Structure-Property Relationships of Surface-Grafted Polymeric Architectures:
From Ultra-Thin Films To Quasi-3D Polymer Assemblies

A dissertation submitted to
ETH ZURICH

for the degree of
Doctor of Sciences

presented by
Ang Li
M.Sc. Polymer Science of Freie Universität Berlin, Humboldt Universität zu Berlin,
Technische Universität Berlin and Universität Potsdam
born on 19, April, 1982
citizen of P.R.China

accepted on the recommendation of
Prof. Dr. Nicholas D. Spencer, examiner
Prof. Dr. A. Dieter Schlüter, co-examiner
Prof. Dr. G. Julius Vancso, co-examiner
Dr. Edmondo M. Benetti, co-examiner

2013
献给我的父亲和母亲
Abstract

Polymeric coatings are widely applied to impart the required surface properties for an application, as well as to protect a buried substrate from processes such as corrosion, wear, and scratching. Anchoring polymers at interfaces is a fundamental issue in numerous technologies, ranging from adhesion and lubrication to the stabilization of colloidal dispersions. In addition, surface-grafted macromolecules are highly relevant in preventing the formation of biofilms in biomedical devices and biomaterials (orthopedic implants, wound healing, ophthalmic and dental care) where maintaining the performance and increasing service life are highly desired. Tethered polymer films have received increasing attention from industry and academia for many years. In particular, end-grafted polymeric chains are found to significantly reduce friction and promote lubrication. These polymeric coatings can also serve as models for understanding the mechanisms of polymer tribology, especially in an aqueous environment.

The main objective of this thesis is to study the relationships between structures of grafted polymeric layers and their properties, as well as to propose new fabrication strategies for the preparation of polymeric surfaces presenting variable structures and characteristics. Poly(acrylamide) nano-films with different crosslink degrees were grafted from a silicon substrate via UVLED surface-initiated photoiniferter-mediated polymerization. The crosslink degree was demonstrated to influence both the physical and morphological properties of chemically identical nano-films. These effects were found to be more marked if compared to the same materials when synthesized in bulk.

Additionally, the nanotribological properties of these films were studied in the presence of solvents with different qualities, by means of colloidal probe microscopy (CPM). The solvent-induced glass transition was observed to cause different pull-off forces for poly(acrylamide) films with varying structures, the interplay between adhesion, friction, crosslinking and solvent quality is discussed correspondingly.
As a follow-up to the first study, poly(acrylamide) films with stratified structures presenting variable crosslink degrees were synthesized. The resulting films, with different tiered combinations in the vertical direction, were distinguished by a set of tandem CPM measurements, according to their differences in mechanical and tribological characteristics.

A novel approach integrating the developed ‘grafting-from’ technique and ‘grafting-to’ deposition of polymers, is proposed to prepare quasi-3D polyelectrolyte complex films. These synthetic polymeric films, prepared by *amplified electrostatic assembly*, present a platform with tailorable interfacial properties that shows great potential in biointerfacial applications.

The findings summarized in this thesis demonstrate how surface-modification strategies by polymer grafting allow control over both interfacial properties and architecture. The investigation of the mechanical properties of polymer films establishes a valuable window into the mechanisms at work in the nanotribological behavior of the films. The overall study demonstrates the highly tailorable physicochemical properties of macromolecules that are anchored on a supporting substrate and, more importantly, it provides an insight into the origins of polymer-assisted aqueous tribology at the nanoscale.
Zusammenfassung


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Introduction

1.1 General Introduction

An interface is the boundary between two phases, and connects the physicochemical properties of a bulk material to its surroundings. Numerous technical applications require tailoring of interfacial properties, in a controlled fashion, to improve surface properties such as wettability, friction, particle stabilization and biocompatibility.

Surface modification by polymer films has gained huge attention over past few decades, as a result of developments of polymer chemistry in the synthesis of surface modifiers coupled to advanced surface deposition techniques, and is hence widely employed, both in industrial applications and in fundamental research. Commercial polymer films and coatings have been used for many decades in areas relating to anti-corrosion and aesthetic coatings as well as in packaging materials. In addition, certain interfacial properties of films can influence the corresponding buried bulk properties. By employing various fabrication and engineering approaches, surfaces with defined structures associated with different functionalization approaches can be achieved, which provides a platform to understand the correlation between the structure and performance of films.

Surface modifications with ultra thin (sub-micrometer) organic films can be achieved by self-assembly and directed-assembly strategies, encompassing Langmuir-Blodgett (LB) films, self-assembled monolayers (SAMs), alternate polyelectrolyte multilayer (LbL) deposition and polymer grafting. These methods provide a versatile approach for surface modification by tailoring the interfacial properties. Among these surface-modification techniques, surface grafting of polymers have received great attention over the past few years due to the unique resulting tethered chain structure. Benefiting from
advances in synthetic polymer chemistry, adapting controlled polymerization techniques for surface modification allows the fabrication of surface-tethered polymer films with well-defined structures, composition and functions, effectively tailoring the nature of the interface.\textsuperscript{5,6}

1.2 Surface-Grafted Polymer Films

1.2.1 Surface-Grafted Polymer Brushes

Polymer brushes are defined as assemblies of polymer chains tethered by one end to a surface (or, in general, an interface) with thicknesses ranging from a few nanometers to several micrometers.\textsuperscript{7} When polymer chains are sparsely grafted (low grafting density) onto the substrate and are not in the presence of a good solvent, tethered polymer chains take on a ‘pancake’ conformation by lying flat on the substrate (Figure 1.1 a). By exposing the chains to a good solvent, a ‘mushroom’ conformation of grafted macromolecules will be adopted (Figure 1.1 b). In a good solvent, upon decreasing the grafting density such that the average distance between adjacent tethering points is smaller than the gyration radius of the grafting macromolecules in an unperturbed state, the surface-attached polymer chains are forced to stretch far away from the anchoring points, to minimize the segment-segment interaction. The overlapping between tethered chains results in a strong osmotic repulsive force, showing interesting interfacial features (lubrication and antifouling) due to this distinctive physical structure (Figure 1.1 c).
Figure 1.1. Artist’s perception of various conformations of surface-grafted polymer chains: (a) ‘pancake’, (b) ‘mushroom’, (c) ‘brushes’.

The first theoretical descriptions of polymer brushes at an interface were proposed by Alexander and de Gennes.\(^8\)\(^{-10}\) They assumed monodisperse polymer chains consisting of \(N\) monomer units that are irreversibly anchored to a flat surface with distance between the grafting sites being smaller than the diameter of the unperturbed chain under an unconfined environment \((2R_g)\). The total free energy of these grafted polymer chains includes the statistical segment interaction energy and the energy difference caused by entropy loss of polymer chains. The minimization of total free energy with respect to the brush equilibrium height \(h\) describes the scaling relationship between the brush height \(h\) and grafting density \(\sigma\) of the brushes in solvents with varying quality:

\[
h \propto N \times \sigma^{1/3} \quad \text{(in good solvent)} \tag{1.1}
\]

\[
h \propto N \times \sigma^{1/2} \quad \text{(in } \Theta \text{ solvent)} \tag{1.2}
\]

However, Alexander and de Gennes model is oversimplified and could not adequately predict the experimentally observed polymer-density profile, therefore, more sophisticated models were required. Over the last few decades, numerical and analytical self-consistent field (SCF), Monte Carlo (MC) and molecular dynamics (MD) methods for polymer brushes with moderate grafting density have been explored in order to resolve segment density profile and to explain osmotic repulsive forces generated under normal and lateral loads. Milner, Witten and Cates (MWC) derived analytical equations for brush profiles that showed a parabolic density profiles in a good solvent (Figure 1.2).\(^11\)
The MWC model also estimates the end-segment-distribution profile of the polymer along the length of surface-attached films in various solvent qualities. In contrast to Alexander and de Gennes’ model, the end-segment-distribution profile in good solvent has a maximum density located within the total brush height instead at the outer interface. However, the height of the maximum in the end-segment distribution for a bad solvent is found to be that of the brush itself (Figure 1.3).12

Figure 1.2. Schematic segment density profiles of surface-grafted polymer chains with different grafting densities. (a) ‘pancake’, (b) ‘mushroom’, (c) ‘brushes’ from Alexander and de Gennes model, (d) ‘brushes’ from MWC model.12

Figure 1.3. Segment density profiles and end segment distributions of surface-grafted polymer chains in (a) good solvent and (b) bad solvent.

Over the years, a huge effort has been made to fabricate polymer brushes with high grafting density. Also, several synthetic routes have been developed to accurately control the structure, composition and functionalization of surface-grafted thin films. In principle,
depending on the brush-anchoring mechanism, the preparation of polymer brushes can be divided into two categories, namely ‘grafting-from’ and ‘grafting-to’ techniques.

The ‘grafting-from’ approach has been studied extensively in the literature and will be employed in this thesis due to the high grafting densities achievable when compared to the ‘grafting-to’ method. Several steps are involved in the formation of well-defined polymer brush films using the ‘grafting-from’ technique. Firstly, initiator molecules are immobilized on a freshly cleaned substrate, and then the polymerization is carried out at the anchored initiator sites under a monomer-enriched medium (Figure 1.4). High grafting density and high polymerization degrees can be achieved due to the convenient diffusion of a monomer to the living radical species during polymerization. Furthermore, a series of controlled polymerization techniques with different mechanisms can be utilized to grow the polymer chains from surfaces, resulting in polymer chains with different polydispersities (PDIs).

![Figure 1.4. General depiction of fabrication of polymer brushes by the ‘grafting-from’ approach. (a) substrate, (b) initiator-modified substrate, (c) polymer brushes.](image)

Despite the fact that high brush densities are achieved by the ‘grafting-from’ approach, a major setback lies in the difficulty in determining the molar mass and grafting density of surface-attached polymer chains. Cleaving the macromolecules from the substrate, via etching of the substrate or delamination of the film, is required to examine their molar mass and PDI by size-exclusion chromatography (SEC)/field-flow fractionation (FFF). However, the amount of polymer, after cleaving, can be insufficient for analysis, due to instrumental uncertainties. An alternative method involves the simultaneous
polymerization in bulk and on the interface, in order to estimate the molar mass and grafting density of polymer brushes, assuming similar rates of polymerization and thus $M_n$ and PDI for both cases. Therefore, from the measured value of the molar mass of polymer chains in the solution and the dry thickness of polymer brushes ($h$), one can estimate the polymer grafting density ($\sigma$) by using the equation (1.3):

$$\sigma = \frac{(h \times \rho \times N_a)}{M_{n,s}} = \frac{(h \times \rho \times N_a)}{M_{n,b}}$$  \hspace{1cm} (1.3)$$

where $\rho$ is the bulk density of the polymers, $N_a$ is Avogadro’s number, and $M_{n,s}$ and $M_{n,b}$ are the number-average molecular weights of polymer chains on surface and in bulk, respectively.

