the sample, and even some with an element of ordering, while the rest as shown are long but disordered, as seen in Figure 4.5.8 3(b, c). Elongation of pores persists at this humidity even for samples at the lower end of the concentration range. However, these are restricted to only a very narrow region near the front of the sample and revert to the standard spherical and coalescent behaviour for the rest of the film. The interpretation of these effects will be presented in the Section 4.5.

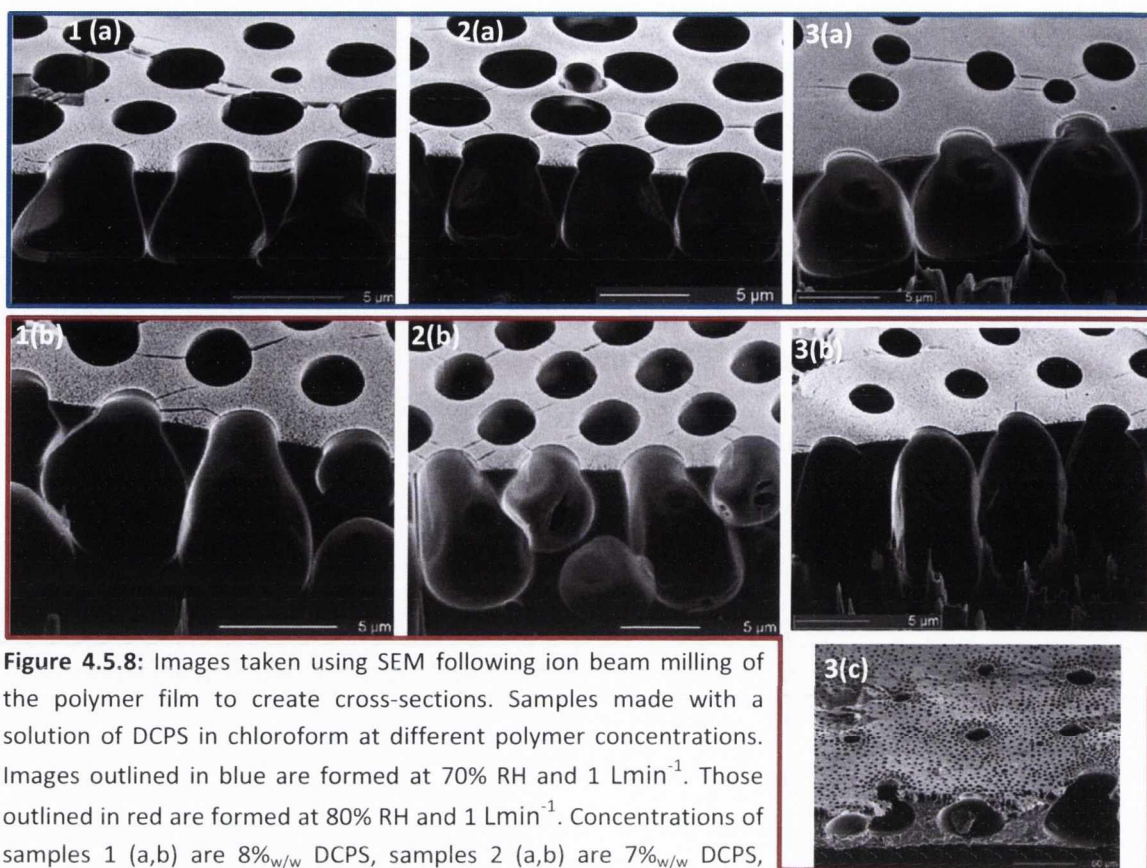


Figure 4.5.8: Images taken using SEM following ion beam milling of the polymer film to create cross-sections. Samples made with a solution of DCPS in chloroform at different polymer concentrations. Images outlined in blue are formed at 70% RH and 1 Lmin^{-1} . Those outlined in red are formed at 80% RH and 1 Lmin^{-1} . Concentrations of samples 1 (a,b) are $8\%_{\text{w/w}}$ DCPS, samples 2 (a,b) are $7\%_{\text{w/w}}$ DCPS, Samples 3 (a,b) are $4.5\%_{\text{w/w}}$ DCPS.

Before this, further results are presented looking at the modification of the environmental conditions during the film formation in an attempt to specifically control the evolving shape of the water droplets and therefore the resulting pores.

4.5.3 Flow and Humidity Modulation

The modulation of conditions during film processing has not, at the time of writing, been discussed by groups working on water droplet templating. A qualitative interpretation of results from the static environment, discussed in Section 4.3.5, led to the more formal approach presented herein to exploring the potential for microstructure control. From the experiments in Chapter 2, it was shown that water droplet templating is not an equilibrium problem and that we are constantly driving the water droplet to grow or evaporate depending on the imposed conditions. Modulating the flow and humidity is intended to find experimentally the extent to which this can be coupled with the dynamics of solvent evaporation and polymer film formation and used to control the resulting pore shapes. Once it was realised, as mentioned earlier in this chapter, that a flow technique provided the potential for microstructure control, the set-up shown in Figure 4.2.1(f) was used for an initial examination into the different combinations of flow rates and humidity values. The aim was to

narrow down the phase space to a reasonable level to allow a more careful analysis and define the conditions where the elongated structures could be reproduced under more controlled circumstances. This initial target was set, due to the earlier observation of such pores and the knowledge that it may be achievable. A set of experiments was carried out that split the flow into two regimes of humidity and flow rate. 10, 5, 3, 1, 0.5 Lmin⁻¹ flows were used for each regime, looked at in nearly all of their combinations (e.g. 10 Lmin⁻¹ → 5 Lmin⁻¹, 10 Lmin⁻¹ → 3 Lmin⁻¹, ..etc) and using a range of values for humidity for each regime. While the target structures of ordered elongated pores were not achieved, vertical growth and destabilisation of the droplets was found and seemed closest to the target results with a combination of a dry flow (<10%RH) at 5 Lmin⁻¹ changing to a 1 Lmin⁻¹ flow at 85% relative humidity. This work however needed to be continued with an improved flow chamber, humidity control and flow control. Further work was therefore carried out once a re-designed and constructed apparatus and procedure was completed as shown in Section 4.2.6.

Using the apparatus and procedures of section 4.2.6, it was found that:

- (i) An optimum initial flow to aid manipulate microstructure is one of 5 Lmin⁻¹ for 30-45 seconds. At shorter durations, very little effect can be seen, while at longer durations the subsequent pore formation is significantly disrupted, leading to very small, disorganised pores that often broaden below the surface as seen in Figure 4.5.9.

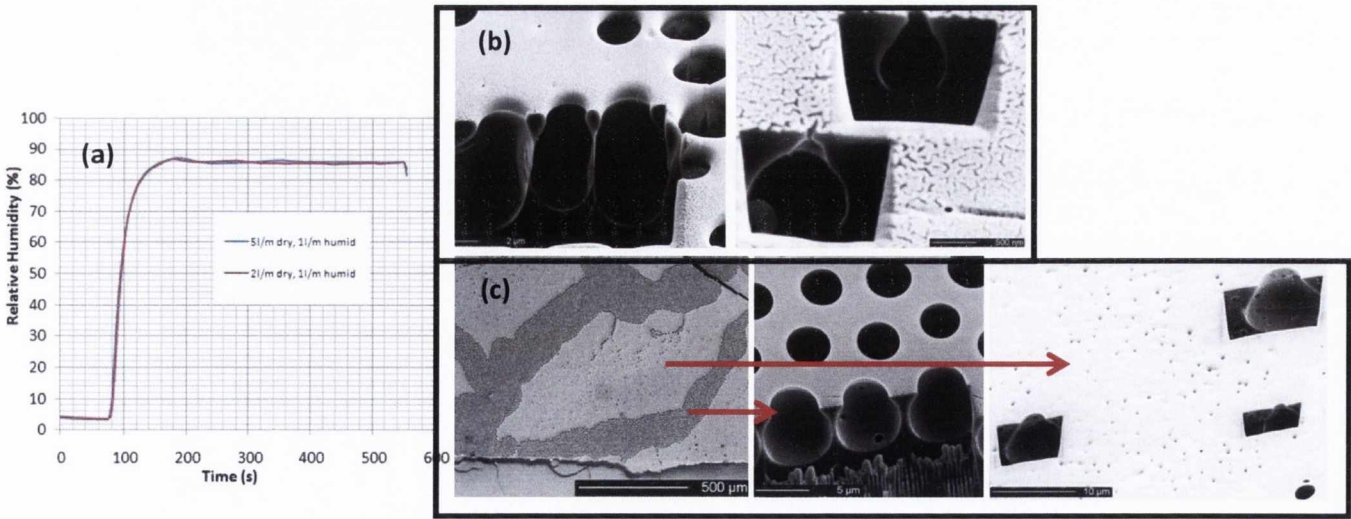


Figure 4.5.9: Graph (a) shows the humidity level recorded over time for two sample runs with time = 0 seconds upon drop-casting. The proceeding set of images are recorded using SEM. The first set, (b), are of a sample formed with an initial dry flow of 5 Lmin⁻¹ for 75 seconds before switching to a humid flow. The second set of images, (c), shows a sample formed with an initial dry flow of 2 Lmin⁻¹ for 75 seconds before switching to a humid flow. The features seen using low magnification are related to the high magnification images using red arrows. Both secondary flows had a rate of 1 Lmin⁻¹.

- (ii) The first flow rate needs to remain at the 5 Lmin^{-1} setting. Lower flow rates, e.g. 3 Lmin^{-1} , are shown in Figure 4.5.9(a,b) to lead to elongated pores, however they are not prevalent, nor as pronounced as when using the higher settings.
- (iii) The second flow needs to be at a high humidity for microstructure control. At a maximum value of 75% or below, highly ordered spherical pores result. At a flow rate of 85% RH or above, stable elongation occurs. The second flow rate was also re-checked in this set-up. A lower flow of 0.5 Lmin^{-1} leads to spherical pores, while a flow rate of 1.5 Lmin^{-1} leads to an increase in coalescence of pores. While the overall experimental results will show a system that is highly flexible and therefore may have alternative regions of phase space to produce different microstructures, our current work shows that a change in humidity shown in Figure 4.5.10 (6) can lead to the novel elongated porous microstructure, Figure 4.5.10 (1,2,3,5).
- (iv) The rate of increase in humidity has been found to be essential for elongated pore formation. A slower rate of increase leads to spherical pores.

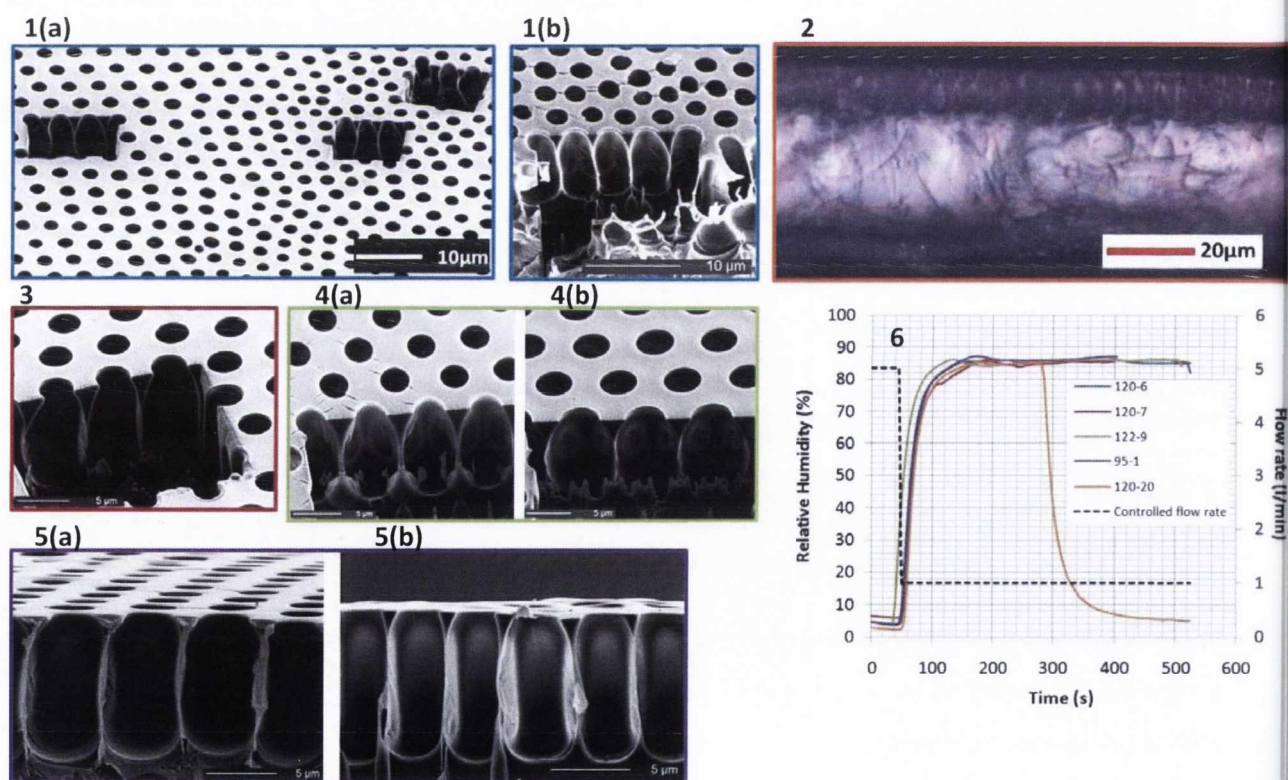


Figure 4.5.10: Images 1, 3-5 are taken using SEM following focused ion beam milling. Image 2 is taken using an optical microscope. Batches 95, 120 and 122 are separate experiments, prepared with the same concentration of 3.5%_{w/w} of DCPS in chloroform. All samples are formed with the same targeted flow and humidity conditions shown in Image 6. Images 1(a,b) - 3 cuts and 1 cross-section into batch 120 sample 6. Image 2- A cross-section of batch 120 sample 20. Image 3- A cut into batch 120 sample 7. Images 4(a,b) - 2 cross-sections of batch 122 sample 9. Images 5(a,b) - 2 cross-sections of batch 95 sample 1. Image 6 – Graphs tracking the humidity of each sample shown during formation on primary axis. This illustrates the repeatability of the flow conditions. The secondary axis shows the noted flow rate for samples in images 1,2,3 & 5.

All samples shown in Figure 4.5.10 are formed using 3.5%_{w/w} concentration of DCPS in chloroform and are formed with the same targeted flow and humidity conditions. As shown in Figure 4.5.10, Samples 6 and 7 from batch 120 and sample 1 from batch 95 (images 1, 3 & 5 respectively) were formed using the optimised settings detailed in Section 4.5.3(i) and show the best examples of elongated pores throughout the front end of the sample. Sample 20 from batch 120 (Figure 4.5.10, image 2) also shows a good coverage of elongated pores.

The simple modulation technique has been used to find a part of the phase space that allows control of the pore microstructure. A set of experiments, shown in Figure 4.5.11 similar to batch 122, sample 9 in Figure 4.5.10 were carried out to test the flexibility of this approach. For this work however, the pulse of humid air was modified with each run to provide shorter and shorter timescales for the condensation event. An initial rapid, dry flow was imposed for each sample as before, using a standard 45 seconds as the guideline. A flow rate of 1 Lmin⁻¹ was then applied from the stream of humidified nitrogen. After the set time for this flow, a third flow was applied at the same rate of 1 Lmin⁻¹ but using just dry nitrogen. The overall drying time was held constant.

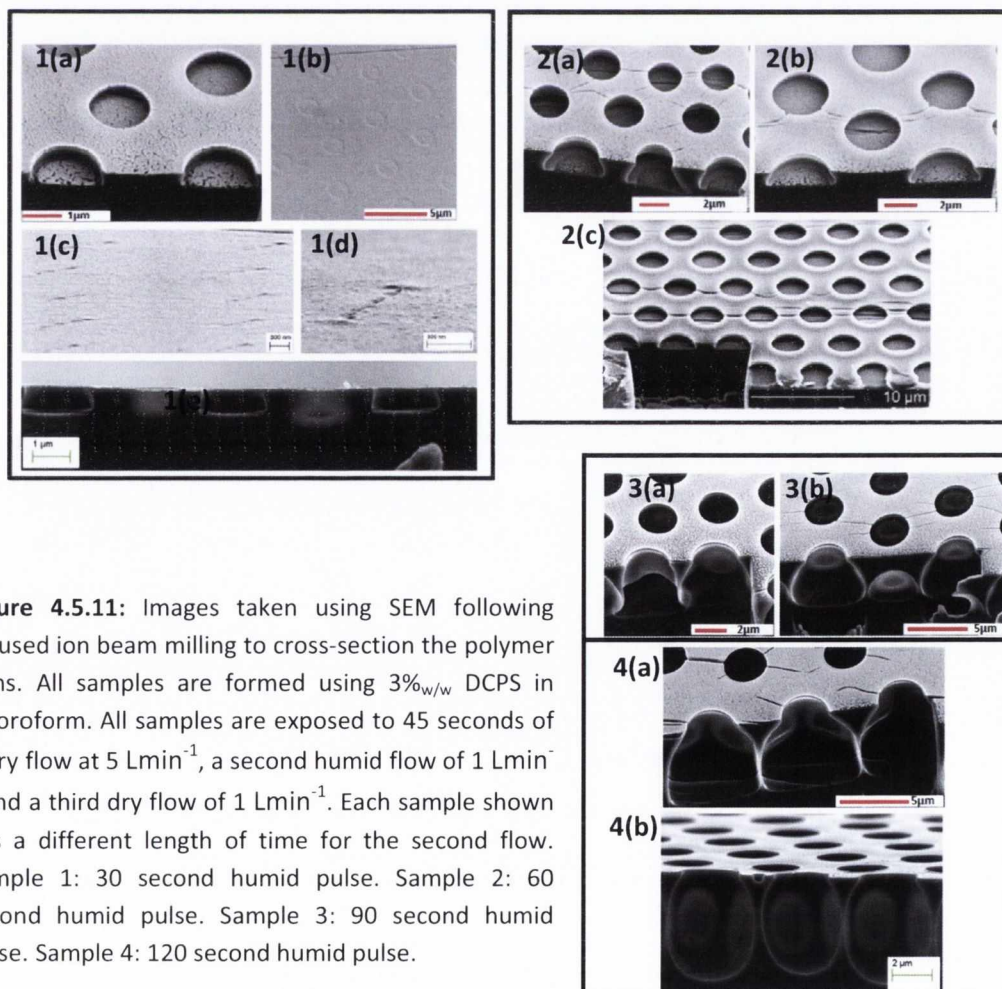


Figure 4.5.11: Images taken using SEM following focused ion beam milling to cross-section the polymer films. All samples are formed using 3%_{w/w} DCPS in chloroform. All samples are exposed to 45 seconds of a dry flow at 5 Lmin⁻¹, a second humid flow of 1 Lmin⁻¹ and a third dry flow of 1 Lmin⁻¹. Each sample shown has a different length of time for the second flow. Sample 1: 30 second humid pulse. Sample 2: 60 second humid pulse. Sample 3: 90 second humid pulse. Sample 4: 120 second humid pulse.

This method can be observed through the side of the glass chamber and it is noted that the surface of the solution becomes white upon introduction of the humid air. As mentioned in Section 1.2.4, this is a sign of breath figure formation and is due to light scattering by the droplets. During the drying phase, this fades or disappears to give the shallow or non-porous surfaces. When using a 30 second pulse of humid air, flat-based shallow pores were formed.

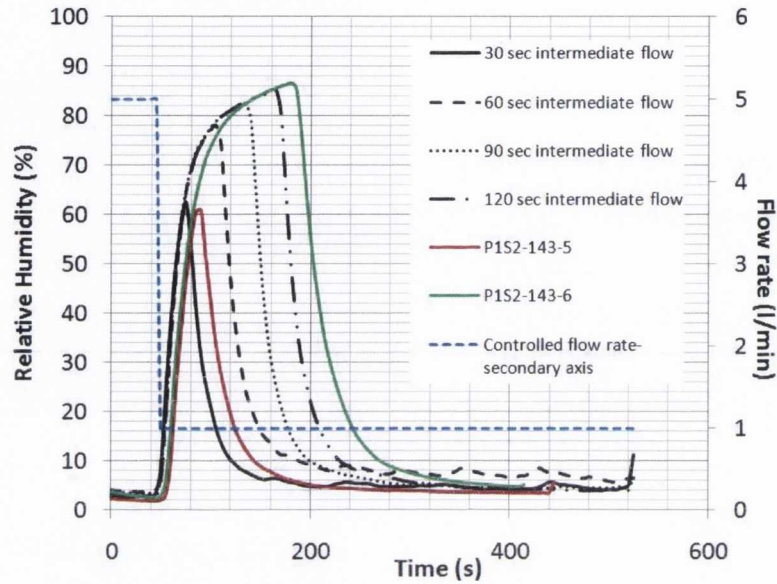


Figure 4.5.12: This plot shows the relative humidity recorded over the course of 7 experimental runs using 3.5%_{w/w} DCPS in chloroform. Each run commences with a 5 Lmin⁻¹ flow of dry nitrogen. Black lines represent a series of experiments where the intermediate humid flow of 1 Lmin⁻¹ lasts 30, 60, 90 or 120 seconds before returning to a dry 1 Lmin⁻¹ flow. A further 30 second (143-5) and 120 second (143-6) sample are shown in red and green respectively to show the scale of experimental error in the timing, which is manually controlled.

Figure 4.5.12 contains a graphical representation of the recorded relative humidity and observed flow rates of a range of samples at 30, 60, 90 and 120 second durations for the humid flow. The cross-sectional view of the 30 second intermediate flow, as shown in figure 4.5.11 (1a), illustrates the shallow nature of the pores. Despite this unusual microstructure, some ordering is observed. The deepest of these shallow pores exist towards the front end of the sample, while further into the sample the pores become more and more shallow. There is a transition from pores to circular rings, as seen in Figure 4.5.11 (1b), which further change to elliptical imprints and finally to ordered lines with a dimple at each edge (1c, d). The humidity data for sample 5 from batch 143 is also shown in red in Figure 4.5.12. This sample did not reproduce the 30 second flow conditions precisely and the pores are slightly deeper but still very shallow with a flat base. A cross-sectional view is shown (4.5.11 (1e)).

A 60 second pulse and its resultant cross-section are displayed in Figure 4.5.11 2(a-c). These pores are observed to be slightly deeper. The ordering is also seen to be greatly improved. 90 second and 120 second humid pulses are also shown (Figure 4.5.11 3,4). Depending on the sample, the results for the longer flow times are less repeatable and sometimes the pore base is slightly flattened, for other flow times it is curved. However, the trend still holds that the longer the intermediate flow duration, the deeper the pores. The timings and humidity changes are crucial but the manual methods used dictate that there will be experimental errors. If the second pulse is greater than approximately 2 minutes, or if the third pulse is abandoned and the humid pulse is allowed to continue, then the system returns to the elongated, cylindrical porous structure observed previously.

In summary, experiments have shown that the standard spherical microstructure observed using a standard DCPS with chloroform can be altered significantly through dynamic influences over the solution evaporation and water condensation events.

4.5.4 Results Tested using Alternative Solvents

As this thesis aims to elucidate the overall mechanism of formation it is important to show that the understanding can transfer to other solvent systems. To explore the applicability to alternative solvents, dichloromethane was also used. As seen in Section 4.4.2 this solvent has a significantly lower critical relative humidity. At 1 Lmin⁻¹ flows, formation of porous films at the critical humidity level also leads to flat based ordered porous microstructures (Figure 4.5.13(a,b)), while a slight increase above this level leads to either slightly submerged droplets near the front end of the sample and spherical pores a little further in (Figure 4.5.13 (d, e)). The ordering under these conditions is excellent (Figure 4.5.13 (c)). This follows the results seen for chloroform. Interestingly, at 85% relative humidity, multi-layers or foam-like structures are observed throughout the film (Figure 4.5.13(g)). The majority of cross-sections viewed show elongated pores, with a destabilised, “wine-bottling” appearance. Some areas have no pores open to the surface but maintain a porous sub-structure (Figure 4.5.13(f)). The ordering on these samples is very poor. Implementing a modulated flow, using the same parameters as with chloroform (5 Lmin⁻¹ dry flow for 45 seconds followed by a 1 Lmin⁻¹ flow at 85% relative humidity for 6 minutes), it is seen that the ordering improves significantly.

The cylindrical pores are straighter and more stable and the porous sub-structure has almost entirely been avoided (Figure 4.5.13(h-j)). Where pores are open to the surface, the ordering of the sample is deceptive when observing with an optical microscope. As can be seen in

Figure 4.5.13(j), the ordering is quite good, but the sizes of the pore openings are often quite different, giving the perception of a poorly ordered surface.

