# Chapter 1

## Introduction

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## 1.1 Historical background

Numerous studies on thin polymer films have confirmed that a number of their physical characteristics displayed traits that significantly differed from their bulk properties, with significant implications for the majority of technological applications based on such thin films. A large number of measurements have shown anomalous reversible and irreversible density changes after annealing below the glass transition temperature ($T_g$) [1-9], unpredicted instabilities of these films [1,10-13], unexpected ageing [14-21], deformed chain conformations, molecular weight independent dewetting processes and much faster kinetics than suggested by bulk-elasticity, clear evidence for residual stresses within these spin-coated thin polymer films and rapid relaxation processes. [22-24]. Some examples of observed contrary polymer dynamics in thin films. The cause of these contradictions is still a debatable topic.

It is undeniable that despite a large number of publications, a clear understanding of thin-film characteristics has not yet been achieved. There is still some debate over the source of some of these complexing characteristics of thin polymer films. The effect of film preparation and confinement on chain conformations is still not fully understood at this time. The effects of the resultant chain conformations, particularly on increasing $T_g$, on the visco-elastic characteristics of thin polymer films are still not fully understood. Whether a conformational state with distinct features is formed when a diluted solution transitions to a dry, glassy state is unclear.

In the conventional method of making films from solutions, the solvent is quickly evaporated, increasing the concentration of the polymer as a result. This process continues until the film hardens while the solvent is still present in significant amounts. It is not definite whether the initially highly separated molecules in solution have sufficient time to merge sufficiently in order to initiate an entangled polymer. It is reasonable that films synthesized this way contain molecules having frozen-in conformations deviating significantly from equilibrium with a reduced degree of inter-chain overlap. It is unclear if film preparation and the consequent non-equilibrium conformations of the polymers affect measurements of visco-elastic characteristics, glass-transition temperature, film stability, diffusion coefficient, etc. Sample preparation may also be a factor for the exceptional behaviour in glassy thin films. In particular, fast evaporation caused during spin-coating may produce samples deviating from equilibrium. The spin coating method was used because this method can produce thin polymer films in the nanometre range. [25,26] The possibility of modifying the film thickness by varying the concentration of the spin coating solution stimulated research into the chain-like character of these macromolecules.

It is still unclear whether polymer properties such as viscosity, chain orientation, chain conformation, mechanical properties and glass transition temperature change when the thickness of film is sufficiently low.

Surprisingly, many of these experiments failed as the films were not stable and destroyed on annealing above the glass transition temperature of the bulk system ($T_g$, bulk) and even below $T_g$, bulk the films were unstable. For chain diffusion stability is required.

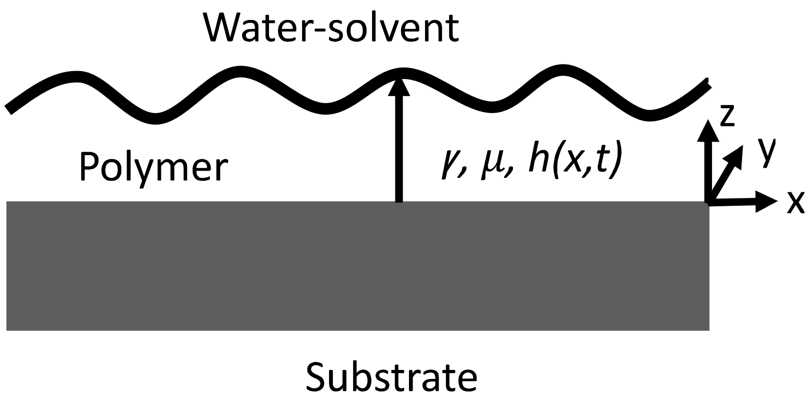

**Figure 1:** Schematic diagram of a thin film instability

## 1.2 Surface instabilities

Surface instabilities in polymer films can be found in unstable highly confined systems or at the mesoscale, where molecular level forces are in control. Even in stable systems, instability can be attained by using external factors to make them become unstable. Various researchers illustrated that the conflict between destabilizing and stabilizing forces directly causes surface instabilities. [27] The destabilizing forces include van der Waals forces, polar interactions, steric interactions or electrostatic interactions. Elastic strain or surface tension is one of the stabilising forces. As a result, we have two different cases:

a) Inherent dynamics lead to instability. This type of film may lead to dewetting.
b) Films that are metastable are susceptible to become unstable when an external stimulus is applied. Applied thermal gradient, electric fields or mechanical forces are commonly applied.

