

CHALMERS



Wettability Gradients Through Chemical Vapor Deposition

Master of Science Thesis

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CHALMERS UNIVERSITY OF TECHNOLOGY
Göteborg, Sweden, 2010

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“Go confidently in the direction of your dreams.
Live the life you have imagined.”

-Henry David Thoreau

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Abstract

Chemical vapor deposition (CVD) has been used to deposit functional paracyclophanes onto surfaces, giving them hydrophilic and hydrophobic properties. By using a custom-built two-source CVD system, wettability gradients have been prepared by combining one hydrophilic and one hydrophobic polymer onto one single surface. This master thesis has shown how existing technologies can be combined in order to achieve successful wettability gradients with a contact angle difference of 30° over a distance of 10 cm. The theoretical maximum predicted for this kind of gradient is $>135^\circ$. The properties of the gradients have however been limited in their strength due to problems with immobilization of polar molecules to the hydrophilic surface. The immobilization has proved successful for hydrophilic, non-gradient surfaces, though. These issues are believed to originate from dynamic effects of the thin polymer film and from mixing of hydrophilic and hydrophobic moieties in the preparation process.

Table of contents

1	INTRODUCTION & BACKGROUND.....	2
1.1	INTRODUCTION	2
1.2	PROJECT GOALS	2
2	THEORETICAL BACKGROUND	3
2.1	REACTIVE POLYMER COATING	3
2.1.1	<i>History</i>	4
2.2	CHEMICAL VAPOR DEPOSITION	4
2.3	CONTACT ANGLE	5
2.4	SURFACE MODIFICATION	5
2.4.1	<i>Citric acid</i>	6
2.4.2	<i>EDC-Chemistry</i>	6
2.4.3	<i>Maleic anhydride</i>	6
2.4.4	<i>Gradients</i>	7
3	MATERIALS & METHODS	7
3.1	SUBSTRATES.....	7
3.2	REACTIVE POLYMER COATING	7
3.3	CHEMICAL VAPOR DEPOSITION	8
3.3.1	<i>One-source CVD</i>	8
3.3.2	<i>Two-source CVD</i>	9
3.4	REACTIONS.....	10
3.4.1	<i>Citric acid</i>	10
3.4.2	<i>Maleic anhydride</i>	10
3.5	CONTACT ANGLE MEASUREMENTS	11
3.6	SURFACE ROUGHNESS	11
4	EXPERIMENTAL PART.....	11
4.1	HYDROPHILIC PART.....	11
4.2	HYDROPHOBIC PART	12
4.3	GRADIENT	12
5	RESULTS & DISCUSSION	13
5.1	HYDROPHILIC PART.....	13
5.1.1	<i>Diamine monomer</i>	13
5.1.2	<i>Surface roughness</i>	14
5.2	HYDROPHOBIC PART	14
5.2.1	<i>Stability</i>	15
5.2.2	<i>Loss of contact angle</i>	17
5.3	GRADIENT	21
5.3.1	<i>Reactions</i>	24
5.3.2	<i>Biotin- hydrazide</i>	28
6	CONCLUSIONS & OUTLOOK.....	30
7	REFERENCES	32
	APPENDIX.....	34

1 Introduction & Background

1.1 Introduction

The objective of this master thesis has been to prepare and study wettability gradients through the use of reactive polymer coatings via chemical vapor deposition (CVD). The project has been performed at the Department of Chemical Engineering at the University of Michigan – Ann Arbor, under supervision by Professor Joerg Lahann. At Chalmers University of Technology, the Department of Chemical and Biological Engineering has served as home department for this thesis and the project has been supervised by Professor Krister Holmberg. Professor Holmberg has also served as examiner of this master thesis.

This thesis explores the use of reactive polymer coatings and how they can be used as a platform for surface modification, with the end goal to create wettability gradients. The motivation behind this project is the increasing interest in surface modifications, the dynamics of surfaces and the control of water spreading, with potential use in e.g. biology and advanced functional surfaces [1]. One application in which gradient surfaces can have great potential is in molecular interaction screening. Here a gradient surface can be used instead of a discrete numbers of surfaces to screen how molecular interactions depend on the surface energy. [2] Other potential applications are fog harvesting and anti fogging surfaces. [1] The use of reactive polymer has earlier been used to create gradients, but not wettability gradients [3]. By being able to prepare wettability gradients, the range of uses for the reactive polymer coatings will be expanded.

1.2 Project goals

The goal for this master thesis is to prepare wettability gradient surfaces by the use of reactive polymer coatings deposited through chemical vapor deposition. The ultimate goal with this gradient is to make it so strong that water will move from one side to the other. The gradients will be achieved by depositing the reactive polymer coatings, i.e. functionalized paracyclophanes, with different chemical properties through a two-source CVD system, allowing two polymer monomers to be deposited onto a substrate surface simultaneously. This enables a surface to have two distinctive properties with a gradual change between the two over the substrate.

The project has its starting point in a paper published by the Lahann group in 2009[3]. The concept of vapor based gradient creation is taken forward in order to produce a wettability gradient using the two-source CVD technique. Creating gradients through chemical vapor deposition of reactive paracyclophanes could have several advantages compared to methods previously used. Since the technique does not require any solvents and can be used on practically any surface or geometry, it can be an important step forward for creating gradient surfaces and expanding the area by introducing a new approach.

2 Theoretical background

2.1 Reactive polymer coating

The main technique used in this project has been the deposition of paracyclophanes through chemical vapor deposition to form reactive polymer coatings, known as poly para-xylylene (PPX) or Parylene. By adding functional groups to the paracyclophanes, functional poly para-xylylene films can be obtained.

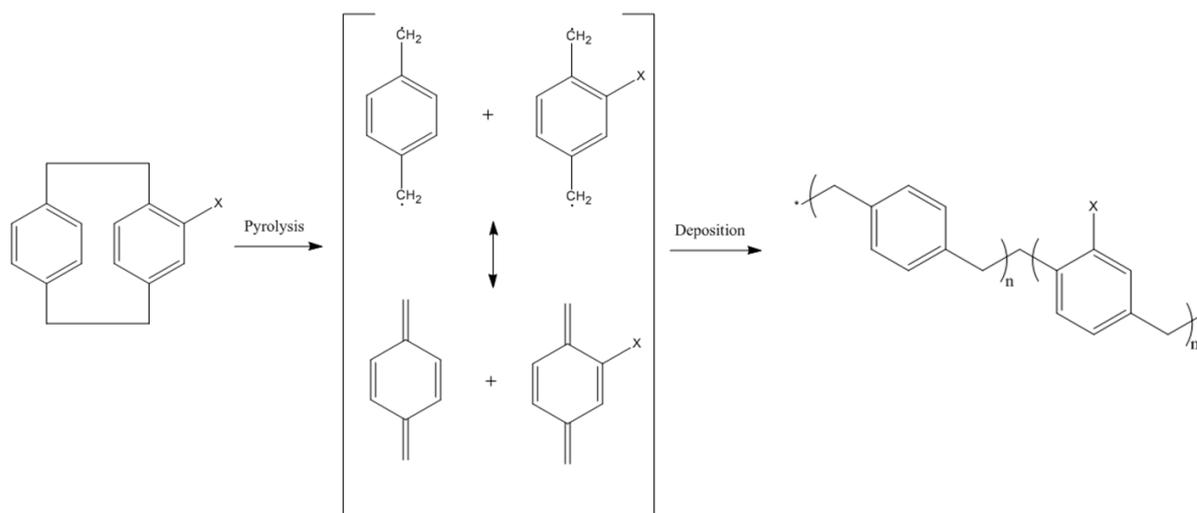


Figure 1. Reaction scheme for the formation of reactive poly para-xylylene (PPX) from paracyclophane (PCP). The polymer properties is determined through the choice of functional group X

The poly para-xylylene (PPX) is a very versatile polymer coating which in its unfunctionalized form is commercially known as Parylene N. Parylene polymers are widely used in industrial coating applications and has usage in several different areas such as medical, automotive and aerospace [4]. The properties that make Parylene coatings so interesting is that it e.g. has good thermal and chemical stability, forms thin conformal and pinhole free coating and can be coated to virtually any material.

Paracyclophanes (PCP) can be functionalized in several different ways and leaves thereby great freedom in creating polymer films with tailored properties. Through synthesis, molecules can be attached to either one or both of the aromatic rings of the paracyclophane. These molecules work as anchoring groups once the polymer film is formed. This will give the coating tailored properties which can further be enhanced or modified through reactions with the functional group. This is where the name reactive polymer coating comes from. The excellent qualities of this type of coating do not end there. Since the polymer film is formed through a CVD process, it will not only form a more conformal coating than a liquid counterpart, i.e. dip coating, but it will not need any kind of solvent. This is of great advantage in for example medical applications since this eliminates potentially toxic residues from the solvents. The coating is also able to coat a wide variety of substrates, making it very versatile.

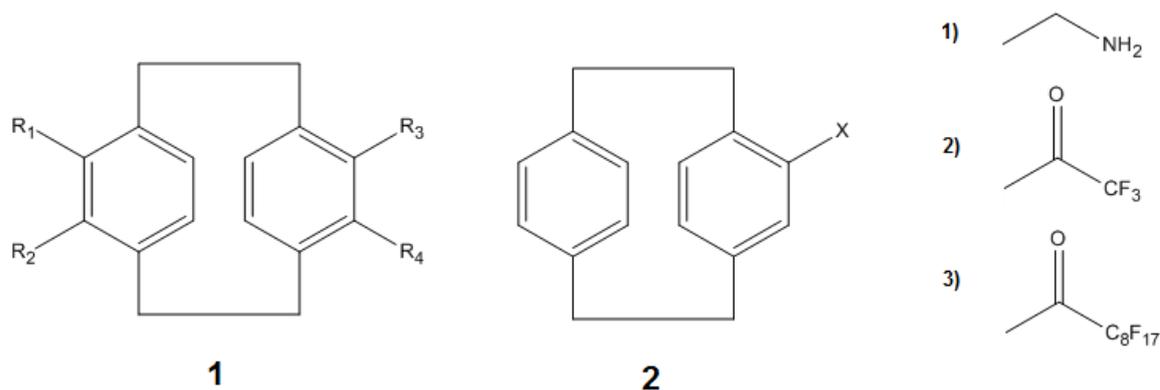


Figure 2. The paracyclophane molecule can be functionalized in many different ways, as can be seen in scheme No. 1. Scheme No. 2 shows examples of functionalized paracyclophanes used in this project

2.1.1 History

Poly para-xylylene (PPX) film was first discovered in 1947 by the physical chemist Michael Szwarc, while he was investigating chemical bonds in different chemical structures. In one of his experiments he discovered that a thin film formed after exposing para-xylene to high temperature. The discovery of this polymer film was found with great interest in the research community and more researchers began study the material. One of them was William Gorham, working for Union Carbide, who improved some of the limitations i.e. reactivity and stability that existed in the initial process by using paracyclophanes as starting material for the polymer film instead of para-xylene. Gorham's work later led to a commercialization of the coating system that today is known as Parylene [5][6].

2.2 Chemical Vapor Deposition

Chemical vapor deposition is a widely use technique for creation of materials. As the name implies, CVD is a method in which a vapor phase is used to chemically build a material through a deposition process. Depending on the material used in the vapor phase, different end materials can be achieved. Thanks to the control that can be achieved through use of the CVD process, materials can be made with very high purity and specific properties. One of the great advantages with CVD is the ability to manufacture very thin coating. CVD films can vary in thickness from a few nanometers to centimeters with tailored composition. Two areas which have found great use of CVD are the electronics industry and metal industry. Both have found great benefits from thin protective coatings that CVD is able to deliver e.g. for circuit boards. Other industries that also use CVD are the automotive industry which uses it to coat car parts before painting.

There are a large number of different types of CVD processes existing, all with their own special properties. The two main differences between these techniques are found in either the process conditions (i.e. pressure) or in the chemical reaction process (e.g. solvents, initiators) [7]. The type of CVD used in this project is a low-pressure system in which the coating is formed through a polymerization reaction on the substrate.

2.3 Contact angle

Contact angle measurements are a method to probe the energy of a surface. It is the surface energy that defines the interactions for surfaces e.g. if a liquid will be able to spread on the surface or not. The most common way to measure the surface energy is to expose the surface to droplets of water. By determining the angle that is formed between the solid and liquid interface, a measure of the surface energy can be obtained. If a surface has a high surface energy it will spread water since the interactions between the water molecules inside the water droplet is weaker than those formed with the surface. In the opposite situation, if the surface energy is weaker the water droplet wants to minimize its exposure to the surface. This will give a high contact angle since the water does not want to interact more than absolutely necessary with the surface.

Contact angle can be understood through the Young's equation:

$$\gamma_{SV} - \gamma_{SL} = \gamma_{LV} \times \cos \theta$$

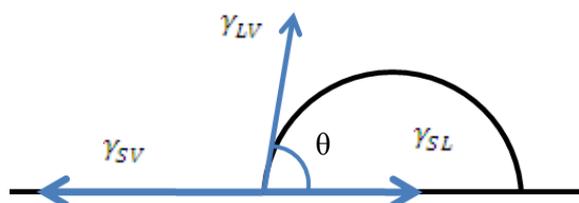


Figure 3. Graphical representation of Young's equation

Where γ_{SV} is the interfacial tension between the solid and the vapor, γ_{SL} is the interfacial tension between solid and liquid and γ_{LV} is the interfacial tension between liquid and vapor. θ is defined as the contact angle [8].