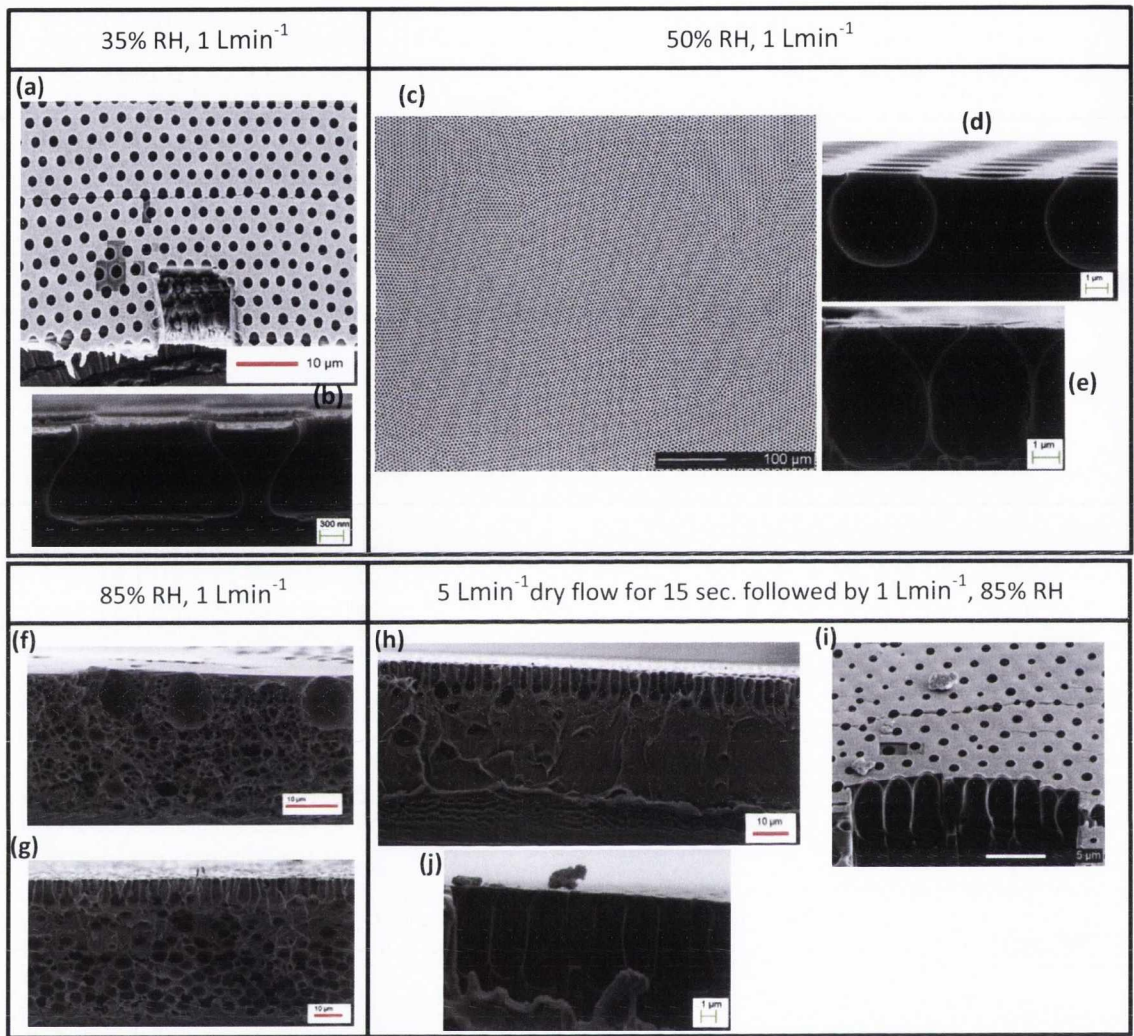


Figure 4.5.13: Images taken using SEM of DCPS in a dichloromethane solution. The concentration was chosen as a molar equivalent to the standard 3%_{w/w} DCPS in chloroform used earlier in this chapter. (a,b) Sample formed at 35% RH, 1 Lmin⁻¹ flow, close to the critical humidity for this solution. (c-e) Sample formed at 50% RH and 1 Lmin⁻¹, (f,g) Sample formed at 85% RH and 1 Lmin⁻¹. (h-j) Sample formed using a dry flow of nitrogen at 5 Lmin⁻¹ for 45 seconds followed by a 1 Lmin⁻¹ flow at 85% RH until the solvent has evaporated.

4.5.5 *In-situ* Observation of Structure Altering Mechanism

In the upcoming discussion section, a hypothesis is put forward regarding the formation of ordered flat pore or imprint arrays. However, it was thought prudent to observe the process as it occurs before finalising an opinion as to its origin. An experiment was carried out using the technique detailed in Section 2.5.1, where droplets of water can be tracked and measured using optical microscopy during the growth process. At the time of the experiment, the optical microscope was located in an open lab and so due to health and safety concerns chloroform

and dichloromethane were not attempted using this method. However, with the use of an extraction unit, toluene was a feasible option. A solution of DCPS in toluene was made up to the equivalent molar concentration of the chloroform and DCM systems.

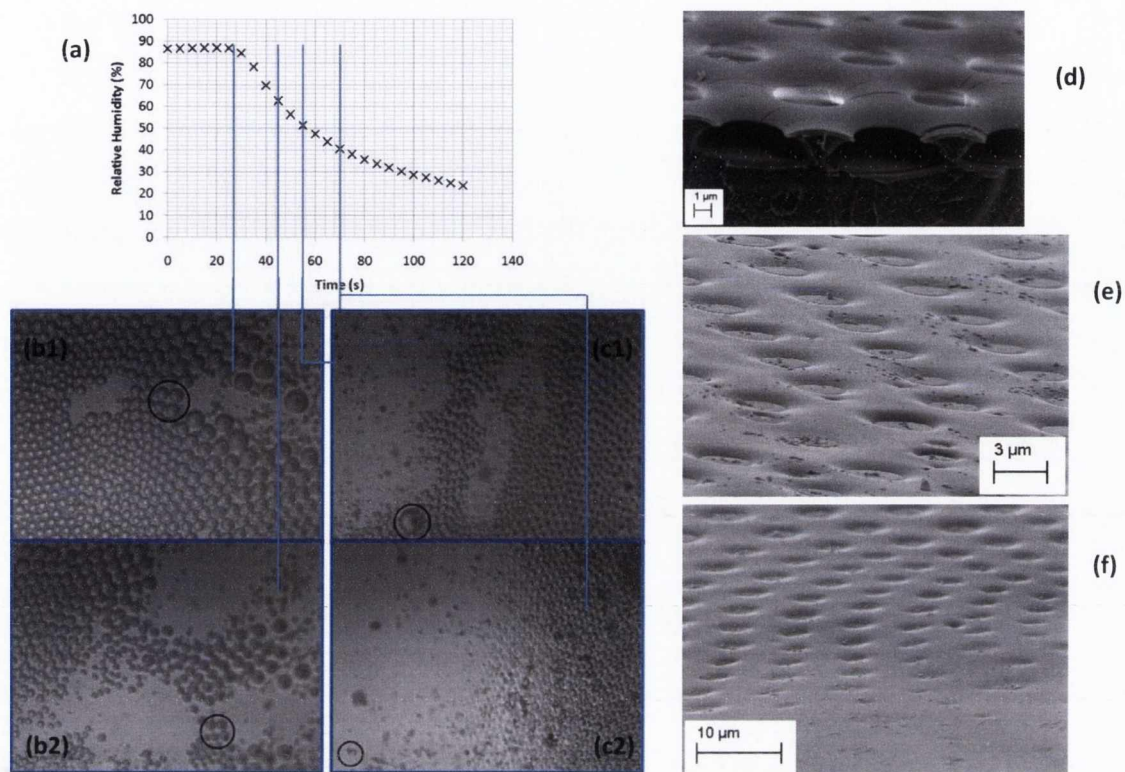


Figure 4.5.14: As shown in Figure 3.1, the relative humidity can be controlled while images of the pore formation process are recorded with the optical microscope shown in Figure 1.3.2 (b). The plot shown in (a) details the relative humidity over time for a sample of DCPS in toluene. As shown moving from (b1) to (b2) water droplets that have been tracked and shown to shrink as the humidity decreases, using optical microscopy. Again using optical microscopy, (c1) and (c2) are seen to show similar behaviour as the humidity decreases further. Using SEM to image the resulting film, (d)-(f) show shallow flat-based pores result from this method as well as shallow indents as seen from these highly tilted image of the surface.

The process of water droplet condensation and ordering at the toluene/air interface was observed and recorded as per the procedure in Section 2.5.1. It was observed that as soon as the humidity was turned off and a lower humidity flow commenced, the droplets began to shrink. Examples of droplets tracked during this process are indicated in Figure 4.5.14(b,c). They would often shrink and not remain attached to their nearest neighbours. A number of videos catch the disappearance of the droplets altogether. Other videos, one of which yielded Figure 4.5.14, show that the round droplets that are normally seen at the end of the process and known to form large arrays of pores with a clear three contact line, in fact become a very faint, dull feature. A subsequent cross-section, as seen in Section 4.4.6, shows that this process yields shallow, flat-based pores in the film that transition to the imprints observed previously.

4.5.6 Polymer Film Surface Characterisation

Finally, before moving to discuss the implications of the experiments described, the microstructure should be detailed. There are no accurate values for wall thickness in the literature, with only vague reports available. The difficulty with accurate measurements is that they can only be achieved with electron or ion based microscopy due to their size and structure. The walls are very thin, contained within the structure and difficult to prepare for imaging. An initial attempt used a focused ion beam to mill downwards through the sample. Figure 4.5.15(a) shows this process part way through the sample, exposing the honeycomb structure that lies beneath the open top pores. Two weaknesses of this approach had to be overcome:

- (i) The wall thickness was below the resolution of the microscope available and so a higher resolution imaging system was required
- (ii) Milling from this direction leads to thinning of the pore walls and they were observed to form interconnections.

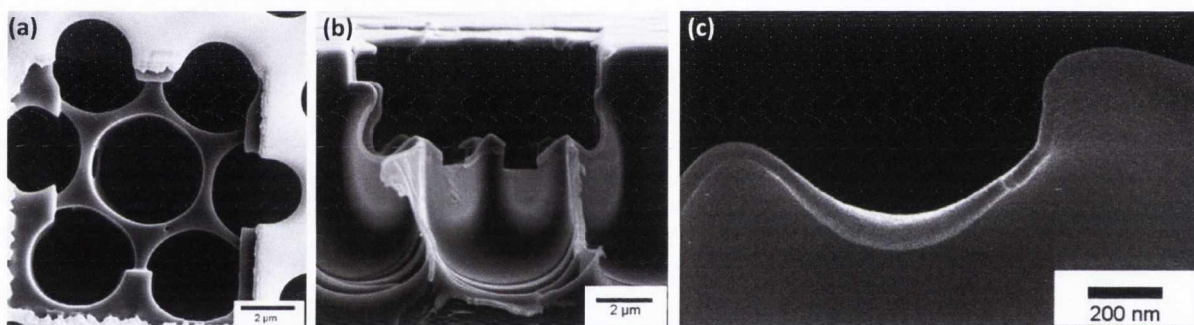


Figure 4.5.15: Analysing a sample prepared using 3.5%w/w DCPS in chloroform under the modulated conditions described in 4.5.3 (i), SEM images reveal in (a) that focused ion beam milling can remove the upper surface and show the sub-structure. (b) Milling from the side of a pore allows careful preparation of thin walls for imaging, (c) The helium ion microscope allows improved imaging and shows extremely thin polymer walls between each pore.

A second approach was therefore used, with elongated, cylindrical pores. These have much larger areas of inter-pore contact and so the thin film is extended. A change in film mounting allowed very low beam current milling of the film from a 90° angle, avoiding the issue of wall thinning. Subsequent imaging with the helium ion microscope, while showing the thinnest point was not quite reached, revealed a wall thickness of approximately 40 nm as seen in Figure 4.5.15. This technique is extremely time consuming and requires a number of technically intricate steps with different high precision tools and so statistical results will be very difficult to achieve for a sample.

Looking at the surface of the porous film, both atomic force microscopy and scanning electron microscopy have been used. It was noticed however that due to the large feature size and

significant depth of the pores, the edges of the pores were not well represented by the AFM technique even with fine tuning. A highly tilted SEM scan with a dynamic focussing technique was instead used to show the morphology. As seen in Figure 4.5.16(b-d), for standard pores, the inter-pore regions are quite flat in general. There does seem to be a slight tilt downwards towards the pores, which then leads to a very small lip at the edge of the pore opening. Shallow pores, however, exhibit a different behaviour and in fact protrude from the surface.

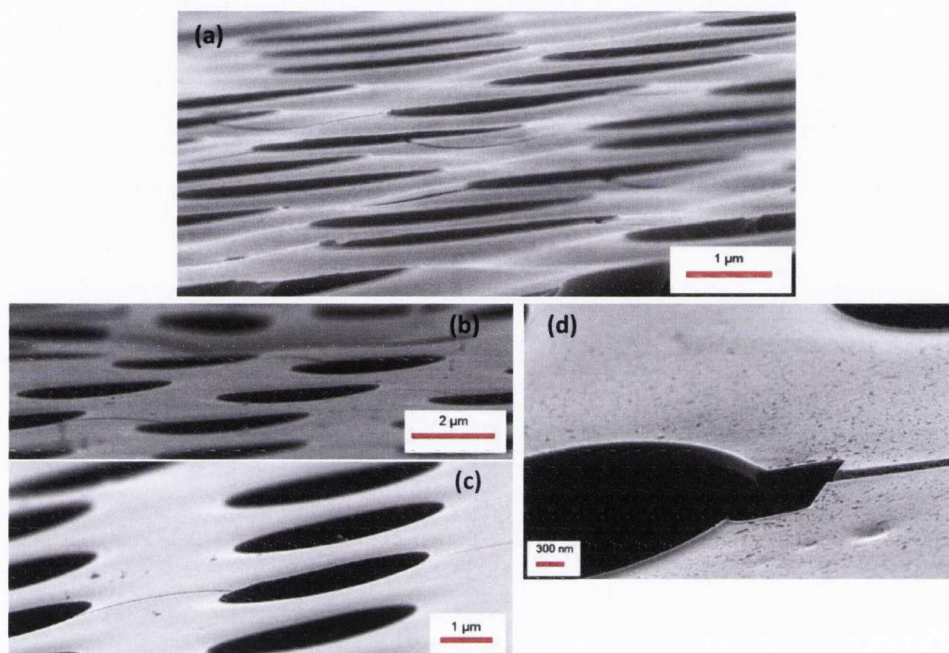


Figure 4.5.16: Images are recorded using SEM of highly tilted polymer film samples. All samples were prepared using DCPS in chloroform. (a) Images show surface of a sample with shallow pores and the protruding pore rims. (b-d) Images are of the surface of a sample with standard spherical pores, showing a flat inter-pore surface with a slight dip towards each hole. A slight rim also exists right at the edge of each pore. In (d) the pore edge has been cut using focused ion beam milling to show the submerged contact angle.

4.6. Discussion

This section focuses on interpreting the results detailed so far regarding breath figure templating. This discussion will be continued at the end of Chapter 5 where further experiments are detailed, following on from the work presented in this chapter. At that point the key discoveries from this chapter and Chapters 2 and 3 will be brought together to present overall conclusions relating to the formation mechanism.

4.6.1 Apparatus Development

It is noted from the work so far discussed, that the method by which water vapour is delivered to the evaporating solution influences the formation mechanism, as too does the volume cast, the substrate conductivity and its wettability with the solution. For this reason, an

experimental set-up (discussed in Section 4.2.5) was built that could be adapted to a number of different experiments, allowing the conditions, quantities and geometries to remain constant throughout. The system is highly dynamic and has highly inter-connected mechanisms that can be affected by many variables and so it is important to keep the conditions as constant as feasibly possible if the resulting data is to be reasonably interpreted. The influence of each of the factors relates mainly to its effect on the evaporation of the solvent. For this reason, the reader is referred to Chapter 5, which focuses almost entirely on polymer solution evaporation, and the discussion therein.

4.6.2 The Influence of Humidity and Flow Rate on Porous Films

At the time of writing, this is the first detailed study of the onset of pore formation or the “critical humidity” with breath figure templating. This is an important study as it defines the lower boundary at which this method is feasible. The analysis, carried out using a 3% DCPS in chloroform solution, showed that such a boundary is variable to some extent. The critical humidity decreases with an increasing flow rate of water vapour entrained nitrogen over the solution surface. This is an important result both in terms of insight into the key drivers of the mechanism and in considering how to apply or develop this technique for dry environments. It is hypothesised that the fast flow rate increases the rate of evaporation and hence cools the surface further. It does this through an addition of kinetic energy to the system, an increased efficiency of removal of the solvent vapour, ensuring a constant drive to evaporate, and also through reduction in the boundary layer and thus aiding mass transport. With a colder solution surface, there is a greater driving force to condense the water vapour. This hypothesis will be examined in further detail in the next chapter, which focuses on solution evaporation dynamics.

The scaling of the critical humidity level with physical properties of the solvent, latent heat of vaporisation, boiling point and vapour pressure, shows that the behaviour is linked to the strength of the intermolecular bonds. Dichloromethane evaporates more rapidly, taking away energy at a fast rate and leading to a cooler temperature, thus inducing condensation at lower values of relative humidity than for chloroform or toluene. Toluene is a volatile solvent but does not evaporate rapidly, hence it has an extremely high critical humidity. Finding a relationship between these known properties and water droplet templating is very useful, as it suggests an ability to choose a solvent to meet specific system requirements. Based on a known property, such as the boiling point of a solvent, this linear trend should yield an

accurate estimate for the critical humidity for other solvents. Examples are shown in Figure 4.6.1.

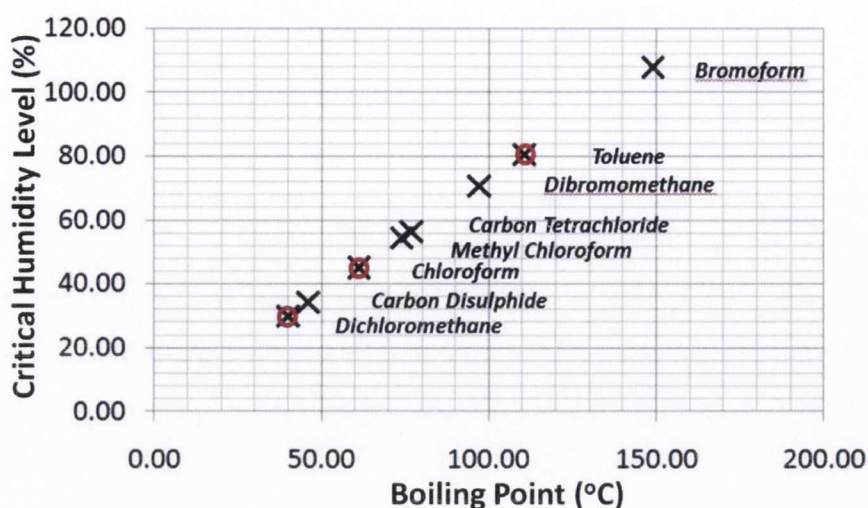


Figure 4.6.1: The critical onset humidity for dichloromethane, chloroform and toluene (highlighted with a red circle) were found experimentally at 1 Lmin^{-1} flow rates and plotted against boiling point. The discovery of this linear relationship should allow a line fit to prediction the critical humidity of other volatile solvents.

The pore counting and measurement used in this report relies upon thousands of results per data point and so is statistically quite robust. Each point also has a distribution to show how representative the average is, while also identifying bi-modal pore size distributions. The improved statistical nature of these results, combined with the random nature of their collection lends further strength to the final trends identified. It is quite clear that with an increased humidity, larger pores are subsequently found as discussed by a number of groups. It is shown here that this is true for a range of flow rates. From the related graphs in Figure 4.5.1 it can also be read that the range of attainable pore sizes increases with an increase in the delivery flow rate. In Srinivasarao *et al.* (32) however, it was remarked that an increase in flow rate led to a decrease in the pore size although no relationship was provided, the level of control is not detailed and the underlying mechanism is not clear.

At higher flow rates, there appears to be a significant compounding of the impact of relative humidity. If the humidity is low, there is still a drive to condense and small droplets form. This growth is relatively slow with respect to the drying of the substrate so the pores are fixed at a small size. If the humidity is high, this evaporative cooling can lead to a significantly larger drive to condense that outperforms the drying of the surface, leading to proportionally more condensation. A relationship between these mechanisms of evaporation and condensation is here being hinted at and if such a mechanism could be refined it would aid in the control of the water droplet templating process. This point will also be picked up again in Chapter 5 upon

examination of the effect of evaporation on the solution temperature throughout the entire formation mechanism.

Figure 4.5.2 shows a trend also not previously discussed, where the dependence of pore opening on the droplet size appears independent of solvent choice. This result shows remarkably that, under the conditions of this experimental set-up, the influences on pore size, which are believed to be the length of time available for the water droplet to grow and the temperature of the surface which drives growth through condensation, are linked so closely that the overall trend is a linear increase in pore size as the humidity increases. This appears true without significant restrictions as to the choice of solvent. Both the time available for the droplet to grow (solvent evaporation time) and the surface temperature (extent of evaporative cooling) are rooted in the strength of the intermolecular bonds, suggesting that for otherwise identical systems, a straight forward relationship exists between certain properties of the chosen solvent, for example the boiling point or Hamaker constant, and the predicted pore size. This result will be examined further in the discussion section of Chapter 5 after further experimental work into the drying process.

The influence of humidity on the pore microstructure is a remarkable one. At low values of humidity, any of the three solvents used result in flat-based shallow pores. This is a highly novel morphology in the field of water droplet templating. The only similar results in the literature are formed using an additional heating step to anneal the polymer as opposed to this one-step method (93). From observations under the optical microscope, these microstructures only appear to form when the water droplets begin to evaporate while there is still enough solvent present in the solution to allow polymer flow.

From this, a great deal can be inferred. This ability of the water droplets to evaporate is discussed later in this section with regard to the modulation of flow. However the drive of the vapour-liquid-equilibrium (VLE) of water towards evaporation is expected at these low relative humidities due to the significantly lower saturation temperature required for condensation to occur. Conversely, at a higher humidity, where the saturation temperature is not so low and water condensation occurs for a longer duration, an increasing pore depth is observed, as shown in Figure 4.5.6. To strengthen this hypothesis, work in Chapter 5 will look at the evolution of the surface temperature over time and what this means to the drive to evaporate or condense water. It is noteworthy that even with polymer flow still enabled due to presence of solvent the surface structures are very difficult to destroy. Figure 4.5.14 illustrates this, showing circular imprints in the polymer film, despite an almost complete recovery of the film

and destruction of the internal porous microstructure. This suggests that at the surface there is a higher concentration of polymeric networks.

The unusual, nanoscale arrays of lines are a further development of this process. Their position and transition from circular imprints to oval shapes and then lines provides consistency to the argument that these are remnants of the water droplets. It appears likely that the mechanical stretching or compressing of this viscous film may have led to these lines in a similar way to (177). These results also provide an insight suggesting that the polymer solution may evoke a concentration gradient during evaporation and it is this that will be explored in the next section.

4.6.3 Influence of Concentration

The effect of an increase in dosing concentration is an important topic to address. Droplets are observed to grow and order at the solution/air interface while evaporation leads to an increasing polymer concentration. Under these conditions, the droplets remain spherical, based on the surface energy balance detailed in Chapter 2, as do the resulting pores. However, upon drop-casting at a higher initial concentration this appears no longer to apply and a range of microstructures can occur, often seemingly at the expense of an ordered structure. Starting with the highest concentration explored, 8%_{w/w} DCPS in chloroform, it is interesting to see that the formation of ordered pores still occurs. More importantly, the internal microstructure does not reflect this order and unstable growth of the water droplets has clearly occurred beneath the solution surface as seen in Figure 4.5.11 (2b). In general the pore openings appear to have a much straighter neck than at standard lower concentrations and become more bulbous further into the film. Such an observation suggests that the water droplet was restricted near the interface but was free to expand at a certain depth. In many cases, this “instability” led to conical flask pores with a flat base. If the system is disrupted through, for example, a reduced capacity for solution evaporation, it is believed as mentioned in the previous paragraph that the water droplets will begin to evaporate and the polymer solution will begin to recover its shape. In the case of the high concentration solutions, the reduced evaporation is seen to be due to a thin polymer film forming over the volatile liquid. A concentration gradient is set up but is so severe that it decreases solvent evaporation and hence sample cooling. It is this action, due entirely to the excessive polymer concentration that also leads to the flat base of the conical flask type microstructure.

At the opposite end of the scale, at 3%_{w/w} DCPS in chloroform, spherical pores are observed and the ordering is significantly improved. However, in between these extremes, it appears

there is a median at approximately 4.5% w/w where the elongated microstructure becomes more stable. However, this does not occur in an ordered film. It is believed in the case of elongated or cylindrical pores that the concentration gradient is descending through the film at approximately the same rate as the droplet growth, stabilising the cylindrical form, as discussed in detail in Chapter 5.

4.6.4 Control of the microstructure through modulation

One of the most important messages from this chapter is that the microstructure of water droplet templated films is not a fixed property of the polymer and solvent system choice. As the literature shows, interconnectivity and elongation of droplets can be promoted through careful polymer design, while shallow pores can be created through further annealing steps. However, drastic influences are feasible through understanding and controlling the dynamic mechanisms of formation. Through control of the humidity and flow rate it was found that with either chloroform or dichloromethane the ordering of the sample could be improved and the pores formed in a range of microstructures from cylindrical to shallow, flat-based pores. It was found that, using the understanding of concentrations and humidity values built up throughout the project, it was sensible to divide the technique into three stages, illustrated in Figure 4.6.2 (a,b).

Stage I involves the initial evaporation process of the solvent. Here we control the flow rate of a dry nitrogen stream to set the temperature of the surface and control the duration of this pulse to set a polymer concentration gradient through the film, in a similar way as happens naturally for higher concentration solutions. The temperature will control the drive to condense water while the concentration gradient will ensure early stabilisation of the droplet at the interface. Next, in stage II the relative humidity is ramped up quickly to a level above the critical humidity for the relevant surface temperature. This induces water condensation at a specific rate dependent on the temperature produced during stage I. The duration of this step has been shown to dictate both the volumetric growth of the droplets and the pore opening diameter. This flow also continues to control the propagation of the higher polymer volume fraction through the solution. Finally a third step reintroduces a slow water-free flow to complete the drying of the film. The timing of this step is key, as it dictates at which point the water droplet vapour-liquid equilibrium (VLE) switches from a condensation to an evaporation process and whether the polymer film has formed or is still fluid, as indicated. If the process in Figure 4.6.2(a) is used and the third flow only evaporates the water droplets and all the solvent has already evaporated then we can expect elongated pores.

