Doctoral Thesis

Gradients of nanotopography in polymers

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Publication Date: 2006

Permanent Link: https://doi.org/10.3929/ethz-a-005294187

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Gradients of nanotopography in polymers

A dissertation submitted to the
SWISS FEDERAL INSTITUTE OF TECHNOLOGY ZURICH
for the degree of
DOCTOR OF SCIENCES

presented by
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Diploma in Physical engineering, (ENSPG, Grenoble, France) 2002

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Zürich, June 2006
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Summary

Materials with gradients in surface properties have been receiving increasing interest due to their importance in various applications. The fabrication of surface gradients is, for instance, an attractive approach to combinatorial studies, since a whole range of conditions can be examined on a single sample. This increases the throughput of the experiments and saves a great deal of time compared to conventional “one sample per condition” experiments. Surface gradients can also provide new properties to surfaces, for example the ability to move liquids or control biological cell locomotion.

This work is concerned with the development of gradients in topography in polymeric materials. A special emphasis has been placed on controlling the length of the gradients. The fabrication of structured surfaces employed the phase separation properties of polymer blends. More precisely, thin polymer blend films on surfaces were made by spin coating on a substrate, solutions containing a mixture of two polymers in a common solvent. During this process, the system phase-separates, leading to a thin structured polymer film on the substrate. This technique, called polymer demixing, was chosen due to the numerous possibilities it offers for tuning the structure size and morphology.

Among the different parameters affecting the phase separation of polymer blend thin films, we focused on the influence of the surface energy of the substrate. The presence of the substrate/polymer interface can indeed modify the phase separation process due to the interplay
between the wetting of the surface by the polymers and the phase separation within the film. A preliminary study was made using separate substrates of different surface energies in order to identify appropriate polymer blend systems. Depending on the polymer blends, different changes in topography were observed on varying the surface energy of the substrate. The next step was the fabrication of gradients of topography along the surface using surface energy dependence. This was divided in two main parts: the fabrication of gradients at the centimetre scale and the sub-millimetre scale.

The substrates with centimetre-scale gradients in surface energy were prepared following a procedure reported in the literature. Following the method, a gold coated substrate was gradually immersed in a dilute solution of methyl-terminated thiols, followed by backfilling with hydroxyl-terminated thiols. The polymer blend solutions were spin coated on these substrates and the resulting gradients in topography were characterized by means of atomic force microscopy. A gradual transition in topography was achieved for each polymer blend along the sample. The lengths and positions of the gradients in topography on the surface-energy gradients depended, however, on the polymer blend used.

For the fabrication of short gradients in topography, wettability gradients at the sub-millimetre scale had to be designed. The wettability gradients were realized using a novel combination of TiO$_2$ photocatalytic lithography with gray-scale lithography. A TiO$_2$-coated glass slide was brought into the vicinity of a surface functionalised with a thiol monolayer. On exposure to UV, the thiol monolayer was degraded due to the photocatalytic properties of TiO$_2$. By designing a photomask with a short gray-scale gradient, the intensity of UV light illuminating the TiO$_2$ gradually varied along the sample, which resulted in a gradual degradation of the thiol monolayer. Polymer blend thin films were then spin-coated on these substrates to achieve short gradients in topography.

The last part of the study focused on the replication of gradients in topography in three different polymeric materials. Appropriate schemes for replication were developed in each case to ensure adequate structure transfer in each material.
L’emploi de matériaux présentant des gradients de propriétés de surface peut être utile dans différents domaines d’applications. L’utilisation de gradients permet, par exemple, de couvrir un grand nombre de conditions expérimentales sur un échantillon unique, ce qui peut être intéressant afin de réaliser des études combinatoires. La présence de gradients de surface permet dans certains cas de procurer aux surfaces de nouvelles propriétés telles que la capacité de contrôler le mouvement de liquides et la motilité cellulaire. Le contrôle de différents critères tels que la longueur et pente du gradient sont déterminant.

L’objectif de ce travail est la réalisation et caractérisation de gradients de topographie dans des matériaux polymères. Un accent particulier a été mis sur le contrôle de la longueur des gradients de surface à l’échelle centimétrique (dits gradients longs) et submillimétrique (dits gradients courts).

La première partie de ce travail concerne l’identification de mélanges de polymères les plus influencés par l’énergie de surface du substrat. L’impact de celle-ci sur la topographie des polymères a été caractérisée par microscopie à force atomique. Ceci a permis de sélectionner les deux mélanges de polymères suivant : PVA/Dextran et PMMA/P2VP.

Dans un second temps, des substrats présentant des gradients d’énergie de surface centimétriques (gradients longs) et submillimétriques (gradients courts) ont été réalisés et caractérisés, puis utilisés pour induire des gradients de topographie dans les mélanges de polymères déposés sur ces substrats.

Les gradients longs d’énergie de surface ont été fabriqués selon une technique basée sur l’immersion graduelle d’un substrat d’or dans une solution de thiols ayant un groupement terminal méthyle. En complétant la monocouche avec un thiol possédant un groupement terminal hydroxyle, un gradient de composition de thiols est obtenu, ce qui génère un gradient d’énergie de surface. Les mélanges de polymères déposés sur ces substrats présentent des transitions graduelles de topographie. Les longueurs et positions des gradients de topographie obtenus le long du gradient d’énergie de surface dépendent cependant du mélange de polymère utilisé. Pour chaque système employé, la transition de topographie s’étend sur 1cm pour une longueur de gradient d’énergie de surface de 2cm.

Concernant la fabrication de gradients à l’échelle submillimétrique, le même principe a été utilisé. La technique développée pour fabriquer les gradients d’énergie de surface à cette échelle combine la lithographie par photo-catalyse de TiO\textsubscript{2} et la lithographie à niveaux de gris. Ainsi, une plaque recouverte de TiO\textsubscript{2} est positionnée face à une surface fonctionnalisée avec une monocouche de thiol possédant un groupement terminal méthyle. Sous rayonnement ultraviolet, des radicaux créés sur la surface de TiO\textsubscript{2} dégradent la monocouche de thiol. En effectuant l’expérience avec un masque de photolithographie présentant des gradients de niveaux de gris, la monocouche de thiol est oxidée de manière graduelle. La longueur du gradient d’énergie de surface et celle du gradient de topographie induit sont contrôlées par le masque utilisé. Plus précisément, une transition de topographie sur une distance de 200µm a été observée lorsqu’un gradient de niveau de gris de 720µm a été employé pour fabriquer le gradient d’énergie de surface.

La dernière partie de ce travail concerne la réplication des surfaces présentant des gradients de structure dans trois différents matériaux polymères : le polydiméthylsiloxane, le Topas\textsuperscript{®} et
l’Affinity™. Dans ce but, des protocoles ont été spécifiquement développés pour chaque matériau en se basant sur les techniques de coulage ou pressage à chaud.
Chapter 1
Introduction

1.1. Potential applications of topography gradients

Advanced materials are taking a more and more important place in everyday applications. The constant interest to develop materials with new or improved properties has led to the emergence of a variety of techniques to tailor and tune, both in surface and bulk characteristics. In many cases, this requires the use of multi-component systems and sophisticated processes. The increasing complexity of the materials produced often demands the optimization of more and more complex structures. In this case, two main benefits can arise from the fabrication of gradients. First, they can play a key role in the optimization process of the material. Since a continuous range of conditions is screened along the gradient, this allows a combinatorial study of the system. Second, materials with surface or bulk gradients may exhibit new properties arising from this specificity. This opens additional routes for the design of new advanced materials and surfaces.

These two approaches have, however, fairly different aims: in combinatorial studies, the objective is to investigate the structure/function relation of the materials. In the second case, the
aim is to control the properties of the material using gradients. There is thus a need to develop techniques specific to each application.

This work deals with the fabrication of surface gradients of tunable dimensions. More precisely, we focused on the fabrication of gradients of nano-topography. The objective was to develop surfaces gradients allowing the investigation and control of the new properties arising from nanostructuring.

1.1.1. Long gradients for combinatorial studies

Historically, combinatorial approaches were first applied to pharmaceutical research where large numbers of parameters have to be investigated to identify the drugs of interest. Already a century ago, techniques were developed to make several experiments in parallel and increase the throughput of the experiments as shown in figure 1-1. The main benefit was the time saved compared with standard “one sample per one measurement” experiments. This advantage has been exploited in other fields like chemistry and materials science where parameter screening is becoming more and more important. This led to the development of more advanced tools for combinatorial studies. The fabrication of advanced materials frequently involves the fine tuning of multi-component systems in terms of surface and bulk chemistry, topography and morphology.

Figure 1-1: Historical parallel stirrer: six solutions could be stirred at the same time (taken from reference [1]).

This often requires a perfect control over numerous experimental parameters such as the composition of the system, the processing temperature, or the control of surface characteristics. These are involved in complex processes like phase transitions, chemical reactions, surface and interfacial phenomena that may occur during fabrication. The increasing complexity of the systems and processes used result in an increased number of variables to treat during the development of the material. Combinatorial techniques present many benefits in such cases. First,
they allow a much more detailed investigation of the system due to the large number of conditions tested during each experiment. Second, the timescale of the development phase is shortened due to parallel processing. Finally, they permit the realization of all the experiments simultaneously under exactly the same environmental conditions.

In many cases, high-throughput studies are made using combinatorial arrays screening numerous conditions in a single experiment. The most advanced setups are fully automated and allow tests of over a thousand conditions in a single run\textsuperscript{[2,3]}\textsuperscript{.} This was successfully applied to high-throughput experimentation in combinatorial chemistry\textsuperscript{[4]}, inorganic materials\textsuperscript{[2,5]} and polymer research\textsuperscript{[6]}. The use of combinatorial arrays already increases the throughput of the experiments compared with standard sequential experiments. However, the number of conditions covered is discrete, which limits the resolution of the technique. Furthermore, many transition phenomena such as phase separation in multi-component systems often result in abrupt changes in properties of the material. A precise determination of the position of such transitions may require very large combinatorial arrays.

One way to overcome this limitation is the fabrication of continuous gradients of the parameters investigated, which increases the number of conditions tested. One good example was reported by Meredith et al concerning polymer-blend phase separation\textsuperscript{[7]}. The authors developed a technique to produce polymer blend films presenting spatial gradients in polymer composition. By annealing the sample on a stage presenting a gradient in temperature, the morphology of the film for all (temperature, composition) conditions was obtained. This permitted the temperature at which the polymer blend phase separated to be identified for all compositions in a single experiment.

The design of the gradient used for combinatorial studies should however be adapted to the tools used to characterize the sample (optical microscopy, Fourier transform infrared spectroscopy, x-ray photoelectron spectroscopy). More precisely, the length of the gradient should be sufficiently large to provide the maximal number of measurements given the resolution of the characterization technique\textsuperscript{[8]}. In practice, gradients fabricated for combinatorial investigations are often several centimetres long, allowing easy characterizations.

1.1.2. **Gradients for materials with new properties**

The presence of bulk or surface gradient in a material can also confer new properties arising from
this specificity. Several examples can be found in nature illustrating the benefits of such materials. For instance, the outstanding mechanical properties of bamboo were found to arise from a structure gradient across the thickness of the culm. A fine analysis of the structure revealed an increase in fibre density from the inner part of the stem to its outer part. This morphology provides bamboo stems with a higher tensile strength than that of equivalent materials with a homogeneous structure. This example inspired the design of new material such as “functionally graded materials”\(^{[9,10]}\). The presence of structure gradients in materials improves properties such as the wear resistance, resistance to contact damage and better redistribution of stress within the material resulting in reduced cracking phenomena. One other well known example is the possibility to improve the interfacial bonding between two different materials by making a smooth composition gradient across the interface\(^{[9]}\).

Another example of new functionalities obtained using gradients can be found in optics. Standard optical lenses are generally made of a homogeneous material and are subjected to spherical aberrations, which limit their focusing capabilities. This problem arises from the difference in focusing between light rays striking the edges of a lens and the light rays closer to the optical axis. These aberrations can be corrected by adjusting the shape of the lens to modify the path of the light rays and correct the focusing. The lenses used in these cases (aspherical lenses) are however expensive to produce compared with standard lenses. Another mean to eliminate spherical aberrations has been suggested by nature: biological optical systems like eyes are also subject to this problem but use a very different strategy to solve it. For instance, in the eyes of some cephalopods, the spherical aberrations are corrected using a spherically symmetric refractive index gradients in the lens\(^{[11]}\). The presence of the gradient in refractive index adjusts the path of the light rays depending on their position relative to the optical axis and correct the aberrations. This led to the development of gradient refractive index (GRIN) lenses which are now commercially available.

In the examples mentioned above, gradients were introduced in the material to obtain a new property that would not exist in a homogeneous material. In these cases, the parameters of the gradient (slope, length) have to be tailored and optimized according to the functionality envisioned. The development of such functional materials thus requires a perfect control over the processes used to fabricate the gradients.
1.1.3. Surface gradients

Various properties of materials such as wettability, bio-compatibility, optical and tribological properties depend strongly on their surface characteristics (e.g. chemistry, topography). The correlation of surface structure and properties has been the focus of many studies in materials science, which led to an increasing interest for surface gradients.

Various studies have focused exclusively on the fabrication of surface gradients for combinatorial studies, which resulted in the development of long wettability, chemical and topography gradients\[12-14\]. This has allowed high throughput investigation of various surface phenomena. For instance, wettability gradients were used to explore the wetting properties of thin homopolymer films\[15\] and the influence of the substrate on the micro-phase separation of block copolymer films\[16\]. Wettability gradients were also widely used for the combinatorial investigation of biological processes such as the adsorption of proteins or the growth and proliferation of cells on surfaces\[12,17\]. Other studies also reported the combinatorial investigation of cell growth using surfaces coated with thin polymer blend films presenting composition gradients\[18,19\].

As mentioned before, the fabrication of surfaces with gradients also provides new functionalities to the materials. For instance the ability to control the wettability of the surface in a graded manner allows liquids to be moved and positioned. This application was first shown by Chaudhury and Whitesides using centimetre-long surface-energy gradients\[20\]. In that pioneering study, a drop of water was deposited on the substrate and the system was vibrated to make the droplet move toward the most hydrophilic side of the gradient. To have a spontaneous movement of the droplet, the design of the wettability gradient needs to fulfil precise criteria concerning the gradient slope and contact angle hysteresis for the drop to move\[21\]. Surface gradients can also be used to control the motion of biological cells on surfaces. Gunawan et al reported the fabrication of gradients of extra-cellular matrix protein for the control of cell migration and polarisation\[22\]. By making a steep enough gradient, the cells were polarized in the direction of the gradient.

Depending on the application envisioned, various kinds of gradients have thus to be designed. As mentioned above, the use of gradients for combinatorial studies requires the fabrication of long gradients in order to screen a maximal number of conditions. For other applications like liquid motion and positioning, the length of the gradient is not an issue, but the steepness of the gradients should be carefully designed. This is also the case for the control of cell migration: if
the slope of the surface gradient is not steep enough, the cells will not detect any preferential
direction to direct their migration.

1.2. Properties of nanostructured surfaces

Nanostructuring has been gaining increasing attention in the last decade due to the wide range of
properties (e.g. optical, mechanical, electronic) arising from the nano-structuring of materials.
Many experimental techniques emerged for both the fabrication and characterization of such new
materials.
The wettability of surfaces can for instance be enhanced by a structuring of the surface. Generally, a suitable chemical treatment of surfaces permits to control its wettability to a given extent. However, the fabrication of surfaces having super-hydrophilic or super-hydrophobic surface require a control of both the structuring and chemistry of the surface.
The optical properties of materials can also be modified in the presence of nanostructures on the
surface. Walheim et al reported for instance the fabrication of nanostructured thin films as antireflection coatings\textsuperscript{[23]}. The nanostructuring at the surface in that case permits in that case the refractive index of the material near the surface to be tuned and the transmission of the light in the material to be improved.
Another very active field of research nowadays is the investigation of the effect of nano-
topography on cell adhesion and proliferation. The presence of micro and nano-scale topography
was already shown to affect the behaviour of cells on surfaces\textsuperscript{[24,25]}. For instance, the presence of groove ridges on the surface can induce the alignment of cells along the ridges even with grooves only a few tens of nanometres deep. More pronounced effects were observed using nano-pitted surfaces, which made the surface completely non adhesive for cells\textsuperscript{[25]}.
The different properties arising from the nanostructuring of surfaces represent a good starting
point for the design of new kinds of topography gradients. For instance, the fabrication of antireflection coatings could be optimized using gradients of nanostructure to identify the best structure. The conditions to obtain super-hydrophobicity/hydrophilicity could also be explored by testing a whole range of conditions on a single topography gradient.
1.3. Fabrication of nanostructured polymer surfaces

Two main approaches can be distinguished for the fabrication of nanostructured surfaces: the top-down and bottom-up approaches. In the first case, the features are written directly in a sensitive layer using photolithography or e-beam lithography techniques. The structures can then be transferred in the substrate using an appropriate etching process. In the bottom up approach, the topography arises from the assembly of basic units into larger structures. The basic units can be for instance molecules such as polymers, block-copolymers or dendrimers. Various means to form the structures can be used depending on the basic unit employed.

The technique we chose to realize nanostructured surfaces was polymer demixing. This method uses the phase-separation properties of polymer blends to produce structured polymer thin films. More precisely, the films were made by spin coating a solution consisting of two polymers and a common solvent on a substrate. During the coating process, the two polymers phase separate and form a structured thin film on the substrate at the end of the process. One great advantage of this technique is the possibility to tune size and morphology with a diversity of parameters, which is a key point for the development of structure gradients. Potential parameters to tune the structure size and morphologies include:

- the polymer blend system chosen
- the composition of the polymer blend
- the molecular weight of the polymers
- the spin speed during spin coating
- the concentration of the starting solution
- the surface energy of the substrate
- the evaporation rate of the solvent
- humidity of the surrounding air

In this work, the effect of some of these parameters was investigated. However, we particularly focused on the effect of surface energy for the fabrication of the gradients of topography. More especially, the aim was to develop a means to transpose the surface energy variations of a substrate into topographic changes. One major part of the work concerned thus the preparation of substrates presenting gradients of surface energy.
1.4. Polymer blend phase separation

1.4.1. Theoretical background of polymer phase separation

The probability that a binary system undergoes mixing or phase separation is governed by its free energy of mixing. The system always evolves toward a minimal free energy, which can result in either a phase separation or a mixing of the components. This general principle is also valid for polymer blends where biphasic and single phase mixtures are observed. One outstanding model that describe the Gibbs free energy of polymer blends was developed by Flory and Huggins\[26\]. The model gives an understanding of the driving force behind phase separation and enables qualitative predictions of polymer blend phase diagrams.

Let us consider a system consisting of two polymers (A and B). Two situations for the system are possible as presented in figure 1-2.

\[
\begin{align*}
\text{Before mixing} & \quad \text{After mixing} \\
 n_A & \quad n_A + n_B \\
 V_A & \quad V_A + V_B \\
 G_A & \quad G_{AB} \\
 n_B & \\
 V_B & \\
 G_B & \\
 & 
\end{align*}
\]

Figure 1-2: Presentation of the variables used in the description of the process of mixing two polymers denoted A and B.

In the first place, the system consists of two phases: \(n_A\) moles of polymer A are contained in a volume \(V_A\) and \(n_B\) moles of polymer B contained in a volume \(V_B\). In the second situation, the two polymers are mixed in a single phase and \(n_A + n_B\) moles of polymer are contained in a volume \(V = V_A + V_B\). The change in Gibbs free energy upon mixing will be expressed as

\[
\Delta G_{\text{mix}} = G_{AB} - (G_A + G_B)
\]

where \(G_A, G_B, G_{AB}\) are respectively the Gibbs free energies of polymer A and B in the separated state and the mixed state. Mixing will occur only if the \(\Delta G_{\text{mix}}\) is
negative.

The Flory-Huggins treatment describe the Gibbs free energy of mixing as the sum of an entropic and an enthalpic term:

$$\Delta G_{\text{mix}} = \Delta G_{\text{loc}} - T \cdot \Delta S_t. $$

This describes the two main aspect of the mixing process. Firstly, mixing leads to an increase in the entropy associated with the motion of the centers of mass of all polymer molecules (translational entropy denoted by $\Delta S_t$) and may also influence the local interactions and motion of the monomers (represented by $\Delta G_{\text{loc}}$).

The increase in translational entropy ($\Delta S_t$) can be expressed as:

$$\frac{\Delta S_t}{R} = n_A \ln \left( \frac{V}{V_A} \right) + n_B \ln \left( \frac{V}{V_B} \right).$$

The volume fractions of the two components in the mixture are represented by: $\Phi_A = \frac{V_A}{V}$, $\Phi_B = \frac{V_B}{V}$

This leads to:

$$\frac{\Delta S_t}{R} = -(n_A \ln(\Phi_A) + n_B \ln(\Phi_B)).$$

We can then introduce the degree of polymerization ($N_A, N_B$) of the polymers:

$$N_A = \frac{V_A}{n_A} = \Phi_A \frac{n_c}{n_A} \quad \text{and} \quad N_B = \frac{V_B}{n_B} = \Phi_B \frac{n_c}{n_B}.$$

Where $v_A$ and $v_B$ are the molar volumes of each polymer given by: $v_A = V \frac{n_A}{n_c}$ and $v_B = V \frac{n_B}{n_c}$. and $v_c$ the molar volume reference unit given by $v_c = \frac{V}{n_c}$ ($n_c$: number of moles per reference unit). This assumes identical monomeric volume for both polymers, equal to $v_c$.

The entropy term can finally be expressed as:

$$\frac{\Delta S_t}{R} = -n_c \left( \frac{\Phi_A}{N_A} \ln(\Phi_A) + \frac{\Phi_B}{N_B} \ln(\Phi_B) \right).$$
The enthalpic contribution ($\Delta G_{loc}$) is expressed using the Flory-Huggins interaction parameter:

$$\Delta G_{loc} = \Phi_A \Phi_B n_C \chi RT$$

$\chi$ can be determined experimentally or can be expressed assuming a lattice model:

$$\chi = z (\varepsilon_{AB} - \varepsilon_{AA} - \varepsilon_{BB}) kT$$

$\varepsilon_{AB}, \varepsilon_{AA}, \varepsilon_{BB}$ represent the energies associated with the interaction between a segment of polymer A and B, A and A; B and B respectively. $z$ is the coordination number per lattice site.

The total Gibbs free energy of mixing finally has the following expression:

$$\Delta G_{mix} = RTn_C \left( \frac{\Phi_A}{N_A} \ln(\Phi_A) + \frac{\Phi_B}{N_B} \ln(\Phi_B) + \Phi_A \Phi_B \chi \right)$$

The Flory-Huggins treatment is the simplest model that describes polymer blend free energies. However, it already gives a lot of information concerning polymer phase separation. For instance, the entropy term, which always favours mixing, is reduced by the degree of polymerization of the polymer. This means that the entropic contribution vanishes for high degrees of polymerization and phase separation will in that case mainly be enthalpy driven. For negative values of $\chi$, the Gibbs free energy of mixing will always be negative and the blend will be miscible. For positive values of $\chi$, a calculation of the Gibbs free energy is needed to draw conclusions.

The Gibbs free energy of mixing versus the composition of the blend can be seen in figure 1-3. The calculation was made with $N_A = N_B = N$. Figure 1-3 a) show the free energy of mixing for different values of $\chi N$. For low $\chi N$ values, the curve is a purely concave shape and has a single minimum, which indicates the formation of a single phase (miscibility). For higher $\chi N$ values, a curve with two minima is obtained, which is typical of phase separating systems. To further analyse the curve, we will now focus on figure 1-3 b) and c) which show the free energy of mixing for $\chi N = 2.6$. 

10
Three situations are encountered:

First, for extreme compositions: \( \Phi_A \leq \Phi_{M1}, \Phi_A \geq \Phi_{M2} \), the system is miscible. Starting from a blend of composition \( \Phi^o \) any fluctuation in composition \( \Phi^+, \Phi^- \) would increase the Gibbs free energy as seen in figure 1-3 c). The system is in a “stable” state.

Second, for blends with compositions \( \Phi_{M1} \leq \Phi_A \leq \Phi_{S1} \) and \( \Phi_{S2} \leq \Phi_A \leq \Phi_{M2} \) the system is in a “metastable” state: small fluctuations in composition \( \Phi^+, \Phi^- \) would lead to an increase in free energy but larger ones \( \Phi^{++}, \Phi^- \) can decrease it.

Third, for composition \( \Phi_{S1} \leq \Phi_A \leq \Phi_{S2} \), any fluctuation in composition would decrease the free energy.
energy of the system. This means phase separation would decrease the free energy of the system. In that case, the system is said “unstable” and phase separation occurs systematically.

A phase diagram can then be plotted by plotting the limits between each case for all $\chi N$ values. This is shown in figure 1-3 d).

The curve separating the one phase from the two phase region is called the binodal line and corresponds to the coordinates $\Phi_{M1}, \Phi_{M2}$ for each $\chi N$ value. The binodal line can be calculated from the condition $\frac{d\Delta G_{\text{mix}}}{d\Phi} = 0$. This leads to the relation: $\chi_{\text{coex}} = \frac{1}{N} \frac{1}{(1 - 2 \cdot \Phi_A)} \ln \left( \frac{1 - \Phi_A}{\Phi_A} \right)$ for $N = N_A = N_B$.

The curve separating the metastable from the unstable states corresponds to the coordinates $\Phi_{S1}, \Phi_{S2}$ for each $\chi N$ value. It can be obtained from the condition $\frac{d^2\Delta G_{\text{mix}}}{d\Phi^2} = 0$ and leads to the relation: $\chi_s = \frac{1}{2 \cdot N \cdot \Phi_A \cdot (1 - \Phi_A)}$ for $N = N_A = N_B$.

One common point in the two cases ”metastable” and “unstable” is that the system will phase separate in order to achieve the lowest Gibbs free energy. The minimal free energy can be reached in both cases by segregating into two phases of compositions $\Phi_{M1}$ and $\Phi_{M2}$. However, the mechanisms to achieve the phase separation are very different. When the system lies within the spinodal line (”unstable” state), it phase separates via a mechanism called spinodal decomposition. If it lies between the binodal and the spinodal line, it will follow a nucleation and growth process. We will now discuss more in detail the main differences between these two mechanisms.