The film morphology evolves toward a more optimal energy state as a result of the surface instability. In order to achieve different surface morphologies and patterns, it is crucial to properly understand the parameters that affect surface instability. Figure 1 depicts the transverse view of the film. Dewetting initiates due to the random perturbations on top of the film. Instability that grows at highest speed will determine λ.

Dewetting is a hydrodynamic process in which the interfacial and intermolecular energy cause a uniform layer of liquid to destabilise and decay into different patterns of stationary droplets. These patterns can now be predicted theoretically, and their numerical evolution may be tracked in striking agreement with experimental findings. Droplet shedding of moving liquid rims and satellite droplet pinch-off during the decay of stationary ridges are two different forms of instabilities that cause the droplet arrays that are seen during the quasistatic evolution. The dissipation at the liquid-solid interface, which is described by an effective Navier slip, is the mechanism responsible for the formation of various droplet patterns.[28]

## 1.3 Surface instabilities utilized to pattern surfaces

### 1.3.1 Dewetting

The free energy of the system controls the evolution of unstable or metastable films to a stable state, which typically results in dewetting, or the film rupturing to generate random morphologies. A random distribution of holes, bi-continuous structures, polygons, and droplets have been seen when this phenomena arises on chemically homogeneous surfaces. However, dewetting can be controlled to pattern polymeric materials. Heterogeneous substrates made by using photolithography, vapour deposition, or microcontact printing are frequently used to achieve this. Dewetting of thin films on regular physically and chemically patterned surfaces, can result in a wide range of surface patterns because the polymer will wet and dewet specific locations.

### 1.3.2 Phase separation of block copolymers and polymer blends

Enclosing polymer blends and block copolymers between surfaces influences the phase separation as a result of one of the components for the interface. Understanding the mechanisms of phase separation in polymer thin films has been the subject of extensive research. [29] Compared to bulk phase separation methods, the presence of substrate/film and film/air interfaces results in additional complications. The complex structures are formed due to small differences on parameters such as film thickness, affinity for the substrate, surface tension of the polymer, molecular weight of the polymer, evaporation speed, polymer concentration, chemical reaction in the blend, addition of additives and temperature. [30,31,32]

### 1.3.3 Template guided structuration

The phase separation process is significantly affected by the presence of an interface. In effect, surface-attractive polymers. Thus, surface-attractive polymers are typically stretched over the substrate surface because the adsorption interaction overcomes the entropy loss caused by extending macromolecular chains (in blends or blocks). As a result, chemically/topographically patterned substrates can alter the phase separation process thus leading to various morphologies.[33]

### 1.3.4 Electrohydrodynamic patterning

In this, a thin polymer film is placed between two plates, with an air gap separating it from the top plate. The polymer-air interface is distorted as a result of surface tension and electrical forces operating at the interface when the polymer is above the glass transition temperature ($T_g$). Moreover, the film becomes unstable when the electrical forces exceed the surface tension thus leading to various morphologies. [34]

### 1.3.5 Surface patterning due to Thermal-gradient

Different morphologies are formed as a result of a morphological instability when a polymer films-air double layer is confined between two plates having different temperatures. As the case using the electric field, an externally applied temperature gradient surface disturbances with a characteristic wavelength that causes the film to break up into various morphologies. [35]

### 1.3.6 Breadth figures

The alignment of ordered water droplet arrays on surfaces is a common phenomenon known as breadth figures. In most cases, breadth figures are created when humid air comes into contact with a cold surface. The moisture condenses on the cold surface if the vapour does not wet the surface, producing water vapours that develop during evaporation and give rise to distinct water droplet arrangements on the surface. Both a thermocapillary and the Marangoni convection, which prevents two droplets of the same liquid from coalescing if there is a significant temperature difference between them, are used to control this process. [36]