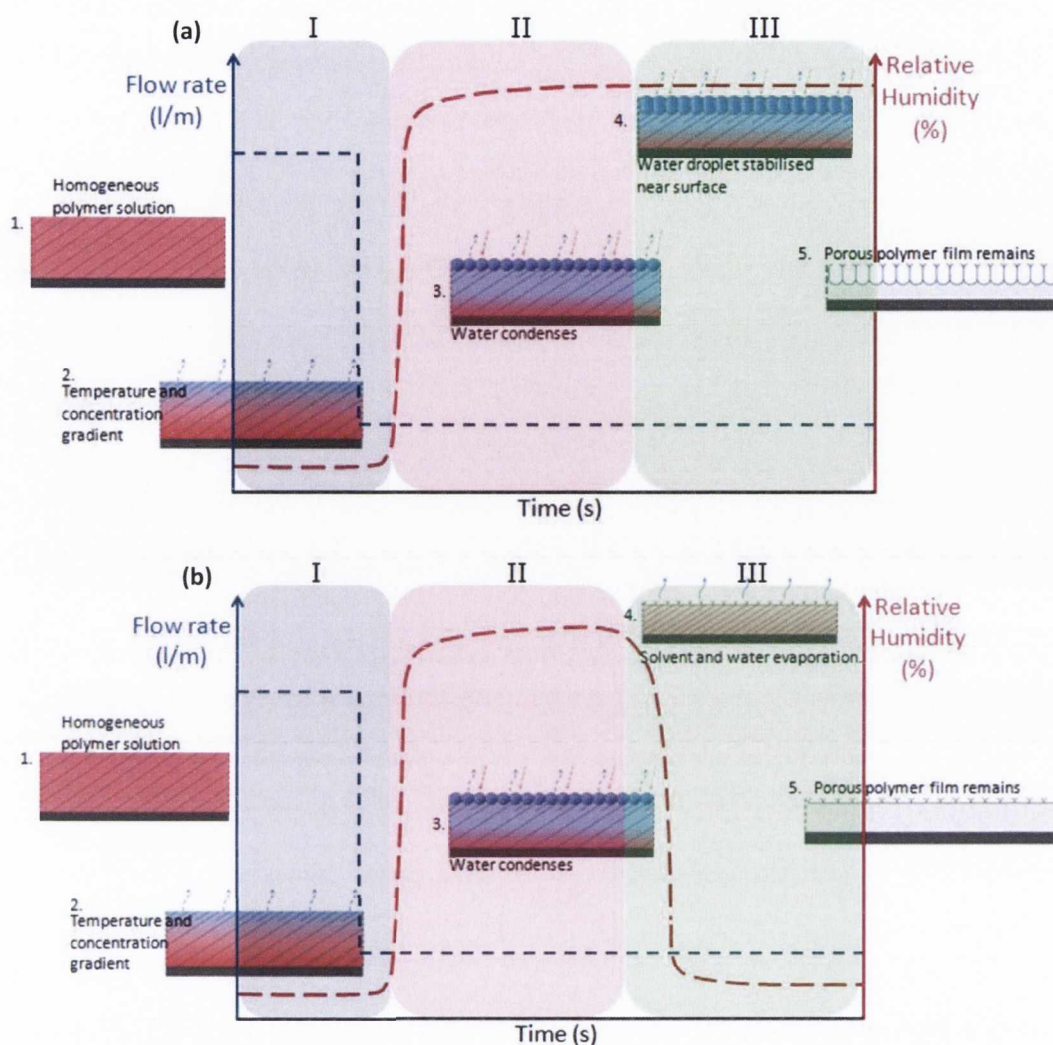


Figure 4.6.2: This figure presents a summary of the proposed mechanism for the formation of elongated or shallow pores in a polymer film. In (a), the modulated flow rate and humidity are shown along with illustrations of the effect on water droplet formation and growth. The conditions in Stage III are identical to Stage II and leads to elongated and cylindrical pores. In (b) the three stage modulation is summarised and shows the method to form flat based pores of controllable depth. In this scenario, Stage III consists of a low flow rate of dry nitrogen. The duration of Stage II is varied to move between the elongated pores of (a) and the shallow pores of (b).

If however the method in Figure 4.6.2 (b) is employed then the timing of this third phase will dictate the extent to which the polymer film can recover its shape. This method for microstructure manipulation affects not only the internal pore shape but also the external surface. The rising of the flattened base appears to lead to a protrusion of the fixed part of the pore leading to a less smooth surface. The wall thicknesses for the shallow pores are extremely large but this is not surprising as the point of closest contact between pores has been re-formed as part of the flat film.

The individual elements of this hypothesis have significant support from the experiments reported in this chapter. However, to understand it to a greater extent, the key driver, the surface temperature of the polymer solution, needs to be explored quantitatively. Chapter 5 will focus on evaporation of polymer solutions and include a look at the theoretically predictable behaviours as well as *in-situ* experimental measurements for our particular flow method. Following this a more detailed and encompassing discussion will provide an overall view of the advances in the field due to this work.

Chapter 5

Breath Figure Templating – Part 2: Dynamic Control of Solution Evaporation

5.1 Introduction

This chapter aims to elucidate the droplet growth behaviour noted in Chapter 4, which appears to originate from changes to the local environment during microstructure formation. Work is presented, calculating, and where feasible quantifying through *in-situ* measurement, the different stages through which the water droplet templating process evolves. Further analysis of these results reveals how the effects of each stage are manifested in the changing physical properties of an evaporating polymer solution.

With this aim, an initial introduction provides a more detailed introduction to polymers than given in Chapter 1, followed by some necessary information, used later in this chapter, regarding polymer solutions and solvent evaporation. This will be followed by a description of the experimental procedures employed in this work before presenting the results and analysis. The discussion will call on points from a number of earlier chapters to present a clearer picture of the water droplet templating mechanism.

5.2 Introduction to Polymer Solutions

Polymers are large molecules (macromolecules) made up of more than one monomer, or chemical unit, that are linked and repeated in various geometries such as lines, combs, stars, rods, etc. One of the key breakthroughs in analysing polymer behaviour in solution was the realisation that they could be considered at a “low magnification”, ignoring the atomic, structural details and viewed as a representative coil. A typical representation of a polymer chain is given in Figure 5.2.1. As noted by de Gennes (178) the flexible nature of the chain can be maintained without taking a high resolution, atomic approach and instead describing the polymer using a series of straight sub-chains of uniform length. The length of these sub-chains must remain below a certain size, depending on the overall chain size, to ensure that a flexible

molecule is still described. The “persistence length” is designated as the length below which the sub-chains do not represent a flexible chain.

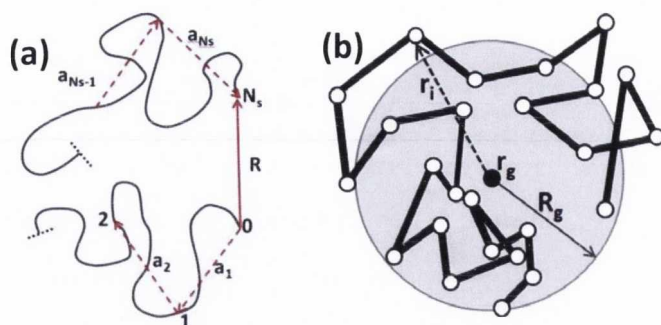


Figure 5.2.1: Illustration of a polymer with (a) segments (a_N) used to describe the chain. In (b) the resulting freely jointed segments are used to model the system. The radius of gyration, R_g . Centre of mass, r_g and distance from centre of mass to each bond monomer join, r_i are indicated. Reproduced from (179).

By setting different permissible behaviours of these sub-chains, mainly related to restricting their relative positions, a range of different models are created, each attempting to predict the behaviour of polymers in solution. The model used within this work is a three dimensional random walk, which determines the conformations of the linear polymers looked at in this thesis. This approach and model considers each segment (or sub-chain) individually. Each sub-chain is added to the end of the previous one in a random step direction and prior steps have no influence over the current one. When forming this structure, a model can choose to allow or prohibit the chain to revisit a site. This leads to the description of ideal and real polymer chains, respectively. The excluded volume term in real chains ensures these are slightly expanded compared with the ideal model due to intermolecular and steric repulsions. While ideal chains do not exist, polymers in their unperturbed state, such as in the melt, highly concentrated solutions or theta-solvents are real chains that behave as if they are ideal. The assumption of an ideal chain is useful in mathematical calculations (179). In this chapter an ideal chain with a three dimensional random walk will be used as the basis for defining polymer geometries in solution.

The definition and estimation of the volume occupied by a polymer molecule is very important for work later in this chapter. The most commonly used characteristic length scale is the radius of gyration. This is the mean square distance from the coil centre of gravity to the segment nodes that make up the random walk as shown in Figure 5.2.1(b). The polymer chain is then assumed to occupy the spherical volume defined by this radius. Other measures often employed are the polymer end-to-end vector (5.1) and the root mean square end-to-end distance (5.2). However, direct measurement of these is not feasible so the radius of gyration is used (5.3). It can be obtained through light scattering experiments.

$$R = \sum_{i=1}^{N_s} a_i \quad (5.1)$$

$$\langle R^2 \rangle = N_s \langle |a_i|^2 \rangle \quad (5.2)$$

$$R_g^2 = \frac{1}{N} \sum_{i=1}^N \langle |r_i - r_g|^2 \rangle \quad (5.3)$$

where $\mathbf{R}$ is the end-to-end vector, N_s is the total number of freely jointed segments, a_i is the length of the i^{th} freely jointed segment, $r_i - r_g$ is the distance from the i^{th} freely jointed segment to the centre of mass. As highlighted by de Gennes (178), the “low magnification” approach to describing polymer behaviour does not accurately apply to solutions without further refinement to allow for molecular weight, concentration and solvent choice. Any change in these parameters influences the polymer interactions in solution and therefore also the scaling laws that have been devised to aid in the prediction of their properties. This is an important point as the system outlined in this thesis traverses a broad scope of concentrations. Chapter 4 showed that there may be an important role for the end of process flow behaviour and to understand this the change in viscosity and glass transition temperature of the solution are important to note and so it is necessary to define which concentration regimes the mechanism passes through and how to deal with each one.

In the dilute regime, the polymers in solution are assumed to have minimal and transient interactions with other chains (180). It is assumed that the dilute regime extends to the level where the mean solution concentration is equal to the mean concentration within a single chain. This critical point signifies the chain overlap concentration and depends on the volume a single chain occupies. This in turn is dependent on the degree of polymerisation and the radius of gyration as shown in Equation 5.4.

$$c^* \left(\frac{4\pi}{3} R_g^3 \right) = \frac{M}{N_A} \quad (5.4)$$

Where c^* is the overlap concentration, R_g is the radius of gyration, M is the molecular weight and N_A is Avogadro’s Number. Prediction of properties in the dilute regime is quite advanced and accurate. Viscosity predictions are based on relationships for a solution of hard spheres. The coils assume the role of these spheres and viscosity can be predicted using equation 5.5 once certain parameters are known for a system (181). The intrinsic viscosity, or viscosity at an infinite dilution, is very well documented for many polymer solvent systems and can be found using published results for the Mark-Houwink equation, 5.6, or experimentally by viscometry.

$$\frac{\eta - \eta_s}{\eta_s c} = [\eta] + k_H [\eta]^2 c + \dots \quad (5.5)$$

$$[\eta] = K M^a \quad (5.6)$$

Where η is the solution viscosity, η_s is the specific viscosity, $[\eta]$ is the intrinsic viscosity, c is the solution concentration, M is the molecular weight of the polymer, K and a are constants for the system. Once above the overlap concentration, new approaches are required for estimating viscosity. There is a range of estimation techniques published in the literature. The

Mark-Houwink equation, Equation 5.6, is used for dilute solutions and also for polymer melts. A method developed by Ford (182), based on a model solution containing hard spheres, is developed (183) to allow viscosity predictions for solutions no longer in the dilute regime. This method is also not suitable at high concentrations of polymer. Predictions then need to be based on a method developed by Van Krevelen (184). This involves calculating the viscosity of the undiluted polymer at the glass transition temperature of the solution and taking into account critical temperature effects and dilution effects. The technique is located in Appendix 5.1.

With a further increase in concentration, the solution reaches the concentrated regime. At this point, the polymer coil is believed to have reached its unperturbed value for the radius of gyration and further dependence on concentration is negligible. The cross over concentration is estimated as (181):

$$c^{**} = \left[\frac{R_g(0)}{(R_g)_0} \right]^8 \cdot \phi^* \quad (5.7)$$

where c^{**} is the crossover concentration from semi-dilute to concentrated solution, $(R_g)_0$ is the unperturbed radius of gyration, $R_g(0)$ is the radius of gyration at infinite dilution, ϕ^* is the volume fraction at the dilute to semi-dilute cross over. The chosen model is also applicable to the concentrated regime. The effect of solvent concentration on the glass transition temperature of the polymer solution must also be estimated and in any regime is associated with the concentration as shown in equation 5.8.

$$\frac{1}{T_g} = \frac{c}{T_g^p} + \frac{1-c}{T_g^s} \quad (5.8)$$

where T_g is the glass transition temperature of the polymer solution, T_g^p is the glass transition temperature of the pure polymer, T_g^s is the glass transition temperature of the pure solvent, c is the concentration of polymer in the solution. Combining the findings from the overlap concentration and the various model details, it should be feasible to cover the range of concentrations and track the change in the polymer with solvent evaporation and specifically the viscosity and glass transition temperature. This will aid understanding of the growth mechanism of the droplets.

This chapter will also explore the key driving force that leads to the change in concentration regime, i.e. the evaporation of the volatile solvent. This appears to be the dictating influence of not just the solution concentration but also, through evaporative cooling, the drive to condense water vapour. Solvents of high vapour pressures and low specific heat capacity are highly volatile and, chosen carefully, can reduce the surface temperature by a significant

amount. A low enthalpy of vaporisation also ensures rapid evaporation at ambient conditions but a higher value will ensure a significant drop in temperature. The result of the evaporation is a polymer solution of increasing polymer volume fraction and cooling of the solution/air interface. This cooling of the surface induces the second key phase change, that of water vapour condensing to droplets.

As part of the general topic of evaporation of drop-cast solutions, there are many constituent mechanisms and phenomena that lead to the overall behaviour. One of the most notable in terms of breath figure behaviour is the presence of convection cells. This is a rich area of research in its own right. Henri Bénard pioneered the scientific approach to documenting and understanding the convective motions observed in shallow fluids with an imposed temperature gradient through heating at the base or cooling from the upper surface. The resulting convection currents took the form of ordered polygonal cells, where the flow was rising at the centre and sinking at the edges. Rayleigh progressed the understanding of convection cells much further, although these were of a slightly different nature. Rayleigh-Bénard (RB) convection cells occur when the vertical temperature gradient induces a change in buoyancy across the film that overcomes the resistance due to viscosity and induces a flow to occur. The difference in density with temperature provides the driving mechanism in this case (185).

The original type of convection current, later explored further by Block and known as Bénard-Marangoni (BM) flow is in fact driven by differences in surface tension. This difference can arise through either concentration or temperature gradients across the thickness of the deposited solution. The difference in surface tensions leads to forces perpendicular to the interface (186). In general it is noted that the more volatile a solution, the greater the temperature difference due to evaporation, hence the presence of higher levels of instabilities and an increased BM convection effect. The buoyancy and surface tension effects need to be disentangled for each scenario to see which is more likely to have the dominant effect. The role of these convection cells in breath figure templating is debated within the literature. It is believed by some groups that the convection cells, often observed during microstructure formation, are responsible for providing nucleation centres for the water droplets (187), ordering the droplets (188), for creating a mesoscopic order to the system (189). It is also reported specifically in terms of breath figures (22) that the main influence of the convection currents is the enhancement of coalescence events. It is generally agreed that it is most likely that while both types of convection are present in these circumstances, the BM type is

dominant. It is less well understood if the temperature or concentration gradient is the key influence over the surface tension.

The establishment of temperature and concentration gradients during solution evaporation is still not fully understood due to the complex nature of the heat and mass transport mechanisms. However, it has been agreed by most authors that upon evaporation of a polymer solution, a region of low solvent concentration is predicted at the solution/air interface (190). This is where the solvent removal is most rapid and so a “rubbery” phase is generally observed here first (191). This concentration gradient can lead to a glassy skin formation at the interface (191), (192) and this transition propagates from the interface towards the substrate as drying continues, until a final glassy film is achieved. A number of models exist to predict the formation of such “skins” or gradients (193), (194) and it has been noted through simulation that when evaporation is high or when the initial polymer concentration is high, a skin or gel phase is predicted to form near the free liquid interface. This polymer-rich region is predicted to have an effect on the flux of solvent at the air interface because the diffusion coefficient is so much greater (193), (195). However, this is not the observed effect of the skin phase in all reports. Some have not found it to interfere with evaporation (192).

The other phase transition that requires an introductory note in this section is that of water condensation. Some notes on condensation have already been presented. In the breath figure system there are many complex issues regarding the non-coalescence, size and positioning of the water droplets, as discussed in Chapter 2. The complexities will not be covered in more detail here but instead a simpler approach to condensation is adopted. Two equations for predicting phase behaviour are used to predict condensation and evaporation of water and do not require a deeper understanding of the growth process to function.

- (i) The Antoine Equation – Used to predict the saturation temperature of water under various relative humidities (196). This should allow a clear picture of the conditions when condensation will occur.

$$\log_{10} p^* = A - \frac{B}{T+C} \quad (5.9)$$

Where p^* is the vapour pressure associated with the liquid at a temperature, T. A, B, C, are tabulated constants for most standard materials.

- (ii) The HKS equation is used to not only predict when evaporation or condensation will occur, but also to provide a quantitative scale depending on the experimental procedures carried out (197).

$$m_{net}^* = \frac{2}{2-\kappa_c} \cdot \left(\frac{M}{2\pi R}\right)^{\frac{1}{2}} \cdot \left\{ \kappa_c \cdot \frac{p_v}{T_v^{0.5}} - \kappa_E \cdot \frac{p_l}{T_l^{0.5}} \right\} \quad (5.10)$$

Where m^* is the net flux of water (kg/s), κ_c is the coefficient of condensation, κ_E is the coefficient of evaporation, M is the molecular mass of water (kg), R is the universal gas constant (J/mol.K), p_v is the partial pressure of water in the chamber environment at temperature T_v , p_l is the vapour pressure associated with the liquid at temperature T_l .

The experiments that now follow explore the influence of environmental conditions on the solution through *in-situ* measurements of mass loss, temperature change and humidity as the microstructure is formed. The theory briefly introduced in this chapter, will enable us to track the viscosity and glass transition temperature. The aim is to explore the interdependencies of the parameters in this highly dynamic system through observation and recording of the changes in physical behaviour with imposed conditions. This will help understand the links with pore microstructure that are observed to occur and previously reported in Chapter 4.

5.3 Introduction to Experimental Approach to Studying Dynamic Mechanisms

The key driving force of the self-organisation method is the evaporation of the solvent. This is the enabling process that induces cooling, thus allowing condensation to occur. It is also, as mentioned in Section 5.2, credited with inducing sufficient surface currents to promote droplet ordering. As part of the analysis of this technique, a range of apparatus was developed to monitor and record the evaporation through *in-situ* mass and temperature measurement during film formation. Evaporation is very sensitive to local flow conditions, as indicated in Chapter 4 where the change in flow rate across the surface of the evaporating solution alters the critical humidity level. To ensure applicability of these measurements to earlier results, the experiments replicate the flow conditions as closely as possible by incorporating the mass balance into the base of the flow chamber and the thermocouple into the chamber itself. With this set-up, a range of conditions were explored and their effects on pure solvent and polymer solution recorded, with particular focus on the flow conditions described in Chapter 4 that access alternative microstructures.

The experiments and results will now be presented, followed by Section 5.7 where the data is further analysed to relate the findings to changes in the concentration, viscosity and solution glass transition temperature. The recorded values are also used to predict condensation of water during the film formation. Finally, the combination of approaches in Chapters 4 and 5 are referenced to discuss the insights they provide for the overall mechanism.

5.4: Recording Evaporation Through Change in Mass

An initial comparison is presented to show the variation in evaporation behaviour between a standard drop-cast sample of pure solvent and an equal dosage volume of the same batch of solvent with a low concentration of dissolved polymer. The solvent used is chloroform and the polymer used is dicarboxy-terminated polystyrene (DCPS), also detailed in Chapter 2 and used in Chapters 3 and 4. The substrate is a glass microscope cover slip and the procedures for cleaning the sample and preparing the flow chamber are the same as in Chapter 4.2.6. For this initial comparison, there is no gas/vapour flow in the system. This is a “static air” experiment only. The ambient conditions are of low humidity and so minimal condensation is expected.

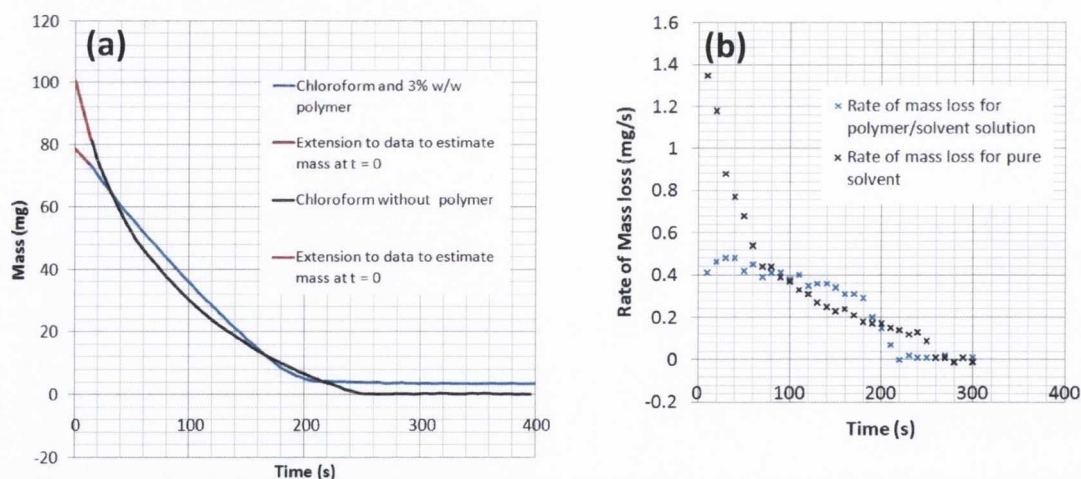


Figure 5.4.1: Plot (a) shows the recorded mass loss as a function of time due to evaporation of pure chloroform and a 3%_{w/w} solution of DCPS in chloroform. These were carried out under static ambient conditions. Plot (b) uses the data from the same experiment and shows the calculated slope of the evaporation curves as a function of time.

Due to fluctuations in the mass recording, inherent in the dosing procedure, the mass balance does not register the actual mass in a stable manner for approximately 10 seconds after dosing. This is due to both the stability of the balance and also the post-dosing re-positioning of the cover used to protect the balance from air currents in the fume hood. The initial slope of

the evaporation curve is extended to the dose time in an attempt to provide a value for the dosing mass. This is an estimate only as it does not take into account the start-up increase in evaporation rate. The red lines in Figure 5.4.1 (a) signify that this estimation has been used and so the values were not recorded as part of an experiment.

Figure 5.4.1(b) is a plot of the instantaneous evaporation rates from Figure 5.4.1 (a). Each data point represents the rate calculated using a range of 10 seconds of the process. This minimises the effect of noise on the recorded values. From these two plots it is clear that the pure solvent commences evaporation at a much greater rate than the polymer solution. The rate of solvent evaporation decreases rapidly at first before changing suddenly to a more gradual decline. There is then a rapid transition to the final, level section of the graph where evaporation is complete. The polymer solution has a more linear response in its evaporation. The rate of evaporation remains relatively constant for the bulk of the sample run before entering a transition towards the end of the evaporation. This transition is notably slower than that of the pure solvent. Four sample runs of each experiment were completed and as these are highly repeatable, the chosen graphs are representative of the standard behaviour of each system.

In Chapter 4 it was seen that, depending on the chosen flow rate, significantly different levels of water vapour were required to form pores. The same mass recording technique is now used to examine a slow and fast flow rate to understand this further. In the following study of the influence of flow rate on evaporation all of the quoted flow rates are for dry nitrogen. This is to allow a separate examination of the influence of humidity on evaporation behaviour. Again, representative samples are chosen for different flow rates in Figure 5.4.2. The data is not from dosing time, but the time when the mass balance measurement stopped fluctuating. The dose time is $t = 0$ for all samples.

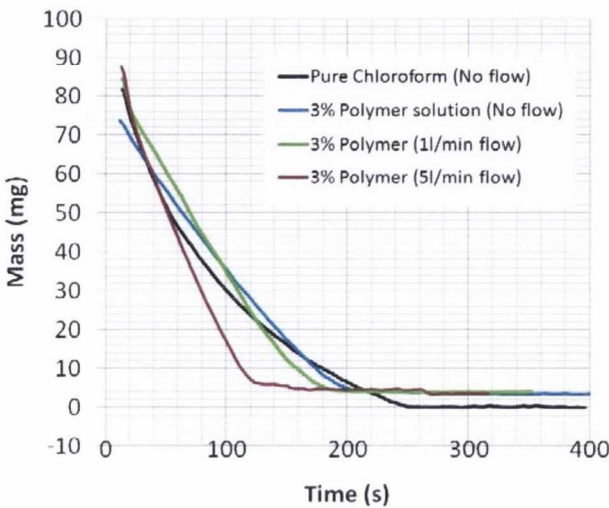


Figure 5.4.2: A comparison of the change in mass over time for three different flow rates, 0 Lmin⁻¹, 1 Lmin⁻¹ and 5 Lmin⁻¹, of nitrogen (no water vapour) over the polymer solution. The solution is 3%_{w/w} DCPS in chloroform. The static evaporation of pure chloroform is included as a reference.

It can clearly be seen in Figure 5.4.2 that increasing the flow rate from 0 Lmin^{-1} to 1 Lmin^{-1} and then 5 Lmin^{-1} shows a steady increase in the rate of evaporation and a significant decrease in the drying time, identified as the duration from dosing until a cessation in the change of mass. The almost linear evaporation trend is present in all polymer-containing samples.