A number of experimental attempts have been carried out in order to verify the abovementioned assumption (equation 1.3). However, contradictory results were reported by different research groups over last few years.\textsuperscript{13,14} Recent Monte Carlo simulations showed a significant difference in the kinetics of controlled radical polymerization in solution and from a 2-D interface. Simulations showed slower growth rate and larger PDI for the surface-initiated polymer chains in comparison to that formed in bulk. Thus, the discrepancy of molar mass between polymers at the interface and bulk polymers can be represented as follows:

$$M_{n,s} = \zeta \times M_{n,b}$$  \hspace{1cm} (1.4)$$

where $\zeta$ is a function representing the effects of confinement on surface-initiated polymerization. This parameter is influenced by the grafting density of the polymer, substrate geometry and polymerization mechanism.\textsuperscript{15,16} Hence, equation (1.3) fails to accurately estimate the grafting density of polymer brushes at the interface.

In the ‘grafting-to’ approach, the polymer chain consists of reactive end groups that can interact either chemically (coupling reaction) or physically (hydrophobic, electrostatic) with the functionally modified interface (Figure 1.5). The polymer chains with reactive
end groups are synthesized by living/controlled polymerization and these mono-dispersed macromolecular chains can be well characterized, prior to the ‘grafting-to’ process, using several surface-sensitive techniques such as SEC/FFF, matrix-assisted laser desorption/ionization time of flight mass spectrometry (MALDI-TOF) and nuclear magnetic resonance (NMR). Thus, this approach helps to provide a more comprehensive understanding of the surface-grafted polymer chains than the ‘grafting-from’ approach. However, high grafting densities cannot to be achieved via ‘grafting-to’ method, as the steric hindrance from the grafted chains will hinder the free polymer chains approaching the grafting sites during adsorption.\textsuperscript{17}

**Figure 1.5.** General depiction for fabrication of polymer brushes by ‘grafting-to’ approach. (a) chain-end functionalized macromolecules, (b) reactive sites-modified substrate, (c) polymer brushes.

Polymer brushes can be applied to various materials, such as metals (oxides), clay minerals, carbon materials, semiconductors and other polymer surfaces.\textsuperscript{18-25} Furthermore, the preparation of polymer brushes is not limited to substrates with two-dimensional geometry (planar surfaces);\textsuperscript{26,27} particles (curved surfaces)\textsuperscript{26,29} and three-dimensional membranes with porous structures\textsuperscript{30,31} can also be functionalized with these assemblies (Figure 1.6).
Thanks to the development of controlled polymerization over recent decades, various polymerization techniques have been successfully applied to surfaces, such as anionic polymerization,\textsuperscript{32} atom transfer radical polymerization (ATRP),\textsuperscript{33} reversible-addition fragmentation chain-transfer polymerization (RAFT),\textsuperscript{34} nitroxide-mediated polymerization (NMP)\textsuperscript{35} and ring-opening metathesis polymerization (ROMP),\textsuperscript{36} resulting in so-called surface-initiated controlled polymerization (SI-CP) to fabricate polymer brushes with tunable thickness, grafting density, composition and architecture. SI-CP has been successfully used to produce polymer films with different structures, e.g. block brushes, random brushes, mixed brushes, gradient brushes, Y-shaped brushes, branched brushes as well as cross-linked brushes, resulting in novel interfacial properties (Figure 1.7).
Figure 1.7. Overview of architecture of polymer films prepared via SI-CP. (a) homogeneous brushes, (b) block brushes, (c) random brushes, (d) cross-linked brushes, (e) branched brushes, (f) binary mixed brushes, (g) Y-shaped brushes, (h) gradient brushes.

Furthermore, a series of patterning techniques (such as micro-contact printing, electron beam-assisted printing, UV irradiation-assisted printing, scanning probe microscopy-assisted printing, nano-imprint and contact lithography) following ‘bottom-up’ or ‘top-down’ strategies have been widely employed to fabricate 2D-structured brush films, finding applications in biomaterials, sensors and micro-electronics.

The chemical composition of the surface-grafted polymer brushes can be tailored to manipulate the conformation of polymer chains upon varying external stimuli. Polymerization of the monomer with well-defined functionalities, solvent-responsive brushes, thermo-responsive brushes, photo-sensitive brushes, pH- and ion-sensitive brushes result in ‘smart surfaces’ with stimuli-responsive features that can specifically adapt to the surrounding environment.
1.2.2 Surface-Grafted Polymer Gels

Surface-grafted polymer gels can be prepared by crosslinking polymer brush films either \textit{in situ} or \textit{ex situ} on the surface (Figure 1.8). The \textit{in situ} crosslinking process requires surface-initiated homo- or copolymerization in the presence of bi-functional monomers. These monomers irreversibly crosslink polymer brushes at the interface to form a surface-grafted quasi-2D network structure.\textsuperscript{58} The \textit{ex situ} crosslinking process generally is carried out during the post-modification of appropriately functional polymer brushes by irreversibly covalently crosslinking or reversibly non-covalently crosslinking (electrostatic interaction or coordination).\textsuperscript{59} The crosslinking process, however, also occurs in a less controlled manner as a result of side reactions during SIP.\textsuperscript{60}

![Figure 1.8. General scheme for fabrication of surface-grafted polymer gels. (a) initiator-modified substrate, (b) polymer gels, (c) functionalized polymer brushes.](image)

1.2.3 Surface-Grafted Stratified Films

The term ‘surface-grafted stratified films’ denotes hybrid polymer films with a combination of gel and brush structures, presenting intriguing material properties in terms of mechanical and tribological behavior. In general, a stratified structure can be realized by building up a second layer on the initial layer. We have used a reinitiation strategy in this thesis in order to covalently graft a second layer on top of the first layer. Depending on the polymerization sequence, tiered polymer films with a gel-brush structure or a brush-gel architecture can be produced (Figure 1.9). It has to be mentioned that the key step for successfully generating a stratified structure lies on the reinitiation process,
which requires correctly choosing the reinitiation conditions. The gel-brush structure can be readily obtained upon reinitiating the brush layer on top of the gel layer in a good solvent (Figure 1.9 b and d). In contrast, the formation of brush-gel architecture upon reinitiating a gel layer on the initial brush layer should be carried out in a bad solvent environment. The adoption of bad solvent in the reinitiation step causes a collapse of the brush layer (transition from a parabolic profile to a step profile), sterically preventing the monomer diffusing to the substrate and guaranteeing the occurrence of reinitiation far away from residual initiator on the substrate. Furthermore, the maximum distribution of reinitiable end groups will be located at the end of brush layer when it is exposed to a bad solvent, which also facilitates the formation of the targeted structure (Figure 1.9 c and e).

Due to the fact that the reinitiable end groups are present throughout the entire initial layer, the resulting stratified films are expected to have a continuous gradient-like interface between the gel and brush layers upon reinitiation.

![Figure 1.9. General scheme for fabrication of surface-grafted stratified films. (a) initiator-modified substrate, (b) polymer gels, (c) polymer brushes, (d) stratified gel-brush films, (e) stratified brush-gel films.](image)

1.2.4 Surface-Grafted Polyelectrolyte Complex (PEC) Films
Surface-grafted polyelectrolyte complex (PEC) films represent polymeric coatings with reversible interfacial (mechanical and tribological) properties, which are fabricated by electrostatically adsorbing polyelectrolytes on surface-grafted oppositely charged polyelectrolyte brushes, as shown in Figure 1.10.

The negatively charged surface-grafted polyanionic brushes can efficiently extend the charge-carrying ability (charge per unit volume), compared to the flat surface, which has a limited charge per unit volume. Therefore, the oppositely charged weak polyelectrolytes in solution can be significantly adsorbed into polyanionic brushes resulting grafted weak PEC films, which are still soluble in water. By carefully adjusting the experimental conditions (grafted weak polyanionic brushes thickness, weak polycationic polymers concentration, adsorption time, pH and salt concentration), the loading mass of weak polycationic polymers in the PEC films can be well tailored.

Furthermore, the adsorption process is fully reversible. By immersing the PEC films in an aqueous solution with high salt concentration, polycationic polymers can be unloaded and the original grafted polyanionic brushes recovered, owing to the breaking of the weak PECs by means of a charge-screening effect upon increasing the ionic strength. In particular, the reversible mechanical and tribological properties make the PEC films with high loading ability a promising platform for biological applications.

Figure 1.10. General scheme for fabrication of PEC films by means of electrostatic complex between two oppositely charged polyelectrolytes. (a) polycationic polymers, (b) surface-grafted polyanionic brushes, (c) grafted PEC films.
1.3 Surface-Initiated Photoiniferter-Mediated Polymerization (SI-PIMP)

Photoiniferter-mediated polymerization was introduced 30 years ago by Otsu, who pioneered modern controlled radical polymerization. A photoiniferter is a chemical compound that acts as initiator, transfer agent and terminator, which mediates radical polymerization with a limited degree of control. Surface-initiated iniferter-mediated photopolymerization was used in this thesis for the fabrication of surface-grafted polymeric architectures, owing to its catalyst-free and simple features.

Surface-grafted iniferter self-assembled monolayers generate one alkyl radical and a dithiocarbamyl radical (a), upon UV irradiation (Figure 1.11). Although the alkyl radical is capable of initiating and further growing monomer, the dithiocarbamyl moiety is barely able to initiate polymerization (b). Due to the high reactivity between the alkyl radical and dithiocarbamyl radical, they tend to rapidly recombine to produce a dormant species, which can again generate the alkyl radical upon photolysis. However, during the polymerization, termination, chain transfer of alkyl radical to the solvent and dimerization of dithiocarbamyl take place, resulting in the loss of the living character. In general, SI-PIMP proceeds as a series of successive reactions in which surface-grafted macromolecular chains grow with the photolysis time.

According to the quasi-living behavior, without considering the chain transfer and termination, the number average molar mass \( M_n \) of the surface-grafted macromolecular chains prepared by SI-PIMP can be written as:

\[
M_n = C \times [M_0] \times [I]^{-1} \times M_{\text{monomer}}
\]

(1.5)

where \( C \) is the conversion coefficient of the polymerization, \( [M_0] \) is the initial monomer concentration, \( [I] \) is the iniferter concentration and \( M_{\text{monomer}} \) is the molecular weight of monomer. It is also known that the conversion coefficient \( (C) \) is proportional to the iniferter concentration and photolysis time, and thus the quasi-living characteristic is validated by demonstrating the linear relationship between the molar mass of grafted chains and the photolysis time.
Due to the intrinsic nature of the *initiferter*, SI-PIMP suffers from low initiation efficiency as well as irreversible termination reactions that result in ‘dead’ polymer chains.\textsuperscript{63} Therefore, grafted polymer films with complex architectures, such as multi-block copolymer brushes, cannot be precisely synthesized upon reinitiation with a second monomer species. However, experimental studies have shown that adding a source of deactivating radicals, such as tetraethylthiuram disulfide (TED), to the reaction mixture during SI-PIMP reduces the extent of irreversible termination, leading to a more controlled growth as compared with that achieved in the absence of added TED.\textsuperscript{64-66} Unfortunately, the extremely poor solubility of TED in water limits its applications in aqueous polymerization.