For a system in the metastable state, only large composition fluctuations lead to phase separation. In order to start the phase separation process, a droplet of the minority phase must be nucleated. The size of the droplet needs to be greater than a critical size in order to grow. The nucleation of the droplets is generally favoured by the presence of interfaces like impurities or surfaces. Once the nucleus is formed, it can increase in size. Growth occurs by diffusion of the polymer chains toward the depleted zone around the nucleated droplet. The final phase morphology is illustrated in figure 1-4: dots of one of the polymer are embedded in the other polymer.
In the case of an unstable state, the phase separation mechanism is very different as is the morphology obtained. As shown in figure 1-4 a), the typical morphology obtained after spinodal decomposition is an isotropic, bi-continuous structure. Different stages occur during spinodal decomposition. At early stages, small fluctuations in composition will initiate phase separation and grow as shown in figure 1-4. However, the fluctuations will grow at different rates depending on their wavelengths. Fluctuations with too long or too short wavelengths will grow slower and an intermediate wavelength will be amplified more strongly. The phase-separated structure will be dominated by this length scale. One striking difference compared with the nucleation and growth mechanism is the direction of the diffusion. In spinodal decomposition, the initial growth of the domains occurs by diffusion of the polymer chains against the composition gradient. In this case, the diffusion coefficient is indeed negative and this phenomenon is called “uphill” diffusion\[27\]. This is due to the fact that diffusion occurs toward a uniform chemical potential in the system and not a uniform composition. The polymer will thus diffuse down the chemical potential gradient, which does not always correspond to a diffusion flux down the composition gradient. The growth in amplitude of the fluctuations occurring in the early stage of spinodal decomposition is however time-limited. As mentioned above, the most favourable energetic configuration is a situation where the system is separated in two phases with well defined
compositions $\Phi_{M1}, \Phi_{M2}$. During the late stages of phase separation, the final compositions of each phase are reached (which is indicated on figure 1-4 by $\Phi_{M1}, \Phi_{M2}$). Since the fluctuations cannot grow further in amplitude, changes in the lateral size of the domains occur.

The Flory-Huggins treatment shows however several limitations. For instance it does not take into account important aspects of phase separation such as the interdiffusion of the polymers. To consider the interface between the two polymers and more generally the composition fluctuations in the polymer blend, an additional term in the Gibbs free energy of mixing was proposed by J.W Cahn and J.E Hilliard $^{[28,29]}$. This led to the following expression:

$$\Delta G(\Phi) = \int \left[ \Delta G_{\text{mix}}(\Phi) + \kappa(\Phi) \cdot (\nabla \Phi)^2 \right] \, dr$$

The additional term $\kappa(\Phi) \cdot (\nabla \Phi)^2$ is called the square gradient term and takes into account the composition gradients in the blend. This more advanced treatment was the basis of bi-dimensional and tri-dimensional numerical simulation of phase separation$^{[29]}$.

### 1.4.2. Wetting and surface-directed phase separation in polymer-blend thin films

The theory presented in the previous section concerned the phase separation of polymer mixtures in the bulk phase. The confinement of the polymer blend in a thin film can, however, greatly affect the phase-separation mechanism. Due to the presence of two interfaces (the substrate-polymer and air-polymer interfaces, the system is subjected to the interplay between the enrichment of the surfaces by the polymers and the phase separation of the polymer blend.

Several studies reported the formation of layered systems depending on the substrate used for the experiment $^{[30-32]}$. Different situations can however be encountered depending on the surface and the polymer blend. Since the polymer blend film is both in contact with the substrate and the air, two cases are expected: first, one polymer is preferentially attracted by the two interfaces (symmetrical case). Second, one polymer is preferentially attracted by the substrate while the other is enriched at the air interface (anti-symmetrical). Furthermore, for each situation we need to distinguish two sub-cases depending on the ability of the polymers to form a partially or completely wetting layer at the interfaces. These cases can be described using the Young’s equation in analogy with the wetting of surfaces by liquid drops. An alternative approach pioneered by Cahn used the square gradient mean field theory to model the wetting of the
polymer on the surface\textsuperscript{[33]}. This permitted later to describe under which conditions (value of $\chi$, $N$, surface energy difference between the pure components) partial or complete wetting can be achieved\textsuperscript{[34]}.

\textbf{Figure 1-5: Schematic illustrating the formation of surface directed spinodal decomposition waves. The process is characterized by uphill diffusion.}

One famous surface-induced phenomenon is the so-called Surface Directed Spinodal Decomposition (SDSD). In the bulk, a system quenched into the unstable state will phase separate following a spinodal decomposition process. The presence of an additional interface will lead to a preferential attraction of one of the polymer at the interface, leaving a depleted region in the bulk (see figure1-5). As explained before, the mutual diffusion coefficient of the polymers is negative for spinodal decomposition (uphill diffusion). The material will thus diffuse against the composition gradient, leading to a more enriched interface and a deeper depleted layer. In this way, composition waves can develop through the depth of the film. In contrast to bulk spinodal decomposition which is isotropic, surface-directed spinodal decomposition is strongly influenced by the surface and the composition waves develop normal to the surface. This results in the formation of layered systems. This phenomenon was first observed by Jones et al \textsuperscript{[34]} using a mixture of poly(ethylene-propylene) and its deuterated equivalent. The analysis of the composition profile of the film revealed oscillatory composition profiles characteristic of surface-directed spinodal decomposition. Other studies reported similar results using other polymer blends\textsuperscript{[30,35]}. This phenomenon was also subjected to several theoretical investigations\textsuperscript{[36,37]}.
1.4.3. Temperature quenched and solvent quenched polymer blends

As mentioned above, the phase separation of polymer blends occurs when the system is brought from a stable state (single phase) to an unstable or metastable state (biphasic). There are however different ways to induce phase separation experimentally; we will now present two of them: the temperature-quench and solvent-quench techniques.

In the first technique, the starting system is a binary polymer blend prepared in the one-phase region to form a homogeneous blend. The system is then subjected to a rapid change in temperature (temperature quench) to bring the blend from the one phase to the two phase region of its phase diagram.

The second approach uses a ternary system composed of two polymers and a good solvent for both polymers. At low polymer concentrations, the polymer chains are well dissolved and do not interact with neighbouring polymer chains. Upon removal of the solvent, the polymer concentration increases until a threshold value above which the system phase separates. The system then undergoes phase separation until it is completely depleted of solvent. The typical phase diagram of a such ternary blend is shown in figure 1-6. The polymer films made using the solvent quench approach are generally made by means of spin coating. This technique is a convenient way to make thin polymer film. When a polymer blend solution is spincoated on a substrate, a thin liquid film first forms due to centrifugal forces. There is then a balance between the centrifugal and viscous forces which determine the thickness of the liquid formed. In a second stage, the solvent evaporate, which leads to an increase in viscosity and initiate phase separation. This process produces a rapid quench of the system which is frozen in a non-equilibrium state. In this case the term “solvent quench” is employed.

One great advantage of the temperature quench approach is that the slow diffusion kinetics of polymer melts allow the different stages of phase separation to be monitored. This can then be compared with the theoretical treatments that have been well developed as presented in the previous section. From the theoretical point of view, the solvent quench technique is more difficult to model since it involves additional phenomena to take into account: for instance solvent evaporation which induces an increase of polymer concentration at the free surface, leading to polymer concentration gradients through the depth of the film. It also leads to cooling of the interface (evaporative cooling) which may affect film formation.
As mentioned in the previous sections, surface-gradients may find many applications in the fields of biology, chemistry and materials science. However, the design of the gradients depends strongly on the application envisioned: gradients designed for combinatorial studies are in
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general long to maximize the number of conditions screened. On the other hand, the length of the
gradient is not the critical parameter when gradients are used to move liquids or direct cell
locomotion. In these last two cases, the slope is the critical parameter to control. This variety of
applications has led to the emergence of different techniques permitting the creation of surface
gradients.

The aim of this section is to review the relevant contributions made by other researchers for the
fabrication of surface gradients. Emphasis was put on the techniques aiming at generating
chemical and topography gradients.

1.5.1. Fabrication of chemical gradients

Various approaches have been reported for the generation of chemical gradients depending on the
kind of gradient envisioned. One of the criteria was the gradient length. Several studies reported
the fabrication of centimetre-long gradients for combinatorial applications. The quality of the
chemistry is in some cases important: some applications only require a wettability gradient
whereas some other need surface gradients of specific functional groups. The generation of the
gradient is generally done by controlling the kinetics of deposition of self assembling molecules
on the surface or by gradually degrading the surface.

Many of the techniques developed used self assembled monolayers like thiols adsorbed on gold
surfaces or silanes deposited on glass or silicon wafers.

Pioneering work by Elwing et al reported the fabrication of wettability gradients based on the
gradual adsorption of silane molecules on a silicon oxide surface\textsuperscript{38}. The silane was dissolved in
a high-density solvent and the solution was then bedded under a low density solvent in which the
silane could diffuse. A silicon wafer was then immersed in the biphasic system. As the silane
diffused from the lower to upper phase of the system, it reacted with the surface, which resulted
in a gradient of silane molecule density along the samples. Two centimetre gradients were made
with water contact angles ranging from 20° to 90°. This technique was however limited to
surfaces reacting with organosilanes such as silicon oxide or glass.

Silane diffusion was also performed in the gas phase as proposed by Chaudhury et al\textsuperscript{20}. The
silane was, in this case, deposited near a silicon wafer. As it evaporated, it diffused in the gas
phase and created a concentration gradient along the sample. This induced a silane surface-
density gradient. Centimetre-long wettability gradients were achieved and successfully used to
control liquid droplet motion\cite{20,21,39}. One drawback of this approach was the difficulty of controlling the length and slope of the gradient. A more advanced procedure also based on silane diffusion in the gas phase was proposed later by Efimenko et al\cite{40}. In that case, the substrate used to make the gradient was a PDMS film. The film was stretched, subjected to UV ozone and exposed to the silane vapours. After release, the PDMS recovered its original shape and the length of the gradient depended on the extent of stretching of the polymer during the process. This allowed fabrication of much shorter gradients (from 5mm to 3cm long) and added a degree of control over the shape of the gradient.

The techniques presented above are based on control of the kinetics of silane deposition on the substrate in order to produce the gradient. An alternative was proposed by Robertson et al based on the gradual oxidation of a silane SAM\cite{41}. A complete SAM was exposed to sub-200nm UV radiation through a photomask with a gray-tone gradient. The amount of oxidizing species (ozone, atomic oxygen) generated by the UV radiation depended on the UV intensity and thus on the gray-tone. This resulted in the formation of a gradually oxidized silane SAM along the sample. The final chemistry of the layer was less controlled than in the previous cases but the shape of the gradient could be tuned using the photomask design.

One noteworthy contribution from Liedberg et al reported the use of thiol chemistry to achieve the gradients\cite{42-44}. Two different alkanethiols were interdiffused through a polysaccharide matrix deposited on a gold surface. The interdiffusion created a compositional gradient along the sample which induced a surface composition gradient. The main advantage of this technique was that a full monolayer was present over all the substrate and only the composition was varied. In the previous examples using silanes, a gradually incomplete monolayer is made.

Alkanethiols were also used in alternative approaches like the gradual adsorption of alkanethiols on a gold surface as reported by Morgenthaler et al \cite{13,45}. A very dilute solution of alkanethiols was made (0.00033mM) and a gold coated substrate gradually immersed into the solution in order to create a gradient of adsorbed alkanethiols along the sample. The sample was then immersed in a solution of a complementary thiol in order to obtain a complete SAM. This led to an alkanethiol composition gradient along the sample. This simple technique generates reproducible, well-defined chemical gradients.

The fabrication of more complex shaped composition gradients was proposed by Kraus et al using the micro-contact printing technique\cite{46}. A PDMS stamp having a thickness gradient was
soaked in a dilute thiol solution. Upon contact with a gold coated substrate, the thiol diffused from the PDMS network to the surface. Since the diffusion depends on the thickness of the stamp, this created a thiol composition gradient.

The techniques presented above lead to gradient lengths ranging from millimetres to centimetres. The fabrication of shorter gradients (sub-millimetre) was also reported but involved different approaches.

Micro-contact printing was used to generate chemical gradients at the micrometre and millimetre scale\[47\]. PDMS stamps with curved surfaces were used to transfer silane molecules on silicon oxide surfaces. The stamp was inked with silane and gradually pressed against the substrate. Due to surface curvature, the contact area between the PDMS stamp and the surface was gradually increased when pressure was applied, which resulted in a variation of contact time between the stamp and the surface along the sample. The shape of the resulting gradient was controlled by the profile of the starting PDMS stamp.

Another approach based on micro-fluidic networks was reported for the fabrication of complex shaped, sub-micrometre gradients\[48-50\]. A composition gradient in solution or on surfaces was achieved by controlling the diffusive mixing of two components flowing in micro-fluidic networks. This led to gradients ranging from hundreds of micrometers to several millimetres.

One alternative using micro-fluidic channels was reported by Fosser et al. \[51\]. PDMS micro-channels were positioned on a surface and filled with a protein-containing solution. By adjusting the filling kinetics of the micro-channels, the protein adsorption on the surface was controlled. The final gradients ranged from hundreds of micrometers to centimetres in length.

Other studies reported the control of thiol self assembly on gold using electrochemistry. By creating an in-plane electrochemical potential gradient, the thiols were gradually desorbed from the gold surface, leaving a gradient in thiol surface density\[52-55\]. The resulting gradient could also be backfilled to obtain a complete SAM\[54,55\]. This approach permitted to obtain centimetre long \[55\] as well as sub-millimetre gradients \[52,53\].

Electrochemical desorption of thiols was also used in a more advanced setup to produce sub-micrometer chemical gradients\[56\]. A scanning tunnelling microscope (STM) was used in order to selectively desorb SAM thiolates at the nanoscale. The amount of thiols desorbed was controlled by adjusting the bias between the STM tip and the surface or the scan rate. The experiment was made in the presence of a complementary thiol solution. The thiols dissolved in solution adsorbed
on the exposed gold regions. This permitted gradients as short as 600nm to be created.

1.5.2. Fabrication of topography gradients

The fabrication of gradients of topography has also been the focus of many studies. Topography can indeed greatly affect many surface phenomena like wetting \cite{57,58} or cell adhesion and proliferation\cite{18,19}. As a consequence, a full description of the surface takes into consideration both chemistry and topography. Various techniques have been developed to create gradients in topography. Most of the studies, however, aimed at fabricating gradient libraries for high-throughput studies\cite{8,59}. Polymers were attractive for that purpose, since they can be processed in different manners.

Temperature gradients were often used to induce morphology gradients in polymer films. As presented before, the phase separation of polymer blends is greatly affected by temperature. Depending on temperature, the polymers may either mix or phase-separate. Phase separation will occur via nucleation and growth or spinodal decomposition depending on the system and the temperature. Upon annealing a polymer blend film on a stage presenting a temperature gradient, Meredith et al were able to obtain a sample presenting a topography gradient\cite{7}. The film was flat and homogeneous at temperatures where the system mixed but structured where phase separation occurred. The complete transition between each region was observed on the sample.

The dewetting of polymer was also investigated using temperature gradients\cite{60}. Upon dewetting, holes are formed in the polymer film and grow at different speeds depending on temperature. By varying the temperature along the sample, a gradual change from large to small holes was observed. For the highest temperatures, the holes grew faster and impinged to form polygons.

Temperature gradients were also used to control the kinetics of polymer crystallization\cite{19,61}. A thin film of a crystalline polymer was brought above its melting point and undercooled on a stage presenting a temperature gradient. After the annealing, the film was quenched to room temperature. The crystallization kinetics were greatly affected by temperature and spherulites only formed at low temperatures. For low undercooling (high temperatures), the film remained flat.

In a slightly different approach, structured polymer films of low-density polyethylene were placed on a heating stage with temperature gradient and annealed to partially melt them\cite{62}. One side of the sample was brought to a temperature well above the melting point of the polymer.
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while keeping the other extremity at room temperature. After annealing, the structure of the film was preserved on the cold side of the gradient only. A progressive flattening of the topography was observed along the sample and the film was completely flat on the heated side. A similar protocol was used by Zhang et al with a monolayer of polystyrene beads\cite{63}. The starting rough sample was a monolayer of polystyrene beads deposited on a substrate. One extremity of the sample was brought above the glass-transition temperature of polystyrene while keeping the other below. The beads coalesced giving a decrease in surface roughness. A gradual change in RMS roughness from 45nm to 15nm was observed.

Temperature is thus an effective way to control the structure of polymer films but the different processes mentioned (crystallization, phase separation, dewetting) can also be tailored by varying other parameters. For instance, the strong dependence of polymer phase separation on the composition of the blend was employed by Meredith et al who developed a casting technique that created gradients of composition\cite{7}. After annealing, the structure of the polymer blend thin film was different depending on the composition.

Crystallization of polymers was also controlled using polymer blends\cite{18}. A polymer blend thin film of poly(L-lactic acid) (PLLA) and poly(D-lactic acid) (PDLA) was made using the casting technique proposed by Meredith et al\cite{7} to obtain a composition gradient along the sample. Upon crystallization, the composition gradient was transposed in a gradient in topography since only PLLA is crystalline. On the PDLA side, the polymer film was flat since it was amorphous and a gradual increase in roughness was observed toward the PLLA rich side. The resulting polymer film had a RMS roughness gradient ranging from 10 to 70nm.

The last technique developed for the fabrication of structure gradients used surface energy gradients. The nature of the substrates supporting thin polymer films plays a key role in many processes like dewetting\cite{15,64}, polymer blend phase separation \cite{31,32,65} and block-copolymer micro-phase separation\cite{66}. This effect was well studied using homogeneous samples but only few reports can be found concerning gradients. For instance, Ashley et al made a combinatorial study of polystyrene dewetting on a substrate bearing a surface energy gradient and observed a transition in the morphology of the topography due to the changes in surface energy\cite{15}. Genzer et al used gradients in surface energy to study the wetting behaviour of a binary polymer blend\cite{67}. The authors however focused on the morphology change through the depth of the film and did not mention how the lateral phase morphology was affected.
1.6. Aim of the thesis

The development of surfaces presenting gradients in properties is motivated by two main fields of applications. First, the fabrication of surface gradients is an attractive approach to realize high throughput studies, since they allow a large number of conditions to be screened during a single experiment. Second, surface gradients play a major role in the development of new functional materials.

Many techniques have been proposed for the fabrication of surface gradients and various applications have already been demonstrated. Until now, however, the techniques proposed all focused on a defined gradient (long or short, smooth or steep) and very few studies aimed at controlling all gradient parameters\(^{[40]}\).

The experiments reported in this thesis were motivated by the need to develop more flexible techniques to create tunable gradients in topography with controlled length and steepness. The main focus was the realization of centimetre-long as well as sub-millimetre gradients of topography using the same approach. Another constraint concerned the kind of topography to be generated. As seen before, various surface properties arise from the structuring of surfaces at the nano-scale; this work aimed at fabricating nano-topography gradients more particularly. The last objective was to avoid the presence of chemical variations along the final gradient since this can modify the properties of the surface. The presence of both chemical and topographical variations along the sample would indeed not permit the influence of topography on the surface properties to be determined.

The method chosen for the fabrication of structured polymer films was based on the phase-separation of polymer blends in thin films. More especially, the influence of surface energy on the phase separation process was used to transpose surface energy gradients into gradients of topography. Emphasis was thus put on both the fabrication of structured polymer films and the fabrication of substrates presenting gradients of surface energy.

1.7. Structure of the thesis

Chapter 2 presents the different polymers and materials and describes the characterization techniques and data-processing procedures used in this work.
Chapter 3 presents the technique developed for the fabrication of the topography gradient. It is based on the influence of surface energy of the substrate on the morphology of phase-separated, polymer-blend thin films. The different polymer-blend systems are first presented. A preliminary study of the effect of surface energy is also made to identify the most promising polymer blends. The selected polymer blends are then subjected to a more detailed study in order to determine over which ranges of surface energy changes are observed. By using a substrate presenting a gradient of surface energy, topography gradients can then be generated. This chapter focuses exclusively on the fabrication of centimetre-long gradients.

Chapter 4 focuses on the fabrication of short structural gradients using the same principle as presented in chapter 3. A technique combining TiO$_2$ photocatalytic lithography and gray-scale photo-lithography is explored to gradually degrade an alkanethiol SAM and produce gradients in thiol composition. This permitted sub-millimetre wettability gradients to be realized. The substrates produced can then be used to realize short structure gradients.

Chapter 5 presents the technique developed for the replication of the structured polymer thin films in other material. This was mainly motivated by the need to create surfaces having gradients of topography without any chemical variations of the surface. The replication in three polymers is investigated and three specific protocols based on casting and hot embossing are presented.

Chapter 6 summarizes the main conclusions of the thesis and the potential directions for future work.

In appendix 1, results of an industrial project made in collaboration with the firm Ilford are presented. The goal of the study is the fabrication of nanoporous polymer layers on ink-jet printer media. The technique developed uses a two step procedures: polymer-blend thin films are first fabricated on flat substrates and then transferred on the ink-jet media. The tunability of the pore dimensions is demonstrated by adjusting various parameters affecting polymer phase separation. This appendix also presents also an approach using photocrosslinking to produce stable structured, polymer layers.
Chapter 2

Materials and Methods

In this chapter, the technical details of the experiments made in this work are given. The different polymers, solvent, substrates used for the study are listed. The cleaning procedures are described, as well as the different protocols used for surface preparation. As mentioned in the introduction, one central point in this work is the fabrication of polymer-blend thin films. The equipment and techniques used to form such films are thus presented as well as the characterization tools used in the study.

2.1. Solvents

Different solvents were used in this study and each of them had a specific role. Some were used to clean substrates, others to dissolve polymers or alkanethiols. The quality of the solvents was very important since they are a source of contaminations. More especially, the substrate surface-energy preparation was a crucial part for the polymer film formation and any contamination of the surface (organic molecules, dust) could affect the polymer film formation. A lot of attention was thus paid to the choice, the handling and the storage of the solvents in order to avoid these potential problems. The table 2-1- describes the different solvents used in the work and their use.
Table 2-1: Description of the different solvents used in the study and their use.

<table>
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<th>Solvent</th>
<th>Quality</th>
<th>Supplier</th>
<th>Use</th>
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<td>Merck</td>
<td>Thiol solvent</td>
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<td>Substrate rinsing, polymer solvent</td>
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</tbody>
</table>

### 2.2. Polymers

This part describes the different polymers used for the work and provides experimental details concerning the fabrication of the polymer blend solutions. The different polymers used are first presented and the polymer blend solutions used are then specified for each experiment.

#### 2.2.1. Homopolymer solutions

Dextran and PDADMAC were dissolved in water at the desired concentration and left overnight to ensure a complete dissolution. PVA did not dissolve spontaneously at room temperature. It could be dissolved by heating the solution at 80°C under continuous stirring for 30mn. The solution was cooled down to room temperature before use.

Concerning the PVA-Sbq, the polymer was received as a 13% w/v solution of polymer dissolved in
buffer. The solution was diluted to 3\% w/v and dialysed with water (molecular weight cut-off of 10000). Since PVA-Sbq is photosensitive, direct contact of the polymer solution with light were avoided during its dialysis and storage.

The dissolution of P2VP in MEK and PS in o-xylene was complete within few hours. PMMA had to be left overnight under shaking to ensure its complete dissolution in MEK or toluene.

Table 2-2: Description of the different polymers used in the study.

<table>
<thead>
<tr>
<th>Polymer name</th>
<th>Abbr.</th>
<th>Supplier</th>
<th>Solvent used</th>
<th>$M_w$ [kDa]</th>
<th>$M_w/M_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly(vinylalcohol), 90% hydrolysed</td>
<td>PVA</td>
<td>Polymer standard service, Mainz, Germany (PSS)</td>
<td>Water</td>
<td>40.50</td>
<td>1.94</td>
</tr>
<tr>
<td>Photosensitive</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Poly(vinylalcohol): SPP-H-13 Bio</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>88% hydrolysed</td>
<td>PVA-Sbq</td>
<td>Toyo Gosei Ltd</td>
<td>Water</td>
<td>70.00</td>
<td>2.19</td>
</tr>
<tr>
<td>Poly(diallylmethyl ammonium chloride)</td>
<td>PDADMAC</td>
<td>PSS</td>
<td>Water, Acetic-acid</td>
<td>44.80</td>
<td>1.47</td>
</tr>
<tr>
<td>Dextran</td>
<td>Dextran</td>
<td>Fluka</td>
<td>Water</td>
<td>50.00</td>
<td>1.30</td>
</tr>
<tr>
<td>Poly(methylmethacrylate) (low quality)</td>
<td>PMMA</td>
<td>Sigma Aldrich fine chemicals, St. Luis, USA</td>
<td>Toluene</td>
<td>102.6</td>
<td>2.12</td>
</tr>
<tr>
<td>Poly(methylmethacrylate) (high quality)</td>
<td>PMMA</td>
<td>PSS</td>
<td>MEK, o-xylene</td>
<td>106.00</td>
<td>1.05</td>
</tr>
<tr>
<td>Poly(2-vinylpyridine)</td>
<td>P2VP</td>
<td>PSS</td>
<td>MEK, Ethanol</td>
<td>79.10</td>
<td>1.05</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>PS</td>
<td>PSS</td>
<td>o-xylene</td>
<td>101.00</td>
<td>1.03</td>
</tr>
</tbody>
</table>

2.2.2. Polymer blends used in the study

Table 2-3 shows the different polymer blends used in this work. The polymer blend solutions were made by simply mixing homopolymer solutions at specific ratios and leaving them to mix under shaking. All the polymer solutions were stored in the fridge to avoid solvent evaporation, but before use they were always allowed to equilibrate to room temperature.
Table 2-3: Description of the different polymer blends used in the study.

<table>
<thead>
<tr>
<th>Polymer 1</th>
<th>Polymer 2</th>
<th>Common solvent</th>
<th>Selective solvent</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVA</td>
<td>PDADMAC</td>
<td>Water</td>
<td>Acetic acid (removal of PDADMAC)</td>
<td>From 10 to 50 mg/mL</td>
</tr>
<tr>
<td>PVA</td>
<td>Dextran</td>
<td>Water</td>
<td>no</td>
<td>From 10 to 50 mg/mL</td>
</tr>
<tr>
<td>PMMA</td>
<td>P2VP</td>
<td>MEK</td>
<td>Ethanol (removal of P2VP) o-xylene (removal of PMMA)</td>
<td>10 mg/mL</td>
</tr>
<tr>
<td>PS</td>
<td>PMMA</td>
<td>Toluene</td>
<td>-</td>
<td>10mg/mL</td>
</tr>
<tr>
<td>PVA-Sbq</td>
<td>Dextran</td>
<td>Water</td>
<td>no</td>
<td>20mg/mL</td>
</tr>
</tbody>
</table>

2.3. Substrate preparation

The thin polymer films were spin coated on different substrate depending on the experiments. The substrates used were either silicon wafers or gold-coated silicon wafers with a thiol monolayer. In the case of surface-energy gradients, more complex preparation protocol were used. This section gives the details of the surface preparation.

2.3.1. Cleaning protocols

Surface preparation was a crucial part of the experiments since it permitted us to have reproducibly clean surfaces. In all cases, the polymer films deposited on the substrates all had sub-100nm thicknesses and any discrepancy due to impurities/dust particles could have influenced the homogeneity and the integrity of the resulting films. Different kinds of substrates were used in the experiments. Silicon wafers (Type: P/Bor, <100>, Thickness: 500µm) were ordered from Siltronix (Archamps, France). Glass slides were purchased from Menzel Gmbh (Braunschweig, Germany).

Silicon wafers and glass slides were cleaned using a Piranha treatment. A blend of sulphuric acid and hydrogen peroxide (4 : 1)v/v was first made. Since the reaction is exothermic, the solution heated up to 100°C. The solution was further heated to 120°C and the substrates were dip for 10 minutes. After removal from the Piranha solution, the substrates were rinsed in flowing MilliQ
water. Since the surfaces obtained after this procedure are highly hydrophilic, they were stored in MilliQ water and nitrogen blow dried when needed.