The measurement of contact angle can be made in two ways, either static or dynamic. When measuring the static contact angle, a water droplet is introduced onto a surface and the contact angle is measured. When measuring the dynamic contact angle, two angles are measured; one advancing and one receding. The advancing contact angle is obtained the water droplet is expanded and the receding is obtained when the same droplet is allowed to contract. Dynamic contact angle is considered the most reliable and reproducible, but due to the simplicity of the static contact angle measurement this is more often used. An advantage with dynamic contact angle is that it gives information about the contact angle hysteresis. The contact angle hysteresis is simply the difference between the advancing and receding contact angle. The hysteresis can give important information about the surface since it depends on three properties; kinetic effects, surface topography and chemical composition. The kinetic effects are due to the ability of mobile groups to flip on the surface depending on its environment. Surface topography depends on if the surface is smooth or rough and the chemical composition depends on if the surface is homogeneous or heterogeneous.

2.4 Surface modification

The application of a reactive polymer coating to a surface enables the surface properties to be modified through chemical reactions. In this project, this potential has been used to enhance the hydrophilic property of the amino methyl paracyclophane. From a general surface

modification point of view, the reactive coating system enables a great control over surface properties. By simply synthesizing a paracyclophane with a desired functional group, this enables the attachment of any molecule of choice, whether it is a biological molecule or any functional group that can change the surface properties. Reactive polymer coating can also be used as a platform onto which molecules can be attached through e.g. click chemistry and prove very valuable in biological applications [9].

2.4.1 Citric acid

Citric acid was one of two molecules used for surface modification of the reactive polymer films. Since citric acid contains three carboxylic groups, it could be attached to the surface and still have as polar groups that would be able to increase water interaction due to its polarity. Since some of the reactive coatings used in this project have functional amine groups, citric acid could be immobilized through EDC chemistry.

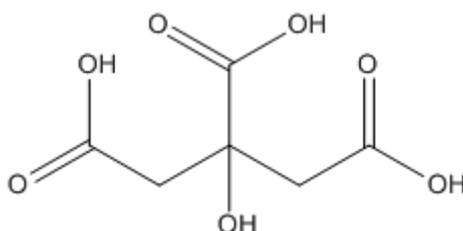


Figure 4. The chemical structure of citric acid

2.4.2 EDC-Chemistry

To attach the citric acid molecule onto the functional amine groups on the reactive polymer coating, EDC-chemistry was used. EDC or [1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride] is a commonly used chemical for biological conjugation chemistry. EDC enables the reaction between the amine and the carboxylate group on the citric acid by making the carboxylate group reactive and thereby able to react with the primary amine on the polymer film. Due to unwanted competitive reactions between water and the active intermediate formed by EDC, reactivity is lost. By adding another chemical, Sulfo-NHS, the intermediate can be stabilized and making the reaction more efficient. EDC and Sulfo-NHS was used in this project to enable an efficient reaction between the citric acid and the functional amine groups present on the surface coating.

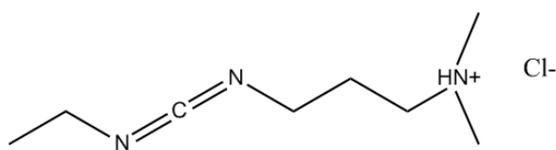


Figure 5. Chemical structure of EDC

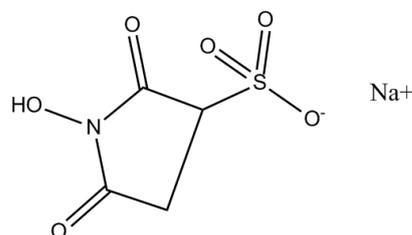


Figure 6. Chemical structure of Sulfo-NHS

2.4.3 Maleic anhydride

Another way to increase the polarity and thereby lower the contact angle is to use maleic anhydride. Maleic anhydride was selected thanks to its polar properties but also since it would be able to work as a compliment to citric acid. The use of maleic anhydride has advantages compared with citric acid; maleic anhydride can easily be dissolved in acetone and reacts by

itself with the functional amine groups without any supporting molecules, compared to citric acid.

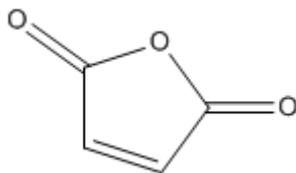


Figure 7. The chemical structure of maleic anhydride

Maleic anhydride soon came to be the preferred method for surface modification. The reason for this was that the maleic anhydride reaction is simpler, since it only requires acetone to be dissolved and no other chemical to make the reaction work. The reaction time for the maleic anhydride reaction is also a little bit shorter than for citric acid. The maleic anhydride reaction was done of 2 hours while citric acid was left to react over night. [10]

2.4.4 Gradients

A gradient is a surface that possesses different properties and has gradual change from one property to the other. In our case the gradient will be between hydrophilic (water loving) property to hydrophobic (water hating) and the gradient will run along a substrate with a length of about 10 cm. The ability to manufacture gradients for different applications has previously been studied by several other research groups. The difference between these has often been in the approaches used to create the gradients or the use of different gradient materials. Some examples of techniques that has been used to create gradients are diffusion [11], self-assembled monolayers [12],[13] and plasma treatment[14].

3 Materials & Methods

3.1 Substrates

The substrates used for this project were silica and gold coated silica. Substrates were used in the shape of squares or slides and were cut from wafers. Before silica substrates were coated, they were first put into a vacuum desiccator and coated with siloxane to improve adhesion of the polymer coating. Siloxane is used to make the substrates more hydrophobic, since the polymer coating is hydrophobic. Application of siloxane is most important when working with glass substrates but it also improves the polymer adhesion for silica substrates. In the gradient experiments, silica slides of about 1 cm width and 10 cm length were cut from silica wafers. The square shaped silica and gold coated silica were of a size of about 1 cm × 1 cm.

3.2 Reactive Polymer coating

The monomers used for coatings were of five different types; (1) [2,2]paracyclophane (PCP), (2) 4-aminomethyl-[2,2]paracyclophane (Amine), (3) 4,15- diamine-[2,2]Paracyclophane (Diamine), (4) 4-trifluoroacetyl-[2,2]paracyclophane (Short chain fluorine) and (5) 4-heptadecafluorononanoyl[2,2]paracyclophane (Fluorine). The paracyclophane and amine monomer are commercial available and is known under the trade name diX-N and diX-AM. The other monomers have been synthesized in the lab.

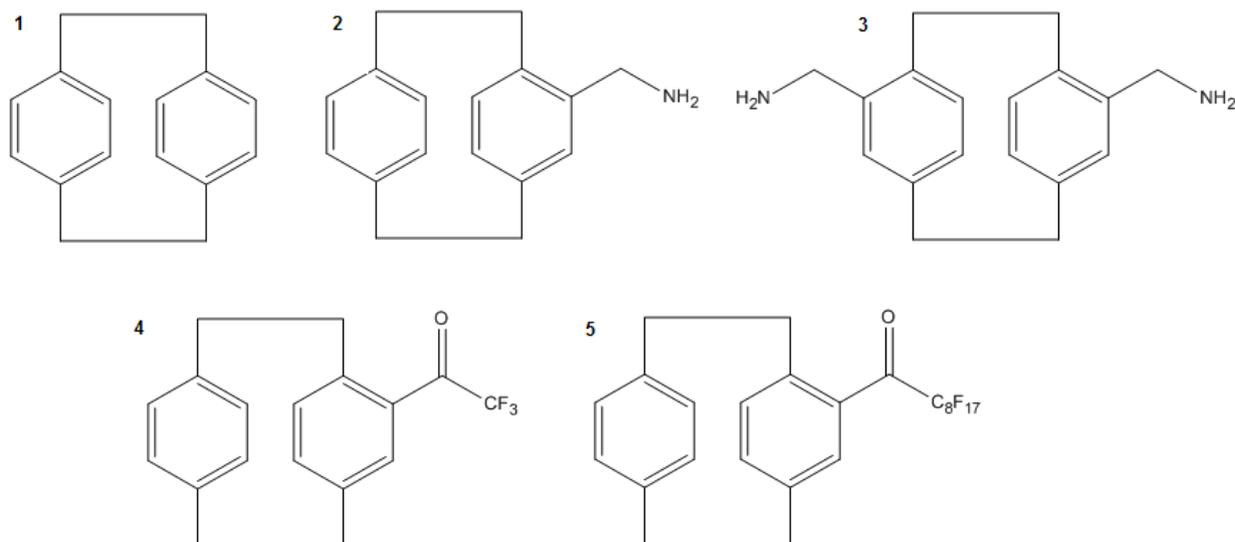


Figure 8. The monomers used in the project and their structures

3.3 Chemical vapor deposition

3.3.1 One-source CVD

The chemical vapor deposition system used in this project was a costume built CVD system with a deposition chamber having one inlet i.e. a one-source CVD system. The system is consisting of a quartz tube, a furnace, a deposition chamber and a vacuum pump. To the quartz tube, an argon gas tank with a belonging gas flow control is attached to provide an inert carrier gas which flow the sublimated monomer into the deposition chamber. In the deposition chamber, a quartz crystal microbalance (QCM) is positioned to monitor the total deposition and the deposition rate. To avoid vapor deposition to anything except the substrates, the walls of the deposition chamber is heated while the stage, at which the substrates are held, is cold. The pressure in the CVD system is monitored through a pressure control, which also controls the vault between the deposition chamber and the vacuum pump.

A general deposition run is started by turning all the equipment on i.e. vacuum pump, furnace, stage cooling, QCM and pressure control. Then the desired monomer is weighed and put in a glass holder. Before the deposition the substrates are put onto the cooled stage inside the deposition chamber and the monomer holder is placed inside the quartz tube. The system is then pressurized by opening the vault towards the pump. When a stable pressure is attained, the carrier gas flow is turned on. When the pressure in the system is stabilized the monomer holder is transferred towards the furnace with the help of a magnet.

By observing the QCM control, the total deposition and current deposition rate be monitored. The deposition rate is controlled by moving the monomer holder closer or further away from the furnace. When a desired thickness has been achieved the run is stopped by moving the monomer holder away from the furnace and there by stopping the sublimation of the monomer. Then the system is re-pressurized by closing the vault to the pump and opening another vault to let argon gas into the deposition chamber. When sufficient pressure is reached, the door to the deposition chamber is possible to open and the coated substrates can be reached.

After a deposition run, the system is cleaned from monomer that deposited onto the quartz tube instead of flowing into the deposition chamber. This is done by pumping down the

system to vacuum again and heating the quartz tube with a heating gun. The final cleaning is a very important step in the process since it otherwise would be an excellent source of contamination.



Figure 9. The one-source CVD used during the project

Table 1. Working conditions for the one-source CVD

Base pressure [mBar]	0.17
Working pressure [mBar]	0.27
Chamber wall temperature [°C]	120
Stage temperature [°C]	14
Carrier gas flow [sccm]	20
Furnace temperature [°C]	610-670 ^A
Monomer amount [mg]	10-150 ^B

^A Monomer dependent, ^B Depends on desired thickness and monomer

3.3.2 Two-source CVD

The gradients were made in a custom built two-source CVD system, see figure 9. This system has one deposition chamber connected with two quartz tubes for vapor transportation. Each tube has its own furnace and a separate carrier gas system which enables the system to work with two different monomers under different temperature and flow conditions. In comparison with the one source CVD, the two-source CVD also has a temperature controlled stage and a heating system for the deposition chamber walls. Most of the settings for the two-source CVD are computer controlled through a LabView program.

The experimental procedures are similar between the one-source and the two-source. What differs is the way of stopping the run. Since there is a distance between the both monomer holders, it makes it impossible to move them away from the furnaces at same time by one operator. Instead, the argon gas is flowed into the chamber before the monomer holders is withdrawn. In this way, the argon gas will fill the deposition chamber from the middle,

pushing the vapor away from the substrates. This is important since one monomer otherwise can give a finishing coat all over the substrates, ruining a gradient.



Figure 10. The two-source CVD system used for gradient manufacturing

Table 2. Working conditions for the two-source CVD

	Fluorine monomer	Amine monomer
Base pressure [Torr]		0.016
Working pressure [Torr]		0.23
Chamber wall temperature [°C]		110.9
Stage temperature [°C]		15
Carrier gas flow [sccm]	7	30
Furnace temperature [°C]	610	660
Monomer amount [mg]	~150	~150

3.4 Reactions

3.4.1 Citric acid

Citric acid, EDC and Sulfo-NHS was first mixed in 50 ml falcon tubes and the introduced to the coated substrates, which were put in a 6-well cell culture.

Citric acid was used in combination with EDC and Sulfo-NHS to be able to react with the functional amine groups. Different amounts and ratios of citric acid, EDC and Sulfo-NHS were evaluated to determine which would have the greatest contact angle lowering potential. In complement of concentration, temperature was also evaluated in order to find out its eventual impact on contact angle. Citric acid, EDC and Sulfo-NHS were bought from Sigma-Aldrich.

3.4.2 Maleic anhydride

Maleic anhydride was dissolved in acetone before it was reacted with the coated substrates in a glass Petri-dish. The concentration of the maleic anhydride solution was 0.1 molar and the reactions were made at room temperature. The maleic anhydride was bought from Sigma-Aldrich.