### 1.3.7 Water-ions induced nanostructuration

A layer of dissolved gases is present at the interfaces when hydrophobic surfaces come into contact with water in ambient conditions. The intimate contact between the two phases is reduced by this effect. However, on degassing the aqueous solution the extent of this layer can be decreased. According to certain researchers, avoiding the presence of a gas layer, increased contact between a hydrophobic polymer film and an aqueous solution can induce a self-assembled nanostructure on the solid surface. This occurs as a result of the water ions (hydroxyl and hydronium) adsorption at the interface. Because of the hydrophobic surface charge, this self-assembled structure was formed. [37]

### 1.3.8 Nanobubble assisted nanopatterning

After being submerged in aqueous media, nanobubbles created by the gas in the solvent are visible on hydrophobic surfaces. They are prone to be placed at hydrophobic solid-liquid interfaces and several recent works confirmed that nanobubbles partially covering the surface interacts with the solid. Particularly, Basal plane highly ordered pyrolytic graphite submerged in aqueous environments may exfoliate more easily as a result of interactions between nanobubbles and the polymer surface. Different surface morphologies can be formed by these nanobubble-polymer interactions.[38]

### 1.3.9 Reaction-diffusion surface patterns

When two or more chemicals diffuse over a surface at varying rates and react with one another, consistent patterns like spots and stripes are produced. This process is known as reaction-diffusion. During the polymerization process, reaction-diffusion dynamics may cause a surface instability. As a result, micro-macroscopic patterns have been derived.[39]

### 1.3.10 Growth processes: crystal growth and aggregation

Non-equilibrium growth techniques such as cluster or crystal growth can produce a variety of patterns. The diffusion of polymer chains or individual particles to the surface of the growing cluster is what causes the aggregation that results in the final shape. The instabilities produced on by the diffusion-limited process are what give rise to the complex structures common in the aggregates, such as dendrites. [40]

### 1.3.11 Surface wrinkling

Instability phenomena like surface wrinkling or folding are frequently observed in polymer films. By applying mechanical stress, a rigid layer is deposited on top of a polymer film. When the applied stress is removed, the film relaxes to form wavy morphology known as "wrinkles". [41]

## 1.4 Patterning of surfaces with polymer

Over the last decade, a wide variety of patterns for polymers have developed rapidly. The variety of existing synthetic and biological polymers and the capacity to "create" new polymer types have sparked a great deal of interest in polymer patterning, making it possible to quickly address the diverse functions of surfaces with polymer patterns. Due to the restricted lateral diffusion of macromolecules, polymer patterns often exhibit great accuracy. Polymers are compatible with a large number of patterning processes, have superior mechanical properties, and are relatively inexpensive.

There are various applications of polymer patterning: fabrication of masks and templates [42,43], the development of plastic electronics, semiconductor microelectronics, and light-emitting displays (LEDs) [44-47], medical and biotechnological research, involving cell and tissue engineering [48-50], key studies in surface science [51,52], the fabrication of optical components like photonic crystals or gratings. [53,54]

The techniques used to fabricate patterned polymer are examined in the sections that follow.

### 1.4.1 Top-down polymer patterning techniques

In a top-down method, the bulk material is broken down into nanoscale structures or particles. Printing or stamping, reproducing a template's shape (moulding or casting), removing material (machining and etching), or selective polymerization can all be used to pattern polymers.

### 1.4.1.1 Mask based patterning technique

Using masks to control the deposition of polymers on a substrate is a typical technique for patterning polymers on a surface. Photolithography is frequently employed in the semiconductor industry to create micrometer and submicrometer-sized patterns. This method involves placing a pattern between the light source (usually UV light) and the photoresist in order to selectively expose and harden the photoresist. The desired designs can be produced by removing unexposed parts of the photoresist. Specialized clean rooms and processing equipment are frequently needed for this method. [55-57]