Following from this, it was decided to explore the response to a modulated flow rate. The aim is to aid understanding of the modulated flow results in Chapter 4 and so the identical flow conditions are employed. An initial flow rate of 5 Lmin^{-1} is set for 45 seconds and this is followed by a 1 Lmin^{-1} flow for the remainder of the drying process.

The change-over between flow rates incorporates the removal of the correction factor discussed in Section 4.2.6.5., resulting in the break in the readings in Figure 5.4.3. The changeover in this case is removed from the graph to avoid reporting an erroneous feature in the evaporation curve. Again, after a series of repeatable runs at each setting, Figure 5.4.3 provides a single set of representative results.

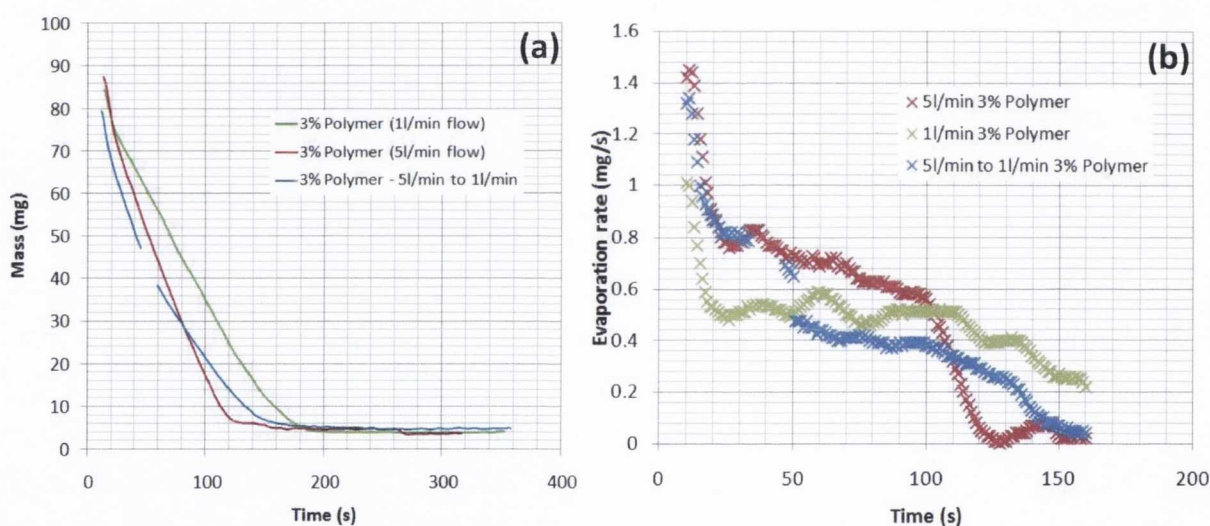


Figure 5.4.3: For a solution of 3%_{w/w} DCPS in chloroform, plot (a) compares of representative curves for the change in mass over time with 1 Lmin^{-1} , 5 Lmin^{-1} and modulated flows. The modulated flow was initially 5 Lmin^{-1} for 45 seconds and then 1 Lmin^{-1} . The beak in the line is the region where instabilities during change over prevent accurate data recording. Plot (b) shows the evaporation rate for each of the curves in (a) over time.

Figure 5.4.3(a) shows the modulated flow evaporation curve with the two reference curves of 1 Lmin^{-1} and 5 Lmin^{-1} flows. (b) details the rate of evaporation for each curve over the duration of the experiment. It can be seen in Figure 5.4.3(a) by eye, and quantitatively in (b), that the modulated flow follows exactly the initial rate of decrease in solvent as the 5 Lmin^{-1} sample. At 45 seconds, when the flows are switched, there is a recovery time where sample points cannot be considered accurate. Next the response switches to a much lower evaporation rate and then steadily decreases towards zero. When comparing four experimental runs of each

technique, the same trend is present. Although subtle, there is a difference in the rate of evaporation in the second part of the modulated flow when compared with the constant flow technique. This rate is lower for the post-rapid flow and the possible reasons are included in the discussion regarding the role of flow rate in Section 5.7.2.

All of the above evaporation experiments were carried out under very low humidity conditions. An experiment was carried out to look at the difference in the mass loss profile between dry and humid flows. A series of samples were prepared at 1 Lmin^{-1} under 75% RH flows and compared with those reported earlier under dry conditions. It appears as if the evaporation profile is identical for the initial period (70-80 seconds) but looking at the rate data in Figure 5.4.4, the evaporation rate of the humid samples starts to level off very gently, decreasing steadily until close to the end of the process where its rate of decline levels off. The dry flows, however, hold at an almost steady evaporation rate and then decrease more rapidly towards the end of the process. It must be emphasised that the differences are minor, but still observable when plotting the evaporation rate data. It can be calculated that approximately 0.1 mg water will condense onto the surface of the solution itself, based on an average droplet diameter of $6 \mu\text{m}$ and using average sample size. However, the total mass expected cannot be calculated as it requires further knowledge of the temperature gradient and surface area of the entire glass substrate as well as taking into account water droplets that sink below the solution surface. However, this experiment shows that the balance chosen is not sensitive enough to estimate the mass condensed.

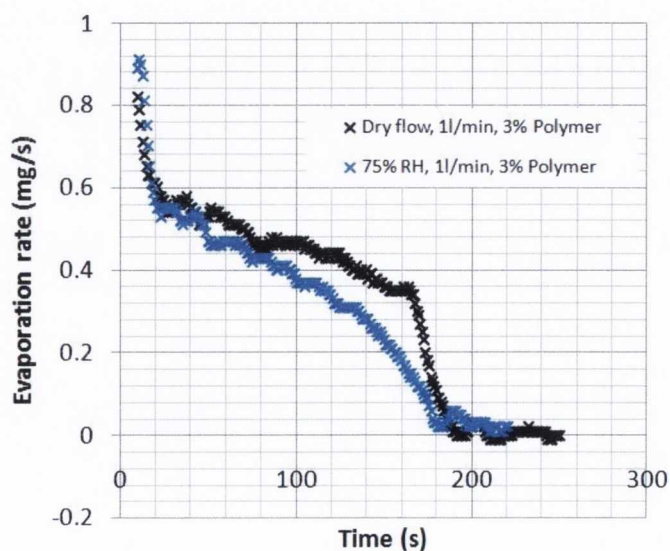


Figure 5.4.4: Comparison of evaporation rates of two samples. The first is recorded for a flow rate of 1 Lmin^{-1} of dry nitrogen. The second has a flow rate of 1 Lmin^{-1} with 75% relative humidity. The solution is 3%_{w/w} DCPS in chloroform.

Evaporation behaviour is discussed further in Section 5.7.3 but it is believed that the covering of the solvent/air interface with water droplets may block or slow the evaporation of the solvent. However, to first build a more complete picture of the changes the system is undergoing, it is necessary to evaluate the change in the solution temperature over time under a variety of conditions, as will be covered in the next section.

5.5: Recording Evaporation Through Change in Solution Temperature

As described in Section 5.2, an ultra-fine Type K thermocouple is installed within the flow chamber to measure the solution temperature during the evaporation driven self-organisation mechanism. The results are collected and filtered and the key results are described below.

Again, commencing with the pure solvent, chloroform, a series of samples were drop-cast onto standard flat glass cover slips. The positioning of the thermocouple junction is not critical in the solvent-only experiments. As noted in the mass measurements, the area of the solvent decreases with evaporation. The thermocouple junction appears to have some attraction to the liquid surface as a slight meniscus arises and this is repeatedly the last portion of the solvent to evaporate. Towards the end of each run, the circumference of the remaining solvent/solution is centred on the junction.

The first set of results looks at a sequence of flow rates to see the change in temperature due to the change in evaporation of the solvent. Representative flows are provided in Figure 5.5.1 (a) showing the temperature profile during drying with 0 Lmin⁻¹, 1 Lmin⁻¹, 3 Lmin⁻¹ and 5 Lmin⁻¹ flows. Only dry nitrogen was used and so the humidity was maintained below the critical onset humidity. The reduction in drying time noted in the mass measurements of Figure 5.4.2 is also reflected in the temperature recording. With this increased rate of evaporation at 5 Lmin⁻¹ flows, the surface temperature for evaporating chloroform reaches values of approximately 4 °C. A similar experiment carried out with chloroform/DCPS solutions shows the same trend of a larger temperature drop at increased flows, as seen in Figure 5.5.1 (b). Firstly it is important to note that in the case of polymer solutions, the location of the thermocouple junction was found to be more important. There appears to be a temperature profile across the evaporating solution. Far more care was exercised in this set-up to position the thermocouple junction in the same location each time, always using the region towards the front end of the sample but away from the edge to try and ensure repeatability.

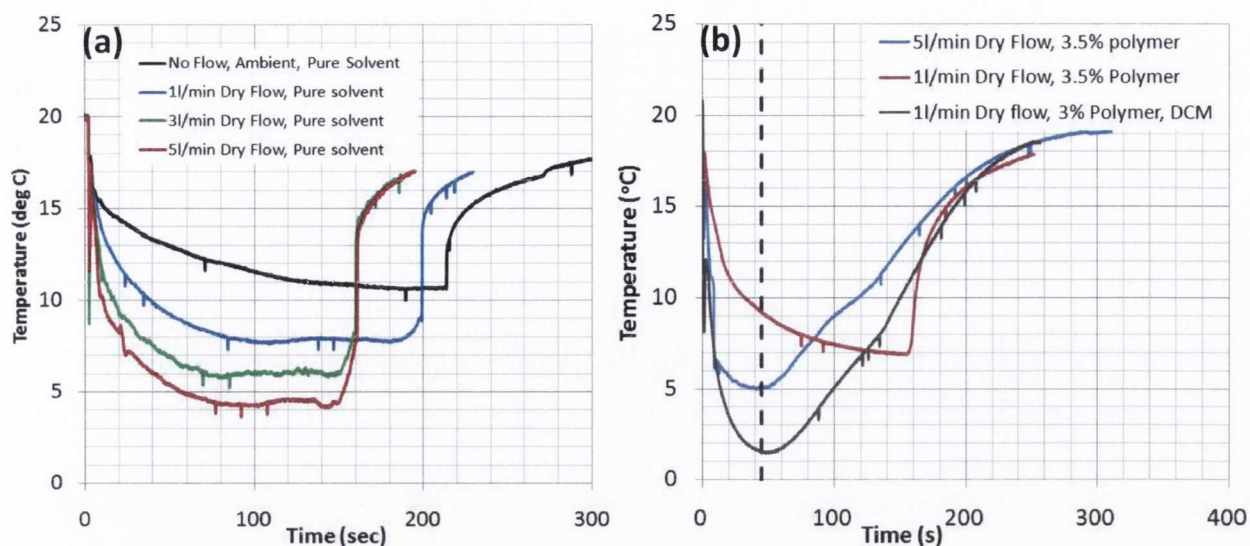


Figure 5.5.1: (a) Comparison of representative temperature curves for evaporation of a dropcast solvent under static, 1 Lmin⁻¹, 3 Lmin⁻¹ and 5 Lmin⁻¹ flows of dry nitrogen. This shows a decrease in the attainable temperature with an increase in flow. Chloroform is used as the solvent in this case. (b) Comparison of 1 Lmin⁻¹ and 5 Lmin⁻¹ flows of dry nitrogen for a chloroform/DCPS solution with a 1 Lmin⁻¹ flow experiment with a dichloromethane/DCPS solution showing a lower temperature is reached when using dichloromethane.

The chloroform/DCPS solutions reported in Figure 5.5.1(b) show that a 5 Lmin⁻¹ flow decreases the temperature significantly over the first 50 seconds when compared with the lower flow rate of 1 Lmin⁻¹. A solution of dichloromethane/DCPS at the same molar concentration as the 3% samples of chloroform was also monitored and shows that at 1 Lmin⁻¹ a significantly larger temperature drop occurs. Also, with the two samples that reached the lowest temperatures (rapid flow over chloroform and standard low flow over DCM), they did not show the same temperature profile as seen previously. The solutions evaporated at lower flow rates show a similar temperature profile as the pure chloroform samples. The sudden recovery in temperature when the last of the solvent has evaporated, as seen in the slower flow rate sample and pure solvents, no longer occurs in the rapidly evaporating samples. These are important points but will be returned to in Section 5.7.2. when coupled with further information. A line has been inserted at the 45 second marker on the x-axis of Figure 5.5.1 (b), where the first modulation of flow normally occurs. The difference in solution temperature at this point is important and will be discussed with reference to the flow modulation later in this section.

The influence of the relative humidity on the evaporation was not very significant or very clear when examining the mass loss data so a number of experiments were carried out to look at any impact on the developing temperature profile. Figure 5.5.2(a) shows a profile of recorded

chamber humidity and solution surface temperature for the evaporation of 60 μL of chloroform from the glass substrate under flow conditions of 1 Lmin^{-1} and approximately 80% RH. It can be seen that the opening of the dosing port when dosing leads to a dip in the relative humidity of 3-4%, close to the y-axis. The temperature drop upon evaporation is again observed. Once the evaporation is complete, the temperature starts to climb and recover. At approximately 200 seconds, the flow was switched to that of a rapid (5 Lmin^{-1}) dry flow and the humidity is seen to drop steeply. In every experimental run with humid air, this step leads to a sudden decrease in the surface temperature. This does not occur when only dry air is used to evaporate the solvent.

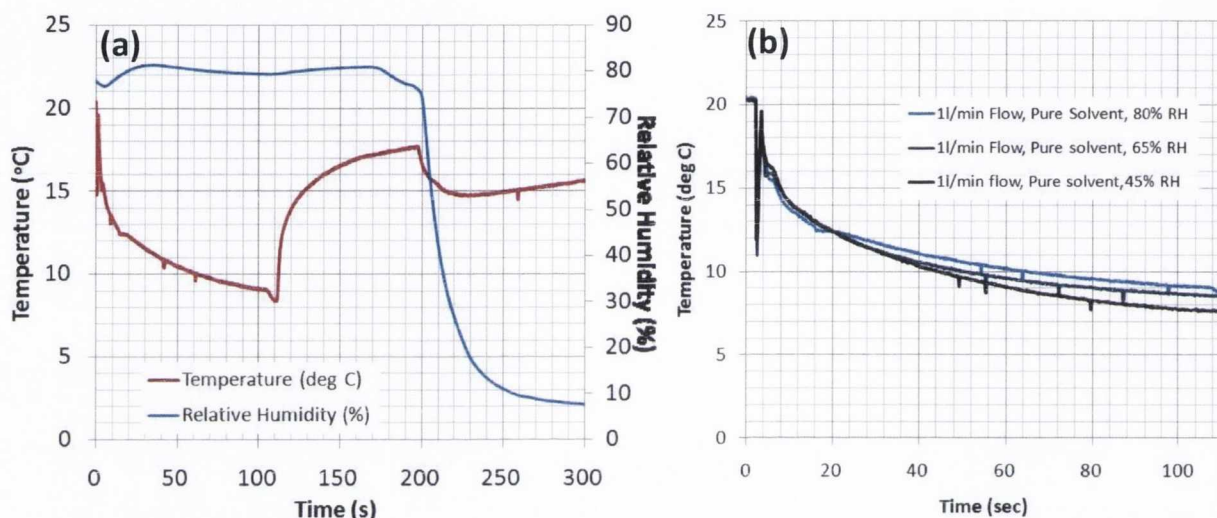


Figure 5.5.2: Plot (a) shows concurrent humidity and temperature recording for the evaporation of pure chloroform under approximately 80% RH at 1 Lmin^{-1} flow. At 200seconds, the flow is modulated to 5 Lmin^{-1} of dry nitrogen. In (b) the temperature data recorded during the evaporation of pure chloroform is presented at conditions of 45%, 65% and 80% relative humidity with a flow of 1 Lmin^{-1} .

This secondary temperature drop is indicative of the fact that water condensation occurs during the chloroform evaporation. When the last of the solvent evaporates, a sudden rapid increase in temperature is observed as the thermocouple junction, in contact with the glass substrate, begins to increase in temperature. A thin film of water remains on the surface and is suddenly under conditions where the vapour liquid equilibrium is driving it to evaporate with a very low presence of water vapour in the ambient surroundings. This evaporation also has an associated cooling effect due to the significant latent heat of vaporisation of water. Once this process is over, the temperature begins to recover without any further decreases. A number of experiments were carried out at different humidity levels. All showed a trend for a slight decrease in the temperature drop with an increase in relative humidity. As shown in Figure 5.5.2(b) when pure chloroform is used, these differences are quite small indeed. The experiment was repeated twice using (i) a solution of 3%_{w/w} DCPS in chloroform and (ii) an

equivalent molar concentration of DCPS in dichloromethane. Samples were formed for each at 6 different levels of humidity. Figure 5.5.3 shows the resulting temperature measurements. It can be seen that the relative humidity values range from close to 0% to 90%. The two dimensional projection is used to show the definite drop in temperature difference across samples with lighter shaded graphs illustrating a higher humidity. Two key observations are taken from this experiment. Firstly, with an increase in humidity there is a noticeable reduction in the scale of the temperature drop. This again is quite subtly different to the chloroform sample, but it is emphasised further with the dichloromethane sample. Secondly, a surprising trend noticed in both the pure solvent samples as well as these polymer solutions is that with the increase in relative humidity, the temperature of the solution begins to recover at an earlier time scale that cannot be accounted for by inherent fluctuations in dosing volumes.

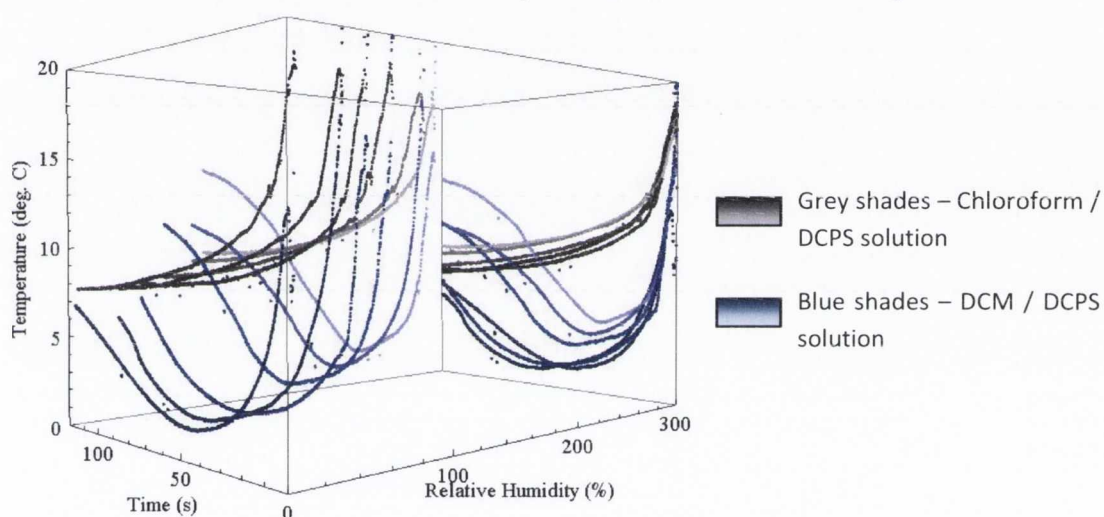


Figure 5.5.3: This plot shows the temperature response for the evaporation of a 3%w/w DCPS/chloroform solution at a range of values of relative humidity and a flow of 1 Lmin^{-1} . This is compared with an identical experiment using a solution with an equivalent molar concentration solution of DCPS in dichloromethane. A 2-D projection of the combed data is shown to the rear of the figure.

5.6: Combined Measurement of Flow, Humidity, Temperature and Mass

A further modification of the apparatus allowed the concurrent measurement *in-situ* of the mass loss due to evaporation, the change in temperature and the ambient humidity during the microstructure formation. The flow rate of humid nitrogen is controlled and recorded manually. This approach to multiple measurements allows a direct comparison between the conditions during a slow constant flow and the modulated flow technique detailed in Chapter 4. Tracking of these properties allows further analysis in the discussion section to corresponding changes in the concentration and viscosity of the solution.

Section 4.2.6.2 describes two different chambers for the combined measurements. The first is a plastic chamber formed using the 3D printer. This however is found to reduce the rate of change of humidity, most likely due to its hygroscopic nature. In an attempt to reproduce as closely as possible the conditions required to form a range of different microstructures, as detailed in Section 4.5.3, a glass chamber is used on a Perspex base, modified to allow inclusion of the mass balance, humidity probe and thermocouple and its holder. The combination of all three devices is expected to disrupt the air flow to some minor extent and induce turbulence. However, it is minimised through careful alignment of all the component parts. There is a slight decrease in the speed of humidity change, most likely due to some loss of the humid air to gaps in the chamber where the mass balance is arranged.

A series of experiments using 3.5%_{w/w} DCPS in chloroform, following the procedures in Section 4.2.6.2, is found to be a highly repeatable method for recording all three parameters simultaneously while also controlling the flow rate feeding the chamber. Representative graphs of a comparison between the two flows are shown in Figure 5.6.1.

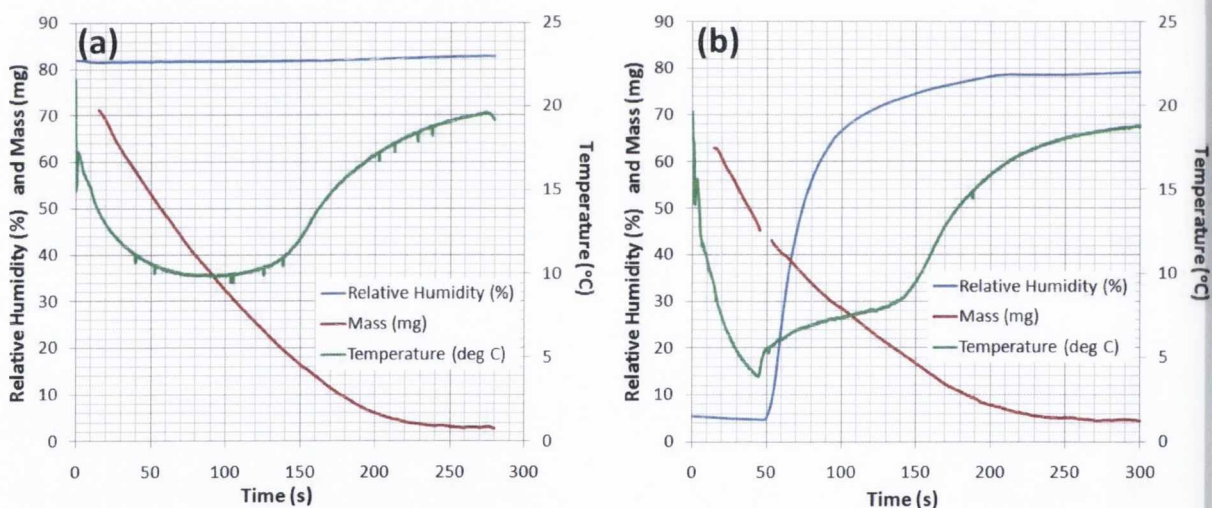


Figure 5.6.1: This figure shows sample results for the experimental approach where the relative humidity, solution mass loss due to evaporation and solution temperature change due to evaporation are all monitored simultaneously. In (a), these details are recorded for a constant 1 Lmin⁻¹ flow at approximately 80% RH for a 60 μ L dose of 3.5%_{w/w} DCPS in chloroform solution. The same approach in (b) records a 5 Lmin⁻¹ dry flow for 45 seconds followed by a 1 Lmin⁻¹ flow at approximately 80% RH.

From these graphs, the hypothesised effects of the modulated flow are clearly recorded and quantified. The initial rapid flow of dry air leads to a significant temperature drop compared with the slow flow. The loss of solvent is at a higher rate also. Figure 5.3.7(b) shows that as soon as the flow regime changes, the temperature begins to recover. However this recovery still ensures a lower temperature than Figure 5.6.1 (a) at the point when the humidity is

introduced. The effects on condensation are explored within the analysis and discussion of Section 5.7.

5.7: Analysis and Discussion

5.7.1 Influence of Polymer

The dissolution of a non-volatile solute, in this case DCPS, has a number of effects on the evaporation of the solution. A lower rate of evaporation is noted. The presence of the solute, whether through enhanced interactions with the solvent or just physically blocking diffusion and the escape of solvent molecules, acts to reduce the vapour pressure. This is true of any non-volatile contaminant in a solvent and this reduction is dependent on the concentration of the solvent and is considered a colligative property (198).

The evaporation rate of pure solvent is shown in Figure 5.4.1 (b) to be less than that of a polymer containing solution for much of the evaporation process. This is not expected, as the presence of polymer normally decreases the vapour pressure of a solvent. Another unusual feature of polymer solution evaporation is the linearity of the mass loss data, as seen in Figure 5.4.1 (a). Both behaviours are believed to be due to the change in surface coverage of the respective evaporating liquids. For a pure solvent, as the evaporation occurs the surface area of the liquid is observed to decrease. The reduced value of surface area and circumference changes the feasible rate of evaporation, which is highly dependent on these factors. The polymer solution, however, remains pinned to its original surface coverage. The evaporation rate will be affected by the change in polymer composition over time, but the key influence of the surface area will remain almost constant. It is noted in Section 5.1 that evaporating polymer solutions form a concentration gradient with a higher volume fraction of polymer existing at the free surface. The build-up is predicted to potentially reduce the rate of evaporation through its influence on the diffusion of solvent molecules to the vapour phase. The solvent and polymer chosen in our experimental work match qualitatively the properties of high volatility and high molecular weight so it is highly likely such gradients are set up.