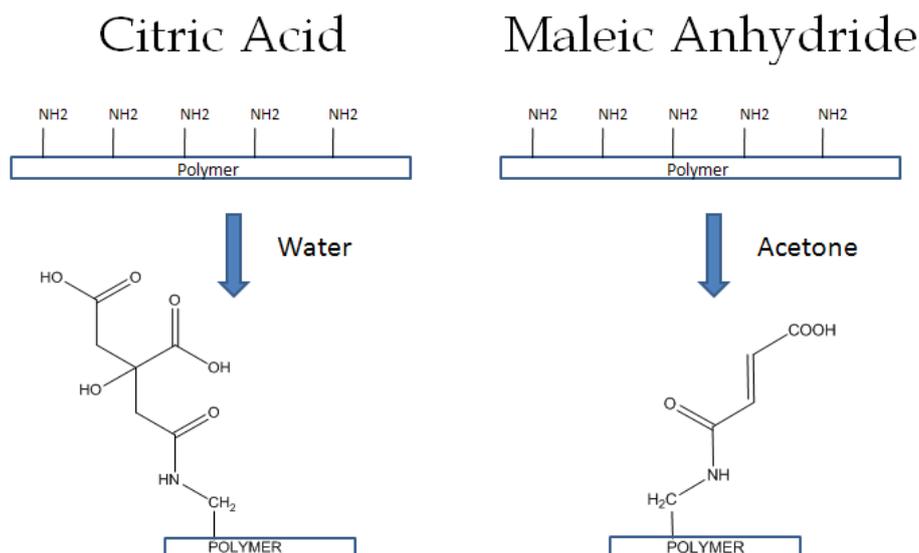


Figure 11. A schematic drawing of how the citric acid and maleic anhydride reacts with the functional amine coating

3.5 Contact angle measurements

Contact angle was measured by applying a 4 μ l droplet by a pipette onto the substrate. An image was taken with a Canon EOS 20D after 20 seconds. The image was processed through ImageJ [14] and the contact angle was determined by using the plug-in software DropSnake.[19]

Dynamic contact angle measurements were performed with a Rame-Hart Model 200 with a manual dispensing system. The contact angle was calculated with the DROPimage Standard software.

3.6 Surface roughness

Surface roughness was used to enhance the contact angle for both the hydrophilic and the hydrophobic surfaces. To create surface roughness, polymer spheres were coated onto the substrates using electrohydrodynamic co-jetting. The material used for the spheres were poly(acrylic acid-co-acrylamide) with molecular weight of 200 kD, supplied by Polysciences. The size of the polymer spheres were in the range of 0.5-1 μ m. The size was chosen to mimic the length scales found on lotus leaves.

4 Experimental Part

4.1 Hydrophilic Part

In order to achieve a hydrophilic coating, amine functionalized paracyclophane (4-aminomethyl-[2,2]paracyclophane) was used as the starting material for the chemical vapor deposition.

This monomer was promising since it would form a polymer consisting of functional amine groups that would give a hydrophilic surface. The amine groups also made it possible to further react the polymer and rendering it even more hydrophilic.

The initial experiments were made on silica and gold substrates which were coated with an amine monomer through CVD. This gave a reactive polymer coating with reactive amine groups on the substrates. To enhance the hydrophilic properties of the surface reactions were made with citric acid and maleic anhydride in order to introduce more polar groups to the polymer.

To enhance the hydrophilic effect, surface roughness was introduced to the substrate. The surface roughness was accomplished by electrohydrodynamic co-jetting of polymer spheres onto the substrate before the polymer coating was added.

Some experiments were also made with a diamine monomer found in the lab. Due to high age the substance its quality was question. The quality was later determined by the use of gas chromatography- mass spectrometry (GC-MS) and nuclear magnetic resonance (NMR)

4.2 Hydrophobic Part

When the investigations of the hydrophilic part had reached a point where a working method had been developed and repeatable results obtained, it was time to move on to the other crucial part of the gradient i.e. the hydrophobic.

From previous research done in the lab, a fluorine functionalized monomer (4-heptadecafluorononanoyl-[2.2] paracyclophane) had already been used and showed results that would be useful in this project. [16]

At this point, since the monomer had already been used in a publication, the work would first be focused on repeating these results and then try to take concept a step further towards the gradient end goal.

During experiments with hydrophobic polymer coatings, it was found that the film was not stable when it was exposed to water. To resolve the problem, different approaches was tried that lead to a multicoating solution that was later used in the rest of the project.

It was also found that the contact angle of the hydrophobic coating lost some of its contact angle when exposed to water but also over time. These observations resulted in experiments trying to determine if there were any dynamic effects that changed the properties of the coating.

4.3 Gradient

When both the hydrophilic and hydrophobic parts were investigated and had reached a state of maturity, it was time to combine them to achieve the primary goal pro this project i.e. a working gradient.

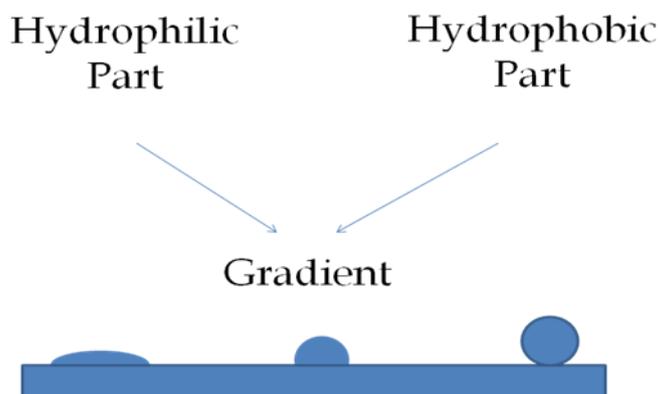


Figure 12. The knowledge gained from the previous experiments were combined in order to manufacture the gradients

The method that was used to manufacture the gradients was a two-source CVD process. The evaluation of the gradient was made primarily with contact angle measurements. The initial contact angle measurements were made with a system camera and were evaluated with the free software, ImageJ. This method provided only a static contact angle. Later in the project, a dynamic contact angle measurements system became available and this gave the opportunity not only to more exact measurements but also to measure contact angle hysteresis. As a complement to contact angle measurements, Fourier transform infrared spectroscopy (FTIR) was used to determine the surface composition along the gradients.

When working gradients were accomplished, the next step became to improve them by trying to lower the contact angle for the hydrophilic part. The methods used for this were the same as for the hydrophilic part i.e. citric acid and maleic anhydride. An experiment with biotin-hydrazide was also made as an alternative approach.

5 Results & Discussion

5.1 Hydrophilic Part

Initial experiments evaluated the contact angles of silica substrates coated with amine functionalized PPX. The effectiveness of the two different immobilization methods using either citric acid or maleic anhydride were investigated to find the most promising. The conclusion from these tests showed that the citric acid in combination with EDC and Sulfo-NHS performed a little bit better at lowering the contact angle than the maleic anhydride. However, the result did not differ by much which led to the decision to use maleic anhydride in the following experiments. The reason for this was that the reaction with maleic anhydride needed less reaction time and was also simpler and cheaper since no extra chemicals besides acetone was needed to make the reaction successful.

5.1.1 Diamine monomer

It was known that the polymer formed with the amine monomer would give a coating which contained unfunctionalized blocks. Since these blocks consist of a benzene ring structure, they would be stable and not particularly interested in having any stronger interaction with water molecules. A way to overcome the negative water interaction of these unfunctionalized blocks would be to use a diamine monomer with amine groups attached to both of its benzene rings in the paracyclophane structure (see fig 7, No. 3). This would give a coating purely consisting of functional amine groups.

Diamine was found in the lab but the problem was that it was very old between 7-9 years. The color of the compound was blackish, which stood in sharp contrast to the amine monomer that is white. Another worrying factor was that if the diamine monomer would turn out to be of usable quality, the amount available would not last long.

As an initial test of the quality, the monomer was used to CVD coat a substrate and the contact angle was measured. This experiment gave a contact angle at 48° and 10° when surface roughness was introduced. This result was promising but since the composition of the monomer was not known, the reason for the lowering of the contact angle may not exclusively depend on the diamine monomer.

As a next step gas chromatography- mass spectrometry (GC-MS) was used to determine composition of the monomer. This method was however not able to answer the question since the components in the tested sample turned out to be to polar. The components of the sample stuck to the chromatography column and where not able to reach the mass spectrometer. The final method for determining the composition and quality became nuclear magnetic resonance (NMR). The NMR was able to determine that the monomer was of poor quality and could not be used (see Appendix A for NMR spectra). Even though the diamine monomer was a promising route, the time it would take to synthesis new monomer was too long to fit into this project.

5.1.2 Surface roughness

The introduction of surface roughness gave a significant enhancement of the of the surface's contact angle properties. For a hydrophilic surface, the introductions of surface roughness decreased the contact angle from 55° to 15°. For hydrophobic surfaces, the contact angles were increased from 100° to 152°.

Table 3. Summary of contact angles

Coating	Contact angle
Amine	75°
Amine (reacted w. Citric acid)	51°
Amine (reacted w. Maleic Anhydride)	55°
Amine with surface roughness	60°
Amine with surface roughness (reacted w. Maleic Anhydrid)	15°
Diamine	48°
Diamine with surface roughness	10°
Fluorine	100°
Fluorine with surface roughness	152°

5.2 Hydrophobic Part

The monomer used to achieve the hydrophobic part was the 4-heptadecafluorononanoyl-[2.2]paracyclophane (see fig 7, No. 5). It is a very attractive monomer for this kind of tasks thanks to its long hydrophobic fluorine tail that was without any modifications capable of delivering a very high contact angle. Contact angles at about 100° were quite quickly accomplished for the substrates, but since the goal was to make it as hydrophobic as possible the way to achieve this was to add roughness to the surface. With surface roughness, the contact angle was increased with about 50° leading to super hydrophobic surfaces. This made the static contact angle measurements somewhat demanding since the water droplets easily rolled of the surfaces.

For the contact angle measurements, particularly on the hydrophobic surfaces it was seen that the contact angle could vary a lot. One contributing factor to this was the inhomogeneous in primarily height but maybe also in particle distribution on the substrates surface. Even though early investigations with SEM showed that the electrohydrodynamic co-jetted particles where rather evenly distributed (see Fig. 13), this will not automatically mean that this is always the case. Still, since the particles are dependent on several parameters connected to the jetting process, the particle distribution can vary between different jetting occasion. There may also

be local clusters formed that give rise to features with larger length scales than the rest of the coating; these formations may not be possible to detect with the naked eye.

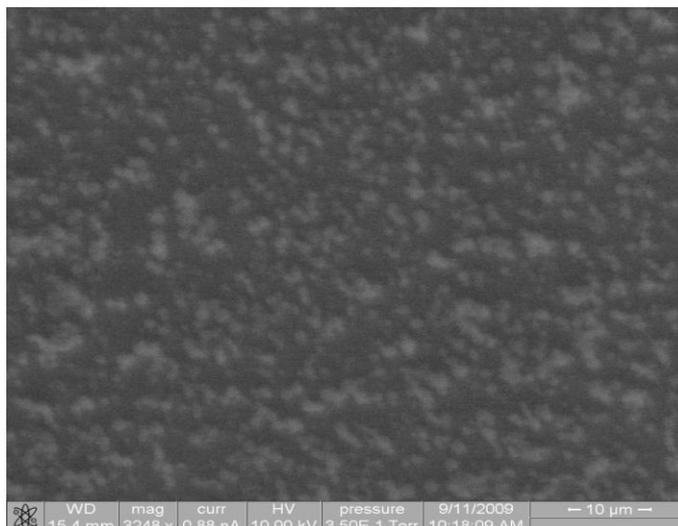


Figure 13. SEM picture of electro jetted substrate surface. The electro jetted particles are distributed fairly evenly distributed without large cluster formations

5.2.1 Stability

A crucial property for the coating is that it should be stable. Since the polymer film was found to break, a series of experiments with different coating thicknesses were investigated in order to find a value that would give a rinse stable film.

The evaluation of the polymer coating was made through a “rinse test” in which the surfaces were rinsed with de-ionized water at an angle of about 45° and observations were made if there were any change in color or of the water repelling properties of the surfaces. In the beginning, the surfaces were only able to withstand this treatment for a short while before they started to allow droplets to stick to the surface. This behavior was only observed for surfaces coated with surface roughness. This raised the question whether the problem was the thickness of the coating or maybe the interaction between the coating and particles. Due to the known properties of the coating the most probable explanation would be the thickness.