### 1.4.1.2 Printing and writing techniques

Direct printing of the polymer is a convenient method for patterning polymers on a substrate. Ink-jet printing is one printing method. In this, droplets of different sizes are discharged from a print head. The print head is controlled by a computer-controlled deposition system to print materials of interest on a substrate. One of the other printing techniques is acoustic printing, which is similar to ink jet printing in that it ejects droplets of the target material. [58] A droplet is released from the reservoir by an ultrasonic pulse used in acoustic printing. [59,60] Acoustic printing's capacity to generate print quantities in the nanoliter to picoliter range can be useful for printing small volumes in close proximity. Similar to photolithography, direct writing techniques like electron beam lithography selectively expose a photoresist to an electron beam (instead of UV) to cause cross-linking. With electron beam lithography, which uses electron beams that can be smaller than the wavelength of light, higher feature resolution can be achieved. The direct writing approach of electron beam lithography can be time-consuming and is frequently employed to pattern small regions, whereas photolithography can quickly generate patterns over large areas.

Using a laser to remove materials from a substrate and generate a patterned surface is known as laser ablation or laser machining or drilling. Making holes in materials rapidly and precisely is possible with laser drilling.[61]

Another writing method that uses a laser to directly expose or polymerize a material is termed laser printing.[62]

### 1.4.1.3 Molding Techniques

The term "soft lithography" refers to a group of related processes that produce micro and nanofabricated structures using elastomeric polymeric mold made of materials like polydimethylsiloxane (PDMS). Since it can produce surface features with high resolution and may be used in standard lab settings, soft lithography is especially appealing for patterning polymers for biological applications. The elastomeric moulds are made by pouring PDMS over a patterned surface and curing it. The PDMS mold is peeled from the wafer after curing. Since the PDMS replica generation is a nondestructive process, several stamps can be produced from a single silicon master. Due to its optical clarity, flexibility, $O_2$ and $CO_2$ permeability, and ability to seal to a variety of surfaces, PDMS is a polymer that works well in *in vitro* applications. Polymers can be patterned on substrates using a variety of various moulding techniques.

## 1.4.2 Bottom-up patterning techniques

Self-assembly is the pattern-based autonomous organisation of components. Self-assembly provides a straightforward and efficient method for creating large periodic structures that top-down techniques might not be able to attain. It is possible to control the self-assembly of macromolecules and nanoparticles on a surface to create patterns with clearly defined topologically or chemically separate regions. The bottom-up approaches for polymeric patterning at various length scales, from macromolecules to nanoparticles, are covered in this section.

#### 1.4.2.1 Macromolecular Assembly

The self-assembly of the macromolecule system into thermodynamically stable structures can be driven by interactions between macromolecules or between the repeating units within a single macromolecule. Although top-down lithographic patterning technologies offer flexibility and improved pattern resolution, top-down techniques are difficult to use for obtaining features smaller than 30 nm.

#### 1.4.2.2 Polymeric nano/microparticle assembly

Highly ordered colloidal crystals, bio - active substrates, and optical and electronic devices can all be generated using the self-organization of nanoparticles. Because metal and silica particles offer the perfect features for electronics and optics, the majority of investigations on nanoparticle assembly have focused on these materials. One example is the self-assembly of polymeric particles by Wang et al, in which PS nanoparticles were induced to self-assemble to create a pattern of microwells on a solid surface.

#### 1.4.2.3 Layer by layer assembly

To create patterned multilayer microstructures, layer by layer assembly can be used in conjunction with other patterning methods. [63-66] While there are many distinct steps in a typical layer-by-layer assembly, it usually starts with dipping a pre-patterned substrate into a diluted solution of the first polymer that will self-assemble. After being cleaned with the appropriate solvent, the substrate that has been patterned with polymer A is dipped into a diluted solution of a second polymer B that can interact with polymer A.

## 1.5 Dewetting

Due to a large number of applications, the generation of nano-microstructured polymer film surfaces has been a challenge during the last decades. Various applications ranging from the fabrication of microchips and microelectromechanical (MEMS) devices to the preparation of substrates for cell growth and adhesion requires patterning of thin polymer films. The progress in the synthesis of structured surfaces to form micro and nano-patterns have been accomplished by basically two ways: adapting techniques such as molding (embossing) or nano/micro imprinting and/or by developing novel techniques consisting laser-ablation, soft-lithography or laser scanning.