An argument in support of a gradient in concentration is also found when looking back at two different scenarios of film formation in Chapter 4. Firstly, the observation of a surface “skin” layer forming when high concentration solutions were used shows both the ability of a highly viscous polymer solution to coexist with a solvent-rich layer and this layer’s ability to restrict

the solvent evaporation. Secondly, reviewing the observation that modifying the length of time a sample is exposed to water vapour allows the tuning of the pore microstructure, it can be seen from the timings of the mass loss measurements that the shallow pores are formed when the droplets are evaporated before the solvent has completed its evaporation. However, even under these circumstances and the subsequent recovery of the solution, the upper surface is often left with the imprints of open pores. This strongly suggests that the upper surface dries out quicker and reaches such a concentration that the viscosity prohibits a full recovery to a flat film. Interestingly, the only similar reported pore microstructures occur when standard breath figure techniques form a standard porous film and then subject it to thermal annealing (199). The material is raised above its glass transition temperature and recovers almost completely. The pore opening imprints remain and are still ordered.

5.7.2 The Influence of Flow Rate

The increase in inlet flow is shown to have a significant influence over the rate of evaporation of the solvent. This is manifested as a decrease in the drying time, an increase in the measured rate of evaporation and an increase in the temperature drop recorded. The efficiency of mass transfer processes between two fluid surfaces is improved through the decreasing thickness of the static boundary region (200), (201), through which all solvent molecules must diffuse. This thickness is directly affected by the relative velocity of the bulk flow. By increasing the flow rate, an improved escape of solvent molecules is stimulated and the evaporative cooling associated with this increases the energy loss, leading to a further drop in temperature.

An interesting feature of the rapidly evaporating samples formed under a dry flow was noted in the results. The temperature profile deviates significantly from the pure solvent and low flow rate samples, as seen in Figure 5.3.4(b). There is no sharply defined drying point and the recovery of the temperature is at a significantly reduced rate. This suggests that evaporative cooling is decreasing but does not cease entirely. Lower evaporative cooling means the solution cannot sustain such a temperature difference. It is also feasible that the expected build up of polymer near the solution/air interface obstructs the evaporation process, reducing the cooling effect.

The rapid flow is only used at the initial stage of our modulated flow experiments and allows a significant difference in temperature to occur by the 45 second time point. Such a rapid evaporation further promotes the build up of a gradient in concentration, with a high volume fraction of polymer at the surface. This is one of the possible explanations for the slight

decrease in the rate of evaporation in the second part of the modulated flow, when compared with constant flow rates. However, the measurement is not sensitive enough to distinguish if this is the case for certain. Another key observation is that the use of a modulated flow can give extremely large domains of well ordered pores. After an initial rapid flow, the viscosity will have increased and so will decrease both the velocity and even the occurrence of convection currents. As mentioned when discussing work by Limaye *et al.* (22) this is predicted to reduce the level of coalescence and so improve the size homogeneity, crucial for good ordering.

5.7.3 The Influence of Relative Humidity

Humidity is clearly necessary as it is the origin of the droplet formation that eventually templates the polymer solution but it still leads to a series of other complex interactions. For this reason it is important to think about the control of condensation and its effects on both the evaporation process and on the end microstructure

It has been shown (Section 5.5) that the humidity has a definite influence over the temperature drop achieved by the drying solution and a more subtle effect on the change in mass recorded. It is already proven, in Chapter 2, that water vapour condenses to droplets over the solution/air interface during the film formation. This must release a latent heat of condensation, most likely absorbed by the solution, the antithesis to the solvent evaporative cooling. It is noted in (201) that this is expected to lead to an increase in the temperature of the water drop if the system does not quickly dissipate the energy. It is feasible that the experiments observing the response to a change in humidity, such as presented in Figure 5.5.3, are measuring this reduction in the temperature drop due to the heat of condensation. Beysens *et al.* also note that this is expected to occur for rapid growth of droplets, which is certainly the case in these experiments at high humidity and low surface temperature. In their case, this was due to a rapid delivery of water vapour, but in the experiments presented within this thesis the source is most likely the significant decrease of the saturation temperature through using a higher partial pressure of water vapour. The higher the relative humidity, the more condensation will occur and the larger this quantity of energy will be, leading to the temperature not dropping as far and recovering earlier in the drying process.

There is only a very subtle effect observed in the change in mass with the introduction of a humid environment. This also suggests that the reduction in the temperature drop may be brought about without the need for significant changes in evaporation. However, without knowing the quantity of water condensing, it is not clear if maybe this is being measured by the balance as well. An alternative suggestion by Nepomnyashchy *et al.* (158) is that the adsorption of water molecules at a liquid/gas interface blocks the solvent from evaporating as

efficiently, similar to the presence of polymer molecules, and so a reduced level of cooling occurs.

As mentioned at the start of this section, the influence on the evaporation mechanism is important but so too is the influence of humidity on droplet and microstructure formation. The results in this chapter can be examined in conjunction with relationships defined in Section 5.1 to interpret the effect of the changing parameters on the growth of breath figures. Taking as an example one of the constant flow measurements discussed in Section 5.6, the data for relative humidity and solution temperature can be used to estimate the onset of condensation and subsequently its control.

In Figure 5.7.1(a) the temperature profile is exhibited for an evaporating chloroform/DCPS solution in high humidity (approximately 80%). Using the Antoine Equation, as detailed at the end of Section 5.2, the saturation temperature, known as the dew point, can be calculated. This is presented as the green line in the figure. If the temperature reduces to a value below this line, condensation is expected to occur as the vapour has risen above the saturation point.

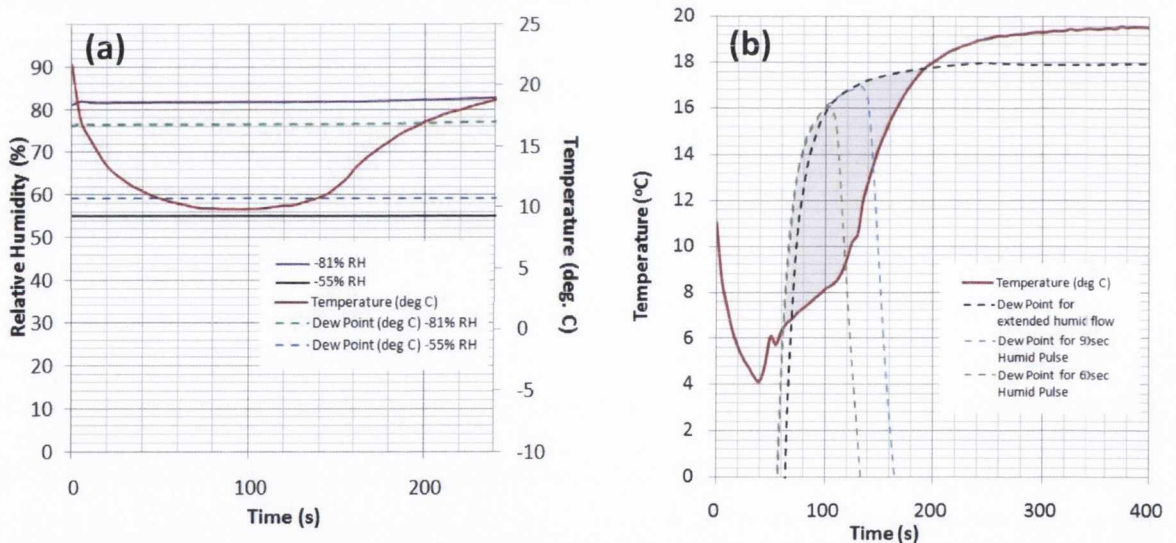


Figure 5.7.1: In (a), a constant 1 Lmin^{-1} flow at approximately 80% RH for a $60 \mu\text{L}$ dose of $3.5\%_{w/w}$ DCPS in chloroform solution. Humidity levels and their associated dew point temperatures are also indicated. Dew point temperatures were calculated using the Antoine equation constants for water, $A=8.10765$, $B=1750.286$, $C=235.0$, from Felder and Rousseau (196). In (b) a 5 Lmin^{-1} dry flow for 45 seconds is followed by 1 Lmin^{-1} flow at approximately 80% RH for the same concentration of solution as in part (a). Recorded temperatures and dew point temperatures are indicated, highlighting the region which suggests condensation can occur.

For this sample, a relative humidity of 55% leads to a lower saturation temperature of approximately 10.5°C . Now, condensation will only be expected to occur for the 80 second period at the centre of the profile, where the blue line signifying the saturation temperature is

above the minimum temperature. In Figure 5.7.1(b) the red line gain signifies the solution temperature profile. This is for a modulated flow experiment, as presented in Section 5.6. Figure 5.7.1(b) also looks at the saturation temperature but this time it changes dramatically due to the significant changes in humidity associated with the modulation of flow and humidity. Two of the three-stage modulation samples, detailed in Section 4.6.4 are used to see this influence on the saturation temperature. For a sample with a 60 second humid pulse, a 90 second humid pulse and a complete humid pulse, the saturation temperature is calculated and included in the graph. The shaded area in Figure 5.7.1(b) shows where the solution temperature decreases below that of the saturation temperature. Depending on the length of the humidity pulse, it can be seen that the area enclosed between the solution temperature and saturation temperature profiles also changes, signifying a change in the duration of the condensational growth of droplets.

Applying the Hertz-Knudsen-Schrage (HKS) equation in Figure 5.7.2, as introduced at the end of Section 5.2, the phase changes experienced by water in the system can be tracked and illustrated more clearly. Three specific samples are considered, namely (i) a 2-stage pulsed flow technique where the flow changes from a 5 Lmin^{-1} dry flow of 45 seconds duration to a 1 Lmin^{-1} 80% humidity flow, (ii) a constant flow technique using a 1 Lmin^{-1} flow at 80% humidity and finally (iii) a 3 stage technique which changes from a 5 Lmin^{-1} dry flow lasting 45 seconds to a 1 Lmin^{-1} high humidity flow for 60 seconds before switching to a dry flow at 1 Lmin^{-1} . The values for ambient and solution temperature are taken from experimental results at these conditions. The vapour pressures of the water both in liquid and vapour phases are calculated using the Antoine equation with Antoine coefficients of $A=8.10765$, $B=1750.286$, $C=235.0$, from Felder and Rousseau (196). The gas constant is $8.314 \text{ Jmol}^{-1}\text{K}^{-1}$ and the evaporation and condensation coefficients were taken from Mareka *et al.* (202). The trends are representative but the quantitative values are only estimates as there is a lack of agreement in the literature regarding condensation and evaporation coefficients, echoed in the wide range of values reported. The study is plotted against time and the result has been modified to show the total quantity condensed up to any given time point. It is hypothesised from experimental results in Chapter 4 that the initial condensation of droplets is essential to forming ordered microstructures but that subsequent reduction of humidity in the system leads to evaporation of the droplets and reforming of the solution to create flat based pores.

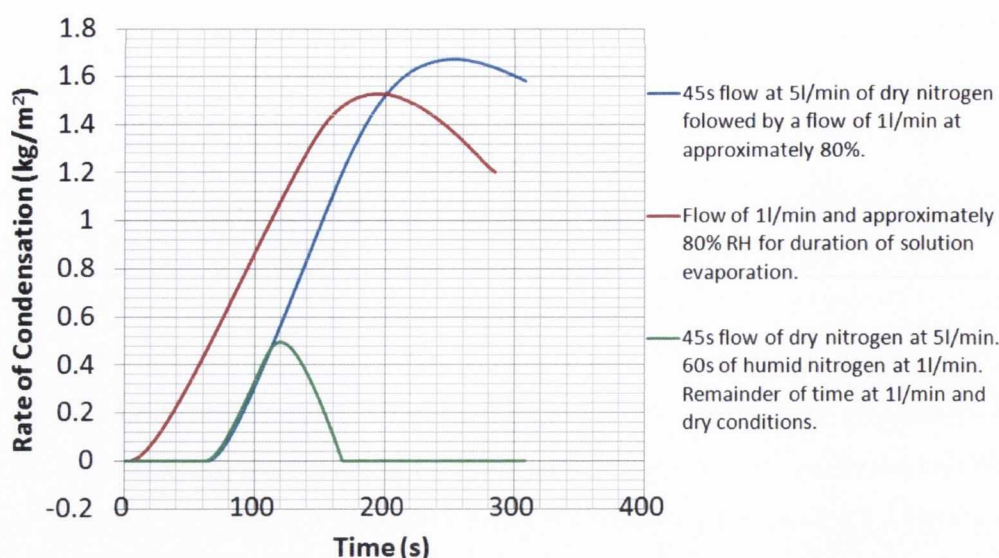


Figure 5.7.2: Using a sample of 3.5%w/w DCPS/chloroform solution, the rate of water condensation onto the solution and water evaporation from the solution is calculated and reported for a 45s flow at 5 Lmin^{-1} of dry nitrogen followed by flow at 1 Lmin^{-1} of approximately 80% RH, a constant flow of 1 Lmin^{-1} and approximately 80% RH and a 45s flow at 5 Lmin^{-1} of dry nitrogen followed by flow at 1 Lmin^{-1} of approximately 80% RH for 60 seconds, followed by a flow of dry nitrogen at 1 Lmin^{-1} . The HKS equation is used for calculation of condensation.

This is illustrated in the HKS approach where the vapour-liquid-equilibrium changes direction from condensation to evaporation of water. It is noted that the rate of increase of condensation is faster for the two and three-stage modulated flow, where the humid air is introduced while the solution is at a significantly lower temperature compared with the standard slow flow. Also, even with the delay before the onset of condensation, the total accumulated condensation value is still higher than for a constant flow method under these conditions. The temperature recovery eventually leads to the cessation of condensation and the reversal of the VLE to induce water evaporation. Normally this occurs at the end of the process when the bulk solvent has almost entirely evaporated and so the porous microstructure remains. However, in Figure 5.7.2, a three stage modulated flow, where a second flow of humid air flows for 60 seconds, shows that condensation commences, is interrupted and then the water is re-evaporated all within the timescale when the solvent is known to be still evaporating. This is one of the procedures that leads to shallow, flat based pores and coupled with the experimental evidence goes further towards understanding the mechanism.

5.7.4 The Influence of Viscosity

Figure 5.7.3 tracks the temperature, mass and humidity of formed samples, as shown earlier in Section 5.6. However, here, each graph is split and incorporates a logarithmic scale graph of

the mass concentration of polymer and the calculated viscosity. The viscosity calculation is described in Appendix 5.1. The calculation requires an estimation of the glass transition temperature as the polymer concentration increases. This is found using Equation 5.8. The estimation techniques used to calculate viscosity are not expected to be highly accurate but certainly of the correct order. The glass transition temperature approaches ambient temperature at about 80-85% weight concentration, after which further flow of the polymer will not occur. However, from about 65% mass concentration or above, the final results are highly sensitive to changes in concentration and even very minor errors in the mass recording (of around 1mg) will give significant differences. However, assuming the initial mass of the dose and the concentration are correct, the samples do not approach the glass transition until very late in the process. This lends credence to the idea of a creeping recovery of a rubbery phase solution near the end of the solvent evaporation process. The minimisation of the surface area would lead to a flattening of the, now empty and dry, pores.

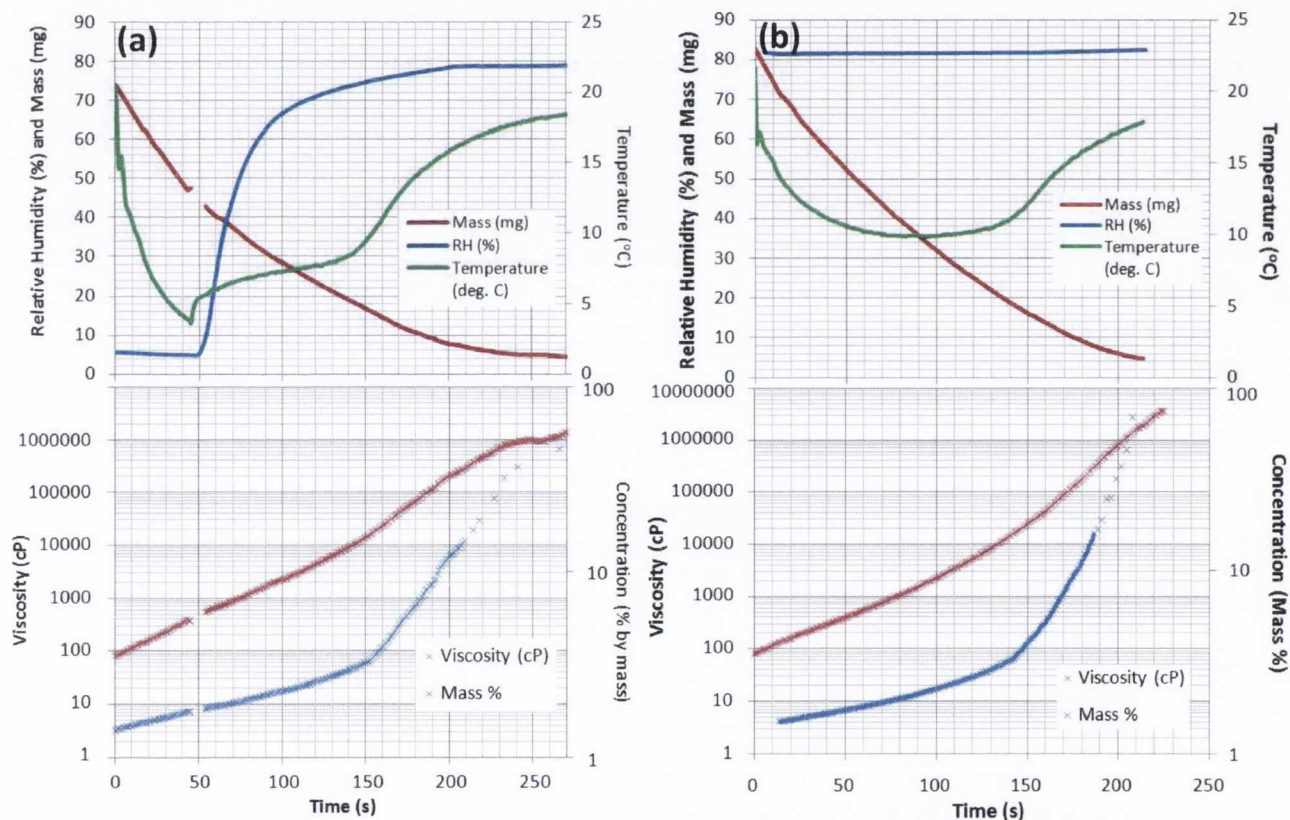


Figure 5.7.3: The split graphs show the recorded temperature, mass and humidity, along with calculated concentration and viscosity for a sample of 3.5%_{w/w} DCPS in chloroform. Sample (a) was exposed to a 5 Lmin⁻¹ flow of dry air for 45s and then 1 Lmin⁻¹ flow at approximately 80%RH. Sample (b) uses a 1 Lmin⁻¹ constant flow technique at just over 80% RH.

5.7.5 Microstructure Control

Reviewing the experimental findings of Chapter 4 and the recorded parameters and estimated physical properties based on established relationships presented within this chapter, a basic

set of heuristic controls can be described as a first step towards a predictive model for this system.

An initial rapid (5 Lmin^{-1}) flow of dry nitrogen induces rapid evaporation and significant temperature drop at the surface. This flow is believed to set up a temperature gradient and a concentration gradient within the polymer film. The initial drop-cast concentration is carefully chosen to avoid the potential stratified layer in this gradient, as reported in Chapter 4 in samples of approximately 8%_{w/w}. The first stage also increases the viscosity of the solution, as seen in Figure 5.7.3. This increase in viscosity must not be to the extent that it reduces the packing and ordering ability of droplets at the interface. It is also known that an increase in viscosity at this stage decreases the velocity and even the occurrence of convection currents and is expected to improve the system ordering and size homogeneity.

A second stage, consisting of a slow (1 Lmin^{-1}) flow of nitrogen with a significant partial pressure of water vapour entrained (approx. 80-85%), is then implemented. The continued evaporation of the solvent maintains a solution temperature below the saturation temperature of water and induces condensation as indicated in Step 2, Figure 5.7.4. Water droplets nucleate rapidly under these humid conditions and grow at the interface. The slow growth rate coupled with the rapid nucleation is referenced (17) as one of the key reasons for homogeneous droplet sizes. The droplet is positioned at the interface as determined solely by interfacial interactions, with surface and three phase interactions playing significant roles. These also dictate the contact angle at the interface and ensure, even with different volume droplets, that the pore openings are homogeneous in size, as detailed in Chapter 2. Figure 5.7.4 shows three alternative routes from this point to complete the formation mechanism. Step 3A represents the continuation of Step 2 until the droplets cease growing due to a significant viscosity and slowing evaporation automatically stopping further growth. It is important in this case to maintain the relative humidity at a sufficiently high level to avoid droplet evaporation before the polymer film has set. It is also important to maintain the flow of humid nitrogen at a low rate to avoid severe concentration gradients developing within the film. Removal of the water, once the film has set, leaves behind arrays of structured pores. The structure depends on the humidity level as described in Section 4.5.1.3 but in general provides deep, round pores.

Step 3B shows that using a 3-stage pulsed flow, the growth of the droplet can be stopped while the polymer concentration and viscosity of the solution are still low enough to allow re-

forming of the solution. This induces flat based pores of various depths, depending on the amount of time provided to the humid pulse. The concentration gradient ensures that the region close to the surface is most fully developed and semi-solid. This is why the surface still retains its ordered nature while the submerged region is free to recover.

Alternatively step 3C uses the concentration gradient in a different manner. It is believed that the gradient in this case stabilises the droplet near the interface, as in 3B. However, in this scenario the droplet growth is increased using high levels of humidity. There is a forced, continued growth of the droplet, stabilised by the development of the concentration gradient within the solution. The droplets will act to stabilise each other as they descend, drawn towards the solvent rich region. This leads to elongated and cylindrical microstructures.

The combination of the improved understanding of the interfacial balance and behaviour of the water droplet, coupled with the controlled formation conditions when forming polymer films and finally the ability to measure *in-situ* the changes that the film undergoes, allowed insights to interpret the rich variety of pore microstructure than is available with this system.

Prior to a concluding section, two of the key collaborations that have been undertaken as part of this thesis are summarised.

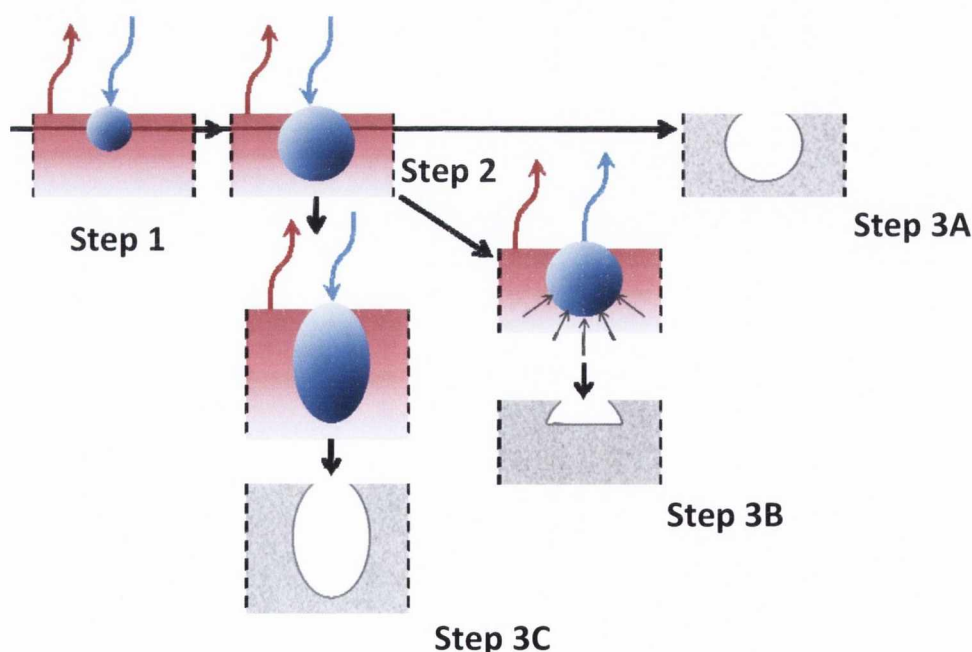


Figure 5.7.4: Illustration of different microstructures and the mechanism of formation. Step 1: Initial water droplet condensation. Step 2: Water droplet growth. Step 3A: Formation of spherical pores through droplet templating. Step 3B: Evaporation of droplet and relaxation of polymer to give flat-based pores. Step 3C: Continued water condensation, matching the progress of the stabilising polymer concentration to allow elongation of pores.

Chapter 6

Collaborations and Applications

6.1 An Examination of the Mechanical Properties of a Porous Polymer Microstructure using Nanoindentation Techniques

- *Collaboration with Dr. Graham Cross, School of Physics and CRANN, Trinity College Dublin, Ireland.*

This chapter summarises some of the collaborative work that has taken place due to the interest in the analysis and application of the porous microstructures detailed in the preceding work.

6.1.1 Introduction

Kinetic energy can be absorbed by a material in the form of elastic or plastic deformation, viscoelastic flow or fracture and fragmentation. In mechanical testing, an axial load is applied to the material of interest to understand a range of its mechanical properties and the method by which it absorbs the energy. There are two reasons why, as a part of this thesis, it was decided to apply mechanical testing techniques to examine the porous polymer films. Firstly, knowledge of the mechanical properties of a material, its ability to dissipate stress and deal with mechanical loads is essential when developing it with an application in mind, such as in microelectromechanical system (MEMS) design (203) or in the processing of high k-dielectric materials (204). There are always processing and usage stresses that it must be able to withstand. Secondly, analysing the stress dissipation and absorption within a porous structure is a topical subject with interesting predicted behaviours. This particular material is quite a novel subject for mechanical testing as it is a microporous material that contains nanoscale components, in the form of ultra-thin walls.