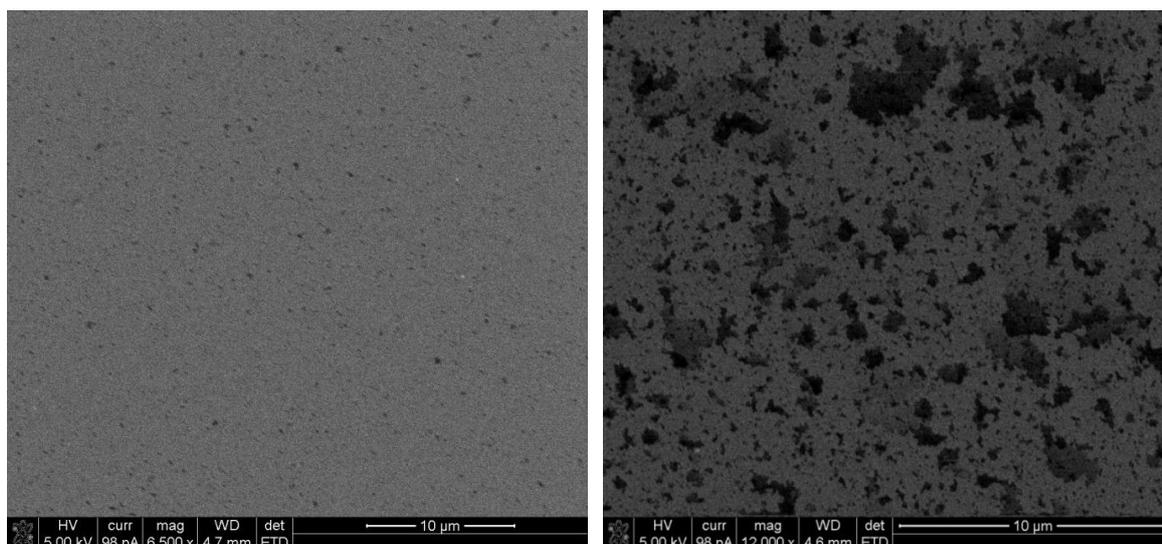


Figure 14. Scanning electron microscopy (SEM) pictures of an unrinsed surface (Left) and a rinsed surface (Right)

The first approach to achieve better film stability was to increase the thickness of the fluorine

coating. This gave an increased stability but the amount of monomer and deposition time also increased, which made this approach disadvantages in a gradient manufacturing situation. As a next step, a two layer approach was tested that consisted of a base coating with unfunctionalized paracyclophane (Parylene N) and on top of this a fluorine coating.

This approach was implemented and different thickness combinations were tried to achieve a completely stable film that would withstand the “rinse test”. The total thickness of the coating was set to be about 50-100 nm because this would not give a significant loss of the surface roughness effect since the jetted particles is in the size range of 0.5-1 μm .

Table 4. Coating thickness vs. stability

Run	Parylene*	Fluorine*	Stability
1	0,177	0,404	No
2	0,195	0,205	No
3	0,452	0,256	Yes ⁿ
4	0,506	0,304	Yes

*Deposition amount according to CVD monitor [0.1 \approx 10 nm]

ⁿ a cluster of particles made a “peak” and resulted in local break of coating during rinse test

The reason for the increase in the required polymer thickness for surfaces with surface roughness may not be very surprising. The introduction of surface roughness will increase the surface area required to be coated quite dramatically.

Investigations of the successful, stable surfaces were made but it was found that the contact angle decreased after being rinsed with water. This leads to an interesting question; what gives raise to this change?

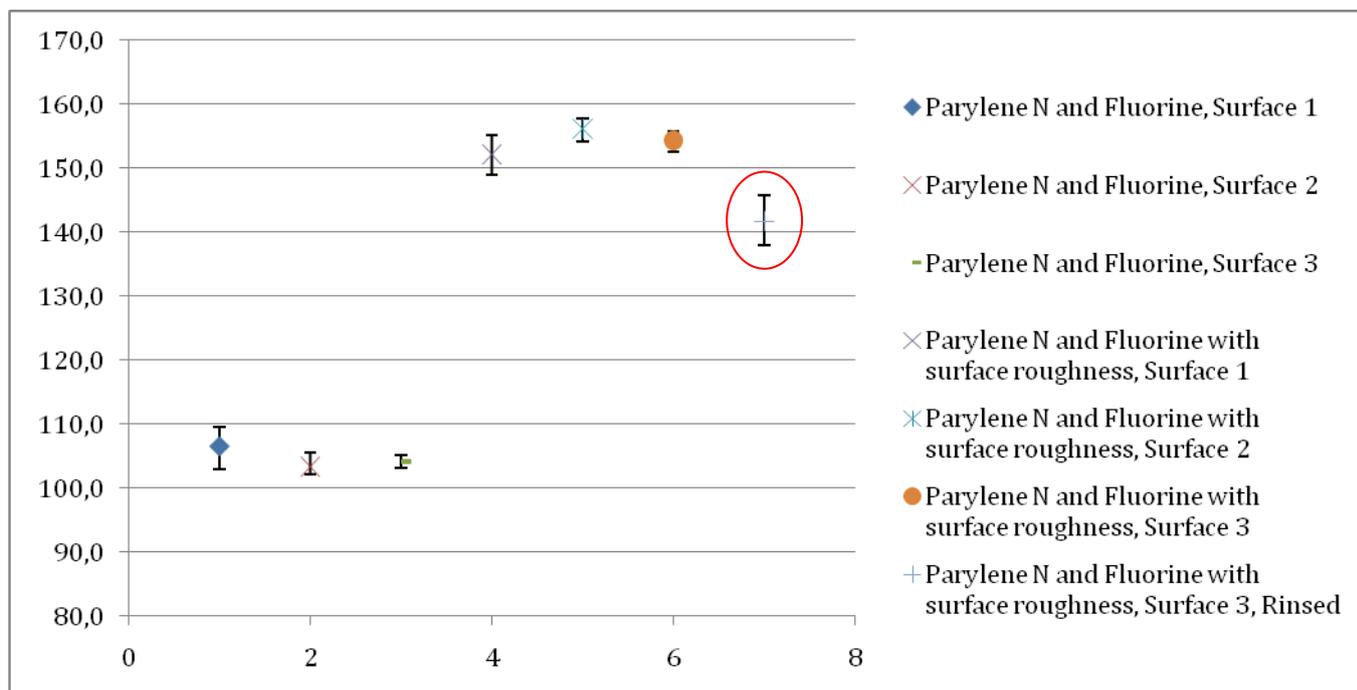


Figure 15. Results from experiments with a rinse test stable combination of non-functionalized paracyclophane (Parylene N) and fluorine. During the experiment a drop in contact angle was noted after the rinse test was conducted

5.2.2 Loss of contact angle

To try to find out why the surfaces show a drop in contact angle after being water rinsed, several different hypotheses were considered. Factors such as contamination and surface dynamics were those found to be most likely. The first variable to consider was contamination from water.

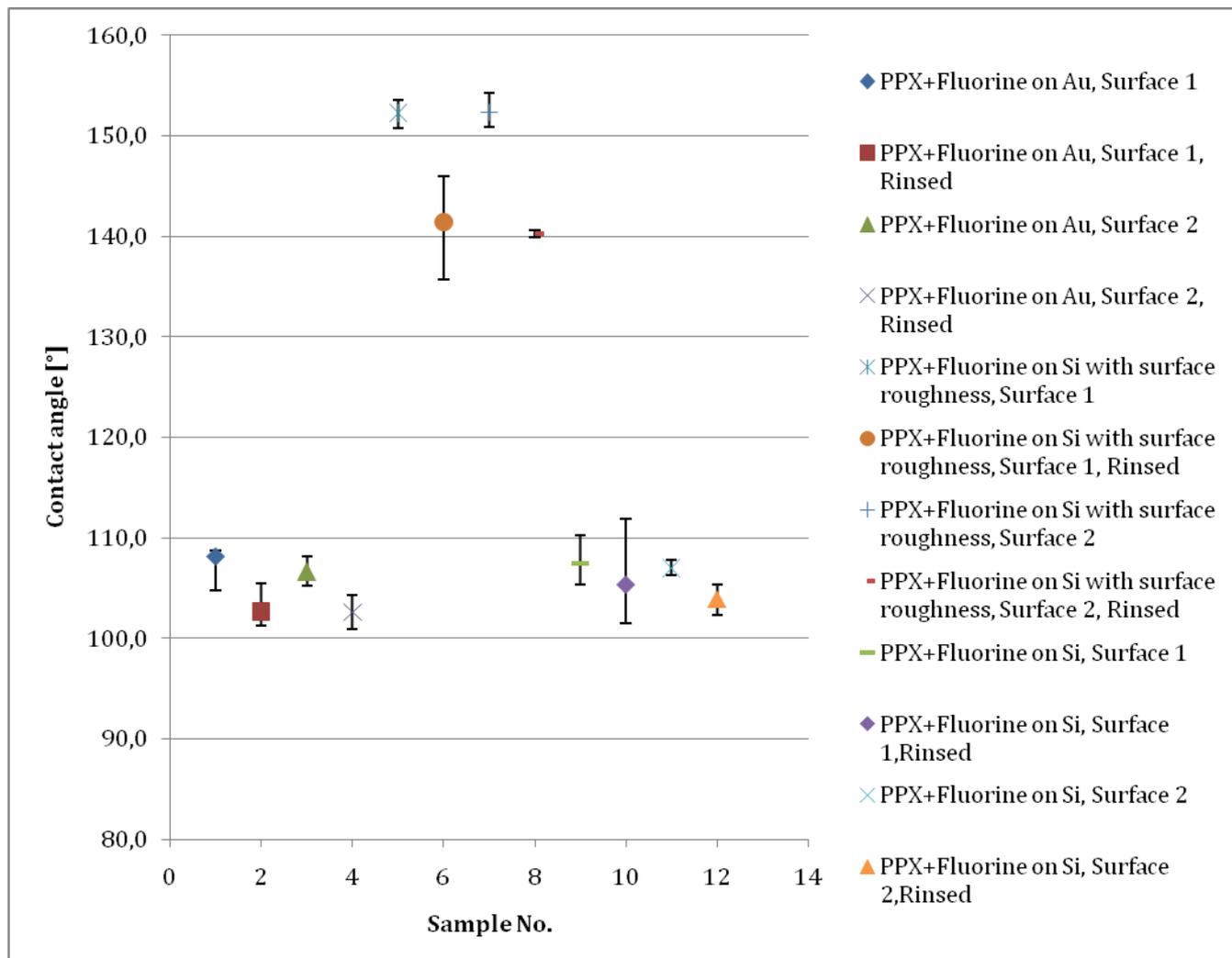


Figure 16. Experiment showing the effect of water rinsing on contact angle for different substrates and coatings. Deionized water was used for rinsing.

The water used for rinsing had been ordinary de-ionized water from one of the student labs. To rule out any issues with water contamination, an experiment was done using DNA grade water and chromatography water. The experiments showed no difference in the results depending on what kind of water that was used. The same characteristic drop in contact angle could be seen for all rinsed surfaces.

During the experiments of finding the reason behind the drop in contact angle after water rinsing, a complimentary experiment was done in order to find other situations that besides water rinsing could cause a drop in contact angle. This experiment investigated a series of fluorine coating with different manufacturing dates.

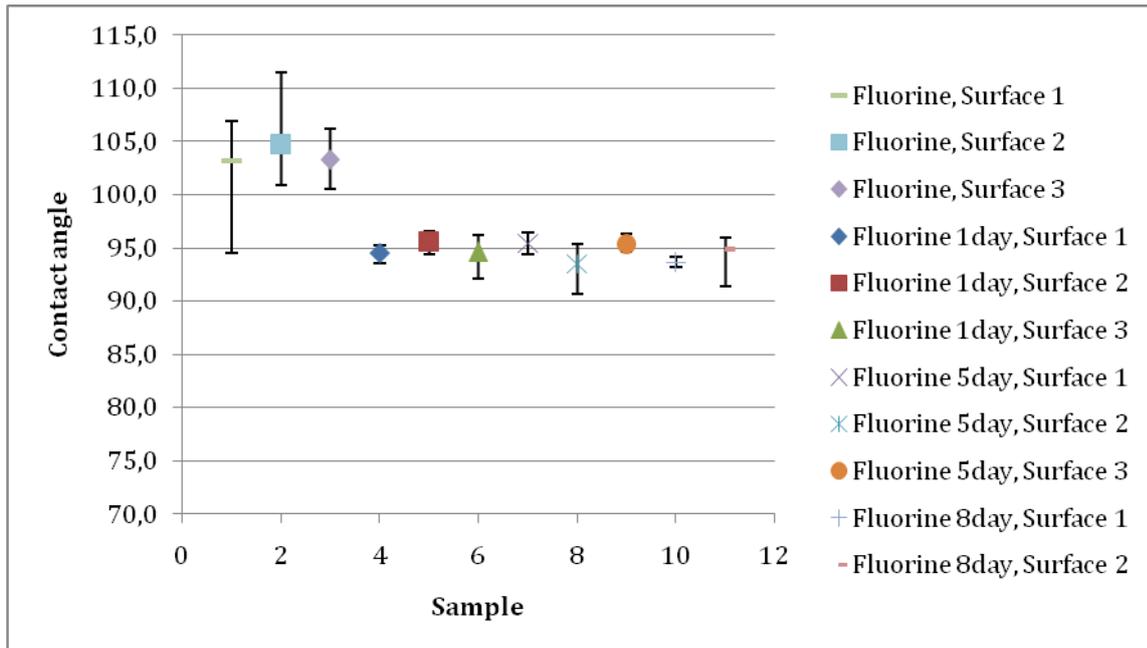


Figure 17. Aging experiment results for fluorine surface with different age. The substrates have no surface roughness

The experiment showed that the surfaces suffered a loss in contact angle that seemed to be stable over time. The question was if these observations could be explained by contamination from the atmosphere or could the exposure to water vapor in the air lead to effects on the hydrophobic fluorine groups?