In contrast to the state-of-the-art tools required by the above mentioned techniques, surface instabilities utilizes the inherent properties of polymers to induce particular surface patterns. Some of the instabilities are established since decades such as film dewetting, phase-separation or water condensation. The considerable interest in using surface instabilities to pattern polymer surfaces relies on the rich and complex patterns obtained by self-organising processes that are rather difficult to fabricate using traditional patterning techniques. Also, depending upon the surface instability, different interesting morphologies have been described. The interpretation of the formation of micro and nanoscale structures and the control of their feature-size is the current focus of many researchers. [67]

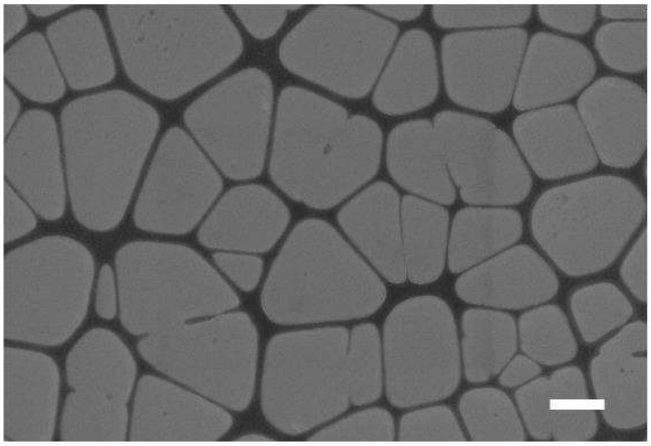

**Figure 2:** Polygons are arranged in a Voronoi tessellation pattern through the coalescence of dewetting holes. (scale: 10 μm)

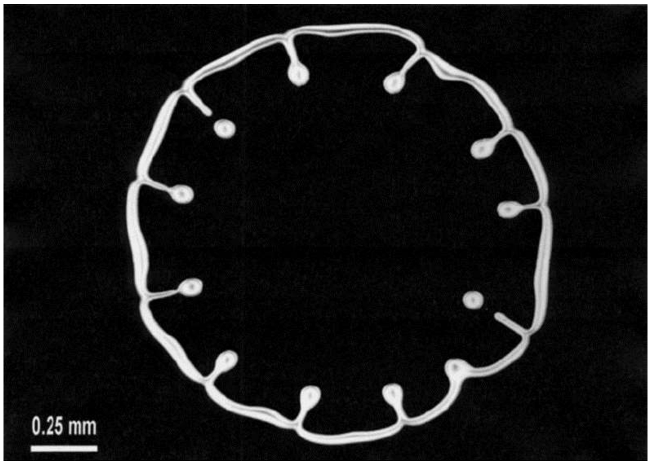

**Figure 3:** Instability of the rim of a circular hole that has formed in a polystyrene film that is 270 nm thick. Reproduced from ref. [95].

Thin film stability and its morphology have been studied extensively for its applications in coatings, adhesives and dielectric layers for its primary scientific interests. In particular, the dewetting phenomenon of thin polymer films has gain much interest. Dewetting is a spontaneous phenomenon in which a thin film on a solid substrate rearranges itself into a collection of separate objects. [68] Dewetting can be observed in day-to-day life for example in hydrophobic surfaces such as dirty window panes or Teflon-coated pan the water layer breaks into droplets. In several cases such as the rupture of a paint or protective film coating, dewetting phenomenon is undesirable. Whereas in other instances, it is useful such as in the industrial processes where rapid drying is needed, in aviation industries the aircrafts wings and fuelage are made unwettable by spraying with anti-ice fluid, in metallurgy, dewetting is required to remove liquid along with its all impurities, dishwasher detergents are formulated to promote water dewetting from the surfaces.[69] For a polymer liquid film with a thickness less than 0.1 μm intermolecular forces in the system is dominant and leads to increase in the fluctuations of film thickness. [70-71] Generally, a film can be destabilized by long-range forces, [72-76] polar interactions, [77-81]and molecular forces in the film having a structure difference due to densification of an interfacial layer at the substrate. [82-84] Most of the studies are for thermal dewetting in which the temperature is increased above the glass transition temperature of the polymer. In the case where the initially homogeneous film is thin, a polygon network of connected strings of material is formed, like a Voronoi pattern of polygons as shown in figure 2. At other film thicknesses, other complicated patterns of droplets on the substrate can be observed, which stem from a fingering instability of the growing rim around the dry patch as depicted in figure 3.