### 1.4 Aqueous Tribology

The bas-reliefs from ancient Egypt have revealed the first example of lubrication in the history of mankind: a man can be seen pouring liquid in front of the pedestal of a statue during its transport, as recorded in the tomb of Tchuti Hetep, El-Bersheh, Egypt, 1800 B.C.\textsuperscript{67} During the renaissance, Leonardo da Vinci (1452-1519) was the first tribologist to quantify friction and measure the dependence of friction on applied normal load. As the industrial revolution boosted the development of tribology, Guillaume Amontons (1663-1705) and Charles-Augustin de Coulomb (1736-1806) formalized three fundamental laws in tribology (1st law: friction force is proportional to the normal force; 2nd law: friction...
force is independent of apparent contact area; 3rd law: friction force is independent of sliding velocity), which are still widely valid for dry friction between two surfaces.

In the 20th century, German engineer Richard Stribeck (1861-1950) described the dependence of the coefficient of friction in lubricated bearings on applied load ($W$), viscosity of the lubricant ($\mu$) and speed of the bearing ($U$),\textsuperscript{68} which is now widely known as the Stribeck curve.

There are generally three lubricating regimes in a Stribeck curve, as shown in Figure 1.12. The \textit{boundary lubrication} regime signifies the sliding of the contacts under severe conditions, i.e. at low speeds and/or at high loads. In this regime, the direct contact between the asperities exists, resulting in high friction coefficients. Surface-adsorbed densely packed molecules/polymer films can act as boundary lubricants and protect the contacting surfaces from extensive wear. Upon significant increase in the Sommerfeld Number ($\mu \times U / W$), a ‘thick’ fluid film is generated by hydrodynamic forces, separating the two counter surfaces, and resulting in low friction and negligible wear in the \textit{hydrodynamic lubrication} regime.\textsuperscript{69} Between these regimes, and moving to lower values of the Sommerfeld number, the hydrodynamically generated film decreases in thickness, such that asperities begin to come into contact. Since areas of the surface are then in boundary lubrication while others are fluid-film lubricated, this is referred to as the \textit{mixed lubrication} regime.
Richard Feynman’s famous lecture at Caltech entitled ‘there’s plenty of room at the bottom’, heralded the arrival of nanoscience and -technology. In its wake, the development of micro- or nano-electro-mechanical systems (NEMS) has promoted the rise of nanotribology in the new century – the study of friction phenomenon at the nanometer scale. From antiquity to the present times, tribology has paralleled the development of human society.

Increased operational costs due to high friction (loss of energy) and wear (loss of materials) in mechanical systems require lubrication strategies such as surface engineering of the material or usage of lubricants at the interface to avoid or reduce the contact area between the sliding parts. The surface texturing method is limited to materials with regular geometry, and requires complex designs and time-consuming fabrication processes. On the other hand, oil-based lubrication is widely used for many engineering surfaces at different contact scales to reduce friction, wear and enhance the lifetime of materials. Oil-based lubricants lead to lubricant retention in the contact, even at high contact pressures, and the avoidance of direct contact between the shearing surfaces, due the high viscosity and pressure-viscosity coefficient of the oils. However,

**Figure 1.12.** Empirical Strubeck curve for lubricated contacts: coefficient of friction is a function of Sommerfeld Number.
oil-based lubricants generate pollutants and harmful contaminants and thus there is constant search for alternative green lubricants that are renewable and environmentally friendly. Lubrication in an aqueous medium has attracted significant attention over the last decade, owing to its environmental compatibility and ready availability of the lubricant, and has potential applications in food, biomedical and pharmaceutical industries. Despite the enormous advantages of water-based lubrication, it is rarely applied as a lubricant due to corrosive nature of water towards ferrous materials and also due its low pressure-coefficient of viscosity. Water at high contact pressures is immediately squeezed out of the contact area, promoting direct asperity-asperity contact and further resulting in significant friction in the boundary lubrication regime.

Nevertheless, lubrication in nature is exclusively achieved with water, which successfully resolves the above-mentioned limitations by employing brush- and/or gel-assisted aqueous lubrication. These heavily hydrated and compliant structures enable extraordinary tribological properties for an enduring time, e.g. in synovial joint lubrication. The water molecules themselves can contribute to the resulting friction by becoming incorporated into the brush-structured proteoglycan to provide a ‘fluid-like’ cushioning layer. Inspired by this approach, it is highly desirable to design and fabricate synthetic water-containing films with complex structures mimicking the natural lubrication mechanism, in an attempt to understand the relationship between film structure and tribological behavior, and potentially enabling the application of aqueous lubrication in relevant industries.

1.5 Scope of The Thesis

This thesis attempts to bridge from synthetic polymer chemistry to tribology, and describe the fabrication ultra-thin organic films with tailorable physical (structure) and chemical (composition) properties. Furthermore, it aims at understanding the structure-property relationships of surface-grafted polymeric architectures in aqueous environments.
First, synthesis and characterization of surface-grafted homogeneous polymer films with tunable crosslink degree and identical chemical composition are described. Second, swelling properties of these polymer films in water-methanol mixtures are studied in terms of different crosslink degrees and solvent quality. The implications of films’ crosslink degree for mechanical, adhesive and frictional properties are systematically discussed at the nanoscale. Third, polymer films with stratified structures are presented; the architecture and nanotribological properties are correlated accordingly. In particular, a new methodology is proposed to qualitatively probe the true structure of tiered poly(acrylamide) films, based on measuring the pull-off force of polymer films at the glass transition, as well as determining the frictional response in a good solvent. Last but not least, quasi-3D amplified polyelectrolyte assemblies are produced by adsorbing positively charged graft copolymers with high mass/charge ratio into surface-tethered weak polyacid brushes. The formation mechanism and structural characteristics of the resulting weak polyelectrolyte complex films are explored by means of various methods in an aqueous environment, which further promotes our understanding of the structure-property relationships of surface-grafted polymeric films.

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Chapter 2

Synthesis of Polymer Films and Characterization Techniques

2.1 Materials

\( p \)-(Chloromethyl)phenyltrimethoxysilane (95\%, ABCR, Germany), acrylamide (99+\%, Acros Organics), \( N,N \)-methylenebis(acrylamide) (>99.0\%, Fluka-Chemie AG, Switzerland), PLL(20k)-g(3.3)-PEG(5k) (SuSoS AG, Dübendorf, Switzerland), PLL(20k)-g(3.3)-PEG(2k)/TRITC (fluorescent red label, TRITC labeling approximately: 4\%, emission wavelength max: 625 nm) (SuSoS AG, Dübendorf, Switzerland), PLL(20k)-g(3.3)-PEG(2k)/FITC (fluorescent green label, FITC labeling approximately: 4\%, emission wavelength max: 514 nm) (SuSoS AG, Dübendorf, Switzerland), methanol (Fluka-Chemie AG, Switzerland), triethylamine (>99.5\%, Sigma-Aldrich, Germany), sulfuric acid (95-97\%, Sigma-Aldrich, Germany) and hydrogen peroxide (30 wt % in water, Merck, Germany) were used as received. Tetrahydrofuran (THF, 99.5\% extra dry, Acros, Germany) and toluene (>99.7\%, Fluka-Chemie AG, Switzerland) were freshly distilled over sodium prior to use. Sodium \( N,N \)-diethyldithiocarbamate (97\%, Fluka-Chemie AG, Switzerland) was recrystallized from methanol. Methacrylic acid (98\%, Fluka-Chemie AG, Switzerland) was first passed through an inhibitor-remover column (Sigma-Aldrich, Switzerland) and subsequently distilled under vacuum prior to use. Water was deionized with a GenPure filtration system (18.2 M\( \Omega \) cm, TKA, Switzerland). HEPES buffer used throughout this study was prepared by adding 1 mM 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid (HEPES, BioChemika Ultra, Fluka-Chemie AG, Switzerland) in Milli-Q water, and adjusting the solution pH to 7.4.

Water and methanol are miscible liquids in any ratio without phase separation. Densities of water and methanol at 20 °C are 1.0 g/cm\(^3\) and 0.8 g/cm\(^3\), respectively. Viscosities of
Water and methanol at 20 °C are 0.001 Pa s and 0.0006 Pa s, respectively. Refractive index of both water and methanol at 20 °C is 1.33.¹ Mixtures of Milli-Q water and methanol at the volume fractions of 0%, 25%, 50%, 75% and 100% were used in this thesis.

2.2 Synthesis of Polymer Films

2.2.1 Synthesis of Photoiniferter

The photoiniferter employed in this thesis was synthesized according to the procedure previously described by de Boer via the classical nucleophilic substitution reaction (Figure 2.1).² p-(Chloromethyl)phenyltrimethoxsilane (13.68 g, 55.4 mmol) and sodium N,N-diethyldithiocarbamate (9.48 g, 55.4 mmol) were dissolved separately in 50 mL of dry THF before the p-(chloromethyl)phenyltrimethoxsilane solution was added slowly to the dissolved N,N-diethyldithiocarbamate solution. After 3 hours of stirring at room temperature under Ar atmosphere, the solution was passed through a filter funnel in order to remove the white NaCl precipitate, and THF was evaporated under reduced pressure. The crude product was further purified by vacuum distillation (180 °C, 0.1 mbar); 4.80 g of a yellowish, viscous liquid was obtained (yield: 24.1%). The freshly synthesized photoiniferter was characterized by ¹H-NMR in order to confirm its purity and kept in a dark and cold place prior to use (Figure 2.2).

¹H-NMR (CDCl₃):  δ 7.61−7.40 (dd, 4H, C₆H₄), 4.55 (s, 2H, CH₂S), 4.05 (q, 2H, NCH₂), 3.71 (q, 2H, NCH₂), 3.61 (s, 9H, Si(OCH₃)₃), 1.25 (t, 6H, CH₃).

![Figure 2.1](image)

**Figure 2.1.** Synthesis of photoiniferter N,N-(diethylamino)dithiocarbamoylbenzyl(trimethoxy)silane (SBDC).
2.2.2 Fabrication of Photoiniferter-Modified Silicon Wafer

The formation of self-assembled monolayers of organosilicon molecules can be obtained by coupling the hydroxyl groups and the alkoxy silane groups via condensation reactions on various surfaces, e.g. glass, mica and metal oxides. The generation of silane SAMs is generally carried out in solution by carefully controlling adsorption conditions (temperature, pH and water concentration), otherwise, SAMs with three-dimensional structures will be produced, which leads to the unresolved coverage. The interfacial silanization normally involves several steps. First, the alkoxy groups undergo the hydrolysis reaction to silanols in the presence of water, which either comes from the surface-bound hydration layer or from the environment. Then, these silanol-bearing molecules diffuse onto the surface and form the hydrogen bonds with interfacial hydroxyl groups. Subsequently, condensation reactions happen at the interface and siloxane bonds form, followed by the liberation of water molecules. Finally, the lateral condensation of silanol groups takes place and generates the targeted silane SAMs.
In this study, the immobilization of photoiniferter (SBDC) on the surface was performed by placing the piranha-cleaned silicon wafer (P/B <100>, Si-Mat Silicon Wafers, Germany) into a freshly distilled toluene solution overnight with 5 mM SBDC and 2 drops of triethylamine (Figure 2.3). Piranha solution is prepared by slowly pouring 30% \( \text{H}_2\text{O}_2 \) into 70% \( \text{H}_2\text{SO}_4 \). This solution is very corrosive and extreme caution should be taken since it reacts violently with any organic materials.