To find out if the atmosphere had any influence on the surfaces, an experiment was designed to test if exposure to air would cause the surfaces to lose some of their properties.

In the experiment, surfaces with surface roughness were coated with fluorine. Then half of the surfaces were rinsed with water, to induce the contact angle lowering seen in pervious experiments. Half of these washed surfaces were then stored in nitrogen while the other half were stored in air. The goal with this study was to see if storage in nitrogen would be able to preserve the contact angle for the unwashed surfaces and recovery the loss of contact angle for the washed surfaces.

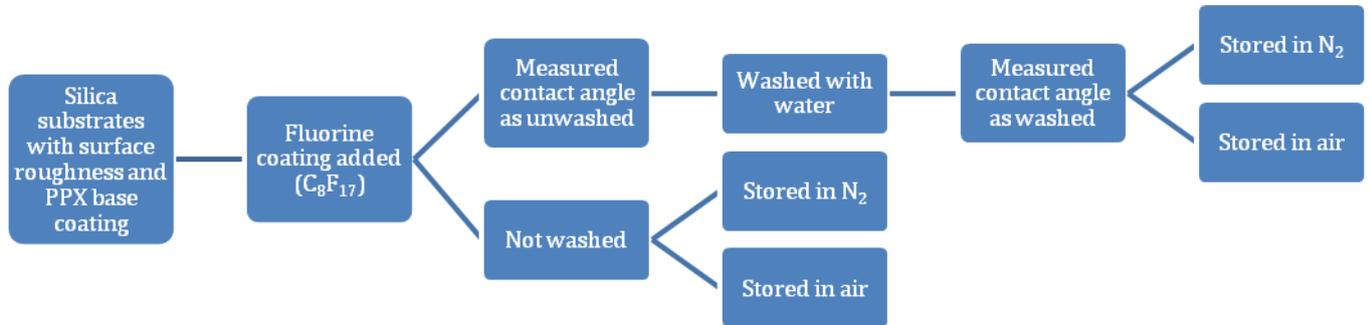


Figure 18. Outline of the surface dynamics experiments

All samples were let to rest for one day in their respective atmosphere before evaluation.

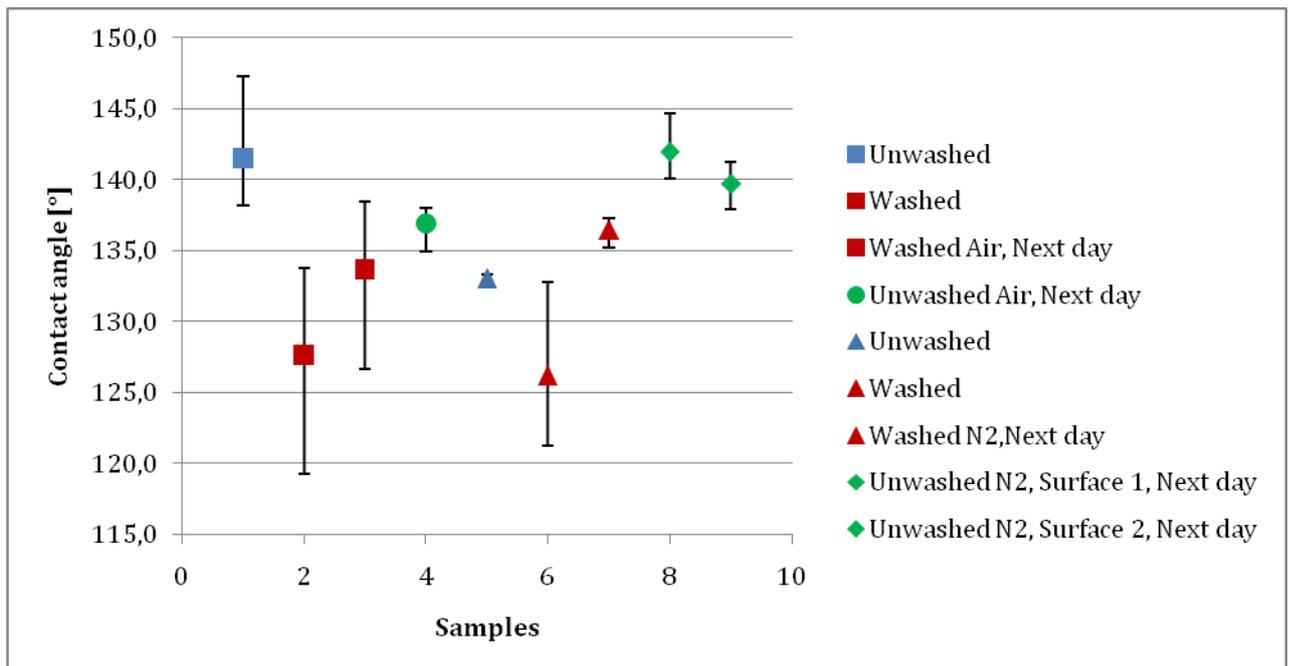


Figure 19. Results from surface dynamic experiment. All surfaces had surface roughness

The results from this experiment are not very clear. The biggest reason for that is the large variation in contact angles on the surface. Generally, substrates with surface roughness will give the highest contact angles but the cost for this is a large variation in contact angles. This can be seen in the contact angle difference between the two unwashed surfaces; these two are made at the same time and in the same way. Still, they differ substantially in contact angle, giving raise to questions about how reliable the result might be if this happens to supposedly identical surfaces.

But some interesting details can be found. The surfaces that were rinsed showed lowering in contact angle after water exposure, which was expected. But from the “next day” samples it can be seen that the unwashed substrate stored in air showed lower contact angle then the substrate that were measure right after manufacturing. This effect was not present for the N_2 stored.

The washed substrate that was stored in air for one day showed a little bit higher contact angle then the directly after rinsing. This trend is also evident for N_2 but stronger.

What puts some questions to these results is the large variation in contact angle that the surface roughness gives rise to. Due to this, none of the results can really be seen as certain. To be able to draw better conclusions from the experiment, it needs to be made again. In the following experiment, the samples were stored for three days before they were measured again. Otherwise the experiment was made the same way.

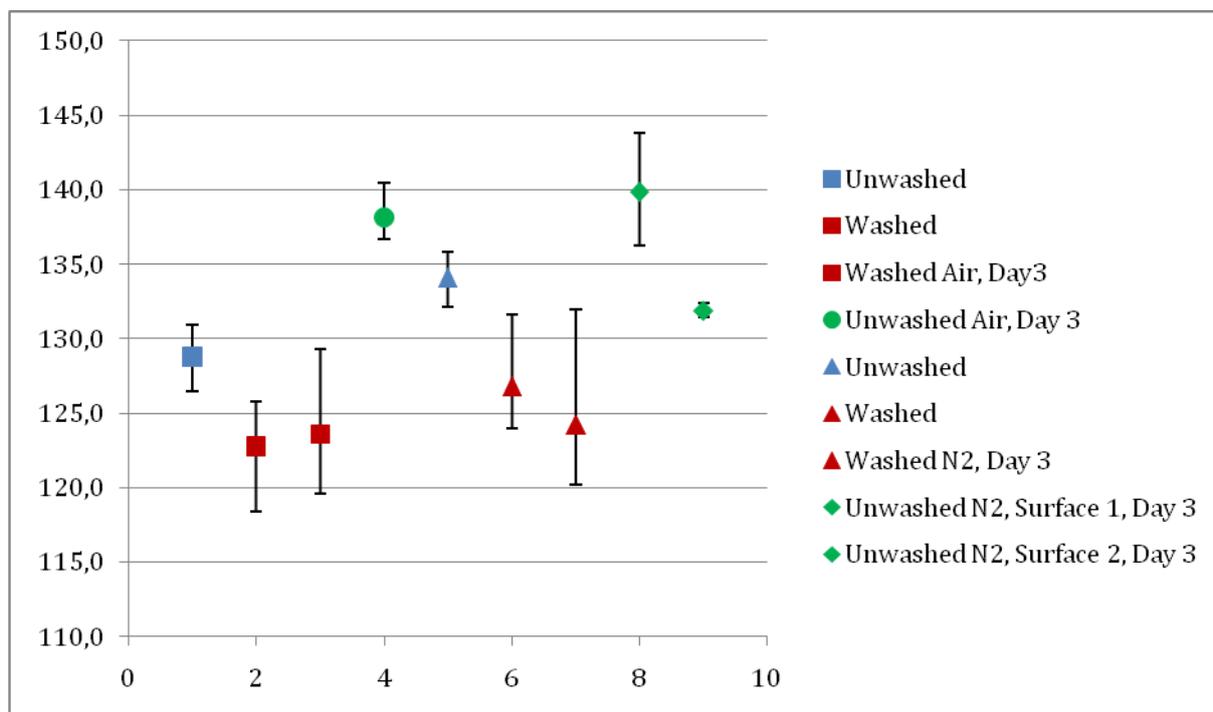


Figure 20. Results from study to determine of different atmosphere will affect contact angle

Again, the contact angles that were made directly after the substrate manufacturing show the same trends as the earlier experiments i.e. contact angle drops after water exposure and there is a contact angle difference between substrates that were to considered identical.

For the surfaces that was stored for three days, both the one that was stored in air and N_2 show a higher contact angle then the ones that was measure the initial day of the experiment. This was not seen in the first experiment and was most likely explained by the difference that surface roughness gives.

The results from the washed substrates (both stored in air and N_2) still show the difference between washed and unwashed. This effect is more obvious in the second experiment than in the first. This indicated that there is no recovery for the surface stored in N_2 then for the one stored in air. The biggest lesson from the experiments was that the surface roughness gives raise to large variations between different measurements both between surfaces and between measurements made on different location on the substrate.

As the project continued towards its main goal, i.e. wettability gradient creation, this question was left unanswered, but only for a while it turned out since the same question returned for the gradients.

5.3 Gradient

The first gradient experiment ended up with no resulting gradient, instead the surface was found to have contact angle at $80^{\circ} \pm 2^{\circ}$ that varied randomly along the silica slide which was used as substrate. It may not have been too surprising that first run would not give a good result but since no gradient was formed, this implied that the problem most likely was to be found in the areas of sublimation control and carrier gas flow rate.

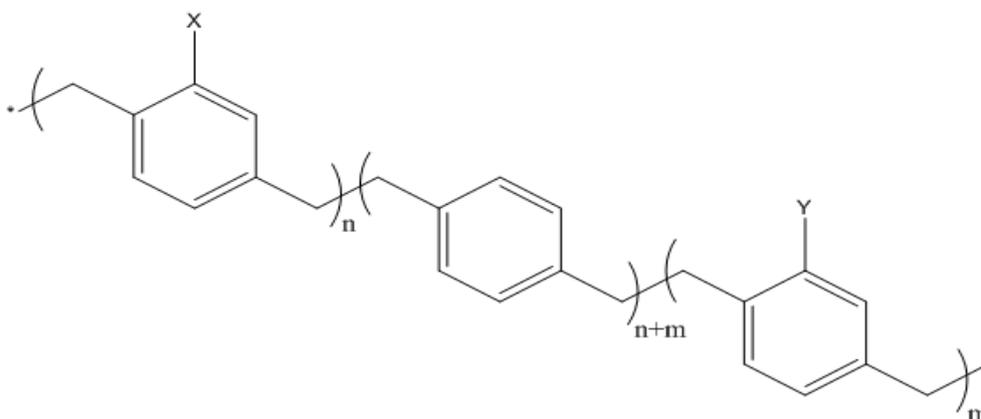


Figure 21. The structure of the polymer coating obtained from the two-source CVD

To resolve the initial problems, contact was made with the previous user of the system. After a discussion and demonstration of e.g. sample holder position new experiments were ready to be undertaken.

With new changes to the operational settings to the two-source CVD, new experiments were carried out. To get more information besides contact angles, the experiments were extended to include gold substrates besides the silica slides. This gave the capability to not only make contact angle measurements but also investigate the surface composition with FTIR.

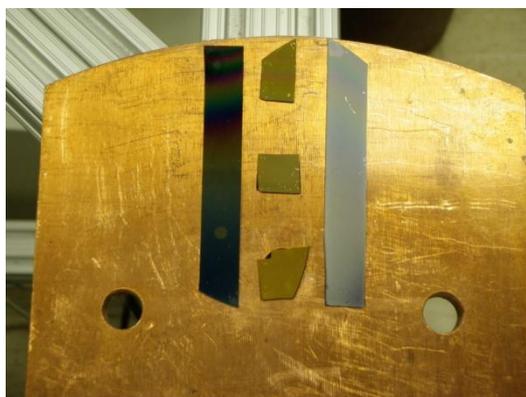


Figure 22. Example of sample placements on the sample holder for a deposition run in the two-source CVD

From the first couple of gradient experiment that was conducted, the later ones showed evidence of a successful gradient creation. These conclusions were drawn from analysis from the IR-spectra's collected from each of the experiment.

FTIR spectras showed that the surface composition change through the CVD process. What can be seen in these spectras is the increase of the fluorine peak while the CH_2/CH_3 bonds, which is present both in the amine groups and in the polymer itself decreases. (see Appendix B)

The following gradient experiments turned out successful and gave two working gradients, one with and one without surface roughness. This proved that concept of manufacturing gradients with variation in contact angle.