In some cases, a gold layer was deposited on clean substrate before further processing. Gold (purity 99.99%) was purchased from Umicore. Gold coated substrates were prepared by evaporation using a Leybold e-beam evaporator. A 30nm chromium layer was first evaporated to improve the adhesion of the gold layer on the substrate. A 120nm thick gold layer was then evaporated on top of the chromium. The gold-coated substrates were always cleaned before use.

For this, the substrate were rinse two times in acetone, then one time in MilliQ water (to remove acetone traces) and nitrogen blow dried. The substrate were then exposed to an oxygen plasma (Exposure time: 3 minutes, Power: 30W, Gas: O₂ 0.250torr). The oxygen plasma was performed with an Oxford Instruments Plasmalab 80 Plus (Oxford Instruments Plasma Technology, Bristol, United Kingdom, equipped with a ENI ACG-3LP4 RF Power Generator, MKS, Wilmington, USA). After oxygen plasma, the substrates were rinse 10 minutes in ethanol to remove the gold oxide formed during the oxygen plasma. The substrates were finally nitrogen blow dried and directly dipped in a thiol solution.

2.3.2. Formation of thiol self assembled monolayers

Gold coated substrates were immersed in thiol blend solutions to form thiol self-assembled monolayers (SAM). Two thiols were used in this study: (CH₃(CH₂)₁₁SH (1-Dodecanethiol 98+%) and (HO(CH₂)₁₁SH (11-Mercapto-1-undecanol 97+%). Both were purchased from Aldrich Chemicals (Milwaukee, WI).

The thiols were dissolved in ethanol at a concentration of 1mM. Different thiol blend solutions were done varying the ratio between the two thiols. The gold coated substrates were then dipped overnight in the thiol solutions to ensure a complete ordering of the thiol monolayer. The surfaces were then rinsed with ethanol and nitrogen blow dried. Surfaces exposed to CH₃(CH₂)₁₁SH solutions were hydrophobic and those exposed to HO(CH₂)₁₁SH were hydrophilic.

2.3.3. Repeating gradients of surface energy

The experimental protocol for photocatalytic lithography experiments was divided in three parts:

- Fabrication and cleaning of the TiO₂ layer.
- Preparation of a thiol SAM and exposure to UV.
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- Backfilling of the thiol layer to have a complete SAM.

2.3.3.1. Fabrication and cleaning of the TiO$_2$ layer

The TiO$_2$ layer was done by spin coating a TiO$_2$ suspension on a glass slide. The TiO$_2$ suspension (STS-01) was kindly supplied by Ishihara Sangyo Gaisha, ltd (Yokkaichi, Japan). 700µm thick glass slides were used. The glass slides were first cleaned with piranha solution as mentioned above and rinsed in MilliQ water. The glass slides were then blow dried with nitrogen and directly put on the spin coater. The substrate was spun at 10000rpm and when the final speed was reached, 200µL of TiO$_2$ suspension were dispensed onto the glass slide. After this coating step, the slides were baked for one hour at 400°C in a furnace (Nabertherm, model L15/12/P320, Bremen, Germany). This step permitted all the organic traces in the layer to be burned out. The last step for the preparation of the TiO$_2$ was the activation of the surface. Before use, the slides were exposed to an oxygen plasma (exposure time: 15minutes, Power: 30W, Gas: O$_2$ 0.250torr). This led to super-hydrophilic TiO$_2$ surfaces that could unfortunately become contaminated in contact with air. The TiO$_2$ coated slides were thus never used more than 10mn after the oxygen plasma.

2.3.3.2. Preparation of the thiol SAM and exposure to UV

The thiol used for the preparation of the SAM was a CH$_3$(CH$_2$)$_{11}$SH, diluted in ethanol at a concentration of 1mM. Gold-coated substrates were then dipped overnight in the thiol solution. After thiol adsorption, the substrates were rinsed in ethanol and blow dried with nitrogen. A home-built holder was used to make the assembly composed of the sample, the TiO$_2$-coated glass slide and the photomask. The photomask used for the experiments was custom designed in order to have four kinds of gradients (one 1.8cm long gradient and three short gradients: 1080, 720 and 360µm long). The mask was fabricated by Photronics (UK) ltd (Manchester, United Kingdom). All the gradients were done with twelve different grey tones (twelve steps). To achieve different gradient lengths, the step sizes were varied. The long gradient had a step size of 1.5mm for a final length of 18mm. The short gradients had step sizes of 90; 60 and 30µm for final lengths of 1080, 720 and 360 µm respectively. Figure 2-1 shows a photograph of the photomask obtained.
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The UV lamp used for the exposures was an Oriel 300W solar ultraviolet simulator, equipped with an Oriel 68851 Light Intensity Controller, an Oriel 84350 Digital timer and UVB/C blocking filter. The irradiance of the lamp was 17mW/cm² at a wavelength of 365nm. The assembly was then exposed to UV for the desired time.

2.3.3.3. Backfilling of the thiol SAM.

After UV exposure, the sample was rinsed in ethanol for 5 minutes. This permitted the thiols degraded during the UV exposure to be wash away. The SAM obtained was not complete and a backfilling step was done using a solution of HO(CH₂)₁₁SH diluted at 1mM in ethanol. The backfilling lasted 10 minutes. The samples were finally rinsed in ethanol and blow dry with nitrogen.

Figure 2-1: a) Photograph of the photomask used. b) Graphs showing the variation of the absorbance along two different gray-tone gradients.
2.4. Polymer film fabrication

2.4.1. Spin coating

The polymer thin films made in this study were all prepared by spin coating. In this process, a drop of the polymer solution is deposited on a flat substrate. The substrate is then spun at a given speed. The solution spreads over the surface due to centrifugal force and a liquid film is formed on the surface. A large amount of solution is thrown off the sample during this stage. In a second step, the solvent of the polymer solution evaporates until the solidification of the polymer. This leads to a thin polymer film forming on the substrate.

![Spin coating process diagram](image)

In this study, the solution for spincoating always consisted of two polymers dissolved in a common solvent. The prepared solution is dilute enough so that the two polymers coexist in a single phase. When the solution is then spin coated onto a substrate, the solvent evaporates, which results in an increase in the concentration of the solution. When a threshold concentration is reached, the system starts to phase separate. The phase separation occurs until the system is completely depleted of solvent. The final film shows a phase-separated morphology. Typical morphologies of thin polymer blend films obtained by spin coating are presented in figure 2-2.

![AFM images](image)
The spin coating was performed in ambient air at spin coating speeds ranging from 1 000 to 10 000 rpm.
Humidity was in some cases controlled using the setup shown in figure 2-3.

![Figure 2-3: Schematic of the setup used to control humidity in the spin-coating chamber.](image)

The ambient temperature was always equal to 21°C. Relative humidity was varied by changing the ratio between dry and moist nitrogen. The gas was flowed in the spincoating chamber. Before each spincoating, the flow was stopped and the system allowed to equilibrate. Relative humidities ranging from 20% to 40% were investigated and the experiments were always performed at 21°C. This corresponded to changes in dew-point temperature from -3°C to 10°C.

One important point in this study was the type of substrate used for the spin coating and more especially its surface energy. In most cases, the substrates used were gold-coated silicon wafers functionalised with a thiol SAM. Different surface energies were used and the substrates were hydrophilic, hydrophobic or even both in the case of gradients. For very hydrophobic substrates (having water contact angle of 110° for instance), a direct use of the substrate may result in a bad quality of the coating due to the dewetting of the solution on the substrate. To overcome this problem, the substrates were scratched on their periphery in order to roughen the surface. This resulted in an increase the contact-angle hysteresis, which prevented the solution from dewetting the surface. Only the centre of the sample was then characterized.

For some polymer blends, the substrates used for spincoating were silicon wafers coated with thin films of PMMA. For this, a solution of PMMA diluted to 3% w/v was spincoated at 3000rpm on a clean silicon wafer. This lead to homogeneous, 100nm thick, PMMA layer. This permitted
to have reproducible hydrophobic surfaces. Such substrates were used with systems where used more particularly with systems consisting of water-soluble polymers.

### 2.4.2. Selective removal of polymers

One important step was the selective removal of one polymer from polymer blend films. This was done for two reasons: first, the selective dissolution permitted us to determine the phase morphology of the polymer blend. By comparing the structure of the polymer film before and after the selective solvent treatment, we could get insight on the lateral and vertical morphology of the polymer film. This was done by dipping the sample in a solvent selectively dissolving one of the components of the blend. This step was investigated in details for the different polymer blend used. To identify the potential selective solvents for each polymer blends, the solubility of the different polymers were investigated for various solvents.

As shown in table 2-4, various selective solvents were identified for each polymer blend. For PVA/PDADMAC blend, acetic acid was used to dissolve selectively PDADMAC. For PMMA/P2VP blend, ethanol was used to remove P2VP.

Table 2-4: Summary of the solubilities of the different polymer used in various solvents.

<table>
<thead>
<tr>
<th>Polymers</th>
<th>Water</th>
<th>Acetic acid</th>
<th>Ethanol</th>
<th>MEK</th>
<th>o-xylene</th>
<th>Toluene</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMMA</td>
<td>-</td>
<td>-</td>
<td>no</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
</tr>
<tr>
<td>P2VP</td>
<td>-</td>
<td>-</td>
<td>yes</td>
<td>yes</td>
<td>no</td>
<td>no</td>
</tr>
<tr>
<td>PVA</td>
<td>yes</td>
<td>no</td>
<td>no</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PDADMAC</td>
<td>yes</td>
<td>yes</td>
<td>no</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Dextran</td>
<td>yes</td>
<td>no</td>
<td>no</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

As can be seen in table 2-4, toluene and o-xylene were two candidates for removal of PMMA. However, this did not lead to a complete removal of PMMA in either case. A special procedure was thus used to remove PMMA: the polymer blend film was first exposed 15mn under UV before rinsing 2min in o-xylene and blow dried with nitrogen. However, no selective solvent was found for PVA/Dextran system.
2.5. **Instruments**

2.5.1. **Atomic force microscopy**

Atomic force microscopy (AFM) was invented in 1986\cite{68}, a few years after the invention of scanning tunneling microscopy in 1982\cite{69,70}. Both of these techniques are nowadays very important tools for the characterization of surfaces on the nanoscale. They indeed permit the investigation of various material properties such as topography, friction, elasticity, electrostatic or magnetic properties with near-atomic resolution. Imaging can also be performed in controlled environments and in liquid. Many commercial systems are now available and we used for this work a scanning probe microscope (Dimension 3100, Veeco Digital Instruments, New York, USA) equipped with a NanoScope IIIa controller (Veeco, New York, USA).

![Dimension3100 AFM](image)

*Figure 2-4: Picture of the Dimension3100 AFM used in the study.*

Atomic Force Microscopy uses the interactions of a probe with the surface of the sample to measure its characteristics locally. By scanning the probe over the surface to analyse, an image of the surface properties can be obtained. In practice, the probe is a micro-fabricated cantilever with a sharp tip at its end that bends when interacting with the surface. To detect the bending of the cantilever, a focused laser beam is reflected off the back of the cantilever and the direction of the reflected beam is monitored using a four-quadrant photo-detector.

As the cantilever bends, the position of the laser beam on the photo-detector changes. By
comparing the signals measured in the lower and upper quadrants, the vertical deflection of the cantilever can be determined. To obtain a characterization of the complete surface, an x-y piezoelectric element is used to scan the tip relative to the surface. A z piezoelectric element is used to control the space between the tip and the surface.

If the tip is scanning the sample at a constant height, the signal recorded is the movement of the laser beam on the photo-detector. Depending on the tip-surface interaction force, the cantilever will bend, which will modify the direction of the reflected laser beam. The system can also be operated in a different mode called constant-force mode. In that case, a working set-point is first given by the user. A feedback loop compares the signal measured on the photo-detector with the set-point and modifies the tip-surface distance until the measured signal matches the set-point. If the feedback-loop parameters are correctly adjusted, the signal measured by the photo-detector should be constant and equal to the set-point value. In that mode, the relevant measurement is thus not the signal of the photo-detector but the vertical position of the tip for each position of the scan.

One of the most common operating mode of AFM is called contact mode. A soft cantilever (typical spring constant of 0.2 N/m) is brought in close contact with the surface and its deflection is monitored during scanning. When it is operated in constant force mode, the feedback is done using the deflection of the cantilever and it corresponds to a constant deflection mode.

While contact mode is well adapted for the characterisation of hard surfaces, it can pose problems with soft surfaces like polymers, since it may cause damage during scanning. However, it permits also the friction properties of the samples to be characterized. In that case, the cantilever is scanned perpendicularly to its main axis. The friction force between the tip and the sample leads to a torsion of the cantilever. This results in a lateral movement of the laser beam spot on the four-quadrant detector. A direct measure of the friction can thus be made. The images obtained reveal the heterogeneities in friction coefficient along the sample which can for instance be due to variations in surface energy or chemistry.

The second most common mode of AFM is tapping mode. In contrast to contact mode, it requires a very stiff cantilever (typical spring constants of 40 N/m). In tapping, the cantilever is oscillated near its resonance frequency using a piezoelectric element. The signal obtained on the photo-detector is an oscillating beam spot. If the tip is brought in the vicinity of the surface, the amplitude of the cantilever oscillation is modified due to the interaction forces. The amplitude of
the oscillation of the beam spot on the photo-detector is thus a direct measurement of the interaction forces. When operated in constant-force mode, the user chooses an amplitude set-point. The feedback is then done using the oscillation amplitude and the system adjusts the tip’s vertical position in order to maintain the amplitude at the set-point value chosen. In tapping mode, the tip just intermittently hits the surface and allows thus the imaging of soft samples. Another measurement can be obtained using tapping mode using the phase of the oscillation. In this so-called phase imaging mode, the phase shift of the oscillating cantilever relative to the driving signal is measured. The phase shift depends on the interactions between the AFM tip and the material; it is very sensitive to variations in material properties such as adhesion and viscoelasticity. It can be useful to differentiate different components in a blend even if the topography is very smooth.

In this work tapping mode was mainly used since it was better adapted to the characterisation of thin polymer film. The topography was recorded for all the samples and phase imaging performed in some cases. Friction measurements were also made in order to characterize the phase morphology of polymer blends. The motorised stage of the AFM was intensively used for the characterisation of the gradient of topography.

2.5.2. Scanning electron microscopy

Scanning electron microscopy is a highly efficient imaging tool to look at micro and nanoscale structures for information such as structure, elemental analysis and distribution. The sample is imaged in vacuum (~$10^{-4}$ - $10^{-5}$ torr) with electron beam used as probe.

The SEM used in this work is a Philips ESEM-FEG XL30 (Philips, Netherlands), equipped with an Energy Dispersive X-ray Spectroscopy (EDAX, Mahwah, USA) for chemical analysis. For cryo-SEM experiment the microscope was equipped with a Gatan Alto 2100cryo transfer module. An electron gun is used to produce electrons having energies ranging between 0.1 and 30 keV. The electron beam is then shaped by means of magnetic lenses and focused on the sample to analyse. By scanning the sample with the beam, a map of the electron/surface interaction is obtained. When the primary electrons strike the surface, they are elastically and inelastically scattered by the atoms in the sample. Through these scattering events, the primary beam effectively spreads inside a sample volume and the interactions in this region lead to the subsequent emission of secondary electrons, back scattered electrons and characteristic X-Ray.
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Figure 2-5: Photograph of the ESEM used in the study.

The best characterization was obtained using secondary electrons since they are the most sensitive to topography. Secondary electrons result from the inner shell ionization of the atoms. Because of their low energy (less than 50eV), only those created within a few nanometres of the sample surface can escape. The intensity of the signal detected depends on the angle between the incident beam and the surface analysed. As the angle of incidence increases, more secondary electrons are emitted, which makes the steep surfaces and edges brighter than flat surfaces on the final image. Since the height of the structures was very small (30nm), the sample holder was tilted at 45° in order to enhance the topography contrast in the images. The primary beam could degrade the polymer films due to high energy electrons impinging on the surface. In that case, a thin (4nm thick) layer of gold was deposited on the surface to improve its conductivity.

Cryo-SEM experiments permitted the sample morphology to be imaged when in contact with a solution. In this work, it was used to obtain a snapshot of the morphology of hydrated cross-linked polymer films. The most important issue was the sample preparation. The samples were mechanically fixed on a cryo-SEM holder. A drop of water was then placed in the centre of the polymer film. The sample was frozen with a very high cooling rate in order to obtain amorphous ice. For this, liquid nitrogen was subjected to vacuum, leading to solid nitrogen. When the pressure was increased, the nitrogen was in a sub-cooled liquid state. The sample was then dipped in liquid nitrogen and placed in the cryo-chamber. The excess ice was removed using a knife edge and the frozen water left was sublimated by maintaining the sample at -95°C and pumping
at $10^{-5}$ mbar for 3h. The sample was then coated with a platinum layer and maintained at -150°C until the end of the characterization.

### 2.5.3. Water contact angle measurements

The substrates used for the spin coating were always characterised in terms of wettability. For that, the water contact angle was determined using a Drop-Shape Analysis System DSA10 provided by Krüss (Hamburg, Germany). Figure 2-6 shows a picture of the setup.

The sample was placed on a holder and a Hamilton syringe filled with MilliQ water was positioned above it. The needle of the syringe was brought close to the sample and a drop of water dispensed on its surface. The volume of the water droplet could be controlled using the syringe. A halogen lamp was used to illuminate the sample from one side. On the other side of the sample, a CCD camera (connected to a computer) imaged the water droplet. Since the samples used were all reflective, the mirror image of the droplet was also seen in the recorded image. A typical result of water contact angle is shown in figure 2-6.

![Diagram of the setup](https://bigwww.epfl.ch/demo/dropanalysis/index.html)  

**Figure 2-6: Schematic of the setup used for the water contact angle measurements.**

To measure the water contact angles, ImageJ software (from NIH) was used in combination with the Drop-Snake plugin developed at the Swiss Federal Institute of Technology, Lausanne (EPFL) (http://bigwww.epfl.ch/demo/dropanalysis/index.html). The algorithm used in this plugin to fit the drop shape permitted to measure the left and right contact angles of the droplet.
Three different measurements could be done to characterise the wetting of the water droplet:

- static contact angle, $\theta_{\text{stat}}$.
- advancing contact angle, $\theta_{\text{adv}}$.
- receding contact angle, $\theta_{\text{rec}}$.

The static contact angle can be measured when a droplet is deposited on the surface and is in equilibrium (the volume of the droplet is constant and the three-phase line does not move). The value obtained when measuring $\theta_{\text{stat}}$ is always smaller than $\theta_{\text{adv}}$ but larger than $\theta_{\text{rec}}$. The advancing and receding contact angles are called dynamic contact angles since the volume of the droplet is changing during the measurements. When the volume of the droplet is increased, the droplet changes shape until the advancing contact angle is reached ($\theta_{\text{adv}}$). Upon further volume increase, the triple line moves toward the solid-gas interface but the contact angle of the droplet remains $\theta_{\text{adv}}$. If the volume of the droplet is decreased, the droplet will change in shape until the receding contact angle $\theta_{\text{rec}}$ is reached. A further decrease of the volume leads to a movement of the triple line towards the centre of the droplet with always $\theta_{\text{rec}}$ as contact angle. The difference between $\theta_{\text{adv}}$ and $\theta_{\text{rec}}$ is called the contact angle hysteresis and gives information about the roughness and chemical heterogeneity of the surface.

For large homogeneous samples, the three contact angles could be measured but only static contact angles were measured when wettability gradients were characterized. In these cases, the droplet diameter should not exceed 1mm and it was difficult in those conditions to make good dynamic contact angle characterizations.

### 2.5.4. Optical microscopy

Optical microscopy was routinely used in order to control the quality of the polymer films. The microscope used was a Reichert Polyvar Met optical microscope (Reichert-Jung, Vienna, Austria). The microscope was operated in both bright and dark field modes.

### 2.5.5. X-ray photoelectron spectroscopy

XPS analyses were performed using a VG Theta Probe spectrophotometer (Thermo Electron Corporation, West Sussex, UK) equipped with a concentric hemispherical analyzer and a two-dimensional channel plate detector with 112 energy and 96 angle channels. Spectra were acquired at a base pressure of $10^{-9}$ mbar or below using a monochromatic Al-K$_\alpha$ source with a spot size of
300µm. The instrument was run in the standard lens mode with electrons emitted at 53° to the surface normal and an acceptance angle of ±30°. The analyzer was used in the constant analyzer energy mode. Pass energies used for survey scans and detailed scans were 200 and 100eV, respectively for gold Au4f, carbon C1s, oxygen O1s, and sulfur S2p. Under these conditions, the energy resolution (full width at half maximum height, fwhm) measured on gold Au4f7/2 is 1.95 and 0.82eV, respectively. Acquisition times were approximately 5 min for survey scans and 30 min (total) for high-energy-resolution elemental scans. These experimental conditions were chosen in order to obtain an adequate signal-to-noise ratio in a minimum time and to limit beam-induced damage. Under these conditions, sample damage was negligible, and reproducible analyzing conditions were obtained on all samples. All recorded spectra were referenced to the gold Au4f7/2 signal at 83.96eV. Data were analyzed using the program CasaXPS [Version 2.3.5 www.casaxps.com]. The signals were fitted using Gaussian-Lorentzian functions and Tauc asymmetry in the case of gold and least-squares-fit routines following Shirley iterative background subtraction. Sensitivity factors were calculated using published ionization cross sections [71] corrected for the angular asymmetry [72] and the attenuation length dependence with kinetic energy.

2.6. Data analysis

As explained before, the characterization of the topography was mainly done by means of atomic force microscopy. To have a more quantitative characterisation, different approaches were used to analyse the topography. The most straightforward one was the determination of roughness parameters: RMS roughness and Skewness. They gave respectively information about the roughness and the peakiness of the surface. The major drawback of RMS roughness was that it only gave information about the vertical structure of the topography. Two different profiles could indeed have the same RMS roughness but very different morphologies. Skewness gave complementary information but it was not sufficient to fully describe the surface. Other approaches were thus considered to characterise the length-scales of the topography. One was based on the power spectral density (PSD) of the image and the other on the analysis of the shape of the feature using particle detection.
2.6.1. Image analysis: roughness, skewness

Topographies can be characterised using their corresponding height histogram. Each point of the height histogram corresponds to the probability that the profile of the surface has a certain height $z$. Figure 2-7 shows three different profiles with their height histograms qualitatively represented.

![Figure 2-7: Schematic showing the three different surface profiles having different skewnesses.](image)

Topography can be characterized using the position, the width and the symmetry of the height histogram. Two roughness parameters, RMS roughness and skewness, were calculated for each image. RMS Roughness was calculated according to the formula presented in Table 2-5 and represents the standard deviation of the topography about its mean plane. It is thus a measure of the width of the height histogram.

| Table 2-5: Definitions of the two roughness parameters used in the study. |
|---|---|---|
| Parameter | Formula | Remarks |
| RMS roughness | $Rq = \sqrt{\frac{\sum_{n} h_n^2}{N}}$ | N: number of pixels in the image, $h_n$: height deviations taken from the mean data plane at pixel n |
| Skewness | $Ssk = \frac{1}{R_q^3} \frac{1}{N} \sum_{j=1}^{N} h_n^3$ | |

Skewness measures the symmetry of the variation of topography about its mean plane. Negative
skewness indicates a predominance of valleys, while positive skewness is seen on surfaces with peaks. It gives a measurement of the asymmetry of the height histogram. The roughness parameters were measured using the proprietary software of the atomic force microscope (Nanoscope III 5.12 r3). The images used to calculate the roughness were 10 µm by 10µm or 5µm by 5µm depending on the polymer blend. The scan size used was always the same for all measurements of a given polymer blend.

### 2.6.2. Power spectral density and particle detection

The Fast Fourier transforms (FFT) of the images gave information about the length-scales of the different topographies. Since the phase separation of the polymer blends led to isotropic patterns, the FFTs were quantified using their 2D isotropic power spectral densities, which are radial averages of the FFTs. Peak positions and full width half maxima (FWHM) of the PSD curves were obtained by fitting them using Igor software (version 4.08). The length-scales of the images were obtained by taking the inverse of the peak position (see figure 2-8).

![Figure 2-8: Description of the different step of image analysis using power spectral density.](image)

In some cases, particle detection was also a relevant characterisation technique. AnalySIS software (Soft Imaging System GmbH) was used to perform particle detection. Figure 2-9 present the different steps to perform particle analysis. A table with the properties of each particle detected was returned by the software and used for the statistical analysis of the data. Even
though many parameters could be measured by the software, only the diameters and area of the particles detected were considered for the analysis.

Figure 2-9: Description of the different step of particle detection.

2.7. Replication of structured surfaces

The structured polymer films of PMMA/P2VP were used as master for replicating in three polymers. Specific protocols were developed for each polymer.

Table 2-6: Properties of the different polymers used for replication.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Melting point °C</th>
<th>Glass transition temperature</th>
<th>Melt flow index ml/10mn</th>
<th>Tensile modulus [MPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>AFFINITY EG 8150</td>
<td>56 (1)</td>
<td>0.5 at190°C (1)</td>
<td>6.62 (1)</td>
<td></td>
</tr>
<tr>
<td>TOPAS 8007S-04</td>
<td>80 (2)</td>
<td>2 at 190°C (2)</td>
<td>2600 (2)</td>
<td></td>
</tr>
<tr>
<td>Crosslinked PDMS</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sylgard 184</td>
<td></td>
<td></td>
<td></td>
<td>3 [73]</td>
</tr>
</tbody>
</table>

(1) Product information: Dow Plastics (2) Product information: Ticona

The first polymer was poly(dimethylsiloxane) (PDMS); the replication technique chosen was in
that case based on casting. Hot embossing was used for the replication in two thermoplastic polymers: AFFINITY™ and TOPAS®. The properties of the polymer used in this section are summarised in table 2-6.

2.7.1. Replication of the structured films in PDMS

The replication in PDMS was made by casting. A mixture of dimethylsiloxane monomers and a crosslinking agent was first made. The mixture obtained was liquid at room temperature and was poured on the master to be replicated. The assembly was then heated to accelerate the crosslinking reaction. At the end of the process, PDMS was cross-linked and could be peeled off the master.

PDMS (Sylgard 184) was purchased from Dow Corning (Wiesbaden, Germany). The PDMS was prepared according to the manufacturer’s directions, by mixing 1 part catalyst with 10 parts base resin. The two components were mixed under continuous stirring for 10 min and placed in a vacuum dessicator for 1 hour in order to eliminate air bubbles from the mixture.

The structured master used in that case was a film made using a PMMA/P2VP (50 : 50)\textsubscript{w/w} solution diluted at 1\%\textsubscript{w/v} in MEK. The solution was spin coated at 6000rpm. The PMMA phase was removed using the technique mentioned above. A thin PS solution in o-xylene was spin coated at 10000rpm on the master to improve the unmoulding of the replica.