![Figure 2.3. Silanization of photoiniferter on a silicon wafer.](image)

2.2.3 Synthesis of Surface-Grafted Homogeneous Poly(acrylamide) Films

For the synthesis of homogeneous poly(acrylamide) (PAAm) films with different crosslink degrees (Figure 2.4), prior to the polymerization, both the acrylamide (AAm) aqueous solution (AAm) (1 M) with a specific amount of crosslinker \( N,N\) -methylenebis(acrylamide) (bisAAm) (\( W_{\text{bisAAm}}:W_{\text{water}} = 0; 0.1; 0.5 \) and 1.0) and the flask containing SBDC-modified wafer were degassed/flushed with Ar for 15 minutes, and the degassed monomer solution was then transferred to the substrate-containing flask under an Ar atmosphere (the resulting polymer films are denoted as PAAm-0, PAAm-0.1, PAAm-0.5 and PAAm-1.0, respectively). The polymerization was started on the SBDC-modified substrate in an aqueous environment under the irradiation of the UVLED setup, which was built in-house and incorporated a LED (NCSU033A, NICHIA Corp., Japan) with a narrow emission spectrum at 365 ± 5 nm (Figure 2.5). The setup incorporated a 5 \( \Omega \) resistor in series with a fan. The use of the LED guarantees polymerization exclusively on the photoiniferter-modified substrate. An optimized irradiation distance (25 mm) was determined in order to maintain a uniform exposure over the entire substrate (20 mm × 20
mm). The operating voltage and current for the UVLED were fixed at 8.5 V and 0.5 A, respectively (Irradiation intensity: 5.5 mW/cm$^2$). The UV irradiation intensity was measured with a radiometer (UVX radiometer with UVX-36 sensor, UVP, Upland, CA, USA). After the polymerization, the polymer-film-bearing substrate was taken out of the flask and rinsed copiously with Milli-Q water, then immersed in water for 2 days, in order to remove any entangled or weakly bonded polymers from the surface before further characterization.

**Figure 2.4.** General scheme for fabrication of homogeneous PAAm films with different crosslink degrees by surface-initiated photoiniferter-mediated polymerization on a silicon wafer.
2.2.4 Synthesis of Surface-Grafted, Stratified Poly(acrylamide) Films

The stratified PAAm films were synthesized by reinitiating the substrate with pre-fabricated homogeneous PAAm thin films in a monomer (crosslinker) medium. For the synthesis of films with gel-brush structure, the substrate bearing PAAm-1 films was placed in a flask filled with degassed AAm aqueous solution (1 M) under an Ar atmosphere; then the UVLED irradiation was applied for a specific time, resulting the films with the targeted structure. In the case of the synthesis of the stratified brush-gel films, the substrate bearing with PAAm-0 films was placed in a flask filled with degassed water-methanol mixtures (volume fraction of methanol: 75%) under an Ar atmosphere (AAm: 1 M, \( W_{\text{bisAAm}}: W_{\text{solvents}} = 1.0\% \)); then the reinitiation was started by applying UV irradiation for a specific time, resulting the stratified brush-gel films. After the polymerization, these polymer-film-bearing substrates were rinsed copiously with Milli-Q water, immersed in water overnight, prior to further characterization.

2.2.5 Synthesis of Surface-Grafted Polyelectrolyte Complex Films

Surface-grafted PMAA brushes were first synthesized from silicon oxide substrates by UV-LED \textit{iniferter}-mediated surface-initiated polymerization (UVLED-SIP), before fabricating the PEC films. The detailed preparation procedure is identical to the above-mentioned synthesis of PAAm-0 brushes (section 2.2.3), with the substitution of methacrylic acid for acrylamide.
Subsequent fabrication of surface-grafted PEC films was carried out by dipping pre-wetted PMAA brush samples into a PLL-g-PEG solution with variable concentrations and different incubation times (Figure 2.6). Following the formation of PEC films, samples were extensively rinsed with Milli-Q water and further incubated in Milli-Q water overnight in order to remove the adsorbed polymer chains prior to characterization.

**Figure 2.6.** Fabrication of surface-grafted polyelectrolyte complex films through electrostatic interaction between two oppositely charged polyelectrolytes.

### 2.3 Characterization Techniques

#### 2.3.1 Variable Angle Spectroscopic Ellipsometry

Spectroscopic ellipsometry (SE) is an accurate and fast optical technique for measuring the dielectric properties, and indirectly the thickness of thin films; it has been used for a large number of fields due to its non-contact and non-destructive features. SE employs broad band light sources, which cover a certain spectral range in the infrared, visible or ultraviolet spectral region. By that the dielectric function tensor or complex refractive index in the corresponding spectral region can be obtained, which gives access to numerous physical properties. Figure 2.7 shows the representative experimental setup for ellipsometer. The incident light is polarized by passing through a polarizer and a
compensator in order to generate a known polarization state; then the polarized light is reflected from the sample surface, where both phase shift and amplitude change take place. Finally, the reflected light after passing through the other compensator is detected by an analyzer. The reflection spectrum is recorded at a specific angle; the amplitude ratio and the phase shift of the reflected light are the measured properties. By fitting the experimental data to a known theoretical model, the film thickness can be determined. For organic films, the Cauchy model is generally used to approximate optical constants and this model is also used throughout this thesis to model the optical constants of an iniferter-modified SAM layer and the whole polymer films.

In this thesis, the dry thickness of the surface-grafted polymer films was determined with a variable-angle spectroscopic ellipsometry (VASE®) (M-2000F, LOT Oriel GmbH, Darmstadt, Germany) in ambient environments with a relative humidity of 28.4%, at three different incidence angles (65°, 70°, 75°), under the assumption that the dry polymer has a refractive index of 1.45. The thickness was determined via the analysis of a four-layer model (software WVASE32, LOT Oriel GmbH, Darmstadt, Germany).

The swelling ratio of the surface-tethered PAAm films with varying crosslink degrees was measured in aqueous methanol mixtures at the chosen volume fractions by ellipsometry. The optical experiments were obtained using a Woollam variable angle spectroscopic ellipsometry (V-VASE®) system. Measurements were performed as a function of photon energy in the range 1.5 eV – 4.5 eV with a step size of 0.1 eV, which corresponds to a wavelength range of 275 nm – 827 nm. All measurements were performed in situ within a dedicated liquid cell. Optical access to the sample was achieved through two windows at a fixed angle of incidence (angle θ of 63°). A third window enabled alignment of the sample at normal incidence and allowed visual inspection of the sample during in situ experiments. The samples were immersed in the aqueous methanol mixture for at least 10 min prior to measurement, to ensure swelling equilibrium. The measured values of amplitude ratio upon reflection and phase shift were used to obtain the optical constants of the wet films with the standard WVASE 32 software package via the analysis of a four-layer model (J. A. Woollam Co.). A Cauchy model, \( n = A + B/\lambda^2 \), was used to describe the refractive index of the wet films by means
of two fitting parameters: offset \((A: 1.353 – 1.444)\) and wavelength dispersion \((B: 0.004 – 0.008)\); these parameters varied with respect to solvent quality and crosslink degree.

![Diagram of ellipsometer setup](image)

**Figure 2.7.** The representative experimental setup for ellipsometer.

### 2.3.2 Static Contact Angle

Contact-angle measurements quantify the wettability of a solid surface by a liquid, and also show how strongly the liquid and solid interact with each other, relative to how strongly each interacts with itself. The thermodynamic equilibrium of a liquid drop on a perfectly smooth solid surface is theoretically defined by Young’s equation (2.1). At equilibrium, the chemical potential in the three phases (vapor-liquid-solid) should be equal. As shown in Figure 2.8, the \(\gamma\) is the interfacial tension between two phases, i.e. solid (S), liquid (L) and gas (V) phase and \(\theta_c\) is the equilibrium contact angle, which is frequently determined by the sessile-drop method. A contact-angle goniometer (Ramé-Hart Instrument Co., Model-100, Netcong, NJ, USA) was employed to determine the static contact angles through the thesis, which consist of the angle that is enclosed by the surface and the liquid-gas phase tangent along the 3-phase line.

\[
\gamma_{sv} = \gamma_{sl} + \gamma_{lv} \times \cos \theta_c
\]  \hspace{1cm} (2.1)
where $\gamma_{sv}$, $\gamma_{sl}$ and $\gamma_{lv}$ are solid, solid/liquid interfacial and liquid surface free energy, respectively.

![Diagram of Young's equation](image)

**Figure 2.8.** The thermodynamic equilibrium status of a liquid drop on a perfectly smooth surface is described by Young’s equation.

2.3.3 Fourier-Transform Infrared Spectroscopy (FT-IR)

Fourier transform infrared spectroscopy (FT-IR) is a very sensitive and widely used quantitative technique for identifying and studying chemical compounds, e.g. stereochemistry, functional groups, molecular conformation and orientation. By passing infrared light through a sample, the light (10 cm$^{-1}$ - 4000 cm$^{-1}$) will interact with sample molecules. The molecule absorbs the infrared light at a particular wavelength, which induces molecular vibrations. The molecule must vary its electric dipole moment via stretching, bending or twisting of chemical bonds in order to absorb infrared light. The absorption can be detected at a specific wavelength that represents the specific bond in the molecule.

To measure the absorption spectrum of a thin polymer layer on a silicon surface, such as surface-grafted polymer films, infrared measurements can be carried out in transmission mode. The polymer films used in this study, as well as the film-bearing silicon substrate, are ideal surfaces for measuring with infrared transmission spectroscopy. FT-IR spectra were recorded on the dried samples by employing an infrared spectrometer (Bruker, IFS 66 V) equipped with a liquid-nitrogen-cooled MCT detector. A background spectrum is collected from a freshly cleaned, bare silicon wafer. For all FT-IR measurements, 32
scans were collected with 8 cm$^{-1}$ resolution. The collected interferograms were processed and baseline-corrected with a polynomial using the instrument software (OPUS, Bruker Optics, Germany).

2.3.4 Confocal Fluorescence Microscopy

The distribution of the fluorophore-labelled PLL-g-PEG in the PEC films has been investigated by means of confocal microscopy. z-stacks were acquired with a Zeiss LSM 780 equipped with a GaAsP detector and a LD C-Apochromat 40x/1.1 W Korr M27 objective. A DPSS 561 nm laser was used for TRITC excitation (red), and a 488 nm Argon laser line for FITC excitation (green). The pinhole was set to 10 µm and z-stacks acquired at an interval of 0.2 µm. Images were visualized and processed with Imaris (Version 7.5.2, Bitplane). Mean fluorescence intensities were determined using ImageJ software (National Institutes of Health, USA).