It is noted in the literature that structures with organised, rather than randomly dispersed, pores are believed to combine the design advantages associated with a low density of material with the mechanical advantages of a truss system. Foam structures are tuned for specific strength and compressibility (205) by linking both to the volume of the pores and the

interstitial truss dimensions. Their joint mechanical response dictates the material's compressive behaviour. Also, there is an especially keen interest in energy absorption in polymer micro and nano-structures (206) as it has been noted that, below certain thicknesses, even a brittle polymer such as polystyrene can behave with ductile, plastic deformation, in effect changing its mode of mechanical failure. For example, this was seen to occur in polystyrene ligaments of approximately 50 nm thickness (207).

A simplified plan view of a single layer, ordered porous film is shown in Figure 6.1.1 (a). The grey regions indicate the top surface pore openings, the adjacent white areas represent the maximum diameter of the pores, submerged in the film. A very thin wall exists where the pores meet (<50 nm), but in the blue interstitial regions, there are thicker trusses of polymer. These are more visible in Figure 6.1.1 (b), which shows the meeting of three spherical surfaces and an example of a single interstitial truss. These are the key supporting elements of the porous film, mentioned in Section 6.1

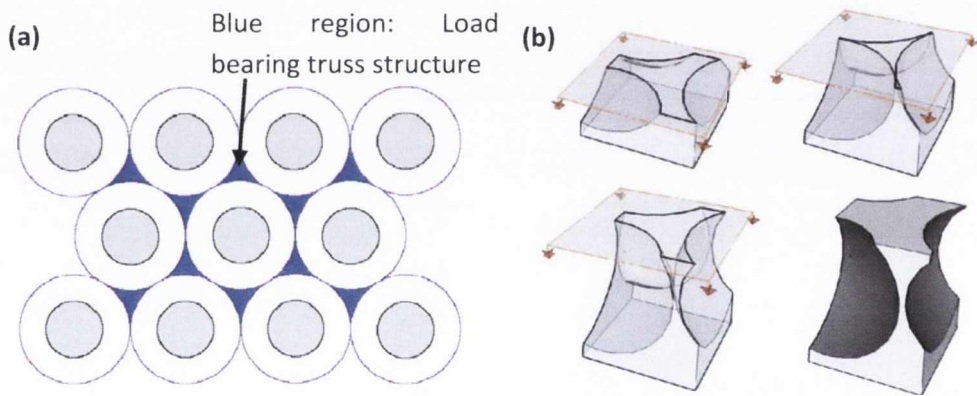


Figure 6.1.1: (a) Diagram of a porous polymer film indicating in grey the pore opening, in white the subsurface maximum diameter of the submerged spherical pores and in blue, the interstitial pillars. (b) A schematic of the interstitial truss is shown with a progression of sections illustrating the change in the shape and diameter with height.

This work aims to test the material mechanically at a range of length-scales in an attempt to understand the failure mechanism of the trusses and their overall impact on the continuous material properties.

6.1.2 Experimental Procedure

Of the available techniques for the testing of films of small volume and in this case of the order of approximately 5-80 μm thick, nanoindentation is the most widely reported in the literature for measuring the elastic modulus (Equation 6.2), hardness (Equation 6.1), stiffness and yield stress (all of which will be defined shortly). The technique traditionally, and as used here,

applies a stress by way of a vertical loading force acting on a very well-defined contact geometry. The loading force is carefully regulated and controlled, while the depth of indent is measured using a highly sensitive capacitive displacement meter with sub-nanometer resolution as detailed in the materials and methods section, 1.3.1.7.

Young's modulus is a commonly used parameter for characterizing the stiffness of a material. In linear elasticity (Hooke's Law), it is the proportionality constant in the relationship between stress (the applied load per unit area) and strain (the deformation induced by the indentation per unit of length). This is a constant value in the elastic portion of the load versus displacement curve. In this chapter, it is found for pyramidal Berkovich indentation by firstly obtaining the reduced modulus, which combines the modulus for the tip as well as the specimen, Equation 6.2. This value can then be divided between the indenter and the sample using Equation 6.3.

The stiffness of a material is generally found from the slope of the unloading curve, which details the ability of a material to recover from an imposed stress. However, using the CSM module of the indenter model described, there is a small oscillation (45 Hz) superimposed on the loading signal (208) and the response is monitored to give a continuous reading of the elastic stiffness, as the indenter progresses into the sample. This allows dynamic calculation of a range of other mechanical properties including the elastic modulus and material hardness at any time point or position in the experiment.

$$H = \frac{P}{A} \quad (6.1.1)$$

$$E_R = \frac{(\sqrt{\pi} \cdot S)}{2\beta \cdot \sqrt{A}} \quad (6.1.2)$$

$$E = \frac{(1 - \nu^2)}{\frac{1}{E_r} - \left(\frac{(1 - \nu_i)}{E_i} \right)} \quad (6.1.3)$$

where H is hardness, P is the pressure, A the area, E_R is the reduced modulus, S is stiffness, β is a geometric correction for tip geometry, A is the contact area with the tip, E is the material's modulus of elasticity, ν is the Poisson ratio, and E_i is the elastic modulus of the tip.

The nanoindenter, sample preparation and loading are described in Section 1.3.1.7. It was found that due to the low stiffness values of the polymer and in particular the porous film, a

crosslinking adhesive could be used to mount the microscope cover slip, with the attached polymer substrate, to the sample stub using the technique detailed in Section 1.3.1.7.

Once the correct indenter is installed and the samples loaded into the nanoindenter, the sample must be positioned at the correct height and moved into position directly below the tip. An initial alignment is required between the tip and the optical microscope to allow an accurate choice of the region to test. Next, if starting a new experimental run, an amorphous silica sample should be tested as a standard and compared with known results. Once aligned over an area of interest, an initial test is completed to ensure the indenter can reach the sample within its optimum extension range.

Three sets of experiments are reported within this section:

- (i) Large flat punch indentation (cylindrical diamond with 20 μm diameter)
- (ii) Small flat punch indentation (cylindrical diamond with 6 μm diameter)
- (iii) Berkovich tip indentation (low angle sharp pyramidal diamond indenter)

As an example of an indent recording, flat punch indents go through six stages during a typical testing program. These are indicated in Figure 6.1.2. Testing commences with an initial routine to locate the surface of interest and ensure the tip is at the correct height. Next, as shown in Figure 6.2(A) to (C) there is a loading portion of the test using a constant load rate, followed by (D), a short hold time chosen by the user where the sample relaxes (creep). At (E) there is an unloading of the sample (usually at the same rate as loading.) (F) indicates an additional holding period once the system reaches 90% unload to allow for correction due to thermal drift and at (G) the unloading is complete. The particular point (B) on the curve indicates the load that leads to the transition from elastic to plastic deformation response, also referred to as the Yield Point.

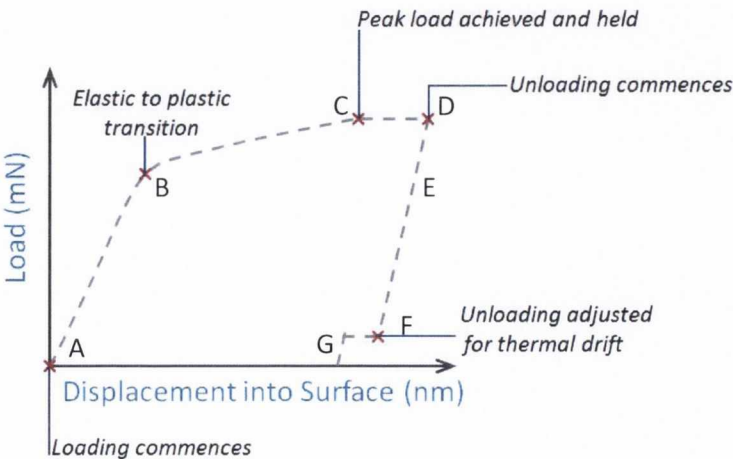


Figure 6.1.2: A typical load-displacement curve is illustrated for a flat punch on a polymer film showing an initial elastic response (A)-(B), an elastic/plastic response (B), a load-holding section (C)-(D) and then the unload region (E)-(G).

6.1.3 Flat Punch Indentation – Wide Punch

To understand the collective structural properties of the porous layer, it is preferable to average over a number of pores simultaneously. To this end a wide, flat, cylindrical indenter tip with a 20 μm diameter and a surface area of 320 μm^2 was formed in diamond using the focussed ion beam tool detailed in Section 1.3.1.3. The surface of the tip was polished using low beam currents to ensure as smooth a surface as possible. This tip has a clearance height of approximately 4 μm to ensure a significant penetration depth and is shown in Figure 6.1.3.

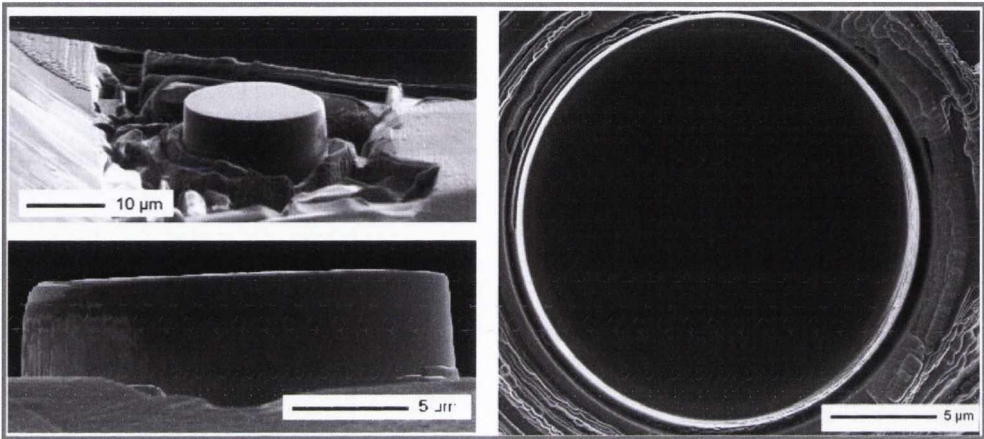


Figure 6.1.3: The images, taken using SEM, are of a flat, cylindrical diamond punch formed for this work using focused ion beam milling.

The flat punch has two advantages. Firstly, due to its geometry, it allows access to the stress/strain data. Secondly, in this case, it allows probing of the average material properties, as it contacts a number of pores and trusses at once.

A series of indentation depths was examined for a film of DCPS on glass, prepared under dry conditions to ensure the absence of pores. At indentation depths of 200 nm and 500 nm, the load displacement curves show elastic responses, as depicted for the 200 nm indent in Figure 6.1.4(a).

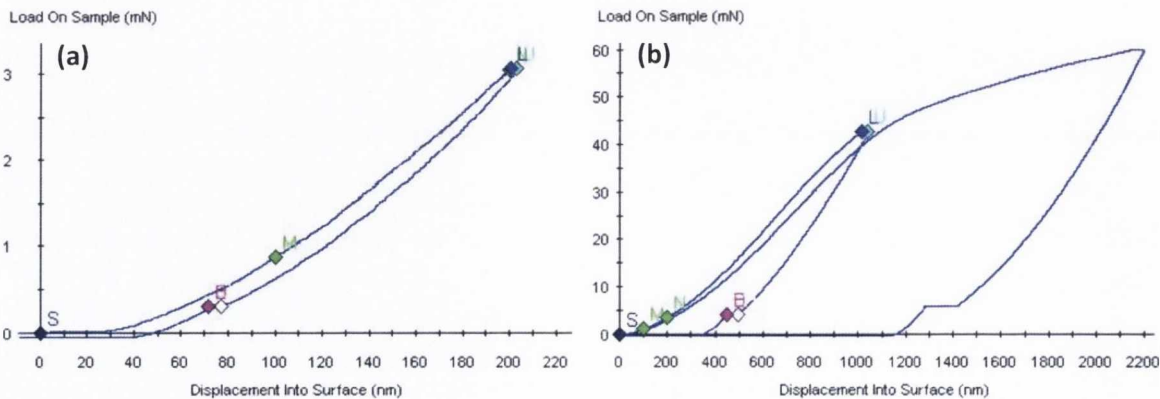


Figure 6.1.4: These plots are from experimental data and show (a) the elastic response of a 200nm deep indent into non-porous DCPS polymer film formed through standard drop-casting in a dry environment, and (b) 1 μm and 2 μm deep indents to show the transition at the yield stress from elastic to plastic deformation.

It appears as if there may be a subtle change in slope upon implementing a depth limit of $1\ \mu\text{m}$. Although it is almost as elastic as previous indents there appears to be a slight change in behaviour towards the maximum load. This is supported by the $2\ \mu\text{m}$ indentation depth result in Figure 6.1.4(b). Here, it is clear that a yield stress occurs when the indentation procedure is close to the $1\ \mu\text{m}$ depth. Taking the value for the load on the sample at the transition from the elastic to plastic regime, a yield stress value can be calculated, by dividing this load by the area indented. This leads to a yield stress of approximately $140\ \text{MPa}$. The same large flat punch was then used to test the mechanical properties of a porous film. Figure 6.1.5 (a) illustrates the geometry of the system being tested when indenting to different depths. A series of indentation depths were examined, namely $0.2\ \mu\text{m}$, $0.5\ \mu\text{m}$, $1\ \mu\text{m}$, $2\ \mu\text{m}$ and $4\ \mu\text{m}$. Figure 6.1.5 (b)-(d) show these indents as compared with the previous non-porous sample, with each figure progressively expanding the data to allow each set to be seen.

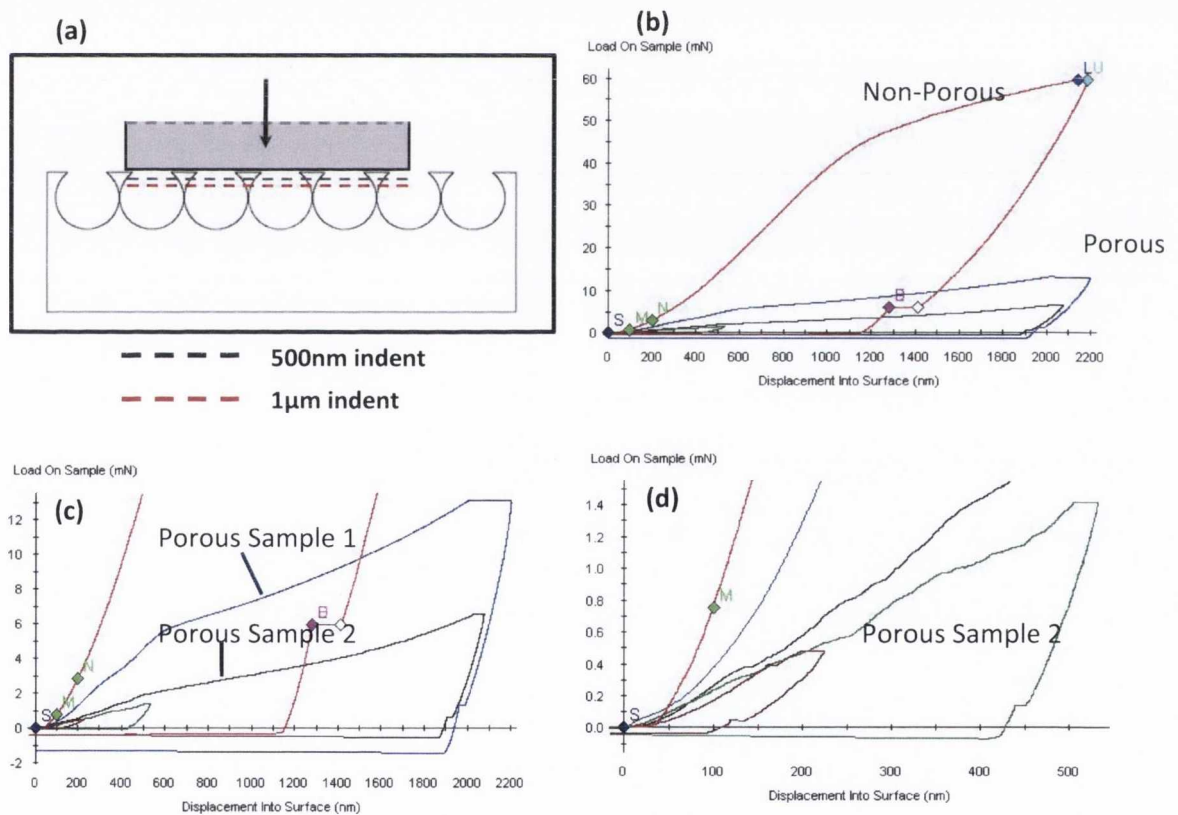


Figure 6.1.5: An illustration of the system is given in (a), showing a large flat punch in contact with porous film. This is drawn to scale and gives an indication of the features and geometries being probed by indents of different depths. In (b) there is a comparison of load/displacement response for one non-porous and two porous samples all at the same depth of indent. Small indents are on this graph but not visible due to their size. Therefore in (c) there is a closer view of the porous film response at $2\ \mu\text{m}$ and $500\ \text{nm}$ indent depths and in (d) there is a closer view of $500\ \text{nm}$ and $200\ \text{nm}$ indent depths.

Even the 0.2 μm and 0.5 μm indents show far less elastic response when compared with their non-porous counterparts. A significant plastic response is seen in samples of larger displacements, as shown in Figure 6.1.5(c) for the 2 μm indent depth. The Yield Stress is also drastically reduced, with an approximate value of 20 MPa. Figure 6.1.5(b) shows a comparison between the load-displacement responses for the non-porous and porous films with this tip. The comparison allows interpretation that the non-porous layer is significantly stiffer than the porous layer. This leads to the first conclusion, that the system can be examined as a layer of pores on a stiff substrate, which infers that stress-strain curves can be calculated based on the truss system alone.

6.1.4 Flat punch indentation – small punch

In an attempt to access more local information regarding the mechanical failure of a truss, a flat, cylindrical diamond indenter of 6 μm diameter (approximately $28 \mu\text{m}^2$) was employed. A polymer film was formed for testing. It is believed from the optical response that the film consists of shallow pores. This specimen featured areas with shallow pores, no pores and a transition region. Tests of 16 indents of both the non-porous and porous regions provided the data shown in Figure 6.1.6(b). An image of each array, taken with an optical microscope is shown in Figure 6.1.6(e) and (f). The results show a clear decrease in the yield strength of the film. The yield stress for the non-porous section is approximately 180 MPa, while for the shallow-pore region is approximately 40% of this value, at 70 MPa. A range of indents was then completed across a region of transition between porous and non-porous as shown in Figure 6.1.7(a), and the load/displacement response was examined.

A closer look at the indents using optical microscopy allowed each to be classified as occurring at a porous or non-porous region.

While the non-porous samples fell on the same load/displacement curve shown in Figure 6.1.6(b), most of the indents on the porous region did not lie on the same load/displacement curve for the porous indents in Figure 6.1.6(b) but instead lie on a separate curve in between the two earlier curves as shown in 6.1.7(c). From the subsequent understanding of shallow pore formation, this is believed to be due to the even more shallow nature of pores at the transition region as opposed to the main porous region. It is important first to note at this point that for flat-punch testing, the alignment of the tip surface with that of the specimen is challenging in the case of these films. Normally, parallel surfaces are achieved through a series of trial indents that are measured by AFM and any tilt measured from the remaining impression can be corrected using a 2-axis tilt stage (209).

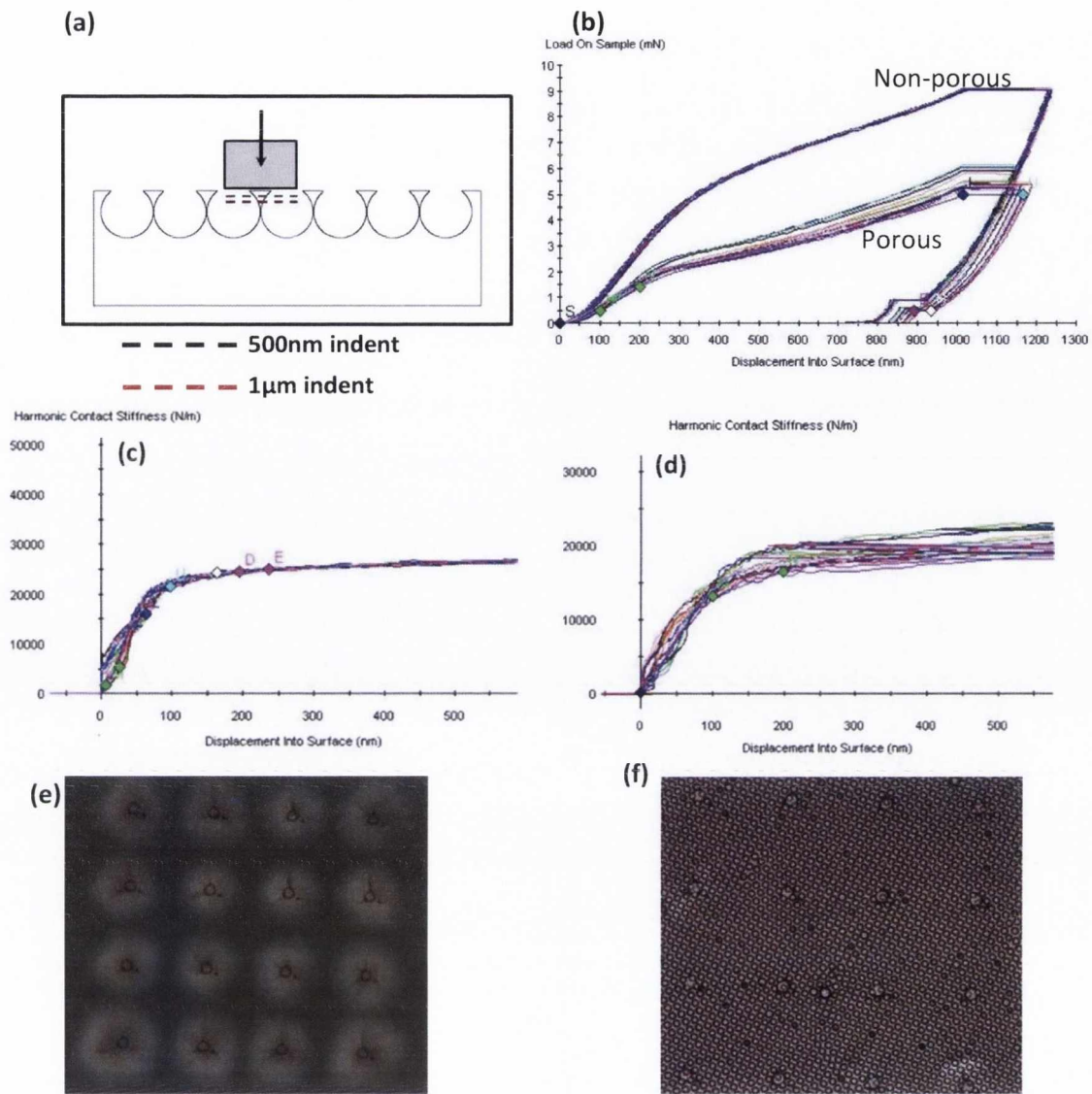


Figure 6.1.6: An illustration of the system is given in (a), showing a 6μm flat punch in contact with the porous film. This is drawn to scale and gives an indication of the features and geometries being probed by indents of different depths. In (b) there is a comparison of load/displacement response for non-porous and porous samples all at the same depth of indent. In (c) and (d) the harmonic contact stiffness is shown for non-porous and porous samples respectively to show the depth when full contact is achieved. Optical microscopy is used in (e) and (f) to show the indents resulting in non-porous and porous films respectively.

However, the samples examined here are not flat across the entire surface and so a simple uniform tilt correction is insufficient. It was decided to proceed without tilt correction and the level of error inherent in each measurement was recorded by looking at a recording of the harmonic contact stiffness with depth of indent. Figure 6.1.6 (c) and (d) show the harmonic contact stiffness versus displacement for indents on non-porous and porous films respectively. The initial steep slope is representative of a growing partial contact of the flat punch surface due to misalignment. The point where the slope levels off was shown by Cross *et al.* (209) to indicate when the flat punch has come into full contact. For example, this is approximately

70 nm and 100 nm for Figure 6.1.6 (c) and (d) respectively. It was found that the alignment was sufficiently accurate that it did not interfere with the interpretation of the elastic/plastic transition. A series of indentation tests at different depths were then carried out on a sample of standard spherical pores, again using the same polymer, substrate and indentation method combination. Figure 6.1.8(a) shows the significant difference between the load/displacement curves of these pores and those of the shallow pores. The yield strength is approximately 10 MPa for the spherical porous system, about 7 times less than shallow pores and 20 times less than the non-porous continuum. Figure 6.8 (c) looks more closely at this new data and shows that the indents consist of mainly plastic response data.

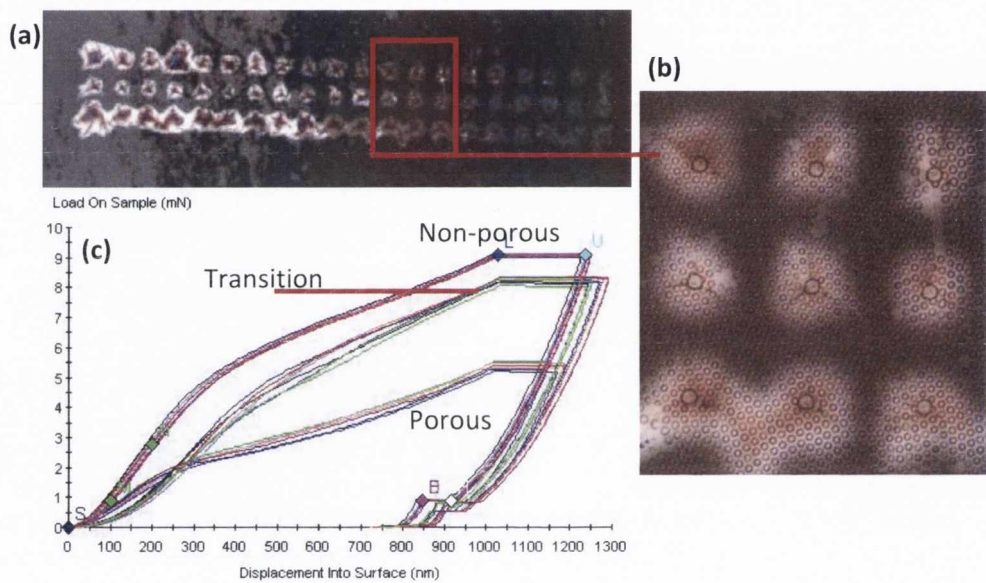


Figure 6.1.7: Image (a) is an optical microscopy image showing an array of 60 indents across a transition between porous and non-porous regions of a polymer sample. The indicated area is shown in more detail in (b). Load-displacement responses for non-porous, very shallow pore and shallow pore regions are indicated in a plot of the data in (c).