The PDMS mixture prepared was cast in the middle of the master. 500µm thick spacers were disposed on each side of the master and a glass slide was placed on top of the PDMS to ensure a constant thickness. The assembly was put in an oven at 80°C overnight and allow to cool down to room temperature after curing.

2.7.2. Replication of the structured films in AFFINITY™

AFFINITY™ EG8150 was kindly supplied by Dow Plastics. The polymer was received in the form of beads. The replication of the structured polymer film was done in two steps (figure 2-10):

- Fabrication of a large wafer of polymer
- Embossing of the structured polymer film in the AFFINITY™

A special mould was designed for the molding of AFFINITY™ wafers. The mould was made of Teflon® and permitted 10cm diameter wafers with a thickness of 4mm to be realized. Polyimide foils (Kapton® 500HN, Dupont-SA) were put on each side of the mold to avoid the sticking of
Chapter 3: Nanostructured Films of Water-soluble Polymers

the polymer upon unmoulding. The holder was put in a vacuum oven at 190°C overnight. Vacuum was applied in order to prevent the polymer from degrading during the process. The mould was then allowed to cool down to room temperature before unmoulding. The wafers were cut in 1.5×1.5cm and put in a blend of ethanol and acetone (50 : 50) for 10min under sonication. Each piece was blow dry with nitrogen. The masters used for the replication were thin films of spin coated PMMA/P2VP. The PMMA phase was removed as aforementioned to enhance the topography.

In the embossing step, the working temperature was 90°C. This was high enough to soften AFFINITY™ and still lower than the glass transition of P2VP (100°C).

A piece of AFFINITY™ was first placed on a clean glass slide and put in the oven at 90°C for 10min without vacuum. The warm piece of AFFINITY™ was then brought into contact with the master and put in the oven for 10min and a pressure of 100kPa was applied. Once the molding step finished, the sample was removed from the oven and allowed to cool down to room temperature before unmoulding. The different steps of the molding process are shown in figure 2-9.

Figure 2-10: Schematic showing two steps made for the replication in AFFINITY™. a) Fabrication of the AFFINITY™ wafer. b) Replication of the structured master.
2.7.3. Replication of the structured films in TOPAS®

The replication in TOPAS® was made by means of hot embossing. TOPAS®-8007S-04 was kindly supplied by Ticona GmbH (Kelsterbach, Germany) and was received as beads of about 2mm diameter. The procedure developed for AFFINITY™ could not be used for TOPAS® due to the different thermal properties of the polymers. A three-step protocol was developed for hot embossing in TOPAS®:

- Fabrication of a TOPAS® wafer
- Replication of the structured master in PDMS.
- Hot embossing with PDMS replica.

TOPAS® beads were placed between two metal plates. Kapton® foils were used to prevent the sticking of the polymer on the metal plates. A 1mm spacer was used to obtain a defined thickness. The assembly was put in the vacuum oven at 190°C overnight and compressed with a pressure of 2kPa. Vacuum was applied to avoid the degradation of the polymer. After cooling down to room temperature, the TOPAS® wafer was easily unmoulded. 1.5×1.5cm and put 10mn in a blend of ethanol and acetone (50 : 50) v/v under sonication before hot embossing. Each piece was blown dry with nitrogen.

The masters used for the replication in TOPAS® were PDMS negative replica of the structured thin film. The negative replica was made following the procedure described above.

A TOPAS® pellet was placed on a Kapton® sheet and placed on a hotplate at 180°C. The negative PDMS replica was placed atop the TOPAS® and a pressure of 100kPa was applied on the assembly. The embossing last 5mn and the sample were let to cool down before unmoulding.
Chapter 3

Fabrication of Long Structure Gradients

This chapter describes the fabrication of centimetre-long structure gradients using polymer-blend demixing by solvent quenching. Various parameters were investigated to control the structure of the polymer-blend films. Among these, we focused on the effect of surface energy. The final goal was to use substrates with surface-energy gradients in order to induce topographical gradients on the surface.

Section 3-1 introduces the principle of demixing of polymer-blends and also presents the different systems used. The effect of some key parameters affecting polymer demixing is also shown.

In section 3-2, the different techniques that were used for controlling the surface energy of the substrates are presented, with special emphasis on the fabrication of long, surface-energy gradients.

In section 3-3, a preliminary study concerning effect of surface energy on different polymer blends is presented. PVA/Dextran, PVA/PDADMAC, PMMA/P2VP and PS/PMMA are discussed in this context.
Finally, section 3-4 demonstrates the fabrication of structure gradients using PVA/Dextran and PMMA/P2VP.

3.1. Introduction

3.1.1. Principle of polymer demixing

The technique used to create structured polymer film was polymer demixing by solvent quenching. Figure 3-1 summarizes the different steps of the process. In a first place, a polymer-blend solution consisting of two polymers and a common solvent was made. The solution was dilute enough to ensure the formation of a single phase. The solution was then spin coated on a surface to form a thin film.

In the early stage of spin coating, the solution spreads on the substrate due to centrifugal forces. During the process, there is a balance between the centrifugal and viscous forces, which determines the thinning of the liquid-film formed. In the late stage, the film continues to thin but solvent evaporation is the dominant effect. As the solvent evaporates, the concentration of the solution increases. Since the system consist in a polymer blend and a solvent, the increase in concentration occurs until a threshold concentration is reached, at which the system phase-separates. Finally, the system is frozen in a non-equilibrium state due to the complete evaporation.
of the solvent. At the end of the process, a phase-separated, structured polymer film is obtained.

The final phase-morphology of the polymer films depended on the following parameters:

- the polymer blend system chosen
- the composition of the polymer blend
- the molecular weight of the polymers
- the spin speed during spin coating
- the concentration of the starting solution
- the surface energy of the substrate
- the temperature of the substrate
- the evaporation rate of the solvent
- humidity of the surrounding air

This technique offers thus numerous handles to tune the structure sizes. Even though the effect of these parameters can be easily observed on separate samples, their use for the fabrication of gradients is not always straightforward. For instance, even if spin speed has a notable influence on the final structure size, it would be difficult to use this parameter in order to induce gradual changes along the sample. Surface energy is attractive with regards this aspect, since various studies in literature have already been reported the fabrication of surface energy gradients.

### 3.1.2. Presentation of the polymer blends used

In this work, four systems were investigated. Two of them involved only water-soluble polymers: PVA/Dextran and PVA/PDADMAC. The two others systems were PMMA/P2VP and PS/PMMA. In the case of PVA/Dextran, PVA/PDADMAC and PMMA/P2VP, one key point was to identify the relative positions of the phase-separated domains in the polymer blend film. PS/PMMA, which has been extensively studied in literature, is presented here more as a comparison with the other three systems\textsuperscript{[32,74]}. In the next two sections, the different polymer blends will be presented into details and the phase morphology of each system identified. The first section will focus on the two polymer blends consisting of water-soluble polymers, while the second section is dedicated to PMMA/P2VP blend. Since PMMA/P2VP system was more used in the work, a more extensive description of it will be made.
3.1.2.1. Polymer blends using water-soluble polymers

The demixing properties of PVA/PDADMAC and PVA/Dextran polymer blends were investigated. The typical composition used for PVA/PDADMAC system was (50 : 50)\(_{w/w}\). In the case of PVA/Dextran, an asymmetric blend was used, with a ratio of (80 : 20)\(_{w/w}\). The substrates used for this preliminary study were silicon wafers coated with thin films of PMMA. Typical polymer blend thin films were made by spin coating a 3\%_{w/v} solution at 3000rpm.

As can be seen on the AFM images shown in figure 3-2 a), the phase separation of PVA/PDADMAC (50 : 50)\(_{w/w}\) led to the worm-like structures typical of the spinodal decomposition process. Selective dissolution of PDADMAC using acetic acid revealed that the elevated domains corresponded to the PVA phase.

As can be seen in figure 3-2 b), the phase separation of PVA/Dextran (80 : 20)\(_{w/w}\) system led to a very different phase morphology in contrast to PVA/PDADMAC system. The presence of dots of one polymer embedded in a matrix of the second polymer suggested a phase separation following a nucleation and growth process.

![AFM images of different polymer films](image)

*Figure 3-2: AFM images of the topography of different polymer films. a) Film of PVA/PDADMAC (50 : 50)\(_{w/w}\) 3\%_{w/v} in water, spin coated at 3000 rpm on a PMMA surface. b) Film of PVA/Dextran (80 : 20)\(_{w/w}\) 3\%_{w/v} in water, spin coated at 3000 rpm on a PMMA surface. c) Film of PVA/Dextran 30mg/mL in water, spin coated at 3000 rpm on a PMMA surface. The (PVA/Dextran) ratio is specified below each image.*
No selective solvent was found for the PVA/Dextran system. In order to find which phase corresponds to the dots, the ratio between PVA and Dextran was changed. As shown in figure 3-2 c), an increase in the size of the dots was observed on increasing the proportion of Dextran in the solution. This demonstrated that the dots corresponded to the Dextran phase, the matrix being PVA.

### 3.1.2.2. The PMMA/P2VP polymer blend

The last system used in this study was a ternary blend of poly(methylmethacrylate) (PMMA) and poly(2-vinylpyridine) (P2VP) diluted in methyl ethyl ketone (MEK). First, a description the system used: typical polymer blend thin films were made by spincoating a 1% w/v PMMA/P2VP (50 : 50) w/w polymer blend solution at 6000rpm. The substrates were gold-coated silicon wafers functionalised with 1-dodecanethiols, which made the surface hydrophobic. As presented in figure 3-3 a), b), the as-cast film obtained consisted of dot-shaped domains embedded in a matrix. Different approaches were combined in order to find the phase morphology of the polymer blend. The first investigation method used atomic force microscopy to probe the changes in friction and phase signals along the sample. As reported by Sprenger et al [75,76], P2VP has a higher friction coefficient than PMMA mainly due to its hygroscopic nature. The slight swelling of water from the ambient air softened the P2VP phase, which led to higher friction signals. The friction image of PMMA/P2VP film in figure 3-3 c), d) clearly shows this contrast. The regions of highest friction coefficient corresponded to the circular domains, whereas the matrix exhibited a lower friction coefficient. The friction signal was observed both in the trace and retrace modes, ensuring that the contrast observed is a real friction signal and is not an artifact from topography, for instance. This suggested the presence of P2VP domains in the bumps and PMMA in the matrix.

The other technique used to investigate the polymer film used selective removal of one of the polymer of the blend using appropriate solvents. We could selectively remove P2VP by rinsing the polymer film in ethanol, which is a poor solvent for PMMA. As can be seen in figure 3-3 e), the polymer film obtained after ethanol treatment consists of the matrix with empty holes. To remove PMMA, o-xylene was chosen as selective solvent but it did not lead to a complete removal of the polymer in a simple rinsing step. To enhance the solubility of PMMA, the polymer film was exposed to UV beforehand. It is known that PMMA undergo main chain scissions when exposed to ultraviolet light [77,78]. The fragmented PMMA chains obtained had
lower molecular weights and were thus more easily solubilised in the selective solvent. This led to a better dissolution of the PMMA phase as shown in figure 3-3 f), leaving P2VP bumps on the surface. This selective solvent analysis confirms the presence of P2VP in the dots and PMMA in the matrix.

The topography of the as-cast polymer film could also be analysed to gain information about the distribution of the two polymers in the film. According to Walheim et al.[32], the topography of thin polymer films made by spin coating arises from solubility differences of the two polymers (PMMA and P2VP) in the common solvent (MEK). During the film formation, PMMA-rich and P2VP-rich phases are created due to phase separation. Moreover, the solvent content of each phase increases with increasing solubility of the polymer in the common solvent. Upon solvent

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Figure 3-3: a), b) AFM image of the topography of a PMMA/P2VP polymer film spincoated at 6000rpm from a (50 : 50)w/w diluted at 1%w/v in MEK on a hydrophobic substrate. c), d) Friction images corresponding to image b), taken in trace and retrace respectively. e) Topography of the thin polymer film after ethanol rinsing (removal of P2VP). f) Topography of the thin polymer film after UV exposure and rinsing in o-xylene (removal of PMMA)
evaporation, the phase containing the polymer with the lower solubility is thicker since it is depleted of solvent more quickly. This argument is often used to explain the presence of topography in polymer blend films. However, a major difficulty in this approach concerns the determination of the quality of the common solvent for each polymer. One possibility would be to make a comparative study of their respective solubility parameters with that of the common solvent. Unfortunately, although solubility parameters are quite well defined for solvents, it is difficult to find consistent data concerning polymers. Moreover, a great deal of care must be taken when using this argument to shown the film morphology. As will be explained in the next section, other effects like humidity can also affect film topography. To avoid the problem of humidity, the polymer films shown in figure 3-3 were fabricated under nitrogen atmosphere. The different techniques employed to characterise the polymer films gave thus consistent results. The PMMA/P2VP polymer film obtained is composed of two phases, the P2VP-rich phase corresponding to the dot-shaped phase and the PMMA-rich one being the matrix.

3.1.3. Effect of spin speed and concentration

A detailed investigation of the effect of spin speed and solution concentration for PVA/Dextran, PVA/PDADMAC systems was also made during the thesis in the frame of an industrial project pursued with the firm Ilford. Spin speed and solution concentration were systematically varied and the polymer films obtained were characterized by means of AFM in order to see the influence of these parameters on the size of the phase separated domains. A complete description of this project, as well as the results obtained is presented in appendix 1.

Figure 3-4: AFM images of the film of PVA/Dextran (80 : 20) w/w made with different solution concentrations: 5, 3, 1% w/v, spin coating was made at 3000 rpm.
In summary, the same trends are observed for both polymer blends. On increasing solution concentration, the length-scales of the structures increase. Figure 3-4 shows the AFM images obtained for PVA/Dextran when the concentration was varied. As can be seen, the dots of Dextran were clearly larger for higher concentration. Image analysis showed that the length-scale of the structures increases linearly with increasing concentration. The influence of spin speed showed a different trend: the length-scales of the structures decreased with increasing spin speed but the dependence was not linear. On increasing spin speeds from 1000 to 4000rpm, the decrease in length-scales was pronounced but further increases in spin speed did not lead to major changes in length-scales.

3.1.4. Effect of humidity on the PMMA/P2VP system

The effect of atmospheric humidity on the formation of the polymer blend thin film was also investigated and was found to be critical for PMMA/P2VP system. As presented in figure 3-5, the relative humidity in the spin-coating chamber was adjusted by controlling the mixing ratio between dry and wet nitrogen. A thin polymer film was made by spin coating a solution of PMMA/P2VP \((50/50)_{w/w}\) diluted at 1\%\(_{w/v}\) in MEK) at 6000rpm on a hydrophobic substrate.

![Figure 3-5: Experimental setup used to achieve different relative humidities in the spin coating chamber. The ambient temperature was equal to 21°C for all measurements.](image)

No clear changes in the lateral size of the domains were observed on increasing the relative humidity but the height of the P2VP domains was modified (see figure 3-6). At low relative humidities, bumps of P2VP embedded in a matrix of PMMA were obtained as mentioned in the
previous section. For higher humidities, the height of the P2VP domains decreased forming holes in the PMMA matrix instead of bumps. This modification in morphology could be explained by the hygroscopic nature of P2VP. Solvent evaporation during spincoating induces phase separation in the system. At this stage, the two coexisting phases (P2VP-rich and PMMA-rich phases) are still liquid due to their high solvent content. Simultaneously with phase separation, evaporative cooling induces a temperature decrease at the free surface. Depending on the dew point temperature of the surrounding air, water molecules may condense on the sample. Due to its hygroscopic character, P2VP swells water during the process, but not PMMA. The drying kinetics of P2VP phase is thus affected since it must be depleted of both MEK and water before vitrification. As a consequence, the PMMA phase is depleted of solvent more quickly than P2VP, resulting in a PMMA phase which is thicker than the P2VP phase.

![AFM images of the PMMA/P2VP spincoated at 6000rpm from a (50/50) w/w diluted at 1% w/v in MEK on a hydrophobic substrate. Different relative humidities were used 20%, 30%, 40% respectively. d) Same polymer film as in a) made under o-xylene vapors. e) Schematic representation of the cross-section of the polymer films showing the thickness variations of PMMA and P2VP phases under the different conditions.](image)

To confirm this explanation, the experiment was repeated using o-xylene vapour instead of water.
vapour. *o*-xylene is a good solvent for PMMA but a poor one for P2VP. We would thus expect a higher uptake of *o*-xylene by PMMA during the spin-coating process. As presented in figure 3-6 d), the polymer film obtained was structured, with high P2VP bumps and a low PMMA phase. As expected, the situation was the opposite of that obtained with high humidity: the PMMA phase was much thinner than the P2VP domains. In this case, P2VP phase was depleted of solvent faster than PMMA phase since it didn't absorb *o*-xylene vapour during the process.

The influence of humidity has been previously reported for other systems containing P2VP\[^{79-82}\]. For instance, Cui et al controlled the order of PS/P2VP phase separated domains using breath patterns\[^{82}\]. The polymer film they used was much thicker (300µm) than in our case. However, they also observed a transition from island-like domains to holes on increasing the humidity.

### 3.2. Self assembly of ω-substituted-alkanethiols to tailor surface energy

The self assembly of ω-substituted-alkanethiols on gold surfaces was used to control the surface energy of the substrates. This well-established method \[^{83,84}\] lead to well-packed, ordered self assembled monolayers (SAM). By adjusting the tail group of the thiol, the surface energy of the surface was modified. Hydrophobic as well as hydrophilic surfaces were produced using methyl and hydroxyl terminated alkanethiols respectively \[^{85}\]. The thiols used were 1-dodecanethiol (HS(CH\(_2\))\(_{11}\)CH\(_3\)) and 11-mercapto-1-undecanol (HS(CH\(_2\))\(_{11}\)OH). The water contact angle obtained for the hydrophobic thiol SAM (HS(CH\(_2\))\(_{11}\)CH\(_3\)) was 110±3°. For the hydrophilic thiol (HS(CH\(_2\))\(_{11}\)OH), water contact angles inferior to 15±3° were observed.

#### 3.2.1. Fabrication of surfaces with intermediate surface energies: mixed thiol SAMs

Intermediate wettabilities were achieved by co-adsorbing the two different thiols on the gold surface \[^{83,86}\]. By adjusting the ratio of methyl to hydroxyl-terminated thiol in the solution, the surface thiol composition was tuned. As presented in figure 3-7, various contact angles were obtained ranging from 105° to 15°.
Chapter 3: Fabrication of Long Structure Gradients

3.2.2. Fabrication of surface energy gradients

Surface energy gradients were made using a technique based on the self assembly of alkanethiols \[13\]. A surface-concentration gradient of adsorbed methyl-terminated thiols was achieved by gradually immersing a gold-coated substrate into a very dilute thiol solution (0.005mM) by means of a linear-motion drive. Subsequent immersion of the substrate into the complementary thiol solution (hydroxyl-terminated thiol) provided a hydrophobicity gradient with a large range of water-contact angles.

Figure 3-8: Water contact angle measured along the surface-energy gradients made by the gradual immersion technique. circles: gradient covering the lowest surface energies, squares: gradient covering the highest surface energies \[1\].

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\[1\] The substrates were kindly supplied by Sara Morgenthaler from the Laboratory of Surface Science and Technology, (ETHZ)
Two kinds of surface energy gradients were produced depending on the experimental conditions as presented in figure 3-8. By gradually immersing a gold coated surface in HS(CH$_2$)$_{11}$CH$_3$ solution at a speed of 30µm/s and backfilling the SAM with a HS(CH$_2$)$_{11}$OH solution, the gradients obtained covered water contact angles ranging from 70° to 105°. When the same procedure was made using an immersion speed of 42.5µm/s, the hydrophobicity gradient ranged from 30° to 80° in water contact angle.

3.3. Effect of surface energy on polymer blends: preliminary study

In this section, polymer-blend thin films were made on surfaces of different surface energies. Self assembly of HS(CH$_2$)$_{11}$CH$_3$ and HS(CH$_2$)$_{11}$OH thiols on gold surfaces was used to provide discrete, homogeneous hydrophobic and hydrophilic substrates, respectively. The polymer-blend solutions were spin-coated on both substrates and characterized by means of AFM. The following ternary systems were investigated: PVA/Dextran/water, PVA/PDADMAC/water and PMMA/P2VP/MEK. A PS/PMMA blend in toluene was also used as a control since it has been widely studied in the past [32,74,87-89]. A change from a hydrophobic to a hydrophilic substrate led to different effects depending on the polymer blend (figure 3-9).

For PS/PMMA, a symmetrical blend diluted in toluene to 3%$_{w/v}$ was spin coated at 3000rpm on the different substrates. Holes were observed in the polymer film made on a hydrophobic substrate. When a similar experiment was done on a hydrophilic substrate, the opposite structure was observed, with islands embedded in a matrix. Walheim et al [32] reported for this polymer blend a preferential wetting of hydrophilic surfaces by the PMMA phase since it is more polar than PS. In the case of hydrophobic surfaces, PS forms a wetting layer on the substrate for the same reason. This surface enrichment affects the phase separation since it induces composition gradients through the depth of the film. In the case of PMMA/P2VP, a symmetrical blend in MEK at 1%$_{w/v}$ was used and spin coated at 6000rpm. For hydrophobic substrates, we obtained bumps of P2VP embedded in a matrix of PMMA. When switching to hydrophilic substrates, no topography was observed. The surface was completely flat, which suggests that the polymer blend adopted a layered morphology as obtained for PS/PMMA.

If a clear change was observed for PS/PMMA and PMMA/P2VP blends this was, however, not the case for PVA/PDADMAC, which was only weakly affected by surface-energy changes. The
spinodal pattern obtained on hydrophobic substrates disappeared and some smaller features appeared. For the PVA/Dextran system, dots of Dextran were observed embedded in a PVA matrix as presented in the previous chapter. For hydrophobic substrates, Dextran pillars were obtained whereas hydrophilic substrates lead to the formation of pits.

![Figure 3-9: Topographies of different polymer blend thin films on hydrophilic and hydrophobic substrates characterized by means of AFM. a), b) PS/PMMA (50 : 50)\textsubscript{w/w} 3\%\textsubscript{w/v} in toluene, spin coated at 3000rpm. c), d) PVA/Dextran (80 : 20)\textsubscript{w/w} 3\%\textsubscript{w/v} in water, spin coated at 3000rpm. e), f) PMMA/P2VP (50 : 50)\textsubscript{w/w} 1\%\textsubscript{w/v} in MEK spin coated at 6000rpm. g), h) PVA/PDADMAC (50 : 50)\textsubscript{w/w} 3\%\textsubscript{w/v} in water, spin coated at 3000rpm.]

Among the four different systems we presented above, we focused on PVA/Dextran and PMMA/P2VP systems for the rest of the study. Since it did not lead to a huge topography change, PVA/PDADMAC/water was not further studied. For the PS/PMMA/toluene system,
additional experiments revealed a very sharp transition occurring at low surface energies. This posed major technical problems for the formation of film of good quality due to dewetting problems with very hydrophobic substrates.

3.4. Effect of substrate surface energy on PVA/Dextran phase separation

3.4.1. Effect of surface energy: investigation on separate samples

The effect of surface energy on the phase separation of PVA/Dextran system was investigated using substrates having water contact angles ranging from 15° to 100°. The concentration of the polymer-blend solution was varied from 1% w/v to 5% w/v and the spin-coating speed was 3000rpm for all experiments.

![AFM images of PVA/Dextran polymer film topography obtained with different wettabilities and solution concentration.](image)

Figure 3-10: AFM images of PVA/Dextran polymer film topography obtained with different wettabilities and solution concentration.
As shown in figure 3-10, for a 3\%w/v polymer blend solution, the phase separation on substrates having water contact angles smaller than 40° led to the formation of pits of Dextran embedded in a PVA matrix. For water contact angles above 80°, a pillar morphology was observed as shown in the previous section. For a 5\%w/v solution, the Dextran domains were bigger since the system had more time to phase separate. On hydrophilic substrates, 15nm deep pits were observed. On hydrophobic substrates, no pillars were observed in contrast to the 3\%w/v polymer blend solution. Instead, Dextran domains were concave and the small depressions were 2-3nm deep. Finally, for the lowest concentration (1\%w/v), pillars were observed at all surface energies and no transition was noticed.

### 3.4.2. Gradual transition from holes to pillars revealed by means of surface-energy gradients

Experiments on gradients of surface energy were carried out for the PVA/Dextran system to observe the transition in morphology, and the surface energy at which it happens. Polymer films were made by spin coating a PVA/Dextran solution on a wettability gradient covering water contact angles from 30° to 80°, since we saw from the preliminary study that the transition occurred between 40° and 80°. The AFM characterisation revealed the same morphology change with surface energy (figure 3-11). On the hydrophobic side, the minor phase (i.e. Dextran-rich domains) formed pillars in contrast to the hydrophilic side, which exhibited pits.

![AFM images showing morphology transition](image)

*Figure 3-11: Evolution of PVA/Dextran (80: 20)_{w/w} polymer blend on a substrate presenting a gradient of surface energy. Several images were made along the gradient. The red circles highlight the presence of small convex domains on the hydrophilic region of the gradient.*

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As the surface energy increased, the pillars flattened more and more. The film then reached an intermediate situation where it was flat. When the surface energy increased further, the Dextran-rich domains formed pits that became deeper and deeper. On the hydrophilic side, a bimodal distribution of the dots also appeared. The big domains were all concave, in contrast to the smallest ones that were still convex, as can be seen in figure 3-11. This meant that only the big domains were affected by the surface energy.

An efficient way to characterize this gradient of structure was to quantify some roughness parameters of the topography for every surface energy. We chose two standard parameters: RMS roughness and skewness. RMS roughness gave insights into the average roughness properties of the topography. We see on figure 3-12 that there was first a decrease on increasing the surface energy. When the flat configuration was reached, the roughness was at its lowest value. If the surface energy increased further, the roughness increased again. RMS roughness measurements thus allow the transition to be located.

![Graphs](image)

Figure 3-12: a) Evolution of RMS roughness of the topography along the gradient. The dashed line indicates the position of the transition between holes and dots. b) Evolution of Skewness of the topography along the gradient. The dashed line indicates the position of the transition between holes and dots.

However, it could not distinguish a rough surface with bumps from a rough surface with holes. This information was given by the skewness, which is a measure of how asymmetric the height distribution is. On the hydrophobic side of the gradient, the height distribution was positively biased since the pits are above the matrix. On the hydrophilic one, it was negatively biased since holes are below the matrix. Figure 3-12 shows the evolution of the skewness along the gradient.
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The switch from holes to pits was found at a water contact angle of 40°. The results obtained using skewness were consistent with what was observed using RMS roughness.