2.3.5 Atomic Force Microscopy (AFM)

Atomic force microscopy (AFM) is an important technique for imaging both conducting and non-conducting solid surfaces, and belongs to the scanning probe microscopy (SPM) family. Nowadays, the versatility of AFM not only allows high-resolution imaging in different media, but also offers capabilities for other surface measurements, e.g. nanoindentation and nanotribometry. The general setup of an AFM can be seen in Figure 2.9 (a). A cantilever keeps scanning the sample surface with a constant tip deflection (contact mode) or a constant oscillation amplitude (tapping mode); the deflection of the cantilever is detected by the reflection of a laser beam, detected by a position-sensitive photodiode (PSD). The PSD allows for the examination of the normal deflection and lateral deflection signals, as shown in Figure 2.9 (b). After processing these position signals and comparing them with the preset values, the feedback electronics further send the command to the piezo-electric scanner, which moves the cantilever accordingly in order to offset the cantilever height and maintain the original deflection (amplitude). By mapping these offset values along the scanning lines, a surface topographic image is produced.
In this thesis, the morphologies of polymer films in dry states were measured by a Dimension AFM with a NanoScope IIIa controller (Digital Instruments, Santa Barbara CA) in Tapping Mode™ with a silicon cantilever (Olympus, Japan) presenting a resonant frequency of 300 kHz and a spring constant of 26.1 N/m, which are the values from the manufacturer.

Morphologies of polymer films in aqueous methanol solutions were obtained by imaging samples in a closed liquid cell with a Cypher™ AFM (Asylum research, Santa Barbara, USA). A triangular-shaped cantilever with a silicon nitride tip (spring constant: 0.32 N/m, model: DNP-S, Veeco, USA) was used for imaging in fluid AC mode to acquire height and phase images over the scanning area (5 µm × 5 µm).

2.3.6 Colloidal Probe Microscopy (CPM)

In contrast to the conventional AFM cantilever configuration, colloidal-probe microscopy utilizes a colloidal particle instead of a sharp tip during measurement, which further expands the functionality of AFM in tribology. The colloidal probe can also be used as a nanoindenter, in order to study the interfacial mechanical properties; furthermore, it significantly increases the contact area during friction measurement, avoiding the severe wear issues that are potentially inherent in the use of a traditional sharp tip.
The apparent elastic moduli of polymer films in water can be estimated from nanoindentation approaching force curves using the Hertz model, and assuming the contact between a sphere and an elastic plane (in case no adhesion is observed):

\[ F = \frac{4}{3} \sqrt{\frac{r_{tip}}{1-v^2}} \times E \times \delta^{3/2} \]  

(2.2)

\[ F = k \times d \]  

(2.3)

\[ \delta = z - d \]  

(2.4)

where \( F \) is the applied load, \( r_{tip} \) is the radius of the colloidal probe, \( v \) is the Poisson’s ratio of the polymer films (assumed to be 0.5), \( E \) the apparent Young’s modulus of polymer films, \( \delta \) is the deformation of the polymer films (calculated from the relative piezo-extension \( z \) and relative deflection of the cantilever \( d \)), and \( k \) is the spring constant of the cantilever. A constant applied force with a specific indenting speed is employed during indentation measurements. The initial 10% of the approach curve (Figure 2.10) is used to measure the Young’s modulus of the polymer films in order to avoid any substrate effect on the measured values. By fitting the force curves acquired during normal-force measurements into Equations (2.2), (2.3) and (2.4), one can obtain the apparent Young’s modulus \( E \) of polymer films in water.

![Figure 2.10. Representative AFM approach curve during a nanoindentation test.](image)
As mentioned above, CPM is also a useful tool for the study of friction at the nanoscale. By rubbing the colloidal sphere against polymer films in aqueous environments, one can obtain comprehensive nanotribological information. However, it is necessary to carry out calibration for applied load and friction force prior to the measurements, in order to convert the photodiode output voltage (V) into force (N).

For the calibration of normal force, the equation (2.5) can be used:

\[ F_N = \frac{K_N}{S_N} \times \Delta V_N \]  

(2.5)

where \( F_N \) (N) is the calibrated normal force, \( K_N \) (N/m) is the cantilever normal spring constant, acquired by thermal-noise tuning function integrated in AFM, \( S_N \) (V/m) is the normal deflection sensitivity of the cantilever, obtained by the slope of deflection-displacement curve upon pressing the colloidal probe against a hard wall (silicon substrate), \( \Delta V_N \) (V) is the measured normal voltage signals.

For the calibration of lateral force, the equation (2.6) should be applied:

\[ F_L = \frac{K_L}{S_L} \times \Delta V_L \]  

(2.6)

where \( F_L \) (N) is the calibrated lateral force, \( K_L \) (N/m) is the cantilever lateral spring constant, acquired by the following equations:

\[ K_L = \frac{K_\phi}{h^2} \times \frac{L}{L'} \]  

(2.7)

\[ K_\phi = 0.1592 \times \rho \times b^4 \times L \times Q \times \omega_i^2 \times \Gamma_i(\omega_i) \]  

(2.8)

where \( K_\phi \) is the torsional spring constant of the cantilever, which can be calculated by equation (2.8), \( h \) is the torsional arm length (diameter of the colloid probe + thickness of the cantilever), \( L' \) is length between the cantilever’s fixed end and the laser spot, \( \rho \) is the
fluid density, $b$ and $L$ are width and length of the cantilever, respectively, $Q_i$ is the quality factor of the fundamental resonance peak of torsional vibration in fluid and $\omega_i$ is the resonant frequency, $\Gamma_i(\omega_i)$ is a hydrodynamic function.

$S_L (\text{V/m})$ is the lateral-deflection sensitivity of the cantilever, obtained by the slope of deflection-displacement curve upon laterally hitting the colloidal sphere against a vertical sidewall (silicon wall), $\Delta V_L (\text{V})$ is the measured lateral voltage signals.

In this thesis, CPM was used in order to guarantee that the nanotribological measurements were in the boundary-lubrication regime. Normal force and friction measurements between a silica microsphere and polymer films under liquid were carried out with an AFM (MFP3DTM, Asylum Research, Santa Barbara, USA) in a liquid cell. The normal spring constant of the Au-coated tipless cantilever (NSC-12, Mikromash, Estonia) was measured by the thermal-noise method and the torsional spring constant was measured according to Sader’s method. Both normal and torsional spring constants of the cantilever were measured before attaching the colloidal microsphere. A silica microparticle (EKA chemicals AB, Kromasil®) was glued with UV-curable glue (Norland optical adhesive 63) to the end of the tipless cantilever by means of a home-built micromanipulator, to be further used for colloidal probe microscopy. In the case of fabricating a gold-coated colloidal probe, the well-attached silica probe was further coated with 2 nm of chromium and 10 nm of gold using an evaporator (MED020 coating system, BAL-TEC, Balzers, Lichtenstein). The lateral-force calibration was carried out by employing the ‘test-probe method’. To determine the lateral sensitivity of the photo detector, a freshly cleaned silicon wafer (1cm × 1cm) was glued ‘edge-on’ to a glass slide. A smooth silicon plane was used as a ‘wall’ for measuring the lateral sensitivity. A test probe (cantilever glued with a silica colloidal sphere of diameter around 40 µm) was moved laterally into contact with the silicon wall without interacting with the glass surface below. The slope of the obtained lateral-deflection-vs-piezo-displacement curve yields the lateral sensitivity used for lateral-force calibration.
For lateral-force measurements, 10 ‘friction loops’ along the same line were acquired at each load in solutions (scanning rate: 1.0 Hz, stroke length: 5.0 μm), from which the average friction force and the standard deviation were calculated.

To characterize the adhesion force, 36 force curves were acquired in solutions over an area of 20 μm × 20 μm. Adhesion histograms were generated from the results and fitted with a Gaussian distribution; the mean and standard deviation of the pull-off forces were calculated accordingly. Both adhesion and friction measurements were repeated at three different locations on the polymeric films.

2.3.7 Nano/Micro-Tribometer

The nano/micro tribometer is the optimal instrument for studying the friction and wear behavior of soft materials (e.g. polymers, gels or biological tissues), with or without lubricant. It allows the coefficient of friction to be directly measured during sliding contact between two interacting surfaces in relative motion, as well as studying the materials lost during the stability test.

The tribometer relies upon the perpendicular deflection of a two-legged cantilever to set the normal force and simultaneously determine the friction force. By using optical fibers or capacitive sensors, differences in the distance between the sensors and the cantilever are detected. Changes in the normal/lateral distances are multiplied by the normal/lateral spring constants of the cantilever and converted into force (Figure 2.11). By varying the load, sliding speed and moduli of pin materials, one can tailor the tribological conditions to a large extent.

In this work, friction tests were performed by using an optical-fiber-based microtribometer (BASALT MUST, Tetra GmbH, Germany), equipped with a stainless-steel cantilever, to which an oxidized PDMS counter-surface was attached. The PDMS elastomer counter surfaces were fabricated by mixing a two-part liquid component silicone kit (Sylgard 184, Dow Corning Corp., Midland, MI) (the weight ratio of base and the curing agent of SYLGARD 184 is 10:1) according to the instruction manual of the
manufacturer and molding in a commercial polystyrene culture cell plate with spherically curved wells (radius = 3 mm, 96 MicroWell Plates, NUNCLON Delta Surface, Denmark). The PDMS counter surfaces were extracted in n-hexane to remove unreacted monomer and afterward plasma treated for 30 s (Harrick plasma cleaner/sterilizer, Ossining, NY) immediately prior to further use. The cantilever attached to the counter surface had a normal force constant of 14.721 N/m and a tangential force constant of 14.752 N/m. Microtribological measurements of polymer films were carried out in HEPES buffer with a sliding speed of 0.1 mm/s and a stroke length of 1 mm. Friction force was acquired from the friction loops under varying loads (0.5–3.0 mN) and the coefficient of friction calculated according to the slope of the friction force–applied load plot. Each measurement was carried out over two cycles.

The capacitive sensors based nanotribometer (NTR2, CSM Instruments, Switzerland) was utilized to study the tribological stability of the surface-grafted polymer films with different crosslink degrees. The cantilever employed here has a normal force constant of 0.5776 mN/μm and a tangential force constant of 1.2088 mN/μm as specified by the manufacturer. The coefficient of friction (μ) for these polymer films was recorded in Milli-Q water by periodically sliding against a counter surface in reciprocating motion (maximum speed: 1 mm/s, sinusoidal) under constant loads (2 mN). The sliding counter surface was a spherical glass pin (Young’s modulus = 80 GPa) with a diameter of 2 mm. The polymer films after tribological tests were rinsed with abundant Milli-Q water and their optical images obtained in situ with an optical microscope built into the nanotribometer (Olympus, M Plan N, 5X).
Figure 2.11. Schematic representation of nano/micro-tribometer.

