Towards Smart "Lining" for Microfluidic Channels with Stimulus Responsive Polymers

Lionel Dos Ramos

Towards Smart “Lining” for Microfluidic Channels with Stimulus Responsive Polymers

Lionel Dos Ramos

Members of the committee:

Chairman	Prof. dr. ir. J.W.M. Hilgenkamp	University of Twente
Promotor	Prof. dr. G. Julius Vancso	University of Twente
Assistant-promotor	Dr. Mark A. Hempenius	University of Twente
Members	Prof. dr. Sabine Szunerits	University of Lille 1
	Prof. dr. Dominik Jańczewski	Warsaw University of Technology
	Prof. dr. Michel Versluis	University of Twente
	Prof. dr. ir. Emile van der Heide	University of Twente
	Dr. Sissi de Beer	University of Twente

The work described in this thesis was performed at the Materials Science and Technology of Polymers (MTP) group, MESA⁺ Institute for Nanotechnology, Faculty of Science and Technology, University of Twente, PO Box 217, 7500 AE Enschede, the Netherlands.

This research was financially supported by the Netherlands Organization for Scientific Research (NWO nano - 11499) and by the MESA⁺ Institute for Nanotechnology of the University of Twente.

© Lionel Dos Ramos, Enschede, the Netherlands, 2016

© Cover design by Geneviève Rietveld, GR-Artworks

Printed by Gildeprint, Enschede, the Netherlands

ISBN: 978-90-365-4089-6

DOI: 10.3990/1.9789036540896

TOWARDS SMART “LINING” FOR MICROFLUIDIC CHANNELS WITH STIMULUS RESPONSIVE POLYMERS

DISSERTATION

to obtain

the degree of doctor at the University of Twente,

on the authority of the rector magnificus,

Prof. dr. H. Brinksma,

on account of the decision of the graduation committee,

to be publicly defended

on Friday, April 1st 2016, at 14:45

by

Lionel Dos Ramos

Born on February 11th 1986

in Saumur, France

This dissertation has been approved by:

Promotor Prof. dr. G. Julius Vancso

Assistant-promotor Dr. Mark A. Hempenius

Table of Contents

Chapter 1	General Introduction.....	1
1.1.	Introduction	1
1.2.	Concept of this thesis.....	3
1.3.	References	4
Chapter 2	Polymeric Systems for Flow Control in Surface- Functionalized Microfluidic Devices.....	7
2.1.	General introduction.....	8
2.1.1.	Definition of surface and interfacial energies.....	8
2.1.2.	Characterization of surface properties	9
2.1.2.1.	Contact angle measurements	9
2.1.2.2.	Atomic force microscopy (AFM)	11
2.2.	Actuators based on surface energy	14
2.2.1.	Passive elements	15
2.2.1.1.	Capillary-driven flow	15
2.2.1.2.	Electro-osmotic flow	19
2.2.2.	Stimulus-responsive systems	21
2.2.2.1.	Light-responsive coatings.....	21
2.2.2.2.	pH-responsive coatings.....	22
2.2.2.3.	Temperature-responsive coatings	23
2.2.2.4.	Redox-responsive coatings	25
2.3.	Movement-based actuators with stimulus-responsive polymer systems ...	27
2.3.1.	Single stimulus responsive systems.....	27
2.3.1.1.	Shape-memory microchannels.....	27
2.3.1.2.	Hydrogel components.....	28

2.3.1.3.	Electrochemical stimuli	31
2.3.1.4.	Magnetic field stimuli.....	33
2.3.2.	Dual stimuli responsive systems.....	36
2.3.2.1.	Dual independent response systems	36
2.3.2.2.	Dual consecutive response systems	36
2.4.	Conclusion.....	38
2.5.	References	39

Chapter 3 Poly(ferrocenylsilanes) with Controlled Macromolecular Architecture by Anionic Polymerization: Applications in Patterning and Lithography..... 45

3.1.	Introduction	46
3.2.	Poly(ferrocenylsilane) synthesis.....	49
3.3.	Reactive ion etching barrier properties of Poly(ferrocenylsilanes)	55
3.4.	Poly(ferrocenylsilane) homopolymers in lithography applications.....	59
3.4.1.	Solvent-assisted microcontact printing.....	60
3.4.2.	Capillary force lithography	62
3.4.3.	Thermal and UV-assisted nanoimprint lithography	64
3.4.4.	Nanosphere assisted lithography	67
3.5.	Poly(ferrocenylsilane)-based block copolymers in “maskless” nanolithography applications.....	69
3.5.1.	Block copolymer microphase separation.....	69
3.5.2.	Block copolymer thin films as nanolithographic templates	75
3.5.3.	Nanostructures with long-range guided order using block copolymer lithography.....	79
3.6.	Conclusion.....	87
3.7.	References	89

**Chapter 4 Controlled Cutting of PNIPAM Brush Chains at their
Roots by Photocleaving to Provide Grafting Density
Variations for Adhesion Hysteresis and Friction Studies..... 101**

4.1.	Introduction	102
4.2.	Results and discussion.....	104
4.2.1.	PNIPAM brushes synthesis and photocatalytic cleavage.....	104
4.2.2.	Swelling characterization with AFM.....	110
4.2.3.	Adhesion hysteresis and friction measurement with AFM	113
4.3.	Conclusion.....	120
4.4.	Experimental section	121
4.5.	Appendix	126
4.6.	References	129

**Chapter 5 Redox-Induced Backbiting of Surface-Tethered
Alkylsulfonate Amphiphiles: Reversible Switching of
Surface Wettability and Adherence..... 135**

5.1.	Introduction	136
5.2.	Results and discussion.....	137
5.2.1.	Synthesis and characterization	137
5.2.2.	Redox properties.....	140
5.2.3.	Wettability switch.....	141
5.2.4.	Adhesion properties via AFM	145
5.3.	Conclusion.....	149
5.4.	Experimental section	151
5.5.	Appendix	155
5.6.	References	157

Chapter 6	Redox Control of Capillary Filling Speed in Poly(ferrocenylsilane)-Modified Microfluidic Channels for Switchable Delay Valves.....	161
6.1.	Introduction	162
6.2.	Results and discussion.....	164
6.2.1.	Surface modification of the microchannel	164
6.2.2.	Redox properties and modelling.....	165
6.2.3.	Redox-induced switching of capillary action	170
6.3.	Conclusions	175
6.4.	Experimental section	176
6.5.	Appendix	180
6.6.	References	188
Chapter 7	Outlook: Towards the Possibility of Electrochemically Switching PNIPAM Polymer Brushes Grafted from a Surface-Anchored PFS Layer.....	193
7.1.	Improvement of the surface energy changes	194
7.2.	Functionalization of surface-anchored PFS with ATRP initiator.....	195
7.3.	Experimental section	198
7.4.	References	199
Summary.....		201
Samenvatting.....		205
Acknowledgements.....		209
About the author.....		215
List of publications.....		216

General Introduction

1.1. Introduction

Over the years, microfluidic devices have aroused great interest in life science applications.^{1,2} With their possibility of handling sub-microliter fluids, microfluidic devices have become perfect tools for cell and biological fluids analysis,³ drug administration⁴ or point-of-care testing.⁵ Common examples of completely automated biochemical analysis tools, which are present on the market nowadays, are pregnancy tests and glucose biosensors. Current research focusses mainly on developing portable, highly sensitive, fast, low-cost and space-efficient platforms for a range of specific biochemical processes, and also for accurate and precise flow control. Indeed, microvalves and micropumps provide the basis for total automation of complex liquid handling when integrated in microfluidic devices.⁶ With decreasing length scales of the microfluidic channels, surface phenomena, such as surface energies and capillary forces, become increasingly dominant over volume phenomena, such as gravity. This allows one to explore passive liquid actuation based on capillary action which results from surface tension and adhesion between the liquid and the inner wall of the microchannel.

Chemical surface modification of the inner walls of microfluidic channels appears to be a key point in the control of the surface energy, and therefore, the flow control by capillary action. A versatile approach to obtain robust, dense and homogenous surface modification is to covalently attach synthetic polymers to form assemblies of tethered chains. Two different procedures exist to obtain such polymeric coatings: “grafting to” and “grafting from” methods. The first technique involves the covalent anchoring of functional macromolecules onto active surfaces.⁷ For example, this technique was used in **Chapter 5** and **Chapter 6** to graft polymeric chains with functional side groups onto an activated surface with functional self-

assembled monolayers. The “grafting from” method consists of growing polymer chains from surface-anchored initiators. Surface-initiated polymerization allows one to obtain higher grafting densities compared to “grafting to” methods. As an example, in **Chapter 4**, a “grafting to” method was used in combination with a controlled and living atom transfer radical polymerization (ATRP) to synthesize well-defined, dense and homogeneous polymer brush layers.⁸

Stimulus responsive polymers are materials that abruptly alter their chain conformation in response to environmental changes induced by an external signal.⁹ This modification of the chain conformation induces a change in the physical properties, such as solubility, stiffness, electronic structure, wettability or adhesion of different species. The stimulus can be a change in temperature, electro-magnetic field, redox state, pH or ionic strength. Stimulus responsive polymers appear to be perfect candidates to switch the surface energy and control the flow inside microfluidic channels. For example, poly(*N*-isopropylacrylamide) (PNIPAM) is a thermo-responsive polymer which has shown considerable benefits, especially for biological applications, since it is biocompatible and presents a lower critical solution temperature (LCST) of 32 °C, close to biological conditions.¹⁰ Among the stimulus responsive systems, redox-responsive polymers stand out, as these materials respond to electrochemical stimuli, a feature that opens new opportunities for their application in microfluidic devices. Indeed, electrical actuation is fast and reversible, it also permits portability and can be localized by employing microelectrodes, features that may be difficult to achieve with the more classical stimuli. Poly(ferrocenylsilanes) (PFSs) are polymers composed of alternating ferrocene and silane groups in their main chain. A wide variety of PFSs have been prepared, possessing different functional side groups, often attached to the PFS silicon atoms as pendant moieties.¹¹ The ferrocene units provide the redox-responsiveness of the polymer and the different functional groups determine properties such as glass transition temperature, melting range, solubility, and permit derivatization or crosslinking reactions.

Since surface energies dominate capillary action in microfluidic channels and are therefore a key factor in controlling flow, a detailed study of the surface properties of the developed materials seems primordial. Contact angle measurements provide information on the wetting at a macroscopic scale of a surface, which can be related to the surface energy. Atomic force microscopy (AFM) permits the precise determination of pull-off forces and friction at a molecular level.¹² Both contact angle and AFM measurements will be conducted as a function of the redox state of the surface-immobilized PFS films to establish the change in hydrophilic/hydrophobic properties as redox stimuli are applied.

1.2. Concept of this thesis

In this thesis, we describe the synthesis and characterization of polymeric systems which can be used as smart coatings for inner microchannel walls. These coatings allow one to switch the surface properties of microfluidic channels.

Chapter 2 provides an overview of surface modifications, stimulus responsive polymers and architectures that have been applied to control flow in microfluidic devices. The first part of this chapter introduces surface energy characterization methods. We then focus on reported applications of stimuli responsive systems in microfluidics.

Chapter 3 is an additional literature overview of the ability and challenges of anionic polymerization of PFS for creating well defined polymeric patterns. The state-of-the-art techniques of microcontact printing and block polymer microphase separation in order to fabricate nanostructures via maskless lithography are presented.

In **Chapter 4**, we develop novel methods to cleave polymer brushes from a titanium dioxide surface via photocatalysis. Nitrodopamine was used as anchor to produce a PNIPAM brush by “grafting from” via surface-initiated atom transfer radical polymerization (SI-ATRP). A full detachment of the PNIPAM chains from

the surface allowed their molar mass and polydispersity characterization. This photocatalytic cleavage also permitted us to tune the grafting density of the polymer brush. We studied the effect of the grafting density on the thermal switching of adhesion hysteresis and friction.

In **Chapter 5**, we describe the synthesis and the characterization of redox-responsive and surface-anchored PFS layers which allow switching of the wettability and the adherence. PFS layers were functionalized with alkylsulfonate amphiphilic chains of which the conformation was changed by attracting or repulsing the polar head depending on the redox state of the PFS. This “backbiting” resulted in a reversible switching of the wetting and adherence.

In **Chapter 6**, PFS chains were anchored onto gold coated microfluidic channel walls. The redox response of the surface-anchored PFS and its ability to reversibly switch the surface energy was employed to reversibly control the capillary filling speed of water through a microchannel.

Finally, in **Chapter 7**, we give an outlook of the possibilities of using a combination of the redox-response of PFS and the swelling response of a polymeric brush. For example, we have successfully managed the functionalization of surface-anchored PFS layers with an ATRP initiator. This system would allow one to control the swelling of a polymeric brush grown from the redox-active surface layer by using external and electrical stimuli.

1.3. References

1. Li, X.J. and Y. Zhou, *Microfluidic Devices for Biomedical Applications*. 2013: Elsevier Science.
2. van den Berg, A. and L. Segerink, *Microfluidics for Medical Applications*. 2014: Royal Society of Chemistry.
3. Zhang, Q. and R.H. Austin, *Applications of Microfluidics in Stem Cell Biology*. BioNanoScience, 2012. **2**(4): p. 277-286.
4. Meng, E. and T. Hoang, *Micro- and nano-fabricated implantable drug-delivery systems*. Therapeutic delivery, 2012. **3**(12): p. 1457-1467.

5. Jung, W., et al., *Point-of-care testing (POCT) diagnostic systems using microfluidic lab-on-a-chip technologies*. Microelectronic Engineering, 2015. **132**: p. 46-57.
6. Au, A.K., et al., *Microvalves and Micropumps for BioMEMS*. Micromachines, 2011. **2**(2): p. 179.
7. Zdyrko, B. and I. Luzinov, *Polymer Brushes by the "Grafting to" Method*. Macromolecular Rapid Communications, 2011. **32**(12): p. 859-869.
8. Matyjaszewski, K., *Atom Transfer Radical Polymerization (ATRP): Current Status and Future Perspectives*. Macromolecules, 2012. **45**(10): p. 4015-4039.
9. Russell, T.P., *Surface-Responsive Materials*. Science, 2002. **297**(5583): p. 964-967.
10. Hoogenboom, R., *Tunable Thermoresponsive Polymers by Molecular Design*, in *Complex Macromolecular Architectures*. 2011, John Wiley & Sons (Asia) Pte Ltd. p. 685-715.
11. Kulbaba, K. and I. Manners, *Polyferrocenylsilanes: Metal-Containing Polymers for Materials Science, Self-Assembly and Nanostructure Applications*. Macromolecular Rapid Communications, 2001. **22**(10): p. 711-724.
12. Vancso, G.J., H. Hillborg, and H. Schönherr, *Chemical Composition of Polymer Surfaces Imaged by Atomic Force Microscopy and Complementary Approaches*, in *Polymer Analysis Polymer Theory*. 2005, Springer Berlin Heidelberg. p. 55-129.

Polymeric Systems for Flow Control in Surface-Functionalized Microfluidic Devices

Surface modification brings to a material a physical, chemical or biological characteristic which differs from the original surface properties of the material. This new surface alters the surface energy of the materials. Since this thesis focusses on different responsive polymeric coatings with the aim of switching surface properties, we start this chapter by introducing some definitions related to surface energetics. Then, we briefly introduce some theoretical aspects concerning contact angle measurements and AFM, which are the two tools we use in this thesis to analyze alterations in surface properties. Contact angle measurements were used to characterize the switch in wetting and AFM was used to measure adhesion forces and friction. Finally, we give an overview of several polymeric systems, used as microfluidic valves and pumps in microfluidic channels to control flow. We divided the systems in two categories: first, the actuators based on a change in the surface energy of the inner wall of microfluidic channels, and second, the actuators based on a movement, such as expansion and collapse, to modify the channel structure. The surface energy change systems were also separated in passive systems which cannot be switched, and active actuators which, on the contrary, can be switched by an external stimulus. The movement-based systems were separated in single response stimulus- and dual stimuli responsive actuators.

2.1. General introduction

2.1.1. Definition of surface and interfacial energies

As we are interested in the wetting and adhesion phenomena at polymer-modified surfaces, and in particular in the switching of surface properties with stimulus responsive polymers, we start by defining some commonly used terms related to surface energetics.¹

Work of adhesion

The work of adhesion W_{12} ($1 \neq 2$) is the free energy change or the reversible work necessary to separate two different surfaces from contact to infinity in vacuum. For two identical media, this energy is the work of cohesion W_{11} .

Surface energy

Inside a homogenous bulk material, all the atoms are surrounded by the same number of atoms. At a surface of a material, disruptions of the intermolecular bonds are present from the lack of bonds of the surfacing atoms compared to the atoms in the bulk material. Atoms at the surface have more energy than the atoms in the bulk material which therefore makes the creation of surfaces energetically unfavorable. This excess of energy at the surface compared to the bulk of a material is quantified by the surface energy γ_1 . It is equivalent to the free energy necessary to separate two half-unit areas from contact $\gamma_1 = W_{12}/2$. The unit of the surface energy is energy per unit of area.

Surface tension

In the case of a liquid, a molecule in the fluid interacts with the surrounding molecules and remains in an equilibrium state. On the contrary, a molecule at the surface of the liquid loses half of its cohesive interactions and reaches a non-equilibrium state. This deviation from equilibrium is compensated by a change in shape to minimize as much as possible the surface area of the liquid with the other phase. The surface tension is then the energy which is necessary to increase the

surface area by one unit. The unit of the surface tension is force per length or energy per area.

Interfacial energy

In the presence of an interface between two non-miscible phases, solid-liquid and liquid-liquid, the surface energy is called interfacial energy. The total free energy is then given by the Dupré's equation:

$$\gamma_{12} = \frac{W_{11}}{2} + \frac{W_{22}}{2} - W_{12} = \gamma_1 + \gamma_2 - W_{12} \quad (2.1)$$

Adherence

Adherence is related to the force needed to separate surfaces in contact, and it is a sum of various chemical and physical factors such as work of adhesion, roughness effects, capillary forces caused by humidity, viscoelastic properties, surface forces (hydrogen bonds, van der Waals forces,...) and other dissipative processes.

2.1.2. Characterization of surface properties

In this thesis, we used two techniques to characterize and quantify the changes of surface energies of the surfaces, modified by the different stimulus responsive polymers. We used contact angle measurements to determine the wetting properties, and atomic force microscopy (AFM) to quantify the adhesion and friction properties.

2.1.2.1. Contact angle measurements

Surface and interfacial energies determine how liquid droplets deform when they adhere to a surface. As shown in **Figure 2.1**, the surface tension γ_{sv} is the tangential stress (in mN/m) at the surface layer and it is a direct measure of the intermolecular forces at the surface. The fundamental equation to obtain solid surface tension via contact angle measurements is the Young's equation:

$$\gamma_{sv} = \gamma_{sl} + \gamma_{lv} \cos \theta \quad (2.2)$$

where γ_{sv} is the solid surface free energy, γ_{sl} is the solid/liquid interfacial free energy, γ_{lv} is the liquid surface tension and θ is the contact angle.

Figure 2.1. Schematic of a liquid droplet contact angle measurement with the representation of the surface and interfacial energies of the Young's equation.

The effect of patterned and chemically heterogeneous surfaces on the contact angle was described by Cassie²:

$$\cos \theta = f_1 \cos \theta_1 + f_2 \cos \theta_2 \quad (2.3)$$

where f_1 and f_2 are the local fractions of the surface with the contact angles θ_1 and θ_2 , respectively.

Israelachvili and Gee³ modified the Cassie model for heterogeneities close to atomic and molecular dimensions:

$$(1 + \cos \theta)^2 = f_1 (1 + \cos \theta_1)^2 + f_2 (1 + \cos \theta_2)^2 \quad (2.4)$$

Surface topography or roughness modify the molecular and effective liquid-solid contact area. Surface roughness is one of the major causes of contact angle hysteresis and permits surfaces to reach superhydrophilic/superhydrophobic states.⁴ The Young-Wenzel equation describes the effect of roughness in the contact angle:

$$\gamma_{lv} \cos \theta = r(\gamma_{sv} - \gamma_{sl}) \quad (2.5)$$

where r is the roughness ratio.

2.1.2.2. Atomic force microscopy (AFM)

Besides the topological imaging of surfaces, AFM allows the measurement of force-distance curves and surface tribological properties, which enables one to characterize surface properties at the microscopic and submicroscopic scales.^{5,6} The ability of using colloid probes from different materials and the possibility of their chemical surface modification, allow a versatile study of colloid-sample interactions.⁷⁻¹⁰

Adhesion forces

From the force-distance curves realized with AFM, pull-off forces can be obtained. As shown in **Figure 2.2**, while approaching the surface, the tip of the AFM cantilever can feel, before contact, attractive surface forces which induce a cantilever deflection. Then, at contact with a hard surface, the deflection is linear with the position. When retracting, the tip remains in contact and the deflection changes linearly with the position. At a certain position from the surface, the tip cantilever is suddenly snapped off the surface. The minimum deflection value is the pull-off force.

Figure 2.2. Schematic of an AFM cantilever deflection as function of the cantilever position during AFM force-distance measurements. Reprinted with permission from 5. © 2005 Springer Berlin Heidelberg.

Contact mechanics theoretical models¹¹ reveal that the adhesion force between a spherical particle (colloid probe or tip from AFM) and a flat surface is controlled by the interfacial tension of the contacting materials. However, a quantitative correlation between measured pull-off forces and theoretical work of adhesion is possible only for non-polar tip-sample interactions. In the case of soft and polar polymeric surfaces, specific interactions complicate the system which can lead to significant deformations.¹² Hertz was the first who studied and described the contact mechanical behavior of two elastic surfaces which are pressed against each other.¹³ The Hertz theory gives the basis of the contact mechanical adhesion theories but does not take into consideration the effect of surface forces. Nowadays, the most commonly used theories to describe surface tension from AFM pull-off force measurements are either Johnson-Kendall-Roberts (JKR) or Derjaguin-Muller-Toporov (DMT) models.¹⁴ The DMT model includes long-range surface forces operating outside the particle-substrate contact area and it is suitable for hard materials having low surface energies and small radii of probe curvature. JKR assumes that attractive forces act only inside the particle-substrate contact area and this model is mostly suitable for relatively soft materials with relatively high surface energy and relatively large probes. The latter model is a more appropriate choice for fitting the AFM measurements of this thesis, since a 5 or 6 μm diameter colloid was used. The relations of the contact radius a , the sample deformation δ and the adhesion force F_{adh} for a spherical tip on a flat surface and according to each model are given in **Table 2.1**. We note here that in these models, the roughness of the surface is not taken into consideration. The size, shape, homogeneity, mechanical properties and distribution of the asperities can affect the AFM measurements.

Table 2.1. Contact area radius a , sample deformation δ and adhesion force F_{adh} for a spherical tip on a flat substrate according to the different models.

	a	δ	F_{adh}
Hertz	$\sqrt[3]{\frac{RL}{E_{tot}}}$	$\frac{a^2}{R} = \frac{L^2}{RE_{tot}^2}$	0
DMT	$\sqrt[3]{\frac{R}{E_{tot}}(L + 2\pi RW)}$	$\frac{a^2}{R} = \frac{(L + 2\pi RW)^{2/3}}{\sqrt[3]{RE_{tot}^2}}$	$2\pi RW$
JKR	$\sqrt[3]{\frac{RL}{E_{tot}}(L + 3\pi RW + \sqrt{6\pi RWL + (3\pi RW)^2})}$	$\frac{a^2}{R} = \frac{2}{3} \sqrt{\frac{6\pi Wa}{RE_{tot}}}$	$\frac{3}{2}\pi RW$

R is the tip radius, W is the adhesion work per unit area, L is the applied force (load) and E_{tot} is the reduced Young's modulus of the substrate.

Adhesion hysteresis

Adhesion during approach and retract can present different values, defined as adhesion hysteresis, which is entirely similar to contact angle hysteresis.¹ With polymeric surfaces, any phenomena which increase the effective surface contact area, such as roughness or chain interdigitations, result in adhesion hysteresis. Irreversible adhesion processes involve energy dissipation through the system. Another effect that creates adhesion hysteresis is viscoelastic junctions that deform during the contact time, and therefore, involve dynamic energy dissipation.

Friction

With contact mode AFM imaging, surface tribological properties can be assessed.⁵ By scanning in the perpendicular direction of the cantilever long axis, the measured tangential forces can be related to tribological properties. The measured friction loops permit the calculation of the friction force from the difference between the trace and retrace lines.

Berman et al.¹⁵ proposed a simple model based on intermolecular forces and thermodynamic considerations, to quantitatively connect the friction force F to the load L and the contact area A .

$$F = \sigma A + \mu L \quad (2.6)$$

where σ is the adhesion-controlled critical shear stress and μ is the friction coefficient. They verified this equation with experiments under different conditions.¹⁵ For smooth and non-adhering surfaces, the first term can be neglected which confirms their results where the friction force was proportional to the load (Amonton's law). Nevertheless, for the case of adhering surfaces, the first term predominated and the friction force was found to be proportional to the molecular contact area.

2.2. Actuators based on surface energy

Switches and valves are important for controlling fluid flow in microfluidic devices, especially in the development of cell culture systems, the construction of labs on a chip and the fabrication and design of chemical microreactors.¹⁶ Electrowetting¹⁷ methods of flow control require integrating electrodes in channels and the flow is controlled externally by an applied electric field. This method requires high voltages, which is energy consuming and reduces the portability of the devices. The versatility of polymer coatings allows one to engineer surfaces to obtain robust, homogeneous and localized properties on various substrates. For responsive systems, these properties can even be varied or switched. These polymer coatings, and especially stimulus-responsive systems, are promising candidates to tackle the numerous challenges regarding addressable components and actuators in microfluidic devices. In this chapter, we offer a non-exhaustive overview of different techniques to control the flow using polymer coatings inside microchannels.

2.2.1. Passive elements

Passive elements are defined as systems where the polymers, covalently bound to a certain portion of a microchannel wall, locally modify the surface properties but cannot be switched externally.¹⁸ The flow behavior can be modified by varying the design of the different covering components and their surface energies inside a microchannel. The flow behavior is mainly driven by capillary and electro-osmotic forces.

2.2.1.1. Capillary-driven flow

The surface tension and adhesive force between the liquid and the wall of a microchannel is the driving force of meniscus motion.^{1, 19} By locally changing the surface energy of the microchannel inner wall using a “smart” design, one can actuate and direct the microfluidic flow.

As shown in **Figure 2.3**, Böhm et al. introduced a novel approach to control and modulate capillary-driven fluid flow inside microfluidic papers.^{20, 21} Such paper based devices are economical alternatives to microfabricated fluidic channels. Hydrophobic PMMA copolymers with photo-reactive benzophenone functional groups were absorbed into a hydrophilic paper by a simple dip-coating process. Then, a lithography mask and UV-light irradiation were used to covalently attach the hydrophobic PMMA network onto the hydrophilic cellulose microfibrils of the paper, via reaction between the benzophenone groups and the aliphatic C-H groups of the cellulose fibers. Physisorbed PMMA macromolecules, remaining on the non-irradiated parts, were removed by simple solvent extraction, resulting in hydrophilic and hydrophobic regions in the paper. The water flow was successfully directed by capillary action exclusively into the non-functionalized paper.

Figure 2.3. Schematic illustration of the process employed by Böhm et al.^{20, 21} to create PMMA-defined channels into paper. The photoreactive polymers were first absorbed onto the cellulose fibers using a dip-coating method. A mask with the shape of the desired channel is used during UV-light illumination, to attach the PMMA network to the non-shaded area. Development of the chemical micro-pattern was achieved by solvent extraction of the non-bound PMMA macromolecules in the shaded areas. Reprinted with permission from 20. © 2014 Springer

Hydrophobic polymer coatings can also be used inside a hydrophilic microfluidic device to stop the flow. For instance, Andersson et al.^{22, 23} used a hydrophobic patch of octafluorocyclobutane (C_4F_8) to create a hydrophobic microvalve inside a silicon microchannel. These authors used the plasma polymerization process of fluorocarbons to coat the inner wall of a hydrophilic silicon/Pyrex microchannel with hydrophobic patches, which after functionalization exhibited a contact angle of 105° . As shown in **Figure 2.4**, the water flow was driven by capillary forces until the meniscus encountered the C_4F_8 patch. An inlet pressure of 0.76 kPa was then necessary to run over the hydrophobic patch microvalve and restart the flow.

Figure 2.4. Optical microscope picture of the hydrophobic C_4F_8 patch in a silicon/pyrex microchannel (a) before and (b) after capillary filling of water from the left. In (b), the water meniscus is observed exactly where the C_4F_8 film starts. Reprinted with permission from 22. © 2001 Elsevier

Soft-lithography techniques have been used to chemically pattern substrates and direct motion or spreading of droplets.^{24, 25} Wang et al.²⁶ reported chemically patterned surfaces with alternative hydrophilic and hydrophobic stripes to create a microvalve and realize an anisotropic flow of water in a microchannel (see **Figure 2.5**). The anisotropic flow was attributed to the different surface energies and anisotropic wettability of the patterned surfaces. The contact angle of a water drop along the stripe direction was 74° and in the perpendicular direction had a value of 104° . Therefore, as shown in **Figure 2.5.b**, the microfluidic flow was directed into the channel with the parallel stripes and stopped at the channel with the stripes perpendicular to the flow direction. An increase of the pressure is then necessary to pass the perpendicular stripes, and this pressure depends on the width of the patterns. Furthermore, as shown in **Figure 2.5.c**, the water was successfully transported along a virtual wall, corresponding to the boundary between the hydrophilic and the hydrophobic areas, positioned in the middle and along the microchannel. To control the microfluidic flow via hydrophilic/hydrophobic patterns, self-assembled monolayers have also been employed.²⁷

Figure 2.5. (a) Schematic illustration of the microvalve fabricated by Wang et al. via alternative hydrophilic and hydrophobic stripes. Optical microscope images of (b) the water flow (arrow) in the Y-shape junction with the position of the meniscus where the flow is stopped (line), and (c) the water microfluidic flow with the virtual wall in the middle of the channel, corresponding to the hydrophilic/hydrophobic boundary. Reprinted with permission from 26. © 2015 American Chemical Society

Instead of completely stopping the flow with fully hydrophobic patches, studies have been done to simply reduce flow internally. For example, the four walls of a hydrophilic glass microchannel with rectangular cross-section have been individually functionalized with hydrophobic poly(neopentylmethacrylamide-*co*-*N*-4-(trimethylsilyl)phenylmethacrylamide) to obtain different combinations of microchannel surface wetting.²⁸ In this work, Sultana et al. demonstrated that the water meniscus shape and the flow rate were strongly dependent on the microchannel surface wetting combination. The decrease of the flow rate dropped with an increased number of hydrophobic surfaces which was attributed to the relatively high adhesion energy at the interface of these hydrophobic surfaces.

Lanotte et al.²⁹ used a different approach to reduce the microfluidic flow. They grafted hydrophilic poly(hydroxyethylmethacrylate) brushes from the inner walls of the silica microchannel. These authors showed that the decrease in the flow velocity induced by the presence of the brush was greater than one would expect simply from the reduced capillary diameter. A maximum velocity reduction of the pressure-driven flow of 35% was observed. These results were supported by molecular simulations. The authors concluded that the flow rate decrease was due to brush polydispersity and to stretching and recoiling of the brushes which resulted in a net backflow close to the channel wall. From this example, we conclude that the wetting property of the microchannel wall is not the only possible actuation method with polymer systems. By modifying the microchannel walls with polymeric systems, such as “hairy” surfaces, the surface geometry could give further control over the flow behavior by movement-driven effects.

The surface modification of 2D flat substrates in order to change wetting properties includes numerous other techniques and designs which could be easily transposed to the modification of microfluidic devices for capillary-driven microfluidic flow.^{30, 31}

2.2.1.2. Electro-osmotic flow

Electro-osmotic flow (EOF)³²⁻³⁴ is the motion of a buffered solution, induced by a potential difference across a porous or microfluidic material. The charged particles in the fluid form a double layer at the fluid and capillary wall interface. The first layer includes the surface charge which can be positive or negative, depending on the surface material. The second layer, also called the diffuse layer, has a net charge opposite of the charge of the surface. By applying a potential difference, the diffuse layer is pulled to one side and therefore drags the neutrally charged bulk solution along with it, thus creating a flow. Electrically driven flow is commonly used in imprinted microfluidic devices, and the direction and rate of the EOF are determined

by the substrate surface charge.^{35, 36} However, the distribution of the surface charge in these devices has been shown to be non-uniform. Polyelectrolyte multilayers have then been employed as coatings to create uniform, reproducible and dense charged surfaces of different materials in microchannels.³⁷⁻³⁹ Because the species in the solution are charged, they can separate in the solution, which is ideal for electrophoresis applications but can be a disadvantage for other applications. However, Joo et al.⁴⁰ fabricated a field-free electro-osmotic pump by coating the two arms of a Y-shaped microfluidic channel with coatings of opposite polarity. By applying an electric field between the two functionalized arms, a field-free flow was generated in the non-functionalized channel. Poly(diallyldimethylammonium chloride) and poly(styrene sulfonate) were used as the cationic and anionic polymer coating, respectively. The direction of the flow was determined by the polarity of the applied field between the two modified channels, and the flow rate was found to be proportional to the applied electric field with a slope of 262.4 nL/min per kV/cm, with a 10 mM phosphate buffer solution at pH 7.0.

Figure 2.6. Schematic of the field-free flow presented by Joo et al.⁴⁰ by modifying the surface of a microfluidic chip with polyelectrolytes. (a) The channels with different surface charge generate a field-free flow in the non-functionalized microchannel in the (b) upward or (c) downward direction depending on the polarity of the applied electric field. Reprinted with permission from 40. © 2007 Elsevier

In the EOF, even if the surface charge of the polymer is static, the flow rate depends on the nature and composition of the electrolytes or surfactants.^{41, 42} The

flow rate is also externally controlled by the potential applied across the channel. This external actuation and control of the flow is one of the requirements that would enhance the performance of actuator parts in microfluidic devices. Passive polymer systems presented in this paragraph do not give the possibility to actively and reversibly switch and tune the microfluidic flow.

2.2.2. Stimulus-responsive systems

Stimulus-responsive polymers^{43, 44} have permitted the fabrication of active systems where the polymer undergoes large and abrupt changes in its chemical and physical properties in response to small variations in its environment, induced by an external stimulus. We offer here an overview of several examples from the literature where the surface wettability switch of stimulus-responsive polymers is used to control microfluidic flow.

2.2.2.1. Light-responsive coatings

Kwong et al.⁴⁵ introduced a vapor phase polymerization process to deposit functional polymer coatings onto paper-based microfluidic devices for chromatography. The fibrous morphology necessary to generate capillary-driven flow was retained and the paper coated with acidic poly(methacrylic acid) (PMAA) and basic poly(dimethylaminoethyl methacrylate) (PDMAEMA) improved the separation of the cationic and anionic analytes, respectively. Furthermore, in this work, the ability of the hydrophobic poly(*o*-nitrobenzyl methacrylate) (PoNBMA) to be converted into hydrophilic PMAA upon exposure to UV-light was used to create a photo-actuated switch and control the path of the fluid. The PoNBMA patch stopped the capillary filling of water in the chromatography paper. After UV illumination, the hydrophobic patch was converted into hydrophilic PMAA which restarted the capillary imbibition in the paper. However, the PoNBMA-to-PMAA

switch was irreversible and its response time was approximately 1h. This response time could be reduced using a higher intensity UV-light but it would remain slow for fast microfluidic applications.

Walsh et al.⁴⁶ presented a photo-controllable microfluidic electro-osmotic pump based on spiropyran-functionalized polymers. The photochromic and monolithic poly(spiropyran-*co*-divinylbenzene) scaffolds were synthesized in poly(tetrafluoroethylene)-coated fused silica capillaries with a diameter of 100 μm . When irradiated with UV light, the uncharged spiropyran molecule was converted into the zwitterionic merocyanine form. This transformation can be reversed by illuminating with visible light. As both states have a zero net overall charge, an acidic electrolyte was used to produce a stable anodic EOF, but both forms have different charge distributions. Irradiating with UV light for 2 min reduced the EOF by 50%. After illumination with visible light, the flow rate increased again from 75 nL/min to 150 nL/min.

In general, we conclude that photo-responsive actuators exhibit a too slow switching to be used as high-throughput and fast microfluidic components, and they are applicable only with transparent devices.

2.2.2.2. pH-responsive coatings

Salim et al.⁴⁷ presented a study to understand the effects of pH-responsive polymers on the EOF in surface-modified microchannels at different pH. Poly(tetraglyme), poly(acrylic acid) and poly(allylamine) were plasma-polymerized on glass microchannel walls which resulted in surfaces with variable charges and charge densities depending on the buffer solution. All of the surface-modified surfaces exhibited a slower EOF compared to non-coated microchannels. The authors observed that the magnitude and the direction of the EOF depended on the pH. Furthermore, they investigated the effect of protein adsorption on the EOF and found that the mobility was dependent on the concentration of the proteins, except

for the poly(tetraglyme)-coated channels. This indicated that the latter polymer is suitable for protein separation in electrophoresis experiments. The three different surface-functionalized and pH-responsive microchannels revealed an effective method for controlling EOF behavior. However, with pH-responsive polymers, the control of the flow depends on the intrinsic properties of the fluid, and therefore, cannot be switched externally for the same fluid.

2.2.2.3. Temperature-responsive coatings

Wang et al.⁴⁸ used poly(*N*-isopropylacrylamide) PNIPAM brushes and their thermal response when crossing the lower critical solution temperature (LCST), to change the wetting properties of a functionalized and patterned microchannel wall. At a temperature below the LCST of 32 °C, PNIPAM brushes are hydrophilic and swollen. Above the LCST, PNIPAM brushes become hydrophobic and collapsed. By modifying the microchannel walls with Janus micropillar arrays (see **Figure 2.7.a**), these authors managed to switch between anisotropic wetting and isotropic wetting. As shown in **Figure 2.7.b**, with a two-step modification process, they decorated the micropillars with a wettability-switchable PNIPAM brush on one side via surface-initiated atom transfer radical polymerization, and with a hydrophilic self-assembled monolayer of 16-mercaptohexadecanoic acid on the other side. At a temperature below the LCST (see **Figure 2.7.c**), the Janus micropillars were uniformly hydrophilic and the water flow in a T-shape junction was anisotropic. At a temperature above the LCST (see **Figure 2.7.d**), the wetting of the micropillar array was asymmetric, which directed the flow in only one channel. Additionally, the authors established a photo-thermal control by using infrared-light to adjust the temperature of the microfluidic system, and therefore, reversibly direct the fluid motion.

Figure 2.7. Schematic illustrations of (a) the fabrication process of the T-shaped microfluidic channel, and (b) the PNIPAM/16-mercaptohexadecanoic acid Janus micropillar with its surface wettability at different temperatures. (c, d) Photographs of a water drop in contact with a flat surface modified with the Janus micropillar array (left) and the fluorescence microscope photographs of the Rhodamine aqueous solution injected into the T-shaped microfluidic channel (right), (c) below and (d) above the LCST. Adapted with permission from 48. © 2015 American Chemical Society

In a different approach, a PNIPAM-based coating was used to switch the adhesion properties and control the adhesion and detachment of living cells in a microchannel. Ernst et al.⁴⁹ cultivated fibroblasts at 37 °C on a hydrophobic and collapsed PNIPAM-based coating on microfluidic channel walls. The cells adhered and spread normally until the temperature was reduced to 25 °C, which is below the LCST. The PNIPAM-based coatings became hydrophilic and the corresponding swelling and hydrophilicity provoked cell detachment. This switching behavior between a cell

adhesive and a cell repulsive state was repeated without any loss of functionality and opens new opportunities in cellular biotechnology applications.

However, a temperature controlled switch is limited in time by the thermal conductivity through the microfluidic process or requires the use of integrated electric heating elements inside the microfluidic device.

2.2.2.4. Redox-responsive coatings

An electrical control of the surface wettability by using a redox-responsive polymer coating gives the advantage of a fast response upon the application of a simple electric stimulus, and the ability to use low voltages, reducing energy consumption and avoiding electrophoresis of the components in the fluid.

By electrically switching the surface energy of the redox-responsive conjugated poly(3-hexylthiophene) (P3HT) in PDMS microchannels, Robinson et al.⁵⁰ demonstrated the possibilities to program a device to direct the flow along a desired path in a junction system. By electrochemically oxidizing the P3HT wall of a PDMS microchannel on only one branch of a Y-junction, these authors changed the polarity of the wall, and therefore, the wetting, which resulted in a favorable route for water.

Tsai et al.⁵¹ presented a precisely controlled droplet manipulation inside a microchannel functionalized with a redox-responsive polymer. The electrochemically tunable wetting property of dodecylbenzenesulfonate-doped polypyrrole (PPy(DBS)) allowed an uphill motion of a salt water droplet in an immiscible organic solvent (dichloromethane). The droplet movement was realized at really low voltages (-1.5 V to 0.6 V). To start, the oxidative potential (0.6 V) was maintained and the microchannel was tilted at 4° to create an asymmetric deformation on the droplet (see **Figure 2.8.a and a'**) which remained at the same location. When the PPy(DBS) layer was switched to the reduced state (-1.5 V), the droplet contact angle increased (more hydrophilic surface) and the water droplet moved uphill (see **Figure 2.8.b and c**). This motion was attributed to the combined

effects of both Marangoni stress and buoyant force (see **Figure 2.8.b' and c'**). When the potential was switched again to the oxidation potential, the droplet stopped moving and it was kept in the initial pinning state (see **Figure 2.8.d and d'**). When the reductive potential was applied again, the droplet was reactivated and resumed the movement (see **Figure 2.8.e and e'**).

Figure 2.8. (Top) Captured images of a salt droplet in a 4°-tilted microchannel immersed in dichloromethane under a square pulse potential (0.6 V to -1.5 V, pulse of 2 s). (Center) Schematics of the droplet behavior in the corresponding position. (Bottom) Graph of the square pulse potential with the position of each picture. Reprinted with permission from 51. © 2013 The Royal Society of Chemistry

Passive and stimulus-responsive switching of the microchannel wall wettability can be combined with patterns or rough architecture to enhance the effect of the hydrophilicity and hydrophobicity.⁵²⁻⁵⁷ These superhydrophilic and superhydrophobic states have been largely studied on 2D substrates and could be transposed to microfluidic channels.⁵⁸⁻⁶² These super states could allow an actuation of the flow with higher back pressure.

2.3. Movement-based actuators with stimulus-responsive polymer systems

Besides possessing a switchable surface energy and wettability, some stimulus-responsive polymeric systems, such as hydrogels or brushes, exhibit a consequent and essentially immediate conformational change. The conformational switch of the polymeric components can be volumetric, geometric or positional, all of which include a movement. As will be discussed in the following sections, these movement-based actuations were used in various designs to control microfluidic flow.