In fluid mechanics, dewetting is one of the processes that can occur at solid-liquid, solid-solid [85] or liquid-liquid interface. Generally, dewetting describes the process of withdrawing of a fluid from a non-wettable surface it was forced to cover. The opposite process-spreading of the fluid is called wetting. Spreading coefficient (S) determines the spontaneous spreading and dewetting of a fluid on a substrate.

$$S=\gamma_{SG} - \gamma_{SL} - \gamma_{LG} \tag{1}$$

where $\gamma_{SG}$ is the solid-gas surface tension, $\gamma_{SL}$ is the solid-liquid surface tension and $\gamma_{LG}$ is the liquid-gas surface tension.

When S>0, the spontaneous spreading is observed and if S<0 partial wetting is observed meaning the liquid will only cover the substrate to some extent.[86] Young-Laplace equation is used to determine the equilibrium contact angle $\Theta_{c.}$

Spreading and dewetting are crucial processes for many applications including lubrication, adhesion, painting, printing and protective coating. For most of the processes, dewetting is an undesired process because it destroys the applied film. Dewetting can be prevented by photocrosslinking the thin film prior to annealing or by including nanoparticles additives into the film.

Surfactants have an important effect on the spreading coefficient. The addition of surfactant decreases the interfacial tension and thus increasing the spreading coefficient(S>0) because when a surfactant is added, its amphiphilic properties cause it to be energetically favourable to migrate to the surface.

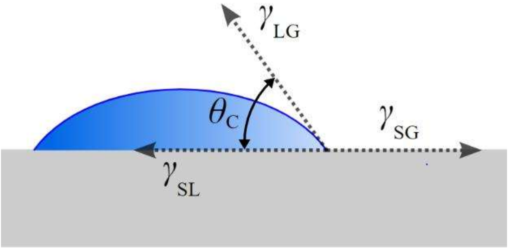

**Figure 4:** Surface tension diagram of a liquid droplet on a solid substrate. Due to Laplace pressure, the surface of the liquid resembles a spherical cap.

### 1.5.1 Reason for polymer to be chosen for film formation

We create a film of a polymer by spin coating and if we take a pure liquid there are going to be issues in spin coating. Spin coating with a pure liquid like an organic solvent on a non-wettable substrate, the liquid will tend to spread. Initially on dispensing it on a surface it will make a finite contact angle, but on spin coating, the vapour pressure of the liquid is high, the liquid will start to evaporate rapidly and the rate of evaporation will enhance as we spread the liquid because the surface area increases. If we take toluene, chloroform, acetone the liquid has definitely spread evenly on a non-wettable surface, but any time-result experiments cannot be done because the liquid has simply evaporated away.

On the other hand, if we take something like water that evaporated very slowly, the problem is that it will spread. Water makes a finite contact angle which it makes with most of the surfaces because water itself is a pretty high surface energy liquid. So, it does not easily wet a surface. It will not evaporate but it will remain in its low viscous state. Now on turning off rotation, it will retract back and dewett in its original configuration. While polymer forms an appropriate model system for these types of study. We make a dilute solution in an organic solvent which is a rapidly evaporating solvent. While spin coating, it spreads and the solvent evaporates. During spin coating, the solvent evaporates away and the solute gets deposited on the surface. So, we get a film on non-wettable surface that remains. The other advantage is that most polymers have long chains so the molecular weight is high, therefore the viscosity is high and therefore, dynamic is slow. So, it allows to track the evolution in minutes or on a realistic time scale.

### 1.5.2 Necessary condition for film to become unstable

Ultra-thin film is a film where there is active van der Waals interactions between its two interfaces. Between two surfaces van der Waals interaction stretches roughly to about 100 nanometers. The sign of the spreading coefficient plays an important role. Even though film is very thin, the first criteria for an instability is the sign of the spreading coefficient. The spreading coefficient do not take the thickness of the film into account. So, even if there is a very thick layer where based on the local surface energies, if the spreading coefficient is negative, that layer is not going to rupture or no instability is going to be manifested because a thick layer is stabilized by gravity and therefore, spreading coefficient despite of having a negative sign will not influence the film instability. The situation become most complex and spontaneous instability is manifested only when the film thickness is thinner than this limit upto van der Waals interaction. The internal kinetic energy of the molecules is responsible to lead to some fluctuations.