A significantly lower volume of polymer material is tested however, as it is not expected to indent through to the more compact layer of polymer beneath the pores. This is shown in Figure 6.8 (d), where a cross-section of a 3 μm indent into the same sample is revealed. This shows the indenter did not penetrate to the other end of the pores and also shows the pore wall collapse where the indent occurred. Figure 6.8 (e) again shows that the tip is in full contact at 100 nm depth, well before the elastic to plastic transition of Figure 6.1.6 (b) at around 200 nm depth. Indents at 150 nm and 500 nm confirmed this as a plastic response was noted for the larger indent but significantly more elastic recovery was seen in the smaller indent.

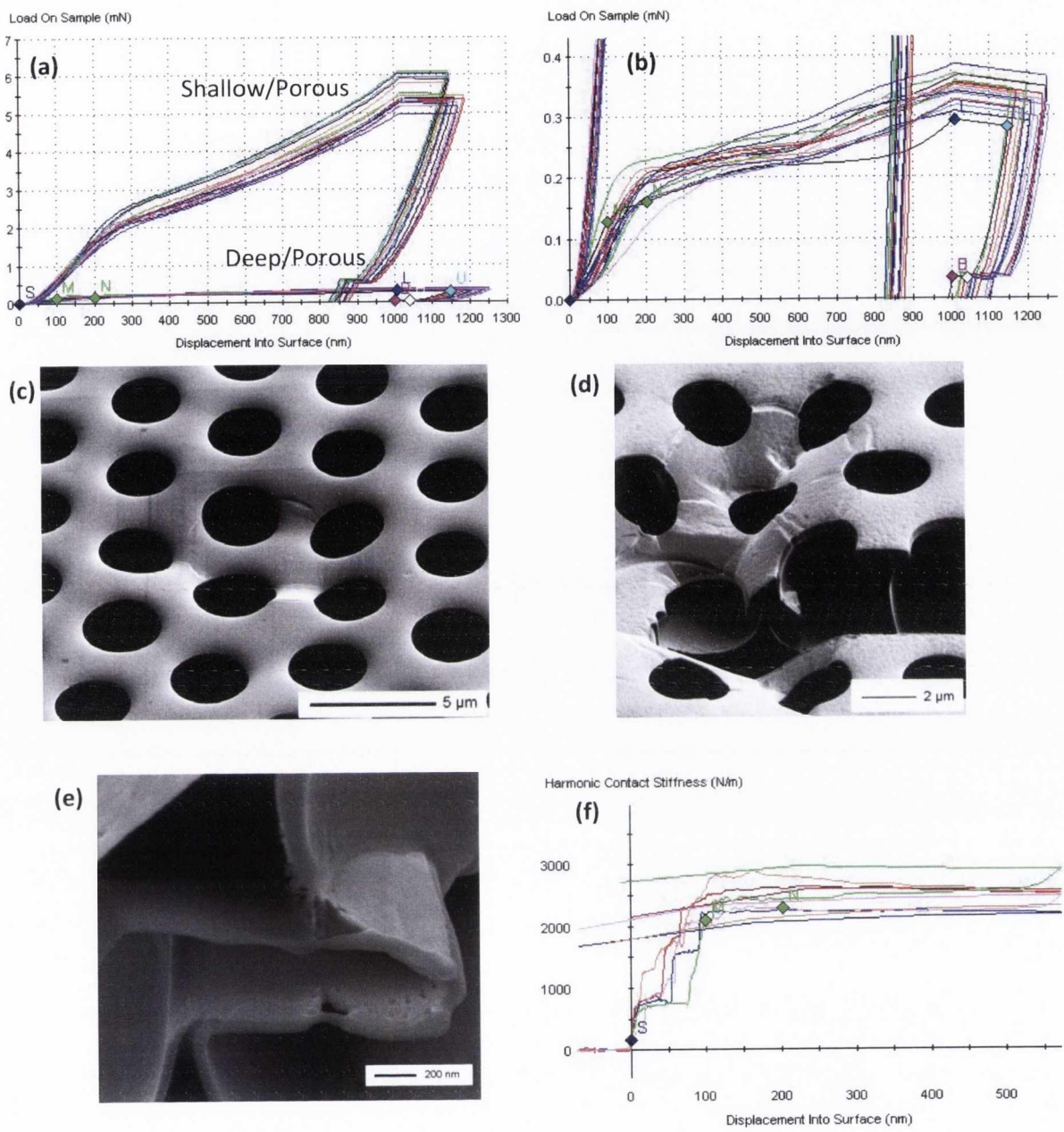


Figure 6.1.8: Using a 6 μ m flat punch, indentation into shallow pores and spherical pores are compared in (a). a closer view of the spherical pore mechanical response is given in (b). SEM is used in (c) to show the plastic deformation from a 500nm deep indent. (d) and (e) show a cross-section using focused ion beam milling and SEM imaging. The plastic deformation takes the form of a wall collapse inside a 3 μ m deep indent region. In (f), the harmonic contact stiffness for the 1 μ m indent on the porous surface is shown, indicating full contact of the punch at approximately 100nm depth.

In summary, the 6 μ m flat punch probes a much smaller region, but still is seen to average the load over too wide a region to probe individual trusses. However it did reveal that the wall-buckling is likely a key mechanical failure mechanism in these samples (Figure 6.1.8(d,e)).

6.1.5 – Berkovich indentation

Work was carried out using a standard load-control indentation method and diamond Berkovich indenter, which is a very low angle three-sided sharp indenter. Figure 6.1.9(a) illustrates the contact involved in this experiment. This diagram is correct to scale, showing the relative angles ($2 \times 71^\circ$) and relative indent depth-to-pore sizes. The point-load-nature of this indenter was hoped to be useful for examining more closely the response of individual trusses.

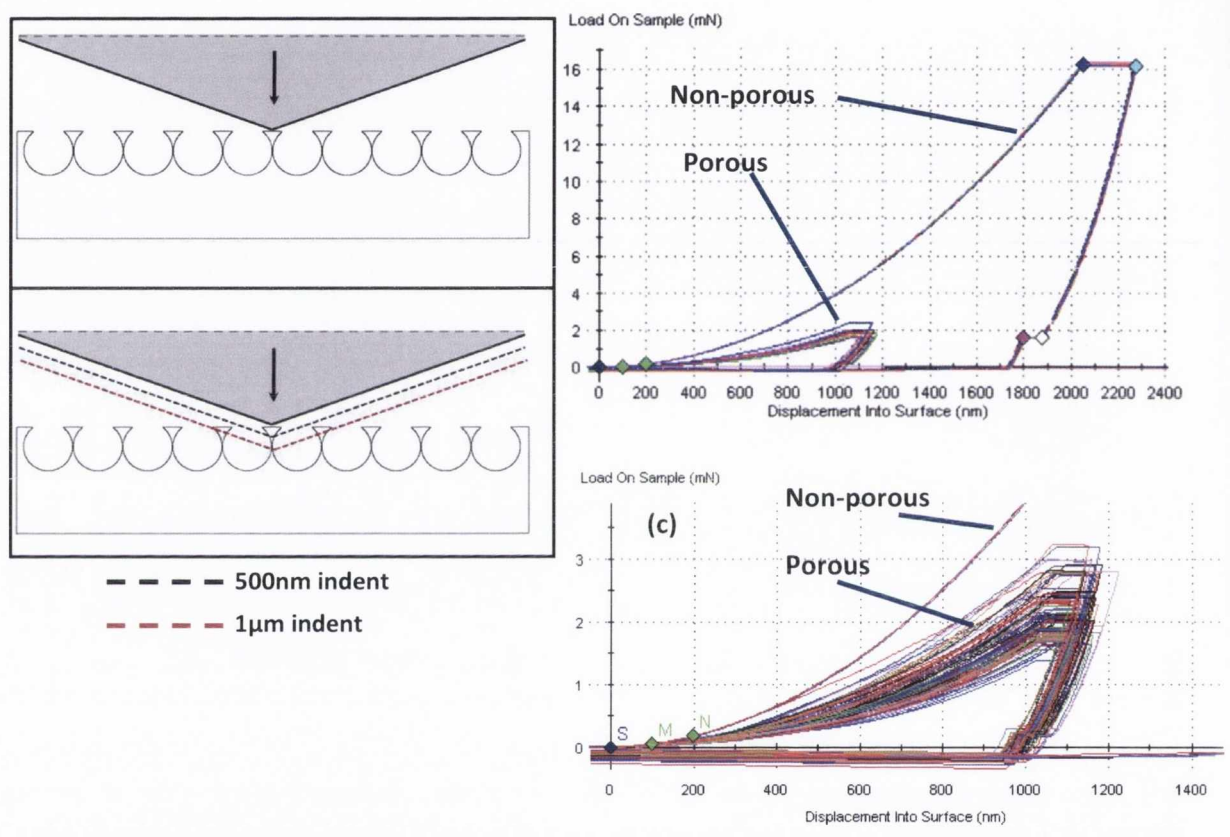


Figure 6.1.9: An illustration of the system is given in (a), showing a Berkovich indenter in contact with the porous film. This is drawn to scale and gives an indication of the features and geometries being probed by indents of different depths. In (b) the data is presented of a load/displacement response for non-porous samples with $2\ \mu\text{m}$ indents. In (c) the data is presented showing load-displacement curves for a 10×10 array of indents on a porous polymer film using $1\ \mu\text{m}$ deep indents.

It can be clearly seen from Figure 6.1.9(a), which includes a series of indents, that the load/displacement response is highly repeatable with almost no scatter to the data ($n=16$), when examining the non-porous, clean, flat continuous polymer film. For the non-porous case, the Berkovich indentation method did show that, with this method of drop-casting and sample preparation, an expected elastic modulus of 4 GPa was achieved, and an average value of hardness 0.23 GPa was also recorded. These values agree with current literature for bulk polystyrene (210). However, the porous sample shows a significant degree of scatter when

recording the mechanical response for a 1 μm deep indent (sample size of 100 indents), as seen in Figure 6.3(b). While there is some evidence that this scatter is related to the position of the indents, the low angle of the indenter prohibits detailed analysis of the trusses alone.

6.1.5 Key Results:

- A tip and procedure are now in place to evaluate the average film properties by indenting over a number of pores.
- The flat punch geometry is advantageous as it allows access to examining the elastic/plastic transition.
- While not conclusive, it appears that the failure of the film occurs due to a buckling of the trusses.
- The stiffness of the non-porous layer shows that this system can be examined as a layer of pores on a stiff substrate.
- There are early indications that the structure of the pores formed will have a signature response to indentation and hence different mechanical properties.

6.1.6 Next steps:

- Another flat, cylindrical tip is going to be formed but with a smaller diameter to allow access to mechanical data for individual trusses.
- Indents are to be cross-sectioned with focused ion beam to (i) examine the failure mechanisms for large and small area punches and (ii) allow calculation of the stress/strain curves.
- Individual trusses are going to be prepared by removing surrounding features by focussed ion beam milling. This will allow an individual truss response measurement to correlate with those situated in a matrix.

6.2: Investigation of Cell Biomimetic and Mechano-Response to Biofunctionalised Regular Architecture Microporous Topographies

- Collaboration with Dr. Adriele Prina-Mello^{1,2} and Ciara Furlong²

1. School of Physics & CRANN, Trinity College Dublin, Ireland

2. Centre for Bioengineering, Department of Mechanical Engineering, Trinity College Dublin, Ireland

6.2.1 Introduction

It can be seen in the literature that there are currently two different approaches to developing polymer substrates made from breath figure templating for studies in Nanobiology. With the possibility to controllably form topographical ordering of arrays of individual cells, there is interest in analysing cellular signalling and associated biochemical pathways to the cell morphological responses in order to deliver new biocompatible nanodevices or nanotemplates for medical applications. This has largely contributed to the expansion in the area of biological sensors with the control mechanism based on any or a combination of the environmental, chemical or physical effects or even the substrate's mechanical properties.

The isolation of cells for such studies can be achieved in a variety of ways (211), one of which is by patterning a self-assembled mono-layer (SAM) on gold to isolate the cells to these shapes. Another method for achieving isolated cells under development by (212) is by using the self-organised films of the same type as those formed during this thesis. They have shown that through careful polymer choice, the pores can be created as arrays of hydrophilic centres where proteins can be attached which will aid the adhesion of cells within each of the pores, leading to cell-based assays useful to drug discovery analysis (211), (212).

A second area of focus, where collaboration is ongoing as a result of the work towards this thesis, uses the micro-structured porous materials in the study of cell-cell and cell-substrate interactions. This is the first key step in an exploratory study into their potential as scaffolds for tissue engineering. It is reported that in regenerative medicine, there is a move away from synthetic implants and tissue grafts towards an approach where tissue engineering on synthetic scaffolds is achievable through building an understanding of the mass transport and biological delivery inherent in a scaffold during the regeneration process (213).

It is known that, *in vivo*, normal functioning of cells only occurs when they remain attached to a substrate and neighbouring cells. The substrate is a connecting tissue made up of a highly

complex composite of biopolymers and is known as the extracellular matrix (ECM). The ECM surrounds and supports cells and is made up of a range of structural proteins that give it its tensile strength (for example collagen and elastin) and a largely amorphous interfibrillary matrix (mainly proteoglycans, glycosaminoglycans solutes, and water) (214) that has a wide range of roles. It can transfer mechanical forces to the cells as well as stimulate it with biochemical signalling, the combination of which control the resulting cell behaviour (215).

So in a move towards developing synthetic means of tissue growth, synthetic scaffolds are currently the focus of much research. The key demands of such a substrate are that it must be biocompatible, biodegradable, adhesive for cells and promote cell growth. A key additional demand is that the cell retains its differentiated function as the ultimate aim would be to provide a material that can be utilised for tissue or organ formation. There is also a specific interest building in three dimensional synthetic scaffolds. It is noted in a recent paper that tissue engineering and cell culturing for biosciences is still dominated by the use of Petri dishes and microscope slides. However this is known to be an unrepresentative environment and in some cases highly unsuitable for analysis (215) - (217). The porous microstructure discussed in this thesis has been formed using similar techniques and examined by a number of groups in terms of its biological applications (51), (218) - (224). However, it is thought that a collaboration would be fruitful due to the improved control and understanding of the microstructure and the local expertise in the field of nanobiology.

To examine the feasibility of using the polymeric porous microstructured films as potential tissue engineering scaffolds, it was first necessary to examine the biocompatibility and cell viability and it is these key results that will be briefly summarised.

6.2.2 Experimental Procedure

Using the methods described in Chapter 4, films of a spherical, porous, ordered microstructure were formed on microscope coverslips. A cytocompatibility study required the samples to be seeded with osteoblast cells (MC3T3-E1) in a sterile 96 well plate (Figure 6.2.1(a) where several substrates, and their control references (positive and negatives) were subjected to the same environmental condition to assess the biocompatibility response of the substrates versus standardized conditions (e.g., normal *in vitro* cell culture on flat PS petri dishes). To achieve this, the samples were removed from the glass substrate, cut into 6mm diameter circles using the punch in Figure 6.2.1(b), placed in between glass slides shown in Figure 6.2.1(c) for 1 hour at 60°C for stress relaxation to ensure removal of the inherent film curvature. F-actin and the nuclei were stained using Phalloidin Bodipy and Hoechst 33258 (Invitrogen, USA) respectively

to allow fluorescent and confocal microscopy to be carried out for the identification of the morphological responses.

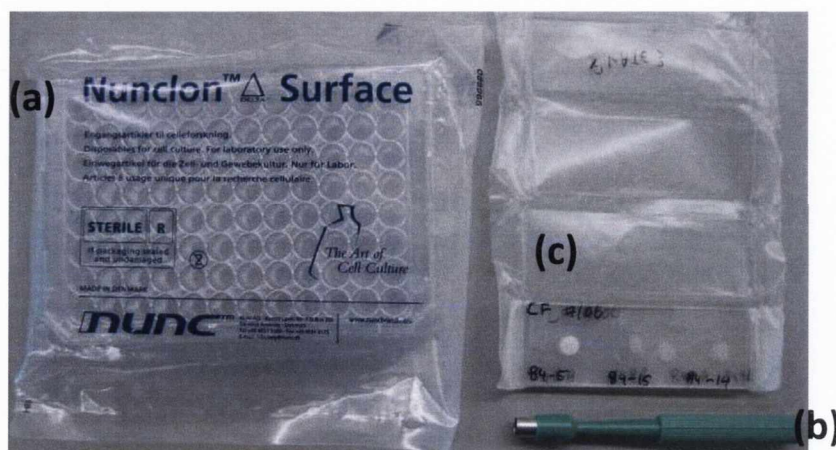


Figure 6.2.1: (a) Sterile 96 well plate, (b) punch to cut porous material to size, (c) samples in between microscope slides after low-heat treatment.

6.2.3 Summary of Results:

The key results summarised from the report (225) are as follows:

- The monitored mitochondrial, lysosomal and endoplasmic reticulum activities quantitatively show that the ordered porous substrate is biocompatible.
- Confocal microscopy showed clearly the adhesion and morphological adaptation of the cells to the porous substrate by a re-organisation of the cytoskeleton (shown in Figure 6.2.2)
- Cell viability assessed at 0 and 24 hour time points showed cell proliferation had not been impaired or altered but it had increased significantly from the plated concentration for both porous and non-porous samples, proving cytocompatibility (e.g., negligible cytotoxicity).

6.2.4 Next Steps

- The results will be repeated for at least one other cell line.
- It was noted in Section 1.2.2.1 that the use of hydrophilic end groups or polymer blocks leads to a preferential coating of these groups inside the pores. During the formation process, it is believed these groups preferentially arrange themselves at the water droplet interface. Initial results using Raman spectroscopy show in our system that a higher concentration of carboxylic acid groups are observed inside the pores when compared with the upper film surface. This approach may lead to a route to functionalise the pores and allow study of the interaction between cell receptors and hydrophilic/hydrophobic terminations.

- With the unique control over pore size and structure, the morphological adaptation of cells to the structures will be examined.
- The optical transparency allows confocal imaging through the material and so it is planned to investigate the morphological adaptation of the cells with samples that are porous throughout and not just at the upper surface with the aim of demonstrating cell adhesion into a 3D scaffold.
- The importance of the mechanical properties of the films to cell response means the techniques developed in Section 6.1 will also be applied to the samples examined in this work.

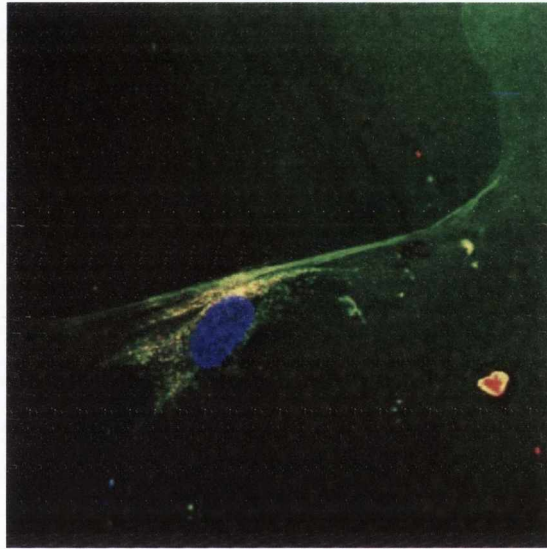


Figure 6.2.2: MC3T3 cell morphologically adapting to porous PS substrate (225).

Chapter 7

Summary and Outlook

7.1 Summary

This thesis examines a complex system of competing mechanisms for a non-equilibrium self-organisation technique that leads to the formation of ordered porous microstructures in polymer films. The mechanism, rather than studied as a whole, was broken down into an examination of (i) the equilibrium force balance of droplets on the solvent surface and (ii) the dynamical behaviour associated with solvent evaporation, water condensation and the evolution of polymer solution concentration.

Part (i) is dealt with in Chapters 2 and 3 where both theoretical and experimental work is completed to understand the ability of micro scale droplets of water to reach a stable position at a solvent/air interface. A model is constructed that shows, Neumann's triangle does not hold true and an additional force is required to explain the existence of the water droplets at the interface for the chosen organic solvents. The excess energy at the three phase contact line, known as line tension, is introduced and explored as the initial solution to this observation.

A method was developed to measure the submerged contact angle of a water droplet and has been applied to a range of droplet sizes for pure solvent. A substantially constant contact angle is observed, fixed at a characteristic value for the solvent concerned. This is unexpected and a selection of likely explanations is presented. The change in the value for line tension with lens size is a likely contributor to this effect, with the predicted change in the magnitude of non-local intermolecular interactions between the droplet and the solvent/air interface. Importantly, similar contact angles are measured whether a pure solvent is used, or a polymer solution. This is a very useful point, as building and testing a model is much simpler when the materials involved can be assumed pure and free of surface active components, especially when dealing with liquid-liquid interfaces. However, it can now be seen that the insights

gained from this approach can be directly translated to the system of interest, a porous microstructure formation.

Part (ii) in chapters 4 and 5, focuses on the dynamic mechanisms of this system and shows that through controlling the ambient humidity and flow conditions during formation, the solution properties can be dynamically tuned during their evolution towards porous films. Tuning these conditions shows that a rich variety of previously unreported pore architectures are achievable with this technique. The effect of these changing conditions is monitored by recording the response of the sample *in-situ*, both in terms of its temperature drop but also the change in its rate of evaporation. This is complimented by the development of focused ion beam milling to allow clear cross-sections to be formed and imaged.

An additional experimental development has been reported in this thesis regarding the monitoring of the formation process by optical microscopy. This is possible while also controlling the ambient flow and humidity. In combination with the approaches summarised above, a clear hypothesis could be formed based on the evolution to explain the mechanism of formation that can give shallow, disc-like pores, spherical pores or elongated and cylindrical pores, to name but a few.

7.2 Outlook

On-going work is focused on:

- (i) Understanding the stability of a water droplet at the solvent/air interface. This will include defining the relative role of line tension and its change with drop size. Also, it will require further examination of the water droplet/air interface to see if a Gibbs layer of solvent can form.
- (ii) Further refinement of the optical measurements of liquid droplets, to reduce the inherent noise.
- (iii) Continuing exploration of the phase space of ambient conditions when forming the porous polymer microstructure in an attempt to understand further the underlying controls and the range of feasible microstructures.
- (iv) The morphological adaptation of cells to the polymer microstructures, taking advantage of the unique sample set of pore geometries available.
- (v) The formation of a diamond flat punch that can probe the local mechanical failures of a polymer truss.

7.3 Outputs

- Two publications in draft format, soon to be submitted, based on output to this thesis regarding the positioning of water droplets and the resulting feasible microstructures.
- One paper in draft for collaboration in Section 6.2.
- (WO/2009/069110) A METHOD FOR PRODUCING AN ARRAY OF PORES OF CYLINDRICAL SHAPE IN A POLYMER FILM, AND A POLYMER FILM PRODUCED ACCORDING TO THE METHOD
- Second patent application filed in October 2010.
- Oral presentation at International Conference on Solid films and Surfaces (ICSFS), July 2008, "Mechanistic Insights from Formation of Novel Pore Morphologies with Breath Figure Templating"
- Poster presentation and runner-up prize, 3rd International Conference on Nanomaterials and Nanomanufacturing, December 2007
- Oral presentation at Materials Research Society Fall Meeting, November 2007, "Mechanistic Insights into Breath Figure Templating of Novel Porous Polymer Morphologies"

Appendices

Appendix 1.1: Physical Properties of Solvents

Property	Toluene	Water	Carbon Disulphide	Dichloromethane	Methyl Chloroform	Chloroform	Bromoform
CAS	108-88-3	7732-18-5	75-15-0	75-09-2	71-55-6	67-66-3	75-25-2
MW (g/mol)	92.14	18.02	76.14	84.93	133.4	119.38	252.73
Boiling Point (deg. C)	110.63	100.00	46.00	40.00	74	61.17	149.10
Melting Point (deg. C)	-94.95	0.00	-112.10	-97.20	-30	-63.41	8.69
$\Delta_{\text{vap}} H f_D$ (kJ/mol)	33.18	40.65	26.74	28.06	29.86	29.24	39.66
$\Delta_{\text{vap}} H f_{25}$ (kJ/mol)	38.01	43.98	27.51	28.82	32.5	31.28	46.05
C_p (J/gK - 1kPa)	1.70	4.18	1.00	1.19	1.08	0.96	0.52
C_p (J/molK - 1kPa)	156.64	75.34	76.14	101.07	144.07	114.60	131.42
Vapour Pressure of 760 mm of Mercury at T: (deg. C)	110.60		-110.80	40.70		61.30	150.50
Vapour Pressure at 25 deg. C (kPa)	3.79	3.17	48.20	58.20	16.5	26.20	0.73
Density (g/cm ³)	0.8668	0.99821	1.2632	1.3266	1.339	1.4832	2.8788

Source: Lide, D. R. 2004, *Handbook of Chemistry and Physics*, CRC Press

Appendix 1.2: Data Sheet for α,ω -Carboxy Terminated Polystyrene

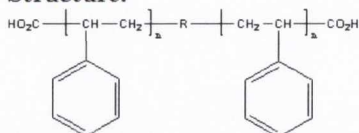
Product and Data Sheet supplied by Polymer Source (www.polymersource.com).