2.3.1. Single stimulus responsive systems

2.3.1.1. Shape-memory microchannels

The dual-shape capability of crosslinked poly(ϵ -caprolactone) (PCL) was used by Ebara et al.⁶³ to fabricate shape-memory microfluidic channels and control the fluidic flow over its melting temperature of 33 °C. The fabrication process of the shape-memory microfluidic devices is shown in **Figure 2.9**. To prepare the shape-memory surfaces with the permanent shape, the PCL macromonomer solution was cured between a glass mold and a flat glass slide for 180 min at 80 °C. The permanent shape could exhibit flat (see **Figure 2.9.a**) or a patterned channels (see **Figure 2.9.b**). Then, to program the opposite temporary surface shape, the PCL films were compressed at 37 °C for 5 min and the stress was then released at 4 °C after 10 min of cooling. Finally, the permanent channel shape was fully recovered by heating at 37 °C. A local heating allowed the authors to dynamically control the destruction (see case in **Figure 2.9.a**) or reconstruction (see case in **Figure 2.9.b**) of the microchannel, and therefore, dynamically direct the flow.

Figure 2.9. Schematic illustration of the fabrication of the shape-memory microchannel patterns which can actively change (a) from a flat pattern to a channel pattern, and (b) from a channel pattern to a flat pattern. Reprinted from 63. © 2011 Chemical and Biological Microsystems Society

In the shape-memory example, the entire microchannel shape is modified by an external temperature stimulus. Since the recovering of the temporary pattern requires a compression step, and therefore the disassembly of the microfluidic device, a dynamic and reversible control of the microfluidic flow is impossible.

2.3.1.2. Hydrogel components

To reach dynamic and reversible actuation, stimulus-responsive polymers have been employed to create the actuating components inside microfluidic devices. For instance, responsive hydrogels which expand and contract according to various stimuli have been used.

Beebe et al.^{64, 65} have demonstrated various examples of autonomous microfluidic valves that can control fluidic flow using the pH response of hydrogels. First, by direct photopatterning from a liquid consisting of acrylic acid, 2-hydroxyethyl

methacrylate, ethylene glycol dimethacrylate and a photoinitiator, these authors fabricated hydrogel structures around prefabricated posts (see **Figure 2.10**). Depending on the fluid pH, the reversible swelling and collapse of the hydrogel structure resulted in the reversible closing (see **Figure 2.10.a**) and opening (see **Figure 2.10.b and c**), respectively, of the channel entrance. The step response for expansion and contraction of the valve was 8 s. Secondly, in a T-junction, the two different branches were gated with hydrogel structures of a unique chemical composition for each branch. The hydrogel for one branch expanded at high pH and contracted at low pH, while the second hydrogel of different composition had opposite behavior. This device automatically directed the fluidic flow to one branch or the other, depending on the fluid pH. Each hydrogel valve performed the sensing, actuating and regulating function. Finally, Beebe et al. also presented a microfluidic valve where the hydrogel did not directly close or open the channel but deformed a flexible membrane that blocked the flow.

Examples of microvalves using the shrinking and expansion of temperature-responsive hydrogels to unblock and block, respectively, the fluid flow entrance in a microchannel have been reported in the literature.⁶⁶⁻⁷⁰

Another tactic to control the flow rate in a microchannel is to switch the diffusive transport rates within a gel network that fill the entire cross-section of the channel. Through the LCST, e.g. in PNIPAM, the pore sizes can reversibly increase or decrease, leading to an active regulation of the transport rate. For instance, Buchholz et al.⁷¹ used thermo-responsive polymer matrices with switchable viscosity for DNA sequencing by capillary and microchip electrophoresis. The viscosity switch decoupled the matrix loading inside the microchannel and the sieving properties, which allowed acceleration of microchannel flow by 3 orders of magnitude.

Figure 2.10. (a) Schematic illustration of the pH-responsive hydrogel around the prefabricated posts in a microfluidic device. (b-d) Microscope pictures of (b) the device after polymerization of the hydrogels, (c) the hydrogel in the swelling conformation, blocking the channel entrance, and (d) the same hydrogels after contraction due to a different pH, which allowed the fluid to flow in the right channel. Reprinted by permission from Macmillan Publishers Ltd: 64 © 2000 Nature

Also with the same principle, Chen et al.⁷² used a crosslinked PNIPAM microvalve that was tuned by changing the mechanical strength of the polymer monolith inside the microchannel via the choice of suitable amounts of monomers and crosslinkers. The pressure-tolerance of the microvalve was enhanced and resisted a leakage pressure of up to 1350 psi. Its opening and closing response times were 4.0 and 6.2 s, respectively. Furthermore, to avoid the complicated microfabrication of embedded heaters, the authors used a simple and inexpensive quartz halogen illuminator with tungsten filament to actuate their high performance microvalve.

2.3.1.3. Electrochemical stimuli

Among all stimuli, electrical stimuli using redox-responsive polymers seem to offer the fastest and most versatile actuation for microfabrication of portable and commercial microfluidic devices. For example, upon applying electrochemical stimuli ($< 1\text{ V}$), conductive polypyrrole changes its redox state, which as seen previously modifies the surface energy, but it also undergoes significant volume changes. Izquierdo et al.⁷³ used this volume switch to fabricate a microactuator which simply pressed or released a flexible PDMS channel until its full closing or opening.

Differently, Kim et al.⁷⁴ modified a PDMS membrane with polypyrrole to fabricate a micropump. When specific voltages were applied across the polypyrrole/PDMS membrane, the resulting deformation to convex or concave shapes drove a diaphragm to perform push or pull actions. This actuator micropump produced a maximum flow rate of $52\text{ }\mu\text{L}/\text{min}$ and a nominal minimum flow rate of $18\text{ }\mu\text{L}/\text{min}$ when operated at $\pm 1.5\text{ V}$.

Wu et al.⁷⁵ demonstrated the possibility to use the electromechanical volume actuation of polypyrrole to develop a low voltage micropump. As shown in **Figure 2.11**, a confined concentric arrangement of polypyrrole actuators, with an appropriate electrical stimulation, induced fluid motion through an inner channel. With an applied potential of -1 V , the polypyrrole coating contracted and closed the liquid channel from the inlet to the end. When the potential was switched to $+1\text{ V}$, the expansion proceeded in the same direction as the contraction. The switch between -1 V and $+1\text{ V}$ created a peristaltic action that enabled fluids to be pumped in a predetermined direction with flow rates of up to $2.5\text{ }\mu\text{L}/\text{min}$ against a back pressure of 50 mbar . This micropump was sufficient to permit fluid motion in a glass capillary channel.

Figure 2.11. (a) Schematic illustration of the polypyrrole-based micropump in the oxidized state, and thereby fully expanded. (b) Pump sequence showing the working mechanism to obtain a peristaltic motion of the fluid inside the channel. Reprinted from 75. © 2005 IOP Publishing, Ltd

2.3.1.4. Magnetic field stimuli

Instead of using the intrinsic properties of a stimulus-responsive polymer, it is also possible to dope a polymer matrix with stimulus-responsive additives which would open opportunities for responsiveness to different stimuli. Magnetic field actuation is one of the examples where the use of polymer composites, generally bearing iron-based nanoparticles, is necessary to assign a new functionality.

Li et al.¹ fabricated a magnetically actuated microfluidic mixer using a carbonyl iron-PDMS composite magnetic elastomer. As shown in **Figure 2.12**, the authors designed a microfluidic mixer where the actuation was realized with integrated electromagnets. The iron-PDMS composite membrane demonstrated high magnetization, good flexibility and stability. The magnetic actuation allowed a large deflection of the elastomer membrane in the microchannels, which resulted in a perfect mixing of two originally laminar flows.

Fahrmi et al.⁷⁶ demonstrated advanced fluid manipulations using ferromagnetic polymeric artificial cilia on the walls of a microfluidic channel. These artificial cilia of 300 μm (see **Figure 2.13**), made of iron nanoparticles and PDMS, were actuated with a homogeneous rotating magnetic field. The rotating magnetic field was created by a quadrupole, as shown in **Figure 2.13.a**. In a microfluidic chamber and in aqueous solution, rotational and translational movements of the cilia (see **Figure 2.13.a, b and c**) generated rotational and translational fluid movements with flow velocities of up to 0.5 mm/s.

Figure 2.12. (a) Schematic illustration of the magnetically actuated mixer design and construction, based on a carbonyl iron-PDMS elastomer membrane. (b) Photograph of the micromixer device. (c-d) Optical microscope images of (c) the channel without magnetic actuation showing the two distinct laminar flows, (d) the same channel after the full mixing. Reprinted with permission from 77. © 2011 Springer

Figure 2.13. (a) Schematic illustration of the quadrupole which generated a rotating magnetic field in the center region where the artificial cilia were placed. (b-d) Top optical microscope view of the movement of the cilia in the rotating magnetic field. The given angles on the top are the angles of the magnetic field H , and the initial residual magnetization $M_{r,0}$ is indicated by the arrows on the left side. Adapted with permission from 76. © 2009 Royal Society of Chemistry

2.3.2. Dual stimuli responsive systems

2.3.2.1. Dual independent response systems

Enhancement of device performance and function can be achieved by using two or more stimuli. For example, a hybrid electrowetting-thermal microvalve has been presented by Ahamed et al.⁷⁸ On the one hand, electrowetting was used to control the position of a polymer droplet at a desired valving location. On the other hand, a temperature-response was used to strengthen the blocking of the microfluidic flow by rigidifying the liquid-like polymer droplet into a hydrogel plug. At low temperature the polymer droplet was liquid-like and could be moved using electrowetting on a metallic electrode inside the microchannel. After positioning the liquid-like droplet close to a channel entrance, the system was heated and the hydrogel valve was formed. Also, the gel blocked the microfluidic flow, and its subsequent liquefaction unblocked the pressurized flow.

2.3.2.2. Dual consecutive response systems

In the previous example, the two stimuli were actuated independently. To maximize actuation versatility, and to give more autonomy to “smart” microactuators, systems with dual consecutive responses have also been developed. A first stimulus triggers a response which becomes the stimulus for the second actuation that causes microfluidic flow control. For instance, Santaneel et al.⁷⁹ encapsulated ferromagnetic nanoparticles (Fe_3O_4) in a thermo-sensitive PNIPAM-based network which was excited by an oscillating magnetic field to induce heat, and subsequently, control the valve action via the temperature-responsive volume switch of the hydrogel. As shown in **Figure 2.14**, the volume shrinkage yield inside the microchannel was around 80%. The oscillating field-actuated de-swelling response time was around 3 s, which is faster than a standard thermal actuation. Furthermore, as the heat generation is controlled by tuning locally the strength of the magnetic

field and the frequency, a series of valves could be actuated separately in the same microfluidic device. However, with this technique the re-swelling caused by the cooling had a longer response time. Indeed, a full re-swelling of the hydrogel inside the microchannel required around 10 min.

Figure 2.14. Optical microscope pictures showing the ferromagnetic-nanoparticle-doped hydrogel modulation, with the induced progressive shrinkage upon heating via an oscillating magnetic field. Adapted from 79. © 2009 IOP Publishing, Ltd

In a different manner, a bi-layered hydrogel structure was introduced by Al-Arife et al.⁸⁰ as a dual light-to-pH-activated microactuator. As shown in **Figure 2.15**, the first layer was a light sensitive polymer network composed of poly(vinyl alcohol) (PVA) and the retinal protein bacteriorhodopsin (bR). The second layer was a blend of PVA hydrogel and a pH sensitive polyethylenimine (PEI). When the first layer was exposed to light, the bR molecules started a multistage photocycle that causes the production of protons which were pumped into the surrounding media. The pH responsive hydrogel, in the second layer, experienced electrostatic repulsive and attractive forces which altered the osmotic pressure within the cross-linked network

and resulted, depending on the type of electrostatic forces, in its swelling or collapse. However, because of the diffusion controlled process, the response was really slow as a full expansion required 2.5 h, and depended on the hydrogel volume.

Figure 2.15. Schematic illustration of the dual response light and pH microactuator with the transfer of hydrogen ions across the interface which resulted in a swelling switch. Reprinted from 80. © 2006 SPIE

2.4. Conclusion

Polymeric coatings in microfluidic channels have been extensively used to create innovative systems for flow control. They open the opportunity for further miniaturization, portability and cheap microfluidic systems dedicated to large scale commercialization. Polymeric coatings which enable the modification of the surface energy have shown great results in capillary flow control, such as in paper, and electro-osmotic flow. Stimulus responsive systems allow an external control of the flow behavior. Different polymer structures and designs permit further control of the flow. Movement-based systems allow relatively high pressures and different applications, such as mechanical mixing at a microscopic scale.

2.5. References

1. Israelachvili, J.N., *Intermolecular and Surface Forces: Revised Third Edition*. 2011: Elsevier Science.
2. Cassie, A.B.D., *Contact angles*. Discussions of the Faraday Society, 1948. **3**(0): p. 11-16.
3. Israelachvili, J.N. and M.L. Gee, *Contact angles on chemically heterogeneous surfaces*. Langmuir, 1989. **5**(1): p. 288-289.
4. Drelich, J., et al., *Hydrophilic and superhydrophilic surfaces and materials*. Soft Matter, 2011. **7**(21): p. 9804-9828.
5. Vancso, G.J., H. Hillborg, and H. Schönherr, *Chemical Composition of Polymer Surfaces Imaged by Atomic Force Microscopy and Complementary Approaches*, in *Polymer Analysis Polymer Theory*. 2005, Springer Berlin Heidelberg. p. 55-129.
6. Samori, P., *Scanning probe microscopies beyond imaging*. Journal of Materials Chemistry, 2004. **14**(9): p. 1353-1366.
7. Ducker, W.A., T.J. Senden, and R.M. Pashley, *Direct measurement of colloidal forces using an atomic force microscope*. Nature, 1991. **353**(6341): p. 239-241.
8. Butt, H.-J., B. Cappella, and M. Kappl, *Force measurements with the atomic force microscope: Technique, interpretation and applications*. Surface Science Reports, 2005. **59**(1-6): p. 1-152.
9. Hodges, C.S., et al., *Forces between Polystyrene Particles in Water Using the AFM: Pull-Off Force vs Particle Size*. Langmuir, 2002. **18**(15): p. 5741-5748.
10. Pericet-Camara, R., et al., *Interaction forces and molecular adhesion between pre-adsorbed poly(ethylene imine) layers*. Journal of Colloid and Interface Science, 2006. **296**(2): p. 496-506.
11. Johnson, K.L. and K.L. Johnson, *Contact Mechanics*. 1987: Cambridge University Press.
12. Feldman, K., et al., *Toward a Force Spectroscopy of Polymer Surfaces*. Langmuir, 1998. **14**(2): p. 372-378.
13. Hertz, H., *Ueber die Berührung fester elastischer Körper*. Journal für die Reine und Angewandte Mathematik, 1882. **1882**(92): p. 156-171.
14. Drelich, J., G.W. Tormoen, and E.R. Beach, *Determination of solid surface tension from particle-substrate pull-off forces measured with the atomic force microscope*. Journal of Colloid and Interface Science, 2004. **280**(2): p. 484-497.
15. Berman, A., C. Drummond, and J. Israelachvili, *Amontons' law at the molecular level*. Tribology Letters. **4**(2): p. 95-101.
16. Nguyen, N.T. and S.T. Wereley, *Fundamentals and Applications of Microfluidics*. 2002: Artech House.

17. Nelson, W.C. and C.-J.C. Kim, *Droplet Actuation by Electrowetting-on-Dielectric (EWOD): A Review*. Journal of Adhesion Science and Technology, 2012. **26**(12-17): p. 1747-1771.
18. Kwang, W.O. and H.A. Chong, *A review of microvalves*. Journal of Micromechanics and Microengineering, 2006. **16**(5): p. R13.
19. Mittal, K.L., *Advances in Contact Angle, Wettability and Adhesion, Volume Two*. 2015: Wiley.
20. Böhm, A., et al., *Engineering microfluidic papers: effect of fiber source and paper sheet properties on capillary-driven fluid flow*. Microfluidics and Nanofluidics, 2014. **16**(5): p. 789-799.
21. Böhm, A., et al., *Photo-attaching functional polymers to cellulose fibers for the design of chemically modified paper*. Cellulose, 2013. **20**(1): p. 467-483.
22. Andersson, H., et al., *Hydrophobic valves of plasma deposited octafluorocyclobutane in DRIE channels*. Sensors and Actuators B: Chemical, 2001. **75**(1-2): p. 136-141.
23. Andersson, H., W. van der Wijngaart, and G. Stemme, *Micromachined filter-chamber array with passive valves for biochemical assays on beads*. Electrophoresis, 2001. **22**(2): p. 249-257.
24. Bliznyuk, O., et al., *Directional Liquid Spreading over Chemically Defined Radial Wettability Gradients*. ACS Applied Materials & Interfaces, 2012. **4**(8): p. 4141-4148.
25. Kooij, E.S., et al., *Directional wetting on chemically patterned substrates*. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2012. **413**: p. 328-333.
26. Wang, S., et al., *Controlling Flow Behavior of Water in Microfluidics with a Chemically Patterned Anisotropic Wetting Surface*. Langmuir, 2015. **31**(13): p. 4032-4039.
27. Nayak, K., et al. *Patterned microfluidic channels using self-assembled hydroxy-phenyl porphyrin monolayer*. in *Nanotechnology, 2007. IEEE-NANO 2007. 7th IEEE Conference on*. 2007.
28. Sultana, S., et al., *Flow behavior in surface-modified microchannels with polymer nanosheets*. Thin Solid Films, 2009. **518**(2): p. 606-609.
29. Lanotte, L., et al., *Flow Reduction in Microchannels Coated with a Polymer Brush*. Langmuir, 2012. **28**(38): p. 13758-13764.
30. Valipour Motlagh, N., R. Khani, and S. Rahnema, *Super dewetting surfaces: Focusing on their design and fabrication methods*. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2015. **484**: p. 528-546.
31. Plawsky, J.L., et al., *REVIEW OF THE EFFECTS OF SURFACE TOPOGRAPHY, SURFACE CHEMISTRY, AND FLUID PHYSICS ON EVAPORATION AT THE CONTACT LINE*. Chemical Engineering Communications, 2008. **196**(5): p. 658-696.

32. Bazant, M.Z., et al., *Towards an understanding of induced-charge electrokinetics at large applied voltages in concentrated solutions*. Advances in Colloid and Interface Science, 2009. **152**(1–2): p. 48-88.
33. Schasfoort, R.B.M., et al., *Field-Effect Flow Control for Microfabricated Fluidic Networks*. Science, 1999. **286**(5441): p. 942-945.
34. David, C.D., et al., *Rapid prototyping of microfluidic switches in poly(dimethyl siloxane) and their actuation by electro-osmotic flow*. Journal of Micromechanics and Microengineering, 1999. **9**(3): p. 211.
35. Locascio, L.E., C.E. Perso, and C.S. Lee, *Measurement of electroosmotic flow in plastic imprinted microfluid devices and the effect of protein adsorption on flow rate*. Journal of Chromatography A, 1999. **857**(1–2): p. 275-284.
36. Roberts, M.A., et al., *UV Laser Machined Polymer Substrates for the Development of Microdiagnostic Systems*. Analytical Chemistry, 1997. **69**(11): p. 2035-2042.
37. Barker, S.L.R., et al., *Plastic Microfluidic Devices Modified with Polyelectrolyte Multilayers*. Analytical Chemistry, 2000. **72**(20): p. 4899-4903.
38. Barker, S.L.R., et al., *Control of Flow Direction in Microfluidic Devices with Polyelectrolyte Multilayers*. Analytical Chemistry, 2000. **72**(24): p. 5925-5929.
39. Kihm, Z.D., et al., *Modification of Electroosmotic Flow for a Polydimethylsiloxane Electrophoresis Microchip via Polyelectrolyte Coating*. Analytical Sciences, 2012. **28**(2): p. 183-183.
40. Joo, S., T.D. Chung, and H.C. Kim, *A rapid field-free electroosmotic micropump incorporating charged microchannel surfaces*. Sensors and Actuators B: Chemical, 2007. **123**(2): p. 1161-1168.
41. Mora, M.F., C.E. Giacomelli, and C.D. Garcia, *Electrophoretic Effects of the Adsorption of Anionic Surfactants to Poly(dimethylsiloxane)-Coated Capillaries*. Analytical Chemistry, 2007. **79**(17): p. 6675-6681.
42. Pumera, M., et al., *Gold Nanoparticle-Enhanced Microchip Capillary Electrophoresis*. Analytical Chemistry, 2001. **73**(22): p. 5625-5628.
43. Urban, M.W., *Handbook of Stimuli-Responsive Materials*. 2011: Wiley.
44. Urban, M.W., et al., *Stimuli-responsive Polymeric Films and Coatings*. 2005: American Chemical Society.
45. Kwong, P. and M. Gupta, *Vapor Phase Deposition of Functional Polymers onto Paper-Based Microfluidic Devices for Advanced Unit Operations*. Analytical Chemistry, 2012. **84**(22): p. 10129-10135.
46. Walsh, Z., et al., *Photochromic spiropyran monolithic polymers: Molecular photo-controllable electroosmotic pumps for micro-fluidic devices*. Sensors and Actuators B: Chemical, 2010. **148**(2): p. 569-576.

47. Salim, M., P.C. Wright, and S.L. McArthur, *Studies of electroosmotic flow and the effects of protein adsorption in plasma-polymerized microchannel surfaces*. Electrophoresis, 2009. **30**(11): p. 1877-1887.
48. Wang, T., et al., *Janus Si Micropillar Arrays with Thermal-Responsive Anisotropic Wettability for Manipulation of Microfluid Motions*. ACS Applied Materials & Interfaces, 2015. **7**(1): p. 376-382.
49. Ernst, O., et al., *Control of cell detachment in a microfluidic device using a thermo-responsive copolymer on a gold substrate*. Lab on a Chip, 2007. **7**(10): p. 1322-1329.
50. Robinson, L., et al., *Electrochemical wettability switches gate aqueous liquids in microfluidic systems*. Lab on a Chip, 2006. **6**(10): p. 1277-1278.
51. Tsai, Y.-T., C.-H. Choi, and E.-H. Yang, *Low-voltage manipulation of an aqueous droplet in a microchannel via tunable wetting on PPy(DBS)*. Lab on a Chip, 2013. **13**(2): p. 302-309.
52. Wang, S., Y. Song, and L. Jiang, *Photoresponsive surfaces with controllable wettability*. Journal of Photochemistry and Photobiology C: Photochemistry Reviews, 2007. **8**(1): p. 18-29.
53. Geissler, A., et al., *Superhydrophobic surfaces fabricated from nano- and microstructured cellulose stearoyl esters*. Chemical Communications, 2013. **49**(43): p. 4962-4964.
54. Shirtcliffe, N.J., G. McHale, and M. I. Newton, *The superhydrophobicity of polymer surfaces: Recent developments*. Journal of Polymer Science Part B: Polymer Physics, 2011. **49**(17): p. 1203-1217.
55. John, T.S., R.H. Scott, and A. Tolga, *Superhydrophobic materials and coatings: a review*. Reports on Progress in Physics, 2015. **78**(8): p. 086501.
56. Wu, Y., et al., *Adhesion-Regulated Switchable Fluid Slippage on Superhydrophobic Surfaces*. The Journal of Physical Chemistry C, 2014. **118**(5): p. 2564-2569.
57. Obeso, C.G., et al., *Modification of paper using polyhydroxybutyrate to obtain biomimetic superhydrophobic substrates*. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2013. **416**: p. 51-55.
58. Ghosh, A., et al., *Wettability patterning for high-rate, pumpless fluid transport on open, non-planar microfluidic platforms*. Lab on a Chip, 2014. **14**(9): p. 1538-1550.
59. You, I., et al., *Polydopamine Microfluidic System toward a Two-Dimensional, Gravity-Driven Mixing Device*. Angewandte Chemie International Edition, 2012. **51**(25): p. 6126-6130.
60. Hong, L. and T. Pan, *Surface microfluidics fabricated by photopatternable superhydrophobic nanocomposite*. Microfluidics and Nanofluidics, 2011. **10**(5): p. 991-997.
61. Zahner, D., et al., *A Facile Approach to Superhydrophilic-Superhydrophobic Patterns in Porous Polymer Films*. Advanced Materials, 2011. **23**(27): p. 3030-3034.

62. Tsougeni, K., et al., *"Smart" polymeric microfluidics fabricated by plasma processing: controlled wetting, capillary filling and hydrophobic valving*. Lab on a Chip, 2010. **10**(4): p. 462-469.
63. Ebara, M., et al. *Design of re-writable and shape-memory microchip materials with dynamically tunable microchannel geometry near biological temperature*. in *15th International Conference on Miniaturized Systems for Chemistry and Life Sciences 2011, MicroTAS 2011*. 2011.
64. Beebe, D.J., et al., *Functional hydrogel structures for autonomous flow control inside microfluidic channels*. Nature, 2000. **404**(6778): p. 588-590.
65. Beebe, D.J., et al., *Microfluidic tectonics: A comprehensive construction platform for microfluidic systems*. Proceedings of the National Academy of Sciences, 2000. **97**(25): p. 13488-13493.
66. Li, A., et al. *Fabrication and testing of hydrogel-based microvalves for flow control in flexible lab-on-a-chip systems*. 2012.
67. Bazargan, V. and B. Stoeber, *Flow Control Using a Thermally Actuated Microfluidic Relay Valve*. Microelectromechanical Systems, Journal of, 2010. **19**(5): p. 1079-1087.
68. Harmon, M.E., M. Tang, and C.W. Frank, *A microfluidic actuator based on thermoresponsive hydrogels*. Polymer, 2003. **44**(16): p. 4547-4556.
69. Yu, C., et al., *Flow Control Valves for Analytical Microfluidic Chips without Mechanical Parts Based on Thermally Responsive Monolithic Polymers*. Analytical Chemistry, 2003. **75**(8): p. 1958-1961.
70. Luo, Q., et al., *Monolithic valves for microfluidic chips based on thermoresponsive polymer gels*. Electrophoresis, 2003. **24**(21): p. 3694-3702.
71. Buchholz, B.A., et al., *Microchannel DNA Sequencing Matrices with a Thermally Controlled "Viscosity Switch"*. Analytical Chemistry, 2001. **73**(2): p. 157-164.
72. Chen, G., F. Svec, and D.R. Knapp, *Light-actuated high pressure-resisting microvalve for on-chip flow control based on thermo-responsive nanostructured polymer*. Lab on a Chip, 2008. **8**(7): p. 1198-1204.
73. Izquierdo, R., et al. *Integration of polypyrrole microactuators and organic optoelectronic devices for lab-on-chip applications*. in *Electronics, Circuits, and Systems, 2009. ICECS 2009. 16th IEEE International Conference on*. 2009.
74. Kim, J.H., et al., *Performance characteristics of a polypyrrole modified polydimethylsiloxane (PDMS) membrane based microfluidic pump*. Sensors and Actuators A: Physical, 2008. **148**(1): p. 239-244.
75. Wu, Y., et al., *TITAN: a conducting polymer based microfluidic pump*. Smart Materials and Structures, 2005. **14**(6): p. 1511.
76. Fahrni, F., M.W.J. Prins, and L.J. van Ijzendoorn, *Micro-fluidic actuation using magnetic artificial cilia*. Lab on a Chip, 2009. **9**(23): p. 3413-3421.

77. Li, J., et al., *Design and fabrication of microfluidic mixer from carbonyl iron–PDMS composite membrane*. *Microfluidics and Nanofluidics*, 2011. **10**(4): p. 919-925.
78. Ahamed, M.J., R. Ben-Mrad, and P. Sullivan, *Electrowetting on Dielectric (EWOD)-Based Thermo-Responsive Microvalve for Interfacing Droplet Flow With Continuous Flow*. *Microelectromechanical Systems, Journal of*, 2013. **22**(3): p. 536-541.
79. Santaneel, G., et al., *Oscillating magnetic field-actuated microvalves for micro- and nanofluidics*. *Journal of Physics D: Applied Physics*, 2009. **42**(13): p. 135501.
80. Al-Arife, K., G.K. Knopf, and A.S. Bassi. *Photo-responsive hydrogel for controlling flow on a microfluidic chip*. 2006.

Poly(ferrocenylsilanes) with Controlled Macromolecular Architecture by Anionic Polymerization: Applications in Patterning and Lithography

In this chapter, the versatility of poly(ferrocenylsilanes) (PFSs) as resists in reactive ion etching (RIE) for nanofabrication, is presented. PFSs, belonging to the class of organometallic polymers, possess skeletal ferrocene and alkylsilane units which provide these solution-processable materials with a very high RIE resistance. First, it is shown that among the different paths for synthesizing PFS, anionic polymerization creates an opportunity to produce well-defined PFSs with a targeted molar mass and low polydispersity. Block polymers and more complex structures can also be realized, which leads to exciting openings in maskless self-assembly lithography for nanopatterning. Then, optimization of the etching process, aimed at maximizing aspect ratios for PFS-based resists, is discussed. Next, several micro- and nanofabrication processes, using PFS homopolymers to fabricate nanoscale structures, are demonstrated. Finally, phase-separation of PFS-block copolymers and their use as self-assembled resists with long-range guided order in nanolithography is discussed. With this technique, various nanopatterns useful for CMOS design could be obtained.

*This Chapter has been published in: Lionel Dos Ramos, Mark A. Hempenius, G. Julius Vancso; In *Anionic Polymerization: Principles, Practice, Strength, Consequences and Applications*, N. Hadjichristidis and A. Hirao, Editors; 2015, Springer Japan: Tokyo; p. 387-427

3.1. Introduction

Complementary metal oxide semiconductor (CMOS) is a technology that was patented in 1967 by Frank Wanlassfor.¹ It is used to construct integrated circuits, such as microprocessors, microcontrollers, static RAM, and other digital logic circuits. CMOS technology is also used for analog circuits, such as image sensors, data converters, and highly integrated transceivers for many types of communication.²

In the race to produce ever smaller, faster and more economical electronic devices, the component density of integrated circuits needs to be ever greater, i.e., component sizes must decrease. One of the main limitations in the fabrication of integrated circuits is the difficulty to further scale down CMOS transistors.³ Most of the patterning processes take place on the wafer in two steps: (1) the patterning of a resist film on top of the functional material, known as lithography; and (2) the transfer of the resist pattern into the functional material, termed etching. Current state-of-the-art photolithographic techniques, such as immersion lithography⁴ and double patterning⁵, combined with a 193 nm UV light source, allow the fabrication of 14 nm-node technology. Electron and ion beam lithography have allowed the creation of features with less than 10 nm wide and continue to be developed in laboratories. However, due to the limits implied by the use of these wavelengths and especially the high costs of implementing these new technologies, alternative techniques capable of producing sub-10 nm-node features must be introduced.

Non-radiation-based resist patterning techniques have been introduced and offer fascinating prospects.^{6, 7} Compared with radiation-based nanopatterning, non-radiation-based patterning methods have major advantages due to the fundamentally different physical principles involved. These techniques have no diffraction limits to resolution, are easily applicable for 3-D patterning, can directly pattern functional materials, thereby reduce fabrication steps, and eliminate the need for complicated and expensive equipment, such as particle sources and optical systems. These

techniques are based on mechanical or chemical patterning processes, and recently the combination of both has attracted research interest.

Mechanical patterning uses a mechanical mold as a template to shape the resist on the substrate, for example through nanoimprinting, or as a stamp to transfer an ink onto the surface, e.g., nanoprinting or soft-lithography.⁸ Chemical patterning methods are bottom-up processes and appear to be a viable alternative for the fabrication of nanoscale features. They exploit the ability of a system to settle at its minimum energy, forming polymeric patterns by self-organization.⁹ Chemical patterning processes include the self-assembly of monolayers on a surface and the phase separation of block polymers.¹⁰ As shown in **Figure 3.1**, several basic structures obtained with block copolymer (BCP) patterning which are useful for CMOS functions, have already been achieved. These patterns include dense and isolated bends, jogs, spots, line terminations, and T-junctions. Nealey and his co-workers obtained these features^{11, 12} by using a lithographically patterned self-assembled monolayer or polymer brushes. These monolayers were subsequently etched with oxygen plasma to define regions with distinct surface tension, which were used to guide the self-organization of a thermally annealed thin block copolymer film.

Figure 3.1. Examples of structures obtained with BCP patterning which can have useful CMOS functions. Reprinted from 13. © 2007 International Technology Roadmap for Semiconductors.

Mixed patterning techniques combine mechanical and chemical methods, such as guided self-assembly in which a larger mechanical or chemical pattern is used to guide the self-assembly of smaller patterns. This technique induces self-organization at predetermined locations with large domain sizes, possessing long range order, instead of the random order and small domain sizes typically resulting from unguided self-assembly.¹⁴

Another challenge in CMOS fabrication and the scaling down of features, is the need for high-performance resists that allow the obtaining of high-contrast features. In this chapter, we focus on poly(ferrocenylsilane) (PFS), an organometallic polymer, which has shown very promising properties as reactive ion etch barrier, and therefore, creates exciting opportunities in maskless self-assembly lithography for nanopatterning.¹⁵

In the second part of this chapter, the synthesis of PFS will be presented and it will be shown that anionic polymerization creates an opportunity to produce well-defined

PFS homopolymers with targeted molar mass and low polydispersity, as well as block polymers or more complex structures. In the third part, the reactive ion etching properties of PFS and the optimization of the etching process to achieve higher contrast will be discussed. The fourth part is dedicated to demonstrating the opportunities of using PFS in various mechanical lithography processes to fabricate nanoscale structures. Finally, in the fifth part, phase-separation of PFS-block copolymers and their use as self-assembled resists with long-range guided order in nanolithography will be discussed.

3.2. Poly(ferrocenylsilane) synthesis

Poly(ferrocenylsilanes) are organometallic polymers composed of alternating ferrocene and silane units in the main chain. These materials were first obtained in 1962 by Rosenberg in a condensation polymerization between a biscyclopentadienide and iron(II) chloride, resulting in oligomers with degrees of polymerization ranging from 1 to 10.¹⁶ Manners and co-workers reported in 1992 a method for synthesizing high-molar-mass PFSs, involving thermal ring-opening polymerization (ROP) of strained silicon-bridged [1]ferrocenophanes.¹⁷ The synthesis of polysilane-poly(ferrocenylsilane) random copolymers by thermal ROP was reported in 1995 by Manners and co-workers.¹⁸ Enhanced control over the molar mass of PFSs was gained by polymerizing [1]silaferrocenophanes in solution using transition metal catalysts.^{19,20} Later, in 1998, transition metal catalyzed ring-opening polymerization was used to synthesize PFSs with regioregular, comb, star and block architectures.²¹ Very well-defined PFSs with unprecedented control over molar mass are obtained by the anionic ring-opening polymerization of [1]silaferrocenophanes.^{22, 23} This method allows one to synthesize near-monodisperse PFS homopolymers, block copolymers, and end-functional PFS chains. Interestingly, [1]silaferrocenophanes can also be polymerized in the solid state using a 60C γ -ray source²⁴ (**Figure 3.2**).

Figure 3.2. Ring-opening polymerization of strained dimethyl[1]silaferrocenophane. With kind permission from Springer Science and Business Media from 25.

Several types of iron-containing macromolecules have been synthesized by polymerizing ferrocenophanes with varying numbers and types of bridging atoms²⁶ and substituents on the cyclopentadienyl rings.^{27, 28}

One of the main advantages of PFS compared to other organometallic polymers is the possibility to adjust the macromolecular characteristics by changing the substituents on the silicon atoms. Polymerization of asymmetrically substituted [1]silaferrocenophanes²⁹ yields amorphous polymers while symmetrically substituted ferrocenophanes yield semicrystalline materials.³⁰ In addition, the glass transition temperature of PFSs can be tuned by varying the size and type of the substituents.³¹⁻³³ The synthesis of water-soluble PFS polyanions³⁴⁻³⁶ and polycations^{37, 38} and their layer-by-layer deposition^{37, 39} to form multilayer thin films was also reported. The introduction of different reactive side-groups allowed the synthesis of hyperbranched structures,⁴⁰ PFS-based hydrogels⁴¹ and recently the covalent fixation of PFS on a substrate.⁴²

Living anionic ring-opening polymerization of silicon bridged[1]ferrocenophanes enabled the synthesis of well-defined and near monodisperse poly(ferrocenylsilane) homo- and block copolymers. A variety of block copolymers with controlled molar masses and low polydispersity have been prepared (see **Table 3.1**). The polymerization mechanism, shown in **Figure 3.3**, involves a nucleophilic attack by an alkyllithium initiator at the bridging silicon atom with a simultaneous cleavage of the ipso-carbon-silicon bond to create a metal-coordinated cyclopentadienyl anion.

The propagation continues from the living anionic chain end until the monomer is consumed. Highly purified monomers, dry solvents and an oxygen-free atmosphere are needed to avoid termination or chain transfer reactions. Under these conditions, predictable molecular weights and narrow molecular weight distributions ($\text{PDI} < 1.2$) are realized.⁴³

Figure 3.3. Reaction scheme for the living anionic polymerization of dimethyl[1]silaferrocenophane. Reprinted with permission from 43. Copyright 1996 American Chemical Society.

Later, in 2004, it was reported that PFS can also be synthesized by living photolytic anionic ring-opening polymerization.^{23, 44} Dimethyl[1]silaferrocenophane was exposed to UV-vis radiation in the presence of an anionic initiator, sodium cyclopentadienylide ($\text{Na}[\text{C}_5\text{H}_5]$), leading to photocontrolled ring-opening polymerization. As shown in **Figure 3.4**, under irradiation at 5 °C, some monomers (M) are photoexcited (M^*) and react with the initiator to form a ring-opened monomer. The propagation proceeds via the opening of more $\text{Fe}-\eta^5\text{-cyclopentadienyl}$ bonds in the photo-excited monomer (M^*) via silyl-substituted cyclopentadienyl anions which are less basic than iron coordinated cyclopentadienyl anions. The chain is terminated with methanol and controlled molecular weights and narrow polydispersities ($\text{PDI} = 1.04\text{--}1.21$) were obtained. Several block copolymers were obtained via this method, see **Table 3.1**, but this approach does not permit the synthesis of acrylate-, methacrylate- or acrylamide-based block copolymers by sequential anionic polymerization as the uncoordinated cyclopentadienyl site is insufficiently reactive.⁴⁵

Figure 3.4. Photocontrolled living anionic ring opening polymerization reaction of [1]silaferrocenophane monomers and the photolytic living ring-opening polymerization mechanism. Reprinted by permission from 44 Macmillan Publishers Ltd: *Nature Materials*, copyright(2006).

Most of the PFS-based block copolymers were synthesized by traditional sequential anionic polymerization, as seen in **Table 3.1**. For block copolymer synthesis, the monomers has to be added following a decrease of the end-group reactivity.⁴⁵ Nevertheless, sequential anionic polymerization has several drawbacks as it cannot be used with monomers containing either an acidic proton, e.g. acrylamide or *N*-alkylacrylamides, or reactive functional groups, such as acrylates or methacrylates. Moreover, some monomers which are suitable for anionic polymerization, e.g. 2-vinylpyridine or ethylene oxide, will not react and polymerize with the propagating PFS anion, and conversely, a propagating poly(2-vinylpyridine) carbanion is not nucleophilic enough to initiate polymerization of dimethyl[1]silaferrocenophane. An elegant way to solve this problem, introduced by Rehahn and co-workers,⁴⁶ involves the end-functionalization of the propagating PFS anion with a strained silacyclobutane to create a living end with enhanced basicity which can be end-capped with 1,1-diphenylethylene. The resulting living end is quite suitable as anionic initiator for acrylic monomers. Anionic ring-opening polymerization also allowed the introduction of functional end-groups, providing access to the synthesis of a broad range of PFS-based block copolymers.⁴⁷ For instance, alkyne-ended PFS chains could be connected to azide-ended poly(*N*-isopropylacrylamide) chains, using a Cu-catalyzed “click” reaction.⁴⁸ **Table 3.1**

gives an overview of PFS-based block copolymers synthesized by anionic polymerization methods.

Figure 3.5. Examples of poly(ferrocenylsilane)-based block copolymers. With kind permission from Springer Science and Business Media from 25.

More complex architectures, such as pentablocks,^{43, 49} dendrimers⁵⁰ or block star terpolymers⁵¹ have been synthesized recently.

Table 3.1. Recapitulative table of the different PFS-based block copolymers synthesized.

Non-PFS block polymer	Synthesis method of PFS block	Synthesis method of non-PFS block	Attachment of the blocks	DP of non-PFS block	PDI of non-PFS block	Year	Ref.
Poly(dimethylsiloxane)	Anionic	Anionic	Sequential Anionic	40/95	1.13	1994	⁵²
	Anionic	Anionic	Sequential Anionic	39/99	1.13-1.15	1996	⁴³
	Anionic	commercial	Click reaction	80	1.10	2013	⁴⁸
Polystyrene	Anionic	Anionic	Sequential Anionic	100	1.08	1996	⁴³
	Anionic	ATRP	Click reaction	29	1.14	2013	⁴⁸
Poly(ethylene oxide)	Pt-catalyzed	commercial	Macromolecular condensation	68	1.13	1999	⁵³
	Anionic	commercial	Click reaction	113	1.16	2013	⁴⁸
Polyisoprene	Anionic	Anionic	Sequential Anionic	450	1.03	2000	⁵⁴
Poly(ferrocenylphenylphosphine)	Anionic	Anionic	Sequential Anionic	1-11	1.01-1.10	2002	⁵⁵
Poly(aminoalkyl methacrylate)	Anionic	Oxyanionic	Sequential with deprotection of hydroxyl-group	52	1.3	2002	⁵⁵
Poly(methyl methacrylate)	Anionic	Anionic	DMSB-mediated end capping	580	<1.1	2004	⁴⁶
	Anionic	ATRP	ATRP macroinitiator end-functionalized	531	1.06	2004	⁴⁷
	Anionic	ATRP	Click reaction	227	1.14	2013	⁴⁸
Poly(γ -benzyl-L-glutamate)	Anionic	NCA ROP	Amino end-capping	95	1.13	2005	⁵⁶
Gly-Ala-Gly-Ala	Anionic	SPPS	Amino end-capping	18	1.00	2006	⁵⁷
Poly(ϵ -benzyloxycarbonyl-L-Lysine)	Anionic	NCA ROP	Amino end-capping	75/180	1.25/1.16	2006	⁵⁸
Poly(lactide)	Anionic	Zn-catalyzed	Hydroxyl-end capping	472	1.41	2007	⁵⁹
Poly(phosphazene)	Anionic	cationic	Phosphorane end-capping	77	1.09	2008	⁶⁰
Poly(ferrocenylmethyl(3,3,3-trifluoropropyl)silane)	PROP	PROP	Sequential Anionic	78	1.02	2010	⁶¹
Poly(cobaltoceniumethylene)	PROP	PROP	Sequential Anionic	50, 75	/	2011	⁶²
Poly(N-isopropylacrylamide)	Anionic	ATRP	Click reaction	105	1.16	2013	⁴⁸
Poly(2-(dimethylamino)ethyl methacrylate)	Anionic	ATRP	Click reaction	400	1.28	2013	⁴⁸

NCA ROP= α -aminoacid-N-carboxyanhydride Ring Opening Polymerization

SPPS= Solid Phase Peptide Synthesis

PROP= Photocontrolled living anionic ring-opening polymerization (ROP)

3.3. Reactive ion etching barrier properties of Poly(ferrocenylsilanes)

In microfabrication, reactive ion etching using oxygen and oxygen-containing plasmas is a common dry etching technology used to selectively remove materials deposited on wafers.⁶³ Two mechanisms, chemical and physical etching, compete during this process.⁶⁴ In chemical etching, the active plasma reacts chemically with the substrate material. Etchant species are adsorbed on the surface and the reactions take place. Then the formed volatile products desorb from the surface and are pumped out. In physical etching, the positive ions are accelerated towards the surface and then mechanically eject substrate material after breaking bonds upon impact. The balance between these two etching mechanisms depends on different parameters, e.g. gas pressure and composition, reactor design and temperature.^{65, 66} Adjusting the relative contribution of these two etching processes is crucial for controlled nanofabrication as contrast is inversely proportional to the etching rate ratio of resist and substrate.