2.4 References

Chapter 3*

Interfacial Properties of Surface-Grafted Homogeneous Poly(acrylamide) Films

Poly(acrylamide) (PAAm) films with different crosslink degrees were fabricated from *initiater*-functionalized silicon substrates by UVLED-initiated photopolymerization and their properties subsequently studied by means of a variety of analytical methods. The employed photografting method allowed the controlled fabrication of very thick films (up to 1 micron) in an aqueous environment, over a period of less than one hour of polymerization and in the absence of side reactions. Covalently crosslinked PAAm films were prepared by feeding trace amounts of the crosslinker bis-acrylamide (up to 1.0 weight% of monomer solution) into the reaction vessel. Both bulk and interfacial properties of these polymer films were found to be strongly influenced by lateral crosslinking of the grafted polymer chains. In agreement with theoretical expectations, the decrease of brush conformational freedom with increasing crosslink density resulted in a substantial increase of film wettability with water. The swelling ratio of covalently crosslinked PAAm brushes, as measured by ellipsometry and atomic force microscopy (AFM), also confirmed the formation of grafted networks and was found to be directly related to the amount of crosslinker in the monomer feed. In addition, the Young’s moduli and tribological properties of PAAm films with different crosslink degrees were tuned by adjusting the crosslinker concentration. Due to the additional constraint given by the surface grafting of each chain end, intermolecular crosslinking generated very high mechanical stresses within the brush structure. Covalently crosslinked brushes thus


The major part of this work was done by Ang Li, including all experiments and writing of the manuscript. Davide Tranchida conducted nanoindentation experiment. Edmondo M. Benetti, Jarred N. Clasohm, Holger Schönherr and Nicholas D. Spencer contributed in discussions and further correcting the paper.
displayed higher moduli and coefficients of friction, when compared to the grafted brush analogues. These films present an opportunity for readily tailoring physical properties, especially as they allow tuning of the physical characteristics of surfaces while maintaining the interfacial chemical composition nearly constant.

### 3.1 Introduction

As was introduced in the previous chapter, research focusing on the fabrication of functional polymer brushes for the modification of surfaces has been increasing substantially over the last decade. The unique characteristics of these films, such as the high polymer grafting density and tunable physicochemical properties have allowed them to be extensively applied in drug-delivery systems, sensors, antibiofouling surfaces, microfluidic devices and lubricant films.

A novel class of hydrogel films is represented by surface-grafted polymer networks (polymer gels or covalently crosslinked brushes), which not only possess some of the characteristics of polymer brushes, but also tunable swelling and mechanical properties. Crosslinked polymer brushes were previously prepared either in situ, by surface-initiated polymerization in the presence of crosslinker or, ex situ, by post-modification of pre-synthesized polymer brushes. These polymer films were subsequently employed as nanoreactors for the controlled synthesis of metal nanoparticles, as coatings for electrophoresis or to fabricate quasi-2D polymer objects. However, none of the previous studies demonstrated a systematic influence of the crosslink degree on interfacial and bulk characteristics of prepared polymer films.

Hydrogel films covalently grafted on surfaces with variable thicknesses and presenting tunable properties show great promise as versatile coating materials. The precise tailoring of interfacial, mechanical and tribological properties of films that are otherwise chemically analogous would be a highly desirable asset in the design of novel systems for surface functionalization.
Following this fundamental objective, we report here on the fabrication and characterization of poly(acrylamide) (PAAm) covalently crosslinked films. These polymer films were prepared by the already introduced UVLED surface-initiated, *iniferter*-mediated photopolymerization (UVLED-SIMP) on silicon surfaces. PAAm films with different crosslink degrees were synthesized by varying the concentration of crosslinker in the polymerization solution. UVLED-SIMP, which was recently reported by us\(^{21}\) as a modification of the well-known *iniferter*-based photografting method,\(^{22,23}\) enabled controlled grafting of polymers exclusively from precursor-modified surfaces. The narrow UVLED emission spectrum, centered at 365 nm, which does not overlap with the monomer absorption band,\(^{24}\) ensured selective activation/deactivation of the dithiocarbamate moieties immobilized on the surface and the avoidance of monomer auto-initiation in the aqueous solution.

*Iniferter*-based photopolymerization has already been reported as a very effective and versatile surface-initiated polymerization approach to the fabrication of polymer films with well-defined micro-architectures.\(^{25}\) In this chapter, we report on UVLED-SIMP applied to acrylamide monomers, which are known to be difficult in atom transfer radical polymerization (ATRP).\(^{26,27}\) UVLED-SIMP showed a quasi-living character for the polymerization of PAAm films, and was performed under mild conditions and for short periods of irradiation.

The chemical composition of the synthesized PAAm films was investigated by Fourier transform infrared (FT-IR) spectroscopy, and confirmed a direct correlation between the amount of crosslinker in the feed and the properties of the resulting covalently crosslinked brush layer.

The bulk and interfacial properties of the prepared films were investigated by a variety of methods, in order to determine the influence of crosslinking within the brushes. Static water contact angle measurements (CA), atomic force microscopy (AFM) and ellipsometry were performed to estimate wettability, Young’s modulus \((E)\) and swelling ratio \((Q)\), respectively, of the grafted PAAm films. Microtribometry was also employed, in order to investigate the tribological properties of the films at the micro scale and the
influence of lateral crosslinking of polymer chains on the films’ lubricating behavior in an aqueous environment.

Analysis of the results showed a substantial influence of crosslinking on the properties of the grafted films. A stiffening of PAAm films due to intermolecular network formation was enhanced by the mechanical stress induced by the surface attachment of each polymer chain. Additionally, the reduced chain conformational freedom within covalently crosslinked hydrogel films—when compared to freely grafted brushes—altered the molecular behavior controlling wettability and friction properties.\textsuperscript{11,29,30}

Covalently crosslinked PAAm brushes were shown to be versatile and chemically stable polymeric films with highly tunable properties at a nearly constant chemical composition.

### 3.2 Results and Discussion

3.2.1 Synthesis and Characterization of Surface-Grafted Homogeneous PAAm Films

PAAm brushes and covalently crosslinked brushes were synthesized by means of UVLED-SIMP initiated by self-assembled monolayers (SAMs) of \textit{iniferter}-bearing silanes on oxidized silicon surfaces. Following the incubation of \((N,N-\text{(diethylamino)dithiocarbamoylbenzyl-}(\text{trimethoxy})\text{silane})\) in a 5 mM freshly distilled toluene solution for 24 hours, the formation of uniform SAMs of photoiniferter was confirmed by static water-contact-angle measurements (CA) and ellipsometry. CA values showed an increase from less than 5°, typical for oxidized silicon substrates, to 70 ± 2° after incubation in SBDC solutions. This finding is consistent with the formation of dithiocarbamate-bearing SAMs, as has previously been reported in the literature.\textsuperscript{31} In addition, the presence of an organic thin layer with average thickness of 1.1 ± 0.1 nm was confirmed by ellipsometry, also consistent with the formation of uniform SBDC-SAMs.

Surface-Initiated \textit{Photoiniferter}-Mediated Polymerization (SI-PIMP) has been reported as a successful approach for the controlled grafting of a wide variety of monomers at ambient temperature and in aqueous media.\textsuperscript{23,32,33} The mild conditions required for this polymerization technique and the fast growth rates have made SI-PIMP attractive. SI-
PIMP is sometimes preferable to ATRP, which has been shown to be less controllable in aqueous environments for the polymerization of acrylamide and often requires high reaction temperatures with the employment of toxic organic solvents.

In this work, acrylamide (AAm) and \( N,N \)-methylenebis(acrylamide) (bisAAm) mixtures were photografted from SBDC-SAMs employing a UVLED illumination setup with a narrow emission wavelength (maximum intensity at 365 nm). We recently reported the SIMP of methacrylic acid by UVLED.\(^{21}\) The very narrow emission spectrum of this source assured the absence of side-reactions, such as auto-initiation of the monomer, in the polymerization solution. This last phenomenon was recently reported to limit the maximum film thickness achievable during SIMP and caused gelation of polymerization medium after long irradiation times. The absence of self-initiation also reduces radical recombination and thus UVLED-SIMP shows faster film-growth rates when compared to systems employing UV sources with broader emission spectra.\(^{34}\)

The film-growth rates for PAAm brushes and covalently crosslinked brushes grafted by UVLED-SIMP were investigated by \textit{ex situ} ellipsometry after drying. In Figure 3.1, the dry thickness of PAAm films is plotted as a function of irradiation time. Different bisAAm feed concentrations were used for the polymerization: 0\%, 0.1\%, 0.5\% and 1.0\%, film samples being denoted as PAAm-0, PAAm-0.1, PAAm-0.5 and PAAm-1.0, respectively. For all feed concentrations studied, very thick films ranging from 400 to 800 nm could be obtained within 30 minutes of irradiation. In all cases, the film growth rates followed a linear trend while the addition of bisAAm in the feed solutions led to an increase in the polymerization rates.

Linear film-growth rates confirmed the quasi-living character of UVLED-SIMP, which has been previously observed for \textit{initiator}-mediated polymerization.\(^{31}\) According to Metters et al,\(^{35}\) who studied the kinetics of SIMP in the case of methyl methacrylate, film-growth rates were proportional to the propagation rate constant, the monomer concentration and the local concentration of surface-attached macro-radicals. The linear trends observed for UVLED-SIMP of AAm/bisAAm systems thus implied negligible termination and chain-transfer reactions during the studied time period. Since the
concentration of both monomer and growing radicals (upon fixing irradiation intensity) could be considered to be constant during polymerization, the faster film-growth kinetics upon addition of bisAAM are ascribed to a higher reactivity of the crosslinker, in comparison to acrylamide.\textsuperscript{36}

![Figure 3.1](image)

**Figure 3.1.** Growth kinetics of PAAm films with different crosslink degrees. Trends of polymer growth were obtained by linear least squares fitting. Crosslinker concentration in the feed was varied from 0\% to 1.0\%.

Monomer-concentration-dependent kinetics was also studied, as shown in Figure 3.2. Upon increasing the monomer concentration during SIMP, the film thickness increases while maintaining constant irradiation intensity and polymerization time. However, when the monomer concentration was too high (≥ 2 M), polymerization in solution was observed. In this case the high concentration of polymerizable species facilitates the chain transfer to monomer thus causing formation of polymer in solution. In contrast, when the monomer concentration was too low during SIMP, termination due to loss of radicals by bimolecular termination becomes more prevalent, as studied by Metters.\textsuperscript{35}
Figure 3.2. Dry thickness of PAAm films as a function of monomer concentration at a constant irradiation intensity of 5.5 mW/cm² and a constant polymerization time of 10 min.

UV-intensity-dependent kinetics were studied, in order to further understand the termination mechanism involved in UVLED-SIMP. The decomposition of the photoinifertor function generates a surface-tethered carbon radical and a dithiocarbamyl radical in solution. The dithiocarbamyl radical can recombine with the surface-tethered radical to form the dormant species, which can then be reinitiated as part of the living-radical photopolymerization mechanism (Figure 1.11). By performing a mass balance on the surface-tethered radicals (STR) and dithiocarbamyl radicals, assuming pseudo-steady state for the surface-tethered radical concentration, we can obtain the scaling relation:}

$$[STR]_0 \propto I_0^{0.5}$$

(3.1)

This equation indicates that all surface-tethered photoinifertors cannot be initiated and the concentration of generated STR prior to any irreversible termination events scales with the square root of the irradiation intensity. According to theoretical predictions, for a fixed polymerization time and monomer concentration, the thickness of polymer films
plateaus at high irradiation intensity if bimolecular termination is the prevailing termination mechanism. However, the chain-transfer model predicts a continuous increase in the layer thickness as intensity is increased and exposure time is held constant.