## 1.6 Motivation

Numerous industries, including optoelectronics [83], nanolithography [84], biotechnology [85], sensors and actuators [86], functional coatings and lubricants [87], microfluidics [88] depend largely on polymer thin films. Due to significant use of thin polymer films in various applications, there are numerous investigations on the dynamics of instabilities and structure creation in these films. Since instability is undesirable in many of these applications, several methods have been proposed to increase the stability of thin films, including the addition of filler (nano)particles and other stabilizing agents. [93-94] Dewetting of ultra-thin films can provide information about the inter-surface forces that cannot be otherwise be directly detected. Additionally, it produces meso and nano patterns over wide areas. This is main motivation for current work to use dewetting of thin polymer films to produce nano-structures. However, the major drawback is the randomness of the dewetted structures that limits its applicability as a potential soft patterning method. To impose a long-range order in the dewetted structures, a number of approaches have been investigated. Combining with other top-down lithographic techniques, such as controlled dewetting on topographically or chemically patterned surfaces, can be used as one of the methods for aligning the structure. The feature size produced by the self-organized dewetting has two major limitations on the pattern resolution and its aspect ratio. The weak van der Waals destabilizing force and high surface tension which both severely restrict the minimum feature size. This restricts the spot size to greater than 1 μm in a model system of polystyrene (PS) thin film on silicon substrate, even for films as thin as 10 nm. Another drawback is the extremely narrow contact angle (<10°), which results in the relatively low aspect ratio of dewetted structures in air. Techniques that allow for a significant improvement in feature size and aspect ratio has been proposed. [95] The films were destabilized by dipping the PS thin films in a suitable solution of solvent (Methyl Ethyl Ketone) and water at room temperature. However, only a fixed composition of the solvent and water was used. The motivation for this work is to tune pattern ratio and its aspect ratio by various techniques such as changing the composition of solvent and water and also by modifying the surface properties such as wettability, etc.

## 1.7 Research Objectives

The global objective of the current thesis is the study of water-solvent induced instabilities in 1D and 2D polymer structures i.e., thin films and nanofibers. The specific objectives related to this are as follows:

- The study of effect of dewetting liquid mixture comprising of solvent and non-solvent on the length-scale parameters of dewetting of polystyrene thin film.
- The study of effect of modulating surface properties on the length-scale parameters of dewetting of polystyrene thin film.
- Formation of aligned droplets by dewetting of electrospinned Polystyrene nanofibers.

## 1.8 Structure of the thesis

The thesis is structured as follows:

**Chapter 2** deals with the role of solvent composition on the dewetting length-scale parameters of the intensified dewetting of polystyrene thin film under water-solvent mixture. In this, the 50 nm thin PS film was dewetted in dewetting mixture of solvent and water. The ratio of water to solvent was varied to study its effect on the length-scale parameters of dewetting i.e., the instability wavelength(λ) and droplet diameter(d).

**Chapter 3** discusses the effect of modulating the surface properties of the substrate on the length-scales of dewetting in water-solvent induced self-organized dewetting of thin polystyrene films. Here, Octadecyltrichlorosilane (OTS) self-assembled monolayer was deposited on cleaned glass substrates under low-pressure in dessicator. Further, the silanized substrates are coated with Polystyrene thin film and then immersed into an optimal mixture of good solvent and non-solvent. The effect of surface hydrophobicity on the length scale parameters of dewetting of thin Polystyrene film is investigated.

**Chapter 4** discusses the formation of aligned droplets by dewetting of electrospinned Polystyrene nanofibers and its comparison with Rayleigh-Plateau's model. Instead, of using film configuration, we had used fiber configuration to get more aligned deposition of nanostructures. The film is initially deposited with fibers and then dewetted and after dewetting again the film is deposited with fibers. Dewetting of fibers on previously dewetted substrates will increase the fiber density.

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