Organometallic compounds are known for their etching barrier properties in oxygen plasmas. Chemical etching products of these compounds are not volatile, contrary to common organic compounds, and therefore they are not desorbed from the surface. The behavior of poly(ferrocenylsilanes) under reactive ion etching conditions was studied.⁶⁷ Due to the presence of iron and silicon in the main chain, PFSs were found to be very efficient oxygen plasma etching barriers compared to common organic polymers. **Figure 3.6** gives a comparison between the etched thickness of poly(styrene) (PS) and poly(ferrocenylsilane) (PFS) as a function of time. During etching, it was established by XPS that a thin iron- and silicon-oxide layer was formed at the surface, which decreased the etching rate considerably.

Figure 3.6. Comparison of the etched thickness by reactive ion etching for PS and PFS as a function of time.

The composition in the depth of PFS films was investigated using Auger electron spectroscopy (AES). In the AES spectra (**Figure 3.7**), the front part corresponds to the sample surface and the increase in sputtering cycles indicates a depth increase. The silicon signal around cycle 90 originates from the underlying silicon substrate. Compared to the film interior, on the surface little carbon and a significant amount of oxygen are present, revealing a thin oxide-rich layer of approximately 10 nm. Interestingly, more silicon is removed from the surface compared to iron during the oxygen plasma treatment. The presence of iron gives a higher resistance than silicon toward removal by oxygen plasma and also provides a high resistivity when fluorocarbon plasmas are applied.

Figure 3.7. Auger electron spectroscopy depth profile of an oxygen plasma etched film of poly(ferrocenyldimethylsilane) of 106 nm. Cycles start at the film surface and end at the substrate. Reprinted with permission from 67. Copyright 2001 American Chemical Society.

Radio-frequency discharges in low-pressure fluorocarbon gases are frequently used for etching silicon, silicon oxide, and silicon nitride.^{68, 69} CF_4 , CHF_3 , C_2F_6 and SF_6 are common gases used in reactive ion etching.⁷⁰ The nature of the plasma and its related etching characteristics can be radically changed by adjusting the composition of the gas.⁷¹ For example, the C/F atomic ratio of the feed gas is a decisive parameter for the nature of the plasma.⁷² An increase of the C/F ratio of the feed-in gas leads to an increase of the concentration of CF and CF_2 radicals which results in polymerization of the plasma. The concurrent deposition of a very thin fluorocarbon film on the substrate enhances the protection to etching, resulting in a significant reduction of the SiO_2 etch rate.⁷³ To overturn this etch stop, the fluorocarbon gases have been diluted with other gases like oxygen.⁷⁴⁻⁷⁶ Oxygen atoms act as scavengers for carbon, and consequently the concentration of fluorine atoms [F] (the etching component) will be relatively higher than the concentration

of fluorocarbons [CFX] (the polymerizing component). **Figure 3.8** (left) shows an example of a structured silicon wafer produced by exposure to CF_4/O_2 reactive ion etching (RIE), using a PFS mask prepared by capillary force lithography.⁷⁷ Under the employed conditions, the etch rate contrast between PFS resist and silicon substrate is on the order of 10:1.

Figure 3.8. (left) SEM image of a patterned silicon substrate after introduction of poly(ferrocenylmethylphenylsilane) lines by capillary force lithography, followed by 10 min of CF_4/O_2 reactive ion etching. (right) SEM image of silicon nanopillars obtained using SF_6 (2 min) in a cryogenic reactive ion etcher with a poly(ferrocenyldimethylsilane) mask. In both cases the polymer mask was subsequently removed using nitric acid. With kind permission from Springer Science and Business Media from 25.

In order to fabricate structures with higher aspect ratios, the rate of the chemical etching of the substrate compared to the polymeric mask has to be increased without compromising the anisotropy of the etching process. This was reached by using SF_6 as the etching gas in a cryogenic reactive ion etcher. The physical and chemical etching parameters were varied independently and conditions for the highest etch rate contrast were optimized.⁷⁸ The substrate temperature was kept at $-110\text{ }^\circ\text{C}$ during processing, resulting in an increase of the chemical etching rate for Si and a drastic decrease of the physical sputtering rate. Using this process, etch rates of 3000 nm/min into Si and around 5 nm/min in the PFS layer were obtained, giving an etch rate contrast of 600:1. Such a high etch rate contrast enables the fabrication of high-

aspect-ratio structures like silicon nanopillars with aspect ratios of 10 as shown in **Figure 3.8** (right).

The etch barrier potential of PFS has now been demonstrated. In the next part we focus on pathways to generate patterns using this resist. The deposition of a very thin resist layer of high etch resistance is a determining step in the fabrication of defined high-aspect-ratio structures, as this minimizes pattern collapse.

3.4. Poly(ferrocenylsilane) homopolymers in lithography applications

With the ongoing miniaturization, polymers have rapidly become crucial in the fabrication of submicron and nanoscale devices, most notably as highly tailorable resist materials. Indeed, their well-defined architecture, wide range of chemical functionalities and ease of processing on micro- and nanoscale were extensively used to fabricate optical systems and microelectronics devices. Nano-imprint lithography, microcontact printing, micro-fluid-contact printing, lift-up, micromolding in capillaries, replica molding, solvent-assisted micromolding with its variations and photolithography were the most used techniques in the past decades. Nevertheless, most of the polymers have low resistivity to etching which is a large disadvantage when high aspect ratio patterns are to be obtained. Poly(ferrocenylsilanes), as seen in paragraph 3.3. , were shown to be ideal materials for one-step resists. The etch barrier potential of poly(ferrocenyldimethylsilane) in O_2 and CF_4/O_2 plasmas was demonstrated for patterns made by micromolding in capillaries.⁶⁷

In the next sections, some examples of microfabrication will be presented, using poly(ferrocenylmethylphenylsilane) (PFMPS) as etch barrier in O_2 and CF_4/O_2 plasmas. The asymmetric substitution on the silicon atoms of PFMPS prevent crystallization of the polymer film, providing excellent homogeneity. The dependence of its glass transition temperature on the number average molar mass was studied.^{29, 77} The extrapolated value of T_g of the polymer with infinite molar mass

was found to be 92 °C. A low molar mass PFMPs of 3700 g/mol, $M_w/M_n=1.07$, was used for its liquidlike behavior above its T_g of 74 °C. At this molar mass, a favorable balance between T_g and viscosity was found, which permits processing at relatively low temperatures. Above its T_g the polymer should be suitable to wet the stamp while below T_g the generated patterns retain their shape.

3.4.1. Solvent-assisted microcontact printing

Microcontact printing, introduced by Whitesides and co-workers,^{79, 80} has become one of the most prominent methods for introducing patterns on flat and curved substrates with feature sizes ranging from micrometers to below 100 nm. Relief patterns on a master poly(dimethylsiloxane) (PDMS) stamp are used to transfer the “ink” to the surface of the substrate by physical contact printing. Usually, small molecules are used as ink and react with the surface, creating self-assembled monolayers (SAMs). When the stamp is removed, the pattern of ink, directed by the stamp shape, remains on the surface of the substrate. One application of the technique is the printing of etch-resistant polymer patterns.

Macromolecular “inks” have been used but poor wetting characteristics of PDMS surfaces by many polymers limit the process. Compared to common polymers, PDMS stamps have a low surface tension which is around 20 mN/m.⁸¹ Indeed, the wetting properties of the ink polymer on the stamp surface will generate a continuous film or discontinuous islands on the substrate. A continuous thin layer of polymer on the surface of the stamp during inking is necessary for the transfer of a well-defined and continuous thin polymer film onto a substrate. In order to form a homogeneous polymer film it is essential to increase the wettability of macromolecules by employing different surface oxidation techniques. For example, oxygen-based plasma treatments were used to increase the surface free energy of PDMS by creating a thin silica-like layer.^{82, 83} However, this thin layer, formed during plasma treatment, thermally expands and generates mechanical stress on the stamp upon

cooling. The relief of compressive stress by buckling of the silica-like thin film that was formed as a result of the plasma exposure induces a periodic wavy structure perpendicular to the pattern of the stamp.⁸⁴ This submicron structure can also be replicated on the PFS ink.^{85, 86}

Nevertheless, less aggressive cleaning and oxidation techniques were found and the corrugation formation was eliminated. A mild ozone/UV environment can be used to clean the PDMS stamp, making the PDMS surface hydrophilic.⁸⁷ This treatment does not result in extensive heating and therefore stress related to thermal expansion is suppressed.

A solution of PFMPs (1 %wt) in toluene was spin-coated on a PDMS stamp treated by the latter method. As shown in **Figure 3.9** (left), the patterns possessed a spacing corresponding to the periodicity of the stamp structure. During printing, the polymer solution dewets between the stamp and the silicon substrate, forming continuous lines in the middle of the protruding stamp contact areas. The lines, with a width on the order of 1 μm , were then etched into the underlying silicon substrate. As shown in **Figure 3.9** (right), after 10 min in O_2 and CF_4/O_2 plasmas, a direct pattern transfer into silicon resulted, with approximately 300 nm of silicon removed. The etch rate contrast between silicon substrate and PFMPs resist was estimated by AFM at 6:1.

Figure 3.9. Schematic diagram (left) and AFM height image with section analysis (right) of solvent-assisted dewetting of PFMPs confined between PDMS stamp and silicon substrate after 10 min of CF₆/O₂-RIE treatment. Adapted with permission from 77. Copyright 2003 American Chemical Society.

3.4.2. Capillary force lithography

In capillary force lithography, a PDMS stamp is used to expel a thin polymer film from areas of contact between the substrate and the stamp. The polymer film was previously deposited on the substrate and heated above its T_g (74 °C for PFMPs). As shown in **Figure 3.10** (left), the polymer diffuses into the grooves along the vertical walls of the stamp due to capillary forces and structures are formed with a shape of a meniscus. A very thin film does not fill the grooves of the stamps completely, hence a double line is formed per groove. An increase of the initial polymer film thickness results in thicker lines and a decrease of the space between the double lines. With a sufficiently high film thickness, the two lines merge and a single line with the dimensions of the groove (**Figure 3.10** (right)) is obtained.

Vancso and co-workers⁷⁷ used a PDMS stamp of 3-μm wide cavity lines spaced by 2-μm wide prominent lines, denoted as 2 x 3 μm. With a 27-nm thin PFMPs film,

patterns with 110 nm high and 500 nm wide features were fabricated. It was observed from the section analysis of AFM height images that a meniscus of the capillary rise is formed in the grooves. The contact angle between PFMPS and PDMS was calculated to be 70° which is in agreement with microscopic measurements ($\theta_{\text{PDMS/PFMPS}} = 67^\circ$). The receding contact angle between the silicon substrate and PDMS was also determined from AFM section analysis and was found to be 5° , whereas the static contact angle was 45° .

Using a $3 \times 5 \mu\text{m}$ stamp, lines with widths of 1.1, 2.1, 2.4 and $5.4 \mu\text{m}$ corresponding to initial film thicknesses of 30, 80, 100 and 150 nm, respectively, were obtained. The gap between the lines can be adjusted from $2.5 \mu\text{m}$ for a 30 nm film to 840 nm for a 100 nm film. With a film thickness higher than 140 nm the two lines merge and a single line with the size of the groove is formed (**Figure 3.10** (right)).

The structures were developed by CF_4/O_2 -RIE into silicon and the remaining PFMPS resist was stripped in HNO_3 . The pattern transferred into the silicon was shown previously in **Figure 3.8** (left). In 10 min of CF_4/O_2 -RIE etching, 300 nm of silicon was removed and the etch rate contrast between silicon substrate and PFMPS resist was determined to be 6:1.

Figure 3.10. Schematic diagram (left) and AFM height image (right) of capillary force lithography of PFMPs after etching and resist stripping for initial film thickness of (A) 30 nm, (B) 80 nm, (C) 100 nm and (D) 150 nm. Adapted with permission from 77. Copyright 2003 American Chemical Society.

3.4.3. Thermal and UV-assisted nanoimprint lithography

Nanoimprint lithography (NIL) allows the fabrication of nanostructures with high resolution and constitutes an alternative to traditional photolithography which uses masks. Thermal NIL^{88, 89} and UV-light-assisted NIL^{90, 91} are two techniques giving access to sub-10-nm features in a low-cost and high-throughput manner. The technique is based on a rigid template or mold with prefabricated topographic features which is used to replicate patterns within a resist layer that can then be employed as an etch mask for further pattern transfer. In thermal NIL, the template is replicated into a thermoplastic material by heating the polymer above its glass transition temperature and applying pressure on the mold. By contrast, in UV-light-assisted NIL, a transparent and rigid template is used to photocure a low-viscosity UV-curing resist material. The main challenge is to find an appropriate fast curable

material that has a low adhesion to the mold, shows a good adhesion to the substrate and a high etch resistance.

Huskens, Vancso and co-workers suggested the use of PFMPS for thermal NIL.⁹² With this technique small features below 100 nm were not precisely transferred on the substrate. Later, in order to obtain a higher contrast, they proposed a bilayer-type step-and-flash imprint lithography using UV-curable resist⁹² covered on the top by PFMPS. After patterning of the UV-curable resist, the template was demolded from the substrate and PFMPS was spin-coated on the top of the structures to form a bilayer structure with a distinctly different etch selectivity between the top layer and the underlying one. Argon sputtering was applied to homogeneously etch down the polymer until the organic imprint material became exposed. Subsequent treatment with oxygen plasma was performed to remove the exposed organic imprint material and keeping the PFMPS lines on the substrate. Finally pattern transfer into the silicon substrate was accomplished by the use of a $\text{CHF}_3/\text{SF}_6/\text{O}_2$ plasma and the resist was stripped off with nitric acid (**Figure 3.11**).

Figure 3.11. Fabrication process of UV-light-assisted nanoimprint lithography using a spin coated top layer of PFMPS. Reprinted with permission from 92. Copyright 2009 American Chemical Society.

With this technique, etch-resistant patterns of PFMS with sizes down to the nanometer range could be created. Nevertheless, because it is a bilayer process, the

final pattern size is defined not only by the imprinting resist but also depends on the subsequent etch processes. PFMPs play an important role here as it provides a very high selectivity over UV-curable resist.

The S-FILTM method⁹³ was used to create PFMPs patterns on a substrate. A template consisting of lines of 100 nm wide pitches of 1:1, 1:2 and 1:3 and with a height of 100 nm was used. By SEM, the thickness of the transfer layer was determined to be 60 nm, the residual UV-curable resist layer after imprinting was about 40-50 nm and the PFMPs after spin-coating in toluene was 60 nm on the top of a line and 120 nm between two lines. The etch rate of PFMPs upon argon sputtering was determined to be 1.5 nm/min. Then the exposed organic imprint layer and the transfer layer material underneath were selectively etched by O₂ RIE. The O₂ RIE etch rates of PFMPs and the organic imprint material were found to be 1 and 60 nm/min, respectively, which results in an etch selectivity of 60. Because of the oxide-layer formation, PFMPs lines stayed intact while the material between the lines was totally removed. PFMPs lines down to 30 nm were obtained after oxygen plasma treatment as shown in **Figure 3.12.b**. Patterning of the silicon substrate was then tested with CHF₃ and SF₆ plasma. The etch rates into Si and PFMPs were 300 and 1 nm/min, respectively, resulting in a etch contrast of 300. This process permitted Huskens, Vancso and co-workers to combine the advantages of UV-NIL with the high etch resistance of PFS to realize the fabrication of feature sizes down to the sub-100 nm range.

Figure 3.12. SEM images of lines fabricated after oxygen RIE of (a) 80 nm PFMPs lines and (b) 30 nm PFMPs lines after 2 min of treatment. (c) 100 nm PFMS lines after 2.5 min treatment. The dark stripes in the images correspond to PFMPs lines. Reprinted with permission from 92. Copyright 2009 American Chemical Society.

3.4.4. Nanosphere assisted lithography

A nanosphere lithography multilayer fabrication process for a freestanding poly(ethersulfone) (PES) membrane with well-defined pore size was proposed by Vancso, Huskens and co-workers.⁹⁴ This procedure employed a self-assembled colloidal silica layer as template, embedded in a PFMPs matrix which acted as etch resist. As shown in **Figure 3.13**, first, a sacrificial layer of cellulose acetate was spin-coated on a silicon substrate, followed by spin-coating of PES. Then a well-ordered and closely packed assembly of silica nanoparticles was deposited by the convective self-assembly method⁹⁵ and PFMPs was spin-coated on the top to fill the pores between the silica particles. Subsequently, argon sputtering was used to remove the top layer of PFMPs and silica particles, exposing a well-ordered surface of half nanospheres surrounded with PFMPs. The ordered hexagonal close-packed pattern was then transferred by oxygen plasma treatment into the PES layer and the sacrificial layer. Contrary to conventional nanosphere lithography, the silica particles are not used as an etch mask but as an inversion mask, PFMPs being the etch mask. Finally, the PFMPs layer was removed by nitric acid treatment and the sacrificial layer of cellulose acetate was dissolved in acetone in order to obtain freestanding PES films.

Figure 3.13. Scheme of freestanding PES membranes by silica nanosphere-assisted lithography. Copyright © 2009 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim from 94.

Figure 3.14. SEM images of (A) a 300 nm silica particle array, (D) particles treated with argon sputtering after PFMPs spin-coating, (G) the substrate after particle removal by HF and (j) the substrate after oxygen plasma and PFMPs removal. (B), (E), (H) and (K) are the corresponding 3D AFM images and (C), (F), (I) and (L) show the corresponding height profile. Copyright © 2009 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim from 94.

The silica particles used were of a size of 300 nm and the PES membrane was shown to have a thickness of 500 nm and a pore size of about 230 nm. The pore size was less than the size of the particles used due to the difference in sputtering rate of PFMPS and silica nanoparticles in a stream of Ar^+ ions. **Figure 3.14** shows the SEM, AFM images and the AFM section profile of freestanding PES films at different stages of the process.

3.5. Poly(ferrocenylsilane)-based block copolymers in “maskless” nanolithography applications

3.5.1. Block copolymer microphase separation

Block copolymers (BCPs) are macromolecules composed of two or more different polymeric segments. Due to this segmented structure, BCPs tend to phase-separate and order themselves into a range of complex periodic domains with a size of tens of nanometers. **Figure 3.15** shows the classical morphologies in diblock copolymer systems depending on the volume fraction of the two phases; here the volume fraction of the black block increases from left to right. These include body-centered-cubic packed spheres, hexagonally packed cylinders and alternating lamellae.

Figure 3.15. The classical morphologies in block copolymer systems. With kind permission from Springer Science and Business Media from 25.

A complete study of microphase separation in block copolymers was done by Leibler in 1980.⁹⁶ In the example of a pure diblock copolymer A-B, the driving force

for phase-separation is due to the free energy cost of contact between block A and B which is described by the Flory-Huggins interaction parameter χ_{AB} . Several experimental methods to determine this parameter exist, including light scattering,⁹⁷⁻⁹⁹ small angle neutron scattering (SANS),¹⁰⁰⁻¹⁰⁴ ellipsometry,¹⁰⁵ melting point depression and comparison of solubility parameters.¹⁰⁶ The equilibrium structure depends also significantly on the degree of polymerization, N , of each block. At large N , the minimization of A-B contacts and phase-separation is thermodynamically more favorable even if there is a loss in translational and configurational entropy due to the separate domains of each block. The magnitude of χN determines whether a block copolymer will phase-separate into an ordered system or remain disordered. The order-disorder transition (ODT) is where the BCP phase-separates when χN exceeds a critical value denoted χN_{ODT} . The relative volume fraction ϕ of A and B defines the morphology that the block copolymer will reach at the equilibrium after phase-separation, while the size of each domain is directed by the degree of polymerization N .

For a BCP system in the strong segregation limit ($\chi N \gg 10$), the width of the interfaces separating block A from block B can be described by $\alpha\chi^{-1/2}$ where α is the characteristic segment length of a monomer unit. Consequently, the creation of sharper interfaces between each block, allowing features with a smaller edge roughness, is possible with higher χ -values. Furthermore, the period of the phase-separated microdomains can be described as $D \sim \alpha N^{2/3} \chi^{1/6}$. This means that a reduction of N while maintaining χN over the critical value for phase-separation, would lead to smaller features with a smaller period.¹⁰⁷ Several organic BCP systems have been studied, e.g., PS-*b*-PMMA, PS-*b*-PI and PS-*b*-PB, but their relatively low χ -values limit the definition of the domains and the scaling down of the features. Inorganic-organic BCPs, such as PFS-based BCPs, tend to have higher χ -values¹⁰⁸ and therefore allow the formation of sharp interfaces separating the domains. Anionic polymerization enabled the preparation of various PFS-based BCPs with

narrow polydispersity and low N , permitting the formation of well-defined microdomains with small size.

The solubility of BCPs in various solvents allows their processing into thin films on solid substrates, for instance by spin-coating. The phase-separation still occurs and detailed studies on the influence of block copolymer composition, molar mass and film thickness on microdomain morphology have been possible using AFM. **Figure 3.16** shows the tapping mode AFM phase images of PI-*b*-PFS of 30 nm thin films with different volume fractions. The morphology of PI-*b*-PFS with a molar mass ratio PI/PFS of 29/15 (in kg/mol for each block), corresponding to 28 vol.% of the organometallic phase, displays an in-plane worm-like cylindrical PFS microdomain structure with an average distance between domains of 32 nm (**Figure 3.16.a**). Parallel orientation is induced by preferential segregation of the lower surface energy PI phase at the surface. A thin film of 31/13, corresponding to 24 vol.% of PFS phase, displays a mixture of the previous worm-like cylindrical structures and also exhibits domains of hexagonally arranged dots. From the 2D Fourier transform, the lattice spacing of these dots was determined to be 29 nm, resulting in a domain spacing of 33 nm (**Figure 3.16.b**). A thin film of 36/12, corresponding to 20 vol.% of PFS, shows a fully hexagonal microdomain morphology with a domain spacing of 30 nm (**Figure 3.16.c**).

Other PFS-based diblock copolymers have also been studied, such as PS-*b*-PFDMS¹⁰⁹, PS-*b*-PFEMS^{110, 111} or poly(styrene)-*b*-poly(ferrocenylisopropylmethylsilane) (PS-*b*-PFiPMS).¹¹² However, in order to obtain a larger variety of ordered structures with more complexity, different copolymer structures have been developed and their phase-separation studied. **Figure 3.17** shows, for example, a simple geometry prediction of the different morphologies that an ABC triblock terpolymer can adopt. These morphologies only take into account the possible combinations of lamellar, cylindrical and spherical microdomains but more complex microdomains have been observed.^{113, 114}

Figure 3.16. Tapping mode AFM phase images of 30 nm PI-b-PFS thin spin-coated films. a) PI/PFS = 29/15 (in kg/mol), i.e., 28 vol.% of PFS. b) PI/PFS = 31/13, i.e., 24 vol.% of PFS. c) PI/PFS = 36/12, i.e., 20 vol.% of PFS. The insets (top right) show the 2D Fourier transform. Adapted with permission from 54. Copyright 2000 American Chemical Society.

Figure 3.17. Possible microdomain morphologies for three-phase structures of ABC triblock terpolymers composed of lamellar, cylindrical and spherical microdomains. Reprinted from 115, Copyright 2002, with permission from Elsevier.

Blends of PFS-based diblock copolymer with the corresponding homopolymers also presented different morphologies.¹¹⁶ As shown in **Figure 3.18**, bicontinuous gyroidic morphologies of blends of PFS-*b*-PMMA in different volume fractions (percentage of each block in subscript) with PFS or PMMA homopolymers (hPFS and hPMMA) have been demonstrated. Annealing temperature was also found to be an important parameter. The influence of annealing temperature on the morphology of the triblock copolymer PS-*b*-PB-*b*-PMMA was presented earlier.¹¹⁷ Solvent annealing is also possible and was studied as well. Later, pentablock copolymer PMMA-*b*-PFS-*b*-PS-*b*-PFS-*b*-PMMA systems⁴⁹ and recently PS-PI-PFS star terpolymer systems⁵¹ have been studied and revealed more complex microdomains as shown in **Figure 3.19** and **Figure 3.20**, respectively.

Figure 3.18. TEM images of (a) PFS36-*b*-PMMA64 + 4% hPFS annealed at 190 °C. (b) PFS37-*b*-PMMA63 + 2% hPFS annealed at 190 °C. (c) PFS40-*b*-PMMA60 + 5 vol% hPFS annealed at 190 °C. (d) PFS45-*b*-PMMA55 + 6 % hPMMA annealed at 190 °C. Adapted with permission from 116. Copyright 2004 American Chemical Society.

Figure 3.19. TEM images and corresponding morphology schemes of a PMMA-*b*-PFS-*b*-PS-*b*-PFS-*b*-PMMA pentablock copolymer presenting different morphologies. (a) Lamellar morphology of PS and PMMA with PFS droplets at the interphase. (b) Spheres-on-spheres morphology. Thin films were cast from dichloromethane solution and annealed for 1 day at 180 °C. Copyright © 2004 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim from 49.

Figure 3.20. TEM images of thin-sectioned bulk films of PFS star terpolymer with the corresponding morphology scheme. (a) Polymer 1 PS/PI/PFS = 12.7/15.5/71.8 wt%, no stain. (b) Same as a) with OsO₄ stain. (c) Polymer 2 PS/PI/PFS = 42.5/29.7/27.7 wt%, no stain. (d) Same as c) with OsO₄ stain. (e) Polymer 2 PS/PI/PFS = 36.3/35.5/28.1 wt%, no stain. (f) Same as e) with OsO₄ stain. Adapted with permission from 51. Copyright 2013 American Chemical Society.

Anionic polymerization has given the opportunity to synthesize well-defined and sophisticated PFS-based structures which opened a broad research of PFS-based block copolymer microdomain phase-separation in bulk and in thin films.

3.5.2. Block copolymer thin films as nanolithographic templates

The ability of block copolymer thin films to self-assemble into tunable and different morphologies makes them suitable candidates for bottom-up lithography processes. The nanoscale ordered structures formed by block copolymer self-assembly can be transferred into an underlying substrate via plasma etching. As traditional photoresists, they act as sacrificial templates but the bottom-up approach obviates the complicated template designs and expensive optical setups. In the late 90's, Register, Chaikin and co-workers, used poly(styrene)-*b*-poly(butadiene) and poly(styrene)-*b*-poly(isoprene) for the fabrication of periodic arrays of densely packed holes.^{118, 119} The self-assembly into a hexagonally packed array of PB cylinders and into body-centered-cubic ordered spheres of PI, both embedded in a PS matrix, allowed the etching of holes with sizes reaching approximately 13 nm and a lattice constant of 27 nm. Later, PS-*b*-PMMA was used for the fabrication of several microelectronic devices, e.g., semiconductor capacitors,^{120, 121} field effect transistors¹²² and flash memory devices.^{123, 124} But as mentioned previously (part 3.5.1.), these block copolymers present low χ -values. Other organic BCP systems with high χ -values exist, e.g., amphiphilic polystyrene-block-poly(4-vinylpyridine) and PS-*b*-PEO, but their low etch selectivity between the organic blocks reduces their potential in the fabrication of nanoscale features with high contrast.

PFS-based block copolymer lithography, because of the high χ -values which allow high contrast of the domains, as discussed in part 3.5.1. , and the good etch selectivity between the PFS block and the organic block, as shown in part 3.3. , appears to be an excellent system for pattern transfer. Vancso, Ross and co-workers used PS-*b*-PFS for the fabrication of an ultra-high density cobalt magnetic dot array via BCP

lithography.¹²⁵ **Figure 3.21** shows the fabrication process of the cobalt magnetic dot array.

Figure 3.21. Fabrication process of a cobalt magnetic dot array via block copolymer lithography. Tilted SEM images of the intermediate stages of cobalt magnetic dot array formation via block copolymer lithography. © 2001 WILEY-VCH Verlag GmbH, Weinheim, Fed. Rep. of Germany from 125.

Figure 3.22. (a) TEM and (b-f) SEM images and the corresponding morphology scheme of: (a) unblended bulk 3 μ -ISF, (b-d) blended 3 μ -ISF with 15 vol% of PS homopolymer on untreated Si wafer with chloroform annealing at (b) 0.7P0, (c) 0.75 P0 and (d) 0.85 P0. (e-f) blended 3 μ -ISF with 15 vol% of PS homopolymer on P2VP-coated surface with chloroform annealing at (e) 0.75P0 and (f) 0.8P0. Samples were stained with OsO4. Thin films (b-f) were etched by O2 RIE before SEM observation, so PFS appears bright and regions formerly occupied by PS appear dark. The film thicknesses were (b-e) 34 nm and (f) 42 nm. Scale bars are 200 nm. Reprinted with permission from 126. Copyright 2013 American Chemical Society.

PS-*b*-PFS diblock copolymer with 20 vol.% of PFS was spin-coated, using a 2% solution, on a multilayer substrate of silica, tungsten and cobalt. After annealing, the 60 nm thin films presented close-packed PFS spheres in a PS matrix. The spheres were found to be about 25 nm in diameter with a periodicity of 50 nm. The block copolymer lithographic mask was formed through an oxygen plasma reactive ion

etching process (RIE). This step removes the PS block and leaves the PFS block with a thin layer of iron and silicon oxide on the top, giving a high etch resistance (see part 3.3.). Then the PFS pattern was transferred into the silicon film using CHF_3 -RIE. The tungsten hard mask was patterned using CF_4+O_2 -RIE. The silicon and residual polymer layers were then removed by high pressure ashing. Finally the cobalt dot array was formed using ion beam etching using the tungsten pattern as hard mask. The cobalt dots after etching had diameters of 20 nm.

Recently, Manners, Ross and co-workers used the self-assembly of 3-miktoarm star terpolymer chains of polyisoprene-arm-polystyrene-arm-polyferrocenylethylmethylsilane ($3\text{ }\mu\text{-ISF}$) thin films to create novel microdomain structures.¹²⁶ Their use as nanolithographic masks was also demonstrated by the transfer of square and triangular hole arrays into a substrate. As shown in **Figure 3.22**, a range of 2D Archimedean tiling was obtained after solvent annealing of $3\text{ }\mu\text{-ISF}$ with PS homopolymer blends. The $3\text{ }\mu\text{-ISF}$ consisted of PI/PS/PFS with a volume fraction of 39/35/26 vol.% and a polydispersity index (PDI) of 1.03, and the homo-PS had a molar mass of 10 kg/mol with a PDI of 1.08. This narrow PDI was obtained by anionic polymerization (see part 3.2.). Furthermore, it was shown that thin films annealed on a substrate with P2VP brushes, which are preferentially wetted by PI, produced additional morphologies (see **Figure 3.22.e-f**). Thin films were then etched by O_2 RIE before SEM observation. PFS appears bright and regions formerly occupied by PS appear dark.

Later, they used solely a $3\text{ }\mu\text{-ISF}$, without adding homopolymer, consisted of PI/PS/PFS with a volume fraction of 34/43/23 vol.% and annealed in chloroform vapor to obtain a “knitting pattern” morphology.¹²⁷ This system allowed the formation of periodic structures consisting of undulating lamellae and alternating cylinders and it was shown that the knitting morphologies could be tuned by varying the film thickness. Furthermore, 90° bends and T-junctions which are generally considered energetically unstable conformations in block copolymers were obtained, due to the unique microdomain structure of the films, as shown in **Figure 3.23**.

Figure 3.23. SEM images of 3μ -ISF thin films with different thickness and different RIE exposure times. The film thicknesses were (a) 28 nm, (b,e,f) 35 nm, (c) 40 nm, and (d) 43 nm. The films were etched in O₂ RIE for (a)–(d) 15 s, (e) 20 s, and (f) 30 s. Samples were stained with OsO₄ before RIE treatment. Scale bars are 300 nm. Adapted with permission from 127. © 2014 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

3.5.3. Nanostructures with long-range guided order using block copolymer lithography

The use of the self-assembling properties of block copolymers for block copolymer lithography has been shown to yield nanoscale patterns over large areas. These patterns present good short-range order but the order is reduced over longer ranges which can be a limitation for block copolymer lithography. The combination of block copolymer self-assembly with long-range ordering methods could permit the fabrication of nanostructures in precise positions on a substrate. Graphoepitaxy is a method that uses surfaces patterned with shallow grooves to order nanostructures formed by the phase-separation of block-copolymers.¹²⁸ Several examples of graphoepitaxy using PFS-based copolymers are presented below.

Figure 3.24 shows how the long-range pattern order of a thin film of PS-*b*-PFS diblock copolymer changes with the width of the grooves in which the film is

deposited.¹²⁹ Within the 500-nm-wide groove, about three rows of close-packed PFS features are aligned parallel to the sidewall (**Figure 3.24.a**). In the 320-nm-wide groove, alignment of the PFS features was observed across the groove, but a significant amount of defects existed (**Figure 3.24.b**). However, in the 240-nm-wide groove, the alignment was almost perfect with a sixfold symmetry and the pattern in each groove has the same orientation, as shown in the superposed fast Fourier transform of the image in **Figure 3.24.c**. The rare domain-packing defects were apparently caused by the edge roughness of the grooves. The patterns were then transferred to the silicon substrate by a single etching step, resulting in arrays of well-ordered silica pillars with 20 nm diameters and aspect ratios above 3.

By using a similar PS-*b*-PFS diblock copolymer thin film, spin-coated in etched channels of 30-80 nm wide, isolated 1D arrays of distorted PFS spheres were obtained.¹³⁰ In the confined channels of width W , approaching the row spacing of the spherical domains, d_0 , a single row of ordered PFS domains was observed over the range $0.6 < W/d_0 < 1.5$ (**Figure 3.25**). The ellipticity of the domains and the orientation of their major axis were controlled by W/d_0 . At $W/d_0 \sim 1.0$, the domain projections were circular, for $W/d_0 > 1.0$, they were elongated perpendicular to the channel, and for $W/d_0 < 1.0$, they were elongated parallel to the channel. Below a W/d_0 of 0.6, the domains were found to be hemispheres and above 1.5, regions consisted of two rows of domains. This method allowed the fabrication of a linear array of dots which is difficult to create by conventional lithography.

Figure 3.24. SEM images of 48 h annealed and plasma-treated PS/PFS 50/12 spin-coated films at 3500 rpm on a silica substrate with (a) 500-nm-wide, (b) 320-nm-wide and (c) 240-nm-wide grooves. Reprinted with permission from 129. Copyright 2002 American Institute of Physics.

Figure 3.25. SEM images of PS-*b*-PFS domains within channels of different confinement widths W , proportional to the equilibrium row spacing, d_0 . Reprinted with permission from 130. Copyright 2006 American Chemical Society.

The influence of topographically patterned substrates on the spherical morphology and close-packing of PS-*b*-PFS domains was also studied by templating thin films within V-shaped grooves.¹³⁰ The V-grooves promoted the formation of a well-ordered face-centered cubic (fcc) close-packed sphere array with (100) planes of the array parallel to the groove walls (**Figure 3.26.b**), while it typically formed a body-centered cubic (bcc) sphere array in bulk. The top surface of the close-packed array, parallel to the substrate, showed a square symmetry (see **Figure 3.26.a**), while a monolayer of spherical domains showed a hexagonal symmetry.

Figure 3.26. SEM images of PS-*b*-PFS films in V-grooves after 72h annealing and etching. (a) Square packing from the top view. (b) Cross-section of the same groove showing a sphere array with 11 rows presenting a fcc packing. Reprinted with permission from 130. Copyright 2006 American Chemical Society.

Successful positioning of PI-*b*-PFS block copolymer spheres in hexagonal grooves was also achieved and complete 2D alignment was demonstrated.¹³¹ **Figure 3.27** shows the alignment of the domains with respect to the six side walls over the entire 800-nm-diameter hexagonal groove. The hexagonal grooves open up the possibility of accurate positioning of the domains, since one single domain is located in each corner, as shown in **Figure 3.27.b**.

Figure 3.27. SEM images of PI-*b*-PFS thin film self-assembly (a) in a 800-nm-wide hexagonal groove and (b) zoom on the corner showing single domain positioning. Copyright © 2007 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim from 131.

The block copolymer architecture and the wettability of the substrate also play a key role in the self-assembly of the domains. **Figure 3.28** illustrates both factors combined with graphoeptaxy by showing the self-assembly of a triblock terpolymer PI-*b*-PS-*b*-PFS blended with PS (ISF/PS), deposited as a thin film within shallow etched grooves in silica. As shown in **Figure 3.28.a**, thin films of the ISF/PS blend presented perfectly ordered cylinders with square-packed morphology and the number of rows was controlled by the width of the grooves. The dots on the top view show PFS cylinders after etching of PS and PI blocks. The influence of the substrate surface chemistry was proved by coating the walls of the grooves with PS brushes. The difference in wettability of the various blocks leads to a different morphology during self-assembly. While an uncoated groove gave square-packed cylinders with the principal axis at 90° of the walls of the trench, PS brush coated grooves provided PFS microdomain arrays with 45° orientation, as shown in **Figure 3.28.b**.

Figure 3.28. (a,b) SEM images of ISF/PS blend self-assembly in shallow grooves after annealing in chloroform vapor for 2.5 h at room temperature, followed by etching with O_2 -RIE to remove PI and PS domains, (a) with uncoated trenches and (b) with PS-brush coated trenches. (c, d) Schematic of the options for packing the microdomains with (c) uncoated trenches and (d) PS-brush coated trenches. Adapted with permission from 132. Copyright 2009 American Chemical Society.

The polymer film thickness of the previous system was investigated and thicker films of $\sim 35 \text{ nm}$ presented different morphologies. As shown in **Figure 3.29.a**, for PS-brush coated trenches the PFS (and PI) cylinders lie in plane perpendicular to the trench walls without contacting the walls. Contrary to the previous examples of cylinders oriented perpendicular to the substrate surface, which was attributed to kinetic effects, the orientation in this case comes from the requirement for the middle PS block to contact the trench walls while maintaining its connectivity to the in-plane PI and PFS cylinders. In contrast, untreated grooves showed regions of mixed parallel and perpendicular cylinders (**Figure 3.29.b,c**). **Figure 3.29.b** presents the case of narrow trenches containing in-plane PFS cylinders parallel to the trench walls and rows of cylinders oriented perpendicular to the substrate surface. **Figure 3.29.c** shows wider grooves containing a variety of morphologies including branched cylinders and 90 and 45° oriented arrays. These results demonstrated that the cylinder microdomain orientation and the principal axes of the cylinder lattice can be controlled by tuning the film thickness and the relative affinity of the groove walls.

Figure 3.29. SEM images of ~ 35 nm thick films of ISF/PS blend assembly in (a) a PS-brush coated template and (b,c) uncoated silica substrates with (b) narrow and (c) wide grooves, after annealing and etching with oxygen RIE. Reprinted with permission from 132. Copyright 2009 American Chemical Society.

In order to gain more control on the positioning and ordering of the PFS cylindrical microdomains over a larger surface areas, topographically guiding walls and posts were recently used by Ross, Manners and co-workers.¹³³ Topographical ridge patterns with a rectangular layout and sparse arrays of posts were prepared by electron-beam patterning of a negative-tone inorganic hydrogen silsesquioxane (HSQ) resist (**Figure 3.30**). To obtain preferential wetting on the sidewalls and nonpreferential wetting on the horizontal substrate surface, the substrate was functionalized with a PEO brush layer and the sidewalls and posts were coated with a PFS brush layer. Highly ordered square patterns with a 44 nm period and an average grain size on the micrometer scale were produced. Topographical templates consisting of rectangular walls could produce “single grain” square symmetry patterns inside the template (**Figure 3.30.a-c**), while single and double HSQ post arrays allowed the authors to accurately align and register the PFS arrays (**Figure 3.30.d-f**). This method shows that a perfect control and positioning of the self-assembled block copolymer domains is possible, enabling the design of lithographic masks which can be used in the fabrication of complex CMOS.

Figure 3.30. (a,d) Schematics and (b,c,e,f) SEM images of highly ordered square arrays of ISF/PS blend self-assembly in HSQ templates consisting on (b) 1.5 and $2\ \mu\text{m} \times 3\ \mu\text{m}$ topographical sidewalls, (c) $0.5\ \mu\text{m}$, $1\ \mu\text{m}$ and $1.5\ \mu\text{m} \times 4\ \mu\text{m}$ topographical sidewalls, (e) $88\ \text{nm} \times 132\ \text{nm}$ single posts and (f) $44\ \text{nm}$ spacing double posts. Adapted with permission from 133. Copyright 2011 American Chemical Society.

3.6. Conclusion

In this chapter, the ability of anionic polymerization to synthesize various well-defined PFS-based copolymers with a narrow molar mass distribution, a low degrees of polymerization, and complex architectures, have been shown. The range of usable monomers was even expanded by the discovery of photoassisted anionic polymerization and the developments in the end-capping of living PFS chains, such

as the use of a silacyclobutane which is acting as a "carbanion pump". Due to the possibility of varying the side groups of PFSs, a wide range of controllable properties has become accessible. Considering its exceptionally high resistance towards plasma etching, PFS may be of considerable value as an etch resist material in CMOS fabrication. The protective layer of silicon-oxide and iron-oxide formed on PFS features during reactive ion etching processes allows high contrasts to be achieved compared to common organic polymers. This contrast can be controlled by adjusting the conditions during the etching process, and one of the remaining challenges is to find the perfect parameter settings for etching, such as gas composition and pressure.