According to our experimental results shown in Figure 3.3, the thickness of polymer films becomes less dependent on irradiation intensity at high irradiation intensities, which is presumably caused by the bimolecular termination owing to a large number of generated radicals, gradually approaching to the saturated value. In contrast, the chain transfer to monomer overwhelms bimolecular termination when the UV irradiation intensity is low (< 5 mW/cm²). The influence of UV intensity on polymer layer growth in our case is similar to that reported by Metters.\textsuperscript{35}

![Graph showing dry thickness (T) of PAAm-0.5 films as a function of irradiation intensity (I₀) at a constant monomer concentration (1 M) and a constant polymerization time of 10 min. Solid fitting line denotes the scaling relation: T ∝ I₀^{0.5}.](image)

**Figure 3.3.** Dry thickness (T) of PAAm-0.5 films as a function of irradiation intensity (I₀) at a constant monomer concentration (1 M) and a constant polymerization time of 10 min. Solid fitting line denotes the scaling relation: $T \propto I_0^{0.5}$.

FT-IR analysis of PAAm brushes and covalently crosslinked brushes was performed in order to determine the chemical composition of the films upon variation of AAm/bisAAm feed ratios. The FT-IR spectra profiles displayed in Figure 3.4, (a) – (d) for PAAm brushes and covalently crosslinked brushes with 0.1, 0.5 and 1.0% of feed
bisAAm respectively, were found to be very similar in all cases. The strong bands at 3338 and 3200 cm\(^{-1}\) were related to N–H asymmetric and symmetric stretching of the NH\(_2\) repeat unit, respectively. The FT-IR signals between 1560 and 1760 cm\(^{-1}\) after Lorentz fitting were assigned to amide I and amide II as shown in Figure 3.5. The amide I bands from both monomer and crosslinker were found at 1655, 1672, 1688 cm\(^{-1}\), and the amide II band from the monomer was found at 1609 cm\(^{-1}\).\(^{37,38}\)

**Figure 3.4.** FT-IR spectra of dried PAAm brushes and covalently crosslinked brushes with varying amount of feed crosslinker. (a) PAAm-0, (b) PAAm-0.1, (c) PAAm-0.5, (d) PAAm-1.0. Dry thicknesses for PAAm-0, PAAm-0.1, PAAm-0.5 and PAAm-1.0 are 150 nm, 100 nm, 260 nm and 250 nm respectively.
Figure 3.5. FT-IR spectra of dried PAAm brushes and covalently crosslinked brushes with varying amount of feed crosslinker after Lorentz fitting. (a) PAAm-0, (b) PAAm-0.1, (c) PAAm-0.5, (d) PAAm-1.0. Dry thicknesses for PAAm-0, PAAm-0.1, PAAm-0.5 and PAAm-1.0 are 150 nm, 100 nm, 260 nm and 250 nm, respectively.

Besides the characteristic absorption peaks of PAAm, addition of bisAAm in the feed with consequent crosslinking of the brushes was revealed by the appearance of a small absorption peak at $1520 \text{ cm}^{-1}$, which corresponds to the N–H bending (amide II band) of secondary amide in the crosslinker. The intensity of this peak increased with the relative concentration of bisAAm in the films. In order to estimate the crosslinker content inside the films with respect to the corresponding concentration in the feeds, the area of the $1520 \text{ cm}^{-1}$ peak was compared to the areas of the signals between $1560$ and $1760 \text{ cm}^{-1}$. The ratio of integral area of amide II of crosslinker to the sum of the integral area of amide I and II bands of monomer and crosslinker was used to obtain a calibration master curve, which finally allowed extrapolation of the relative content of bisAAm in the films. For each feed concentration, the corresponding bisAAm content in the brush films was thus derived.

In order to determine the absolute crosslinker content in surface-grafted hydrogel films, a calibration curve was made based on the spectral ratios of a series of AAm/bisAAm
mixtures with varying percentages of bisAAm. Spectral ratio is defined as the ratio of the integral area of amide II of crosslinker to the sum integral area of amide I of both monomer and crosslinker and amide II of monomer in the IR spectrum (wavenumber between 1560 and 1760 cm\(^{-1}\)).

\[
\text{Spectral Ratio} = \frac{A_{\text{amide II, crosslinker}}}{A_{\text{amide I, monomer}} + A_{\text{amide I, crosslinker}} + A_{\text{amide II, monomer}}} \quad (3.2)
\]

The IR spectra of AAm/bisAAm/KBr mixtures with varying bisAAm percentages were collected and their spectral ratios plotted against the crosslinker percentage in the mixture (Figure 3.6).

![Graph showing spectral ratio vs. calibration mixture (bisAAm mol%)](image)

**Figure 3.6.** Spectral ratio of AAm/bisAAm mixtures with varying bisAAm percentages. The spectral ratios of PAAm brushes and covalently crosslinked brushes with varying feed amounts of crosslinker were acquired by integration of their corresponding FT-IR spectra, then the actual crosslinker content in the polymer films was calculated accordingly.

As expected, due to the higher reactivity of bisAAm, compared to AAm, a preferred incorporation of crosslinker in the films was found in all cases as seen in Figure 3.7. The
bisAAm content varied linearly from 0.36 to 4.8% for feed bisAAm concentrations ranging from 0.1 to 1.0%.

![Graph showing the relationship between crosslinker content in films and the feed crosslinker content.](image)

**Figure 3.7.** Relationship between crosslinker content in films and the feed crosslinker content.

It could be concluded that due to the similar chemical structures of AAm and bisAAm, the crosslink degree of PAAm hydrogel thin films could be tuned without significantly changing the overall chemical composition.

### 3.2.2 Interfacial Properties of Covalently Crosslinked PAAm Hydrogel Films

Variation of the crosslink degree in surface-grafted PAAm films was expected to strongly influence the interfacial and bulk properties of the fabricated films. AFM and static water contact angle (CA) analyses were performed, revealing changes in morphology and wettability, respectively, as a function of crosslink degree.

Surface morphologies of PAAm brushes and covalently crosslinked brushes with varying amounts of crosslinking were determined by tapping-mode AFM in the dry state. PAAm brush surfaces showed a uniformly smooth morphology and presented an average RMS roughness of 0.4 nm (calculated over an area of 5 µm × 5 µm, Figure 3.8 (a)). The addition of crosslinker led to a clear roughening of the dry film surface, presumably due
to spatial variations in crosslink density during polymerization, leading to clustering of the growing chains. Similar clustering effects have been observed upon crosslinking in cast films. The roughness of PAAm-0.1 brush films reached 0.7 nm while in the cases of PAAm-0.5 and PAAm-1.0, values of RMS roughness of 3.2 and 5.7 nm, respectively, were found.

![AFM images of PAAm brushes and crosslinked brushes](image)

**Figure 3.8.** AFM images of dried PAAm brushes and covalently crosslinked brushes with varying amounts of feed crosslinker. (a) PAAm-0, (b) PAAm-0.1, (c) PAAm-0.5, (d) PAAm-1.0. (a) and (b) share the same height-scale bar (0 – 20 nm); (c) and (d) share the same height-scale bar (0 – 50 nm).

In order to qualitatively confirm the crosslinking behavior, surface-grafted PAAm-0 brushes and PAAm-1.0 gels were separated from silicon substrate by immersing them in HF aqueous solution (48%) for 5 min. Being a selective etching chemical for SiO₂, HF can efficiently detach the whole PAAm films from the silicon wafer. As shown in Figure 3.9 (a), there are no visible films after HF etching of PAAm-0 brushes. However, freestanding hydrogel films with thicknesses of a few hundred nanometers were observed after HF etching of PAAm-1.0 gels as shown in Figure 3.9 (b). The structures of PAAm
films with different crosslink degrees at the nanoscale essentially determine their macroscopic properties.

![Optical images of PAAm films on silicon substrate](image)

**Figure 3.9.** Optical images of PAAm films on silicon substrate (1 cm × 1 cm) after 5 min HF etching. (a) PAAm-0, dry thickness: 106 nm, (b) PAAm-1.0, dry thickness: 115 nm.

In addition to the effects on the surface morphology, the increase of crosslinking also strongly influenced the wettability of the resulting polymer films. Surfaces modified with polymer brushes usually show finite contact-angle values, even when wetted by good solvents. This phenomenon has been reported as being due to a ‘bridging effect’ of the grafted polymer chains at the solvent-vapor interface, which generates partial wetting and non-zero surface pressure. The lateral crosslinking of surface-grafted chains is assumed to strongly hinder chain conformational freedom, thus inhibiting the bridging effect and causing an increase in wettability.

By varying the crosslinker concentration in the feed from 0.1 to 1.0% (Figure 3.10) and monitoring the CA values of the covalently crosslinked PAAm films formed, the breaking of the ‘bridging effect’ could be studied. Uncrosslinked PAAm brushes showed a CA of 22°, while addition of crosslinker led to a continuous decrease of CA to, for a bisAAm concentration in the feed of > 0.6%, below 5°. Thus, ‘bridging effects’ by grafted polymer chains were found to be completely absent above a certain bisAAm content in the films (approximately 2.8 mol%) and the covalently crosslinked brush surfaces showed greatly increased wettability compared to freely grafted brush films. For bisAAm feed concentrations in the range 0 – 0.6% the surface wettability was precisely tunable as a function of the crosslink degree (and thus conformational freedom of brushes)
in the prepared films. To our best knowledge, this study first experimentally showed the breaking of ‘bridging effect’ by covalently crosslinking the polymer brushes.

![Figure 3.10](image)

**Figure 3.10.** Static contact angles of dried PAAm brushes and covalently crosslinked brushes with varying amounts of feed crosslinker. Sessile drops on three different surfaces shown in inset: (a) PAAm-0, dry thickness: 128 nm with 0% feed crosslinker, (b) PAAm-0.3, dry thickness: 181.9 nm with 0.3% feed crosslinker, (c) PAAm-1.0, dry thickness: 146.1 nm with 1.0% feed crosslinker.

It is well known that the wetting of solid surfaces is influenced by the roughness; however, in this study the decrease of the contact angle cannot be caused by such a small increase of surface roughness (0.4 nm – 5.7 nm) according to the prediction of Wenzel equation:

\[
\cos \theta^* = r \times \cos \theta
\]  

(3.3)

where \( \theta^* \): apparent contact angle, \( \theta \): Young contact angle, \( r \): roughness ratio.