3.4.3. Discussion

As observed above, the transition from holes to dots was more pronounced when a higher polymer concentration was used and completely disappeared at very low concentrations. To understand this difference, we propose the following analysis of the film formation during spin-coating. On decreasing the concentration of the starting solution, its viscosity is decreased. During the initial stage of spin-coating, a balance between centrifugal forces and viscous forces leads to a gradual thinning of the spin-coating solution. At this stage, the film contains a large amount of solvent and has a thickness that depends on spin speed and the viscosity of the solution. A lower viscosity leads to a thinner liquid film. The subsequent stage of spin-coating is dominated by solvent evaporation. The lower the concentration of the solution, the faster the evaporation since the amount of solvent to be evaporated is lower in a thinner film. A lower concentration thus means a shorter time in which the system can phase separate before vitrification. Moreover, solvent evaporation occurs at the air/solution interface and is accompanied by a local increase in concentration. As a consequence, the nucleation of Dextran domains probably initiates at this interface.[90] To explain the disappearance of the transition for low concentration, we suggest that the evaporation of the solvent was too fast to let enough time for the system to react to surface energy. Likewise, the use of a higher concentration permitted the system to phase separate for a longer time and led a more pronounced transition.

A similar transition from a hole to pillar morphology upon changing the substrate surface energy was reported by Budkowski et al.[91,92] The system used in this study was a blend of polystyrene (PS) and polyisoprene (PI), spin coated from a toluene solution. The final films exhibited dots of PS embedded in a matrix of PI. The PS protrusions were concave for hydrophobic substrates and convex on hydrophilic ones. The authors also observed that small protrusions always remained convex in contrast to larger ones that switch from convex to concave. The transition observed was the opposite of our observations, in which pillars were observed for hydrophobic surfaces and holes for hydrophilic ones. The system we used was however very different. In their case, the two polymers were both apolar contrary to PVA and Dextran and the solvent (toluene) much less polar than water.
3.5. Effect of substrate surface energy on PMMA/P2VP phase separation

3.5.1. Effect of surface energy: investigation on separate samples

The effect of surface energy on PMMA/P2VP phase separation was investigated using substrates of different hydrophobicities with water contact angles ranging from 10 to 100°. Figure 3-13 shows the different morphologies obtained.

A flat morphology was observed for surfaces with contact angles below 75°. For surfaces with contact angles above 85°, the polymer film was structured with dots of P2VP embedded in a PMMA matrix. A slight increase in the dot size was observed when the polymer film was made on a substrate with 85° contact angle compared with 100°. AFM was systematically used to characterize the topography quantitatively but the changes were also qualitatively observed using dark-field microscopy. Indeed, the scattering of light was different depending on the structure of the polymer film. For films made on hydrophilic surfaces, nothing was observed in dark-field since the films were flat but the structured films obtained on hydrophobic surfaces led to a strong scattering of the incident light. One example of this optical effect is given in the next chapter, in figure 4-10.

![Figure 3-13: AFM images showing the evolution of the topography of PMMA/P2VP polymer films spin coated on substrates of different surface energies.](image)

This preliminary study did not allow the transition between the two extremes to be fully characterized, but it gave an estimation of its position. Given these results, we chose a surface-energy gradient covering contact angles from 50° to 100° in order to create the topography gradients.
3.5.2. Transposition of chemical gradients into structural gradients

Polymer films were made by spin coating a PMMA/P2VP solution on a wettability gradient covering water contact angles from 50 to 105°. The topographies of the films were characterised along the entire gradient, with measurements every 500 micrometers. The wettability gradient was two centimetres long. Figure 3-14 shows some AFM images of the film, as cast, and after removal of the P2VP phase. The topography of the film was clearly different on the hydrophilic and the hydrophobic surfaces. On the hydrophobic end of the sample, the polymer film consisted of holes in a matrix, while on the hydrophilic end the film was very flat and laterally phase-separated domains were not observed. A gradual transition from one regime to the other took place over a defined range of surface energies: from water contact angles of 100° to 75°. Outside this range of surface energies, no changes in the film topography were observed.

The transition in morphology observed from the hydrophobic to the hydrophilic side can be separated into two parts. At the hydrophobic extreme the polymer film consisted of holes embedded in a matrix. Moving towards higher surface energies, the diameter of the holes increased and a change in their morphology was observed; from holes embedded in a matrix, the morphology gradually became bi-continuous. This constituted the first part of the transition. In the second part, the bi-continuous morphology broke down and gave way to isolated domains embedded in a matrix. As the surface energy increased, the size and density of the isolated domains decreased. At the highest surface energies, the film surface became flat.

A selective solvent study was also made in order to better understand the micro-phase structure of the film. The sample was broken in half lengthways and one half was dipped in ethanol, which selectively removed the P2VP phase while leaving the PMMA phase in place. After the ethanol treatment, the morphology of the hydrophobic side of the gradient remained qualitatively unchanged compared to the as-cast film. The holes were, however, much deeper than before.

The topography gradient observed after removal of P2VP revealed the differences between the two phases of the transition. During the first part of the transition, the film consisted of holes embedded in a PMMA matrix. In the second part of the transition, the morphology was reversed, with islands in a matrix.
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Figure 3-14: AFM topographies recorded along the gradient. The position on the substrate is indicated on the left: a) Topography of the film as cast. b) After removal of the P2VP phase. c) Height histogram of the topographies obtained in b). d) Schematic drawings of the cross section of the PMMA phase.
The selective solvent study demonstrated that the islands correspond to PMMA domains and also revealed the formation of a PMMA wetting layer at lower contact angles. This can be observed in the height distribution of the topographies after the selective solvent wash. On the hydrophobic side two peaks were present in the histogram, corresponding to the bottom of the holes and the matrix. As the substrate became more hydrophilic a PMMA layer formed thin rims around the islands, which could be observed as a third peak in the histogram. Higher surface energies resulted in broader PMMA rims but smaller isolated PMMA islands; the formation of the rims depleted the upper part of the film in PMMA, which resulted in a reduction in the size and density of the PMMA domains. When the surface energy was high enough, the rims interconnected to form a layer of PMMA. On the most hydrophilic surfaces, there was only one peak in the histogram since the PMMA layer was complete and there were no islands.

From this initial analysis of the AFM images we could divide the influence of the surface energy on the micro-phase structure of the polymer film into four regimes: at very low surface energies (contact angle>100°) the polymer blend is not affected by the surface energy; in a second regime the domains increase in size and their morphology changes; the third step corresponds to the formation of a PMMA wetting layer on the substrate surface; finally, for high surface energies (contact angle<75°), the polymer blend forms a layered system on the substrate and is not affected by further increases in surface energy.

A more quantitative characterisation of the structure gradient was carried out using image analysis of the AFM results obtained. This gave the locations of transitions between the different regimes of micro-phase structure along the gradient. The analysis was made on the images taken after removal of the P2VP phase since it provided better contrast.

The first parameter used to characterise the gradient of topography was RMS roughness. figure 3-15 shows the graph of RMS roughness along the gradient. The curve obtained can be separated into three parts: at low surface energies the surface has a RMS roughness of 18nm. This remains constant up to a substrate contact angle of approximately 85°. The changes in domain (hole) shape and size observed in the AFM images were not reflected in the RMS roughness measurements. At intermediate substrate surface energies (75°<contact angles<85°), the roughness dropped from 18nm to 4nm: this corresponds to the formation of the PMMA wetting layer on the substrate surface and to the reduction in size and density of the islands of PMMA associated with it. For the highest surface energies (contact angles<75°) the RMS roughness
remained constant at 4nm.

RMS roughness thus revealed and located the formation of the PMMA wetting layer on the surface-energy gradient. It did not, however, describe the transition from dots in a matrix to bi-continuous morphology observed for low surface energies. Analysis of this transition required quantification of either the area or the lateral size of the domains. The mean area of the domains was analyzed by means of particle-detection software on the AFM images and an analysis of the particle area distribution. Alternatively, the fast Fourier transform of the images was used to derive the 2D power spectral density (PSD), which described the distribution of distances in the image. The inverse of the mean of the PSD was a characteristic length of the images.

Figure 3-16 a) shows the mean area of the domains as a function of the water contact angle. For water contact angle below approximately 93°, the mean area of the domains was significantly higher, reflecting the more interconnected morphology. At higher water contact angles, the mean area of the domains was decreasing on increasing water contact angle, reflecting the formation of smaller dots.

Figure 3-16 b) shows the inverse mean PSD value as a function of the water contact angle. For a water contact angle of 85°, the length scale was large since it corresponded to the bi-continuous structure. For contact angles between 85° and 95°, the length scale of the domains decreased, corresponding to the elongated domains. For the highest contact angles, the length-scale decreased further, corresponding to the smaller domains observed for the most hydrophobic substrates.
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3.5.3. Discussion

As presented in the previous section, thin films of PMMA/P2VP spin coated from a MEK solution can lead to either a structured or layered film depending on the wettability of the surface. The influence of substrate surface energy on polymer-blend thin films has been widely studied in the past both experimentally\cite{34,67,88,89,93-96} and theoretically\cite{30,97,98}. It however concerned mostly temperature-driven, polymer-blend phase separation. Studies on spin-cast films were also made\cite{31,91,92,99} with an emphasis on the influence of surface patterning\cite{32,100-102}. The presence of interfaces often leads to the preferential attraction of the polymers to the interfaces. This leads to composition gradients through the depth of the film and the appearance of composition fluctuation waves normal to the surface\cite{103}. This phenomenon called surface-directed spinodal decomposition greatly affects the phase-separation process.

The morphology of phase-separated, polymer-blend thin films is thus governed by the interplay between lateral phase separation in the polymer film and the enrichment of the interfaces by the polymers. Different cases are encountered due to the presence of two interfaces (air/polymer or substrate/polymer). Both interfaces can indeed preferentially attract the same polymer of the blend (symmetrical case). Similarly, the substrate can have more affinity for one of the polymer while the other polymer is more attracted at the air/polymer interface (anti-symmetrical case). Between these two cases, there is a situation of non-preferential wetting, where both polymers
have the same affinity for the interfaces.

Figure 3-17: a) Schematic showing the different structures of the film depending on the hydrophilicity of the substrate. b) Schematic showing the different vertical morphologies of the polymer blend thin films encountered depending on the surface energy of the substrate.

Another aspect is the possibility to have either a complete or partial wetting of the interfaces by the enriched polymer layers\cite{30}. This leads to four cases (see figure 3-17 b)) that were initially proposed for the theoretical investigation of phase separation in thin films\cite{37}. We decided to add the case of non-preferential wetting which is important for the formation of bi-continuous structures.

On the hydrophilic end of the wettability gradient, we observed a layered morphology. This was a situation of complete wetting according to the classification. Other studies reported the appearance of wetting both for temperature-quenched \cite{67,89,93,104} and solvent-quenched systems\cite{31,65,99}. In our case, the layered morphology disappeared upon decreasing the substrate surface energy and a bi-continuous phase morphology arose. This modification may be explained by a progressive change from complete wetting of the substrate by one of the component to a
situation of partial wetting of the surface. Bruder at al also reported a switch from a layered to structured morphology due a change from complete to partial wetting of the substrate\textsuperscript{[30]}. According to Winesett et al\textsuperscript{[89]}, the presence of a bi-continuous morphology indicates a situation of non-preferential wetting: both polymers are equally attracted by each interface. The authors proposed a non-preferential wetting condition taking into account the energy cost of the polymer/polymer interface and the interfacial energy of each polymer with the substrate:

\[ \gamma_{A/B} \geq \left| \gamma_A/\text{Substrate} - \gamma_B/\text{Substrate} \right| \]. This relation reflects the interplay between phase separation and wetting.

For lower surface energies, the bi-continuous structure disappeared and dots of P2VP in a PMMA matrix appeared. No clear surface enrichment was observed from the AFM measurements but the lateral morphology was fairly modified. As mentioned in the previous section, on increasing the water contact angles from 85° to 100°, the bi-continuous structure was lost and dots of P2VP in a PMMA matrix were observed. The transition between the two situations was not sharp and intermediate morphologies with elongated, but not interconnected, P2VP domains were observed. For a water contact angle of 85°, the system was in a situation of non preferential wetting as indicated by the bi-continuous morphology \textsuperscript{[89]}. On the most hydrophobic side of the gradient, the polymer film was confined between two interfaces attracting the lower-surface-energy phase (symmetrical situation). The preferential attraction of the polymer was however not strong enough to lead to a situation of complete wetting. AFM revealed that both polymers were wetting each interface (partial wetting situation). According to Das et al, similar changes were simulated in temperature-quenched systems\textsuperscript{[37]}. For partially wetting, symmetrical case, they obtained a dots in a matrix morphology whereas an anti-symmetrical situation led to a bi-continuous structure. However, our results can only be qualitatively compared with their simulations, since the experiments were made using polymer demixing by solvent-quenching and the simulations made for temperature quench polymer blends.

In summary, we classified the structure gradient obtained as such:

- On the hydrophilic side, the progressive change from a layered morphology to a bi-continuous structure was assigned to a change from a complete wetting situation to a case of partial wetting.
- The bi-continuous situation obtained in the middle of the transition corresponded to a case
of partial wetting where there was no preferential wetting of the surfaces by the polymers\[^{[89]}\].

- For the lowest surface energies, the progressive change from bi-continuous to dot shaped domains was attributed to a switch to symmetrical case with partial wetting. The film was indeed confined in that case between two hydrophobic interfaces (air/polymer and substrate/polymer).

### 3.6. Conclusion

A method to generate gradients of structures in polymer blend thin films was described. The technique developed used surface-energy gradients to control polymer blend phase separation and induce structure gradients along the substrate. It was applied to two polymer blends: PVA/Dextran and PMMA/P2VP.

Self assembly of \(\omega\)-substituted-alkanethiols on gold surfaces was an efficient tool to control substrate surface energy. Separate samples of different surface energies were made by co-adsorbing two thiols to produce mixed SAMs. Such substrates were used in preliminary studies to investigate the influence of surface energy on polymer blend thin films.

Centimetre-long surface energy gradients were also produced using a newly developed technique\[^{[13]}\]. The first strength of these substrates was the range of surface energies covered on a single sample. It allowed a combinatorial study of the effect of surface energy to be carried out for the two polymer blends selected. The influence of substrate surface energy was however different depending on the system considered. In the case of PVA/Dextran polymer blend, a transition from bumps to holes was observed when going from the hydrophobic to the hydrophilic side of the gradient. The PMMA/P2VP system showed a different structure transition. A layered morphology was observed on the hydrophilic side of the gradient, whereas the film was structured on the hydrophobic one. A progressive change between the two extreme cases was observed and the polymer film adopted a bi-continuous morphology in the middle of the transition.

Using this technique, structure-gradients in thin polymer films were produced in a single step. To obtain a bigger structure contrast, one phase of the polymer blend was removed using a selective solvent. This could be done for PMMA/P2VP system. After this step, RMS roughness of the topography was ranging from 3 to 18nm along the gradient and the transition spread over 1.2cm.
Similar gradients in terms of roughness and length were reported using polymer crystallization and applied to cell growth investigation. Such topography gradients could constitute an interesting platform for similar high-throughput studies.

Finally, the critical importance of one of the process parameters: relative humidity was highlighted. We showed that it can greatly affect the phase separation of the polymer blend. This effect was pronounced in our case due to the presence of a hygroscopic polymer (P2VP) in the blend.
Chapter 4

Fabrication of Short Wettability and Structure Gradients

As discussed in chapter 3, the fabrication of chemical and topographical gradients is a very active field of research, since it finds many applications in combinatorial studies. Such applications require the maximum number of conditions on the gradient, in order to screen a large number of experimental conditions on a single sample. There are however other potential applications for gradients that require different criteria in terms of both gradient slope and length. For instance, chemical gradients have been already used to control the motion of liquid drops on surfaces \[105-107\]. Designing shorter gradients can be attractive to control the motion and positioning of liquids on the sub-millimetre scale \[105\]. Short gradients can also find applications in biology. Cells’ response to protein, short gradients has already been investigated in previous studies with gradients ranging from 100µm to 1mm \[108,109\].

In this chapter, we focus on the realization of sub-millimetre structure gradients combining short wettability gradients with polymer demixing. Since the gradual immersion technique used in the previous chapter cannot be used for the creation of very short gradients, an alternative technique was developed. The central point of this chapter is the fabrication of short wettability gradients.
Chapter 4 : Fabrication of Short Wettability and Structure Gradients

After a short review of the already existing methods, our technique will be introduced and the results presented.

4.1. Introduction

4.1.1. Literature review

Different techniques were already reported for the creation of short chemical gradients and various gradient lengths were achieved ranging from hundreds of nanometres to millimetres. Pioneering studies reported the control of surface density of photoactive molecules using photolithographic techniques \cite{108,109}. The emergence of soft-lithography in the last decade instigated various techniques based on stamping or micro-fluidic networks \cite{47,49}. The state of the art in terms of length of the gradients is obtained using STM replacement lithography, where gradients as short as 600nm can be obtained \cite{56}. Table 4.1 presents the main techniques reported. More technical details about the different approaches were given in the main introduction.

Table 4-1: Review of the different techniques reported for the generation of sub-millimetre gradients.

<table>
<thead>
<tr>
<th>Approach</th>
<th>Length of the gradients</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Photo-immobilization of molecules</td>
<td>250µm to 1mm</td>
<td>Photosensitive molecules were gradually immobilized by varying the light exposure time \cite{108,109}.</td>
</tr>
<tr>
<td>Microstamping.</td>
<td>200µm</td>
<td>Hemispherical and hemicylindrical PDMS stamps are used to silane molecules on a silicon wafer. The stamp is gradually pressed on the surface to induce a gradient in silane density \cite{47}.</td>
</tr>
<tr>
<td>STM replacement lithography</td>
<td>600nm</td>
<td>A thiol SAM is gradually desorbed using a STM tip and replaced by a second thiol \cite{110}.</td>
</tr>
<tr>
<td>Microfluidic networks</td>
<td>300 to 900µm</td>
<td>Microfluidic networks are used to create gradients in solution composition \cite{48,111}.</td>
</tr>
<tr>
<td>Electrochemical</td>
<td>100 to 400µm</td>
<td>Creation of a gradient in surface electrochemical potential to gradually desorb a thiol SAM adsorbed on gold. \cite{52,53,112-114}.</td>
</tr>
</tbody>
</table>
4.1.2. Principle of photocatalytic lithography

The technique we developed here is based on the gradual oxidation of a thiol SAM by means of TiO$_2$ photocatalytic remote oxidation. Before going into more details about the experiment itself, a presentation of the fundamentals of photocatalysis will be given.

TiO$_2$ is one of the most used semiconductors for photo-catalysis. A lot of work was already reported in this field both for scientific and technological purposes [115-119]. TiO$_2$ only weakly absorbs visible light but shows a strong absorbance in the UV since it has a band-gap of 3.2eV (for the anatase form of TiO$_2$). When a photon with an energy $h\nu$ higher than the band gap of TiO$_2$ is absorbed, an electron is promoted from the valence band to the conduction band, leaving a hole in the valence band. The system can then undergo different processes. In the first place, the electron-hole pair created can recombine both in the volume or the surface of the material. The electron hole pairs have however sufficiently long lifetimes in semiconductors to enable other mechanisms. Another pathway for the relaxation of the system is the charge transfer of electrons or holes from TiO$_2$ to adsorbate molecules. The electrons formed in the conduction band can diffuse to the TiO$_2$ surface and be involved in the reduction of an electron-acceptor molecule. Similarly, holes formed the valence band can migrate to the surface and oxidize electron donor molecules. The ability of TiO$_2$ to undergo photo-induced charge transfer depends on the positions of its conduction and valence bands.

![Figure 4-1: Illustration of the different de-excitation pathways after photo-generation of electron-hole pairs](119).

The position of the conduction band will determine the reduction potential of the photoelectrons. Likewise, the position of the valence band will give insights on the oxidizing power of the holes.
When photocatalysis occurs in an electrolyte, the positions of the conduction and valence bands can be compared with the redox potentials of the adsorbed species to know if the reduction or oxidation is possible \[^{[116,119-121]}\]. However, the redox potentials are measured compared with the Standard Hydrogen Electrode (SHE) and the SHE energy level relative to vacuum is known (-4.5V) but the redox potentials are measured in solutions. If gas-phase photocatalysis is performed, the redox potentials may not be the right parameter to consider, since the reaction does not happen in liquid.

The final efficiency of the photocatalysis depends on the competition between the charge-transfer process, which is responsible of the photocatalytic activity of the semiconductor and the electron-hole recombination, which is detrimental for the photocatalytic efficiency. It also depends on the environment in which photocatalysis is performed (liquid or gas-phase). The technique we developed uses only gas-phase degradation. In that case, TiO\(_2\) photocatalysis was found to be greatly influenced by the relative humidity and the oxygen content of the atmosphere \[^{[116,117,122-124]}\]. When a molecule adsorbs on the TiO\(_2\) surface, one pathway for its degradation is its direct reduction/oxidation as an acceptor/donor molecule. However, many studies reported that gas phase degradation is mediated by the water and O\(_2\) molecules present on the TiO\(_2\) surface \[^{[115,122,125]}\]. The O\(_2\) molecules adsorbed on TiO\(_2\), which are strong electron acceptors, can act as efficient electron traps that inhibit the recombination process. Upon charge transfer of a photogenerated electron to an adsorbed O\(_2\) molecule, superoxide (O\(_2^−\) or HO\(_2^•\)) can be produced. The superoxide is highly active and can degrade other molecules present in its vicinity.

---

**Generation of an electron-hole pair**

\[ \text{TiO}_2 \xrightarrow{\text{UV}} \text{TiO}_2 + (h^+ + e^-) \]

**Oxidation of H\(_2\)O:**

\[ H_2O + h^+ \rightarrow HO^+ + H^+ \]

**Reduction of O\(_2\):**

\[ O_2 + e^- (+H^+) \rightarrow O_2^−(\text{or HO}_2^•) \]

followed by hydroxyl radical creation:

\[ 2HO^• \rightarrow H_2O_2 + O_2 \]

\[ H_2O_2 \xrightarrow{\text{UV}} 2HO^• \]

---

*Figure 4-2: Summary of the different chemical reactions taking place upon UV illumination of TiO\(_2\) in air.*

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Concerning the effect of water, several viewpoints were reported \[115,116\]. On the one hand, water molecules adsorbed on the surface represent electron-hole recombination centres, leading to a decrease in photocatalytic efficiency. On the other hand, it was reported that water molecules and hydroxyl groups can act as hole traps, thus favouring the charge separation of the electron-hole pair. Moreover, the oxidation of water molecules by photogenerated holes produces hydroxyl radicals (HO\(^\cdot\)) which mediate other oxidation reactions. In practice, humidity was reported to either inhibit or enhance the photocatalysis depending on the system studied.

The composition of the surrounding atmosphere was thus a critical parameter to understand the reaction mechanism. Furthermore, more sophisticated pathways for the creation of oxidizing radicals were reported. For instance, the generation of hydrogen peroxide (H\(_2\)O\(_2\)) from superoxide (HO\(_2\)^{\cdot}\)) and its decomposition in two hydroxyl radicals (HO\(^\cdot\)) due to the presence of UV was reported \[115\]. The different pathways for the creation of radicals are presented in figure 4-2.

Another source of debate concerns the diffusion of the oxidizing radicals (O\(_2\)^{\cdot}\) or HO\(^\cdot\)) in the vicinity of the surface. Some studies support the fact that radicals can diffuse and oxidize non-adsorbed molecules \[126\]. The oxidizing radicals involved are however very reactive and another viewpoint is that the reaction has to take place close to the surface \[127\]. There are nevertheless several studies that have been performed in the gas phase that prove that the diffusion of the radicals can happen over long distance (>100µm) \[115,125,128-131\]. In these studies, a glass surface was coated with a probe species (polymer film, soot, thiol or silane SAM, soot) and degraded using photocatalysis. A TiO\(_2\) surface was brought into the vicinity of the sample surface and an air gap was maintained between both. The gap ranged from tens to one hundred micrometers. Upon UV exposure, oxidizing radicals were produced as explained above and had long enough lifetimes to diffuse across the air gap and oxidize the molecules on the sample surface.

This technique named photocatalytic remote oxidation (PCO) lead to the emergence of photocatalytic lithography. In photocatalytic lithography, the TiO\(_2\) surface is illuminated with UV light through a patterned photomask. Since UV is necessary for the generation oxidizing species, only illuminated regions of the TiO\(_2\) surface are producing radicals. If a small enough gap is maintained between the TiO\(_2\) surface and the sample surface, the UV pattern can be transferred in a chemical pattern on the surface.
Figure 4-3: Fluorescent micrograph of 11-mercaptop-1-undecanoic acid modified gold surface after photocatalytic lithography through a patterned photomask. Rhodamine 6G was casted on the surface to obtain the fluorescent contrast (taken from reference [130]).

Results from Notsu et al are presented in fig 4-3 as illustration. Photocatalytic lithography was already used for the formation of surface patterns in thiol and silane SAMs [129,130,132].

4.1.3. Generation of sub-millimetre chemical gradients

The previous sections introduced the basic principles of photocatalysis and the concept of photocatalytic lithography. We will now present the concept proposed for the fabrication of short chemical gradients.

The alternative technique we developed to create wettability gradients combines photocatalytic lithography and gray-scale lithography. Gray-scale lithography is generally used in microtechnology to create 3D profiles in photosensitive materials (photoresists) [133,134]. This is done by varying the UV dose received by the material along the sample. In practice, the UV dose contrast is achieved using gray-tone gradients on the photomask. For this work, we designed a photomask having gray-tone gradients of various lengths from 360µm to 1.8cm (see figure 4-4 a)).

The gray-tone gradients were not truly continuous but made of 12 different gray-tones. The short gradients were repeated several times along the photomask. The variation in transmission along two gradients is illustrated in chapter 2, figure 2-1. The photomask was then used to perform photocatalytic lithography.

By creating a gradient of UV intensity along the sample, the amount of radicals created at the TiO$_2$ surface could be progressively modified, leading to a gradual oxidation of the surface.
Figure 4-4: a) Photograph of the 5inches photomask designed for the experiments. On the left, the long grayscale gradient is shown. The three short repeating gradients are also shown on the right side. b) Schematic representation of the setup used to gradually degrade thiol SAMs using photocatalytic lithography. The TiO$_2$ layer is brought close to the sample surface and a photomask is positioned above this assembly to create a gradual UV exposure.

4.2. Fabrication sub-millimetre chemical gradients

4.2.1. Principle

The experiment was done in four steps: first, the fabrication of a homogeneous thiol SAM. Second: the degradation of the SAM by means of photocatalytic lithography. Third: removal of the oxidized thiol by rinsing in ethanol. And fourth: backfilling of the SAM using a complementary thiol.

A homogeneous 1-dodecanethiol SAM was adsorbed on a clean, gold-coated substrate. The water contact angle measured after thiol adsorption was 110±3°. A TiO$_2$ coated glass slide was faced to
the thiolated gold coated substrate, separated by a 60µm air gap (figure 4-4 b)). Other studies report the use of thinner spacers (up to 12.5 µm) or thicker (up to 125 µm)[125]. The use of thicker spacers leads to a slower degradation, since the radicals have to cross the air gap to reach the surface of interest. Furthermore, the use of very thin spacers posed big technical problems, since the experiment was not done in a clean room. 60µm was a good compromise between these two constraints. The photomask having grey-tone gradients was then positioned at 800µm from the surface. This large gap was chosen to blur deliberately the UV intensity gradient due to diffraction effect. This permitted to improve the continuity of the gradient which actually arises from a twelve step gray-tone gradient. Since the photocatalytic activity of the TiO₂ depends on the intensity received, the amount of radical created was gradually varied along the TiO₂ surface. As the radical could diffuse through the air gap, this led to a gradual degradation of the thiol SAM. The sample was then backfilled with another thiol to complete the thiol SAM and obtain a thiol-composition gradient.