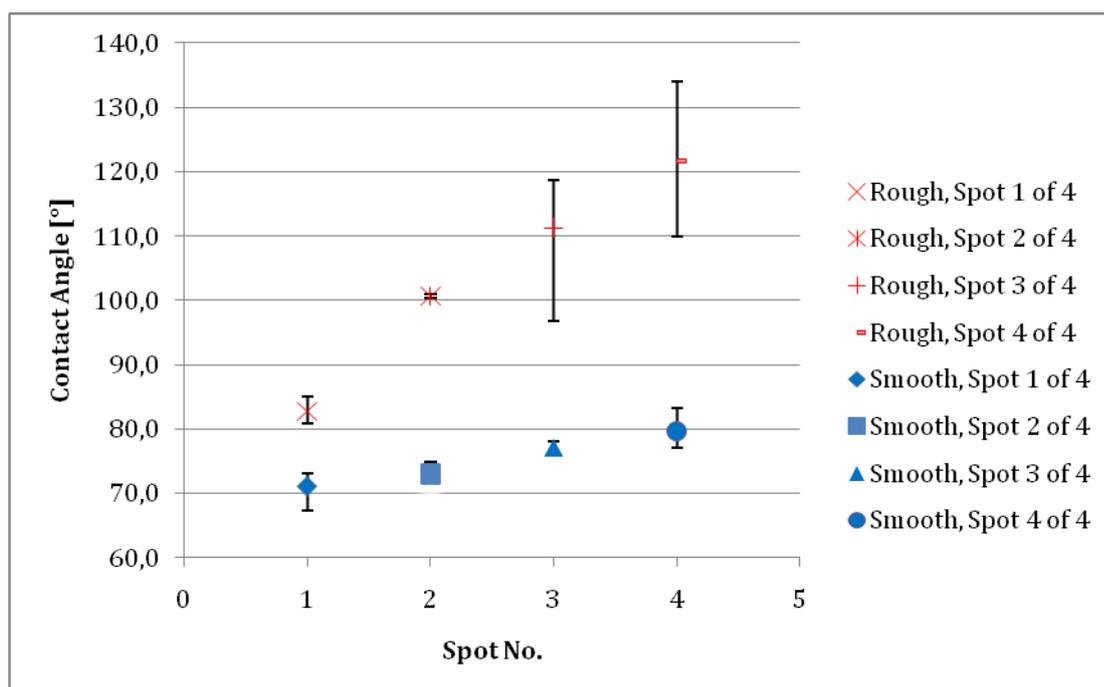


Figure 23. Static contact angle of the gradient measured at four different locations along the gradient

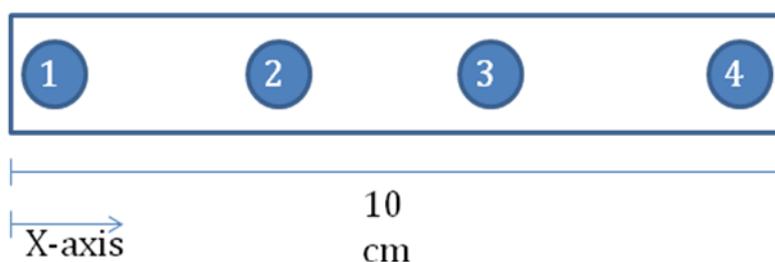


Figure 24. Scheme showing the spots used for contact angles measurements on the gradients

From the lessons learned about stability of the polymer film form the hydrophobic substrates, the concept of a multilayer or sandwich coating was also used for the gradient. When coating the gradient substrates, a PPX coating of about 100 nm was applied. This thickness was chosen since it would provide a good protection for the surface and any eventual surface roughness, but it would still be thin enough to not smoothen out the surface roughness effect given by the polymer spheres. The thickness of the gradient coating achieved by the two-source CVD is hard to estimate correctly. From the deposition control it would be in the range of a few hundred nanometers, but when visually inspection of the surfaces it was obvious that there was a thickness gradient as well. This could be seen due to color changes, mainly on the

hydrophilic side of the gradient. The reason for this might be that since the sample holder is tilted towards the fluorine source there may be turbulence in the flow going over the edge of the sample holder, resulting in an uneven thickness distribution in this area.

Thanks to the Tuteja lab at the Department of Materials Science and Engineering, the opportunity to do dynamic contact angle measurements was given. This made it possible to make measurements that is more accurate and repeatable but which also gives the chance to determine the hysteresis of the polymer film.

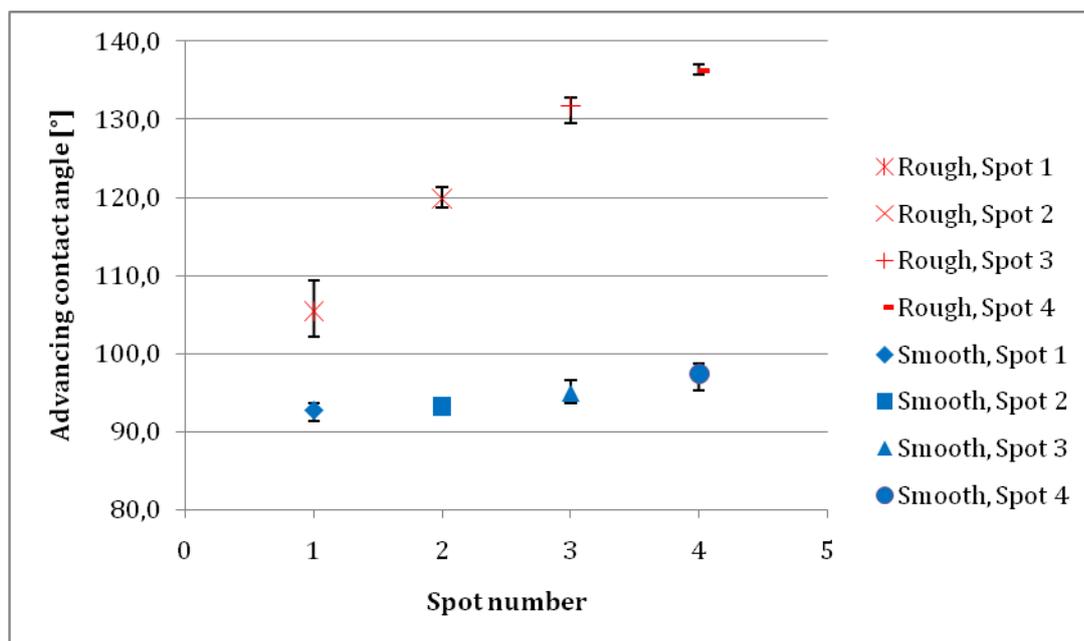


Figure 25. Advancing contact angle of the gradient measured at four different locations. Same gradients as in Figure 21 but this time with advancing contact angle.

When comparing the results from the contact angle measurements, one should note that some are static while the later ones are dynamic (advancing). This makes them not directly comparable. However, the trend in the both cases gives a clear picture of the gradient properties.

From investigating the contact angles measured for the gradients it is clear to see that they are generally higher for the hydrophilic part and lower for the hydrophobic part, compared to the experiments made earlier stage of the project. Since the creation of the gradient is a rather complex process which is not easily controlled, several different variables might be to blame for difference in contact angle. One is of course that the use of the two monomers will lead to a mixture in composition. It is very hard to get a perfect and even transition from one property to the other. There is likely some hydrophobic monomer that reaches in to the hydrophilic regime and vice versa. Another explanation is that the when working with two monomers there will be a larger amount of unfunctionalized monomer parts than in the case of only on monomer. This will of course led to a different composition of the polymer coating which will have implications on its properties.

By using the Cassie equation [17], it is possible to calculate the fractions of the amine and fluorine in the final polymer.

$$\cos \theta = f_1 \cos \theta_1 + f_2 \cos \theta_2$$

θ = contact angle for the heterogeneous surface

θ_1 / θ_2 = contact angle for the homogeneous surface

Since we have two components in the system, f_2 can be described as $1 - f_1$

Table 5. Results of compositional calculations

Gradient part	Topography	Component	Amount	Component	Amount
Hydrophilic	Smooth	Amine	69%	Fluorine	31%
Hydrophobic	Smooth	Fluorine	54%	Amine	46%
Hydrophilic	Rough	Amine	56%	Fluorine	44%
Hydrophobic	Rough	Fluorine	75%	Amine	25%

The calculations show that both sides of the gradient contain a fairly large contamination from the other monomer. Since the fluorine monomer has a long tail, it would be likely that this tail can due to its length give a negative effect for the hydrophilic side by reaching out and interact with the water before the shorter amine can. This can explain why the hydrophilic side on the gradients shows such a high contact angle. However, these calculations are not exact but can give a clue to the experimental data.

5.3.1 Reactions

The results from the gradients experiments showed that successful gradient had been accomplished. The difference between the hydrophilic and the hydrophobic parts are clearly visible from the contact angle measurements. Since the gradients are made with a reactive polymer coating, it is now time to use this feature to it full extent. From the early experiments in this project, reactions were used to achieve substantially lower contact angles than seen on the gradients so far. Even though the gradients are made in an environment without the same degree of control as can be obtained when only working with one monomer, the results should still give a hint about what, at least in theory, contact angles that could be achieved for the gradients.

To lower the contact angle of the gradients, maleic anhydride dissolved in acetone were introduced to react with the gradients.

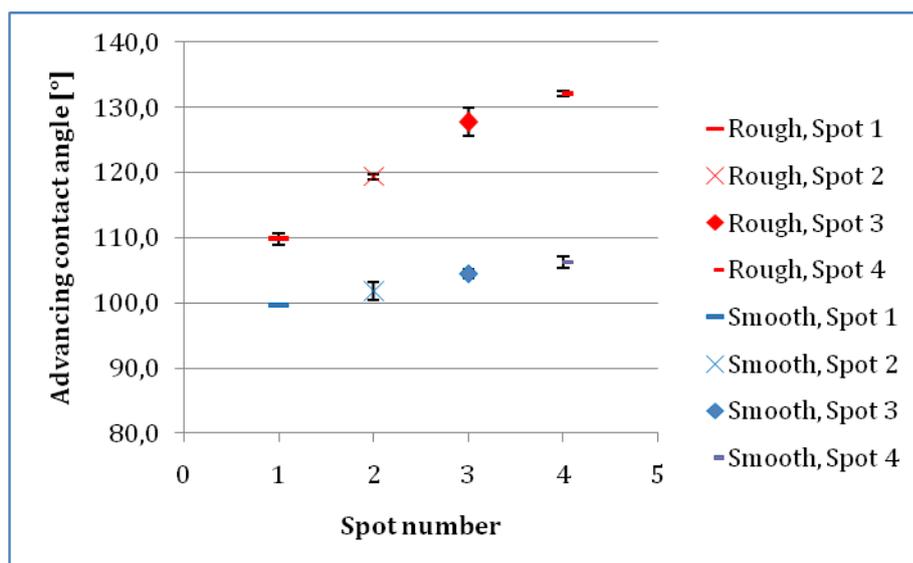


Figure 26. Contact angle measurements on the gradient **before** reaction with maleic anhydride

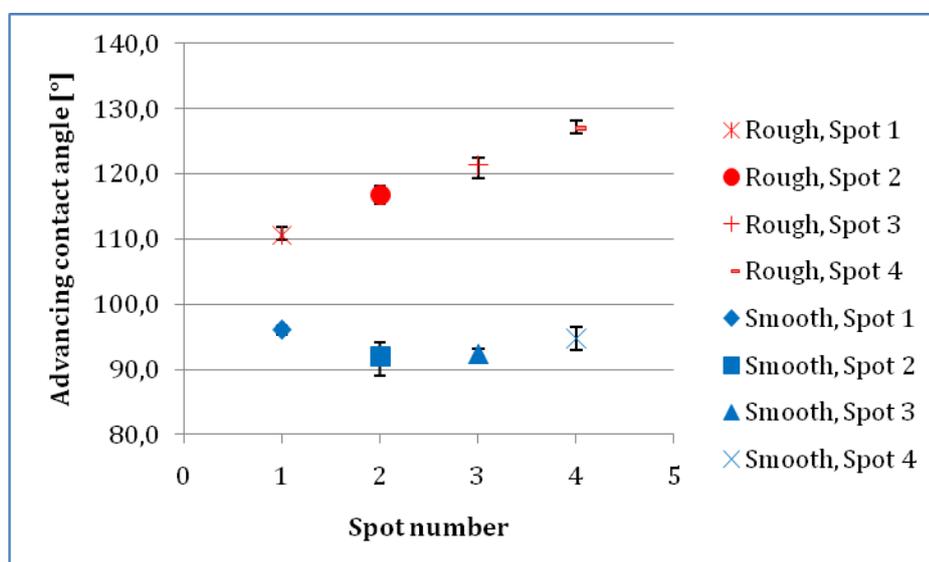


Figure 27. Contact angle measurements on the gradients **after** reaction with maleic anhydride

Since the contact angle after reactions with maleic anhydride did not show much improvement, the questions were raised whether the reactions worked as they should. From the earlier experiments, the citric acid was also used to successfully lower the contact angle. To get some perspective to the results obtained with maleic anhydride, citric acid was used as a comparison.