PFSs may be used as resists in soft lithography-based patterning approaches. Such patterning methods are both versatile and cost-effective, and enable the generation of patterns at the micro and submicrometer scales. PFSs have also been employed as resists in nanoimprint lithography processes, which offers advantages compared to conventional optical lithography techniques, due to the suppression of resolution limitations caused by diffraction. Several examples in which PFS was used as a resist in soft lithography, nanoimprint lithography and nanosphere-assisted lithography, have been presented. These examples demonstrate the utility of PFS in both micro and nanofabrication.

Nevertheless, for sub-10-nm-node fabrication, challenging techniques remain to be developed and bottom-up lithography seems to hold the greatest potential. PFS-based BCPs are optimal candidates for bottom-up resists because of their low polydispersity, accurately controlled degrees of polymerization, high χ -value, high selectivity to etching, and long-range order of the microstructures. Polymer thin film physics differs from the bulk; therefore, properties, such as thermal transitions and surface viscoelasticity need to be studied separately for each system. Precise and quantitative molar mass characterization is also required to obtain PDIs for both components and blocks. Edge roughness and defects must be reduced to improve pattern fidelity. The microphase separation patterns and the phase separation kinetics remain to be studied in detail. Long-range order has been induced using

graphoepitaxy and several controlled geometries have been fabricated by this method. The ability to form ordered 3D arrangements makes BCPs attractive for the templated self-assembly of nanoscale periodic arrays. The coating of substrates by polymer brushes provides access to additional morphologies and constitutes an important tool in guided BCP self-assembly. Surfaces of underlying substrates and of topographic features in graphoepitaxy can be tailored to preferentially attract one block. Therefore, insight in creating both neutral and block-selective surfaces is needed. Substrate engineering opens several new research avenues by giving opportunities to control grafting type, i.e. "to" or "from", grafting density and composition, and chain length. Furthermore, solvent and high temperature annealing must be optimized to reduce both fabrication time and chemical costs, and make these processes more feasible. In addition to BCP self-assembly, it would be of interest to create patterns of etch resistant materials with thicknesses of 1 or 2 nm. The assembly of nanomaterials into such ultrathin barrier layers, is expected to further improve resolution in the fabrication of nanoscale CMOS.

BCPs, soft matter and inorganic materials, such as nanooptics and QD emitters, could also be integrated into complex systems with applications in areas, such as sensing and bionanomedicine. Resist development for CMOS fabrication, requiring ever smaller feature sizes and low defect densities, will continue to challenge polymer scientists in the years ahead.

3.7. References

1. Wanlass, F.M., *Low stand-by power complementary field effect circuitry*. 1967, FAIRCHILD CAMERA INSTR CO: United States.
2. Baker, R.J., *CMOS: Circuit Design, Layout, and Simulation*. 2011: Wiley.
3. Haron, N.Z. and S. Hamdioui. *Why is CMOS scaling coming to an END?* in *Design and Test Workshop, 2008. IDT 2008. 3rd International*. 2008.
4. Kusumoto, S., et al., *Advanced materials for 193 nm immersion lithography*. *Polymers for Advanced Technologies*, 2006. **17**(2): p. 122-130.

5. Hori, M., et al., *Sub-40-nm half-pitch double patterning with resist freezing process*. 2008: p. 69230H-69230H.
6. Pease, R.F. and S.Y. Chou, *Lithography and Other Patterning Techniques for Future Electronics*. Proceedings of the IEEE, 2008. **96**(2): p. 248-270.
7. Acikgoz, C., et al., *Polymers in conventional and alternative lithography for the fabrication of nanostructures*. European Polymer Journal, 2011. **47**(11): p. 2033-2052.
8. Kaufmann, T. and B.J. Ravoo, *Stamps, inks and substrates: polymers in microcontact printing*. Polymer Chemistry, 2010. **1**(4): p. 371-387.
9. Hadjichristidis, N., S. Pispas, and G. Floudas, *Block Copolymers: Synthetic Strategies, Physical Properties, and Applications*. 2003: Wiley.
10. Hamley, I.W., *Developments in Block Copolymer Science and Technology*. 2004: Wiley.
11. Stoykovich, M.P. and P.F. Nealey, *Block copolymers and conventional lithography*. Materials Today, 2006. **9**(9): p. 20-29.
12. Stoykovich, M.P., et al., *Directed Assembly of Block Copolymer Blends into Nonregular Device-Oriented Structures*. Science, 2005. **308**(5727): p. 1442-1446.
13. Team, E.R.M., *International Technology Roadmap for Semiconductors: Emerging Research Materials*, I.T.R.f. Semiconductors, Editor. 2007.
14. Chi, L., *Nanotechnology: Volume 8: Nanostructured Surfaces*. 2010: John Wiley & Sons.
15. Nunns, A., J. Gwyther, and I. Manners, *Inorganic block copolymer lithography*. Polymer, 2013. **54**(4): p. 1269-1284.
16. Rosenberg, H. and M.D. Rausch, *Silicon-containing dicyclopentadienylmetal compounds and polymers and methods for preparing same US Patent 3060215*. 1962.
17. Foucher, D.A., B.Z. Tang, and I. Manners, *Ring-opening polymerization of strained, ring-tilted ferrocenophanes: a route to high-molecular-weight poly(ferrocenylsilanes)*. Journal of the American Chemical Society, 1992. **114**(15): p. 6246-6248.
18. Fossum, E., et al., *Polysilane-Poly(ferrocenylsilane) Random Copolymers*. Macromolecules, 1995. **28**(1): p. 401-402.
19. Gómez-Elipé, P., P.M. Macdonald, and I. Manners, *Architectural Control in the Transition-Metal-Catalyzed Ring-Opening Polymerization of Silicon-Bridged [1]Ferrocenophanes*. Angewandte Chemie International Edition in English, 1997. **36**(7): p. 762-764.
20. Ni, Y., et al., *Transition metal catalyzed ring-opening polymerization of silicon-bridged [1]ferrocenophanes at ambient temperature*. Macromolecular Rapid Communications, 1995. **16**(9): p. 637-641.
21. Gómez-Elipé, P., et al., *Transition Metal Catalyzed Ring-Opening Polymerization (ROP) of Silicon-Bridged [1]Ferrocenophanes: Facile Molecular Weight Control and the Remarkably Convenient Synthesis of*

- Poly(ferrocenes) with Regioregular, Comb, Star, and Block Architectures*. Journal of the American Chemical Society, 1998. **120**(33): p. 8348-8356.
22. Rulkens, R., A.J. Lough, and I. Manners, *Anionic ring-opening oligomerization and polymerization of silicon-bridged [1]ferrocenophanes: Characterization of short-chain models for poly(ferrocenyldimethylsilane) high polymers*. Journal of the American Chemical Society, 1994. **116**(2): p. 797-798.
23. Tanabe, M. and I. Manners, *Photolytic Living Anionic Ring-Opening Polymerization (ROP) of Silicon-Bridged [1]Ferrocenophanes via an Iron-Cyclopentadienyl Bond Cleavage Mechanism*. Journal of the American Chemical Society, 2004. **126**(37): p. 11434-11435.
24. Rasburn, J., et al., *Solid-State Synthesis and Morphology of Poly(ferrocenyldimethylsilane)*. Chemistry of Materials, 1995. **7**(5): p. 871-877.
25. Korczagin, I., et al., *Surface Nano- and Microstructuring with Organometallic Polymers*, in *Ordered Polymeric Nanostructures at Surfaces*, G.J. Vancso, Editor. 2006, Springer Berlin Heidelberg. p. 91-117.
26. Nelson, J.M., H. Rengel, and I. Manners, *Ring-opening polymerization of [2]ferrocenophanes with a hydrocarbon bridge: synthesis of poly(ferrocenylethylenes)*. Journal of the American Chemical Society, 1993. **115**(15): p. 7035-7036.
27. Nelson, J.M., A.J. Lough, and I. Manners, *Synthesis and Ring-Opening Polymerization of Highly Strained, Ring-Tilted [2]Ruthenocenophanes*. Angewandte Chemie International Edition in English, 1994. **33**(9): p. 989-991.
28. Gallei, M., et al., *Defined Poly[styrene-block-(ferrocenylmethyl methacrylate)] Diblock Copolymers via Living Anionic Polymerization*. Macromolecular Rapid Communications, 2009. **30**(17): p. 1463-1469.
29. Foucher, D., et al., *Synthesis, Characterization, and Properties of High Molecular Weight Unsymmetrically Substituted Poly(ferrocenyldimethylsilanes)*. Macromolecules, 1994. **27**(14): p. 3992-3999.
30. Foucher, D.A., et al., *Synthesis, characterization, glass transition behavior, and the electronic structure of high-molecular-weight, symmetrically substituted poly(ferrocenyldimethylsilanes) with alkyl or aryl side groups*. Macromolecules, 1993. **26**(11): p. 2878-2884.
31. Manners, I., *Polymer science with main group elements and transition metals*. Macromolecular Symposia, 2003. **196**(1): p. 57-62.
32. Kulbaba, K. and I. Manners, *Polyferrocenyldimethylsilanes: Metal-Containing Polymers for Materials Science, Self-Assembly and Nanostructure Applications*. Macromolecular Rapid Communications, 2001. **22**(10): p. 711-724.

33. Manners, I., *Poly(ferrocenylsilanes): novel organometallic plastics*. Chemical Communications, 1999. **0**(10): p. 857-865.
34. Hempenius, M.A., F.F. Brito, and G.J. Vancso, *Synthesis and Characterization of Anionic and Cationic Poly(ferrocenylsilane) Polyelectrolytes*. Macromolecules, 2003. **36**(17): p. 6683-6688.
35. Wang, Z., A. Lough, and I. Manners, *Synthesis and Characterization of Water-Soluble Cationic and Anionic Polyferrocenylsilane Polyelectrolytes*. Macromolecules, 2002. **35**(20): p. 7669-7677.
36. Hempenius, M.A. and G.J. Vancso, *Synthesis of a Polyanionic Water-Soluble Poly(ferrocenylsilane)*. Macromolecules, 2002. **35**(7): p. 2445-2447.
37. Hempenius, M.A., et al., *Organometallic Polyelectrolytes: Synthesis, Characterization and Layer-By-Layer Deposition of Cationic Poly(ferrocenyl(3-ammoniumpropyl)-methylsilane)*. Macromolecular Rapid Communications, 2001. **22**(1): p. 30-33.
38. Power-Billard, K.N. and I. Manners, *Hydrophilic and Water-Soluble Poly(ferrocenylsilanes)*. Macromolecules, 1999. **33**(1): p. 26-31.
39. Ginzburg, M., et al., *Layer-by-Layer Self-Assembly of Organic–Organometallic Polymer Electrostatic Superlattices Using Poly(ferrocenylsilanes)*. Langmuir, 2000. **16**(24): p. 9609-9614.
40. Wurm, F., S. Hilf, and H. Frey, *Electroactive Linear–Hyperbranched Block Copolymers Based on Linear Poly(ferrocenylsilane)s and Hyperbranched Poly(carbosilane)s*. Chemistry – A European Journal, 2009. **15**(36): p. 9068-9077.
41. Sui, X., et al., *Preparation of a Rapidly Forming Poly(ferrocenylsilane)-Poly(ethylene glycol)-based Hydrogel by a Thiol-Michael Addition Click Reaction*. Macromolecular Rapid Communications, 2010. **31**(23): p. 2059-2063.
42. Sui, X., et al., *Electrochemical sensing by surface-immobilized poly(ferrocenylsilane) grafts*. Journal of Materials Chemistry, 2012. **22**(22): p. 11261-11267.
43. Ni, Y., R. Rulkens, and I. Manners, *Transition Metal-Based Polymers with Controlled Architectures: Well-Defined Poly(ferrocenylsilane) Homopolymers and Multiblock Copolymers via the Living Anionic Ring-Opening Polymerization of Silicon-Bridged [1]Ferrocenophanes*. Journal of the American Chemical Society, 1996. **118**(17): p. 4102-4114.
44. Tanabe, M., et al., *Photocontrolled living polymerizations*. Nat Mater, 2006. **5**(6): p. 467-470.
45. Rider, D.A. and I. Manners, *Synthesis, self-assembly, and applications of polyferrocenylsilane block copolymers*. Polymer Reviews, 2007. **47**(2): p. 165-195.

46. Kloninger, C. and M. Rehahn, *1,1-Dimethylsilacyclobutane-Mediated Living Anionic Block Copolymerization of [1]Dimethylsilaferrocenophane and Methyl Methacrylate*. *Macromolecules*, 2004. **37**(5): p. 1720-1727.
47. Korczagin, I., M.A. Hempenius, and G.J. Vancso, *Poly(ferrocenylsilane-block-methacrylates) via Sequential Anionic and Atom Transfer Radical Polymerization*. *Macromolecules*, 2004. **37**(5): p. 1686-1690.
48. Zhang, M., et al., *Modular Synthesis of Polyferrocenylsilane Block Copolymers by Cu-Catalyzed Alkyne/Azide "Click" Reactions*. *Macromolecules*, 2013. **46**(4): p. 1296-1304.
49. Datta, U. and M. Rehahn, *Synthesis and Self-Assembly of Styrene-[1]Dimethylsilaferrocenophane-Methyl Methacrylate Pentablock Copolymers*. *Macromolecular Rapid Communications*, 2004. **25**(18): p. 1615-1622.
50. Kim, K.T., et al., *Synthesis, Characterization, and AFM Studies of Dendronized Polyferrocenylsilanes*. *Macromolecules*, 2006. **39**(23): p. 7922-7930.
51. Nunns, A., C.A. Ross, and I. Manners, *Synthesis and Bulk Self-Assembly of ABC Star Terpolymers with a Polyferrocenylsilane Metalloblock*. *Macromolecules*, 2013. **46**(7): p. 2628-2635.
52. Rulken, R., Y. Ni, and I. Manners, *Living Anionic Ring-Opening Polymerization of Silicon-Bridged [1]Ferrocenophanes: Synthesis and Characterization of Poly(ferrocenylsilane)-Polysiloxane Block Copolymers*. *Journal of the American Chemical Society*, 1994. **116**(26): p. 12121-12122.
53. Resendes, R., et al., *A Convenient, Transition Metal-Catalyzed Route to Water-Soluble Amphiphilic Organometallic Block Copolymers: Synthesis and Aqueous Self-Assembly of Poly(ethylene oxide)-block-poly(ferrocenylsilane)*. *Macromolecules*, 1999. **33**(1): p. 8-10.
54. Lammertink, R.G.H., et al., *Nanostructured Thin Films of Organic-Organometallic Block Copolymers: One-Step Lithography with Poly(ferrocenylsilanes) by Reactive Ion Etching*. *Advanced Materials*, 2000. **12**(2): p. 98-103.
55. Wang, X.S., M.A. Winnik, and I. Manners, *Synthesis and Solution Self-Assembly of Coil-Crystalline-Coil Polyferrocenylphosphine-b-polyferrocenylsilane-b-polysiloxane Triblock Copolymers*. *Macromolecules*, 2002. **35**(24): p. 9146-9150.
56. Kim, K.T., et al., *Organometallic-Polypeptide Block Copolymers: Synthesis and Properties of Poly(ferrocenyldimethylsilane)-b-poly-(γ -benzyl-L-glutamate)*. *Macromolecules*, 2005. **38**(12): p. 4958-4961.
57. Vandermeulen, G.W.M., et al., *Metallopolymer-Peptide Conjugates: Synthesis and Self-Assembly of Polyferrocenylsilane Graft and Block Copolymers Containing a β -Sheet Forming Gly-Ala-Gly-Ala Tetrapeptide Segment*. *Biomacromolecules*, 2006. **7**(4): p. 1005-1010.

58. Wang, Y., et al., *Organometallic–Polypeptide Block Copolymers: Synthesis and Self-Assembly of Poly(ferrocenyldimethylsilane)-b-Poly(ϵ -benzyloxycarbonyl-L-Lysine)*. Chemistry – A European Journal, 2008. **14**(28): p. 8624-8631.
59. Roerdink, M., et al., *Poly(ferrocenylsilane)-block-Polylactide Block Copolymers*. Macromolecular Rapid Communications, 2007. **28**(22): p. 2125-2130.
60. Soto, A.P. and I. Manners, *Poly(ferrocenylsilane-b-polyphosphazene) (PFS-b-PP): A New Class of Organometallic–Inorganic Block Copolymers*. Macromolecules, 2008. **42**(1): p. 40-42.
61. Smith, G.S., et al., *Photocontrolled Living Anionic Polymerization of Silicon-Bridged [1]Ferrocenophanes with Fluorinated Substituents: Synthesis and Characterization of Fluorinated Polyferrocenylsilane (PFS) Homopolymers and Block Copolymers*. Macromolecular Chemistry and Physics, 2010. **211**(3): p. 303-312.
62. Gilroy, J.B., et al., *Main-Chain Heterobimetallic Block Copolymers: Synthesis and Self-Assembly of Polyferrocenylsilane-b-Poly(cobaltoceniumethylene)*. Angewandte Chemie International Edition, 2011. **50**(26): p. 5851-5855.
63. d'Agostino, R., *Plasma deposition, treatment, and etching of polymers*. London: Ed. 1990, Academic Press, INC.
64. Manos, D.M. and D.L. Flamm, *Plasma Etching: An Introduction*. 1989: Academic Press.
65. van Roosmalen, A.J., J.A.G. Baggerman, and S.J.H. Brader, *Dry Etching for VLSI*. 1991: Springer.
66. Flamm, D. and V. Donnelly, *The design of plasma etchants*. Plasma Chemistry and Plasma Processing, 1981. **1**(4): p. 317-363.
67. Lammertink, R.G.H., et al., *Poly(ferrocenyldimethylsilanes) for Reactive Ion Etch Barrier Applications*. Chemistry of Materials, 2001. **13**(2): p. 429-434.
68. Knizikevičius, R., A. Galdikas, and A. Grigonis, *Real dimensional simulation of anisotropic etching of silicon in CF₄+O₂ plasma*. Vacuum, 2002. **66**(1): p. 39-47.
69. Kokkoris, G., E. Gogolides, and A.G. Boudouvis, *Etching of SiO₂ features in fluorocarbon plasmas: Explanation and prediction of gas-phase-composition effects on aspect ratio dependent phenomena in trenches*. Journal of Applied Physics, 2002. **91**(5): p. 2697-2707.
70. Henri, J., et al., *A survey on the reactive ion etching of silicon in microtechnology*. Journal of Micromechanics and Microengineering, 1996. **6**(1): p. 14.
71. Oehrlein, G.S. and H.L. Williams, *Silicon etching mechanisms in a CF₄/H₂ glow discharge*. Journal of Applied Physics, 1987. **62**(2): p. 662-672.

72. Coburn, J.W. and E. Kay, *SOME CHEMICAL ASPECTS OF THE FLUOROCARBON PLASMA ETCHING OF SILICON AND ITS COMPOUNDS*. Solid State Technol, 1979. **22**(4): p. 117-124.
73. Strobel, M., et al., *Plasma fluorination of polyolefins*. Journal of Polymer Science Part A: Polymer Chemistry, 1987. **25**(5): p. 1295-1307.
74. Mogab, C.J., A.C. Adams, and D.L. Flamm, *Plasma etching of Si and SiO₂---The effect of oxygen additions to CF₄ plasmas*. Journal of Applied Physics, 1978. **49**(7): p. 3796-3803.
75. Donnelly, V.M., et al., *Anisotropic etching of SiO₂ in low-frequency CF₄/O₂ and NF₃/Ar plasmas*. Journal of Applied Physics, 1984. **55**(1): p. 242-252.
76. Egitto, F.D., L.J. Matienzo, and H.B. Schreyer, *Reactive ion etching of poly(tetrafluoroethylene) in O₂--CF₄ plasmas*. Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films, 1992. **10**(5): p. 3060-3064.
77. Korczagin, I., et al., *Surface Micropatterning and Lithography with Poly(Ferrocenylmethylphenylsilane)*. Chemistry of Materials, 2003. **15**(19): p. 3663-3668.
78. Legtenberg, R., et al., *Anisotropic Reactive Ion Etching of Silicon Using SF₆/O₂/CHF₃ Gas Mixtures*. Journal of The Electrochemical Society, 1995. **142**(6): p. 2020-2028.
79. Xia, Y. and G.M. Whitesides, *Soft Lithography*. Angewandte Chemie International Edition, 1998. **37**(5): p. 550-575.
80. Kumar, A. and G.M. Whitesides, *Features of gold having micrometer to centimeter dimensions can be formed through a combination of stamping with an elastomeric stamp and an alkanethiol "ink" followed by chemical etching*. Applied Physics Letters, 1993. **63**(14): p. 2002-2004.
81. Clarson, S.J. and J.A. Semlyen, *Siloxane Polymers*. 1993: PTR Prentice Hall.
82. Donzel, C., et al., *Hydrophilic Poly(dimethylsiloxane) Stamps for Microcontact Printing*. Advanced Materials, 2001. **13**(15): p. 1164-1167.
83. Hillborg, H. and U.W. Gedde, *Hydrophobicity recovery of polydimethylsiloxane after exposure to corona discharges*. Polymer, 1998. **39**(10): p. 1991-1998.
84. Chua, D.B.H., H.T. Ng, and S.F.Y. Li, *Spontaneous formation of complex and ordered structures on oxygen-plasma-treated elastomeric polydimethylsiloxane*. Applied Physics Letters, 2000. **76**(6): p. 721-723.
85. Lammertink, R.G.H., et al., *Metal-Containing Polymers for High-Performance Resist Applications*, in *Macromolecules Containing Metal and Metal-Like Elements*. 2003, John Wiley & Sons, Inc. p. 115-133.
86. Bowden, N., et al., *Spontaneous formation of ordered structures in thin films of metals supported on an elastomeric polymer*. Nature, 1998. **393**(6681): p. 146-149.

87. Efimenko, K., W.E. Wallace, and J. Genzer, *Surface Modification of Sylgard-184 Poly(dimethyl siloxane) Networks by Ultraviolet and Ultraviolet/Ozone Treatment*. Journal of Colloid and Interface Science, 2002. **254**(2): p. 306-315.
88. Chou, S.Y., P.R. Krauss, and P.J. Renstrom, *Imprint of sub-25 nm vias and trenches in polymers*. Applied Physics Letters, 1995. **67**(21): p. 3114.
89. Chou, S.Y., P.R. Krauss, and P.J. Renstrom, *Imprint Lithography with 25-Nanometer Resolution*. Science, 1996. **272**(5258): p. 85-87.
90. Bender, M., et al., *Fabrication of Nanostructures using a UV-based imprint technique*. Microelectronic Engineering, 2000. **53**(1): p. 233-236.
91. Colburn, M., et al., *Step and flash imprint lithography: a new approach to high-resolution patterning*. 1999: p. 379-389.
92. Acikgoz, C., et al., *Direct surface structuring of organometallic resists using nanoimprint lithography*. Nanotechnology, 2009. **20**(13): p. 135304.
93. Resnick, D.J., S.V. Sreenivasan, and C.G. Willson, *Step & flash imprint lithography*. Materials Today, 2005. **8**(2): p. 34-42.
94. Acikgoz, C., et al., *Fabrication of Freestanding Nanoporous Polyethersulfone Membranes Using Organometallic Polymer Resists Patterned by Nanosphere Lithography*. Advanced Materials, 2009. **21**(20): p. 2064-2067.
95. Ling, X.Y., et al., *An in Situ Study of the Adsorption Behavior of Functionalized Particles on Self-Assembled Monolayers via Different Chemical Interactions*. Langmuir, 2007. **23**(20): p. 9990-9999.
96. Leibler, L., *Theory of Microphase Separation in Block Copolymers*. Macromolecules, 1980. **13**(6): p. 1602-1617.
97. Sun, Z. and C.H. Wang, *Determination of Flory--Huggins interaction parameter and self-diffusion coefficients in ternary polymer solutions by quasielastic light scattering*. The Journal of Chemical Physics, 1995. **103**(9): p. 3762-3766.
98. Posharnowa, N., et al., *Polymer--polymer interaction parameters for homopolymers and copolymers from light scattering and phase separation experiments in a common solvent*. The Journal of Chemical Physics, 2001. **115**(20): p. 9536-9546.
99. Fukuda, T., M. Nagata, and H. Inagaki, *Light scattering from ternary solutions. I. Dilute solutions of polystyrene and poly(methyl methacrylate)*. Macromolecules, 1984. **17**(4): p. 548-553.
100. Nedoma, A.J., et al., *Measurements of the Composition and Molecular Weight Dependence of the Flory--Huggins Interaction Parameter*. Macromolecules, 2008. **41**(15): p. 5773-5779.
101. Lee, J.H., et al., *Thermodynamics and Phase Behavior of Block Copolymer/Homopolymer Blends with Attractive and Repulsive Interactions*. Macromolecules, 2002. **35**(20): p. 7748-7757.

102. Lefebvre, A.A., et al., *Determination of the Phase Boundary of High Molecular Weight Polymer Blends*. *Macromolecules*, 2002. **35**(20): p. 7758-7764.
103. Zirkel, A., et al., *Small-Angle Neutron Scattering Investigation of the Q-Dependence of the Flory–Huggins Interaction Parameter in a Binary Polymer Blend*. *Macromolecules*, 2002. **35**(19): p. 7375-7386.
104. Ryu, D.Y., et al., *Phase Behavior of Deuterated Polystyrene-block-poly(*n*-pentyl methacrylate) Copolymers*. *Macromolecules*, 2003. **36**(8): p. 2894-2902.
105. Elbs, H. and G. Krausch, *Ellipsometric determination of Flory-Huggins interaction parameters in solution*. *Polymer*, 2004. **45**(23): p. 7935-7942.
106. Marsac, P., T. Li, and L. Taylor, *Estimation of Drug–Polymer Miscibility and Solubility in Amorphous Solid Dispersions Using Experimentally Determined Interaction Parameters*. *Pharmaceutical Research*, 2009. **26**(1): p. 139-151.
107. Bates, F.S. and G.H. Fredrickson, *Block Copolymer Thermodynamics: Theory and Experiment*. *Annual Review of Physical Chemistry*, 1990. **41**(1): p. 525-557.
108. Eitouni, H.B., et al., *Thermodynamic Interactions in Organometallic Block Copolymers: Poly(styrene-block-ferrocenyldimethylsilane)*. *Macromolecules*, 2002. **35**(20): p. 7765-7772.
109. Xu, J., et al., *A Novel Crystallization Scheme in Poly[styrene-block-(ferrocenyl dimethylsilane)] Diblock Copolymers*. *Macromolecular Chemistry and Physics*, 2010. **211**(21): p. 2276-2285.
110. Rider, D.A., et al., *Diblock Copolymers with Amorphous Atactic Polyferrocenylsilane Blocks: Synthesis, Characterization, and Self-Assembly of Polystyrene-block-poly(ferrocenylethylmethylsilane) in the Bulk State*. *Macromolecules*, 2005. **38**(16): p. 6931-6938.
111. Gwyther, J., et al., *Double-Gyroid Morphology of a Polystyrene-block-Poly(ferrocenylethylmethylsilane) Diblock Copolymer: A Route to Ordered Bicontinuous Nanoscale Architectures*. *Macromolecular Chemistry and Physics*, 2011. **212**(2): p. 198-201.
112. Gwyther, J. and I. Manners, *Diblock copolymers with an amorphous, high glass transition temperature, organometallic block: synthesis, characterisation and self-assembly of polystyrene-b-poly(ferrocenylisopropylmethylsilane) in the bulk state*. *Polymer*, 2009. **50**(23): p. 5384-5389.
113. Mogi, Y., et al., *Tricontinuous morphology of triblock copolymers of the ABC type*. *Macromolecules*, 1992. **25**(20): p. 5412-5415.
114. Breiner, U., et al., *Structural Characterization of the “Knitting Pattern” in Polystyrene-block-poly(ethylene-co-butylene)-block-poly(methyl methacrylate) Triblock Copolymers*. *Macromolecules*, 1998. **31**(1): p. 135-141.

115. Yamauchi, K., et al., *Synthesis and morphological studies of polyisoprene-block-polystyrene-block-poly(vinyl methyl ether) triblock terpolymer*. Polymer, 2002. **43**(12): p. 3563-3570.
116. Kloninger, C. and M. Rehahn, *Bicontinuous Gyroidic Morphologies in Ferrocenyldimethylsilane-b-Methyl Methacrylate Diblock Copolymer Blends*. Macromolecules, 2004. **37**(22): p. 8319-8324.
117. Corté, L., et al., *Annealing and Defect Trapping in Lamellar Phases of Triblock Terpolymers*. Macromolecules, 2003. **36**(20): p. 7695-7706.
118. Park, M., et al., *Block Copolymer Lithography: Periodic Arrays of ~1011 Holes in 1 Square Centimeter*. Science, 1997. **276**(5317): p. 1401-1404.
119. Mansky, P., et al., *Nanolithographic templates from diblock copolymer thin films*. Applied Physics Letters, 1996. **68**(18): p. 2586-2588.
120. Black, C.T., et al., *Integration of self-assembled diblock copolymers for semiconductor capacitor fabrication*. Applied Physics Letters, 2001. **79**(3): p. 409-411.
121. Black, C.T., et al., *High-capacity, self-assembled metal-oxide-semiconductor decoupling capacitors*. Electron Device Letters, IEEE, 2004. **25**(9): p. 622-624.
122. Black, C.T., *Self-aligned self assembly of multi-nanowire silicon field effect transistors*. Applied Physics Letters, 2005. **87**(16): p. 163116-3.
123. Black, C.T., et al., *Polymer self assembly in semiconductor microelectronics*. IBM Journal of Research and Development, 2007. **51**(5): p. 605-633.
124. Guarini, K.W., et al. *Low voltage, scalable nanocrystal FLASH memory fabricated by templated self assembly*. 2003.
125. Cheng, J.Y., et al., *Formation of a Cobalt Magnetic Dot Array via Block Copolymer Lithography*. Advanced Materials, 2001. **13**(15): p. 1174-1178.
126. Aissou, K., et al., *Ordered Nanoscale Archimedean Tilings of a Templated 3-Miktoarm Star Terpolymer*. Nano Letters, 2013. **13**(2): p. 835-839.
127. Choi, H.K., et al., *Thin Film Knitting Pattern Morphology from a Miktoarm Star Terpolymer*. Advanced Materials, 2014. **26**(16): p. 2474-2479.
128. Segalman, R.A., H. Yokoyama, and E.J. Kramer, *Graphoepitaxy of spherical domain block copolymer films*. Advanced Materials, 2001. **13**(15): p. 1152-1155.
129. Cheng, J.Y., et al., *Fabrication of nanostructures with long-range order using block copolymer lithography*. Applied Physics Letters, 2002. **81**(19): p. 3657-3659.
130. Cheng, J.Y., et al., *Self-Assembled One-Dimensional Nanostructure Arrays*. Nano Letters, 2006. **6**(9): p. 2099-2103.
131. Roerdink, M., et al., *Substrate Wetting and Topographically Induced Ordering of Amorphous PI-b-PFS Block-Copolymer Domains*. Small, 2007. **3**(8): p. 1415-1423.

132. Chuang, V.P., et al., *Templated Self-Assembly of Square Symmetry Arrays from an ABC Triblock Terpolymer*. Nano Letters, 2009. **9**(12): p. 4364-4369.
133. Son, J.G., et al., *Highly Ordered Square Arrays from a Templated ABC Triblock Terpolymer*. Nano Letters, 2011. **11**(7): p. 2849-2855.

Controlled Cutting of PNIPAM Brush Chains at their Roots by Photocleaving to Provide Grafting Density Variations for Adhesion Hysteresis and Friction Studies

The grafting density of polymer brushes on titanium dioxide substrates was tuned by detaching the anchored chains from the surface via photocatalysis. Surface-initiated atom transfer radical polymerization was used to create a dense poly(*N*-isopropylacrylamide) (PNIPAM) brush layer using nitrodopamine as anchor on the titania substrates. Then, the photocatalytic properties of titania was used to detach the polymer chains from the surface. The polymer grafting density was fine-tuned using 366-nm UV irradiation and was reduced from 0.43 to 0.01 chain/nm² after 200 minutes of exposure. Longer irradiation times (300 min) permitted a full detachment of the polymer brush, which allowed its molar mass and polydispersity characterization via gel permeation chromatography. Adhesion hysteresis and friction force for these well-defined systems of different grafting densities were studied via atomic force microscopy, using a polystyrene colloid probe in water, and for temperatures at, below and above the lower critical solution temperature (LCST).

*Lionel Dos Ramos, Edmondo M. Benetti, Bernard D. Kieviet, Hubert Gojzewski, Sissi de Beer, Mark A. Hempenius, G. Julius Vancso; Manuscript in preparation

4.1. Introduction

In the field of materials science, scientists are interested in the relation between molecular structure and physical properties.¹⁻³ In the case of grafted polymer systems, the structure is primarily related to the chemical composition of the chains, the grafting density, the chain length and its distribution. Polymer brushes are polymer systems where one end of the chain is covalently tethered on solid substrates with a high grafting density of polymer chains.⁴ Polymer brush systems, immersed in solvent, present a competition between entropy and osmotic pressure/steric hindrance contributions to the free energy which determines its brush height and surface properties. The degree of swelling regulates then the adhesion and the friction properties. The degree of stretching of the surface-anchored macromolecules is determined by the solvent quality. A good solvent is absorbed into the brush layer which results in its swelling and the stretching of the chains. In contrary, a poor solvent stays out of the polymer brush layer, resulting in a collapsed dense film. Swollen polymer brushes are especially an efficient method for tailoring surface properties, such as antifouling ability,^{5, 6} biocompatibility,^{7, 8} stabilization of colloidal particle suspensions⁹ or lubrication.¹⁰⁻¹²

Stimulus-responsive polymers experience a large change in their chemical and physical properties upon a small variation in their environment, modifying directly its affinity with the solvent. Typical stimuli include variations in pH,¹³⁻¹⁸ ionic strength,¹⁹ electric field^{20, 21} and temperature.²²⁻²⁵ Therefore, with smart brush systems, the surface properties can be conveniently controlled and sometimes reversibly switched by an external stimulus. For instance, poly(*N*-isopropylacrylamide) (PNIPAM) in water is a temperature responsive polymer with a phase transition at the lower critical solution temperature (LCST) of 32 °C.²⁶⁻²⁸ Indeed, below the LCST, PNIPAM presents an expanded state, which switches to a collapsed state above the LCST.

“Grafted to” polymer brushes allow for a characterization of the chains prior to the grafting process.²⁹ But these “grafting to” methods do not give a dense and homogeneous brush layer.³⁰ “Grafting from” methods using controlled and living polymerization, such as surface-initiated atom transfer radical polymerization (SI-ATRP), result in length-controlled, dense and homogeneous polymer brush layers. Nevertheless, the molar mass and polydispersity of the chains is notoriously difficult to characterize experimentally. Several methods have been used to access a characterization of the system. For instance, free sacrificial initiator molecules have been added to the polymerization solution to obtain indirectly the molar mass and distribution of the chains.³¹ The comparison between the polymer brush and the free chain in solution is limited by the kinetics difference between a free initiator in solution and a surface-anchored initiator due to confinement. To directly characterize the brushes after surface-initiated polymerization, the cleavage of polymer brushes has been performed using harsh and dangerous chemicals. For example, hydrofluoric acid³² or tetrabutyl ammonium fluoride³³ were employed to cleave brushes from silica surfaces. An alternative method to detach PNIPAM polymer brushes on gold substrates using a solution of iodine in methylene chloride has also been used.³⁴ But these cleavage methods need to be used with precautions handling, and require also an extra purification procedure.

Here, we present an easy and environmental-friendly approach using photochemistry to both accurately measure the chain length of the “grafted from” polymer brushes, and tune the grafting density. The photocatalytic ability of titanium dioxide was used to cleave polymer brushes from a titania substrate for exact molar mass and polydispersity characterization with gel permeation chromatography (GPC) measurements. The mild and controlled detachment of the surface-anchored chains allowed for tuning the grafting density and studying its effect on the tribo-mechanical properties of the PNIPAM brushes at different temperatures. Contact mode atomic force microscopy (AFM) in water with a polystyrene (PS) colloid probe was used to measure the adhesion hysteresis and friction.

Previous works on this subject have studied various surface property-changes of PNIPAM brushes below and above the LCST. For instance, the change in surface wettability of PNIPAM brushes was investigated with static contact angle measurements of water droplets.³⁵ Changes in adhesion have also been studied with the surface force apparatus³⁶ and AFM.^{7, 24, 37-40} The conformation of PNIPAM brushes upon continuous increase of the temperature near the LCST has also been investigated.^{26, 41} It was found that the temperature-range of the collapse/hydration transition takes place over a broad range of temperatures compared to free PNIPAM chains in bulk solution. Previous work from our group using an AFM colloid probe showed that the grafting density of PNIPAM brushes has an influence on the mechanical properties, and more specifically on the apparent Young's moduli.⁷ Another of our studies also revealed that the adhesion hysteresis and the friction force between a dense PNIPAM brush and a colloid AFM probe are maximum at the LCST.²⁷ To complement our earlier works and understand the effect of the grafting density of PNIPAM brushes on adhesion hysteresis and friction force, a precise characterization and synthesis at the molecular level of the PNIPAM brushes is necessary.

4.2. Results and discussion

4.2.1. PNIPAM brushes synthesis and photocatalytic cleavage

PNIPAM brushes were “grafted from” titanium dioxide substrates via SI-ATRP, using nitrodopamine as anchor. The ATRP initiator was fixed in a two-step procedure to the titania substrates. First, a self-assembled monolayer (SAM) of nitrodopamine in water and at room temperature was formed. Nitrodopamine was shown to provide a dense and stable immobilization layer on metal oxides.⁴² Then, the ATRP initiator was attached to the anchored nitrodopamine via nucleophilic coupling of the anchored amine groups to the acyl halide group of α -bromoisobutyryl

bromide. This reaction creates an amide group, which ensures a stable and dense coupling of the ATRP initiator onto the substrate. PNIPAM brushes were then “grafted from”, employing the living and controlled ATRP. The photocatalytic properties of titanium dioxide were finally used to cleave the PNIPAM brushes, as shown in Scheme 1. Titanium dioxide is a semiconductor with a band gap of 3.2 eV which corresponds to the UV region of the electromagnetic spectrum ($\lambda \leq 387.5$ nm).⁴³ During the photocatalysis process, electrons from the valence band are excited to the conduction band by light of higher energy than the respective band gap. This results in the creation of electron/hole pairs that initiate redox reactions on the catalyst surface. On the one hand, conduction band electrons are strong reducing agents that can reduce O_2 to superoxide radicals ($\text{O}_2^{\cdot-}$). On the other hand, valence band holes are strong oxidizing agents that can oxidize H_2O or HO^- molecules, adsorbed on the surface, into hydroxyl radicals ($\text{HO}^{\cdot}$), hydrogen peroxide (H_2O_2), and protonate superoxide radicals ($\text{HOO}^{\cdot}$).

Scheme 4.1. Schematic representation of the photocatalytic cleavage of the surface-anchored polymer brushes on titania.

A simple long-wave UV lamp ($\lambda = 366$ nm, 8 W) used normally in an UV Cabinet for Thin-Layer Chromatography observation, was used to illuminate the titania substrates in water at room temperature. We note here that no study on the anatase content, which is the titanium dioxide phase presenting photocatalysis, or on the band gap energy of the titanium dioxide layer was performed. Of course, one could optimize the efficiency of the photocatalytic cleavage by tuning the percentage of the anatase phase present on the surface, by adjusting the sputtering method⁴⁴ or by thermal annealing.⁴⁵ The band gap of the titania layer could also be measured and the wavelength of the UV lamp could be selected to match this band gap energy. Our study was focused on the possibility to use common lab facilities, such as this UV cabinet, to cleave polymer brushes for length characterization or for varying the grafting density and avoid the use of harmful chemicals for cleavage. The cleavage of the polymer brush can be attributed to two photocatalytic mechanisms: first, the direct oxidation of the organic molecules on the created holes,⁴⁶ and second, the indirect oxidation of the organic molecules with the hydroxyl radicals and superoxide created at the surface.⁴⁷ In both cases, we argue that the polymer chains are broken at the anchor point and not randomly along the chain. Indeed, when considering the first mechanism, the holes oxidize only the organic molecules present at the titania surface. For the second mechanism, the short lifetime of the hydroxyl and superoxide radicals would only permit cleavage of molecules very close to the surface,⁴⁸ making random polymer chain scission unlikely.

For GPC measurements, brushes were grown on a 2.5×4 cm² substrate to obtain a maximum amount of material. After PNIPAM brush polymerization, the dry height of the layers was found to be $110 \text{ nm} \pm 2 \text{ nm}$ by ellipsometry. The layer was dense and homogeneous along the entire sample surface. Cleavage of the brush was achieved by illuminating the substrate for 300 min in water. The polymer layer was totally removed from the titania substrates. This was confirmed by ellipsometry measurements on the substrates which gave a polymer layer thickness of 0 nm (with fitting parameter A of the Cauchy dispersion relation, fixed at 1.45). The water used

during the detachment of the PNIPAM chains was collected and partially evaporated. After freeze-drying, the small amount of PNIPAM chains was dissolved in 0.2 mL of THF for GPC measurements. The amount of cleaved PNIPAM chains can be estimated to be 0.1 mg, by considering a bulk volume density ρ for PNIPAM of 1.1 g/cm³.⁴⁹ For a polymer brush layer with a thickness of 110 nm, a number-average molar mass M_n of 169 kg/mol, a weight-average molar mass M_w of 281 kg/mol and a polydispersity index M_w/M_n of 1.66 were established by GPC (see **Appendix 4.1**). This polydispersity index agrees well with results in the literature for polymer brushes grown via SI-ATRP.⁵⁰ These molar mass characteristics confirm our assumption that the polymer brushes are cleaved from the substrate at the anchor point. Indeed, if the brush chains were cleaved randomly along the polymer chain, the polydispersity index would be much higher than the one obtained. The initial grafting density σ was then calculated by using the equation $\sigma = h_{\text{dry}} \rho N_A / M_n$, where h_{dry} is the dry height of the polymer brush layer and N_A is Avogadro's number. A grafting density of 0.43 chain/nm² was found. This value is also comparable with previous grafting densities of dense polymer brushes.^{27, 50}

As seen previously, a long exposure (300 min) to UV irradiation results in the cleavage of the entire polymeric brush layer. This observation sparked the idea to use shorter UV exposure times, allowing one to detach only a desired fraction of brush chains and therefore tune the grafting density. A brush was grown on a large substrate (2.5×4 cm²) simultaneously with the brush grown for the GPC measurement to obtain identical, dense and homogeneous polymer brush layers. Then, the large substrate was cut in eight smaller pieces of 1.25×1 cm². For each small substrate, the brush thickness was measured individually with ellipsometry (**Figure 4.1.a**). The initial dry thickness after polymerization and before UV exposure was $104 \text{ nm} \pm 2 \text{ nm}$. After various UV irradiation times (2, 5, 10, 20, 50, 100 and 200 min), the substrates were extensively rinsed with water and ethanol, and dried under a nitrogen stream. The dry height was measured again by ellipsometry. **Figure 4.1.a** shows the dry brush height as a function of the UV irradiation time.