To show the feasibility of the technique, the long gray-tone gradient was used in order to fabricate a 1.5cm long wettability gradient. The characterization of long gradients could be done by means of contact-angle measurements. In a second time, the technique was applied to the fabrication of shorter gradients.

4.2.2. Fabrication of TiO₂ layers

The TiO₂ nanoparticles used in the study were obtained as a 30%w/w suspension in water. The nanoparticles were stabilised with nitric acid. According to the supplier, the nanoparticles had diameters 7nm, as measured from X-ray diffraction and the TiO₂ crystalline structure was anatase. TiO₂ layers were made by spin coating a suspension of TiO₂ nanoparticles on a clean glass substrate. Once coated, the layers were calcinated at 400°C to remove all organic compounds. The calcination was an important step to ensure that only TiO₂ was on the surface. If the TiO₂ layers were not clean before photocatalysis, the radicals created would have first reacted with the traces of organic compounds and cleaned the TiO₂ surface. The surface was also subjected to oxygen plasma before each experiment for the same reason.

The morphology, structuring and thickness of the layers were critical to know, since they were shown to affect the photocatalytic process. For instance, Tatsuma et al reported a decrease in photocatalytic remote oxidation as the TiO₂ layer thickened[129] due to absorption of UV by the
TiO$_2$ layer itself. An AFM and SEM characterization of the TiO$_2$ layers was thus performed. The thickness was measured using AFM and was 600nm±60nm.

*Figure 4-5: a) SEM image of the TiO$_2$ used for the study. b) AFM image of the nanotopography of the TiO$_2$ layer.*

The layers obtained were finely cracked but homogeneous over the substrate (figure 4-5). As can be seen on the SEM image, the cracks were few micrometers long and 200nm in width. A nanostructure was also observed within the TiO$_2$ domains as shown on the AFM image. The topography had a granular morphology with grain diameters of about 50nm. As mentioned before, the nanoparticles were, however, only 7nm diameter in suspension. One explanation of this difference may be that the nanoparticles aggregated during the spincoating process.

### 4.2.3. Feasibility of the experiment: generation of long gradients

First trials were done using the longest gray-tone gradient. After 7min UV exposure, no relevant changes in wettability. However, the contact angles were clearly changing along the sample after rinsing and backfilling the sample with 11-mercapto-1-undecanol (figure 4-6). On the most hydrophobic side, the water contact angles measured were 90° (average over four samples). The decrease in wettability was not linear and the slope of the gradient was decreasing toward the most hydrophilic side. Contact angles measured on the hydrophilic side were 50°. When the experiment was repeated but the backfilling done with a 1-dodecanethiol solution, no gradients were observed and the final contact angle was lower than in the case of the untreated SAM. The fact that the maximal water contact angle obtained is 90° may be explained by the oxidation of the alkyl chain during the process.
XPS measurements were performed to further understand the mechanism of the photo-catalytic degradation on the thiol SAM. For these measurements, no gray-scale gradients were used during the photocatalytic oxidation of the SAM: the samples were homogeneous. XPS spectra in the S2p region were measured on the sample at each step of the process. For the 1-dodecanethiol monolayer, two peaks were obtained at 162.12eV and 163.3eV corresponding to the S2p\textsubscript{3/2} and S2p\textsubscript{1/2} of thiolate head-groups, respectively. On exposure to UV, a third sulphur peak appeared at binding energy of 168eV. This was attributed to the formation of sulphonate compounds. After ethanol rinsing, the sulphur peak at 168eV disappeared indicating that the sulfonate species dissolve in ethanol. When the SAM was backfilled with 11-mercapto-1-undecanol, the sulphur content was closer to that of a full monolayer.
Chapter 4: Fabrication of Short Wettability and Structure Gradients

![Figure 4-7](image)

(a) X-ray photoelectron spectra in the S2p regions of the thiol SAMs measured at the different steps of the process. (1) full 1-dodecanethiol SAM, (2) after 7mn photocatalytic remote oxidation (PCO), (3) after 7mn PCO and 5mn ethanol rinsing, (4) after 7mn PCO, 5mn ethanol rinsing and 10mn backfilling with 11-mercapto-1-undecanol. The spectra are displaced along the y axis for clarity. (b) Table presenting the positions of important XPS peaks and their attributions.

<table>
<thead>
<tr>
<th>Average binding energy [eV]</th>
<th>Attribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>S2p_{3/2}</td>
<td>162.12</td>
</tr>
<tr>
<td>S2p_{1/2}</td>
<td>163.30</td>
</tr>
<tr>
<td>S2p</td>
<td>168</td>
</tr>
</tbody>
</table>

The results obtained from contact angle and XPS measurement permit to propose a degradation mechanism of the thiol monolayer, when subjected to photocatalytic lithography through a gray-tone gradient. This is illustrated in figure 4-8.

On exposure to UV, a gradient in UV intensity is obtained on the TiO_2 layer due to the presence of the gray-tone gradient. This result in a gradient in radical concentration on the TiO_2 surface, the most exposed areas producing more radicals than the less exposed. Then, the radicals diffuse through the air gap and oxidize the thiol into sulfonate species. The oxidation of the alkyl chain may also occur during the process. Since there is a gradient in radical concentration on the TiO_2 surface, the numbers of oxidized thiols gradually increase toward the most UV exposed region of the sample. When the samples are rinsed, the sulfonates dissolve in ethanol and the thiol SAM becomes incomplete except on the less exposed side of the sample. When the samples are back filled, the free anchoring sites that appeared after ethanol rinsing are available for new thiols and the SAM is completed. If the thiol used for backfilling is different than the starting thiol, a composition gradient is obtained along the sample.
4.2.4. Fabrication of short wettability gradients

The approach proposed for the generation of thiol composition gradients was successfully applied to the fabrication of long gradients. We will now focus on the application of this technique to the fabrication of short gradients, which was the main challenge. The experiment was repeated using the 720µm grey tone gradient. The experimental protocol was strictly the same as for long gradient. However, the characterization could not be done by means of contact angle measurement because of the length of the gradient. To obtain a qualitative view of the gradient, the wettability of ethanol and water on the substrates having gradients was investigated. When a droplet is deposited on a homogeneous surface, it adopts a perfectly round shape in order to minimize the interfacial energy. This was not the case when the droplet was in contact with a surface having a surface energy gradient. During the ethanol rinsing step, we could see a first evidence of the presence of a gradient on the surface.
Figure 4-9: a) Photographs showing the dewetting of ethanol on a surface having gradients. The characterization was performed after 7 min of photocatalytic lithography. The sample was 1.5 cm wide. b) Transmission images of the 720 µm gray-tone repeating gradients. The images are aligned with the images in c) to show the correspondence between the gray-tone and the shape of the water droplet. c) Dark field images of water droplets deposited on the surface bearing 720 µm gradient. The characterization was performed after 7 min of photocatalytic lithography, 5 min ethanol rinsing and 10 min backfilling with 11-mercaptop-1-undecanol.
As presented in figure 4-9 a), ethanol was dewetting the most hydrophobic areas of the samples and was spreading into the hydrophilic region of the gradient. Since the gradient was repeating along the sample, stripes of ethanol were observed. No changes in the wettability of water were noticed at this stage of the experiment. On the other hand, a clear change in the shape of sessile water droplets was seen after backfilling with 11-mercapto-1-undecanol. At the centimetre scale, the droplet was round but the triple line was continuously changing along the gradient at the millimetre scale. On the hydrophobic areas, the droplets was dewetting more than on the hydrophilic one. Since the short wettability gradient was repeating along the sample, this resulted in the formation of a wave-shape triple line.

The striking difference in spreading between ethanol and water on the substrates may be explained by the difference in surface tension of these two liquids. On hydrophobic areas of the gradients, the surface energy of the substrate is low and it is energetically more favourable for both ethanol and water to dewet the surface. On the most hydrophilic side, the surface energy of the substrate is high and the total energy of the system can be decreased when the surface is completely wetted by a liquid having a low surface tension. Since the surface tension of water is 72.8mN/m, while that of ethanol is only 22.4mN/m, ethanol will be more likely to spread over the hydrophilic parts of the gradient than water.

4.2.5. Phase separation of polymer blends on repeating gradients

The wettability gradients were also characterized using polymer-blend thin films. As seen in the previous chapter, phase separation of polymer blends is strongly influenced by the surface energy of the substrate. Thin, polymer-blend films can indeed have various morphologies depending on the surface energy of the substrate. Moreover, many studies about phase separation of polymer blends on patterned substrates showed that wettability changes at the micrometer scale could induce changes in polymer structure \(^{[65,135-137]}\). This showed that phase separation of polymer blend can be used as a sensitive probe to characterize the wettability changes of the substrate at the micrometer scale.

Thin films of PMMA/P2VP were made by were spin-coated polymer blend solution (PMMA/P2VP (50 : 50)\(_{w/w}\), dissolved at 1\(_{w/v}\) in MEK) at 6000rpm on the substrate bearing the 720\(\mu\)m repeating wettability gradients. The wettability gradients were made as explained before
with an exposure time of five minutes. As evoked in the previous chapter, the phase separation of this polymer blend on hydrophobic substrates led to an optical effect which was not present when the polymer film was made on hydrophilic ones. The structure changes could thus be seen optically directly after the spin coating.

Figure 4-10 a) shows clearly the transition between the structured to non-structured areas. On the left part of the image, the polymer film was homogeneous since the substrate was not subjected to photocatalytic remote oxidation. On the right hand side, periodical structure changes were seen since the wettability gradients were repeating along the sample. A more quantitative analysis was obtained by making AFM images along the gradient.

Figure 4-10: a) Optical image of the thin polymer film after spincoated on a short wettability gradient. b) AFM images of the PMMA/P2VP polymer blend film. The contact angles presented on the above the images were determined by comparing the morphology of the structures with the results obtained with long gradients c) AFM images of the PMMA/P2VP polymer blend film after PMMA phase removal.
The polymer films were characterized after spin coating and after PMMA phase removal. As expected, the morphology of the polymer film was varying periodically along the sample. The transition from structured to flat morphologies could be seen, as in the case of the long wettability gradient. Figure 4-10 b), c) presents a series of AFM images taken at different positions along the gradient.

On the hydrophobic part, the polymer film was structured, with islands. For the most hydrophilic part, the film was flat. For intermediate hydrophilicities, a gradual change was seen as reported in the previous chapter. The gradient was spreading over 200µm. The RMS roughness was measured for each image and plotted versus the lateral position. As presented in figure 4-11, the as cast polymer blend film did not exhibit a huge change in RMS roughness along the gradient. However, after PMMA phase removal, a clear topographical contrast was observed. On the flat part of the gradient, the RMS roughness was very low (2-3nm) but increased to 15nm on the most hydrophobic side.

![Figure 4-11: RMS roughness evolution along the gradient. The roughness was measured on the as cast films (circles) and after PMMA removal (squares).](image)

We know from the results obtained on long gradients that the structure transition observed for PMMA/P2VP system occurred between 95° and 75°. Moreover, we just saw that the polymer blend film has a structure transition over two hundred micrometers. This shows that the short wettability gradient extends from 95° to less than 75°. Since the structure of PMMA/P2VP film
remains flat for surfaces having contact angles smaller than 75° it is difficult to draw a conclusion concerning the most hydrophilic part of the gradient.

### 4.3. Discussions

#### 4.3.1. Influence of the morphology of the TiO$_2$ layer

As mentioned above, the TiO$_2$ layers prepared were finely cracked all over the coating. An issue was to know if the cracked morphology of the TiO$_2$ layer could be transferred in the thiol SAM during photocatalysis. For that, more information about the resolution of photocatalytic lithography had to be found. This problem was already addressed in studies dealing with the patterning of surfaces by means of photocatalytic lithography.$^{[128-130]}$ When photocatalytic lithography is performed using a patterned photomask, radicals are created on the illuminated areas of the TiO$_2$ surface. Then, the radicals diffuse through the air gap and oxidize the surface facing TiO$_2$. The final resolution may depend on the diffusion of the radicals within the air gap, and thus on its thickness. The resolution may also be influenced by more complex mechanisms, as suggested by Kubo et al.$^{[115,128]}$ According to the authors, hydrogen peroxide, which is created in the vicinity of TiO$_2$ surface and diffuse through the air gap, may decompose into hydroxyl radicals in the vicinity of the surface to degrade. Since the decomposition of hydrogen peroxide into hydroxyl radicals occurs in presence of UV (figure 4-2), this would happen only on the illuminated regions of the target surface. There would thus be an increased degradation in these areas.

In practice, 10µm large features were resolved with spacer thicknesses of 12.5µm or 100 µm.$^{[128]}$ Since the cracks present on our TiO$_2$ layers were long (micrometers) but only 200nm wide, they were too small to be resolved. The risk to induce the cracked morphology in the SAM was thus limited.

#### 4.3.2. Comments on the photo-oxidation of thiol SAMs

The photocatalytic oxidation of thiol SAM was, until now, only scarcely studied. Notsu et al reported results concerning the patterning of thiol SAMs by means of photocatalytic lithography.$^{[130]}$ However, the photo-oxidation of alkanethiolates using UV was widely studied. The goal of this paragraph is to review the different mechanisms of thiol SAM photo-oxidation reported in
literature and compare them with our results. Among the previous studies, various setups were used to investigate thiol photo-oxidation. In all cases, a UV lamp was used to illuminate a thiol SAM adsorbed on a gold or silver coated substrate. The different results are difficult to compare since the irradiiances of UV lamps used and their spectrum (broad spectrum, ozone generating or ozone free lamp) were not always the same. The studies however agree that thiol photo-oxidation results in the formation of sulfonate species\textsuperscript{[138-144]}. This could be observed on XPS spectrum with the appearance of a peak at 168eV typical of sulfonate species upon UV illumination and the disappearance of the thiolate peak at 163eV\textsuperscript{[139,144-146]}. Sulfonate groups like (SO$_3$)$^-$, (HSO$_4$)$^-$ also appeared in Static SIMS spectra\textsuperscript{[142,143,146]}. If all the studies agree on the generation of sulfonate species, there are still debates concerning the underlying mechanism. When ozone generating lamps were used ($\lambda$$<$200nm) the main process of photo-degradation was reported to be ozonolysis and the oxidation of the alkyl chains was even observed during the process\textsuperscript{[138,145,147-149]}. However, other groups showed that thiol photo-oxidation could occur with ozone free lamps\textsuperscript{[142]}. The mechanism proposed in that case involve the generation of “hot” electrons in the gold layer upon absorption of a photon, which initiate the oxidation process. This explanation was first proposed in the work of Huang and Hemminger\textsuperscript{[139]}.

Concerning TiO$_2$ photocatalytic oxidation, Notsu et al reported some results about the remote oxidation of octanethiol, 1H-1H-2H-2H-perfluorodecanthiol, 11-mercaptoundecanoic acid and 2-aminodecanethiol\textsuperscript{[130]}. In their study, the contact angles and XPS measurement were made after photocatalytic degradation but no backfill was performed. For octanethiol, a decrease in contact angle from 100° to less than 10° was observed. XPS results suggested the formation of sulfonate species during the process. However, a large increase in oxygen content was observed together with a decrease of carbon content. They concluded that oxygen containing groups (e.g. -OH, C=O, -COOH) were formed and that alkyl chains were degraded during the photocatalytic process. For long exposure times, oxidation of gold was even observed. This could be seen on the XPS spectrum, and explained why contact angle of less than 10° were measured. We did not see so large changes in water contact angle just after the photocatalytic process. This may be explained by the difference in irradiation since our lamp was ten times less intense. Nevertheless, we also observed the 168eV peak due to the formation of sulfonates upon photocatalytic remote oxidation.
4.3.3. Fabrication of short structure gradients

The dependence of polymer demixing on substrate surface energy was used to characterize the short wettability gradients. Polymer can indeed react to surface-energy variations on the micrometer scale \[^{[65,102,150]}\]. In addition to the fact that it is useful as a characterization means, the fabrication of polymer demixed thin films on substrates having wettability gradients is an efficient technique to produce samples with very short topography gradients. As mentioned above, 200µm long structure gradients with RMS roughness ranging from 2 to 15nm were made. Long gradients with similar RMS roughness changes were already fabricated for a combinatorial cell growth study \[^{[19]}\]. Our approach permits shorter structure gradients to be created, which would not be interesting for high throughput studies but would provide new templates for other applications such as cell locomotion investigation where the slope and length of the gradients are critical.

4.4. Conclusion

A new technique to achieve long as well as short wettability gradients was proposed. This technique is based on the gradual photo-oxidation of thiol SAMs. The proposed method combines photocatalytic lithography and gray-tone lithography. 1-dodecanethiol modified, gold-coated substrates were subjected to TiO\(_2\) photocatalytic lithography with a photomask having gray-tone gradients. The degree of degradation of the thiol SAM could locally be controlled by the grey tones on the photomask. This led to a gradual degradation of the thiol SAM. After photocatalytic remote oxidation, the samples were backfilled with a different thiol to create a compositional gradient and to ensure a complete thiol SAM.

The water contact angle measurements made along the long gradient revealed a non-linear wettability gradient with water contact angles ranging from 90° for the most hydrophobic side to 50° for the most hydrophilic one. The backfilling appeared to be critical, since no gradients were observed when the back filling was performed with 1-dodecanethiol.

The precise mechanism of the photocatalytic remote oxidation of thiols was elucidated using XPS. The apparition of a sulphur peak at 168eV showed that thiols were oxidized into sulphonate species. The sulfonates were then removed from the surface by rinsing the sample in ethanol. A degradation mechanism proposed was supported by the results of other studies concerning thiol photo-oxidation \[^{[115,130,142]}\].
Short wettability gradients were also made by using a short gray-tone gradient. If the characterization of the long wettability gradients was straightforward, this was an issue for short gradients. The gradients were qualitatively observed from the shape of sessile drops on the gradient surfaces. The second characterization technique used the wettability dependence of PMMA/P2VP films morphology. We could conclude that short gradients were varying from 95° to less than 75° over a distance of 200µm. However, this technique did not give details about the most hydrophilic side of the gradient.

One challenging point, now, is to know how short the wettability gradients can be using this technique. The lower limit for the length of the gradient was not investigated but would require modifications of the setup. The fabrication of shorter gradients would require working with smaller air gap to improve the resolution of the system, which would modify the kinetics of degradation \[126\]. This would require also a perfect control of all environmental parameters. As for many techniques developed for the fabrication gradients, the process presented here relies on the kinetics of reaction. In some approaches, this is for instance the kinetics of diffusion or adsorption of the thiols\[13,43\]. Here, the kinetics of photocatalytic oxidation of the thiol SAM is exploited. The control of the kinetics is however not critical in other applications of photocatalysis such as surface patterning, where the goal is to obtain either oxidized or non-oxidized areas. For example, we evoked in the introduction the importance of humidity in the degradation process. Modifications in the photocatalytic activity were indeed already reported depending on this parameter \[122,151\]. We would, for instance, expect a change in gradient slope and length due to humidity variations.
Chapter 5
Replication of Structured Thin Polymer Films

This chapter focuses on the replication of the structured polymer films previously presented. Three different polymers were used for the replication and individual protocols were used in each case.

5.1. Introduction

We showed in the previous chapters that long as well as short structure gradients could be produced. The next step of the study was to use these substrates to investigate the effect of topography on cell growth. Among the different systems explored, we decided to focus on the PMMA/P2VP system, since it led to the most pronounced topographical contrast. The aim was to replicate the structure gradients presented in chapter 3 in different polymeric materials. The necessity to develop a replication technique was motivated by three limitations of our process. In the first place, the structured polymer films were made using a polymer blend and led to chemically heterogeneous samples. Friction measurements revealed, indeed, the presence of PMMA and P2VP at the air/polymer interface of the as-cast films. Selective solvent treatment did
not solve this problem since the polymer structures obtained were surrounded by the thiolated gold substrate. This was a major drawback to study the effect of topography, since the chemistry of the surfaces also varied along the sample. Replication of the structured polymer film eliminated the chemical variations along the sample, leading exclusively to the topographical contrast.

Another drawback was the time needed to produce each sample. Biological applications often require the use of numerous samples, since statistics plays a major role. The fabrication of the structured thin polymer films was divided in three steps: the preparation of the gold surface (creation of long or short surface-energy gradients); the fabrication of the thin polymer film and a last step to selectively remove one polymer of the blend. Each step required working sequentially and the time per sample varied from thirty minutes when long gradients were made to more than one hour in the case of short gradients. The second goal of replication was thus to decrease the time needed to produce the samples.

The last point concerned the morphology of the samples made by polymer demixing. The roughness and length scales of two samples made under similar conditions were always the same since these measurements are averaged over the sample. However, the morphology of the film can never be exactly the same due to the stochastic nature of the topography obtained. If the same master is used for all replicas, the study can be done by rigorously using the same structured gradients.

Concerning the potential techniques for replication, we focused on hot embossing and casting, which were already reported for the replication of micro and nano-structured surfaces\textsuperscript{152-154}. In hot embossing, the polymer is heated well above its glass transition temperature and pressed against the structured master for replication. The moulds are usually made of silicon or metal to withstand high processing temperatures (from 150°C to 200°C)\textsuperscript{155}. Some recent studies reported also the use of PDMS soft intermediates, which is an attractive alternative to nickel shim since it does not\textsuperscript{156}. Casting techniques do not need such high temperatures, since the polymer is not processed in a melt. The polymer is usually cross-linked after casting either chemically or using UV. The most widely used polymers are silicone based elastomers (PDMS)\textsuperscript{157,158}. They can be easily processed and only moderate temperatures are required to chemically cross-link them (80°C).
Three main issues had to be resolved to use these techniques to replicate the gradients:

- First, the master we used consisted of a structured polymer thin film deposited on a gold-coated silicon wafer. The main problem concerned the processing temperature, which had to be less than the glass-transition temperature of the polymer used to make the master. A temperature that was too high would have resulted in a degradation of the master.
- Second, the process had to be suitable for sub-micrometer structures. The features present on the structured master were only 30 nm high but the lateral dimensions were in some cases as small as 200 nm.
- Third, the un-moulding step was also critical since it could affect the quality of the replica. The adhesion of the replica on the master had to be low enough to avoid the deformation of the replica during un-moulding or the lift off of the thin film from the substrate.

The three different materials used for the replication were poly(dimethylsiloxane) (PDMS) and two thermoplastic polymers: AFFINITY EG8150 and TOPAS 8007S-04. The physical and thermal properties of the polymers are presented in table 5-1. The three materials had very different properties and a specific replication protocol was developed for each case. After a presentation of the replication techniques for the three materials, initial cell growth results will be showed.

*Table 5-1: Summary of the properties of the polymers used for replication.*

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Melting point °C</th>
<th>Glass transition temperature</th>
<th>Melt flow index ml/10min</th>
<th>Tensile modulus [MPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>AFFINITY EG 8150</td>
<td>56 (1)</td>
<td>0.5 at 190°C (1)</td>
<td>6.62 (1)</td>
<td></td>
</tr>
<tr>
<td>TOPAS 8007S-04</td>
<td>80 (2)</td>
<td>2 at 190°C (2)</td>
<td>2600 (2)</td>
<td></td>
</tr>
<tr>
<td>PDMS Sylgard 184</td>
<td></td>
<td></td>
<td>3 [73]</td>
<td></td>
</tr>
</tbody>
</table>

*(1) Product information: Dow Plastics (2) Product information: Ticona*
5.2. Replication in PDMS

PDMS is an elastomer commonly used in soft lithography\textsuperscript{[153,159]}. Micrometre-scale features were reported to be accurately replicated but more sophisticated approaches using hard PDMS have been developed for a good replication of sub-micrometer features\textsuperscript{[158]}. Attempts were even made to replicate sub100nm features\textsuperscript{[160]}. Due to its good replication properties and transparency, PDMS has been used for various applications like the fabrication of microfluidic networks\textsuperscript{[161]}, optical devices\textsuperscript{[162]} and was extensively used in soft lithography techniques like microcontact printing and micromolding in capillaries\textsuperscript{[153]}.

The structured polymer thin films replicated here were PMMA/P2VP (50/50)\textsubscript{w/w} films spin coated at 6000rpm from a 1\%\textsubscript{w/v} solution. PMMA was removed to obtain a more pronounced topographical contrast. As will be explained later, an additional PS layer was spin coated on the thin film to improve the quality of the replication (figure 6-1). PDMS was prepared using a (10:1)\textsubscript{w/w} monomer/cross-linker ratio. The stamp was made by casting the mixture on the structured master (figure 5-1) and curing it overnight. The choice of the curing temperature was critical since the master was composed of a polymer. The glass transition temperature of the polymer we used were all above 100°C and possibly higher due to the confinement of the polymer in a thin film\textsuperscript{[163]}. The PDMS was thus cured at a temperature of 80°C and released after cooling to room temperature.

![Figure 5-1: Schematic representation of the replication procedure.](image)

Figure 5-2 presents the AFM characterisations of the masters used for the replication and the PDMS stamp. Two kinds of masters were used: one without the additional PS layer, the other
with. As can be seen, the features present on the first master could hardly be replicated. Holes were observed in the PDMS replica but were much deeper (>60nm) than the height of the starting pillars (30-35nm). This was not observed when a thin PS film was spincoated on the structured film. By making a scratch on the polymer thin film, the thickness of the PS film was measured as can be seen on the section presented in figure 6-2. The PS was 10nm thick, which decreased the height of the feature but permitted drastic improvements in the accuracy of the replication. However, a discrepancy was observed concerning the depth of the holes compared with the height of the starting pillars. For 22nm height pillars in average, the corresponding holes in PDMS were only 18nm. Other studies report a similar tendency when replicating with PDMS\textsuperscript{[73,160]}.

![Figure 5-2: Optimization of the replication process. a) Left: AFM images of the master without the PS layer: centre: section of the polymer film; right: corresponding PDMS replica. b) Left: AFM images of the master with the PS layer: centre: section of the polymer film; right: corresponding PDMS replica.](image)

The poor quality of replication in absence of the PS layer might be due to an adhesion that was too strong between PDMS and the substrate between the pillars. This resulted in a deformation of
the stamp during the releasing step. The PS layer acted thus as an anti-adhesive layer.

Figure 5-3: Series of AFM images taken along the structure gradient of: a) the master and b) the PDMS replica. The position of each measurement along the gradient is precised on the left part of the image.
The replication of polymer thin films bearing structure gradients was also made following the same procedure. Figure 5-3 presents AFM images of the topography taken along the gradient. As can be seen the progressive transition from a structured to a flat morphology is observed. As a comparison, the structure gradient obtained for a PMMA/P2VP film after PMMA removal is displayed on the right hand side.

### 5.3. Replication in polyolefin elastomer

The first thermoplastic used for the replication was a poly-olefin plastomer (POP). These polymers result from the copolymerization of ethylene and an α-olefin, such as butene or octene. The thermal and physical properties can be tuned by varying the co-monomer content. This new class of polymers has already been shown to be an effective alternative to PDMS for micro-contact printing applications\[^{164}\]. The replication of features as small as 100nm was already reported using the hardest elastomers\[^{164}\]. In this study, a copolymer of ethylene and octene was used (AFFINITY™ EG 8150).