Sample Name:

α,ω -Carboxy Terminated Polystyrene

Sample #: P423-S2COOH

Structure:

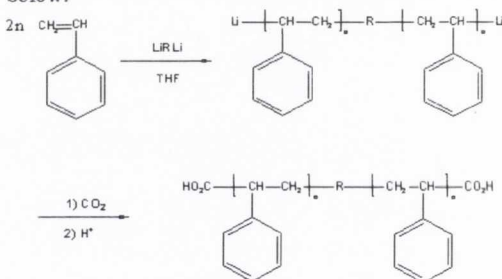


Composition:

$M_n \times 10^3$	PDI
93.8	1.07
Functionality	>1.93
T_g (°C)	104

Synthesis Procedure:

The functionalized polymer was prepared by anionic living polymerization of styrene using bifunctional as initiator in THF followed by terminating the polymerization reaction with dried CO_2 . The scheme of the reaction is illustrated below:



Characterization:

The molecular weight and polydispersity index of this polymer were determined before the addition of the carboxy function by size exclusion chromatography (SEC) using a Varian liquid chromatograph equipped with a UV and refractive index detector. In our columns the polymer after termination with CO_2 the elution is retarded. This is because of the strong interaction with the column packing material. Furthermore the M_w/M_n broadens because of that reason. Polymer functionality was determined by the titration with NaOH using phenolphthalein as the indicator.

Thermal analysis:

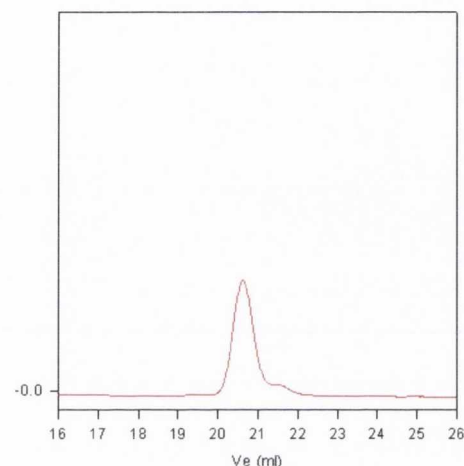
Thermal analysis of the samples was carried out on a TA Q100 differential scanning calorimeter at a heating rate of $10^\circ\text{C}/\text{min}$. The midpoint of the slope change of the heat flow plot of the second heating scan was considered as the glass transition temperature (T_g).

Solubility:

Polymer is soluble in THF, Dioxane, CHCl_3 and precipitated out from methanol/water, and in cold hexane.

SEC of Sample:

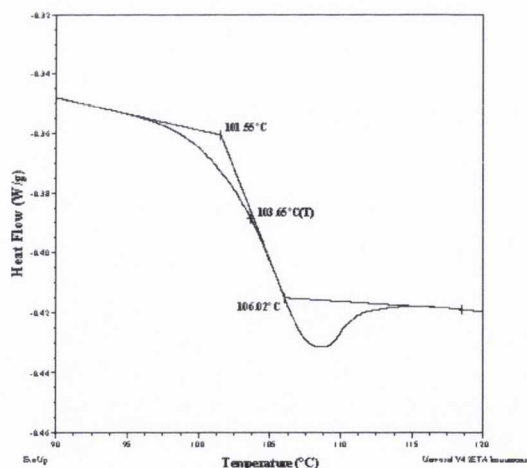
P423-S2COOH



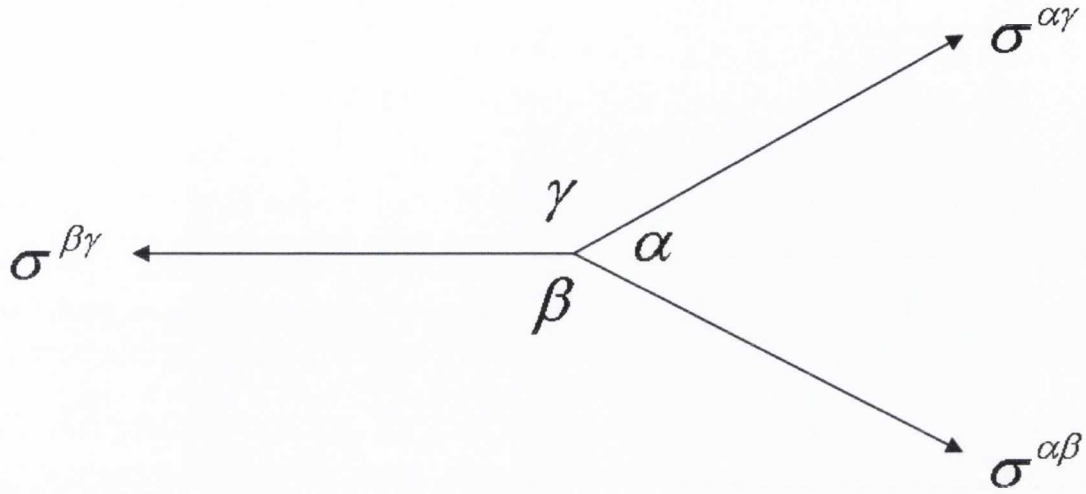
Size exclusion chromatography of α,ω -dicarboxy terminated polystyrene.

$M_n=93800$, $M_w=100400$, $M_z=105700$, $PI=1.07$, functionality=1.93.

DSC thermogram for the polymer:



Appendix 2.1: Derivation of Contact Angle Definition in Terms of Surface Tensions for a Three Liquid-Phase System (i.e. Neumann's Triangle)



- $\alpha + \beta + \gamma = 2\pi$

Resolving forces with respect to each vector σ^{ij} gives:

$$(i) \quad \sigma^{\alpha\gamma} = -\sigma^{\alpha\beta} \cos \alpha - \sigma^{\beta\gamma} \cos \gamma$$

$$(ii) \quad \sigma^{\beta\gamma} = -\sigma^{\alpha\beta} \cos \beta - \sigma^{\alpha\gamma} \cos \gamma$$

$$(iii) \quad \sigma^{\alpha\beta} = -\sigma^{\beta\gamma} \cos \beta - \sigma^{\alpha\gamma} \cos \alpha$$

Substitute equation (i) into equation (iii) to remove the $\sigma^{\alpha\gamma}$ term:

$$\sigma^{\alpha\beta} = -\sigma^{\beta\gamma} \cos \beta - [(-\sigma^{\alpha\beta} \cos \alpha - \sigma^{\beta\gamma} \cos \gamma) \cos \alpha]$$

$$\Rightarrow \sigma^{\alpha\beta} + \sigma^{\beta\gamma} \cos \beta - \sigma^{\alpha\beta} \cos \alpha - \sigma^{\beta\gamma} \cos \gamma \cos \alpha = 0$$

Re-group to give:

$$\Rightarrow \sigma^{\alpha\beta} (1 - \cos^2 \alpha) + \sigma^{\beta\gamma} (\cos \beta - \cos \gamma \cos \alpha) \quad \mathbf{A}$$

Substitute equation (i) into equation (ii) & repeat procedure:

$$\Rightarrow \sigma^{\beta\gamma} (1 - \cos^2 \gamma) + \sigma^{\alpha\beta} (\cos \beta - \cos \gamma \cos \alpha) \quad \mathbf{B}$$

With $\cos^2 \theta + \sin^2 \theta = 1$
 $\Rightarrow 1 - \cos^2 \theta = \sin^2 \theta$

Divide **A** by **B**:

$$\Rightarrow \frac{\sin^2 \alpha \cdot \sigma^{\alpha\beta}}{\sin^2 \gamma \cdot \sigma^{\beta\gamma}} = \frac{\sigma^{\beta\gamma} (\cos \beta - \cos \gamma \cos \alpha)}{\sigma^{\alpha\beta} (\cos \beta - \cos \gamma \cos \alpha)}$$

$$\Rightarrow \frac{\sigma^{\beta\gamma}}{\sigma^{\alpha\beta}} = \frac{\sin \alpha}{\sin \gamma} \quad \mathbf{C}$$

Alternatively:

$$\text{from equation (ii)} \Rightarrow \cos \gamma = \frac{-\sigma^{\alpha\beta} \cos \beta - \sigma^{\beta\gamma}}{\sigma^{\alpha\gamma}} \quad \mathbf{D}$$

$$\text{from equation (i)} \Rightarrow \cos \alpha = \frac{-\sigma^{\beta\gamma} (\cos \gamma) - \sigma^{\alpha\gamma}}{\cos^{\alpha\beta}} \quad \mathbf{E}$$

Substitute **D** into **E**

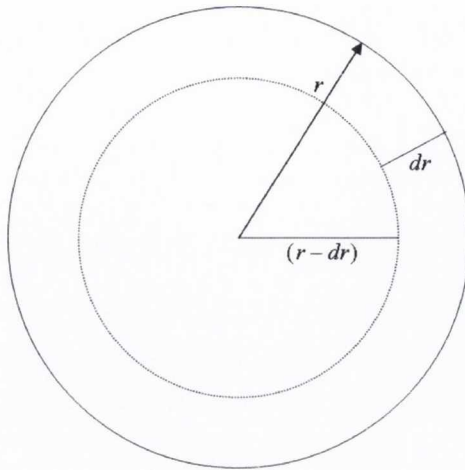
$$\Rightarrow \cos \alpha = \frac{\sigma^{\beta\alpha} \cdot \sigma^{\alpha\beta} \cos \beta + (\sigma^{\beta\gamma})^2 - (\sigma^{\alpha\gamma})^2}{\sigma^{\alpha\beta} \cdot \sigma^{\alpha\gamma}}$$

Then substitute in equation (iii)

$$\Rightarrow \sigma^{\alpha\beta} + \sigma^{\beta\gamma} \cos \beta + \frac{\sigma^{\beta\gamma} \cdot \sigma^{\beta\gamma} \cos \beta + (\sigma^{\beta\gamma})^2 - (\sigma^{\alpha\gamma})^2}{\sigma^{\alpha\beta}}$$

$$\text{Tidy to show, } \cos \beta = \frac{(\sigma^{\alpha\gamma})^2 - (\sigma^{\beta\gamma})^2 - (\sigma^{\alpha\beta})^2}{2\sigma^{\alpha\beta} \cdot \sigma^{\beta\gamma}}$$

Appendix 2.1: Derivation of Two Dimensional Equivalent of the Laplace Pressure.



- 1) Energy associated with outer circumference, where σ is the interfacial energy.

$$= 2\pi r \cdot \sigma$$

- 2) Energy associated with inner circumference

$$= 2\pi r \sigma - 2\pi(r - dr)\sigma$$

$$= (2\pi r - 2\pi r + 2\pi dr) \cdot \sigma$$

$$= \sigma \cdot 2\pi dr \quad \mathbf{A}$$

- 3) Energy associated with area is pressure working against it.

$$\left[\pi r^2 - \pi(r - dr)^2 \right] P_\sigma$$

$$= 2\pi dr \cdot P_\sigma \quad \mathbf{B}$$

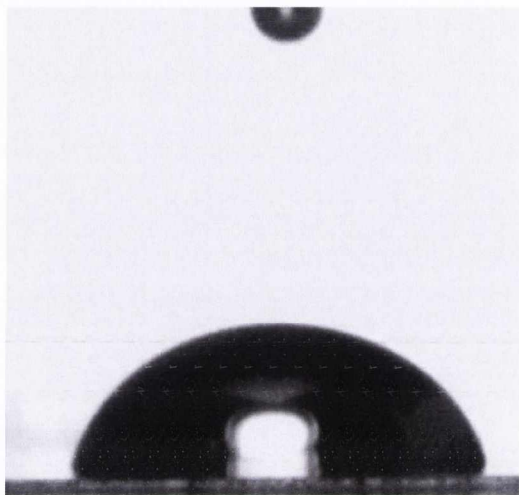
- 4) Equate **A** & **B**

$$\Rightarrow 2\pi dr \sigma = 2\pi dr P_\sigma$$

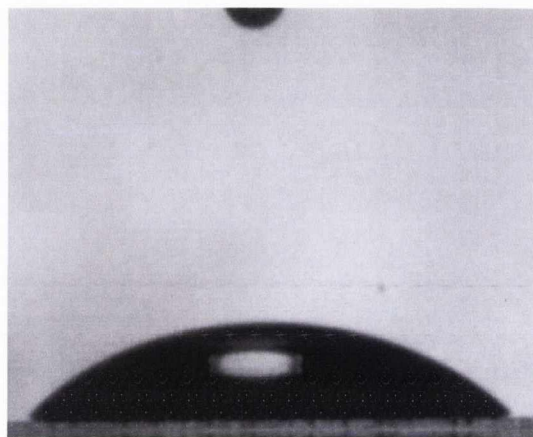
$$\Rightarrow P_\sigma = \frac{\sigma}{r}$$

Appendix 3.1: Change in Water Contact Angle with Cleaning Technique

Glass cover slips are used as a substrate for porous film formation throughout this thesis. The contact angle of water can be seen to change depending on the cleaning method used. Contamination free samples are essential for line tension measurement.



Glass cover slips, without cleaning.



Glass cover slips, with sonication in isopropanol to clean



Cleaned by soap/water, acetone sonication, water rinse, methanol sonication, water rinse, N₂ dry and O₂ plasma clean.

Appendix 3.2: Effect of Temperature and Curvature of the Water Droplet on Surface Tension Values

Initially it was considered that the temperature or curvature dependence of surface tensions was in fact altering the surface energies sufficiently so that they balance as per the Neumann relation. This would ensure a constant contact angle.

Surface tension has an almost linear response to the change in temperature. The following temperature dependencies were found by looking at (i) temperature coefficients for solvents (<http://www.surface-tension.de>) and (ii) where these were unavailable, turning to the Eötvös Rule (113):

$$\gamma \cdot V^{\frac{2}{3}} = k \cdot (T_c - T) \quad (3.4)$$

where γ is the surface tension, V is the molar volume, T_c is the critical temperature, T is the temperature of interest, and k is a constant found to be approximately 2.1 ergs/K. Figure 4 shows the response to temperature for each of the solvents in our current work.

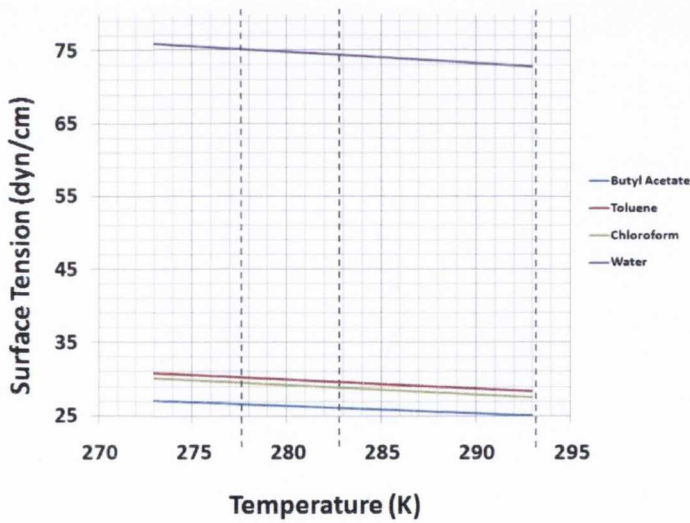


Figure 3.2.1: This figure shows the calculated change in surface tension over the range of expected temperatures in the breath figure formation process for three different solvents and the water droplets.

Modifying the individual surface tensions based on the above temperature relationships and then using these to look at the trend of interfacial tensions using the following equation (111),

$$\gamma^{1/2} \approx \gamma^1 + \gamma^2 - 2 \cdot \sqrt{\gamma_1^d \cdot \gamma_1^d} \quad (3.5)$$

shows that in fact the interfacial tensions remain almost constant.

Using the Mathematica, the surface tension range was explored to see if any of the systems showed any unusual behaviour or may be sensitive to temperature according to our model.

Each system showed that an additional force is required for the droplet to be present at the interface, at any of the temperatures that we may encounter in the experiment.

(i) Surface tension dependence on curvature

An alternative reason for the unexpected behaviour of the micron scale water droplets was that the surface tension values were significantly altered from their literary values due to a curvature of the lens. This is a theory put forward in detail in (173). The Laplace equation illustrates the pressure drop across a curved surface. This represents a change in molar free energy of a substance depending on its curvature. The free energy is often related to the vapour pressure of a substance and the Kelvin equation below shows the change in vapour pressure with surface curvature (162):

$$RT \cdot \ln \left(\frac{P}{P_o} \right) = \gamma \bar{V} \left(\frac{1}{R_1} + \frac{1}{R_2} \right) \quad (3.6)$$

where P_o is the normal vapour pressure, P is the vapour pressure over the curved surface, R_i are the principle radii of curvature.

If the curvature is sufficient, the value of surface tension is also affected. This relationship is known as the Tolman equation, below, and has been shown to be only relevant at radii of a few nm and is extremely important in the understanding of nucleation events. However, this is not expected to impact our force balance.

$$\gamma = 1 - \frac{\delta}{R_m}, \text{ where } \delta = \frac{2 \cdot c_o \cdot K}{\gamma^o} \quad (3.7)$$

where R_m is the mean radius of curvature, c_o is the spontaneous curvature, K is the bending elastic modulus.

Appendix 3.3: Surface Energy Measurement of Dicarboxy-terminated Polystyrene

Method:

1. Films of DCPS were formed by spin casting the polymer in solution onto a clean glass coverslip.
2. Ultra clean water was dosed using a new, clean glass syringe, rinsed thoroughly with ultr-pure water.
3. Ten drops were recorded using a CCD camera mounted in the plane of the substrate, in device in the School of Physics set up to allow contact angle measurements (example image in Figure A.5.3.1).
4. Contact angles were fitted using ImageJ software with LB-ADSA Drop Analysis plug-in.

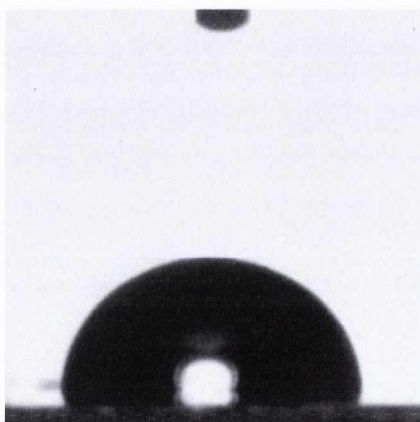


Figure A.3.3.1: Water drop on DCPS film as recorded by CCD camera.

5. The surface energy was calculated using a method discussed in (184) as follows:

$$\cos \theta = 2\varphi \left(\frac{\gamma_s}{\gamma_l} \right)^{\frac{1}{2}} - 1, \quad \text{where,} \quad \varphi = \frac{4(V_s V_l)^{\frac{1}{3}}}{\left(V_s^{\frac{1}{3}} + V_l^{\frac{1}{3}} \right)^2}$$

With γ_s the surface tension of the solid DCPS film, γ_l the surface tension of the water, θ the average measured contact angle, and V the molar volume.

With an average contact angle of 89° this led to a surface tension of 0.022J/m^2 . One other literature value found gives a contact angle of 83° , which translates to a value of 0.027J/m^2

Appendix 4.1: Thermocouple Calibration

The type K thermocouple is connected via a National Instruments connection box to a laptop. Running LabView, it is possible to record readings from the probe.

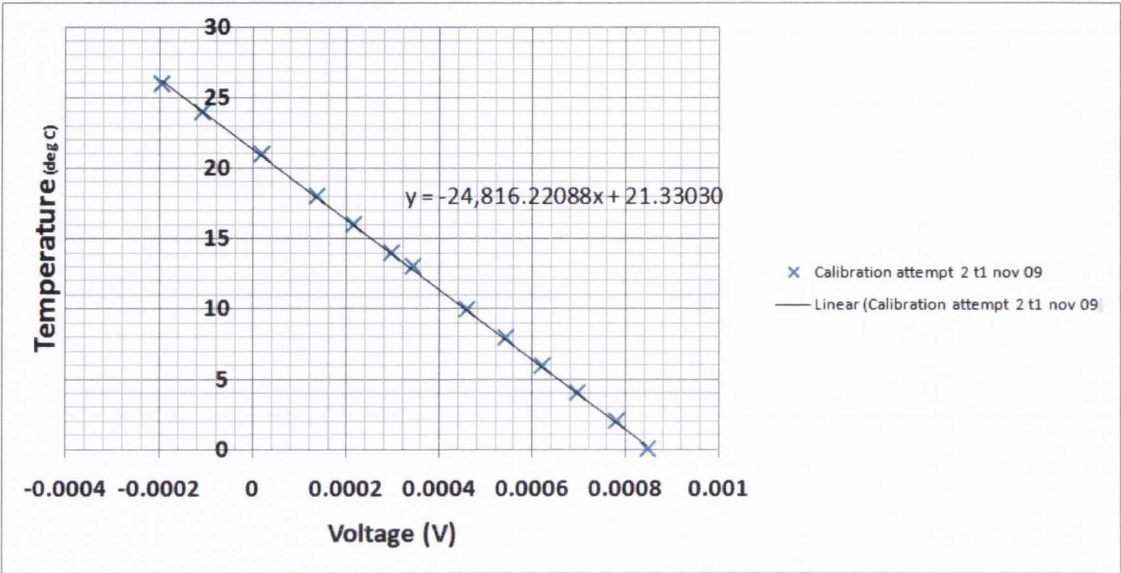


Figure A.4.1.1: Calibration chart for a type K thermocouple based on data recorded at a range of known temperatures.

However, prior to use, it needs to be calibrated. This was carried out regularly to ensure accuracy. Calibration was carried out by submerging the tip and holder into iced water stored in an insulated glass beaker and allowed to equilibrate. Readings are then taken, recording for 300 data points. A tested, accurate and narrow temperature range thermometer is used as the calibration. The temperature calibration is completed with a range of temperatures of interest. The temperature of the water slowly increases naturally. This has been found to proceed slowly enough that it doesn't affect the readings significantly. This happens very slowly and gives the probe time to equilibrate. This technique gives an excellent straight-line response, as seen in Figure A. 4.1.1 and is used as a calibration equation in Labview. Due to numerous repairs and significant usage, regular calibrations were performed to ensure accuracy.

Appendix 5.1: Viscosity Estimation Techniques

Two methods are used to estimate the viscosity of polymer, DCPS, in chloroform over a range of concentrations.

The first method is chosen as it is shown to be accurate for lower concentration solutions (183). It is most accurate when based on a single known viscosity. Without this measurement, the estimate was carried out using the limiting viscosity based on the Mark-Houwink formula noted in Section 5.2, as suggested in the report.

The method is based on the approach of modelling the solution as a Newtonian flow of polymer spheres:

$$\frac{\eta_0}{\eta} = 1 - 2.5\phi + 11\phi^5 - 11.5\phi^7$$

Where η_0 is the intrinsic viscosity (at infinite dilution), η is the solution viscosity at the concentration of interest, ϕ is the volume fraction of polymer and is calculated by:

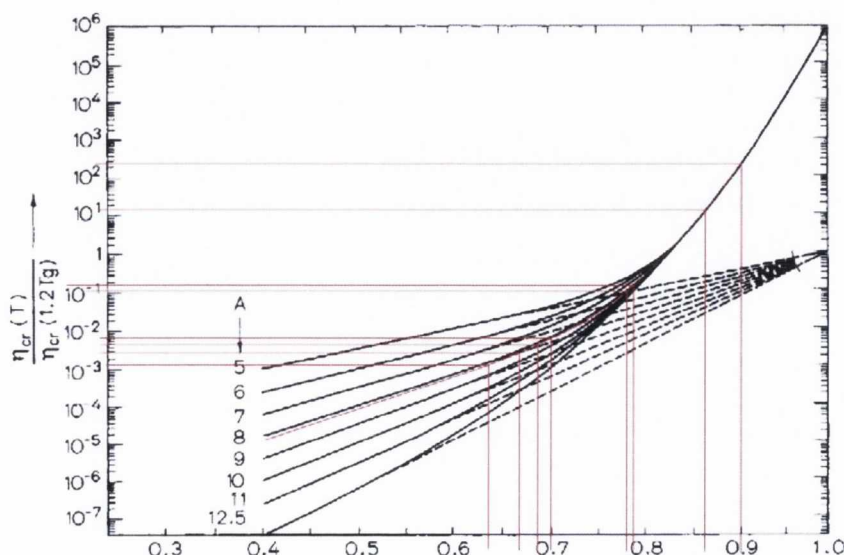
$$\phi = \frac{0.524c_{\epsilon_0}}{0.524\rho + c(\epsilon_0)}$$

Where ρ is the density, c is the concentration in g/cm^3 and ϵ_0 is obtained from the intrinsic viscosity:

$$\epsilon_0 = \frac{\rho[\eta]}{2.5}$$

These equations give the initial part of the curve up to a volume fraction of 0.2. An estimate for volume fraction is used to track the progress of the solution based on the mass loss recordings. This estimate is simply based on the densities of the involved components.

Once the volume fraction is above 0.2, a method for estimating the viscosity of more concentrated solutions is used (184).



The viscosity relationship was constructed to take into account both the dilution effect of the solvent and also its plastisizing influence on the glass transition temperature.

With an estimation of the glass transition temperature, the Mastercurve is used to then take into account the effect of the change in plastisizing effects. With a value for $\frac{T_g}{T}$, the Mastercurve can then be used to find a value for the correlated y-axis:

$$\frac{\eta_p^*}{\eta_p(1.2T_g^P)}$$

Where η_p^* is the contribution, due to the plastisizing effect, to the viscosity of the polymer solution at its new concentration, η_p is the value for the viscosity of the pure polymer at its glass transition temperature. The value for this ratio is found using $A=8.2$ as the intersecting line, highlighted above, the reported value for polystyrene. Finally this is combined with the contribution to viscosity due to dilution, using:

$$\log \eta = \log \eta_p^* + 5 \log \phi_p$$

As the initial value for η_p is unknown, this is estimated by assuming we know the concentration for the first point, where it overlaps with the previous method. This was on the order of values for similar systems but a correct value would be useful.

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