Figure 4.1.b displays the resulting relative thickness decrease (%) as function of the UV irradiation time. Since the dry height is proportional to the grafting density, it can be concluded that the grafting density decreases rapidly in the beginning of the irradiation and slows down progressively. Indeed, within 10 min, the grafting density decreased by 50 %. Afterwards, more than 200 min of irradiation were necessary to reduce the remaining 50 % to 0 %. The fast decrease in the beginning could be explained by the high probability of breaking the anchoring bonds at the surface, since these are densely packed initially. Holes and radicals formed by photocatalysis would rapidly encounter anchored chains in their vicinity, which would result in chain scission. When the grafting density decreases progressively, the probability of a hole or radical to encounter, react with and break an anchored molecule decreases as well, resulting in a reduction of the cleavage reaction rate. We note here that the effect of the 366-nm-light absorption by PNIPAM is negligible as shown in **Appendix 4.2**. PNIPAM brush layers with initial thickness of 450 nm have also been successfully cleaved to obtain different grafting density but the GPC measurements were impossible since the molar mass of the obtained chains exceeded the range of our GPC columns. Other polymeric brushes could be characterized with our method, for example we realized the same cleavage with polyacrylamide brushes, which resulted to the same homogeneous detachment.

Figure 4.1. a) The dry thickness of the PNIPAM brush layers before and after the UV-irradiation, and b) the resulting relative thickness decrease as function of UV irradiation time.

We considered the initial grafting density of the samples subjected to UV irradiation to be identical to the grafting density of the substrate used for GPC, as these substrates were decorated with brushes simultaneously, in the same reaction flask. Considering an initial grafting density of 0.43 chain/nm^2 for all of the substrates, we can calculate the average molar mass of the polymer brushes for each sample. Subsequently, we calculated back the grafting density value for each

irradiation time. **Figure 4.2** displays the decrease of the grafting density with the irradiation time.

Figure 4.2. The calculated grafting density as function of irradiation time. The estimated statistical error is 5%.

4.2.2. Swelling characterization with AFM

AFM images of dry polymer brushes were recorded in tapping mode, after exposure to UV radiation for 2, 5, 10, 20, 50, 100 and 200 minutes (**Figure 4.3**). The polymer brush layers, possessing decreasing grafting densities, exhibited a homogeneous and smooth surface after irradiation and displayed the same homogeneity as the polymer brush before UV irradiation (0 min) which proves that detachment of brush polymer chains via our method occurred homogeneously over the entire sample surface. AFM images in contact mode were also taken of the same samples swollen in water, using a PS colloid probe (**Appendix 4.3**). In the swollen state, the PNIPAM brush layers with their varying grafting densities kept their homogeneity, confirming the homogeneous detachment of brush chains upon UV

irradiation. We note here that the efficiency of our system was not studied and optimized as already mentioned earlier. This non-optimized system gives a slow cleavage kinetics that might be the origin of this homogeneous detachment of the polymer chains. It might be possible that an optimization of the system, and therefore, an increase of the cleavage reaction rate, results in an inhomogeneous detachment of the chains.

Figure 4.3. AFM images taken in tapping mode of the scratch made in the polymer brush. On the left part of each image, the polymer brush is displayed and on the right, the scratch revealing the titania underneath the polymer brush layer can be seen.

From the AFM images (see **Appendix 4.3**) in water at 25 °C with contact mode, using a PS colloid probe over a scratch on the polymer brush, the swollen thicknesses of the PNIPAM brushes with different grafting densities were obtained. **Figure 4.4** shows the evolution of the swollen ratio $(h_{\text{swollen}} - h_{\text{dry}}) / h_{\text{dry}}$ with the grafting density. For the highest grafting density 0.43 chain/nm², the swelling ratio was 2.7, which is similar to previous studies.^{27,36} With the decrease of the grafting density, the swelling ratio increases until a maximum of 5.3 for a grafting density of 0.1 chain/nm². For even smaller grafting densities, the swelling ratio decreases until reaching 1 for 0.01

chain/nm². We observed a maximum swelling ratio for intermediate grafting densities. This is comparable to the trend observed in previous studies monitoring the conformational transition upon temperature and using high molecular weight PNIPAM brushes.^{36, 51} This trend is also in good agreement with the prediction of Mendez et al. for dense brushes of long chains, using a self-consistent-field calculation.⁵² The transition between two regimes of the swelling ratio is related to the transition between brush-to-mushroom regimes.³⁶ In our experiment, this transition occurs between 0.04 and 0.1 chain/nm². A recapitulative table with all the quantitative results for the different substrates is present in the **Appendix 4.4**.

Figure 4.4. Swelling ratio of the PNIPAM brushes on titania as function of their grafting density.

We note here that the AFM images (see **Appendix 4.3**) of the swollen brush height were realized using the minimal force possible for each sample. This minimal force before losing contact with the brush surface compresses slightly the brush. This compression is stronger for lower densities. Indeed, by reducing the grafting density, the brush density profile at the surface becomes less pronounced and it becomes

easier to compress it. Thus, the lower the grafting density is, the bigger the errors on the swollen brush height and the swelling ratio are.

4.2.3. Adhesion hysteresis and friction measurement with AFM

Figure 4.5 shows the typical force-separation curves, which were obtained with a PS colloid AFM probe upon approach towards and retract from the PNIPAM brushes of different grafting densities and at three different temperatures. **Figure 4.6** shows the histograms representing the statistical distribution of the corresponding adhesion hysteresis (work per compression cycle), which is the area between the approach and the retract curves.

At temperatures T below the LCST (25 °C) (see **Figure 4.5.a**), and for the two highest grafting densities (0 and 2 min), the approach and the retract curves overlap. This means that the work of adhesion is small, as confirmed in **Figure 4.6.a**. For $T < \text{LCST}$, water is a good solvent for the PNIPAM brushes and the osmotic pressure inside the brush is high. Therefore, the brush is only slightly compressed and the interaction with the PS colloid is small, which minimizes the dissipation. When the grafting density is reduced, the osmotic pressure of the water inside the brush becomes smaller. The colloid compresses the brush much more than for high grafting densities, such that more water is squeezed out causing an increase in the contact area between the PS colloid and the brush. For the brush with the lowest grafting density (200 min), corresponding to 0.01 chain/nm^2 , this work of adhesion is really high compared to the other densities (see **Figure 4.6.a**). This can be explained by the long-range interactions that are observed for the smaller densities (see **Figure 4.5.a**). This long-range interaction can be attributed to an increase of the polymer segment-colloid contacts, resulting in stretching of the polymer chains over almost $1 \mu\text{m}$ when the colloid is moved away from the surface. The same effect was observed in our previous study.²⁷

At a temperature of 32 °C, which is generally considered to be the LCST of a PNIPAM brush as found in the literature,^{27, 36, 53, 54} the hysteresis increases considerably and a similar long-range interaction stretches the brushes at all the densities. For the highest brush densities, corresponding to the brush regime (0, 2 and 50 min), this stretching reaches 1 μm whereas for the lowest densities, corresponding to the mushroom regime, this stretching occurs only over 750 nm. This stretching at the LCST affects directly the value of the hysteresis, which, as seen in UV-visible spectrum of PNIPAM is increasing with the increase of the grafting density.

At a temperature of 37 °C, above the LCST, the water is a poor solvent for PNIPAM, the polymer-polymer interactions become more favorable and the PNIPAM brushes collapse.^{27, 36, 53, 54} **Figure 4.5.c** and the **Appendix 4.5** show that the adhesion force between the collapsed PNIPAM brush and the PS colloid is strong but the stretching of the brush is reduced and below 250 nm (**Figure 4.5.c**). This means that the chains resist stretching during the retraction of the PS colloid.

Figure 4.5. Graphs representing examples of force-separation curves between a PS colloid probe and PNIPAM brushes depending on the irradiation time at a) a temperature below the LCST, b) at the LCST and c) above the LCST.

Figure 4.6. Histograms showing the distribution of the adhesion hysteresis between a PS colloid probe and PNIPAM brushes depending on the irradiation time at a) a temperature below the LCST, b) at the LCST and c) above the LCST.

We expect that the maximum in the dissipation, attributed to chain stretching and observed at the LCST, affects directly the tribo-mechanical properties of the PNIPAM brushes.²⁷ In order to validate this hypothesis and study the effects of the grafting density and the temperature on the tribo-mechanical properties, we realized friction measurements. A PS colloid of 5 μm diameter was slid laterally on the surface of the PNIPAM brushes over 10 μm and at a velocity of 10 $\mu\text{m/s}$. **Figure 4.7** shows the evolution of the friction forces as function of the applied load below, above and at the LCST. Other studies of the temperature effect on friction for PNIPAM brush or hydrogel systems have been performed.^{7, 55-61} However, the change of the tribo-mechanical properties during the transition around the LCST was poorly investigated. Here, we consider both the grafting density effect and the particular behavior at the LCST. We note here that the tribological properties of a PNIPAM brush will also depend on the degree of polymerization and the sliding velocity.

Figure 4.7. Graphs representing the friction force as function of the load between a PS colloid probe and PNIPAM brushes depending on the irradiation time at a) a temperature below the LCST, b) at the LCST and c) above the LCST. The lines represent the linear fit when applicable.

In agreement with Amonton's law, for many systems consisting of solid objects on a solid substrate under dry conditions, the friction force does not depend on the apparent contact area and is proportional to the loading force.⁶² These relations do not always hold, e.g. in the case of a soft elastic object or with the addition of a lubricant, the tribological properties are modified significantly.⁶³ In our experiments, we observe that for most temperatures and grafting densities, the friction (**Figure 4.7**) changes nonlinearly with the normal load. Only at $T > \text{LCST}$ and for the low grafting densities (100 and 200 min) at $T = \text{LCST}$, the friction increases linearly as function of the load. For the temperatures below the LCST and for the high densities (0, 2 and 50 min) at the LCST, where the polymer brush layers are swollen and the chains are stretched, the change of the surface contact upon the increase of the load deviates from the classical relation given by the contact mechanic models between the surface contact area and the load.^{62,64} This deviation is due to the polymer density changes with the height of the brush, such that the elasticity becomes a function of the normal load, which is enhanced by the polydispersity. Furthermore, the deviation between the theory and the experiments is also affected by the surface quality which is influenced for instance by the surface inhomogeneity, the defects, the stability of the AFM tip or the roughness.⁶⁵ By applying higher loads, the roughness of the polymer brush surface varied considerably which contributes even more to this non-trivial relation between the contact area and the load. In **Figure 4.7.a**, at $T < \text{LCST}$ where the brushes are swollen, and for loads lower than 120 nN, the lower grafting densities (100 and 200 min) result in a higher friction force than the higher grafting densities (0, 2 and 50 min). For loads larger than 120 nN, this effect is reversed. We attribute the high friction forces to the situation where the number of contacts between PNIPAM and the PS colloid are high. For loads below 120 nN, the strong osmotic pressure for the brushes of high grafting densities reduces these contacts, while for the low grafting densities these contacts are high. For $T > \text{LCST}$ (**Figure 4.7.c**), the friction force changes according to the ideal linear relation with the applied load. Since the PNIPAM brushes are collapsed, the systems behave ideally

with a linear increase of the contact area with the applied load. In the particular case of $T = \text{LCST}$ (**Figure 4.7.b**), the lower grafting densities (100 and 200 min) are mostly collapsed and the friction force changes linearly with the load. As seen previously, the stretching of the chains is also lower for these grafting densities compared to the high grafting densities. For the highest grafting densities at the LCST, the friction is really strong (> 12 nN) and does not behave linearly with the load. We notice that the grafting density of 0.28 chain/nm^2 (2 min) results in a higher friction force of 18 nN compared to 0.43 and 0.1 chain/nm^2 (0 and 50 min, respectively) which results in friction forces around 12 and 6 nN, respectively. It seems that the friction is maximized at this particular and intermediate density due to a maximization of the stretching of the brush.

4.3. Conclusion

In conclusion, by using the photocatalytic properties of titanium dioxide, the PNIPAM brushes grafted from titania surfaces via SI-ATRP, were cleaved from the surface. The molecular mass and the polydispersity of the brushes were then successfully characterized by GPC. For a polymer brush layer with a thickness of $110 \text{ nm} \pm 2 \text{ nm}$, a number-average molar mass M_n of 169 kg/mol, a weight-average molar mass M_w of 281 kg/mol and a polydispersity index M_w/M_n of 1.66 were found.

Different irradiation times under UV-light, resulted in a homogeneous detachment of the anchored chains, allowing the formation of homogeneous polymer brush layers with different grafting densities. The grafting density was tuned between 0.43 and 0.01 chain/nm^2 within 200 minutes of UV irradiation. It was shown experimentally that the grafting density of PNIPAM brushes affects the magnitude of the swelling ratio. Such a result is primordial for applications where a large thickness change is needed, such as in flow control actuation inside microchannels.^{61,}

⁶⁶ The easy-to-use detachment could also be implemented for gradient formation by

irradiating a substrate with a mask moving progressively. These grafting density gradients could be used in cell adhesion and motion studies, for example.^{67, 68}

A study of the changes in the work of adhesion and friction, depending on the temperature and the grafting density of the PNIPAM brushes, was performed with a PS colloid probe using AFM in water. The effect of the PNIPAM brush's grafting density on the tribology is different for temperatures below, at and above the LCST. Below the LCST, the brush was swollen and friction as function of load was nonlinear. The reason for the latter was that the traditional contact mechanics models could not describe the change in contact area between the colloid and the brushes as a function of the normal load. This deviation is attributed to long-ranged interactions and stretching of the brushes occurred, and the brush density which is not constant over the height of the brush. The work of adhesion and the long-ranged interactions increased with the decrease of the grafting density. At the LCST, all the studied grafting densities showed long-ranged interactions (up to 1 μm). High grafting densities showed high friction forces, but at intermediate grafting densities (0.28 chain/nm²) the highest friction forces were measured. At temperatures above the LCST, the brushes were collapsed and the friction force as function of the load was linear for all the studied grafting densities. Long-range interactions were no longer present but a strong adhesion force between the PS colloid and the collapsed PNIPAM brushes was seen. This adhesion force was attributed to hydrophobic interaction between the PS colloid and the hydrophobic collapsed PNIPAM brushes in water.

4.4. Experimental section

Substrates and chemicals. The titania wafers used in this study, are silicon wafers with a native SiO₂ layer obtained from Si-Mat Silicon Materials, Landsberg/Lech, Germany. The wafers were coated with a TiO₂ layer (17-nm-thickness according to ellipsometry measurements) by physical vapor deposition (PVD, reactive magnetron

sputtering) at the Paul Scherer Institute, Villigen, Switzerland. The titania substrates ($2.5 \times 4 \text{ cm}^2$) were cut from these titania wafers with a diamond pen. *N*-Isopropylacrylamide (NIPAM, 97%) was purchased from Sigma-Aldrich and purified twice by recrystallization from toluene/hexane solution (50% v/v), and dried under vacuum for 48h at room temperature. Copper(I) bromide (CuBr, 98%) was also purchased from Sigma-Aldrich and purified by stirring three times in acetic acid (glacial, Sigma-Aldrich), filtered and rinsed excessively with ethanol and dried under vacuum for 24h. *N,N,N',N'',N''*-Pentamethyldiethylenetriamine (PMDETA, 99%), α -bromoisobutyryl bromide (98%), triethylamine ($\geq 99\%$), copper(II) bromide ($\geq 99\%$) were purchased from Sigma-Aldrich and used as received. Methanol (absolute AR, Biosolve), tetrahydrofuran (THF, AR, Biosolve) and ethanol (absolute, Merck) were used as received. All the water used is ultra-pure water dispensed through a Milli-Q Advantage A10 purification system from Millipore Corporation.

Synthesis of 6-Nitro-3-hydroxytyramine Hemisulfate Salt (Nitrodopamine).

Nitrodopamine was synthesized according to the method described by Rodenstein et al.⁶⁹ 3-Hydroxytyramine hydrochloride (4.0 g, 21 mmol) and sodium nitrite (3.2 g, 46 mmol) were dissolved in water (50 mL) and cooled to 0 °C. Then, sulfuric acid (34.8 mmol in 20 mL of water) was added dropwise to the mixture. After complete addition of the sulfuric acid solution, the reaction was left to proceed under stirring at 0 °C for 1h, and subsequently at room temperature overnight. The yellow precipitate was filtered, rinsed with cold water and methanol, and recrystallized from 80 °C to room temperature in water. The nitrodopamine was then dried under high vacuum for 2 days. Yield: 2.97 g (63%). ¹H NMR (D₂O, 300 MHz): 7.73 ppm (s, 1H, aromatic), 6.90 ppm (s, 1H, aromatic), 3.32 ppm (t, 2H, -CH₂), 3.23 ppm (t, 2H, -CH₂).

Surface attachment of the Atom Transfer Radical Polymerization (ATRP)

Initiator. Prior to functionalization, the titania substrates ($2.5 \times 4 \text{ cm}^2$) were sonicated consecutively for 30 min in toluene and 2-isopropanol, dried under a

stream of nitrogen and treated with oxygen plasma for 30 min. Immediately after, substrates were immersed in a 0.5 mM solution of nitrodopamine in water at room temperature, overnight, to allow the formation of a dopamine self-assembled monolayer. The substrates were then rinsed extensively with water and ethanol, and dried under a stream of nitrogen. Coupling of the ATRP initiator to the surface-anchored amine groups was then performed under anhydrous conditions. The dopamine-functionalized titania substrates were placed on the bottom of a 300 mL Erlenmeyer (2 substrates of $2.5 \times 4 \text{ cm}^2$ per Erlenmeyer) which was sealed with a septum and purged with argon for 1h. Afterward, anhydrous chloroform was added (30 mL), and under stirring, triethylamine (0.1 mL) and α -bromoisobutyryl bromide (0.1 mL) were added. After 2h of reaction, the substrates were rinsed extensively with toluene and ethanol, dried under a stream of nitrogen and kept in the dark.

Surface-Initiated Atom Transfer Radical Polymerization (SI-ATRP) of PNIPAM brushes. NIPAM monomer (5.7 g, 100 mmol) and the ligand PMDETA (464 μL , 2.22 mmol) were added to a water (20 mL) and methanol (20 mL) mixture. The solution was then purged for 30 min with argon. CuBr (63.2 mg, 0.44 mmol) and CuBr₂ (6.3 mg, 0.028 mmol) were added into another reaction flask and flushed with argon for 30 min. Next, the monomer and ligand solution were added into the flask containing the copper salts and stirred until total dissolution of the copper by complex formation with the ligand. The solution was then transferred into a flask containing the initiator-functionalized titania substrates and which was beforehand sealed with a rubber septum, protected with aluminum foil from light, and purged with argon for 1h. After reaching the reaction time of 120 min, the substrates were extensively rinsed with water and ethanol, and subsequently dried under a stream of nitrogen. The titania substrates functionalized with the PNIPAM brush layer were kept in the dark in a nitrogen box.

Polymer brush detachment. The polymer brushes were cleaved from the substrates by using the photocatalytic properties of titania under UV irradiation. The substrates were placed flat in a petri dish and immersed under approximately 0.5 cm

of water. A long-wave UV lamp (366 nm, 8 W, UV Cabinet for Thin-Layer Chromatography, CAMAG) was used to irradiate the titania substrates for different periods of time. The distance from the substrates to the lamp was approximately 8 cm. After a specific irradiation time, the substrates were rinsed extensively with water. For molar mass characterization by gel permeation chromatography, a full cleavage of the PNIPAM brushes from the titania substrate ($2.5 \times 4 \text{ cm}^2$) was obtained after 300 min of irradiation time. For the grafting density variation, after PNIPAM brush formation, the large titania substrates ($2.5 \times 4 \text{ cm}^2$) were cut in 8 pieces of $1 \times 1.25 \text{ cm}^2$. Then, following the same procedure, each substrate ($1 \times 1.25 \text{ cm}^2$) was removed after a certain irradiation time (2, 5, 10, 20, 50, 100 and 200 min).

Gel permeation chromatography (GPC) measurements. GPC measurements were carried out in THF (flow rate 2.0 mL/min) at 25°C, using microstyragel columns (bead size 10 μm) with pore sizes of 10^5 , 10^4 , 10^3 and 500 Å (Waters) and a dual detection system consisting of a differential refractometer (Waters model 410) and a differential viscometer (Viscotek model H502). Molar masses were determined relative to polystyrene standards in THF. After full detachment of the polymer brushes, the water from the petri dish and the rinsing water containing the PNIPAM chains were collected. After evaporation of most of the water by rotary evaporator, the detached PNIPAM chains were dried via a freeze drying procedure. The PNIPAM chains were then dissolved in a minimal amount of THF (0.2 mL) to keep the highest concentration possible for GPC analysis.

Ellipsometry. The dry thickness of the polymer brush layer on the titania substrates was measured using a rotating analyzer ellipsometer (J.A. Woollam VASE) at wavelengths ranging from 380 to 800 nm and at an angle of incidence of 70°. Thickness determinations were performed on at least 3 spots for each sample. The Cauchy dispersion relation ($n(\lambda) = A + B/\lambda^2 + C/\lambda^4$) was used to model the titania and polymer brush layers. The thickness, and constants A and B were fitted, and constant C was fixed at 0. From a bare titania substrate, the thickness of the titania layer on the silicon wafer was found to be 17 nm and the parameters A and B were

determined to be 2.23 and 0.0452, respectively. Afterwards, as the ellipsometric data of the PNIPAM brushes were fitted, the parameters of the 17-nm-thick titania layer were fixed. For the PNIPAM layer model, the constants A and B were 1.45 ± 0.03 and 0.005 ± 0.002 , respectively. Similar values have been reported in the literature.³⁷

Atomic Force Microscopy (AFM) measurements. AFM measurements were performed in water using a standard Bruker liquid cell in a Multimode 8 atomic force microscope (Bruker, USA) with a NanoScope V controller. For the step height measurements, a scratch was made in the polymer brush layers with a Teflon tweezer to avoid the damage of the layer of titania underneath. A polystyrene sphere with a diameter of 5 μm (determined by scanning electron microscopy) was glued using a microcontroller under a microscope to an AFM cantilever (TL-CONT-50, sQube, Germany). The cantilever does not have a coating, which reduces the thermal sensitivity such that the temperature could be changed without realigning the laser. The spring constant of the PS colloidal probe fabricated in this way was determined using the thermal noise method⁷⁰ which gave a value of 0.3 N/m. The heating setup was located on the scanner stage below the sample, and the temperature was monitored via a thermocouple immersed in the water inside the liquid cell. After increasing the temperature, the system was equilibrated during 30 min before measurements. The deflection sensitivity was determined for each sample measurement and each temperature on bare titania. To obtain the force-separation curves between the PS colloid probe and the PNIPAM brush layer, the cantilever deflection was monitored upon approach to and retract from the surface⁶⁴ over a distance of 2.5 μm at a velocity of 3 $\mu\text{m/s}$ and a maximum applied force of 32 nN for each measurement. At least 150 force-separation curves were obtained at 3 different areas for each data set and analyzed with a Matlab program to extract the pull-off forces, the adhesion hysteresis. The friction was measured by moving the sample in the lateral direction (with a scan angle of 90°) over a scan size of 10 μm and a velocity of 10 $\mu\text{m/s}$ at different normal loads between 20 and 210 nN. The lateral sensitivity factor of the PS colloid cantilever, necessary for the friction force

calculations, was obtained using the non-contact method of Vezenov⁷¹, resulting in a value $S_x = 34.6 \text{ nN/V}$.

4.5. Appendix

Appendix 4.1. GPC data of detached 110-nm-thick PNIPAM brushes in THF measured against the PS standard curve.

Appendix 4.2. UV-visible spectrum of PNIPAM.

Appendix 4.3. AFM images with contact mode, using a PS colloid probe, of the swollen PNIPAM brush after different UV irradiation time.

Irradiation time (min)	Initial dry height ^a (nm)	Calculated molar mass (kg/mol)	Dry height after UV irradiation ^a (nm)	Grafting density after irradiation (chain/nm ²)	Swollen height ^b (nm)	Swelling ratio ^c
0	104	160	104	0.43	351	2.7
2	104	160	68	0.28	251	3.3
5	107	164	61	0.25	261	4.0
10	102	157	52	0.22	231	3.9
20	106	163	38	0.15	191	5.0
50	104	159	25	0.10	106	5.3
100	101	156	10	0.04	47	3.8
200	100	154	2	0.01	4	1.0

^a obtained by ellipsometry; ^b obtained by AFM step height with a minimal load force; ^c the swelling ratio is taken as $(h_{\text{swollen}} - h_{\text{dry}}) / h_{\text{swollen}}$.

Appendix 4.4. Table summarizing the quantitative results obtained during the study.

Appendix 4.5. Histograms showing the statistical distribution of the pull-off forces between a PS colloid probe and PNIPAM brushes depending on the irradiation time at a) a temperature below the LCST, b) at the LCST and c) above the LCST.

4.6. References

1. Andrews, E.H., *Structure-Property Relationships in a Polymer*. Angewandte Chemie International Edition in English, 1974. **13**(2): p. 113-121.
2. Jancar, J., et al., *Current issues in research on structure–property relationships in polymer nanocomposites*. Polymer, 2010. **51**(15): p. 3321-3343.
3. Marek, W.U. and D.C. Clara, *Structure-Property Relations in Polymers*. Advances in Chemistry. Vol. 236. 1993: American Chemical Society. 852.
4. Milner, S., *Polymer brushes*. Science, 1991. **251**(4996): p. 905-914.
5. Guo, S., et al., *Surface charge control for zwitterionic polymer brushes: Tailoring surface properties to antifouling applications*. Journal of Colloid and Interface Science, 2015. **452**: p. 43-53.
6. Gao, G., et al., *Antibacterial Surfaces Based on Polymer Brushes: Investigation on the Influence of Brush Properties on Antimicrobial Peptide Immobilization and Antimicrobial Activity*. Biomacromolecules, 2011. **12**(10): p. 3715-3727.
7. Sui, X., et al., *Polymer Brushes: Probing the Collapse Dynamics of Poly(N-isopropylacrylamide) Brushes by AFM: Effects of Co-nonsolvency and Grafting Densities (Small 10/2011)*. Small, 2011. **7**(10): p. 1274-1274.
8. de las Heras Alarcon, C., et al., *Bioadhesion at micro-patterned stimuli-responsive polymer brushes*. Journal of Materials Chemistry, 2005. **15**(21): p. 2089-2094.
9. Sun, N., X. Zhao, and Z. Xiao, *Synthesis and Characterization of Hollow TiO₂ Particles Coated with Polyimide Brushes by Click Chemistry*. Journal of Nanoscience and Nanotechnology, 2015. **15**(6): p. 4676-4681.
10. Chen, M., et al., *Lubrication at Physiological Pressures by Polyzwitterionic Brushes*. Science, 2009. **323**(5922): p. 1698-1701.
11. Lee, S. and N.D. Spencer, *Sweet, Hairy, Soft, and Slippery*. Science, 2008. **319**(5863): p. 575-576.
12. de Beer, S. and M.H. Müser, *Friction in (Im-) Miscible Polymer Brush Systems and the Role of Transverse Polymer Tilting*. Macromolecules, 2014. **47**(21): p. 7666-7673.
13. Benetti, E.M., H.J. Chung, and G.J. Vancso, *pH Responsive Polymeric Brush Nanostructures: Preparation and Characterization by Scanning Probe Oxidation and Surface Initiated Polymerization*. Macromolecular Rapid Communications, 2009. **30**(6): p. 411-417.
14. Lee, H., et al., *pH-Programmable Sequential Dissolution of Multilayer Stacks of Hydrogen-Bonded Polymers*. ACS Macro Letters, 2013. **2**(10): p. 924-927.

15. Hiller, J.A. and M.F. Rubner, *Reversible Molecular Memory and pH-Switchable Swelling Transitions in Polyelectrolyte Multilayers*. *Macromolecules*, 2003. **36**(11): p. 4078-4083.
16. Yang, S.Y. and M.F. Rubner, *Micropatterning of Polymer Thin Films with pH-Sensitive and Cross-linkable Hydrogen-Bonded Polyelectrolyte Multilayers*. *Journal of the American Chemical Society*, 2002. **124**(10): p. 2100-2101.
17. Chung, A.J. and M.F. Rubner, *Methods of Loading and Releasing Low Molecular Weight Cationic Molecules in Weak Polyelectrolyte Multilayer Films*. *Langmuir*, 2002. **18**(4): p. 1176-1183.
18. Kuckling, D., C.D. Vo, and S.E. Wohlrab, *Preparation of Nanogels with Temperature-Responsive Core and pH-Responsive Arms by Photo-Cross-Linking*. *Langmuir*, 2002. **18**(11): p. 4263-4269.
19. Li, H., F. Lai, and R. Luo, *Analysis of Responsive Characteristics of Ionic-Strength-Sensitive Hydrogel with Consideration of Effect of Equilibrium Constant by a Chemo-Electro-Mechanical Model*. *Langmuir*, 2009. **25**(22): p. 13142-13150.
20. Hempenius, M.A., et al., *Poly(ferrocenylsilane) Gels and Hydrogels with Redox-Controlled Actuation*. *Macromolecular Rapid Communications*, 2010. **31**(9-10): p. 772-783.
21. Osada, Y., H. Okuzaki, and H. Hori, *A polymer gel with electrically driven motility*. *Nature*, 1992. **355**(6357): p. 242-244.
22. Jonas, A.M., et al., *Thermo-Responsive Polymer Brushes with Tunable Collapse Temperatures in the Physiological Range*. *Macromolecules*, 2007. **40**(13): p. 4403-4405.
23. Moghadam, M.N., et al., *Controlled release from a mechanically-stimulated thermosensitive self-heating composite hydrogel*. *Biomaterials*, 2014. **35**(1): p. 450-455.
24. Benetti, E.M., S. Zapotoczny, and G.J. Vancso, *Tunable Thermoresponsive Polymeric Platforms on Gold by "Photoiniferter"-Based Surface Grafting*. *Advanced Materials*, 2007. **19**(2): p. 268-271.
25. Szuwarzyński, M., et al., *Pulsatile Releasing Platform of Nanocontainers Equipped with Thermally Responsive Polymeric Nanovalves*. *Chemistry of Materials*, 2013. **25**(3): p. 514-520.
26. Balamurugan, S., et al., *Thermal Response of Poly(N-isopropylacrylamide) Brushes Probed by Surface Plasmon Resonance*. *Langmuir*, 2003. **19**(7): p. 2545-2549.
27. Yu, Y., et al., *Stretching of collapsed polymers causes an enhanced dissipative response of PNIPAM brushes near their LCST*. *Soft Matter*, 2015. **11**: p. 8508-8516.
28. Heskins, M. and J.E. Guillet, *Solution Properties of Poly(N-isopropylacrylamide)*. *Journal of Macromolecular Science: Part A - Chemistry*, 1968. **2**(8): p. 1441-1455.

29. Advincula, R.C., et al., *Polymer Brushes*. 2006: Wiley.
30. Minko, S., *Grafting on Solid Surfaces: "Grafting to" and "Grafting from" Methods*, in *Polymer Surfaces and Interfaces*, M. Stamm, Editor. 2008, Springer Berlin Heidelberg. p. 215-234.
31. Matyjaszewski, K., et al., *Polymers at Interfaces: Using Atom Transfer Radical Polymerization in the Controlled Growth of Homopolymers and Block Copolymers from Silicon Surfaces in the Absence of Untethered Sacrificial Initiator*. *Macromolecules*, 1999. **32**(26): p. 8716-8724.
32. Welch, M.E. and C.K. Ober, *Characterization of Polymer Brush Membranes via HF Etch Liftoff Technique*. *ACS Macro Letters*, 2013. **2**(3): p. 241-245.
33. Patil, R.R., et al., *Direct Measurement of Molecular Weight and Grafting Density by Controlled and Quantitative Degrafting of Surface-Anchored Poly(methyl methacrylate)*. *ACS Macro Letters*, 2015. **4**(2): p. 251-254.
34. Plunkett, K.N., et al., *PNIPAM Chain Collapse Depends on the Molecular Weight and Grafting Density*. *Langmuir*, 2006. **22**(9): p. 4259-4266.
35. Sun, T., et al., *Reversible Switching between Superhydrophilicity and Superhydrophobicity*. *Angewandte Chemie International Edition*, 2004. **43**(3): p. 357-360.
36. Malham, I.B. and L. Bureau, *Density Effects on Collapse, Compression, and Adhesion of Thermoresponsive Polymer Brushes*. *Langmuir*, 2010. **26**(7): p. 4762-4768.
37. Chen, Q., et al., *Collapse from the top: brushes of poly(N-isopropylacrylamide) in co-nonsolvent mixtures*. *Soft Matter*, 2014. **10**(17): p. 3134-3142.
38. Jones, D.M., et al., *Variable Adhesion of Micropatterned Thermoresponsive Polymer Brushes: AFM Investigations of Poly(N-isopropylacrylamide) Brushes Prepared by Surface-Initiated Polymerizations*. *Advanced Materials*, 2002. **14**(16): p. 1130-1134.
39. de Beer, S., et al., *Solvent-induced immiscibility of polymer brushes eliminates dissipation channels*. *Nat Commun*, 2014. **5**: p. 3781.
40. Svetushkina, E., et al., *A comparative study on switchable adhesion between thermoresponsive polymer brushes on flat and rough surfaces*. *Soft Matter*, 2011. **7**(12): p. 5691-5696.
41. Liu, G. and G. Zhang, *Collapse and Swelling of Thermally Sensitive Poly(N-isopropylacrylamide) Brushes Monitored with a Quartz Crystal Microbalance*. *The Journal of Physical Chemistry B*, 2005. **109**(2): p. 743-747.
42. Malisova, B., et al., *Poly(ethylene glycol) Adlayers Immobilized to Metal Oxide Substrates Through Catechol Derivatives: Influence of Assembly Conditions on Formation and Stability*. *Langmuir*, 2010. **26**(6): p. 4018-4026.

43. Etacheri, V., et al., *Visible-light activation of TiO₂ photocatalysts: Advances in theory and experiments*. Journal of Photochemistry and Photobiology C: Photochemistry Reviews, 2015. **25**: p. 1-29.
44. Huang, H.H., et al., *Preparation of rutile and anatase phases titanium oxide film by RF sputtering*. Journal of Nanoscience and Nanotechnology, 2008. **8**(5): p. 2659-2664.
45. Yoo, D., et al., *Effects of annealing temperature and method on structural and optical properties of TiO₂ films prepared by RF magnetron sputtering at room temperature*. Applied Surface Science, 2007. **253**(8): p. 3888-3892.
46. Fujishima, A., T.N. Rao, and D.A. Tryk, *Titanium dioxide photocatalysis*. Journal of Photochemistry and Photobiology C: Photochemistry Reviews, 2000. **1**(1): p. 1-21.
47. Richter, H.W. and W.H. Waddell, *Mechanism of the oxidation of dopamine by the hydroxyl radical in aqueous solution*. Journal of the American Chemical Society, 1983. **105**(16): p. 5434-5440.
48. Wu, M.J., et al., *Photocatalysis of Titanium Dioxide for Water Disinfection: Challenges and Future Perspectives*. International Journal of Photochemistry, 2014. **2014**: p. 9.
49. Reufer, M., et al., *Temperature-sensitive poly(N-Isopropyl-Acrylamide) microgel particles: A light scattering study*. The European Physical Journal E, 2009. **28**(2): p. 165-171.
50. Wu, T., et al., *Formation and Properties of Anchored Polymers with a Gradual Variation of Grafting Densities on Flat Substrates*. Macromolecules, 2003. **36**(7): p. 2448-2453.
51. Yim, H., et al., *Effects of Grafting Density and Molecular Weight on the Temperature-Dependent Conformational Change of Poly(N-isopropylacrylamide) Grafted Chains in Water*. Macromolecules, 2006. **39**(9): p. 3420-3426.
52. Mendez, S., et al., *Computational Modeling of the Temperature-Induced Structural Changes of Tethered Poly(N-isopropylacrylamide) with Self-Consistent Field Theory*. Macromolecules, 2005. **38**(1): p. 174-181.
53. Rahane, S.B., et al., *Swelling Behavior of Multiresponsive Poly(methacrylic acid)-block--poly(N-isopropylacrylamide) Brushes Synthesized Using Surface-Initiated Photoiniferter-Mediated Photopolymerization*. Advanced Functional Materials, 2008. **18**(8): p. 1232-1240.
54. Bittrich, E., et al., *Temperature-Sensitive Swelling of Poly(N-isopropylacrylamide) Brushes with Low Molecular Weight and Grafting Density*. Langmuir, 2012. **28**(7): p. 3439-3448.
55. Banquy, X., E. Charraut, and S. Giasson, *Normal and Lateral Interactions between Thermosensitive Nanoparticle Monolayers in Water*. The Journal of Physical Chemistry B, 2010. **114**(30): p. 9721-9728.

56. Nordgren, N. and M.W. Rutland, *Tunable Nanolubrication between Dual-Responsive Polyionic Grafts*. Nano Letters, 2009. **9**(8): p. 2984-2990.
57. Chang, D.P., J.E. Dolbow, and S. Zauscher, *Switchable Friction of Stimulus-Responsive Hydrogels*†. Langmuir, 2007. **23**(1): p. 250-257.
58. Dedinaite, A., et al., *Friction in aqueous media tuned by temperature-responsive polymer layers*. Soft Matter, 2010. **6**(11): p. 2489-2498.
59. Wu, Y., et al., *Switching Friction with Thermal- Responsive Gels*. Macromolecular Rapid Communications, 2013. **34**(22): p. 1785-1790.
60. Pitenis, A.A., et al., *Polymer fluctuation lubrication in hydrogel gemini interfaces*. Soft Matter, 2014. **10**(44): p. 8955-8962.
61. Ernst, O., et al., *Control of cell detachment in a microfluidic device using a thermo-responsive copolymer on a gold substrate*. Lab on a Chip, 2007. **7**(10): p. 1322-1329.
62. Israelachvili, J.N., Y.-L. Chen, and H. Yoshizawa, *Relationship between adhesion and friction forces*. Journal of Adhesion Science and Technology, 1994. **8**(11): p. 1231-1249.
63. Otsuki, M. and H. Matsukawa, *Systematic Breakdown of Amontons's Law of Friction for an Elastic Object Locally Obeying Amontons's Law*. Scientific Reports, 2013. **3**: p. 1586.
64. Butt, H.-J., B. Cappella, and M. Kappl, *Force measurements with the atomic force microscope: Technique, interpretation and applications*. Surface Science Reports, 2005. **59**(1–6): p. 1-152.
65. Szożkiewicz, R., et al., *Correlations between adhesion hysteresis and friction at molecular scales*. The Journal of Chemical Physics, 2005. **122**(14): p. 144708.
66. Lokuge, I., X. Wang, and P.W. Bohn, *Temperature-Controlled Flow Switching in Nanocapillary Array Membranes Mediated by Poly(N-isopropylacrylamide) Polymer Brushes Grafted by Atom Transfer Radical Polymerization*†. Langmuir, 2007. **23**(1): p. 305-311.
67. Ren, T., et al., *Complementary Density Gradient of Poly(hydroxyethyl methacrylate) and YIGSR Selectively Guides Migration of Endothelial Cells*. Biomacromolecules, 2014. **15**(6): p. 2256-2264.
68. Ren, T., et al., *A complementary density gradient of zwitterionic polymer brushes and NCAM peptides for selectively controlling directional migration of Schwann cells*. Biomaterials, 2015. **56**: p. 58-67.
69. Rodenstein, M., et al., *Fabricating Chemical Gradients on Oxide Surfaces by Means of Fluorinated, Catechol-Based, Self-Assembled Monolayers*. Langmuir, 2010. **26**(21): p. 16211-16220.
70. Hutter, J.L. and J. Bechhoefer, *Calibration of atomic-force microscope tips*. Review of Scientific Instruments, 1993. **64**(7): p. 1868-1873.
71. Wagner, K., P. Cheng, and D. Vezenov, *Noncontact Method for Calibration of Lateral Forces in Scanning Force Microscopy*. Langmuir, 2011. **27**(8): p. 4635-4644.

Redox-Induced Backbiting of Surface-Tethered Alkylsulfonate Amphiphiles: Reversible Switching of Surface Wettability and Adherence

The synthesis and characterization of electrode-supported poly(ferrocenylsilane) (PFS) films bearing iodopropyl (PFS-I) and undecanesulfonate (PFS-SO₃⁻) surface moieties are presented. The redox-responsiveness of these PFS films allows for controlled and repeatable switching of the surface energy of the PFS-I and PFS-SO₃⁻ layers under electrochemical control. Static water/surface contact angle measurements showed a change in contact angle values for PFS-I from 80° (reduced state) to 70° (oxidized state), over repeated cycles. However, an opposite change in wettability was observed for PFS-SO₃⁻ where the values observed varied from 59° (reduced state) to 77° (oxidized state). Nanoscale adherence was assessed with colloid probe AFM. The adhesive forces between these surfaces and a polystyrene (PS) colloid probe in water alternated between 130 nN (reduced state) and 30 nN (oxidized state) for PFS-I layers, and between 75 nN (reduced) and 180 nN (oxidized) for the PFS-SO₃⁻ films. The reversed response of PFS-I films to oxidation compared to PFS-SO₃⁻, in both contact angles and adhesive forces, suggests a different underlying mechanism for switching.

5.1. Introduction

Controlling the interfacial properties of surfaces enables a variety of applications from anti-biofouling coatings^{1, 2} and biomedical glues³ to controllable bioelectrocatalysis⁴ and flow control actuation in microchannels.⁵ The interfacial energy of surfaces can be altered by electric fields⁶ or by changing the chemical composition of the surfaces,⁷ for example by surface functionalization with stimuli-responsive molecules.^{8, 9} Several examples of responsive systems, which can reversibly change their surface properties,¹⁰ can be found in literature. Reversible alterations of surface characteristics are generally controlled by pH,¹¹ temperature,^{12, 13} UV-visible light,^{14, 15} magnetic,^{16, 17} solvent/water,^{18, 19} mechanical,^{20, 21} electrical^{22, 23} and redox^{24, 25} stimuli.