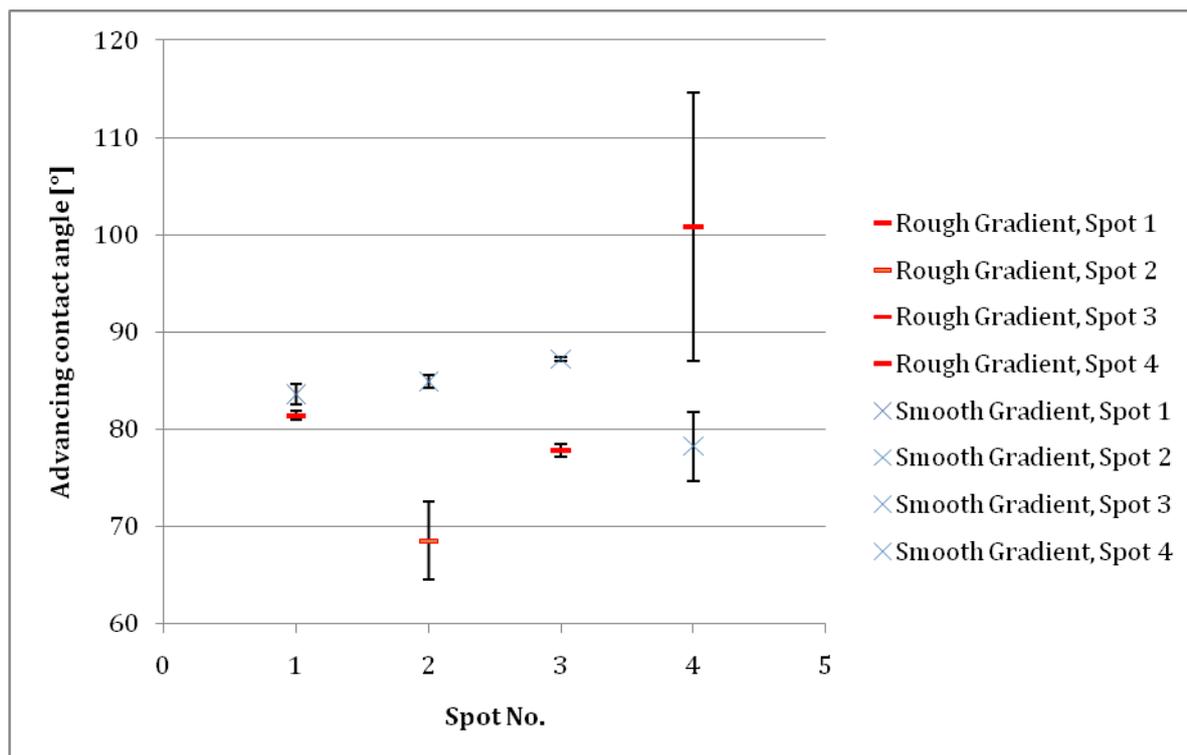


Figure 28. Contact angles of gradients reacted with citric acid

The reaction with citric acid did not give a result that deviated a lot from what was achieved previously with maleic anhydride. Since the surfaces are very sensitive, especially the ones with surface roughness, makes it very difficult to clearly determine if the deviating measurements are due to modifications made to the surface or just results of surface defects. From the citric acid gradient reaction it can be seen that the contact angle does not differ substantially from when maleic anhydride was used. By studying the results from the gradient without surface roughness, i.e. smooth, the difference compared to maleic anhydride reacted smooth gradient is about 10-20°. This difference is in the same range as what was seen earlier in the project for the hydrophilic surfaces. This implies that the reaction have been working to some extent and that the results are probably the best that can be achieved for the presently existing system.

The big question that still was unanswered was why the contact angle of the hydrophilic part would not get any lower when it was reacted with more polar molecules. An idea came up while thinking of how the surface would look like on a molecular scale. What would happen if the fluorine chain, which is longer than the amine, is present on the hydrophilic part? Even if the amount would be small, maybe the length and dynamics of the chain still is sufficient to hinder the immobilization process of the more polar molecules, i.e. maleic anhydride or citric acid onto the amines? To find out, a gradient experiment was run but this time with a fluorine monomer with a shorter fluorine chain.

In the experiment, 4-trifluoroacetyl[2,2]paracyclophane (Fig. 7 no.4) was used instead of the previously used 4-heptafluorononanoyl[2,2]paracyclophane. This monomer is in the same size range as the amine and would not be able to interfere with its surrounding environment as much as the more long chained fluorine would be able to.

The experiment was conducted in the same way as the previously gradient experiments; the only difference was that the flow rate for the short chain fluorine monomer was set to 7 sccm,

due to the difference in molecular weight. This flow rate had also been used in earlier experiments and reported in literature [3].

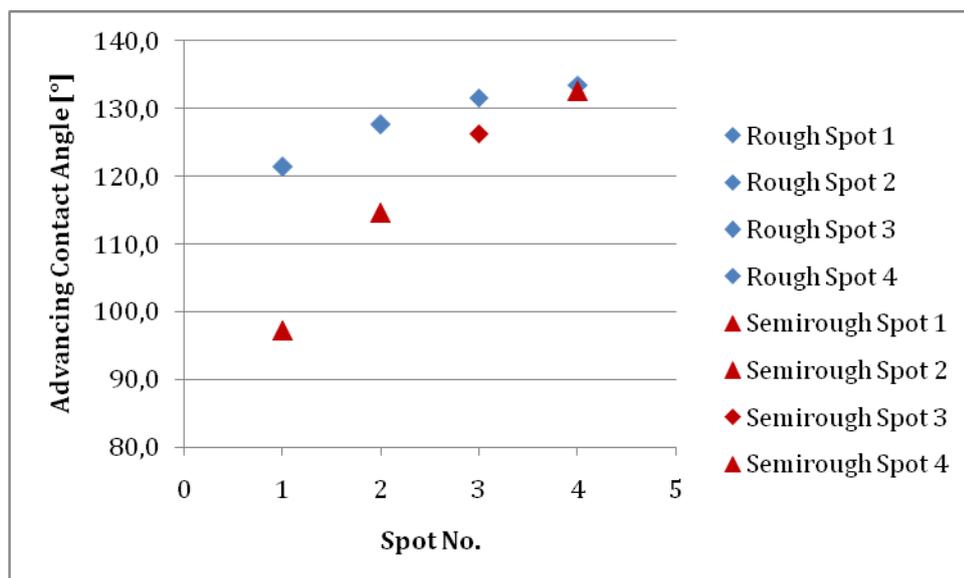


Figure 29. Contact angle for the short chain fluorine monomer.

One of the surfaces used for the experiment had not been coated completely and was there for denoted “semirough”. The part that was not completely coated was the part closest to the amine monomer inlet i.e. the hydrophilic part. This should be taken into consideration when viewing the values for the contact angle since this will give a lower value than if coated completely.

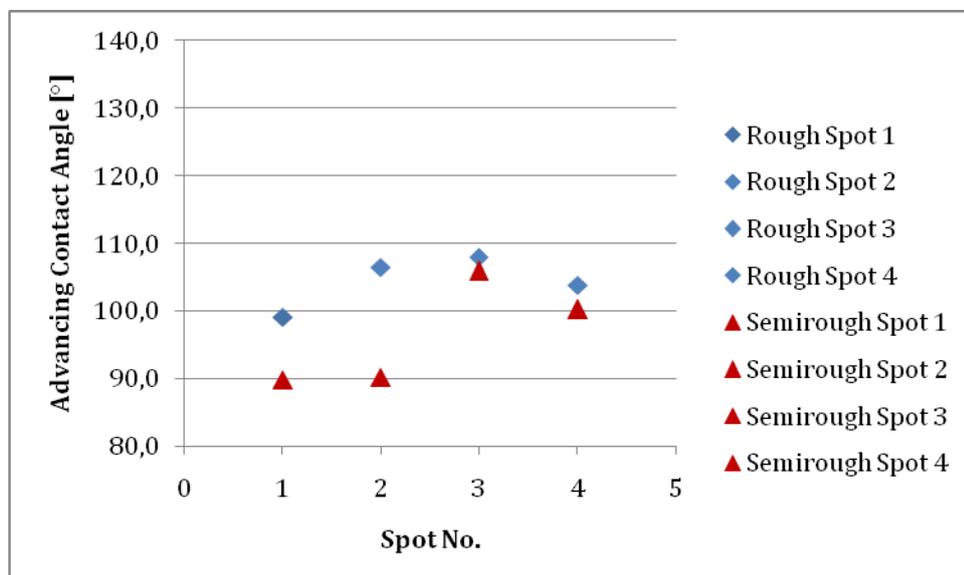


Figure 30. Contact angles for the reacted gradient

After reacting the gradients with maleic anhydride, the previous gradient properties were pretty much lost. This result gave a clear indication that the fluorine chain length did not have any negative impact on the contact angle; it instead showed that something must be wrong with the reaction. Clearly, what was seen in the early parts of the project, i.e. maleic anhydride lowering the contact angle for amine functionalized substrates to 15°, could no longer be seen.

5.3.2 Biotin- hydrazide

Since the reactions designed to lower the contact angle for the hydrophilic part of the gradient did not seem to work for either maleic anhydride or citric acid, it was time for a new approach. A molecule that was often used in the lab was biotin-hydrazide.

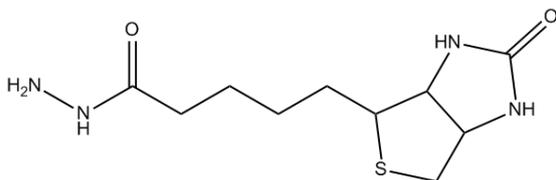


Figure 31. Chemical structure of biotin-hydrazide

This molecule would bind to the keto group (C=O) present on the hydrophobic part i.e. lower part of the fluorine chain. With this reaction, the hydrophilic side with its amine groups would become the part with highest contact angle while the previously hydrophobic part now would become hydrophilic.

New gradient surfaces was made and reacted with biotin-hydrazide in PBS buffer. The reaction lasted for about one hour before the gradients were rinsed. Contact angle measurements were then performed.

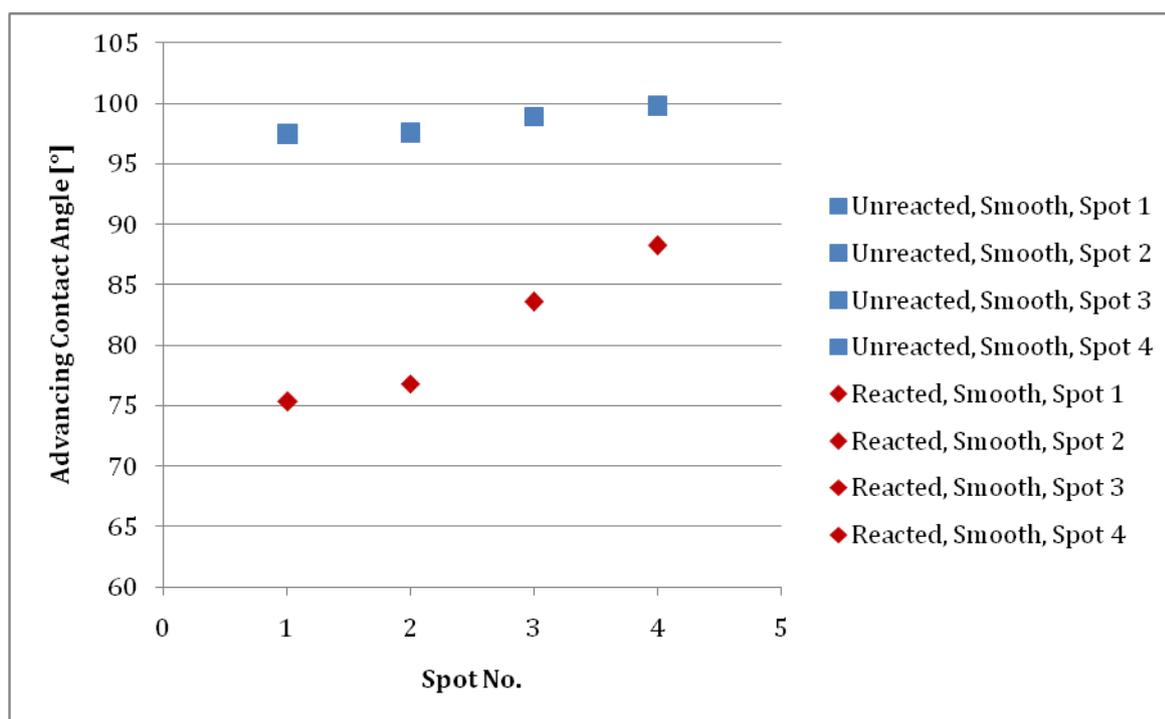


Figure 32. Contact angle measurements of biotin-hydrazide reacted gradient

A rather surprising result was found when the hydrophilic part of the gradient i.e. amine containing turned out to be the part that lowered its contact angle. This was of course an unexpected turn out but it might also be important to understand the gradient, and there through maybe also a large part of the project.

If the biotin-hydrazide reacts with keto groups, this means that keto groups must be available on the hydrophilic gradient side. This is a result consistent with the theoretical calculations

previously made from the change in contact angle between the gradient and the earlier made hydrophobic/hydrophilic surfaces.