![Figure 5-4 : Schematic representation of the replication procedure.](image)

The polymer was received as beads and a first moulding step to form flat pellets was necessary (figure 5-4 a)). One advantage of this material for the replication was its low melting point (56°C), which permitted moderate processing temperature to be used without compromising the
replication time. As for PDMS, the temperature used for the replication had to be lower than the glass-transition temperature of the polymer forming the master. The master used in that case was a structured polymer thin film of PMMA/P2VP (50/50)\textsubscript{w/w} spin coated at 6000rpm from a 1\%\textsubscript{w/v} solution. PMMA was removed to obtain a more pronounced topographical contrast. Contrary to PDMS, no anti-adhesive layer was needed to ensure a good release of the replica. The hot embossing was performed at 90°C and lasted ten minutes per sample (figure 5-4 b)).

![AFM images](image)

**Figure 5-5:** a) AFM image of the master used for the replication. b) AFM image of the AFFINITY™ replica. c) RMS roughness of the master and the replica.

AFM images of the starting master and of the AFFINITY™ replica are presented in figure 5-5. The general quality of the polymeric replica was good, with an accurate reproduction of the lateral size of the domains. As can be seen on the sections, the vertical dimensions of the features were fairly well replicated. A finer analysis revealed however that the depth of the holes was smaller than the height of the starting pillars. This led to a decrease of the roughness of the surface as shown in figure 5-5.
Chapter 5: Replication of Structured Thin Polymer Films

Other studies reported the replication of sub-micrometer structure using elastomers\cite{165,166}. According to the authors, the replication of features sizes below 500nm was difficult, due to the softness of the material. In our case, the width of the structures were small (200nm for the smallest), but the height of the features were only 30nm. This small aspect ratio may explain why the features could be replicated.

Figure 5-5: Series of AFM images taken along the gradient in topography for: a) the master and b) the replica in AFFINITY™. The position of each measurement along the gradient is precised on the left part of the image.

*Figure 5-5: Series of AFM images taken along the gradient in topography for: a) the master and b) the replica in AFFINITY™. The position of each measurement along the gradient is precised on the left part of the image.*
As shown in figure 5-5, gradients of structures were also replicated in AFFINITY™. The different morphologies of the transition were observed in the AFFINITY™ replica.

## 5.4. Replication in TOPAS®

TOPAS® is a cyclic olefin copolymer made by copolymerization of ethylene with a cyclic olefin: norborne. The thermal properties of the resulting material can be tailored by adjusting the ratio between the monomers. TOPAS® has already been shown to be suitable for the replication of micro and nanostructures by means of nano-imprint lithography\[155,167,168\]. Its low shrinkage and low surface energy make it indeed attractive for replication purposes. In this work, the TOPAS® used had a glass-transition temperature of 80°C. The process developed for the replication in AFFINITY™ could unfortunately not be used due to the too high glass transition temperature of TOPAS®. As mentioned before, the glass-transition temperature of PMMA and P2VP is situated at 100°C. Furthermore, several studies reported a processing temperature of 170°C for replication in TOPAS®\[167,169\]. Such a high temperature would certainly alter the structure of the polymer thin film. Another kind of master had thus to be developed. Among the previous studies, replication in TOPAS® was reported using nickel shims\[155\] or fluorinated silicon masters\[169\]. Another approach less investigated was the use of soft intermediates such as PDMS stamps to perform the embossing. This was already applied to the embossing of polystyrene and PMMA\[156,170\]. Since the cross-linked PDMS stamp withstands temperatures until 200°C, a hot embossing is possible without degrading the master. Moreover, we showed in a previous section that the structure gradients obtained in the polymer thin film can be replicated in PDMS.

For TOPAS®, we thus made a two step replication: first, a PDMS negative replica of the structured polymer thin film was produced using the technique presented above. It was then used as a master to transfer the structures to TOPAS® by means of hot embossing. The embossing temperature was 180°C and the process lasted 5mn per sample. One advantage of PDMS was that a good conformal contact was directly set when brought into contact with the surface of TOPAS®. After cooling down, the master was easily removed. The resulting TOPAS® was then characterized by means of AFM. Figure 5-6 presents the AFM images of the PMMA/P2VP thin film (covered with a thin PS film) that serve as master for PDMS. The negative PDMS replica obtained exhibited holes slightly less deep than the height of the starting pillars as described in the previous sections. The final TOPAS® replica had the same morphology as the starting
polymer thin film. The hot embossing in TOPAS® was very effective and the height pillars obtained in the replica corresponded to the depth of the holes in PDMS.

![Figure 5-6: a) Starting structured polymer thin film. b) Negative replica in PDMS. c) Replica in TOPAS®. The red line show where the sections presented on the right hand side were taken.](image)

More than ten embossing steps could be made using the same PDMS replica without affecting the replication quality. This allowed series of replica to be made. The replication of the gradients was also demonstrated. As presented in figure 5-7, the structure gradients were successfully transferred into TOPAS®. The final gradient had a similar morphology to the starting polymer thin film, since the PDMS stamp was a negative replica of the starting master. The replicated features were however less high than the original due to the replication step in PDMS, which led to a loss in definition.
Figure 5-7: Series of AFM images taken along structure gradients in a) the starting master, b) the PDMS negative replica c) the TOPAS® replica. The position of each measurement along the gradient is precised on the left part of the image.
5.5. Initial cell growth experiments

Preliminary investigations were made concerning the effect of topography on cell growth. This work was made in collaboration with the University of Glasgow. The three different structured polymer surfaces were used as substrates for the growth of HTERT fibroblasts. The cells were grown in complete medium for periods of time ranging from 24h to 72h. After fixation, the cells were analysed using light microscopy or SEM.

The cell adhesion and growth on PDMS and AFFINITY™ surfaces was very weak and no characterization could be made due to the lack of cells on the sample. However, TOPAS® was found to be more suitable for cell growth. The density and shape of the cells were first analysed by means of optical microscopy after a Coomassie blue staining. No relevant effects were observed concerning the influence of structuring on cell density or morphology (area, shape). However, on the microscopic scale, SEM revealed changes in the formation of the filopodias of the cells as illustrated by figure 5-8.

Figure 5-8 : SEM images of HTERT-fibroblasts grown 72H on a TOPAS® surface.
5.6. Discussion

As presented above, the three materials chosen were successfully replicated using three specific replication techniques. As mentioned above, the thermal and physical properties of the different polymers were very different, which influenced the molding process. For instance, we observed that the two soft polymers (PDMS and AFFINITY™) always led to shallower replicas. TOPAS®, which was much harder, did not show this problem. Other studies reported the need for a hard material to realize high-resolution replication of sub-micrometer structures\(^\text{[73,158]}\). Special techniques were for instance developed using “hard” PDMS\(^\text{[3]}\) to overcome the limitations of the standard grade. Similar problems were also noticed when replicating in other elastomers\(^\text{[165,166]}\). Two points should be addressed concerning the quality of the replication: first the ability of the polymer to establish a conformal contact over the whole structure to be replicated, second, the ability of the polymer to maintain the moulded structure after processing (after crosslinking and cooling in the case of PDMS, after hot embossing and cooling for thermoplastics).

In the molding process, the first step is the filling of the structures with polymer during moulding. This can be affected by the wettability of the polymer on the master. Moreover, in the case of hot embossing, the viscosity of the polymer melt and the pressure applied will also play a role. An incomplete filling of the features by the polymer would be the first source of imperfection in the replication. In a second step, the system is cooled down and the polymeric replica released. At the end of the process, the polymer replicas are no longer confined in the master and the polymer surfaces are subjected to surface-tension effects. In the case of elastomers, the low modulus does not permit the moulded shapes to be retained after release from the master. The sharp details are smoothed due surface tension forces. In the case of harder materials, the surface-tension forces are not strong enough to modify the shape of the replica. This effect already reported in literature justify the need of hard materials for high resolution replication\(^\text{[158,171]}\). This can be critical when sub-micrometer features have to be replicated. Finally, another contribution to the loss of resolution during the replication is the shrinkage of the polymer during the process. This can originate from the polymerization (in the case of PDMS) and from cooling (thermal shrinkage)\(^\text{[171]}\).

The different effects presented above, all contribute to loss of resolution during replication. The effect of surface tension however only affects materials with a low Young’s modulus like the two
elastomers used in this study. This restricts the use of elastomers to the replication of large features.

5.7. Conclusion

The structure gradients presented in chapter 4 were replicated in three different polymers: PDMS, AFFINITY™ and TOPAS®. Three specific techniques were used due to the different thermal and physical properties of the polymers.

Replication in PDMS was done by pouring a mixture of monomers and crosslinking agent onto the master and thermally crosslinking the polymer. This technique was the most time consuming due to the long curing time of the polymer. For the two other polymers, hot embossing was used to perform the replication. This permitted the replication to be made in less than 10mn for each sample. The masters could be used for several replication steps.

As mentioned in the introduction, three conditions had to be met to ensure good replication: first, the possibility to replicate at a temperature below the glass transition temperature of the polymer forming the master. Second, the possibility to replicate sub-micrometre features. Third, avoid the sticking of the replica on the master upon demoulding.

Concerning the first point, the replication in PDMS and AFFINITY™ was made at temperatures below to the glass transition temperature of the polymer constituting the master. The high glass-transition temperature of TOPAS® did not permit replication at such low temperature. An alternative technique using a PDMS negative replica to hot emboss in TOPAS® was used.

Second, in all cases the quality of the replication was good but in the case of the two elastomers, a slight loss in definition was observed. This effect, already reported in literature, was attributed to surface tension. After release, surface tension deformed the surface of the replica due to the low Young modulus of the elastomers. Harder materials like TOPAS® do not have this problem and permit the replication of sub-micrometer features more accurately.

Finally, the unmoulding step was problematic only for PDMS. In that case, a deformation of the PDMS replica was observed upon demoulding. To solve this problem, a thin PS film was spin coated onto the master as an anti-adhesive layer. This drastically improved the quality of the replication.

Initial cell-growth investigations were made using H-TERT fibroblasts on the different substrates. Among the three materials, only TOPAS® was found to be suitable for cell growth.
No relevant effect of topography on the cell morphology and density were observed. On the micrometer scale, the formation of filopodia by the cells was found to be influenced by the presence of structures.
The aim of this work was the fabrication and replication of gradients in topography. Except for the work concerning replication, the fabrication of structured surfaces was made by means of polymer demixing by solvent quenching. Various parameters were investigated in order to tune the morphology and sizes of the structures produced. Emphasis was put on the effect of surface energy which was used to fabricate gradients of topography.

6.1. Fabrication of long gradients of topography

The confinement of polymer blends in thin films can greatly affect the morphology of the phase separated domains due to the presence of the substrate/polymer and air/polymer interface. Indeed, there an interplay between the enrichment/wetting of the interfaces by polymers and the phase separation. By controlling the surface energy of the substrate, the morphology of the resulting film can be tuned.

Among the different polymer blends tested, different effects of surface energy were observed. In the case of PVA/PDADMAC, the effect of surface energy was very weak and only slight changes were observed in the morphology. For the two blends studied in more detail (PVA/Dextran and PMMA/P2VP), different topographies were observed on hydrophilic and hydrophobic substrates. This was highlighted using gradients of surface energy in order to probe the transitions between
the two extreme surface energies. In the case of PVA/Dextran blend, a transition from pillars to pits was observed on increasing surface energy. In contrast, PMMA/P2VP showed a more complex transition from a dotted morphology on the hydrophobic side of the gradient to a layered morphology on the hydrophilic side. In the middle of the transition, the polymer film had a bi-continuous morphology. The position of the transition also depended on the system chosen: Although the transition was observed at a water contact angle of 40° for the PVA/Dextran system, this was not the case for PMMA/P2VP, which exhibited a transition at 85°. For both polymer blends, the transition in morphology spread over more than a centimetre, whereas the gradient of wettability took place over 2cm. To obtain a gradual transition in morphology over the whole sample, a specific gradient of wettability should be designed according to the characteristics of the transition (position and range of contact angles).

In addition to its interest for the fabrication of topography gradients, the method developed here could also be useful as a tool for the investigation and the control of other polymer blends. There is for instance a growing interest in films of conductive polymer blends, which play an important role in the fabrication of organic light emitting diodes (OLEDs). One key point is the control of the morphology of the blend which can affect the performance of the device. The use of surface energy gradients would permit the investigation of the dependence of blend morphology on surface energy and would allow the structure/function relation of the OLED to be elucidated on a single sample.

6.2. Fabrication of short gradients of topography

The fabrication of sub-millimetre gradients of topography was also demonstrated. We used the same polymer blend (PMMA/P2VP) as for the long gradients and focused on the development of substrates presenting sub-millimetre long wettability gradients.

The technique explored was based on the gradual degradation of an alkanethiol SAM. For this, we developed a technique combining TiO₂ photocatalytic lithography and gray-scale lithography: a glass slide coated with TiO₂ placed in front of the surface to be modified with a small intervening air gap. On exposure to UV, oxidizing radicals were created on the TiO₂ surface. These diffused through the air gap and degraded the thiol SAM. Since the amount of radicals created depends on the intensity of illumination, the degradation of the SAM was controlled along the sample using a gray-scale photomask. Once subjected to photocatalytic lithography, the
samples were backfilled with a complementary thiol to obtain a complete SAM.
The feasibility of the experiment was shown by first making 1.5 cm long wettability gradients. For this, we used a long gray-scale gradient to perform the photocatalytic lithography. Water contact angle measurements revealed changes in wettability along the sample but the final gradient was not linear: the slope indeed decreased towards the hydrophilic end of the gradient. We also observed that the type of thiol chosen for backfilling led to significant changes in wettability and was critical for the fabrication of the gradients.

The experiment was then performed using a 720 µm long gray-scale gradient. Here, the main problem encountered was the characterization of the final gradients. We got insights into the wettability changes along the gradient by analysing the shape of sessile water droplets deposited on the surface. The droplets wet more the substrate in the hydrophilic regions of the gradient in contrast to the hydrophobic areas, where the water dewetted. This led to a wave-shaped triple line on the water droplet. This showed that the surface could also be modified using short gray-scale gradients. However, it was difficult to draw any quantitative conclusions concerning the length and slope of the gradient obtained.

As mentioned above, the goal of this chapter was the fabrication of short structure gradients. Polymer blend thin films were thus made on the substrates. A gradual transition in the morphology of the polymer blend film was observed along the sample. A 720 µm long gray-scale gradient was used to fabricate a wettability gradient of wettability and the final gradient of polymer structure was 200 µm long. In addition to showing that structure gradients can be made using this technique, the morphology of the polymer blend thin film gave information on the water contact angles of the substrate. As seen in chapter 3, the transition in morphology observed for PMMA/P2VP is obtained at precise water contact angles (from 95° to 70°); we could thus use the polymer blend thin film as a tool to characterize the surface. Since the water contact angle/morphology relation is known, we obtained a measure of the water contact angle of the substrate from the morphology of the polymer blend thin film. We concluded that the short wettability gradient covered water contact angles ranging from 95° to 70° along 200 µm. However, the extremities of the gradients (lowest and highest water contact angles) could not be determined using this approach.

Other potential application can, however, be envisioned. The combination of photocatalytic and gray-scale lithography presented here is an interesting basis for the realization of wettability
gradients with complex shapes: the photomask designed for this study had linear gray-scale gradients of different lengths. However, we can imagine creating other kinds of gradients (radial, non-linear slopes) by simply adjusting the design of the photomask.

Another outlook would be the investigation of the limits of such the technique proposed. The smallest gray-scale gradient used in this study was 720µm. However, previous studies reported that surface patterning of features down to 10µm was possible with photocatalytic lithography. One challenge would thus be to see how small the gradients can be done. The fabrication of very short gradients (from 10 to 100µm long) would require a perfect control over the different parameters affecting the photocatalytic degradation. More precisely, emphasis should be put on the control of the kinetics of photo-degradation, on which the creation of the gradient relies.

6.3. Replication of the structured, thin polymer films

The surfaces presenting gradients in topography were also used as masters for replication. Only one polymer blend was used in this part: PMMA/P2VP (50 : 50)\textsubscript{w/w}. The replication was made in three polymers: PDMS, AFFINITY™ and TOPAS®. Since each polymer had specific properties, the replication techniques were adapted to each case. The three methods were either based on casting or hot embossing. The major problem concerned the sensitivity of the master to temperature; a processing temperature above the glass-transition temperature of the polymer forming the master would result in degradation of the master. The size of the structures to be replicated was also an issue since the features were only few tens of nanometre deep and hundreds of nanometre wide. The last problem to overcome concerned the adhesion of the replica to the master, which often poses problems for the unmoulding of the replica.

The replication in PDMS was done by casting. A direct use of the structured polymer thin film as a master was however not successful due to PDMS sticking to the film. An anti-adhesive layer was thus added to the master to improve the demoulding and the quality of the replica. The final replica was, however, always smoother than the master. This was attributed to the deformation of the replica after demoulding due to the effect of surface tension combined with the low Young’s modulus of PDMS.

In the case of AFFINITY™, the replication was done by hot embossing. The advantage of AFFINITY™ was its low melting point, which allowed replication of the master at a temperature
below the glass-transition temperature of the structured polymer film. In contrast to PDMS, no anti-adhesive layer was necessary to ensure good replication. However, the final replica was again smoother than the master. The Young’s modulus of the AFFINITY™ used was also low, which may lead to the same deformation problems as observed for PDMS.

The last polymer used was TOPAS®. Replication was performed by hot embossing. The high glass-transition of the TOPAS® did not allow the master to be directly replicated. The hot embossing was made using a negative replica of the master in PDMS. This allowed a higher moulding temperature. Moreover, the use of PDMS was an attractive alternative to nickel shims, which are often employed for hot embossing but require more expensive equipments.

The different replicated surfaces were then used for preliminary cell growth experiments. One advantage of using replicas was that, for each material, exactly the same gradient in topography was used since all replicas were made using the same master. H-Tert fibroblasts were grown on the different samples but did not show notable changes in cell morphology or density along the gradients. However, SEM characterization revealed that the formation of filopodia of the cell was affected by the presence of the nanostructures on the surface.
Appendix 1

Nanostructured Films of Water-soluble Polymers

This appendix describes the fabrication of nanoporous polymer films of water-soluble polymers and their transfer to ink-jet printing media. In the first part, the fabrication of tunable structured polymer thin films using polymer-blend phase separation will be demonstrated. The study involved two polymer blends composed of water-soluble polymers. In the second part, a technique developed to transfer the polymer films to ink-jet printing media will be presented. Finally, we describe a method to obtain more stable layers using a photo-crosslinkable polymer.

A1.1. Context

The emergence of digital photography has led to an increasing interest in ink-jet printing techniques. Photo-like quality images can be obtained using commercially available printers and ink-jet printing media. This level of quality was reached due to the improvement made in the last decade to optimize properties such as the rapidity of ink-uptake, the drying time of the ink, the resolution of the printed image, the gloss of the surface and the stability of the printed images. However, there are still compromises to find during the development of such ink-jet media. Indeed, the technologies allowing the best resolution generally lead to the less stable images and
those giving the highest stability produce less resolved images.

In this appendix, we focus on the problems of stability and fading of ink-jet printed images with time. There are several factors affecting the lifetime of the images: the two main sources of degradation of ink-jet printed images are light fading and gas fading. We more especially focused on this last case. Gas fading is caused by contact of the image with the surrounding air, which results in the degradation of the colorant, mainly by ozonolysis.

Various kinds of inks and ink-jet media currently exist on the market but there resistance toward gas-fading is very variable.

Two kinds of inks are generally used to ink-jet print: the dye-based and the pigment-based inks. The dyes used in the dye-based inks are usually organic molecules that are generally easily degraded on exposure to ambient air, which decreases the lifetime of the images. They, however, allow the best printing resolution. In the case of pigments-based inks, the images obtained are much more stable since the colorants are inorganic particles. The main problem with this technology is the production of particles as small as possible. Too big pigments generally lead to lower printing resolution.

Gas fading depends also strongly on the kind of ink-jet media used and more especially on its ink-receptive layer. Two trends emerged for the fabrication of such coatings: the use of polymer layers and the use of nanoporous metal-oxide layers. In the first case, a polymer layer that can swell the ink is deposited on the paper. When the ink droplet strikes the surface of the media, the polymer swells the ink and embeds the ink components (dyes or pigments). Such media generally provide a good stability of the images but require long drying times. The printing resolution is also not optimal due to the diffusion of the ink in the polymer layer. In the second case, metal-oxide nanoparticles are used to form a nanoporous layers on the surface of the paper. The layer obtained has a large specific area and porosity at the nano-scale, which results in a very fast ink-uptake due to capillary effects and permits the highest image quality to be achieved. However, the dyes and pigments are in that case deposited within the nano-pores and not embedded, as in a polymer coating. Since there is a huge specific area due to the nanoporosity, this results in a greater exposure to the surrounding air and makes these media more sensitive to gas fading.

In this study, we investigate a potential route to improve the stability of the ink-jet media having a metal-oxide nanoporous layer. More precisely, the goal was to deposit a thin nanoporous polymer film on top of the ink-jet media and try to improve the gas fading properties of the media.
while maintaining fast ink uptake and high resolution.

Various constraints had to be respected for the development such layers:

- The process had to be environmentally friendly. The techniques employed to fabricate the ink-jet media presented above generally avoid the use of organic solvent and harmful chemicals and we had to take this aspect into account.
- The nanoporous polymer layer had to be tunable. The pore size and pore volume play indeed a key role in the ink-media interaction during printing.
- The nanoporous polymer layer had to be deposited on ink-jet printing media coated with a metal-oxide nanoporous layer. This was a real challenge since such substrates have very special properties (porosity, roughness, chemistry).

The technique proposed to realize such layers is based on a polymer demixing. In this simple technique, a solution composed of two polymers and a solvent is spin coated onto a substrate. During the process, the evaporation of the solvent led to a demixing of the two polymers and a phase-separated structure is formed. By selectively removing one component of the blend, a porous film can be obtained. We restricted ourselves to water-soluble polymers and avoided organic solvents to keep an environmentally benign procedure. Polymer demixing was widely studied in the past and permits the formation of structured polymer films with feature sizes on the micrometers to nanometre scale \[31,32,173\]. To date, this technique was, however, used almost exclusively with organic-solvent-based, polymer-blend solutions \[31,32,87\].

A detailed investigation was first made to determine which kind of phase-separated structures can be obtained using water-based systems and to get insights on the tunability of the technique. Two parameters (spin speed and solution concentration) were systematically varied in order to achieve different structure sizes. In this first part of the study, we used model substrates (silicon wafers). In a second part, a technique was developed to realize the nanoporous polymer layers on the ink-jet media. Finally, we investigated the possibility to produce more stable layers using a cross-linkable polymer.

### A1.2. Polymer demixing with water-soluble polymers

The technique used in this part to create structured polymer films was polymer demixing by solvent quenching. As mentioned above, the final goal was the fabrication of a nanoporous polymer layer with tunable pore sizes. To fabricate a porous layer from the phase-separated
polymer film, one of the polymers of the blend was selectively dissolved. The size of the pores could then be controlled via the size of the phase separated domains. To tune the structure sizes in the polymer film, two parameters affecting the phase-separation process were intensively investigated: the polymer concentration in solution and the spin speed. The two blends used were PVA/PDADMAC (50 : 50)\textsubscript{w/w} diluted to 3\%\textsubscript{w/v} and PVA/Dextran(80 : 20)\textsubscript{w/w} diluted to 3\%\textsubscript{w/v}. Details about the phase-separation of these two polymer blends were already given in chapter 3 since both systems were investigated for the fabrication of gradients in topography. In this study, the substrates used were always the same and consisted of silicon wafers coated with thin films of PMMA. As will be explained later, the PMMA film was used as a sacrificial layer during the transfer to the ink-jet media. The whole study was thus made using these substrates.

A1.2.1. Effect of spin speed

Spin speed was an important parameter that affected the kinetics of phase separation of the spin-coated film. Indeed, the spin speed influences the centrifugal force undergone by the polymer solution during the spin coating, which in turn modifies the shear thinning of the film. Moreover it also modifies the relative speed of the air flow above the spinning sample, which changes the evaporation rate of the solvent\textsuperscript{[174]}. These two phenomena peculiar to the spin coating process had to be taken into account to understand the film formation. The samples prepared were made at spin velocities ranging from 1000 rpm to 10000rpm.

For a PVA/Dextran polymer blend, we observed an increase in the size of the domains on decreasing the spin speed as shown in figure A1-1 b). The typical nucleation and growth morphology remained, however, for all the spin speeds. Actually, spin coating at higher spin speed reduced the time in which the system could phase separate, which led to smaller domains. The trend of this change was quantified by means of particle analysis. The effect of spin speed occurred mostly between 1000rpm and 4000 rpm. Above this limit, all the domains had the same size (figure A1-2 c). For PVA/PDADMAC, the images obtained clearly showed the progressive changes in morphology as well as in structure size on varying the spin speed (figure A1-1 a)). For the highest spin velocities (\(\omega = 6000\) rpm), thin and convoluted domains were obtained. At intermediate spin velocities (\(\omega =3000\) rpm), a bi-continuous structure was observed with PVA and PDADMAC domain shapes being very similar. At low velocities (\(\omega =2000\) rpm), the PDADMAC domains became bigger and rounder.
Appendix 1: Nanostructured Films of Water-soluble Polymers

Figure A1-1: a) Film of PVA/PDADMAC (50:50) \(\text{w/w}\) 3%\(\text{w/v}\) in water, spin coated at 2000, 3000 and 6000 rpm on a PMMA surface. The Fast Fourier transform of each image is displayed in top left hand corner. b) Film of PVA/Dextran (80:20) \(\text{w/w}\) 3%\(\text{w/v}\) in water, spin coated at 2000, 3000 and 6000 rpm on a PMMA surface.

This progressive transition to round shaped domains was essentially due to the surface tension between the PVA and PDADMAC phases. At lower spin velocities, the time during which the PVA-rich and PDADMAC-rich phases separated was longer (before the structure was ‘frozen’ into two solid phases). This allowed more time for the phase structure to approach equilibrium, minimising the surface energy of the system.

These images obtained in real-space gave qualitative information about the topographies of the different samples but more quantitative insights were obtained working in reciprocal space\(^{175,176}\). The samples’ structures were thus quantified using 2D fast Fourier transform analysis (2D FFT). As can be seen in figure A1-1 a), the resulting 2D FFT ring indicated that the phase structure was isotropic, with no preferred direction, and with a characteristic spatial frequency given by the maximum of the power spectral density (PSD). Figure A1-2 a) presents the PSD for different spin velocities. The curves were fitted to measure the PSD peak position frequency.
We also calculated the typical length scale of the images by taking the inverse of the PSD peak frequency (figure A1-2 b)). The characteristic length scale of the demixed polymer film clearly decreases with increasing velocity. The curve of the PVA/PDADMAC length scale corroborates the results obtained with PVA/Dextran showing that the change mainly occurred between 1000rpm and 4000rpm. After this point, continued increases in spin speed did not induce major structure modifications. This allowed us to demonstrate, as previously reported \cite{74}, that the structure length scale and film thickness do not depend linearly on the spin speed.