In contrast to most stimulus-responsive materials, redox-switchable materials with electrochemical activity allow for an external and localized actuation by the use of micro- or nano-electrode design.²⁶ Poly(ferrocenylsilane)s (PFSs) are prime building blocks for creating redox-responsive surfaces as these materials can form robust polymer layers on a variety of surfaces including gold,²⁷ silicon oxide²⁸ or polymeric surfaces.²⁹ PFSs can be reversibly oxidized and reduced by chemical and electrochemical methods. Cyclic voltammograms display typical double oxidation and reduction waves, caused by intermetallic coupling between the ferrocene units in the PFS main chain. Complete electrochemical oxidation of PFSs is achieved at redox potentials below 1 V.^{27, 30, 31} PFSs can be incorporated into polymer architectures by copolymerization^{32, 33} and can form dual responsive systems via side group modification,³⁴ opening possibilities for the fabrication of complex material structures such as hydrogels³⁴ or porous membranes.³⁵

An interesting alternative method which gives a significant change in surface energy has been reported for a low-density self-assembled monolayer (SAM) of (16-mercapto)hexadecanoic acid on gold substrates using a molecular backbiting transition. This transition was, however, driven by *high*-voltage electric fields.³⁶ We

aim here at assessing the variations in wettability and adherence at *low* voltages. To do so, we compare unsubstituted PFS and PFS bearing charged sulfonate groups to obtain insights about the role of polarity and conformational changes of the surface grafts. Electrode-supported PFS films, possessing either iodopropyl- or undecylsulfonate surface groups (PFS-I and PFS-SO₃⁻, respectively), were oxidized and reduced electrochemically and characterized by water contact angle measurements and atomic force microscopy (AFM) measurements using a polystyrene (PS) colloid in water. Oxidation of PFS-I modifies the polarity of the surface by creating positively charged ferrocenium (Fc⁺) centers, which increase the surface energy. When reduced, the PFS-I layer returns to its neutral, hydrophobic state neutrality and consequently, the surface energy is again decreased.³⁷ However, this change in surface energy is not large ($\Delta\theta = 10^\circ$). By substitution of the iodopropyl group by a dangling undecylsulfonate group, a backbiting method²⁵ can be employed resulting in much stronger variations of the surface energy ($\Delta\theta = 20^\circ$). For this system, the exposed alkanesulfonate groups, in the reduced state, create a hydrophilic surface. Upon oxidation, the Fc⁺ units attract the negatively charged sulfonate head-group, resulting in backbiting of the head-groups towards the PFS surface. This exposes the hydrophobic undecyl spacer and reduces the surface energy. The attraction between the sulfonate group and Fc⁺ competes with counter-ions in the electrolyte solution. In acetonitrile, a favorable affinity of the sulfonate group compare to PF₆⁻ for the Fc⁺ centers was found, in agreement with the Hofmeister series.³⁸⁻⁴⁰

5.2. Results and discussion

5.2.1. Synthesis and characterization

Surface-immobilized PFS-I films were obtained in a two-step synthetic procedure. For PFS films functionalized with PFS-SO₃⁻, an additional step was required

(**Scheme 5.1**). First, an amine-terminated self-assembled monolayer (SAM) was formed on a gold substrate. Then, a solution of PFS-I in THF was spin-coated on this layer followed by heating at 50 °C to covalently bind the PFS chains to the Au surface via amination of the iodopropyl side groups.²⁸ The non-chemisorbed PFS-I chains were then removed by immersion of the substrate in THF. PFS-SO₃[−] layers were fabricated by treating the unreacted iodopropyl groups of the surface-immobilized PFS-I films with a sulfonate-ended alkanethiol. The thiol-end group of sodium 11-mercaptoundecanesulfonate was first deprotonated with sodium methoxide in methanol under an inert atmosphere to enhance its reactivity. The sodium 11-mercaptoundecanesulfonate solution was then added to the PFS-I surface-modified substrates and left for several days.

Scheme 5.1. Schematic representation of the covalent surface-attachment of PFS-I chains on gold substrates followed by the modification of unreacted iodopropyl groups by sulfonate-terminated alkanethiol to obtain PFS-SO₃[−] films.

XPS was performed to prove the presence of PFS-I and PFS-SO₃[−] layers on the gold substrates. As shown in **Appendix 5.1**, the expected elements for PFS-I and PFS-SO₃[−] are present in significant amounts. Furthermore, successful functionalization of PFS-I with sulfonate-ended alkanethiol to obtain PFS-SO₃[−] was verified by observing the binding energy in the region of the chemical shift of sulfur S2p. Indeed, as shown in **Figure 5.1**, XPS spectra of PFS-I do not show any sulfur, while for PFS-SO₃[−], sulfur atoms, bound in two typical ways, are present. The S2p peak around 169 eV originates from the sulfonate group, and the S2p around 164 eV is characteristic of the sulfur in a thioether group. The sulfur of the cysteamine monolayer that is bound to gold is not visible for both PFS-I and PFS-SO₃[−], because of its relatively low amount which is, furthermore, covered by the PFS layers of 14 nm. The amount of PFS units functionalized with sulfonate-ended alkanethiol in PFS-SO₃[−] was estimated at 67%, by comparing the atomic concentration of sulfur with the atomic concentration of iron (see **Appendix 5.1**).

Figure 5.1. XPS spectra of PFS-I and PFS-SO₃[−] in the region of the chemical shift of sulfur S2p. PFS-I layers do not show any peaks in this region. PFS-SO₃[−] layer shows 2 peaks at 169 and 164 eV, corresponding to sulfonate and thioether groups, respectively. Each S2p peak is the combination of 2 peaks, namely S2p_{1/2} and S2p_{3/2}.

5.2.2. Redox properties

The redox-response of surface-immobilized PFS-I and PFS-SO₃⁻ films was studied with cyclic voltammetry (CV) from +0.1 V to +0.9 V in acetonitrile, using 0.1 M tetrabutylammonium hexafluorophosphate (NBu₄PF₆) as supporting electrolyte. As demonstrated previously, relatively dense PFS-I layers are obtained which display a high stability during repeated oxidation and reduction cycles, in both aqueous and organic solvents.²⁸ Stable cyclic voltammograms in acetonitrile, a good solvent for PFS, provide evidence for the robustness of the covalent attachment to the gold surface. PFS-I and PFS-SO₃⁻ films show similar cyclic voltammograms (see **Figure 5.2** and **Appendix 5.2**), indicating that functionalization of PFS-I with sodium 11-mercaptopundecanesulfonate does not influence the oxidation and reduction potentials of the PFS chains. In **Figure 5.2.a**, the cyclic voltammograms of PFS-SO₃⁻ films recorded at scan rates between 5 and 100 mV/s are presented. The CV curves show a reversible electrochemical process with the double oxidation and reduction waves characteristic of PFS.³¹ At 100 mV/s scan rate, the two oxidation peaks i_{pox1} and i_{pox2} are at the potential of +0.54 V and +0.67 V, respectively. The two reduction peaks i_{pred1} and i_{pred2} are found at the potential of +0.41 V and +0.52 V, respectively. The surface coverage of ferrocene units was determined from electrochemical measurements by integrating the current-potential signals, and typical values of 2.2×10^{-9} mol/cm² were found. This value is in agreement with literature and indicates the presence of a thin, uniform and relatively dense PFS film at the electrode surface.²⁸ The linear dependency of the current peak height with scan rate (**Figure 5.2.b**) provides evidence for a surface-confined redox reaction.⁴¹

Figure 5.2. (a) Cyclic voltammograms of surface-immobilized PFS-SO₃⁻ films on a gold substrate at different sweep rates. The PFS-modified gold substrates were used as the working electrode; counter- and reference electrodes were of platinum, and the electrolyte was a 0.1 M NBu₄PF₆ solution in CH₃CN. (b) Graph representing the peak heights of *i*_{pox2} and *i*_{pred2} of PFS-SO₃⁻ layers as a function of scan rate.

5.2.3. Wettability switch

Static water contact angle measurements were performed to study interfacial energy changes of the PFS-I and PFS-SO₃⁻ layers in the reduced and oxidized states, respectively. Full oxidation of the PFS films was achieved electrochemically in 0.1 M NBu₄PF₆ solution in acetonitrile by applying a constant potential of +0.8 V for 5

min. Complete reduction of the PFS-modified layers was achieved using an applied potential of +0.1 V. PFS layers are known to keep their redox state for some hours after being disconnected from an electrochemical setup followed by rinsing and drying, which allowed us to perform experiments following redox reactions.³⁴ In **Figure 5.3**, the static contact angles of a water droplet on dried PFS-I (dashed line) and PFS-SO₃⁻ (full line) films are presented for four redox cycles. PFS-I layers display a reversible change in average contact angle from 80° to 70° when converted from the reduced to the oxidized states. The change in the contact angle values can be explained by the alteration of the polarity of the surface. When oxidized, PFS-I layers become positively charged, as ferrocene units are turned into ferroceniums. The induced polarity increases the wettability of the surface. When the PFS-I layer is reduced, the film becomes neutral again and consequently the wettability decreases, as is evident from the increased water contact angle. In contrast, PFS-SO₃⁻ films show a change in contact angle from an average value of 59° in the reduced state to 77° in the oxidized state. The reversed switching behavior of PFS-SO₃⁻ films from a mild hydrophilic to a more hydrophobic state indicates a different underlying mechanism.

Figure 5.3. Graph representing the static water/surface contact angle during four redox cycles of PFS-I (dashed line) and PFS-SO₃⁻ films (full line). The applied potentials were +0.1 V and +0.8 V for reduction and oxidation, respectively, vs. a platinum wire electrode in 0.1 M NBu₄PF₆ in CH₃CN.

In the case of PFS-SO_3^- films, the presence of sulfonate-terminated alkane groups at the PFS surface give, in the reduced state, a higher surface energy compared to neutral reduced PFS-I. The high polarity of the free sulfonate groups increases the wettability of the PFS-SO_3^- films. When the PFS-SO_3^- films are oxidized, positively charged ferrocenium centers are created. The Fc^+ centers attract the negatively charged sulfonate groups. The consequent bending of the alkane chain exposes the hydrophobic hydrocarbon chain at the interface and reduces wettability (**Scheme 5.2**). We note that a similar conformational transition was described with a low-density SAM of (16-mercapto)hexadecanoic acid on gold substrates.³⁶ Their reported relative change in wettability was similar to our system ($\Delta\theta = 20^\circ$). However, our contact angles are close to 90° which allows for capillary filling transitions.⁴² In their work, the collective molecular reorientation of the alkylcarboxylate moieties was found to occur only for SAMs with a low surface coverage. In fact, with a high density SAM of the same alkylcarboxylate, the wettability change was absent. In the case of the PFS-SO_3^- films however, the alkylsulfonate groups are spaced at a sufficiently large distance to avoid steric hindrance, allowing for dynamic molecular motion and bending.

Scheme 5.2. Schematic representation of the conformational transition of alkylsulfonate side groups upon oxidation and reduction of PFS-SO_3^- films in 0.1 M NBu_4PF_6 in CH_3CN .

Another factor that can influence the conformational transition of the sulfonate-terminated alkane is the electrolyte solution which is used during electrochemical oxidation and reduction of PFS-SO₃⁻. When PFS-SO₃⁻ is oxidized, Fc⁺ units acquire negatively charged counterions. When compensating the positive charge of the Fc⁺ centers, a competition may occur between the sulfonate group and the anions of the supporting electrolyte in solution. This phenomenon should be related to the Hofmeister's series. The Hofmeister's series ranks cations and anions depending on their affinity to polymeric systems, e.g. proteins. Affinity is specific for each system, as it depends on the charge of the ions, the hydrophilicity of the studied polymer³⁸ and also on the solvent.³⁹ In the specific case presented in this chapter, the combination of NBu₄PF₆ in acetonitrile and PFS-SO₃⁻ results in a favorable affinity of the sulfonate group for the Fc⁺ centers of PFS-SO₃⁻ compared to PF₆⁻ anions.

The same experiment was performed in 0.1 M aqueous sodium perchlorate (NaClO₄) as electrolyte for the electrochemical redox. Contact angles changed for the PFS-SO₃⁻ films as they changed for PFS-I upon redox. When oxidized, the contact angle was lower (within 10°) than in the reduced state. This reveals that for PFS-SO₃⁻ films in aqueous NaClO₄, no bending of the sulfonate-ended alkane occurred and that only polarity changes of the films affected the wettability. In water, ClO₄⁻ anions seem to have a higher affinity for the Fc⁺ centers of PFS-SO₃⁻ than the sulfonate groups. This observation is in a good agreement with the Hofmeister's series for similar systems.⁴⁰ For the positively charged amino-proteins in water, anion affinity was ranked as: H₂PO₄⁻ < HCOO⁻ < CH₃SO₃⁻ < Cl⁻ < NO₃⁻ < CF₃COO⁻ < BF₄⁻ < ClO₄⁻ << PF₆⁻. According to this series, the sulfonate anion (underlined) has less interaction with the ammonium groups of the protein than ClO₄⁻ (underlined) in water.

5.2.4. Adhesion properties via AFM

Grafting of PFS-I chains to amine-functionalized surfaces is known to produce thin, homogeneous and relatively dense polymer layers.²⁸ However, since surface roughness influences wettability,⁴³ tapping mode AFM images were acquired and the RMS roughness of the image (500 nm x 500 nm) was calculated. As shown in **Figure 5.4**, both PFS-I (**Figure 5.4.a**) and PFS-SO₃⁻ films (**Figure 5.4.b**) possessed a low roughness, which varied similarly between reduced and oxidized states for these films. In the reduced state, PFS-I and PFS-SO₃⁻ films had typical roughness values R_q of 2.93 nm and 2.89 nm, respectively, for a scan size of 500 x 500 nm². In the oxidized state, R_q changed to 1.65 nm and 1.23 nm for these films, respectively. These surface and thickness roughness values are consistent with the literature.²⁸ As PFS-I and PFS-SO₃⁻ films displayed a similar trend in surface roughness but different wettability behavior upon redox, it can be concluded that surface roughness changes are not responsible for the observed contact angle changes.

Figure 5.4. Tapping mode AFM images in air of (a) PFS-I and (b) PFS-SO₃⁻ films upon redox at a scan size of 500 nm and a z-scale of 20 nm.

Figure 5.5. Representative force-distance curves of a surface-immobilized PFS-I in (a) reduced and (b) oxidized state with a PS colloid probe in water. The arrows indicate the evolution of the curves with the approach and retraction between the PS colloid and the surface. The adhesive force is displayed on the y-axis with the same scale for better comparison. (c) Histograms of pull-off forces of this PFS-I layer recorded for reduced and oxidized state. For each redox state, at least 600 force-distance curves were collected over 3 different spots. The histograms were fitted with a Gaussian distribution.

Figure 5.6. Representative force-distance curves of a PFS-SO₃⁻ layer in (a) reduced and (b) oxidized state with a PS colloid probe immersed in water. The arrows indicate the evolution of the curve during the approach and retraction process of the PS colloid from the surface. The adhesive force is displayed on the y-axis with the same scale for better comparison. (c) Histograms of pull-off forces on PFS-SO₃⁻ films recorded for reduced and oxidized states. For each redox state, at least 600 force-distance curves were performed over 3 different spots. The histograms were fitted with a Gaussian distribution.

AFM force measurements can provide detailed information on the hydrophilicity or hydrophobicity of surfaces by measuring adhesive forces between *e.g.* a colloidal probe attached to an AFM cantilever and the surface of interest.⁴⁴ In order to obtain support for the arguments we provided to explain the observed trends in wetting, we carried out detailed force curve studies by employing colloidal probe AFM. A PS colloid probe was used to obtain force-distance curves on PFS-I and PFS-SO₃⁻ layers, immersed in water. The values of the pull-off force between the hydrophobic colloidal sphere and the PFS surfaces were extracted. **Figure 5.5** shows an example for a force-distance curve for reduced PFS-I (**Figure 5.5.a**) and oxidized PFS-I films (**Figure 5.5.b**), respectively. In **Figure 5.5.c**, the histogram represents the distribution of the pull-off forces, which correspond to the adhesive forces between the two surfaces. A Gaussian function was then used to fit each histogram. The average adhesive force value for reduced PFS-I was around 130 nN, and was approximately 30 nN in the case of oxidized PFS-I. In the reduced state, the hydrophobic PFS-I displays a high adherence with the hydrophobic PS colloid which can be attributed to hydrophobic interactions. When PFS-I is oxidized, the polarity of the surface makes it more hydrophilic.⁴⁵ This increases the wetting of the PFS-I surface and reduces the adherence with the PS probe. **Figure 5.6** presents force-distance curves of reduced (**Figure 5.6.a**) and oxidized (**Figure 5.6.b**) PFS-SO₃⁻ layers with the same PS colloid. In **Figure 5.6.c**, the distribution of the adhesive forces for each PFS-SO₃⁻ redox state is illustrated. The inverse trend for the water contact angles displayed earlier by the PFS-I and PFS-SO₃⁻ films under electrochemical oxidation and reduction was also seen in the adhesive force measurements. PFS-SO₃⁻ films in the reduced state and the PS colloid had an adhesive force of around 75 nN. When PFS-SO₃⁻ was oxidized, the adherence increased to 180 nN. In the reduced state, the PFS-SO₃⁻ film surface is polar due to the exposed sulfonate groups, which leads to a low adhesive force with the PS colloid. When PFS-SO₃⁻ is oxidized, the interface hydrophobicity increases, resulting in an increased hydrophobic interaction between the surfaces in water and

consequently a higher pull-off force. Even though the presence of surface charges on the hydrophobic PS beads used in the adhesive force measurements cannot be completely excluded,^{46, 47} our results can be explained entirely on the basis of hydrophobic interactions between PFS film and PS colloidal tip, and are fully consistent with earlier electrochemical AFM studies where hydrophobic silicon nitride tips were employed to probe tip-film interactions as a function of redox state.^{28, 37} From the colloid probe AFM force curve experiments, we conclude that the redox-induced variation of PFS film polarity and the redox-induced changes in electrostatic interactions between the immobilized PFS film and its pendant sulfonate groups as evident from contact angle observations, are fully supported by the AFM data.

5.3. Conclusion

Two redox active poly(ferrocenylsilane) thin films, immobilized on electrode surfaces and possessing either iodopropyl- or undecylsulfonate surface groups were employed to study the variation of surface polarity and wetting under electrochemical control. The surface characteristics of these films could be reversibly switched between hydrophobic and hydrophilic states as was demonstrated by both the contact angle of a water droplet and the adhesive forces with a PS colloid in water. For surface-immobilized PFS-I, the formation of Fc^+ units during oxidation yielded to low contact angle and low adhesive force values with the hydrophobic surface of a PS colloidal probe. When PFS-I was brought back to the reduced state, the polarity of the film was minimized, which reduced the wettability and increased the adhesive force with the PS colloid. Next, the PFS-I films were derivatized to PFS-SO_3^- films possessing alkylsulfonate moieties at their surface. Compared to PFS-I, the obtained PFS-SO_3^- films exhibited a reversed trend upon electrochemical oxidation and reduction for both water contact angles, and the adhesive forces with a PS colloid in water. Electrochemical oxidation of PFS-SO_3^-

films caused a conformational transition resulting from electrostatic interactions between the sulfonate groups and the Fc^+ centers. This transition exposed the alkane chain to the interface and increased the hydrophobicity of the surface. Additionally, the hydrophobic PS colloids used in the adhesive force measurements in water could exhibit negative surface zeta potential, depending on the pH and the ionic strength, which would also add electrostatic interactions with the PFS-SO_3^- layers. The particular choice of the electrolyte solution plays an important role in this backbiting process. Both the nature of the supporting electrolyte salt and the solvent affect Hofmeister's interaction of the sulfonate groups and the anions in solution, with the Fc^+ units on the film surface. The strength of the interaction between the cations in solution and the sulfonate groups, compared to the affinity of the Fc^+ units for the sulfonate groups, also play a role. Supporting electrolytes such as NMe_4PF_6 , which will provide PFS-SO_3^- films with lower contact angles in the reduced state compared to NBu_4PF_6 , may expand the range over which contact angles and adhesive forces are switched. Unfortunately, the observed switching of the PFS-SO_3^- films was not possible in water which restricts the use of this system for in-situ applications in aqueous solutions, e.g. in microchannels for flow control or for "pick and place" techniques.⁴⁸ A full study of other electrolytes from the Hofmeister's series would, therefore, be beneficial for a better understanding of the system behavior in other conditions. Furthermore, super-hydrophilicity and super-hydrophobicity states could be achieved with this system, for example, by designing a particular roughness distribution on the surface.^{12, 13} Moreover, the bending transition triggered in the PFS-SO_3^- films may also change the friction between the surface and a counter-surface, which would be a topic of great interest to study.^{49, 50}

5.4. Experimental section

Materials. Gold substrates (1 x 1 cm²) were cut from a silicon wafer coated with 100-nm-sputtered Au on 10 nm Cr. Poly(ferrocenyl(3-iodopropyl)methylsilane) (PFS-I) was prepared by platinum-catalyzed ring-opening polymerization according to established procedures.⁵¹ (GPC against polystyrene standards: $M_w = 199$ kg/mol, $M_n = 116$ kg/mol, $M_w/M_n = 1.7$) 11-Bromo-1-undecene (95%), sodium sulfite ($\geq 98.0\%$), benzyltriethylammonium bromide (99%), thioacetic acid (96%), 2,2'-azobis(2-methylpropionitrile) (98%), hydrochloric acid, sulfuric acid and sodium methoxide (25 wt% in methanol) were purchased at Sigma-Aldrich and used as received. Methanol, diethyl ether, tetrahydrofuran (THF) and ethanol were purchased from Merck and used as received. All the water used is ultra-pure water dispensed through a Milli-Q system from Millipore Corporation.

Sodium 11-mercaptoundecanesulfonate synthesis. Sodium 11-mercaptoundecanesulfonate was synthesized following a 3-step reaction route as reported in literature.⁵² First, 11-bromo-1-undecene (1.24 g, 5 mmol) was refluxed with sodium sulfite (1.26 g, 10 mmol) and benzyltriethyl ammonium bromide (14.8 mg) in methanol (8 mL) and Milli-Q water (18 mL) for 16h. The aqueous mixture was extracted with diethyl ether (3 x 30 mL) and cooled down to 0 °C until precipitation of the sodium undec-10-enesulfonate. The white solid obtained was filtered and dried. Then, the terminal alkene group of sodium undec-10-enesulfonate was converted into a thiol functionality by refluxing it with thiolacetic acid (2 mL, 26 mmol) with azobisisobutyronitrile (10 mg) in methanol (20 mL) for 6h. The volatiles were removed under vacuum overnight and the residue was washed with diethyl ether (4 x 20 mL), filtered and dried. Finally, the thiol of 11-acetylthioundecanesulfonate, obtained previously, was deprotected by refluxing in 10% hydrochloric acid (20 mL) for 2h. The residue was dried under vacuum overnight and recrystallized in water to obtain pure sodium 11-

mercaptoundecanesulfonate. ¹HNMR (D₂O): 2.68 (t, 2H), 2.33 (t, 2H), 1.52 (m, 2H), 1.38 (m, 2H), 1.1 (br s, 14H).

Attachment of poly(ferrocenyl(3-iodopropyl)methylsilane) films to gold. PFS-I chains were covalently attached to gold via a cysteamine self-assembled monolayer as reported previously.²⁸ Gold substrates were cleaned with Piranha solution (H₂SO₄:H₂O₂ 3:1) for 30 s and extensively rinsed with water and ethanol. The cleaned gold substrates were directly immersed in a 10 mM cysteamine solution in ethanol for 16h to form the cysteamine SAM. The substrates were then rinsed with ethanol and dried in a stream of nitrogen. A solution of PFS-I in THF (10 mg/mL, 100 μ L per sample) was immediately spin-coated (3000 rpm for 60 s, Spincoater Model P6700 from Specialty Coating Systems, Inc.) on the substrates which were left to react overnight at 50 °C in a vacuum oven. The PFS-I-modified substrates were then immersed in THF (3x 1h) to remove any physisorbed polymer chains.

Side group modification of surface-anchored poly(ferrocenyl(3-iodopropyl)methylsilane) with sodium 11-mercaptoundecanesulfonate (PFS-SO₃⁻). The unreacted iodopropyl side groups of surface-attached PFS-I were modified with sodium 11-mercaptoundecanesulfonate. In order to enhance its reactivity, the thiol group was deprotonated. A solution of sodium 11-mercaptoundecanesulfonate (104 mg, 0.36 mmol) in methanol (10 mL) was purged with a flow of argon for 30 min. Then, sodium methoxide solution in methanol (0.1 mL, 0.46 mmol) was added. A separate 100 mL Erlenmeyer flask containing the PFS-I-modified gold substrates was closed by a septum and also purged with a flow of argon for 30 min. The sodium 11-mercaptoundecanesulfonate solution was then added with an argon-purged syringe, by completely immersing the substrates. The flask was left at room temperature in the dark for 4 days. The substrates were washed with methanol and ethanol successively, and dried under nitrogen flow. Yield of reaction and characterization of the sample by X-ray photoelectron spectroscopy (XPS) are discussed in the results section.

Static contact angle measurements. Static contact angle measurements were performed with a 2 μl sessile drop using an OCA15 instrument from Dataphysics, Germany, equipped with an electronic syringe unit. The drop contour was fitted by the Young-Laplace equation and at least 3 different measurements on each sample were performed.

Electrochemistry. Cyclic voltammetry and redox reactions of PFS were performed in a 0.1 M solution of tetrabutylammonium hexafluorophosphate (NBu_4PF_6) in acetonitrile. The gold substrate underneath the PFS was used as working electrode, a Pt wire as reference electrode and a Pt counter-electrode was employed. Cyclic voltammograms were recorded between +0.1 V and +0.9V, vs. Pt, at different scan rates. PFS was oxidized and reduced by applying a constant potential of +0.8V and +0.1V for oxidation and reduction, respectively, during 5 min. The full oxidation and reduction of the film, during these 5 min, was confirmed with the visualization of the current-time (i-t) curves, as shown in **Appendix 5.3**. To determine the surface coverage, first, the total surface charge Q is extracted from the CV curves by using the equation $Q = \int i/v \, dE$, with v being the scan rate used during the CV measurements, i being the current and E the applied potential. Next, the surface coverage of the ferrocene groups on the surface Γ was calculated using the equation $\Gamma = Q/(n F A_s)$, where n is the number of electrons involved in the ferrocene/ferrocenium redox reaction (here $n = 1$), F is the Faraday constant and A_s is the total surface area of the working electrode. As we used an electrochemical cell with an O-ring, A_s is the inner area of this O-ring.

X-ray photoelectron spectroscopy. XPS was performed to confirm the presence of PFS-I tethered films after substrate anchoring and to evaluate the concentration of sulfonate groups in PFS-SO_3^- after functionalization with sodium 11-mercaptoundecanesulfonate. XPS spectra were obtained by a Quantera SXM instrument from Physical Electronics, using monochromatized Al $K\alpha$ radiation (1486.6 eV) with an X-ray beam diameter of 200 μm at the standard beam-input and detector input angle of 45° . The atomic concentration is calculated with the formula

$C_x = (I_x/S_x)/(\sum_i^n I_i/S_i)$ with I_i the peak area off a photoelectron peak and S_i the relative sensitivity factor of the peak.

Ellipsometry. The thickness of dry layers was measured using a rotating analyzer ellipsometer (J.A. Woollam VASE) at the wavelengths from 380 to 800 nm at the angles of incidence of 65, 70 and 75°. Thickness determinations were performed on at least 3 spots for each sample. The Cauchy dispersion relation ($n(\lambda) = A + B/\lambda^2 + C/\lambda^4$) was used to model the PFS layers on 100 nm gold material. The constant A was fixed at 1.687, B at 0.01 and C at 0.⁵³ The dry thickness of PFS-I and PFS-SO₃⁻ layers was found to be 14.3 ± 0.2 nm for both layers.

Atomic Force Microscopy (AFM) measurements. AFM measurements were performed in water using a NanoScope V multimode 8 atomic force microscope (Bruker, USA) equipped with a standard liquid cell. A polystyrene colloidal probe (sQube, Germany) with a spring constant of 0.2 N/m (determined using the thermal noise method⁵⁴) and a colloid diameter of 6 µm (determined by Scanning electron microscopy (SEM), see **Appendix 5.4**) was used in the experiments. The cantilever deflection was monitored upon approach to and retract from the surface⁵⁵ over a distance of 1.5 µm at a velocity of 3 µm/s. At least 600 force-distance curves were obtained at 3 different spots for each data set and analyzed with a Matlab program to extract the adhesive force. To determine the roughness of the sample, tapping mode imaging was employed using a relative amplitude setpoint of 80% and a drive frequency ($f_{\text{drive}} = 296.32$ kHz) just below the resonance frequency of the cantilever (MPP-11100, Bruker, $f_{\text{res}} = 296.5$ kHz). The roughness was quantified by calculating the RMS roughness amplitude $R_q = \sqrt{\frac{1}{n} \sum_{i=1}^n y_i^2}$ over each image of size 500 x 500 nm².

5.5. Appendix

Element Sample	C	N	O	Na	Si	S	Fe	I	Au
PFS-I	75.40	0.88	2.42	0.40	7.05	0.70	5.32	1.88	5.94
PFS-SO ₃ ⁻	64.51	0.59	10.40	0.97	7.28	5.19	3.86	1.11	6.10

Appendix 5.1. XPS spectra of PFS-I and PFS-SO₃⁻ on gold substrates and table of the atomic concentration for each element.

Appendix 5.2. Cyclic voltammograms of surface-immobilized PFS-I films on a gold substrate at different sweep rates. The PFS-modified gold substrates were used as the working electrode, counter- and reference electrodes were of platinum, and the electrolyte was a 0.1 M NBu₄PF₆ solution in CH₃CN.

Appendix 5.3. Current-time (*i-t*) curves during oxidation at 0.8 V and reduction at 0.1 V for PFS-I films in a 0.1 M NBu_4PF_6 solution in CH_3CN . The current reaches a plateau at 0 A, showing that no more electrons are involved in redox reactions, and therefore, proving that the entire film was oxidized or reduced after 5 min. The plateau is not exactly at 0 A because of the resistance of the system itself. Furthermore, 5 min of oxidation and reduction is a long time for this fast redox system (less than 60 s is required), but this time was chosen on purpose to ensure that the entire film was completely oxidized or reduced.

Appendix 5.4. SEM image of the PS colloid probe used for AFM pull-off force experiments with PFS-I and PFS-SO_3^- . The scale bar for both images is 1 μm .

5.6. References

1. Krishnan, S., C.J. Weinman, and C.K. Ober, *Advances in polymers for anti-biofouling surfaces*. Journal of Materials Chemistry, 2008. **18**(29): p. 3405-3413.
2. Brzozowska, A.M., et al., *Biomimicking Micropatterned Surfaces and Their Effect on Marine Biofouling*. Langmuir, 2014. **30**(30): p. 9165-9175.
3. Meddahi-Pellé, A., et al., *Organ Repair, Hemostasis, and In Vivo Bonding of Medical Devices by Aqueous Solutions of Nanoparticles*. Angewandte Chemie International Edition, 2014. **53**(25): p. 6369-6373.
4. Wan, P. and X. Chen, *Stimuli-Responsive Supramolecular Interfaces for Controllable Bioelectrocatalysis*. ChemElectroChem, 2014. **1**(10): p. 1602-1612.
5. Kieviet, B.D., P.M. Schon, and G.J. Vancso, *Stimulus-responsive polymers and other functional polymer surfaces as components in glass microfluidic channels*. Lab on a Chip, 2014. **14**(21): p. 4159-4170.
6. Satoh, W., M. Loughran, and H. Suzuki, *Microfluidic transport based on direct electrowetting*. Journal of Applied Physics, 2004. **96**(1): p. 835-841.
7. Whitesides, G.M. and P.E. Laibinis, *Wet chemical approaches to the characterization of organic surfaces: self-assembled monolayers, wetting, and the physical-organic chemistry of the solid-liquid interface*. Langmuir, 1990. **6**(1): p. 87-96.
8. Mendes, P.M., *Stimuli-responsive surfaces for bio-applications*. Chemical Society Reviews, 2008. **37**(11): p. 2512-2529.
9. Stuart, M.A.C., et al., *Emerging applications of stimuli-responsive polymer materials*. Nat Mater, 2010. **9**(2): p. 101-113.
10. Xin, B. and J. Hao, *Reversibly switchable wettability*. Chemical Society Reviews, 2010. **39**(2): p. 769-782.
11. Dai, S., P. Ravi, and K.C. Tam, *pH-Responsive polymers: synthesis, properties and applications*. Soft Matter, 2008. **4**(3): p. 435-449.
12. Sun, T., et al., *Reversible Switching between Superhydrophilicity and Superhydrophobicity*. Angewandte Chemie International Edition, 2004. **43**(3): p. 357-360.
13. Geissler, A., et al., *Thermo-responsive superhydrophobic paper using nanostructured cellulose stearoyl ester*. Cellulose, 2014. **21**(1): p. 357-366.
14. Schenderlein, H., et al., *Preparation and Characterization of Light-Switchable Polymer Networks Attached to Solid Substrates*. Langmuir, 2013. **29**(14): p. 4525-4534.
15. Wan, P., et al., *Tuning surface wettability through photocontrolled reversible molecular shuttle*. Chemical Communications, 2008(44): p. 5710-5712.
16. Zhang, M., et al., *Superparamagnetic Hybrid Nanocylinders*. Advanced Functional Materials, 2004. **14**(9): p. 871-882.

17. Wan, P., et al., *Graphene Carrier for Magneto-Controllable Bioelectrocatalysis*. Small, 2014. **10**(4): p. 647-652.
18. de Beer, S., et al., *Solvent-induced immiscibility of polymer brushes eliminates dissipation channels*. Nat Commun, 2014. **5**.
19. Edmondson, S., et al., *Co-Nonsolvency Effects for Surface-Initiated Poly(2-(methacryloyloxy)ethyl phosphorylcholine) Brushes in Alcohol/Water Mixtures*. Langmuir, 2010. **26**(10): p. 7216-7226.
20. Vogel, M.J. and P.H. Steen, *Capillarity-based switchable adhesion*. Proceedings of the National Academy of Sciences, 2010. **107**(8): p. 3377-3381.
21. Chan, E.P., et al., *Surface Wrinkles for Smart Adhesion*. Advanced Materials, 2008. **20**(4): p. 711-716.
22. Mugele, F. and J.C. Baret, *Electrowetting: From basics to applications*. Journal of Physics Condensed Matter, 2005. **17**(28): p. R705-R774.
23. Pei, Y., J. Travas-Sejdic, and D.E. Williams, *Reversible Electrochemical Switching of Polymer Brushes Grafted onto Conducting Polymer Films*. Langmuir, 2012. **28**(21): p. 8072-8083.
24. Chung, H.J., J. Song, and G.J. Vancso, *Tip-surface interactions at redox responsive poly(ferrocenylsilane) (PFS) interface by AFM-based force spectroscopy*. Applied Surface Science, 2009. **255**(15): p. 6995-6998.
25. Tabard-Cossa, V., et al., *Redox-Induced Surface Stress of Polypyrrole-Based Actuators*. The Journal of Physical Chemistry B, 2005. **109**(37): p. 17531-17537.
26. Bani-Yaseen, A.D., *Fabrication of Electrochemically Deposited Microelectrodes for Microfluidic MEMS Applications*. International Journal of Electrochemical Science, 2010. **5**(12): p. 1837-1846.
27. Péter, M., et al., *Electrochemistry of Surface-Grafted Stimulus-Responsive Monolayers of Poly(ferrocenyldimethylsilane) on Gold*. Langmuir, 2005. **21**(11): p. 5115-5123.
28. Sui, X., et al., *Electrochemical sensing by surface-immobilized poly(ferrocenylsilane) grafts*. Journal of Materials Chemistry, 2012. **22**(22): p. 11261-11267.
29. McDowell, J.J., et al., *Electroactuation of Alkoxysilane-Functionalized Polyferrocenylsilane Microfibers*. Journal of the American Chemical Society, 2010. **132**(10): p. 3236-3237.
30. Wang, X.-J., et al., *Electrochemical behaviors of poly(ferrocenylsilane) solutions*. Journal of Applied Polymer Science, 2007. **103**(2): p. 789-794.
31. Rulkens, R., et al., *Linear Oligo(ferrocenyldimethylsilanes) with between Two and Nine Ferrocene Units: Electrochemical and Structural Models for Poly(ferrocenylsilane) High Polymers*. Journal of the American Chemical Society, 1996. **118**(50): p. 12683-12695.
32. Bellas, V. and M. Rehahn, *Polyferrocenylsilane-Based Polymer Systems*. Angewandte Chemie International Edition, 2007. **46**(27): p. 5082-5104.

33. Resendes, R., et al., *Supramolecular Organometallic Polymer Chemistry: Multiple Morphologies and Superstructures from the Solution Self-Assembly of Polyferrocene-block-Polysiloxane-block-Polyferrocene Triblock Copolymers*. Chemistry – A European Journal, 2001. **7**(11): p. 2414-2424.
34. Sui, X., et al., *Poly(N-isopropylacrylamide)-poly(ferrocenylsilane) dual-responsive hydrogels: synthesis, characterization and antimicrobial applications*. Polymer Chemistry, 2013. **4**(2): p. 337-342.
35. Zhang, K., et al., *Breathing Pores on Command: Redox-Responsive Spongy Membranes from Poly(ferrocenylsilane)s*. Angewandte Chemie International Edition, 2014. **53**(50): p. 13789-13793.
36. Lahann, J., et al., *A Reversibly Switching Surface*. Science, 2003. **299**(5605): p. 371-374.
37. Feng, X., et al., *Adhesion forces in AFM of redox responsive polymer grafts: Effects of tip hydrophilicity*. Applied Surface Science, 2014. **292**(0): p. 107-110.
38. Schwierz, N., D. Horinek, and R.R. Netz, *Anionic and Cationic Hofmeister Effects on Hydrophobic and Hydrophilic Surfaces*. Langmuir, 2013. **29**(8): p. 2602-2614.
39. Cacace, M.G., E.M. Landau, and J.J. Ramsden, *The Hofmeister series: salt and solvent effects on interfacial phenomena*. Quarterly Reviews of Biophysics, 1997. **30**(03): p. 241-277.
40. Roberts, J.M., et al., *Influence of the Hofmeister Series on the Retention of Amines in Reversed-Phase Liquid Chromatography*. Analytical Chemistry, 2002. **74**(19): p. 4927-4932.
41. Bard, A.J. and L.R. Faulkner, *Electrochemical methods: fundamentals and applications*. 2001, USA: John Wiley & Sons.
42. Böhm, A., et al., *Photo-attaching functional polymers to cellulose fibers for the design of chemically modified paper*. Cellulose, 2013. **20**(1): p. 467-483.
43. Quéré, D., *Wetting and Roughness*. Annual Review of Materials Research, 2008. **38**(1): p. 71-99.
44. McNamee, C.E., N. Pyo, and K. Higashitani, *Atomic Force Microscopy Study of the Specific Adhesion between a Colloid Particle and a Living Melanoma Cell: Effect of the Charge and the Hydrophobicity of the Particle Surface*. Biophysical Journal, 2006. **91**(5): p. 1960-1969.
45. de Gennes, P.G., *Anomalous friction at a 'Janus interface': the possible role of blisters*. Advances in Colloid and Interface Science, 2003. **100–102**(0): p. 129-135.
46. Ohsawa, K., M. Murata, and H. Ohshima, *Zeta potential and surface charge density of polystyrene-latex; comparison with synaptic vesicle and brush border membrane vesicle*. Colloid and Polymer Science, 1986. **264**(12): p. 1005-1009.

47. Kolská, Z., et al., *Electrokinetic Potential and Other Surface Properties of Polymer Foils and Their Modifications*. Polymer Science. 2013.
48. Sitti, M. *Survey of nanomanipulation systems*. in *Nanotechnology, 2001. IEEE-NANO 2001. Proceedings of the 2001 1st IEEE Conference on*. 2001.
49. Song, J. and G.J. Vancso, *Responsive Organometallic Polymer Grafts: Electrochemical Switching of Surface Properties and Current Mediation Behavior*. Langmuir, 2011. **27**(11): p. 6822-6829.
50. Labuda, A., et al., *Switching Atomic Friction by Electrochemical Oxidation*. Langmuir, 2011. **27**(6): p. 2561-2566.
51. Hempenius, M.A., F.F. Brito, and G.J. Vancso, *Synthesis and Characterization of Anionic and Cationic Poly(ferrocenylsilane) Polyelectrolytes*. Macromolecules, 2003. **36**(17): p. 6683-6688.
52. Uzun, O., et al., *Water-soluble amphiphilic gold nanoparticles with structured ligand shells*. Chemical Communications, 2008(2): p. 196-198.
53. Cumurcu, A., et al., *Sub-nanometer expansions of redox responsive polymer films monitored by imaging ellipsometry*. Nanoscale, 2014. **6**(20): p. 12089-12095.
54. Hutter, J.L. and J. Bechhoefer, *Calibration of atomic-force microscope tips*. Review of Scientific Instruments, 1993. **64**(7): p. 1868-1873.
55. Butt, H.-J., B. Cappella, and M. Kappl, *Force measurements with the atomic force microscope: Technique, interpretation and applications*. Surface Science Reports, 2005. **59**(1-6): p. 1-152.

Redox Control of Capillary Filling Speed in Poly(ferrocenylsilane)-Modified Microfluidic Channels for Switchable Delay Valves

We present a method to reversibly change the wetting of gold-coated microchannel walls, and, as a result, alter the capillary filling speed of water inside such modified microchannels. To this end, we employ the redox-response of surface-anchored poly(ferrocenylsilane) (PFS) films, which allows for a controlled and repeatable switching of the surface energy under low voltages (<1 V). Cyclic voltammetry and chronoamperometry were used to confirm the presence of PFS coatings, to determine surface coverage and to study the redox reaction kinetics of the films inside of microchannels where a 0.1 M sodium perchlorate aqueous solution served as electrolyte. SEM images attested thin, uniform and selective surface modification of the gold electrode by PFS films. The velocity of the meniscus was reversibly switched between 1.8 ± 0.1 mm/s (reduced state) and 3.4 ± 0.1 mm/s (oxidized state). Model calculations, based on the Lucas-Washburn equation and adapted to our specific channel setup and partial surface modification, showed a linear dependency of the meniscus position on our observation time interval, in agreement with our experimental results. Meniscus velocities predicted by the model agreed well with the experimentally determined capillary meniscus velocity.