If now fluorine groups are present at the hydrophilic part of the gradient, the question is how this will affect the amines? There are two possibilities; since the polymer film is dynamic this might result in that the hydrophilic amine groups will minimize its exposure to air by hiding these groups in the polymer film. At the same time, the hydrophobic fluorine chain will migrate to the polymer film surface to maximize its exposure to the air and thereby lower their energy.

What also might occur is the opposite; since water is present in the air, this will form a thin film on all surfaces that is in contact with it. This fact is a problem in corrosion. If this is what happens, the fluorine groups should be hiding while the hydrophilic groups reach for the polymer surface, under the condition that the water film is able to influence the surface to such an extent.

From the results obtained, it seems more likely that the hydrophobic molecules are more present on the surface than the hydrophilic. This would explain the high contact angle for hydrophilic part of the unreacted gradients compared with the reacted surfaces earlier in the project. It would also explain the results from the biotin-hydrazide experiment. If it would be true that the dynamics of the surface changed the surface properties, it might explain why our reactions do not seem to work.

Since the hydrophilic surface has been that part of the gradient that not achieving satisfactory results, an experiment was made just to confirm that nothing had changed with the amines during the project. Smooth silica substrates were coated with a base coating of Parylene N and on top of this a layer of amine functionalized PPX.

Table 6. Dynamic contact angle for the hydrophilic surfaces

Coating	Dynamic contact angle	
	Advancing	Receding
Amine	92°	59°
Amine (Reacted)	79°	4°
Amine (Reacted w. Roughness)	66°	6°
Silica (i.e. No coating)	42°	21°

The result confirmed the earlier measurements that were made in the project, but what was noted was that the hysteresis was high, about 40°. This is not what is desired when the goal is to get water to move by itself over the gradient. According to Whitesides and Chaudhury [12], a hysteresis less than 10° is required to make water move.

Going back to contact angle hysteresis, three contributing factors are available i.e. topography, kinetic effect and surface composition. Since the substrates were smooth the topography component can be eliminated. The kinetic effects, which is the ability of molecular groups on the surface to lower their total energy by hiding in the polymer underneath is an explanation that previously been considered likely.

The hysteresis can also depend on the surface composition since the polymer we make, both with the one- and two-source CVD, is made up from building blocks with different chemical properties. In the one source CVD, the surface depends on the assembly of one functionalized

part and one unfunctionalized part which will form the final polymer. However, since the amount of monomer in a CVD process is very large the statistics predicts that the polymer composition formed will be even with respect to its components i.e. the resulting surface coating done with amine monomer will get a even distribution of functionalized and unfunctionalized groups. This will give raise to a difference in surface composition, i.e. heterogeneity.

6 Conclusions & Outlook

The work done in this project has shown that it is possible to prepare wettability gradients by using chemical vapor deposition (CVD) in combination with functional paracyclophanes. The experiments have resulted in successful gradients with a wettability difference at 20-30° degrees. This was however achieved without a functioning immobilization process that would have been capable of creating even stronger gradient.

Through the project, successful strategies have been developed to enhance the wettability properties of these functional paracyclophanes. By using simple chemical and physical modifications, the properties of the polymer coatings formed through CVD processes with paracyclophanes have been modified and controlled. This project has shown the opportunities existing within this technology but also revealed some underlying phenomena that need to be further understood in order to gain more control over the system.

The immobilization problems for the gradient are thought to depend on the dynamics of the polymer surface. This conclusion has been drawn from the experimental results indicating a large contact angle hysteresis together with unsuccessful chemical surface modification. By consulting the underlying theory for hysteresis, three possible explanations are possible: topography, kinetic effect and surface composition. The topography component, i.e. surface roughness, can be disregarded considering the experimental results. Since the other effects are likely to be responsible for the problems that have been encountered, it would be of interest to explore them further. A possible first step would be to try to eliminate one of remaining effects. This can be done by synthesizing the diamine monomer and measure the dynamic contact angle. Since the only existing explanation to any eventual hysteresis would be the kinetic effect such as surface reconstruction, this could be of great help for understanding the surface. If it would turn out to be the kinetic effect, a next step could be to investigate the surface with SIMS. It is however known that polymer surfaces have a greater mobility then the bulk and since these coatings are very thin, they are likely to have high mobility.

If the hysteresis would be present also on a diamine coated surface a more thorough investigation into the CVD process should be done. Since surface composition may then be the problem, an investigation into the statistical process of the polymer formation and any possible implications that the equipment might have could be helpful.

Besides the previous question about the surface coatings properties there are other things that can improve the system. When it comes to gradient, a better understanding for the flow conditions can most likely improve the quality.. By learning to optimize these conditions the contamination issue can be minimized. One way that this can be done is by modeling the flow within the two-source chamber with computational fluid dynamics to reveal problems such as turbulence when a sample holder is used. Another way to improve the understanding of the

flow conditions it to make an experimental design investigating the effects of flow rate and position of monomer holder on the coating.

Another possible improvement of the system would be to micro fabricate the surface roughness. This would give a greater control over the roughness and also eliminate any possible interaction problems that may occur if another polymer is used.

As a final conclusion to the whole project, I think it is fair to say that knowledge and use of the chemical vapor deposition of reactive polymer coating have been extended. This project has investigated and showed the potential use of these two concepts for creation of wettability gradients. Even though the main goal, i.e. to move water, was not accomplished and that the reactions at the hydrophilic gradient part did not turn out successful, this project has highlighted the need for more understanding of the basic properties of the polymer and how these should be used. Such a study will be comprehensive and may give interesting and important findings.

7 References

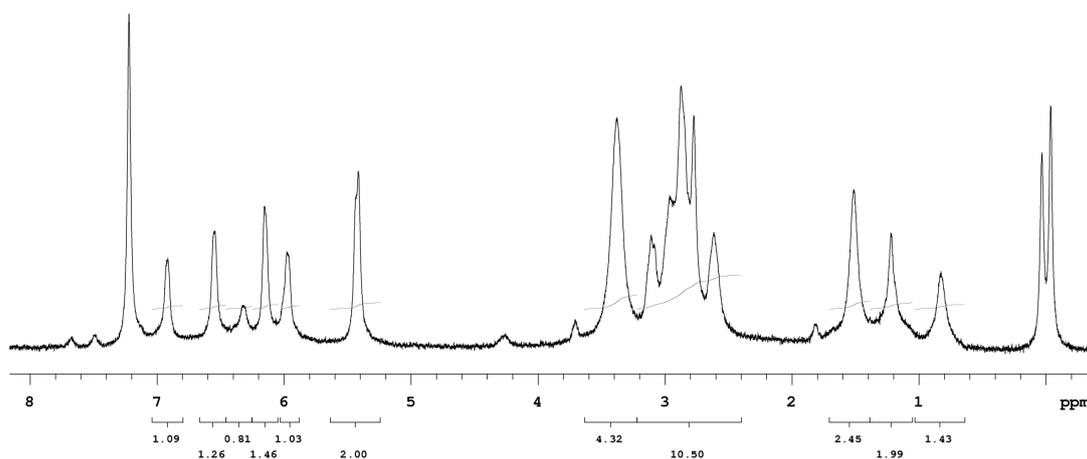
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Appendix

Appendix A – Diamine NMR

PPX-amine
Sample Name:
Data Collected on:
Zr.Chem.LSA.UMich.edu-inova400
Archive directory:
Sample directory:
FidFile: PPX-amine
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Mar 11 2010



Appendix B – Gradient FTIR

Table 7. Interesting FTIR peaks [18]

Group/Bonds	Characteristic peak [cm^{-1}]
N-H	3500-3300
C-H	2960-2850
C=O	1725-1700
C-F	1365-1120
Aromatic C-H	900-770

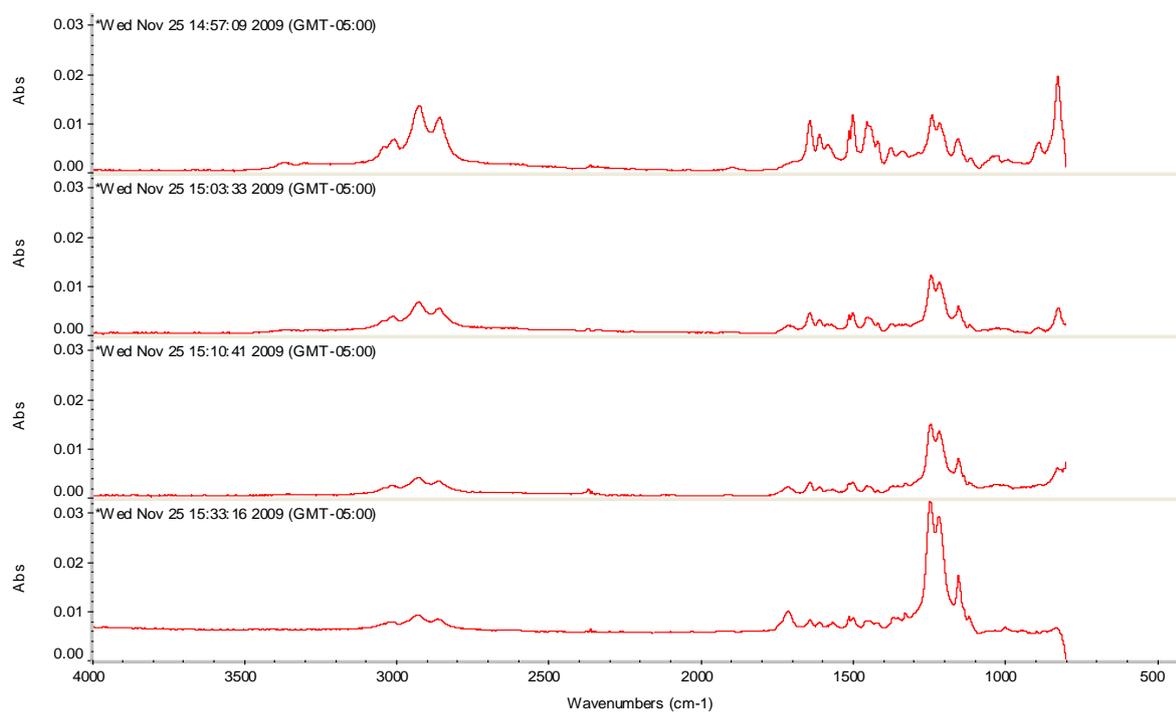


Figure 33. IR spectra from gradient experiment #2

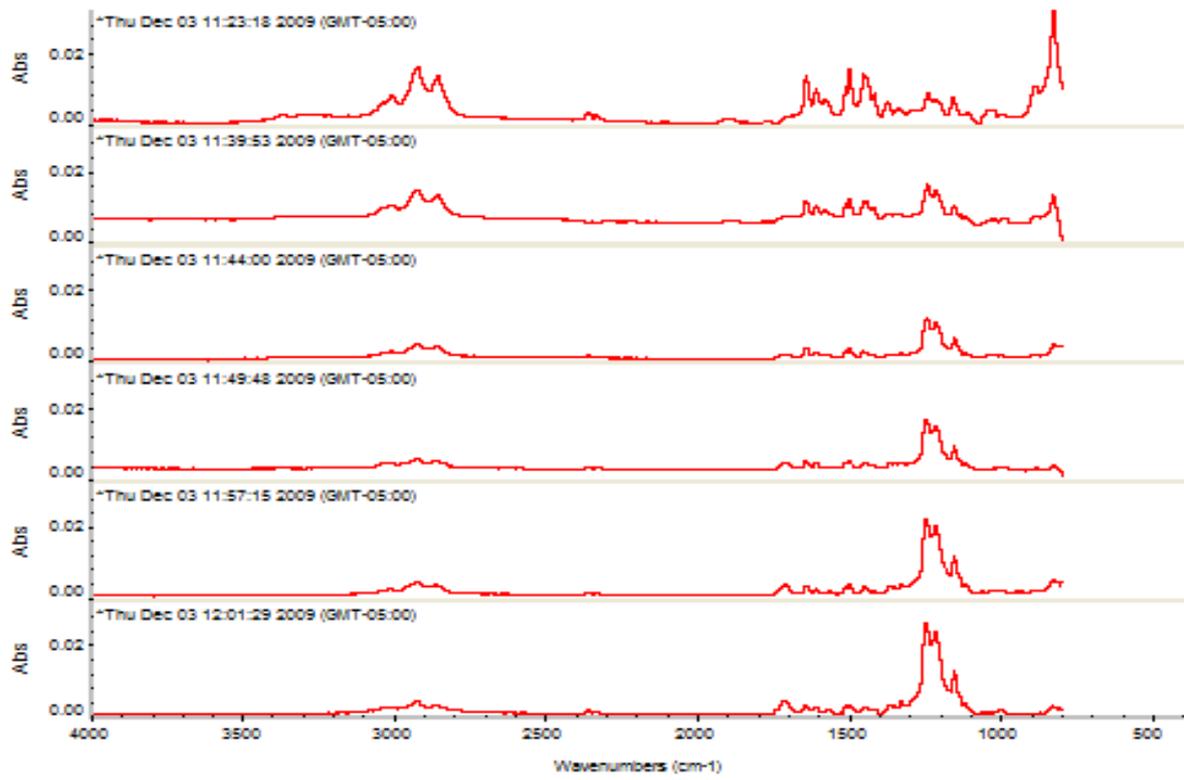


Figure 34. IR spectra from gradient experiment #3