### A1.2.2. Effect of the concentration

The second parameter we tuned was the initial concentration of the polymer blend solution. It is also an important parameter in spin cast films since it influences the viscosity of the solution, which mainly influences the hydrodynamics during the spin coating process. The polymer blend solution was prepared as described above, the spin speed was set to 3000rpm and different concentrations were investigated (ranging from 1 to 5\%_{w/v}).
Figure A1-3: a) Film of PVA/PDADMAC (50:50)\textsubscript{w/w} 5, 3 and 1\textsubscript{w/w} in water, spin coated at 3000 rpm on a PMMA surface. The Fast Fourier transform of each image is displayed in top left hand corner. b) Film of PVA/Dextran (80:20)\textsubscript{w/w} 5, 3, 1\textsubscript{w/w} in water, spin coated at 3000 rpm on a PMMA surface.

Figure A1-3 shows the resulting AFM images. As with spin speed, a clear effect can be seen on the morphology of both the demixed film.

For PVA/Dextran blend, the diameter of the domains increased on increasing the concentration. The morphology of the domains remained the same as on changing spin speed. However, image analysis revealed that the two parameters did not affect the polymer film topographies in the same way. In the case of concentration, the dependency was clearly linear in contrast to spin speed (figure A1-4c).

For PVA/PDADMAC, small convoluted domains were obtained at low concentrations. At higher concentrations the domains were bigger and rounder, indicating that the “freezing-in” of the structures occurred later than at lower concentrations.
Appendix 1: Nanostructured Films of Water-soluble Polymers

Figure A1-4: a) PVA/PDADMAC: PSD for different concentrations. b) PVA/PDADMAC: Length scale of the topography versus concentration. c) PVA/Dextran: mean diameter of the Dextran domains versus concentration

The same image processing was carried out as before. Figure A1-4 a) shows the power spectral densities obtained at different concentrations while figure A1-4 b) shows the changes in the length scale of the topography. We can see that the higher the concentration, the bigger the domains. As for PVA/Dextran, a linear dependence can be observed. Similar dependence of the domain size on the initial polymer concentration in polymer demixed films was previously reported by P. Cyganik et al although their study was performed with a system consisting in three polymers and a common solvent [76].

We thus saw, for both blends, an increase in the domain sizes on increasing the polymer concentration. More concentrated solutions gave a thicker liquid film in the early stages of spin-coating because of higher viscosity. It thus took more time for all the solvent to evaporate during spin coating. Since the polymers diffused and phase separated for longer time before the solvent quench, larger domains were observed. The image processing revealed that domain size depends linearly on concentration in contrast to spin speed.
Appendix 1: Nanostructured Films of Water-soluble Polymers

A1.3. Transfer of the nanoporous layer on the ink-jet media

A1.3.1. Principle

The fabrication of thin polymer films on the ink-jet media raised many technical problems. The fabrication of polymer demixed films by spin coating is generally made using substrates such as silicon wafers or glass slides. Here, the substrate was an ink-jet media having a highly porous layer of metal-oxide nanoparticles. A trial was made to spin coat the polymer blend solution directly on the media but this resulted in an uptake of the solution in the porous film. Instead of spreading on the surface of the media, the solution was directly spreading inside the porous layer, which led to a very inhomogeneous film. A direct use of the media as substrate was thus impossible. An alternative method was then explored to overcome this problem: the aim was to fabricate the polymer blend thin film on a well defined substrate and transfer it onto the ink-jet media. The transfer was made as follow: first, a multilayer composed of a PMMA film and a polymer blend thin film was made on a silicon wafer (figure A1-5). In a second step, the multilayer was brought in contact with the ink-jet media and immersed in a selective solvent for one polymer of the blend and PMMA.

Figure A1-5: Schematic of the transfer method
This resulted in lift-off the polymer film from the silicon wafer due to the dissolution of PMMA and the formation of a porous polymer layer due to the dissolution of one component of the polymer blend. The PMMA film acted actually as a sacrificial layer during the transfer process.

**A1.3.2. Transfer of the polymer film**

The system chosen to realize the nanoporous polymer layer was a PVA/PDADMAC (50 : 50)\textsubscript{w/w} polymer blend diluted to 3\%\textsubscript{w/v} in water. The solution was spin coated at 3000rpm on a substrate coated with a 100nm thick PMMA layer. Acetic acid was used for the transfer, since it allows both PMMA and PDADMAC to be dissolved. The PVA/Dextran system was not used since no selective solvents were found for this polymer blend. The ink receptive layer of the ink-jet media used consisted of nanoparticles of Bohemite (gamma-AIOOH). The media was placed in the acetic acid bath and the multilayer was then brought in contact with the media. The assembly was maintained 30mn in acetic acid to ensure the complete dissolution of both PMMA and PDADMAC. After separation, the ink-jet media was coated a porous PVA layer. The nanoporous polymer film transferred on the ink-jet media was characterized by means of optical microscopy to control the quality of the transfer. Figure A1-6 shows an optical image of a nanoporous polymer film transferred on the ink-jet media. The image was taken at the edge of the nanoporous film to show the contrast between the bare and coated media. The upper part of the image corresponds to the bare ink-jet media while the lower part corresponds to the area coated with the nanoporous polymer layer. As can be seen, a homogeneous film was obtained after the transfer. The brighter part in the middle of the image coincides with the edge of the nanoporous polymer film. This was not due to the transfer process but the spin coating. There is indeed always an edge effect when a polymer solution is spin coated on a substrate, which result in a thicker film at the edges of the sample.

The samples were also characterized by means of Tapping-mode AFM in order to see the micro and nanostructuring of the surface. The images corresponding to the bare and coated media are displayed on figure A1-6. The bare ink-jet media had an RMS roughness of 15nm and exhibited different levels of structuring. The peak to peak height was about 100nm. At a smaller scale, nanostructures were observed due to the nanoporosity of the metal-oxide layer. After the transfer, the surface of the media was clearly modified. The small features of the PVA nanoporous
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polymer film were observed.

Figure A1-6: Characterization of the transferred nanoporous film: a) Optical image of the nanoporous polymer film transferred on the Ink-jet media. b) AFM image of the bare Ink-jet media. c) AFM image of the Ink-jet media coated with the nanoporous polymer layer.

The homogeneity was however not as good as on the silicon substrate. To obtain a more quantitative view, the 2D isotropic power spectral densities were calculated for the bare ink-jet media, the nanoporous polymer layer on the PMMA coated silicon and the Ink-jet media coated with the nanoporous polymer layer. The results are presented in figure A1-7.

The PSD of the polymer film spincoated on the PMMA coated silicon wafer had a clear peak at 0.25µm, corresponding to the mean size of the features. The PSD of the bare ink-jet media did not have a peak but showed high values at long wavelengths. This derived from the coarse structure of the bare media. The PSD of the nanoporous polymer layer transferred on the ink-jet
media clearly showed the characteristics of both the nanoporous layer and the ink-jet media: the peak obtained for the nanoporous layer on the PMMA coated silicon wafer was also observed after transfer; the PSD showed also high value at long wavelength typically obtained for the ink-jet media.

![Graph](image)

*Figure A1-7: 2D isotropic power spectral density calculated for: a) The bare Ink-jet media. b) The nanoporous polymer layer transferred on the ink-jet media. c) The nanoporous polymer layer on the PMMA coated silicon wafer.*

In summary, the fabrication of a polymer nanoporous layer on ink-jet media was demonstrated. The main constraint encountered arised from the nature of the substrate to coat. The starting ink-jet media was indeed highly porous, which did not permit a direct spin coating of the polymer blend. A two-step procedure was developed to fabricate the polymer film separately and transfer it on the media. The process was based on the selective dissolution of a sacrificial layer on which the polymer thin film was deposited. AFM characterisation revealed the presence of the nanostructures on the media after the transfer. This was highlighted by calculating the PSD of the bare and coated ink-jet media.
A1.4. Fabrication of cross-linked structured polymer films

As described in the previous section, nanoporous PVA polymer film were transferred onto ink-jet media. The polymers used were water-soluble to have an environmentally friendly process. However, the thin films were also sensitive to water and humidity after deposition. One way to improve the film stability but keep a water-based formulation is to crosslink the polymer after deposition. Furthermore, the polymer we used to create the nanoporous polymer layers (PVA) is widely used in many practical and industrial applications \[177-179\] and several techniques have been developed for its crosslinking.

In this section, a first review of the different crosslinking techniques of PVA is given followed by a more detailed description of the technique chosen. The last part will show that cross-linked structured PVA film can be obtained using this procedure.

A1.4.1. Review of the different approaches to crosslink PVA

Various techniques were developed to crosslink PVA depending on the application envisioned. Cross-linked PVA has been used in different fields like paper manufacturing and phosphor screen fabrication \[177,180,181\] but also in biological and biomedical applications such as soft contact lens fabrication \[178,182\] or enzyme immobilisation for sensors \[179,183\]. This diversity of applications led to the development of very different approaches to crosslink PVA. Some references are given in table A1-1.

One of the most commonly used procedures is the crosslinking mediated by borate ions. If borate ions are present in a PVA solution, they coordinate with four hydroxyl groups of the PVA chains and act as crosslinks. This reaction is generally performed in solution, but gas phase treatment using trimethylborate has also been reported \[184\].

Another widely used technique is the photocrosslinking of dichromated PVA films. In this case, a blend of PVA and ammonium dichromate is made. Upon exposure to UV the chromium ions form complexes with PVA chains via hydroxyl groups. This method has the advantage that crosslinking only occurs in the presence of UV light. It has been widely used for patterning applications and in phosphor screen fabrication \[181,185\]. Nevertheless, one drawback is the presence of chromium in the system, which poses environmental problems.
The use of glutaraldehyde for PVA crosslinking is less common but has also been reported\textsuperscript{[186]}. 

Table A1-1: Review of the different techniques to crosslink PVA.

<table>
<thead>
<tr>
<th>Technique</th>
<th>Principle</th>
<th>refs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Freezing and Thawing</td>
<td>A PVA solution is frozen and slowly warmed to room temperature. The freezing and thawing cycles are repeated in order to obtain the crosslinking.</td>
<td>[187,188]</td>
</tr>
<tr>
<td>Complexation with sodium borate</td>
<td>Sodium tetraborate is added to the PVA solution. The borate ions form a complex with polyvinyl alcohol.</td>
<td>[189-193]</td>
</tr>
<tr>
<td>Glutaraldehyde</td>
<td>Condensation reaction between glutaraldehyde and the hydroxyl groups of PVA.</td>
<td>[186,194]</td>
</tr>
<tr>
<td>Photocrosslinking: Photosensitive PVA</td>
<td>Photosensitive groups (styrylpyridinium) are grafted on PVA and act as crosslinking points when UV irradiated</td>
<td>[195-198]</td>
</tr>
<tr>
<td>Irradiation</td>
<td>Expose the PVA film to $\gamma$-irradiation, e-beam or microwaves.</td>
<td>[199,200]</td>
</tr>
<tr>
<td>Exposure to dichromate</td>
<td>Ammonium or potassium dichromate is added to the PVA solution. Upon UV irradiation, chromium ions form a complex with PVA.</td>
<td>[181,201, 202]</td>
</tr>
</tbody>
</table>

The three technique mentioned above all involve the hydroxyl groups of PVA in the crosslinking mechanism. For these techniques, the final degree of crosslinking of the polymer is thus very dependent on the degree of hydrolysis of the PVA. Other techniques like freezing and thawing use very different properties of PVA to obtain crosslinks in the polymer. When PVA is subjected to repeated freezing and thawing cycles, it partially crystallizes and the crystallites act as crosslinks in the polymer. The polymer is in this case only physically crosslinked and its crosslink density depends on the crystallinity of the starting PVA. One great advantage is that no crosslinking agents have to be used. Another alternative technology is to use PVA modified with photosensitive pendent groups like styrylpyridinium (PVA-Sbq). Upon exposure to UV, the polymer is crosslinked via the photosensitive groups. The crosslinking depends in this case on the number of pendent groups per PVA chain.

A determining criterion in the choice of the crosslinking technique was the possibility to preserve the structure of the polymer film during and after the process. Any water-based post treatment of the film was thus impossible since it would result in the dissolution of the polymer. The most
straightforward method to address this issue was to use a UV curing technique. Despite the fact that di-chromated PVA was widely used in the past, we focused on the use of photosensitive PVA (PVA-Sbq) to avoid the use of chromium in the process.

After a description of the photo crosslinking process of PVA-Sbq, the results obtained for the fabrication of crosslinked structured PVA films on silicon wafers will be presented.

### A1.4.2. Photohardening of PVA-Sbq

The synthesis of PVA-Sbq was first reported in the early eighties by Ichimura et al.\(^{196,198}\). This is now a commercial product and has already been used in screen printing\(^{177}\) and biocatalyst immobilisation\(^{179,183}\). The crosslinking of PVA-Sbq is mediated by its styrylpyridinium groups. Upon UV illumination, a dimerisation of the styrylpyridinium groups occurs, which create crosslinks in the polymer (figure A1-8). The reaction is specific to the styrylpyridinium, which means that the crosslinking density depends on the amount of Sbq pendant groups.

**Figure A1-8**: Schematic showing the crosslinking reaction of PVA-Sbq when exposed to UV light\(^{203}\).

Shindo et al studied the swelling properties of the hydrogel obtained depending on the pH of the swollen gel and the extent of photo-dimerisation of the styrylpyridinium groups\(^{204}\). They observed that the swelling was maximal at a pH of 7 and decreased for lower and higher pH values. The authors also reported a decrease in swelling on increasing the extent of photo-dimerisation.

### A1.4.3. Fabrication of cross-linked structured PVA film

The first step was the fabrication of a homogeneous polymer-blend solution. PVA-Sbq was diluted and mixed with Dextran or PDADMAC solution at different ratios as made in the
previous section with normal PVA. PVA-Sbq and Dextran solutions were miscible at all ratios, but PVA-Sbq / PDADMAC did not lead to a homogeneous solution. Aggregates formed upon blending the two solutions. This immiscibility may arise from the presence of the Sbq groups on the PVA chains. The only other difference compared to the PVA used in the previous section was the molecular weight of the PVA (40kDa for the standard PVA and 80kDa for PVA-Sbq), which should not affect to this extent the miscibility of the polymer solutions.

We thus focused on the PVA/Dextran blends. The PVA-Sbq /Dextran solutions were spin coated on clean silicon wafers. The samples were exposed to UV light for 10mn. Half of the samples were rinsed in water to partially remove the Dextran phase. Figure A1-9 shows the topographies obtained as determined by AFM in ambient conditions for different PVA-Sbq/Dextran ratios. Typical demixed structures were observed for all conditions tested. For PVA-Sbq/Dextran ratios of (90 : 10)$_w$/w and (80 : 20)$_w$/w, PVA-Sbq formed a matrix with Dextran domains embedded in it. The domains were smaller on decreasing the Dextran content. For lower PVA-Sbq proportions isolated PVA-Sbq domains were observed, surrounded by a Dextran matrix. The boundary between the rinsed and non rinsed part of the sample was clearly observed by AFM. On the non-rinsed side of the samples, Dextran filled pores that were emptied upon rinsing.

However, the use of PVA-Sbq in the polymer blend led to notably different structured polymer films compared with what was obtained using standard PVA. First, the morphology of the structured obtained were different: for PVA/Dextran ratios of (90 : 10)$_w$/w and (80 : 20)$_w$/w, perfectly round Dextran domains embedded in a PVA matrix were observed with standard PVA. In contrast, PVA-Sbq/Dextran blend led to round Dextran domains only at a ratio of (90 : 10)$_w$/w; and the domains were more elongated and interconnected at a ratio of (80 : 20)$_w$/w. Second, the sizes of the features were always smaller and denser when PVA-Sbq was used.

There are two potential explanations for these differences:

- the molecular weight difference between the PVA used in the previous section and PVA-Sbq.
- the change in chemistry due to the presence of the photosensitive pendant groups on PVA-Sbq.
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Figure A1-9: AFM images of the PVA-Sbq/Dextran polymer films for ratios of a) (90 : 10) w/w, b) (80 : 20) w/w, c) (70 : 30) w/w. The upper images show the limit between the rinsed and non-rinsed part of the sample.

As mentioned above, the molecular weight of PVA-Sbq was larger than that of the normal PVA used in the first section, which plays a key role in the phase separation of the polymer blend. Affrossmann et al \cite{affrossmann2008} suggested that changes in polymer molecular weight affect phase separation in two ways. In the first place, they can modify the position of the binodal and spinodal lines on the phase diagrams of the polymer blends. If the molecular weight of only one polymer of the blend is changed, the critical composition of the system will be shifted. Moreover, an increase in molecular weight will lead to an increase in the viscosity of the polymer solution. Since both PVA used in this study were 80% hydrolysed, the viscosity of the solution containing PVA-Sbq (Mw=80kDa) was higher than that of normal PVA (Mw=40kDa). A higher viscosity first affects the spreading of the polymer solution during spin-coating, modifying the thickness of the final polymer film. Moreover, once phase separation has started, the diffusion and coalescence of the Dextran domains is hindered due to the higher viscosity of the surrounding PVA matrix.

Furthermore, the change in chemistry of PVA due to the presence of Sbq groups may also affect its phase separation with Dextran. Several studies reported that slight differences in polymer
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Chemistries such as deuteration or bromination can be sufficient to induce or modify the phase separation of polymer blends\cite{99,205}. One striking example was shown in this section: if a PVA-Sbq and a PDADMAC solution are mixed, this results in the formation of aggregates, which was not the case with standard PVA.

Initial AFM characterizations were performed in air. The PVA film obtained was insoluble in water but could however absorb water when in contact with an aqueous solution\cite{204}. The last part of the characterization was thus to investigate the water absorption properties of the polymer film and its morphology in the swollen state.

The first method used to characterize the swollen polymer films was AFM in liquid. This technique was useful to quantify the swelling of the polymer by measuring the changes in film thickness upon swelling. Homogeneous films were made by spin coating 2%\text{w/v} solutions of PVA-Sbq at 4000 and 6000rpm. The thickness of the polymer films was measured both in the dry and swollen state using contact mode AFM. For all the measurements, the contact force was 5nN.

As shown in table A1-2, a two fold increase in thickness was observed in average.

\textit{Table A1-2: Thicknesses of the PVA/Sbq layers measured using AFM in the dried state and in liquid environment}

<table>
<thead>
<tr>
<th>Sample</th>
<th>Thickness in the dry state $h_d$</th>
<th>Thickness in the swollen state $h_{sw}$</th>
<th>$h_{sw}/h_d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVA-sbq 2%(w/v) H$_2$O, 4000rpm</td>
<td>63nm</td>
<td>148nm</td>
<td>2.3</td>
</tr>
<tr>
<td>PVA-sbq 2%(w/v) H$_2$O, 6000rpm</td>
<td>51nm</td>
<td>92nm</td>
<td>1.8</td>
</tr>
</tbody>
</table>

The structure of the polymer film in the swollen state was also characterized using the cryo-SEM technique. Polymer films were made by spin coating a 2\%\text{w/v} solution of PVA-Sbq / Dextran with a ratio of (80 : 20)\text{w/w} at 1000rpm. A very low spin speed chosen deliberately in order to obtain large structures more easily resolved by SEM. After exposure to UV and rinsing of the polymer film with water, the sample was prepared for cryo-SEM.
A drop of Millipore water was deposited on the film to swell the crosslinked PVA. The sample was rapidly frozen in order to obtain amorphous ice. After sublimation of the ice, the polymer film kept its structure in the swollen state. Since the water drop did not fully wet the polymer film, its structure in both the dry state and the swollen state could be characterized on a single sample as shown in figure A1-10 f).

In the dry state (fig A1-10 a, b)), the structures observed had morphologies similar to those seen
Appendix 1: Nanostructured Films of Wate soluble Polymers

in AFM (figure A1-9). The structure sizes were larger since the spin speed used was lower. On the swollen part of the sample, drastic changes in the film morphology were observed. A highly porous film was obtained with a much rougher surface than in the dry state. The contrast can be clearly seen on the image showing both swollen and dry morphologies figure A1-10 f).

A1.5. Conclusion

A technique for the fabrication of nanoporous polymer layers on ink-jet media has been developed. The goal of the study was to develop this technique respecting the following constraints: first, develop an environmentally friendly process. Second, have the possibility to tune the size of the pores in the polymer film since it has a primary influence on the ink-uptake. Third, make the polymer thin film on an ink-jet printing media.

The first constraint was solved by employing only water-soluble polymers and solvents such as acetic acid. Moreover, PVA was employed in both polymer blends investigated and was also the final polymer remaining on the ink-jet media after the transfer. This was a particular advantage since PVA is already used in the fabrication of ink-jet media.

The technique used to fabricate the porous polymer was based on polymer demixing by solvent quenching. This method involves the spin coating of polymer blend solution in order to create phase separated polymer blend thin films. On rinsing in a selective solvent, one component of the blend is dissolve, which results in a porous film. As presented in the main introduction of the thesis, various parameters can affect the final film structure using this technique. Among the different parameters, spin speed and the concentration of the polymer solution were investigated. For both blends, we observed an increase of the feature size on increasing the concentration of the solution. Data analysis revealed a linear dependency of the length scale with concentration. Concerning spin speed, both blends showed also the same trend and a decrease of the feature size on increasing the spin speed was observed. The length scale did not depend linearly on the spin speed in contrast to the effect of concentration.

The last constraint concerned the type of substrate used: the ink-jet media used was coated with a highly porous layer of metal-oxide nanoparticles. A direct use of this substrate for spincoating was unsuccessful. An alternative technique was thus developed based on the transfer of the thin polymer film to the ink-jet media. This part was made using PVA/PDADMAC polymer blend. The polymer blend thin films were made on PMMA coated silicon wafers. The sample was then
brought in contact with the ink-jet media in presence of acetic acid. This resulted in the
dissolution of PMMA which allowed the thin film to be lifted off the silicon wafer. PDAMAC
was also dissolved by acetic acid, leaving a porous PVA layer on the ink-jet media. Optical
microscopy and AFM confirmed that the nanoporous film was transferred on the ink-jet media.
The nanoporous polymer films produced using the technique presented above were thin and still
water soluble, which made them sensitive to external parameters like humidity. In the final
section, a method was proposed to fabricate more stable layers. The aim was to cross-link the
structured polymer film. For this, a polymer blend containing a UV photo-crosslinkable PVA,
PVA-Sbq, was used. After crosslinking of the polymer film, its morphology both in the dry and
swollen state were investigated using AFM and cryo-SEM characterization. We could observe
qualitatively the morphology change of the film on swelling of water.
In summary, the approach investigated permitted to realize nanoporous PVA layer on ink-jet
media. The technique allowed to vary the size of the pores in the PVA layer, which is critical
since the porosity of the layer will affect the uptake of the ink while printing. Although efficient,
the technique we used to transfer the film to the ink-jet media would, however, not be easily
scaled up and adapted to currently used ink-jet media fabrication techniques. However, this
would permit to figure out the potential benefits of such nanoporous polymer layers on the
quality and stability of ink-jet printed images.
I would like to thank Dr. Martha Liley, my supervisor at CSEM. I really appreciate the scientific discussions we had together. More particularly, I would like to thank Martha for the outstanding supervision and guidance she gave me all along my PhD while letting me enough liberty for my research.

I would like to thank Prof. Dr. Nicholas. D. Spencer who accepted to be my academic supervisor at the ETHZ. I thank Nic for the time he has taken to follow my research through regular meetings despite the distance between Neuchâtel and Zürich. I am also grateful for his help to integrate the LSST team.

I thank Prof. Dr. Diethelm Johannsmann and Prof. Dr. Walter Steurer for accepting to be a part of my doctoral committee.

I thank CSEM SA for giving me the opportunity to pursue my PhD among a multidisciplinary and multicultural team of researchers and in an international working environment.

I also thank ETHZ for accepting me in the materials science doctoral school and giving me access to the facilities.

I would like to thank my colleagues from CSEM for maintaining a nice and stimulating atmosphere in the laboratory and the office every day. I am grateful to my sector head Dr. Raphaël Pugin and division head Dr. Harry Heinzelmann for being good team leaders as well as friendly colleagues. I would like to thank all the people of the “nano-bio” team I have been
Acknowledgements

working with during that time: Dr. Sivashankar Krishnamoorthy for the numerous scientific discussions, Dr. André Meister for his precious help concerning AFM, Dr. Rolf Eckert, Dr. Caterina Minelli and Dr. Myriam Losson for their help and support, Dr. Rolf Steiger, Véronique Monnier, Marta Giazzon, Dr. Emmanuel Scolan, Dr. Jérôme Polesel-Maris, Dr. Christian Hinderling, Dr. Christian Santchi, Anna-Maria Popa, Silvia Angeloni, Dr. Silvia Jeney, Maria Juvet, Dr. Erika Gyorvary. I also want to thank Dr. Kaspar Cottier, Eric Bernard, Réal Ischer, Dr. Guy voirin, Dr. Rino Kunz, Dr. Stephanie Pasche from the bio-sensing group.

I thank all the members of the Laboratory for Surface Science and Technology (LSST) for their welcome, help and advice when I came in Zürich or at the annual group meetings. More especially, I thank Sara Morgenthaler for the fruitful collaboration and for the supply of the substrates presenting surface-energy gradients. I thank Stefan Zürcher for the XPS measurements, Seughwann Lee for the characterization of samples using AFM in liquid. I am also grateful to Lydia Feller for the interesting discussion and to Tobias Künzler for the supply of AFFINITY polymer and his advice for the replication work.

I would like to thank Mathis Riehle for welcoming me in his laboratory, teaching me the basics of cell growth, and for the fruitful scientific discussions. I also thank Elena Martines and Lucia Csaderova.

I thank Martin Staiger, Stefan Schuettel and Rolf Steiger from Ilford Imaging who made possible the project Papillon concerning the fabrication of nanoporous polymer layer on ink-jet printing paper. I thank Top-nano 21 project for their financial support in this project.

I would like to thank the COMLAB for the facility for characterization equipments (AFM, SEM).
I thank Dr. Massoud Dadras and Mireille Leboeuf for their help and support for the SEM, ESEM and cryo-SEM measurements.

I am also grateful to Günter Reiter for the fruitful and interesting scientific discussions we had and for coordinating the network POLYNANO, which contributed to the financing of my PhD.

I thank the members of Arrayon Biotechnology SA for giving me access to their equipment. More especially I thank Hans Siegrist, Sylvie Guinchard and François Crevoisier for their help and support.

I thank Gilles Weder and Prof. Bruno Betschart for the nice and friendly collaboration.

To finish, I would like to thank my family, all my friends in Neuchâtel and in France. I thank Elodie for her patience and support during this important period of my life.
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Conferences:

- Blondiaux et al: *Gradients of polymeric structures induced by surface energy* (poster), Swiss User Group Surfaces and Interfaces, 21th Annual Meeting, 21 January 2005, Fribourg, Switzerland

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