6.1. Introduction

Microfluidic flow control is important for a wide variety of applications involving microfluidic fuel cells¹ or lab-on-a-chip devices.^{2, 3} In such devices, fluid transport can be manipulated by employing valves which regulate liquid flow inside a microchannel.⁴⁻⁶ A particularly simple and non-mechanical method for controlling liquid intake in a microchannel involves variation of the capillary force. Fluid transport driven by capillary forces is relevant for further device miniaturization and may lead to simplified handheld microfluidic analysis systems which do not require the use of external accessories such as micropumps.⁷⁻⁹

Capillary intake can be controlled using principles including passive capillarity, thermocapillarity and electrocapillarity. Thermocapillarity is induced by a temperature gradient on the surface.^{10, 11} Electrocapillarity, also known as electrowetting, results from a localized potential difference at the surface.^{12, 13} These last two techniques are energy consuming and limit miniaturizability and mobility of the devices because of the external equipment or the high voltages needed. Furthermore, electrocapillarity is often used to drive microvalves with a movable membrane for gas flow regulation^{14, 15} rather than for liquid flow control because of the electrolysis of liquids at high voltages.^{16, 17} On the contrary, passive capillary filling can be tuned by the geometry (or path design) of the microchannel by forming a pressure drop¹⁸⁻²⁰, by the topography of the microchannel wall²¹⁻²³ or the surface coating (hydrophobic or hydrophilic surfaces).²⁴⁻²⁶ Hydrophobic coatings can be combined with geometry-based valves^{27, 28} and surface topography-based valves²⁹⁻³¹ to obtain superhydrophobic coatings and provide an even higher retention force. Thus, the meniscus speed can be controlled in microfluidic devices by modifying channel geometry, surface patterns, roughness and surface wettability.

Stimulus-responsive polymers show great promise as reversible actuators for controlling flow delivery.³² For example, Londe et al. described a thermo-actuated capillary valve in microfluidic channels based on the reversible

hydrophobic/hydrophilic switching of PNIPAM.^{33, 34} The system was controlled by the interfacial tension of the liquid–air–solid interface, and not by the swelling and shrinking of PNIPAM as its lower critical solution temperature (LCST) was traversed.

We recently reported a redox-responsive system for switching wettability, using poly(ferrocenylsilane) (PFS) films on 2D flat substrates.^{35, 36} PFSs can be oxidized and reduced chemically or electrochemically with full reversibility, in the latter case requiring only low voltages (< 1 V),³⁷⁻³⁹ and so, as opposed to electrowetting, allowing one to prevent the electrolysis of liquids. The change in surface polarity allowed a switch in surface properties, such as wetting, adhesion and friction.^{35, 40, 41} PFSs with reactive side groups can form robust polymer layers on different surface materials, including gold^{35, 42} and indium tin oxide (ITO).^{43, 44} Furthermore, PFSs provide the opportunity to fabricate dual responsive systems via copolymerization.⁴³ Due to these characteristics, reactive PFSs are suitable as microfluidic surface coatings for controlled capillary filling.

In this chapter, we present a method to control the capillary filling speed in microfluidic channels, which involves a reversible changing of the interfacial energy of the microchannel wall. To this end, a partially gold-coated glass microchannel was modified with a redox-responsive PFS layer. The uniformity of the layer was studied by imaging the inside wall of the modified microchannels with SEM. The redox-response of the surface-anchored PFS layer was studied via cyclic voltammetry and chronoamperometry. The capillary filling speeds, depending on the redox state of the PFS, inside the modified microfluidic channels were obtained by recording the marching of the meniscus under an optical microscope. The experimental capillary filling speeds were then compared to the theoretical speeds obtained from a model based on the Lucas-Washburn equation.

6.2. Results and discussion

6.2.1. Surface modification of the microchannel

The gold electrode in the microchannel was modified with a poly(ferrocenyl(3-iodopropyl)methylsilane) (PFS-I) layer, which was anchored to the electrode surface via a cysteamine self-assembled monolayer (SAM) in an amine alkylation reaction (**Scheme 6.1**).^{35, 42} After PFS immobilization, only the covalently bound PFS-I remained on the electrode while physisorbed PFS-I in the microchannel was rinsed away (**Appendix 6.1**).

Scheme 6.1. Schematic representation of the modification of gold substrates with a PFS-I film anchored via a cysteamine monolayer.

Figure 6.1.a and **Figure 6.1.b** show a top view of the sputtered gold microelectrode in the glass microchannel. The bare gold surface exhibits a grainy topography, typical of this sputtered gold. Attachment of PFS-I chains to the electrode surface resulted in the formation of a film with some holes, which might be caused by dewetting,⁴⁵ still revealing the tops of the underlying gold, appearing as bright spots in the images (**Figure 6.1.c** and **Figure 6.1.d**). Unfortunately, charging of the glass during the SEM measurements prevented imaging at higher magnification and therefore an estimation of the PFS film thickness was not possible. However, successful surface modification was confirmed by electrochemistry.

Figure 6.1. SEM images of microchannel cross-sections, providing a top view of (a, b) the bare gold microelectrode and (c, d) the surface-immobilized PFS-I layer on the gold microelectrode. Scale bars represent 200 nm.

6.2.2. Redox properties and modelling

In previous studies, similar PFS-I layers immobilized on 2D surfaces were found to be dense, uniform and robust under electrochemical oxidation and reduction in organic and aqueous electrolytes.^{35, 42, 43, 46} Due to these characteristics, these layers were successfully employed in sensing applications and for the reversible switching of surface wettability and adhesion.^{35, 42} In the current study, the modified gold microelectrode was used as working electrode and platinum wires were used as reference and counter electrode at the inlet and outlet of the microchannel. The obtained cyclic voltammogram (**Figure 6.2.a**) displays the double oxidation and reduction waves characteristic of PFSs.^{38, 39, 47} Nevertheless, in our system, the two peaks are broad and overlap which indicates inter- and intramolecular electron

transfer. These double peaks are attributed to oxidation and reduction of the ferrocene units in an alternating fashion, resulting from intermetallic coupling between the ferrocene units in the PFS main chain (**Scheme 6.2**).³⁸ The surface coverage of ferrocene units on the gold microelectrode was calculated by using the relation $\Gamma = Q / (n \cdot F \cdot A)$, where Q is the charge, n is the number of electrons involved per redox reaction of a single ferrocene unit (here $n = 1$), F is Faraday's constant (96 485 C/mol), and A is the surface area of the working electrode ($3.20 \times 10^{-3} \text{ cm}^2$). The charge Q involved in the redox process was obtained by integrating the CV curve, since $Q = \int i/v \text{ d}E$, with v being the scan rate. The surface coverage by ferrocene units Γ on the gold electrode in the microfluidic channel was found to be $2.28 \times 10^{-10} \text{ mol/cm}^2$. This value is ten times lower than the surface coverage found previously with a 15-nm-PFS-I layer prepared with the same chemical procedure on a 2D gold flat substrate ($2.20 \times 10^{-9} \text{ mol/cm}^2$).^{35, 42} The reason for our thinner layer is the smaller amount of PFS-I available for reaction during the deposition in the microchannels, compared to the 2D procedure.

Scheme 6.2. Schematic representation of the redox reaction of PFS and the associated parameters used to model the redox reaction.

In **Figure 6.2.b**, the current-time (i-t) curves captured during the oxidation and the reduction of the PFS-I films on the gold electrode are presented. These i-t curves were recorded using the chronoamperometry mode. Full oxidation and reduction of PFS-I was obtained after 2 min at 0.7 V and -0.4 V, respectively. The i-t curves

reach a plateau which indicates that full oxidation and reduction were achieved. As mentioned, the oxidation and reduction of PFSs may be represented by a two-step process featuring a half oxidized form as intermediate state (**Scheme 6.2**). To fit the *i*-*t* curves of **Figure 6.2.b**, the oxidation and reduction reactions of PFS-I were considered separately as two different irreversible two-step consecutive reaction sequences, $A \rightarrow B \rightarrow C$ and $C \rightarrow B \rightarrow A$, with A the fully reduced state, B the alternating half oxidized and C the fully reduced state. A first order approximation of the current as a function of time for redox species confined to an electrode surface and following this irreversible two-step consecutive reaction mechanism was proposed by Chambers et al.⁴⁸

Figure 6.2. (a) Cyclic voltammogram at 20 mV/s and (b) current-time curves during redox reactions of immobilized PFS-I films on the gold microelectrodes, performed in 0.1 M NaClO₄ aqueous solution. The gold microelectrode was used as working electrode, and platinum wires as counter and reference electrodes.

For oxidation and reduction, the i - t curves were thus fitted with:

$$i(t) = i_0 + FAF_T \left(k_1 + \frac{k_1 k_2}{k_2 - k_1} \right) \times e^{-k_1(t-t_0)} - FAF_T \left(\frac{k_1 k_2}{k_2 - k_1} \right) \times e^{-k_2(t-t_0)} \quad (6.1)$$

$$i'(t) = -i'_0 - FAF_T \left(k'_1 + \frac{k'_1 k'_2}{k'_2 - k'_1} \right) \times e^{-k'_1(t-t'_0)} + FAF_T \left(\frac{k'_1 k'_2}{k'_2 - k'_1} \right) \times e^{-k'_2(t-t'_0)} \quad (6.2)$$

where i_0 is the current through the system due to the resistance of the connections, F is the Faraday constant, A is the area of the gold working electrode ($3.20 \times 10^{-3} \text{ cm}^2$), Γ_T is the total surface coverage by ferrocene units which was calculated previously ($2.28 \times 10^{-10} \text{ mol/cm}^2$), t is the time, t_0 is the experimental delay time, and k_1 and k_2 are the rate constants of the first and second oxidation step, respectively, as indicated in **Scheme 6.2**. The parameters of equation (6.2) are the same as in equation (6.1) except that the prime was used to refer to the inverse reaction. Because in electrochemistry, reduction currents are taken as negative, equation (6.2) is equation (6.1) multiplied by -1 . In chronoamperometry, the current vs. time response for surface-confined redox species following an irreversible two-step consecutive reaction mechanism, presents a double exponential decay profile corresponding to the two-stage redox process. The various parameter values after fitting of the i - t curves from **Figure 6.2.b** are shown in **Table 6.1**. We calculated the characteristic time of each redox step via $\tau_i = 1/k_i$ with i the step number.

Table 6.1. Fitting parameter results after fitting the experimental *i-t* curves with equations (6.1) and (6.2) for oxidation and reduction, respectively.

	Oxidation	Reduction
Current (A)	$i_0 = 5.0 \times 10^{-9} \pm 1.3 \times 10^{-9}$	$i'_0 = -7.4 \times 10^{-10} \pm 1.6 \times 10^{-10}$
First step rate constant (s^{-1})	$k_1 = 0.6 \pm 0.4$	$k'_1 = 1.0 \pm 0.2$
Second step rate constant (s^{-1})	$k_2 = 0.070 \pm 0.014$	$k'_2 = 0.079 \pm 0.008$
First step relaxation time (s)	$\tau_1 = 2.3 \pm 1.6$	$\tau'_1 = 1.0 \pm 0.3$
Second step relaxation time (s)	$\tau_2 = 14.6 \pm 3.3$	$\tau'_2 = 12.8 \pm 1.4$

The characteristic times of the system were found to be 2.3 ± 1.6 s and 14.6 ± 3.3 s for each of the two steps of the oxidation, and 1.0 ± 0.3 s and 12.8 ± 1.4 s for each step of the reduction. These relaxation times show that the system quickly reaches the half oxidized state while the second step towards full oxidation or reduction is the rate limiting step. The somewhat slow redox response of our system may be due to the full coverage of the gold electrode by the cysteamine SAM which may hinder electron transport between the electrode and the ferrocene units. On the contrary, in a previous study,^{49, 50} a similar ferrocene unit coverage was obtained with thiol-ended PFS chains which were end-grafted to a gold surface. This differently tethered PFS layer, lacking a dense SAM between electrode and ferrocene units, allowed completion of redox reactions within 200 ms under similar applied potentials. Likely, the barrier to be overcome by the electrons in the latter system was smaller, allowing faster redox reactions. The somewhat slow response of the current redox layer is similar to the response times of stimulus responsive polymers in microfluidics.⁵¹ We note that the rate constants are in fact dependent on the potential difference between the applied potential during the redox reactions and the potential at equilibrium

which is the peak potential of the CV curve in **Figure 6.2.a**.⁵² Therefore, increasing this potential difference will reduce the activation energy and thus enhance the redox reaction kinetics. In our case, we chose an oxidation potential of 0.7 V while the anodic peak potentials are at 0.25 and 0.35 V, and a reduction potential at -0.4 V while the cathodic peak potentials are at -0.05 and 0.1 V. The potential differences are then 0.35 V and 0.45 V for oxidation and 0.35 V and 0.5 V for reduction. This asymmetry in the applied voltage for oxidation and reduction does not allow for an exact comparison. Nevertheless, the relaxation times observed for the oxidation and reduction processes are very similar.

6.2.3. Redox-induced switching of capillary action

To study the influence of the surface-immobilized PFS-I redox state on the capillary filling speed inside the microchannel, we recorded the position of the water meniscus as a function of time inside the dried microchannel at the level of the PFS-I-modified gold electrode. Full oxidation or reduction of the PFS film was achieved as described above, and subsequently, the microchannel was rinsed with water and dried under a nitrogen flow. A droplet of water was placed at the entrance of the microchannel and the meniscus was followed while travelling a distance of 1.6 mm along the modified microchannel wall. The movies were analyzed with Matlab and the relative position of the meniscus versus the relative time for three redox cycles was plotted in **Figure 6.3.a**.

Figure 6.3. (a) The relative meniscus position with time and (b) the change of the capillary filling speed along the observation window of the microchannel, modified with PFS-I on a gold microelectrode, for three redox cycles. In (a), the dots are the measured points and the lines are a linear fit of the corresponding dots. The meniscus speed in (b) corresponds to the slope of the linear fits for each redox state.

The position of the meniscus changed linearly with time within the observation interval. To validate the experimental results with theory, we considered a model to describe the flow in our microchannel. We employed a Lucas-Washburn type model,^{53, 54} adapted to our specific channel setup and partial surface modification. The full theoretical derivation and calculation of the progressing meniscus position in the microchannel can be found in the **Appendix 6.2**. The meniscus position

follows equation (6.3) which has a square root dependency with time over a long period of time (≥ 180 s) as presented in the **Appendix 6.3**.

The meniscus position η is described by:

$$\eta(t) = -L_{wc} \left(\frac{P_{wc} A_{nc}}{A_{wc} P_{nc}} \right)^4 + \left(\frac{A_{nc}}{P_{nc}} \right)^4 \sqrt{L_b^2 \left(\frac{P_{wc}}{A_{wc}} \right)^8 + 8 \left(\frac{P_{nc}}{A_{nc}} \right)^4 \frac{\gamma \cot(\theta) \pi}{\mu W_{nc} H_{nc}^2} t} \quad (6.3)$$

where L_{wc} is the length of the wider entrance channel ($L_{wc} = 1.2$ cm), A_{wc} and P_{wc} are the area and perimeter of this wider entrance channel ($A_{wc} = 3080.5 \mu\text{m}^2$ and $P_{wc} = 256.5 \mu\text{m}$), A_{nc} and P_{nc} are the area and perimeter of the studied narrow microchannel ($A_{nc} = 1800.5 \mu\text{m}^2$ and $P_{nc} = 176.5 \mu\text{m}$), W_{nc} and H_{nc} are the width and the height of the studied narrow channel ($W_{nc} = 70 \mu\text{m}$ and $H_{nc} = 32 \mu\text{m}$), θ is the water contact angle with the microchannel wall, γ is the surface tension of water ($\gamma = 0.072$ N/m), μ is the dynamic viscosity of water ($\mu = 0.001$ Pa.s), and t is the time. and P_{nc} are the area and perimeter of the studied narrow microchannel ($A_{nc} = 1800.5 \mu\text{m}^2$ and $P_{nc} = 176.5 \mu\text{m}$), W_{nc} and H_{nc} are the width and the height of the studied narrow channel ($W_{nc} = 70 \mu\text{m}$ and $H_{nc} = 32 \mu\text{m}$), θ is the water contact angle with the microchannel wall, γ is the surface tension of water ($\gamma = 0.072$ N/m), μ is the dynamic viscosity of water ($\mu = 0.001$ Pa.s), and t is the time.

As shown in the theoretical curves in **Figure 6.3.a** obtained from the model, on a short time interval (less than 1 s), the position of the meniscus vs. time can be approximated with a linear fit. For that reason, we fitted our experimental data points with a linear fit. The speed of the meniscus for each redox state was thus taken as the slope of the linear fit.

Table 6.2. Static contact angle results obtained for a reduced and oxidized PFS-I-immobilized film on flat gold substrates and meniscus speeds obtained theoretically and experimentally. The theoretical meniscus speed in the microchannel was obtained with equation (6.3) and using the equivalent contact angle values of 2D flat substrates for oxidized and reduced states. The experimental meniscus speeds are the mean of the meniscus speed of **Figure 6.3**.

	Oxidation	Reduction
Static contact angle on 2D flat substrates ($^{\circ}$)	$70^{\circ} \pm 3^{\circ}$	$82^{\circ} \pm 2^{\circ}$
Theoretical meniscus speed (mm/s)	4.9	1.9
Experimental meniscus speed (mm/s)	3.4 ± 0.1	1.8 ± 0.1

The experimental speed of the meniscus switches from an average of 1.8 ± 0.1 mm/s in the reduced state to 3.4 ± 0.1 mm/s in the oxidized state (**Table 6.2**). As shown in **Figure 6.3.b** over three cycles, this change in speed is reversible. In a previous study,³⁵ the PFS redox state was shown to change the surface energy due to a change in polarity of the PFS films. Indeed, as shown in **Table 6.2**, in the reduced state a 2D flat substrate with a PFS-I layer exhibited a contact angle of $82^{\circ} \pm 2^{\circ}$. After oxidation, the contact angle was reduced to $70^{\circ} \pm 3^{\circ}$ due to the formation of ferrocenium centers which increase the polarity of the surface, and therefore, increase the hydrophilicity. The theoretical curves in **Figure 6.3.a** and the theoretical meniscus speed in **Table 6.2** were obtained by using these contact angle values. Equation (6.4) is the time derivative of equation (6.3), and therefore, gives the speed of the meniscus vs. time. A combination of equation (6.3) and (6.4) allows the expression of the meniscus speed depending on the position in the microchannel (equation (6.5)).

$$\dot{\eta}(t) = \frac{4\gamma \cot(\theta) \pi}{\mu W_c H_c^2} \frac{1}{\sqrt{L_b^2 \left(\frac{P_b}{A_b}\right)^8 + 8 \left(\frac{P_c}{A_c}\right)^4 \frac{\gamma \cot(\theta) \pi}{\mu W_c H_c^2} t}} \quad (6.4)$$

$$\dot{\eta}(t) = \frac{4\gamma \cot(\theta) \pi}{\mu W_c H_c^2} \left(\frac{A_c}{P_c}\right)^4 \frac{1}{\eta(t) + L_b \left(\frac{P_b A_c}{A_b P_c}\right)^4} \quad (6.5)$$

By using equation (6.5) and the static contact angle values from flat substrates, it was possible to obtain the average theoretical meniscus speed in a section of the narrow microchannel, between 1.7 mm and 3.3 mm from its junction with the wider channel (**Appendix 6.2** and **Appendix 6.4**). The average theoretical meniscus speeds were 1.9 mm/s and 4.9 mm/s for reduced and oxidized states, respectively (**Table 6.2**). For the reduced state, the match between the theoretical and experimental meniscus speeds shows that our model, used to obtain an estimate of the theoretical speed, is in good agreement with the experimental data but slightly overestimates the velocity. The deviation can be attributed to a difference in surface coverage between the 2D flat substrates, used for contact angle measurements, and the microchannel. Indeed, a lower surface coverage was found for the PFS-immobilized on the gold electrode inside the microchannel. This lower surface coverage of ferrocene units results in a smaller change in polarity, and therefore, in a lower hydrophilicity and lower meniscus speed. Moreover, the change in surface roughness for the 2D substrates might differ from the roughness alteration in the microchannel, resulting in different changes in the contact angles. Furthermore, we note that our model is a simplification of the real channel setup, since we assume a constant contact angle at all microchannel walls even though our top wall consists of bare glass and is thus chemically different. Nevertheless, our model confirms the linear evolution of the meniscus position over the time interval used during the measurement, and accurately predicts a value for the meniscus velocity inside such channels

6.3. Conclusions

Gold electrodes covering a microchannel wall were successfully modified with a surface-anchored poly(ferrocenylsilane) film via a cysteamine SAM. These robust layers were reversibly oxidized and reduced electrochemically inside the microchannel. By means of these redox reactions, the surface energy of the microchannel wall could be switched reversibly, which resulted in a change in the water meniscus speed during capillary filling of the dried and surface-modified microchannel.

SEM images showed that the surface modification occurred selectively on the gold electrode inside the glass microchannel to produce a thin, uniform redox-active films. CV enabled the quantification of the ferrocene unit surface coverage on the gold electrode inside the microchannel, which exhibited a value ten times lower than the surface coverage of a 15-nm-layer of the same immobilized PFS-I on a 2D gold flat substrate. Chronoamperometry was performed to study the rate constants of the two-step oxidation and reduction process of the poly(ferrocenylsilane) layer. The current versus time profile was fitted by a model for redox species confined to an electrode surface which describes an irreversible two-step consecutive redox reaction mechanism. For both oxidation and reduction, the rate constants showed a faster reaction towards the intermediate half oxidized PFS state than towards the fully oxidized or fully reduced states. Complete oxidation and reduction was therefore rate-limited, by the second step of the process, which revealed a characteristic time below 20 s. By changing the redox state of the surface-immobilized PFS film, its wettability could be switched, allowing for a reversible alteration of the capillary filling speed of water inside the modified microchannel between 3.4 ± 0.1 mm/s (reduced state) and 1.8 ± 0.1 mm/s (oxidized state). The change in the meniscus speed was consistent with theoretical calculations for which we used water contact angle values of the same surface-anchored PFS-I layer on flat substrates. The employed Lucas Washburn model accurately predicted capillary

filling speeds for the various redox states of the PFS films. The reversible surface hydrophilicity change inside the microchannel opens opportunities towards microfluidic delay valves. Combining our surface modification with surface-topography and geometry based microfluidic valves may broaden flow control opportunities within a single device.

6.4. Experimental section

Materials. As shown in **Figure 6.4** and **Appendix 6.5**, we used glass microchannels composed of two successive parts: 1) a wide entrance channel of 28 μm deep (H_{wc}), 111 μm wide (W_{wc}) and 1.2 cm long (L_{wc}), followed by 2) a narrow channel of 28 μm deep (H_{nc}) and 73 μm wide (W_{nc}) which was partially covered with 100-nm-thick gold electrodes on the bottom wall (10 nm Cr as adhesive layer, 3 mm length). The design and fabrication of the microfluidic chip will be described elsewhere.³⁶ Poly(ferrocenyl(3-iodopropyl)methylsilane) (PFS-I) was prepared by platinum-catalyzed ring-opening polymerization according to established procedures,⁵⁵ $M_{\text{w}} = 199 \text{ kg/mol}$, $M_{\text{n}} = 116 \text{ kg/mol}$, $M_{\text{w}}/M_{\text{n}} = 1.7$, measured by GPC against narrow polystyrene standards. Cysteamine ($\geq 98.0\%$) and sodium perchlorate ($\geq 98.0\%$) were purchased from Sigma-Aldrich and used as received. Tetrahydrofuran (THF, AR) and ethanol (absolute for analysis) were obtained from Merck KGaA. Water used in this study was ultra-pure quality dispensed through a Milli-Q system from Millipore Corporation.

Figure 6.4. Schematics of the microchannels which were used for the capillary filling measurements representing (a) the top view of the microchannel, (b) the side view cross-section, and (c) a cross-section of the microchannel at the level of the gold electrode. The shape of the channel cross-section, consisting of two quarter of a circle and one rectangle, is typical from the isotropic wet etching of glass.³⁶ (d) Camera view picture of the gold-coated microchannel (horizontal) and the connecting gold electrode (vertical). The scale bar is 200 μm .

Attachment of Poly(ferrocenyl(3-iodopropyl)methylsilane) (PFS-I) Chains to the Gold Electrodes Inside the Microchannel. PFS-I chains were attached to the gold electrode surface using the reaction between the iodine of PFS-I and the amine group of a cysteamine self-assembled monolayer (SAM) as published previously.^{35, 42} First, the microfluidic chip was taken from its sealed package and treated with an oxygen plasma for 1 h in order to clean the gold electrode inside the microchannel. Next, the freshly cleaned gold microelectrodes were immediately covered with a cysteamine by slowly perfusing a 10 mM cysteamine solution in ethanol overnight

with a flow rate of 0.01 mL/h. The microchannel was subsequently rinsed with ethanol at a flow rate of 0.5 mL/h for 8 h and dried under vacuum overnight. Afterwards, to cover the microchannel walls with a PFS-I film, the microchannel was filled by capillary imbibition with a PFS-I solution in THF (10 mg/mL) and left to dry under ambient conditions. To covalently bind the PFS-I film to the cysteamine SAM on the gold microelectrodes, the microfluidic chip was left overnight in a vacuum oven at 50 °C. Finally, physisorbed polymer chains, which did not bind to the cysteamine SAM, were removed by flushing the glass microchannel with THF, which is a good solvent for PFS-I, for 8 h at a flow rate of 0.6 mL/h. The microfluidic chip was then dried under vacuum overnight.

Scanning Electron Microscopy (SEM). To characterize the PFS film inside the channel, SEM images of the channel cross-section were taken with a Zeiss MERLIN high resolution SEM. The glass microfluidic chip was cut perpendicularly to the channel at the gold microelectrode level. An Inlens Secondary Electron detector was used with an operating voltage of 1.4 kV. Because of charging of the glass, a low probe current of 50 pA was employed. No conducting coating was applied.

Electrochemistry. Cyclic voltammetry and redox reactions of the PFS-I films in the microchannels were performed using 0.1 M aqueous NaClO₄ as electrolyte. The gold microelectrode in the microchannel was used as the working electrode. Platinum wires were employed as the reference electrode and the counter-electrode, and placed at the inlet and outlet of the microchannel, respectively. Cyclic voltammograms were recorded between −0.4 V and +0.7 V vs. Pt, at a scan rate of 20 mV/s. PFS-I was oxidized and reduced by applying a constant potential of +0.7 V and −0.4 V for oxidation and reduction, respectively, for 2 min. Then, the microchannel was rinsed with water, at a flow rate of 0.6 mL/h, and dried under a nitrogen flow.

Contact Angle Measurements. Static contact angles of a 2 µL water sessile drop were measured on 2D gold flat substrates with an OCA15 instrument from Dataphysics, Germany. The drop contour was fitted by the Young-Laplace equation.

For contact angle measurements, the 2D gold flat substrates were modified with PFS-I as reported in previous studies.^{35, 42} Oxidation and reduction reactions were performed under the same conditions as previously mentioned for the modified gold microelectrode.

Capillary Filling Speed Measurements Inside the Microchannel. The speed of the meniscus inside the microchannel, at the level of the PFS-modified gold electrode, was visualized under an Olympus BX60 optical microscope with a magnification of 20 $\times$ and illumination from the top. A 5 μ L water drop was deposited in the powder blasted inlet of the microchannel. A video of the meniscus motion at the level of the gold electrode inside the glass microchannel was recorded with a Sony Hyper HAD color video camera at 20 frames per second.

The videos were analyzed with a home-written Matlab program to record the position of the meniscus with time (**Figure 6.5**). The script was based on background subtraction that highlights the change in intensity due the filling of the capillary. This treatment was followed by a median convolution filtering in order to remove the noise while preserving the edges (**Figure 6.5**). An average was then performed in the horizontal direction, leaving only one line. This line, representative of the moving front, was scaled and fitted to an arctangent function, from which the inflection point was extracted and defined as the position of the front.

Figure 6.5. Examples of a complete frame sequence from a movie analyzed with Matlab to follow the position of the meniscus inside the channel. The blue color corresponds to the channel filled with water and the red color corresponds to the empty channel.

6.5. Appendix

Appendix 6.1. SEM images of (a) the narrow channel cross-section and (b) the corresponding zoomed-in image on the inner glass channel wall, showing that PFS-I immobilization occurred exclusively on the gold electrode via the cysteamine SAM and not on the inner glass channel wall. The scale bars are (a) 10 μm and (b) 1 μm .

Appendix 6.2. This appendix presents the dimensions of the microfluidic channel, used in the model, followed by the full derivation to obtain the theoretical position and speed of the meniscus inside the microchannel as a function of time.

The wider channel has a depth H_{wc} of $28 \mu\text{m}$, a width W_{wc} of $111 \mu\text{m}$ and a length L_{wc} of 1.2 cm . The narrow channel which is partially covered with a gold electrode, has a depth H_{nc} of $28 \mu\text{m}$ and a width W_{nc} of $73 \mu\text{m}$. The gold electrode starts at a distance of 1 mm from the beginning of the narrow channel and has a length of 3 mm . The observation window with the camera, and therefore the observed meniscus position η , is between 1.7 and 3.3 mm from the beginning of the narrow channel. Because we consider having a channel which is wider (y-direction) than high (x-direction), the y-direction is not taken into account in all the parameters of the system which, therefore, depend only on x and z .

First, the Laplace-Young equation at the meniscus gives:

$$P(\eta, x, t) - P_0 = \gamma \frac{\partial^2 \eta}{\partial x^2} \quad (6.6)$$

where P is the pressure in the fluid, P_0 is the atmospheric pressure, η is the position of the meniscus in the narrow channel, x is the coordinate of the parabolic meniscus on the channel depth direction, γ is the surface tension of water ($\gamma = 0.072 \text{ N/m}$) and t is the time.

Then, because we consider having a laminar flow (Reynolds number $Re = 6.4 \times 10^{-2}$), the velocity of the fluid changes only in z :

$$\vec{v} = v(z, x) \vec{e}_z$$

Navier- Stokes equation gives:

$$-\frac{1}{\rho} \frac{\partial P}{\partial x} = \frac{\partial v_x}{\partial t} + v_x \frac{\partial v_x}{\partial x} + v_z \frac{\partial v_x}{\partial z} + \frac{\mu}{\rho} \frac{\partial^2 v_x}{\partial z^2}$$

where μ is the dynamic viscosity of water ($\mu = 0.001$ Pa.s) and ρ is the density of water ($\rho = 1000$ kg/m³). Since we consider a steady state flow ($\frac{\partial v_x}{\partial t} = 0$) which is incompressible ($v_x \frac{\partial v_x}{\partial x} = 0$ and $v_z \frac{\partial v_x}{\partial z} = 0$), it reduces to:

$$\frac{\partial P}{\partial x} = 0 \quad (6.7)$$

In the other direction (z -direction):

$$-\frac{1}{\rho} \frac{\partial P}{\partial z} = \frac{\partial v_z}{\partial t} + v_x \frac{\partial v_z}{\partial x} + v_z \frac{\partial v_z}{\partial z} + \frac{\mu}{\rho} \left(\frac{\partial^2 v_z}{\partial z^2} + \frac{\partial^2 v_z}{\partial x^2} \right)$$

Because we consider a steady state flow and an incompressible fluid ($\frac{\partial^2 v_z}{\partial z^2} = 0$), it simplifies to:

$$\frac{\partial P}{\partial z} = \mu \frac{\partial^2 v_z}{\partial x^2} \quad (6.8)$$

Next, we consider that the pressure inside the water droplet at the entrance of the channel is the same as the atmospheric pressure P_0 . Therefore, the pressure difference through the meniscus between the pressure inside the fluid P_l and outside the fluid P_0 from equation (6.6) is the same as the pressure difference through the channel from equation (6.7). This implies:

$$\frac{\partial (P_l - P_0)}{\partial x} = 0$$

So:

$$\gamma \frac{\partial^3 \eta}{\partial x^3} = 0$$

Which has the general solution:

$$\frac{\partial \eta}{\partial x} = \alpha x + \beta$$

With α and β constants that we determine by considering the following boundary conditions:

$$\begin{aligned}\left. \frac{\partial \eta}{\partial x} \right|_{x=0} &= 0 \\ \left. \frac{\partial \eta}{\partial x} \right|_{x=d} &= \cot(\theta) \\ \left. \frac{\partial \eta}{\partial x} \right|_{x=-d} &= -\cot(\theta)\end{aligned}$$

Where d is half of the channel height and θ is the contact angle of the meniscus with the channel wall. We find:

$$P_l - P_0 = \frac{\gamma \cot(\theta)}{d} \quad (6.9)$$

Furthermore, the derivatives of equations (6.7) and (6.8) to z and x , respectively, give:

$$\begin{aligned}\frac{\partial^2 P}{\partial x \partial z} &= 0 \\ \frac{\partial P}{\partial x \partial z} &= \mu \frac{\partial^3 v_z}{\partial x^3} = 0\end{aligned}$$

Therefore, the speed of the meniscus in the microchannel has the following functional dependence:

$$v = a(x - d)(x + d) = a(x^2 - d^2)$$

Where a is a constant that we will determine by using the conservation of the flow ϕ over a cross-section area S of the channel:

$$\phi = \int_S v dS$$

Thus:

$$\phi = a W_{nc} \int_{-d}^d (x^2 - d^2) dx$$

This gives:

$$\phi \approx a \frac{4dx^3}{3} W_{nc} \approx \frac{4H_{nc}^3 a W_{nc}}{3 \times 8}$$

Thus:

$$\phi \approx \frac{aH_{nc}^3 W_{nc}}{6} \quad (6.10)$$

Moreover, the hydraulic resistance R_H of the entire channel (wide and narrow) is defined as:

$$\Delta P = R_H \times \phi \quad (6.11)$$

With $R_H = R_{wc} + R_{nc}$, where R_{wc} is the hydraulic resistance of the wide channel and R_{nc} is the hydraulic resistance of the narrow channel.

By considering a Poiseuille flow, the hydraulic resistance of the wide channel R_{wc} can be written:

$$R_{wc} = \frac{8\mu L_{wc}}{2\pi r_{hwc}^4} \quad (6.12)$$

With L_{wc} the length of the wide channel, and r_{hwc} the hydraulic radius which is defined without any consideration of the channel cross-section geometric shape as:

$$r_{hwc} = \frac{2A_{wc}}{P_{wc}} \quad (6.13)$$

Where A_{wc} is the area of the wide channel (cross-section) and P_{wc} its perimeter. Thus:

$$R_{wc} = \frac{\mu L_{wc}}{2\pi} \left(\frac{P_{wc}}{A_{wc}} \right)^4 \quad (6.14)$$

Similarly:

$$R_{nc} = \frac{\mu}{2\pi} \left(\frac{P_{nc}}{A_{nc}} \right)^4 \eta \quad (6.15)$$

Where A_{nc} is the area of the narrow channel and P_{nc} is its perimeter.

By substituting equations (6.10), (6.14) and (6.15) into equation (6.11) we obtain:

$$\Delta P = \frac{aH_{nc}^3 W_{nc} \mu}{12\pi} \left[L_{wc} \left(\frac{P_{wc}}{A_{wc}} \right)^4 + \eta \left(\frac{P_{nc}}{A_{nc}} \right)^4 \right] \quad (6.16)$$

Moreover, from equation (6.9) and $d = H_{nc}/2$, we get:

$$\Delta P = \frac{2 \gamma \cot(\theta)}{H_{nc}} \quad (6.17)$$

Such that we find a to be:

$$a = \frac{24\pi \gamma \cot(\theta)}{H_{nc}^4 W_{nc} \mu \left[L_{wc} \left(\frac{P_{wc}}{A_{wc}} \right)^4 + \eta \left(\frac{P_{nc}}{A_{nc}} \right)^4 \right]} \quad (6.18)$$

To find an expression for η , we consider that the average velocity in the channel is defined by:

$$v_m = \frac{\phi}{S} \quad (6.19)$$

Which, by using equation (6.10) and by considering $S = H_{nc} \times W_{nc}$, becomes:

$$v_m = \frac{a H_{nc}^2}{6} \quad (6.20)$$

By replacing the value of a from equation (6.18), the average velocity becomes:

$$v_m = \frac{4\pi \gamma \cot(\theta)}{\mu W_{nc} H_{nc}^2} \times \frac{1}{L_b \left(\frac{P_{wc}}{A_{wc}} \right)^4 + \eta \left(\frac{P_{nc}}{A_{nc}} \right)^4} \quad (6.21)$$

By considering $v_m = \dot{\eta}$, equation (6.21) can be rewritten:

$$\dot{\eta} \left[L_{wc} \left(\frac{P_{wc}}{A_{wc}} \right)^4 \right] + \dot{\eta} \eta \left(\frac{P_{nc}}{A_{nc}} \right)^4 - \frac{4\pi \gamma \cot(\theta)}{\mu W_{nc} H_{nc}^2} = 0 \quad (6.22)$$

For simplification, we introduce δ to be:

$$\delta = \frac{4\pi \gamma \cot(\theta)}{\mu W_{nc} H_{nc}^2} \quad (6.23)$$

And we notice that:

$$\dot{\eta} \eta = \frac{1}{2} \frac{\partial}{\partial t} (\eta^2)$$

So by integration of equation (6.22) over time, we obtain:

$$\eta L_{wc} \left(\frac{P_{wc}}{A_{wc}} \right)^4 + \frac{\eta^2}{2} \left(\frac{P_{nc}}{A_{nc}} \right)^4 - \delta t = \varepsilon$$

Due to the boundary condition $\eta(t = 0) = 0$, the constant $\varepsilon = 0$. So we can write:

$$\eta L_{wc} \left(\frac{P_{wc}}{A_{wc}} \right)^4 + \frac{\eta^2}{2} \left(\frac{P_{nc}}{A_{nc}} \right)^4 - \delta t = 0 \quad (6.24)$$

We recognize a quadratic equation, and therefore, can calculate the discriminant Δ :

$$\Delta = L_{wc}^2 \left(\frac{P_{wc}}{A_{wc}} \right)^8 + 2 \left(\frac{P_{nc}}{A_{nc}} \right)^4 \delta t \quad (6.25)$$

From which we take only the positive solution, since the direction of the meniscus displacement, and therefore, the sign of the meniscus velocity, is determined by the sign of $\cot(\theta)$:

$$\eta = -L_{wc} \left(\frac{P_{wc} A_{nc}}{A_{wc} P_{nc}} \right)^4 + \left(\frac{A_{nc}}{P_{nc}} \right)^4 \sqrt{L_{wc}^2 \left(\frac{P_{wc}}{A_{wc}} \right)^8 + 2 \left(\frac{P_{nc}}{A_{nc}} \right)^4 \delta t}$$

Which by replacing δ by its full expression from equation (6.23) give the expression of the meniscus position depending on the time:

$$\begin{aligned} \eta(t) &= -L_{wc} \left(\frac{P_{wc} A_{nc}}{A_{wc} P_{nc}} \right)^4 \\ &+ \left(\frac{A_{nc}}{P_{nc}} \right)^4 \sqrt{L_{wc}^2 \left(\frac{P_{wc}}{A_{wc}} \right)^8 + 8 \left(\frac{P_{nc}}{A_{nc}} \right)^4 \frac{\gamma \cot(\theta) \pi}{\mu W_{nc} H_{nc}^2} t} \end{aligned} \quad (6.26)$$

By taking the derivative with respect to time, we get the velocity of the meniscus:

$$\dot{\eta}(t) = \frac{4\gamma \cot(\theta) \pi}{\mu W_{nc} H_{nc}^2} \frac{1}{\sqrt{L_{wc}^2 \left(\frac{P_{wc}}{A_{wc}} \right)^8 + 8 \left(\frac{P_{nc}}{A_{nc}} \right)^4 \frac{\gamma \cot(\theta) \pi}{\mu W_{nc} H_{nc}^2} t}} \quad (6.27)$$

Finally, by combining equations (6.26) and (6.27), we obtain the expression of the meniscus velocity depending on the meniscus position:

$$\dot{\eta}(t) = \frac{4\gamma \cot(\theta) \pi}{\mu W_{nc} H_{nc}^2} \left(\frac{A_{nc}}{P_{nc}} \right)^4 \frac{1}{\eta(t) + L_{wc} \left(\frac{P_{wc} A_{nc}}{A_{wc} P_{nc}} \right)^4} \quad (6.28)$$

Appendix 6.3. Graph representing the theoretical meniscus position inside the channel as a function of time for a microchannel wall presenting a water contact angle value of 70° (PFS-I in oxidized state) and 82° (PFS-I in reduced state).

Appendix 6.4. Graph representing the theoretical meniscus speed as a function of the meniscus position inside the channel for a microchannel wall presenting a water contact angle value of 70° (PFS-I in oxidized state) and 82° (PFS-I in reduced state). The range of the x-axis values corresponds to the location of the channel where the meniscus position was experimentally recorded.

Appendix 6.5. SEM images of (a) the wide entrance channel and (b) the studied narrow channel cross-sections. The scale bars are 10 μm.

6.6. References

1. Kjeang, E., N. Djilali, and D. Sinton, *Microfluidic fuel cells: A review*. Journal of Power Sources, 2009. **186**(2): p. 353-369.
2. Shui, L., J.C.T. Eijkel, and A. van den Berg, *Multiphase flow in microfluidic systems – Control and applications of droplets and interfaces*. Advances in Colloid and Interface Science, 2007. **133**(1): p. 35-49.
3. Srinivasan, V., V.K. Pamula, and R.B. Fair, *An integrated digital microfluidic lab-on-a-chip for clinical diagnostics on human physiological fluids*. Lab on a Chip, 2004. **4**(4): p. 310-315.
4. Kwang, W.O. and H.A. Chong, *A review of microvalves*. Journal of Micromechanics and Microengineering, 2006. **16**(5): p. R13.
5. Safavieh, R. and D. Juncker, *Capillaries: pre-programmed, self-powered microfluidic circuits built from capillary elements*. Lab on a Chip, 2013. **13**(21): p. 4180-4189.
6. Novo, P., et al., *Control of sequential fluid delivery in a fully autonomous capillary microfluidic device*. Lab on a Chip, 2013. **13**(4): p. 641-645.
7. Walker, G.M. and D.J. Beebe, *A passive pumping method for microfluidic devices*. Lab on a Chip, 2002. **2**(3): p. 131-134.

8. Ichikawa, N., K. Hosokawa, and R. Maeda, *Interface motion of capillary-driven flow in rectangular microchannel*. Journal of Colloid and Interface Science, 2004. **280**(1): p. 155-164.
9. Liu, K.-K., et al., *Microfluidic Systems for Biosensing*. Sensors (Basel, Switzerland), 2010. **10**(7): p. 6623-6661.
10. Glockner, P.S. and G.F. Naterer, *Surface tension and frictional resistance of thermocapillary pumping in a closed microchannel*. International Journal of Heat and Mass Transfer, 2006. **49**(23-24): p. 4424-4436.
11. Yang, Y., A. Odukoya, and G.F. Naterer. *Droplet meniscus motion of thermocapillary pumping in a closed microchannel with external heating*. in *Thermal and Thermomechanical Phenomena in Electronic Systems (ITherm)*, 2010 12th IEEE Intersociety Conference on. 2010.
12. Lee, J., et al., *Electrowetting and electrowetting-on-dielectric for microscale liquid handling*. Sensors and Actuators A: Physical, 2002. **95**(2-3): p. 259-268.
13. Berre, M.L., et al., *Electrocapillary force actuation of microfluidic elements*. Microelectronic Engineering, 2005. **78-79**(0): p. 93-99.
14. Sato, K. and M. Shikida, *An electrostatically actuated gas valve with an S-shaped film element*. Journal of Micromechanics and Microengineering, 1994. **4**(4): p. 205.
15. Goll, C., et al., *An electrostatically actuated polymer microvalve equipped with a movable membrane electrode*. Journal of Micromechanics and Microengineering, 1997. **7**(3): p. 224.
16. Sung Kwon, C., et al. *Towards digital microfluidic circuits: creating, transporting, cutting and merging liquid droplets by electrowetting-based actuation*. in *Micro Electro Mechanical Systems, 2002. The Fifteenth IEEE International Conference on*. 2002.
17. Sang-Chung, Y. and L. Cheng-Hsien. *An electrolysis-bubble-actuated micropump using electrowetting on dielectric (EWOD) for 1xN micro-sample switches*. in *Solid-State Sensors, Actuators and Microsystems Conference, 2009. Transducers 2009. International*. 2009.
18. Glière, A. and C. Delattre, *Modeling and fabrication of capillary stop valves for planar microfluidic systems*. Sensors and Actuators A: Physical, 2006. **130-131**(0): p. 601-608.
19. Zimmermann, M., P. Hunziker, and E. Delamarche, *Valves for autonomous capillary systems*. Microfluidics and Nanofluidics, 2008. **5**(3): p. 395-402.
20. Dong Sung, K., et al., *Micro-channel filling flow considering surface tension effect*. Journal of Micromechanics and Microengineering, 2002. **12**(3): p. 236.
21. Ji Won, S. and C. Jun-Hyeong, *Capillary flow control using hydrophobic patterns*. Journal of Micromechanics and Microengineering, 2007. **17**(4): p. N11.

22. Huang, W., Q. Liu, and Y. Li, *Capillary Filling Flows inside Patterned-Surface Microchannels*. Chemical Engineering & Technology, 2006. **29**(6): p. 716-723.
23. Kim, J. and H.-Y. Kim, *On the dynamics of capillary imbibition*. Journal of Mechanical Science and Technology, 2012. **26**(12): p. 3795-3801.
24. Andersson, H., et al., *Hydrophobic valves of plasma deposited octafluorocyclobutane in DRIE channels*. Sensors and Actuators B: Chemical, 2001. **75**(1–2): p. 136-141.
25. Andersson, H., W. van der Wijngaart, and G. Stemme, *Micromachined filter-chamber array with passive valves for biochemical assays on beads*. Electrophoresis, 2001. **22**(2): p. 249-257.
26. Lung-Jieh, Y., Y. Tze-Jung, and T. Yu-Chong, *The marching velocity of the capillary meniscus in a microchannel*. Journal of Micromechanics and Microengineering, 2004. **14**(2): p. 220.
27. Sang-Ho, L., et al., *Quantitatively controlled nanoliter liquid manipulation using hydrophobic valving and control of surface wettability*. Journal of Micromechanics and Microengineering, 2003. **13**(1): p. 89.
28. Riegger, L., et al., *Dye-based coatings for hydrophobic valves and their application to polymer labs-on-a-chip*. Journal of Micromechanics and Microengineering, 2010. **20**(4): p. 045021.
29. Handique, K., et al. *Microfluidic flow control using selective hydrophobic patterning*. 1997.
30. Mukhopadhyay, S., et al., *Nanoscale surface modifications to control capillary flow characteristics in PMMA microfluidic devices*. Nanoscale Research Letters, 2011. **6**(1): p. 411.
31. Tsougeni, K., et al., *"Smart" polymeric microfluidics fabricated by plasma processing: controlled wetting, capillary filling and hydrophobic valving*. Lab on a Chip, 2010. **10**(4): p. 462-469.
32. Kieviet, B.D., P.M. Schon, and G.J. Vancso, *Stimulus-responsive polymers and other functional polymer surfaces as components in glass microfluidic channels*. Lab on a Chip, 2014. **14**(21): p. 4159-4170.
33. Londe, G., et al., *Microfluidic valves based on superhydrophobic nanostructures and switchable thermosensitive surface for lab-on-a-chip (LOC) systems*. Sensors and Actuators B: Chemical, 2008. **132**(2): p. 431-438.
34. Chunder, A., et al., *Conformal switchable superhydrophobic/hydrophilic surfaces for microscale flow control*. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2009. **333**(1–3): p. 187-193.
35. Dos Ramos, L., et al., *Redox-Induced Backbiting of Surface-Tethered Alkylsulfonate Amphiphiles: Reversible Switching of Surface Wettability and Adherence*. Langmuir, 2015. **31**(23): p. 6343-6350.
36. Kieviet, B.D., et al., to be published.

37. Péter, M., et al., *Electrochemistry of Surface-Grafted Stimulus-Responsive Monolayers of Poly(ferrocenyldimethylsilane) on Gold*. Langmuir, 2005. **21**(11): p. 5115-5123.
38. Rulkens, R., et al., *Linear Oligo(ferrocenyldimethylsilanes) with between Two and Nine Ferrocene Units: Electrochemical and Structural Models for Poly(ferrocenylsilane) High Polymers*. Journal of the American Chemical Society, 1996. **118**(50): p. 12683-12695.
39. Foucher, D., et al., *Synthesis, Characterization, and Properties of High Molecular Weight Unsymmetrically Substituted Poly(ferrocenylsilanes)*. Macromolecules, 1994. **27**(14): p. 3992-3999.
40. Chung, H.J., J. Song, and G.J. Vancso, *Tip-surface interactions at redox responsive poly(ferrocenylsilane) (PFS) interface by AFM-based force spectroscopy*. Applied Surface Science, 2009. **255**(15): p. 6995-6998.
41. Song, J. and G.J. Vancso, *Responsive Organometallic Polymer Grafts: Electrochemical Switching of Surface Properties and Current Mediation Behavior*. Langmuir, 2011. **27**(11): p. 6822-6829.
42. Sui, X., et al., *Electrochemical sensing by surface-immobilized poly(ferrocenylsilane) grafts*. Journal of Materials Chemistry, 2012. **22**(22): p. 11261-11267.
43. Sui, X., et al., *Poly(N-isopropylacrylamide)-poly(ferrocenylsilane) dual-responsive hydrogels: synthesis, characterization and antimicrobial applications*. Polymer Chemistry, 2013. **4**(2): p. 337-342.
44. McDowell, J.J., et al., *Electroactuation of Alkoxysilane-Functionalized Polyferrocenylsilane Microfibers*. Journal of the American Chemical Society, 2010. **132**(10): p. 3236-3237.
45. Reiter, G., *Dewetting of thin polymer films*. Physical Review Letters, 1992. **68**(1): p. 75-78.
46. Feng, X., et al., *Covalent Layer-by-Layer Assembly of Redox-Active Polymer Multilayers*. Langmuir, 2013. **29**(24): p. 7257-7265.
47. Foucher, D.A., et al., *Organometallic Ferrocenyl Polymers Displaying Tunable Cooperative Interactions between Transition Metal Centers*. Angewandte Chemie International Edition in English, 1993. **32**(12): p. 1709-1711.
48. Kertesz, V., J.Q. Chambers, and A.N. Mullenix, *Chronoamperometry of Surface-Confined Redox Couples for Irreversible Two-Step and Three-Step Consecutive Reaction Mechanisms*. Analytical Chemistry, 1999. **71**(17): p. 3905-3909.
49. Peter, M., et al., *Synthesis, characterization and thin film formation of end-functionalized organometallic polymers*. Chemical Communications, 1999(4): p. 359-360.
50. Péter, M., et al., *Electrochemical AFM on surface grafted poly(ferrocenylsilanes)*. Macromolecular Symposia, 2001. **167**(1): p. 285-296.

51. Beebe, D.J., et al., *Functional hydrogel structures for autonomous flow control inside microfluidic channels*. *Nature*, 2000. **404**(6778): p. 588-590.
52. Kertesz, V., J.Q. Chambers, and A.N. Mullenix, *Chronoamperometry of surface-confined redox couples. Application to daunomycin adsorbed on hanging mercury drop electrodes*. *Electrochimica Acta*, 1999. **45**(7): p. 1095-1104.
53. Lucas, R., *Ueber das Zeitgesetz des kapillaren Aufstiegs von Flüssigkeiten*. *Kolloid-Zeitschrift*, 1918. **23**(1): p. 15-22.
54. Washburn, E.W., *The Dynamics of Capillary Flow*. *Physical Review*, 1921. **17**(3): p. 273-283.
55. Hempenius, M.A., F.F. Brito, and G.J. Vancso, *Synthesis and Characterization of Anionic and Cationic Poly(ferrocenylsilane) Polyelectrolytes*. *Macromolecules*, 2003. **36**(17): p. 6683-6688.

Outlook: Towards the Possibility of Electrochemically Switching PNIPAM Polymer Brushes Grafted from a Surface-Anchored PFS Layer

In this last chapter, we propose an outlook with different methods to enhance the surface property changes of our smart polymers which could be applied in microfluidic devices. The increase of the contact area of the surface by increasing the roughness or porosity would allow superhydrophilic and superhydrophobic states. The ability to create chemical heterogeneity by decorating the surface of the microchannels with PFS patterns would open opportunities in flow control. Furthermore, we suggest a method using the chemical versatility of PFS layers to electrochemically control the conformation of PNIPAM brushes. Indeed, we describe the reaction path to obtain PFS layers functionalized with ATRP initiators on the side groups. This would allow the formation of polymer brushes on the top of a redox-responsive PFS layer.

7.1. Enhancement of the surface energy changes

Stimulus responsive polymer systems have demonstrated their great ability in switching the surface properties and in controlling the flow inside microfluidic channels. The singular behavior of PNIPAM brushes at the LCST, shown in **Chapter 4**, which is also dependent on the grafting density, could find many applications in microchannels, such as in cell biology with microreactors.¹

An increase of the surface energy changes in the systems that we presented in this thesis, could be reached by increasing the contact area via an increase of the roughness or porosity. Superhydrophilic and superhydrophobic states are then possible.²⁻⁴ Patterns and chemical heterogeneity could be introduced using our presented systems. For instance, masks or titania patterns could be used to locally detach the brushes, as shown in **Chapter 4**, and create patterned surfaces with heterogeneous wetting, adherence or friction. In **Chapter 5** and **Chapter 6**, the electrical actuation of the redox-responsive PFS systems has demonstrated its utility in the switching of surface properties at low voltages (< 1 V). Patterned gold microelectrodes could also be designed to locally modify predefined areas with PFS.

Furthermore, the versatility of PFS chemistry and its ability to create well-defined and ordered patterns, as presented in **Chapter 3**, could be used to tune the surface energy changes. For examples, PFS-based copolymers with more hydrophobic polymers, such as fluorinated polymers,⁵ would shift the contact angle to higher values. Micro- or nanopatterns could be designed in such a way that they direct the flow inside microfluidic channels.

Nevertheless, the temperature stimulus is relatively slow and needs either a heating device or a cooling device, which are energy-consuming for microfluidic flow control. In a previous study from our group,⁶ the versatility of PFS allowed the fabrication of dual responsive systems. Indeed, PFS and PNIPAM copolymer hydrogels were synthesized. It was shown that the redox state of the PFS affected

the LCST of the hybrid hydrogel. This shift in the LCST could be used as actuator to induce a swelling or collapse via electrical stimuli.

7.2. Functionalization of surface-anchored PFS with ATRP initiator

With the same idea of fabricating hybrid polymeric systems, polymer brushes have been grafted from conducting polypyrrole by Pei et al.⁷ In their system, the redox reaction of polypyrrole resulted in a change in the ionic composition of the zwitterionic polymer brush environment which induced a switch of its conformation. The fully reversible conformation switch caused a change in wettability. In view of these results, we propose as an outlook the synthesis of surface-anchored PFS layers which are functionalized with an ATRP initiator. Such layers would give the opportunity to graft polymer brushes on the top of the redox-responsive PFS layer. The oxidation of the PFS layer, and the resulting positively charged ferrocenium groups, would repulse the cations from the polymer brush layer and attract the anions inside. This ionic composition change would affect the LCST of PNIPAM brushes.⁸⁻

10

First, PFS-I was attached to gold substrates via a cysteamine SAM, as presented in **Chapter 5**. Then, as shown in **Scheme 7.1**, remaining iodopropyl groups on the surface of the PFS-I film were functionalized with an ATRP initiator (PFS-ATRP) in a four-step reaction mechanism. Potassium 1,1,3,3-tetramethyldisilazide $\text{KN}(\text{SiMe}_2\text{H})_2$ was used as aminating agent of the iodopropyl groups (PFS-NP). The free amine group was obtained by deprotection and successive deprotonation of PFS-NP via a pH change. Finally, the ATRP initiator was coupled to the amine groups of the surface-immobilized poly(ferrocenyl(3-aminopropyl)methylsilane) (PFS-NH₂) under inert conditions.

Scheme 7.1. Schematic reactions of the functionalization with ATRP initiator (PFS-ATRP) of the side groups of surface-anchored PFS-I.

The success of the functionalization of the surface-anchored PFS layers was verified by XPS. As shown in **Figure 7.1**, the presence of Fe, Si and C prove the stability of the PFS layer during the successive reactions (see **Figure 7.1.a, b and c**). Iodine I is present in PFS-I but disappeared after the amination by reaction of $\text{KN}(\text{SiMe}_2\text{H})_2$ with the alkyl halide (see **Figure 7.1.d**) which is proven by the appearance of the nitrogen N peaks (see **Figure 7.1.f**). The presence of bromine Br is observed only in the PFS-ATRP layer (see **Figure 7.1.e**).

Figure 7.1. XPS spectra of surface-anchored PFS-I, PFS-NP, PFS-NH₂ and PFS-ATRP on gold substrates at the binding energies corresponding to the elements a) Fe 2p, b) Si 2p, c) C 1s, d) I 3d, e) Br 3d and f) N 1s.

7.3. Experimental section

Synthesis of surface-anchored poly(ferrocenyl(3-aminopropyl)methylsilane) (PFS-NH₂). First, PFS-I was attached to gold substrates which were beforehand functionalized with a cysteamine SAM, as described in **Chapter 5**. Then, KN(SiMe₂H)₂ was used as aminating agent for the iodopropyl groups.¹¹ To do so, in the glove box, 1.25 mL KH dispersion in oil (30 wt % in mineral oil, Sigma-Aldrich) was washed three times with 10 mL anhydrous toluene, and 10 mL of anhydrous THF was added to the flask. The flask was closed, remove from the glove box and kept under overpressure of argon. 1,1,3,3-Tetramethylsilazane (97%, Sigma-Aldrich) was purged with argon and 1.33 mL was added dropwise to the previous KH solution and stirred under argon for 1 h. Aside, 0.19 g of 18-crown-6 (99%, Sigma-Aldrich) was flushed with argon, dissolved in 3 mL of anhydrous THF, and added to the previous KH solution. The resulting KN(SiMe₂H)₂ solution was then added to the PFS-modified substrates which had been placed in a flask and flushed with argon. The PFS-modified substrates were left to react overnight with stirring under overpressure of argon. To remove the silane protecting groups, 0.1 M HCl solution was added until the pH reached 1 for 30 min. Then, the polycation was deprotonated by slowly increasing the pH to 11 by adding 0.1 M NaOH solution. The substrates were removed from the flask, rinsed extensively with water, dichloromethane and ethanol, and finally dried under a stream of nitrogen.

ATRP initiator coupling on surface-anchored PFS-NH₂. Coupling of the ATRP initiator to the surface-anchored amine groups of PFS-NH₂ was performed under anhydrous conditions. The substrates modified with PFS-NH₂ were placed on the bottom of a 300 mL Erlenmeyer which was sealed with a septum and purged with argon for 1h. Afterward, anhydrous toluene was added (30 mL), and under stirring, triethylamine (0.1 mL) and α -bromoisobutyryl bromide (0.1 mL) were

added. After 2h of reaction, the substrates were rinsed extensively with toluene and ethanol and dried under a stream of nitrogen.

7.4. References

1. Šalić, A., A. Tušek, and B. Zelić, *Application of microreactors in medicine and biomedicine*. Journal of Applied Biomedicine, 2012. **10**(3): p. 137-153.
2. Lafuma, A. and D. Quere, *Superhydrophobic states*. Nat Mater, 2003. **2**(7): p. 457-460.
3. Erbil, H.Y., et al., *Transformation of a Simple Plastic into a Superhydrophobic Surface*. Science, 2003. **299**(5611): p. 1377-1380.
4. Li, X.-M., D. Reinhoudt, and M. Crego-Calama, *What do we need for a superhydrophobic surface? A review on the recent progress in the preparation of superhydrophobic surfaces*. Chemical Society Reviews, 2007. **36**(8): p. 1350-1368.
5. Hester, J.F., et al., *ATRP of Amphiphilic Graft Copolymers Based on PVDF and Their Use as Membrane Additives*. Macromolecules, 2002. **35**(20): p. 7652-7661.
6. Sui, X., et al., *Poly(N-isopropylacrylamide)-poly(ferrocenylsilane) dual-responsive hydrogels: synthesis, characterization and antimicrobial applications*. Polymer Chemistry, 2013. **4**(2): p. 337-342.
7. Pei, Y., J. Travas-Sejdic, and D.E. Williams, *Reversible Electrochemical Switching of Polymer Brushes Grafted onto Conducting Polymer Films*. Langmuir, 2012. **28**(21): p. 8072-8083.
8. Zhang, Y., et al., *Effects of Hofmeister Anions on the LCST of PNIPAM as a Function of Molecular Weight†*. The Journal of Physical Chemistry C, 2007. **111**(25): p. 8916-8924.
9. Zhang, Y., et al., *Specific Ion Effects on the Water Solubility of Macromolecules: PNIPAM and the Hofmeister Series*. Journal of the American Chemical Society, 2005. **127**(41): p. 14505-14510.
10. Karg, M., et al., *Temperature, pH, and Ionic Strength Induced Changes of the Swelling Behavior of PNIPAM–Poly(allylacetic acid) Copolymer Microgels*. Langmuir, 2008. **24**(12): p. 6300-6306.
11. Itsuno, S., et al., *Synthesis of Primary Amines Using Potassium 1,1,3,3-Tetramethyldisilazide as Aminating Agent of Alkyl Halides*. Synthesis, 1995. **1995**(02): p. 150-152.

In this Thesis, the development and the characterization of polymeric films with the ultimate goal of switching the properties of functionalized microchannel surfaces is presented. The coatings were mainly based on two types of stimulus responsive polymers, temperature responsive poly(*N*-isopropylacrylamide) (PNIPAM) and redox-responsive poly(ferrocenylsilane) (PFS). These polymers allow one to control wettability, adhesion force, and friction which are important variables for preparing designer microchannels. Surface switching was primarily studied by colloid probe AFM. The motivation for the choice of PNIPAM and PFS is rationalized by their responsiveness and by the opportunities for anchoring these polymers to solid substrates, allowing one to functionalize the inner walls of microfluidic devices and tune the surface properties of these walls to control flow. As a proof of concept, we present a study of PFS functionalized channels for switchable delay valves.

First, a brief introduction of the topics relevant for this Thesis, and the motivation for the reported research are presented in **Chapter 1**.

Chapter 2 starts with some definitions of commonly used terms associated with surface energetics. Then, a brief introduction to the theories behind contact angle measurements and AFM, allowing one to connect the contact angle values or the adhesion hysteresis and friction to the surface properties of a material, is given. Finally, we offer an overview of recent polymeric microvalves and micropumps, used in microfluidic devices to control the flow. The examples are divided in two categories: first, polymeric systems which use surface energy changes to influence capillary action, and second, polymeric systems based on movement, such as expansion and collapse, to manipulate the flow behavior inside microchannels. The first category is separated into the passive elements which cannot be actuated, and the stimulus responsive systems which permit an active switch. The movement-based actuators are classified in single and dual stimuli responsive systems.

In **Chapter 3**, we propose an additional literature overview of the opportunities offered by anionic polymerization of silaferrocenophanes for synthesizing well-defined PFS patterns. Microcontact printing and block polymer microphase separation techniques show immense potential for creating well-ordered patterns at the nanoscale. PFS-based patterns are shown to be perfect candidates for maskless lithography. The creation of patterned surfaces may be easily applied in microfluidic fabrication or simply to alter surface properties.

In **Chapter 4**, we develop a novel method to detach polymer brushes from a titanium dioxide surface via photocatalysis. Nitrodopamine was used as anchor to immobilize an atom transfer radical polymerization initiator for the surface-initiated growth of PNIPAM brushes. Detachment via UV-light irradiation resulted in both, a full cleavage of the brushes, and a controllable, partial and homogeneous detachment, depending on the exposure time. A full detachment of the PNIPAM brushes from the surface allowed the precise molar mass and polydispersity characterization via gel permeation chromatography (GPC). Then, the partial photocatalytic cleavage permitted us to tune the grafting density of the polymer brush from 0.43 to 0.01 chain/nm². Having established a well-characterized system, we were able to study the effect of the grafting density on the thermally induced switching of adhesion hysteresis and friction. At the LCST, a particular behavior of the brush which held long range interactions with the PS colloid, induced a stretching of the brushes and an increase of the adhesion hysteresis and the friction. This phenomenon was maximized at an intermediate grafting density of 0.28 chain/nm².

In **Chapter 5**, we describe the synthesis and the characterization of redox-responsive and surface-anchored PFS layers which allow switching of the wettability and the adherence. First, a poly(ferrocenyl(3-iodopropyl)methylsilane) (PFS-I) layer permitted a reversible change in contact angle values from 80° (reduced state) to 70° (oxidized state), over repeated cycles. Then, this PFS-I layer was functionalized, at the side groups, with alkylsulfonate amphiphilic chains (PFS-SO₃⁻) of which the conformation was changed by attracting or repulsing the polar head depending on

the redox state of the PFS. The resulting “backbiting” caused an inverse switch of the wetting compared to the PFS-I layer, since the contact angle values changed from 59° (reduced state) to 77° (oxidized state). Nanoscale adherence with a PS colloid AFM probe confirmed the two different switching mechanisms for both layers.

In **Chapter 6**, as a proof of concept, we present a study of PFS-I functionalized channels for switchable delay valves. The redox response of the surface-anchored PFS-I and its ability to switch reversibly the surface energy was used to functionalize a gold coated microfluidic device. The switchable surface energy allowed a reversible control of the capillary filling speed of water through a microchannel. The velocity of the meniscus was reversibly switched between 1.8 ± 0.1 mm/s (reduced state) and 3.4 ± 0.1 mm/s (oxidized state).

Finally, in **Chapter 7**, we give an outlook of the possibilities of using a combination of the redox-response of PFS and the swelling response of a polymeric system, such as a brush or hydrogel. For example, we have successfully managed the functionalization of surface-anchored PFS layers with an ATRP initiator at the side groups. This system would allow one to control the swelling of the polymeric layer by using external and electrical stimuli.

In dit Proefschrift worden de ontwikkeling en karakterisering van polymeerfilms beschreven, die op de wanden van microkanalen kunnen worden aangebracht. Door gebruik te maken van polymeren met schakelbare eigenschappen kunnen de eigenschappen van de microkanalen reversibel worden beïnvloed. De polymeercoatings bestaan uit twee typen op stimuli reagerende polymeren, namelijk temperatuurgevoelig poly(*N*-isopropylacrylamide) (PNIPAM) en het op redox stimuli reagerende poly(ferrocenylsilaan) (PFS). Deze polymeren maken het mogelijk om bevochtiging, adhesiekracht en wrijving te sturen, wat belangrijke parameters zijn voor het fabriceren van specifieke microkanalen. De schakelbaarheid van oppervlakte eigenschappen werd voornamelijk bestudeerd door middel van colloïd probe atomic force microscopy. De keuze voor PNIPAM en PFS is gebaseerd op hun mogelijkheid om te reageren op stimuli en op de diverse manieren waarop deze polymeren kunnen worden gehecht aan oppervlakken, zodat de wanden van microfluidische kanalen kunnen worden gefunctionaliseerd en de oppervlakte eigenschappen van de wanden kunnen worden beïnvloed om zo de doorstroming van de kanalen te kunnen sturen. Om de werking van het concept aan te tonen werden met PFS gefunctionaliseerde kanalen gefabriceerd die dienen als schakelbare delay valves.

Eerst wordt een korte inleiding van de onderwerpen, relevant voor dit Proefschrift, en de motivatie voor het beschreven onderzoek gepresenteerd in **Hoofdstuk 1**.

Hoofdstuk 2 begint met enkele definities van veelgebruikte termen op het gebied van oppervlakte energie. Daarna volgt een korte inleiding in de achtergonden van randhoekmetingen en atomic force microscopy (AFM), zodat randhoekwaarden of adhesiehysterese en wrijving kunnen worden gerelateerd aan de oppervlakte eigenschappen van een materiaal. Tenslotte geven we een overzicht van recente polymeer microkleppen en micropompen die gebruikt worden in microfluidische apparatuur om vloeistofstroming te sturen. Voorbeelden zijn onderverdeeld in twee

categorieën: eerst worden polymeer gebaseerde systemen besproken die veranderingen in oppervlakte energie gebruiken om capillaire werking te beïnvloeden, daarna worden polymersystemen die gebruik maken van beweging, zoals expansie en samentrekking, om vloeigedrag in microkanalen te beïnvloeden, behandeld. De eerste categorie wordt onderverdeeld in passieve elementen die geen beweging vertonen, en in op stimuli reagerende systemen die als actieve schakelaar kunnen dienen. De op beweging gebaseerde actuatoren worden onderverdeeld in op enkelvoudige, en op meervoudige stimuli reagerende systemen.

Hoofdstuk 3 bevat een literatuuroverzicht van de mogelijkheden verschaft door anionische polymerisatie van silaferrocenophanen voor de synthese van goed gedefiniëerde PFS patronen. Microcontact printen en blokcopolymeer microfasescheiding bieden enorme mogelijkheden om regelmatige patronen op nanometerschaal te fabriceren. PFS patronen zijn bijzonder geschikt voor maskless lithography. Oppervlakken met nanometerschaal patronen kunnen van belang zijn in microfluidische fabricage, maar ook om oppervlakte eigenschappen te beïnvloeden.

In **Hoofdstuk 4** wordt een nieuwe methode ontwikkeld om polymeerborstels van een titaniumoxide oppervlak los te maken via fotokatalyse. Nitrodopamine werd gebruikt als anker om een atom transfer radical polymerization (ATRP) initiator aan het TiO_2 oppervlak te hechten voor de oppervlakte geïnitieerde groei van PNIPAM borstels. Het losmaken van polymeerketens via bestraling met UV licht leidde tot zowel een volledige verwijdering van de borstels als tot een gecontroleerde, gedeeltelijke en homogene verwijdering van polymeerborstels, afhankelijk van de bestralingsduur. Volledige verwijdering van de PNIPAM borstels van het oppervlak maakte een precieze karakterisering van de molecuulmassa en polydispersiteit mogelijk door middel van gel permeatie chromatografie (GPC). Vervolgens maakte de gedeeltelijke fotokatalytische splitsing het mogelijk om de grafting dichtheid van de polymeerborstel te sturen, tussen 0.43 to 0.01 ketens/ nm^2 . Nadat hiermee een goed gekarakteriseerd systeem was gerealiseerd, waren we in staat om de invloed van grafting dichtheid op de thermisch geïnduceerde verandering

van adhesiehysterese en wrijving te bestuderen. Op de lower critical solution temperature (LCST) leidde een bijzonder gedrag van de borstel, die interacties op langere afstand onderhield met het polystyreen colloid, tot het strekken van de polymeerketens in de borstel en een toename in de adhesiehysterese en wrijving. Dit verschijnsel was maximaal bij een gemiddelde grafting dichtheid van 0.28 ketens/nm².

In **Hoofdstuk 5** beschrijven we de synthese en karakterisering van op redox stimuli reagerende, oppervlakte verankerde PFS films die het mogelijk maken om oppervlaktebevochtiging en -adhesie te schakelen. Eerst maakte een poly(ferrocenyl(3-iodopropyl)methylsilaan) (PFS-I) laag een reversibele verandering in randhoek mogelijk van 80° (gereduceerde toestand) naar 70° (geoxideerde toestand), in meerdere cycli. Vervolgens werden de zijgroepen van deze PFS-I laag gefunctionaliseerd met alkylsulfonaat amfifiele zijgroepen (PFS-SO₃⁻) waarvan de conformatie werd veranderd door aantrekken of afstoten van het polaire uiteinde, afhankelijk van de redox toestand van het PFS. Het resulterende “backbiting” leidde tot een omgekeerde verandering van de bevochtiging vergeleken met de PFS-I laag, omdat de randhoekwaarden veranderden van 59° (gereduceerde toestand) naar 77° (geoxideerde toestand). Nanoschaal adhesie met een polystyreen colloid AFM probe bevestigde de twee verschillende schakelmechanismen voor deze lagen.

Hoofdstuk 6 beschrijft het gebruik van PFS-I gefunctionaliseerde kanalen als schakelbare delay valves waarbij de werking van het concept wordt gedemonstreerd. De redox activiteit van oppervlakte-geïmmobiliseerd PFS-I en de capaciteit van deze films om de oppervlakte energie reversibel te veranderen waren de aanleiding om goud-gefunctionaliseerde microfluidische kanalen te coaten met deze PFS films. De schakelbare oppervlakte energie maakte reversibele controle over de capillaire vulsnelheid van een microkanaal door water mogelijk. De meniscus snelheid werd reversibel geschakeld tussen 1.8 ± 0.1 mm/s (gereduceerde toestand) en 3.4 ± 0.1 mm/s (geoxideerde toestand).

Tenslotte geven we in **Hoofdstuk 7** een vooruitblik van de mogelijkheden om de reacties van PFS op redox stimuli en de zwellingsrespons van een polymeersysteem zoals een borstel of een hydrogel te combineren. We zijn er bijvoorbeeld in geslaagd om oppervlakte geïmmobiliseerde PFS lagen te functionaliseren met ATRP initiator groepen, als PFS zijgroepen. Zwelling van een polymeerborstel, gegroeid vanaf deze redox actieve laag, zou kunnen worden gestuurd door externe en door elektrische stimuli.

Et voilà! A little bit more than five years have passed, here, in Enschede, with my master internship and my PhD. And of course, during all these years in this international environment, I have met so many people that have played an important part in my life. I am sure I will forget some names, and I already apologize for that, but I would like to let you all know that I had really a great time with all the amazing people I have met.

First, I would like to thank my promotor **Julius Vancso** for welcoming me in his group for my master internship, and later on for offering me the PhD position. Dear **Julius**, I am sure that at a certain point we both doubted this decision but at the end, with ups and downs, we went through it successfully. ☺ And from you, I will always keep in mind a quotation you regularly use for science: “*There are no problems, but only challenges*”. Thanks to this experience, I have learned a lot about being an independent scientist but also about myself.

I would never be able to go through certain chemical challenges without the help of my supervisor **Mark Hempenius**. Dear **Mark**, thank you for your amazing chemical tips and tricks. You have always been accessible and always managed to propose a solution or explanation for these chemical brain-teasers we went through.

Being a chemist, I have been tempted by **Sissi de Beer** to explore steep roads of physics via AFM. Dear **Sissi**, I have already told you many times but I would like to repeat it again: thank you for being my lighthouse who guided me from the darkness towards the calm and “*cool*” lands of physics. With your eternal good mood, patience, and passion for science that you transmitted to me during our never-ending discussions, you helped me to put some sense in all these theories, equations, and even more... Without you, this thesis would never be what it is now. Also, I hope that from now on, every time you will taste a “*real brie cheese*” with wine, you will remember the crazy French chemist who was continuously bothering you, but always with affection.

I would also like to thank **Edmondo M. Benetti** for the collaboration I had with him. Dear **Eddy**, unfortunately you were in Enschede only a few days per month but I really enjoyed every moment we spent together discussing about chemistry, and also after work over a burger. Furthermore, I appreciated the warm welcome from you and your team at the ETH in Zurich.

Next, I would like to thank my two officemates, friends and paranymphs, **Michel** and **Andreas**. I had the chance to share every single moment of this PhD adventure with them, so it was obvious to have them at my side for my “*grand final*”. Dear **Michou**, starting at MTP by being your first master student played of course an important role on my choice in continuing with this PhD. Thank you for being always available, for the numerous Dutch translations, discussions, but mostly for the fun and the moral support you gave me with your legendary tranquility. Dear **Schnoufy**, from the first day you had joined the office, we had immediately fun and quickly became friends. Thank you for the passionate discussions, your homemade cocktails and your craziness which have always been a blast.

Furthermore, I would like to especially thank **Clemens Padberg** for all his technical support. Dear **Clemens**, without you around to fix all these little challenges that I came across daily, from GPC measurements to computer bugs and even broken screws, my life would have been more difficult. Also, thank you for all the fun we had playing table football.

Dear **Geneviève** and **Marion**, thank you for taking care of all the administrative paperwork in a joyous and relaxed atmosphere. And special thanks to **Geneviève** for being able to harmoniously assemble all my ideas in this beautiful thesis cover.

Dear **Aysegul**, I really appreciated all the discussions and fun we had together during the numerous coffee breaks, lunches and dinners. Also thank you for all the fashion help you provided to me during the exhausting shopping sessions.

Dear **Bart**, thank you for helping me analyzing my uncountable data with your Matlab skills but also for all the help, discussions and mostly fun that I had with you during these years.

During my PhD research, I had the opportunity to supervise some students. Dear **Ludger, Henrieke, Lidia, Mathies** and **Simone**, it was a pleasure to be in the lab with you all. I hope you have learned from me as much as I have learned from you guys, and I wish you all the best in your future life.

For all my others MTP colleagues during my stay there: **Joost, Peter, Edit, Bram, Wilma, Lucie, Hubert, Hairong, Xueling, Xiaofeng, Shanqiu, Yunlong, Kaihuan, Keshav, Maria, Marta** and all the other Bachelor and Master students who passed the group. We have all survived with fun and humor all the “chemical attacks” in the lab. Thank you for your help in the lab but also the great time we had at the coffee corner or at the various group activities.

At the beginning of my stay in Enschede, I was living at the campus and I have met there really nice people. Dear **Indré**, you are the very first person I met here. Even though your first impression was not so enthusiastic, we manage to have a lot of fun, joined later by **Ruta** and **Bas**. Dear **Daian, Deepak, Gigi** and **Alex**, thank you for the great time we had during the numerous parties and trips around Europe.

Later, I grew up and moved in a house with still quite international company. Dear **Andrea**, “*grazie mille*” for teaching me how to cook properly pasta. Cher **Guillaume**, merci pour ton aide et tous les bons moments au boulot mais surtout dans la vie privée. **Marco Garcia Porcel**, muchas gracias por cocinar para mí las increíbles cenas y especialmente la paella. Querida **Inês**, por mais que te custa, tu serás sempre a minha “*Totozinha*” preferida; foi um prazer partilhar a casa contigo e desejo-te muita sorte para o teu futuro. Dear **Marco Cirelli**, I cannot “*image*” how would have been my writing process without your communicative craziness. Thank you for all the fun and as you always say “*see youuuuu!*”.

As a good French, I always managed to find cheese lovers to surround myself with. Aux expats français aux Pays-Bas : **Guillaume et Fenna, Séb, Khalid, Audrey et Yannick, Vanessa, Julie et Chris, Anne et Mathieu, Jonathan et Kasia, Géraldine et Jeroen, Élise, Adeline, Claire**, je vous remercie pour tous ces moments que nous avons passés autour d'un dîner, sur les pistes de ski ou accrochés aux arbres. Ensemble nous pouvions enfin nous plaindre librement de la bouffe hollandaise et parler avec nostalgie de la gastronomie française! :p Tous ces moments passés en votre compagnie m'ont aidés à surmonter l'éloignement, et ont fait que ces années sont passés rapidement avec joie et bonne humeur. Et un merci particulier à **Guillaume, Séb et Khalid** pour ces interminables et passionnés dîners et débats politiques.

Because of my family roots, I always felt comfortable and happy surrounded by Portuguese culture. So I would like to thank my Portuguese friends who help me to keep this so familiar nest in Enschede. Aiii turminha! **Joana, Ana** (R'driginhes), **Ana** (Maria), **Davidinho e Carlito**, mais que uns amigos aqui nos Países Baixos, vocês foram a minha família de substituição. Obrigado por todos os bons momentos que passámos juntos, desde Enschede, a Castelo Branco, passando por Deventer, Amsterdão, Maastricht e até Paris (de France). As nossas jantaras portuguesas com “de vez em quando” um toque francês, ajudaram-me a matar as saudades. Graças a vocês também acabei por aperfeiçoar o meu Português. E, claro que não podia acabar sem citar a letra de um fado para exprimir como vocês marcaram a minha *bida* aqui, em Enschede: “As coisas vulgares que há na vida, não deixam saudades, só as lembranças que doem ou fazem sorrir. Há gente que fica na história, da história da gente, e outras de quem nem o nome lembramos ouvir. São emoções que dão vida, à saudade que trago, aquelas que tive contigo e acabei por perder...” (Mariza, Chuva) Meninos, com certeza que me recordarei para sempre, e cada vez que comer bolacha Maria, da nossa história debaixo da chuva holandesa!

My life in Enschede would not have been so fun without all the other people that I have crossed during all these years. Dear **Maike, Pablo, Joana, Marina,**

Khalid, Afrodite, Pantelis, Aikatarina, Pepito, Machete, Rodolfo, Corina, Ioana, it has been a pleasure to meet you and share good moments with you.

Finally, I would like to thank all my friends and family in France and Madeira for their support. A ma **famille et amis en France**, merci pour me faire sentir si confortable comme si je n'avez jamais quitté la France, à chaque fois que je rentre auprès de vous. Malheureusement, on ne s'est vu que trop peu mais chaque moment en votre compagnie m'a permis de me libérer l'esprit. A minha **familia e amigos na Madeira**, obrigado por me receber sempre com tantos carinhos cada vez que vou aí. Estes momentos passados em vossa companhia me ajudaram a voltar mais forte para afrontar o frio do norte e o doutoramento.

Maman et Papa, merci pour votre soutien durant toutes ces années et pour m'avoir offert l'éducation qui m'a permis d'avancer dans la vie.

A handwritten signature in cursive script, reading "Lionel", with a long horizontal flourish extending to the right.

Lionel Dos Ramos was born on the 11th of February, 1986 in Saumur, France. In 2004, he started the “Classes Préparatoires”, an intensive course to get entrance into a “Grande Ecole”, specializing in Physics and Chemistry at “Lycée Chaptal” in Paris.

Successively, he went to “Ecole Nationale Supérieure de Chimie de Mulhouse”, the National Graduate Chemistry School of Mulhouse in France, where he obtained, in 2011, an engineering degree in Materials and Polymers Chemistry. In parallel, Lionel also obtained a Master’s degree in Inorganic and Organic Materials Synthesis at the University of Haute-Alsace in Mulhouse, France.

During his Master’s degree, Lionel had the opportunity to spend a gap year (2009-2010) at the R&D department of Albemarle Catalyst Company in Amsterdam, where he performed research in catalysts for biofuels.

His Master’s research project was accomplished at the University of Twente in collaboration with both Materials Science and Technology of Polymers (MTP) group, and Tissue Regeneration (TR) group. He worked under the supervision of Prof. dr. G. Julius Vancso and Dr. Lorenzo Moroni, on the adhesive behavior of stem cells on gradient polymer brushes.

Starting from October 2011, Lionel continued as a PhD student at the MTP group, under the daily supervision of Dr. Mark Hempenius and Dr. Sissi de Beer. His research was funded by the Netherlands Organization for Scientific Research (NWO).

In 2014, he also got the chance to do research at the Eidgenössische Technische Hochschule (ETH) Zürich in Switzerland. During this period, he worked together with Dr. Edmondo M. Benetti on the titania functionalization and photocatalytic cleavage of polymer brushes. Parts of the results are presented in this thesis in Chapter 4.

Duvigneau J., Kutnyanszky E., Phang I.Y., Chung H.J., Wu H., Dos Ramos L., Gädt T., Yusoff S.F.M., Hempenius M.A., Manners I., Vancso G.J.; *Raft crystals of poly(isoprene)-block-poly(ferrocenyldimethylsilane) and their surface wetting behavior during melting as observed by AFM and NanoTA*. Polymer (United Kingdom). **2014**; 55(11); p. 2716-24.

Cumurcu A., Feng X., Dos Ramos L., Hempenius M.A., Schön P., Vancso G.J.; *Sub-nanometer expansions of redox responsive polymer films monitored by imaging ellipsometry*. Nanoscale. **2014**; 6(20); p. 12089-95.

Dos Ramos L., Hempenius M.A., Vancso G.J.; *Poly(ferrocenylsilanes) with controlled macromolecular architecture by anionic polymerization: Applications in patterning and lithography*. In *Anionic Polymerization: Principles, Practice, Strength, Consequences and Applications*, Hadjichristidis N. and Hirao A., Editors; **2015**, Springer Japan: Tokyo; p. 387-427.

Dos Ramos L., de Beer S., Hempenius M.A., Vancso G.J.; *Redox-induced backbiting of surface-tethered alkylsulfonate amphiphiles: reversible switching of surface wettability and adherence*. Langmuir. **2015**; 31(23); p. 6343-50.

Dos Ramos L., Lajoinie G., Kieviet B.D., de Beer S., Versluis M., Hempenius M.A., Vancso G.J.; *Redox Control of Capillary Filling Speed in Poly(ferrocenylsilane)-Modified Microfluidic Channels for Switchable Delay Valves*. **2016**; Submitted

Kieviet B.D., Dos Ramos L., Hempenius M.A., Duvigneau J., Schön P.M., Vancso G.J.; *In-line sensing of sodium ascorbate using a poly(ferrocenylsilane)-coated microfluidic device*. **2016**; Submitted

Dos Ramos L., Benetti E.M., Kieviet B.D., de Beer S., Hempenius M.A., Vancso G.J.; *Controlled cutting of PNIPAM brush chains at their roots by photocleaving to provide grafting density variations for adhesion hysteresis and friction studies*. **2016**; Manuscript in preparation