The surface area and projected surface area of grafted PAAm films with varying crosslink degrees were acquired by using Veeco software (Nanoscope Version 5.12), and the roughness ratios were calculated by the same software. According to the apparent
contact angle (22.0°) and the roughness ratio (1.00084) of the PAAm-0, the apparent contact angle (21.1°) of the PAAm-1.0 covalently crosslinked brushes is obtained by using Wenzel’s mode (roughness ratio of PAAm-1.0: 1.00736). However, the variation of the contact angle (> 20.0°) by increasing the crosslink degree of the films in this study cannot be justified by such a small change of contact angle (< 1.0°) according to the Wenzel’s mode, hence it is believed that the decrease of contact angle is mainly due to the breaking of the ‘bridging effect’.

<table>
<thead>
<tr>
<th></th>
<th>Surface Area (μm²)</th>
<th>Projected Surface Area (μm²)</th>
<th>Roughness Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAAm-0</td>
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<td>25</td>
<td>1.00084</td>
</tr>
<tr>
<td>PAAm-0.1</td>
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<td>25</td>
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</tr>
<tr>
<td>PAAm-0.5</td>
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<td>25</td>
<td>1.00068</td>
</tr>
<tr>
<td>PAAm-1.0</td>
<td>25.184</td>
<td>25</td>
<td>1.00736</td>
</tr>
</tbody>
</table>

**Table 3.1.** Roughness ratios of PAAm brushes and covalently crosslinked brushes with varying amount of feed crosslinker.

3.2.3 Mechanical and Swelling Properties of Covalently Crosslinked PAAm Films

In order to study how the mechanical and swelling properties of PAAm films with different crosslink degrees were influenced by the lateral crosslinking of grafted chains, AFM-based nanoindentation was employed.\(^{42,43}\) As shown in Figure 3.11, PAAm brush films immersed in buffer solution were indented by an AFM tip and the characteristic load-penetration depth profiles were recorded for all samples. PAAm brushes and covalently crosslinked brushes presenting similar dry thicknesses (around 35 nm measured by ellipsometry) showed markedly different load-penetration curves, due to the different degrees of swelling for films with different levels of crosslinking. From these profiles, the hydrated thicknesses of PAAm films could be measured as a depth difference between the tip-brush contact point (the distance at which the measured force first rises above the baseline) and the region where the underlying substrate was sensed upon further compression (as indicted by a the pronounced increase of the slope of the applied load against penetration depth, since the AFM tip cannot indent the stiff silicon
substrate). Since the dry films were shown in independent measurements to possess elastic moduli of ~10 GPa, the compressed (dehydrated) films may have been too stiff to be indented at large penetration depths, thus leading to an underestimate of film thickness and swelling ratio (vide infra). PAAm-0 brushes presented a hydrated thickness of 880 nm, while covalently crosslinked brushes, as expected, showed lower values of 300, 190 and 90 nm in the case of PAAm-0.1, PAAm-0.5 and PAAm-1.0, respectively.

![Figure 3.11](image)

**Figure 3.11.** Applied-load-versus-penetration-depth curves for PAAm brushes and covalently crosslinked brushes in HEPES buffer with varying amount of feed crosslinker

Dry thicknesses for PAAm films with 0%, 0.1%, 0.5% and 1.0% feed crosslinker are 33.9 nm, 38.9 nm, 44.5 nm and 30.8 nm, respectively.

Due to surface confinement of polymer brush films, the effective swelling of the layers could be considered as mainly perpendicular to the surface\(^{44,45}\) and it was previously observed to be larger than the mono-dimensional swelling of bulk networks at constant crosslink density.\(^{44}\) According to this, we defined the swelling ratio as:

\[
Q = \frac{V_{\text{wet}}}{V_{\text{dry}}} = \frac{d_{\text{wet}}}{d_{\text{dry}}}
\]  

(3.4)
where $V_{\text{wet}}$ and $V_{\text{dry}}$ are swollen and original volume of unconstrained hydrogel; $d_{\text{wet}}$ and $d_{\text{dry}}$ are wet and dry thickness of covalently crosslinked PAAm hydrogel films, respectively, measured by AFM and ellipsometry.

PAAm-0 brushes were thus shown to swell profusely when immersed in a good solvent ($Q = 25.9 \pm 1.0$). The lateral crosslinking of the brushes effectively decreased the hydration of PAAm films, as previously reported by the groups of Rühe and Hilt.$^{45,46}$ The presence of even a small amount of crosslinks, e.g. for PAAm-0.1, led to a 70% decrease in the swelling ratio of the PAAm brushes ($Q = 7.7 \pm 1.0$). Further addition of crosslinker turned the films into rather rigid structures, which were far less capable of incorporating water into their structures. PAAm-0.5 and PAAm-1.0 showed very low values of $Q$: 4.3 ± 1.0 and 2.9 ± 1.0, respectively.

The Young’s moduli ($E$) of PAAm brushes and covalently crosslinked brushes were evaluated according to Sneddon’s model$^{43}$ from the region of the force curves corresponding to penetration depths smaller than 10 nm, in order to avoid substrate effects. The values of $E$ are reported in Figure 3.12, where they are correlated with the corresponding swelling ratios $Q$ of the films. In general, the elastic moduli of PAAm brush and covalently crosslinked brush films were found to lie within the range 20–700 kPa, comparable with reported moduli for bulk PAAm hydrogels.$^{47-49}$

The Young’s moduli for the different brush films could be precisely tuned by varying the amount of crosslinker in the formed films. While PAAm brushes behaved as very compliant films mainly constituted of water, a considerable stiffening of the covalently crosslinked PAAm brushes was observed upon increasing the concentration of bisAAM in the feed.
Chapter 3

Figure 3.12. Young’s modulus versus swelling ratio for PAAm brushes and covalently crosslinked brushes with varying amounts of feed crosslinker. Dashed line denotes $E \propto Q^{1.57}$ (1D swelling), solid line denotes $E \propto Q^{2.25}$ (3D swelling), dry thicknesses for PAAm films with 0%, 0.1%, 0.5% and 1.0% feed crosslinker are 33.9 nm, 38.9 nm, 44.5 nm and 30.8 nm, respectively.

In the case of isotropic bulk polymeric networks, different Young’s moduli have been obtained by varying the equilibrium polymer volume fraction when immersed in a good solvent. According to de Gennes and Candau,\textsuperscript{50,51} Young’s modulus $E$ and the swelling ratio $Q$ (the reciprocal of the equilibrium polymer volume fraction) scale with an exponent equal to $-2.25$. In contrast to the 3D swelling, the anisotropic 1D swelling of the covalently crosslinked PAAm thin films in this study shows a scaling exponent of $-1.57$ (Figure 3.12). For the uncrosslinked brushes the point of contact is difficult to detect precisely, while for the covalently crosslinked PAAm brushes with a high crosslink degree the compressed films may have become dehydrated, resulting in such a substantial stiffening that the soft AFM cantilevers used cannot indent the film completely. Although the AFM nanoindentation measurements may have underestimated the true swelling ratio, as alluded to above, the discrepancy of the two scaling exponents suggests that the scaling law of $E$ and $Q$ of hydrogel is swelling-dimension dependent.
According to the rubber elastic theory, the average mesh size of uncharged hydrogels can be estimated by employing the polymer volume fraction as reported by Peppas:\textsuperscript{52,53}

\[
\xi = (C_n \times n)^{1/2} \times l \times Q^{1/3}
\]  

(3.5)

where \(C_n\) is the characteristic ratio of poly(acrylamide) (the value of 14.8 was used),\textsuperscript{54} \(l = 1.54\ \text{Å}\) is the \(sp^3\) C – C bond length, \(n\) is the molar ratio of monomer and crosslinker, and \(Q\) is the polymer swelling ratio obtained from AFM (the ratio of swelling thickness to dry thickness), assuming the similar density for polymer and water. Average mesh sizes (\(\xi\)) (network correlation length) of the surface-tethered gels with respect to various crosslink degrees in water can be calculated accordingly as shown in Table 3.2 and Figure 3.13.

The surface-grafted PAAm gel films present an average mesh size of 19.5 nm, 6.3 nm and 3.8 nm when the crosslink degree of the films is 0.36\%, 2.28\% and 4.8\%, respectively. These average mesh sizes are similar to the ones determined from macroscopic PAAm gels.\textsuperscript{55} We can conclude that the average mesh size of the PAAm films in water decreases upon enhancing the crosslink degree.\textsuperscript{56,57}

<table>
<thead>
<tr>
<th></th>
<th>(C_n)</th>
<th>(n)</th>
<th>(l) (nm)</th>
<th>(Q)</th>
<th>(\xi) (nm)</th>
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<td>0.154</td>
<td>2.9</td>
<td>3.8</td>
</tr>
</tbody>
</table>

Table 3.2. Molecular parameters for calculating average mesh size of PAAm films.
Figure 3.13. Average mesh size of PAAm films with different crosslink degrees.

3.2.4 Microtribological Properties of Covalently Crosslinked PAAm Hydrogel Films

PAAm brushes and covalently crosslinked brushes are expected to display different tribological characteristics as the crosslink degree is changed. Thus, in order to investigate the influence of crosslinking on the frictional properties of PAAm films, microtribological tests were performed.58,59

Microtribological measurements were carried out in aqueous buffer by operating a microtribometer setup with a hydrophilic, oxidized poly(dimethylsiloxane) (Ox-PDMS) spherical counter surface60 glued to a cantilever with known normal and tangential force constants. The coefficients of friction for PAAm brushes and covalently crosslinked brushes were thus obtained by sliding the cantilever in contact with the films’ surfaces at normal loads ranging from 0.5 to 3.0 mN. As shown in Figure 3.14, the friction coefficient of PAAm films sliding against a hydrophilic counter surface increased dramatically upon increasing the crosslink degree in the films.

The range of contact pressures in the microtribological studies (22.3 – 40.5 kPa) was too small to produce any wear track that could be discerned by optical microscopy. Thus it is
believed that the dramatic increase in the coefficient of friction is mainly due to the changes in the structure of the thin films upon crosslinking, rather than dissipative processes associated with wear.

**Figure 3.14.** Coefficient of friction of PAAm films with varying amount feed crosslinker measured by microtribometer in HEPES buffer with a sliding speed of 0.1 mm/s and a stroke length of 1 mm. Friction force was acquired from the friction loops under varying loads (0.5 – 3.0 mN). Dry thicknesses of PAAm-0, PAAm-0.1, PAAm-0.5, and PAAm-1.0 are 238 nm, 265 nm, 208 nm and 155 nm, respectively.

We also expect the microtribological properties of PAAm films to be related to the extent to which mobile, brush-forming polymer chains are present in the outermost layer of the films. As the crosslink degree increases, the chains are less available for the formation of the highly hydrated brush architecture that has been widely reported to facilitate sliding.\(^8,9\)

The decrease in free surface chain conformation has already been discussed above in the context of the wettability results. The degree of swelling is also related to the presence of the brush-forming, free chains: PAAm-0 presented a swelling ratio value of \(Q = 25.9\), which corresponds to 96.1% of water. The increase of crosslinking for PAAm-0.1, PAAm-0.5 and PAAm-1.0 films led to a decrease in the water content inside the layers to 87.0%, 76.7% and 65.5%, respectively. As the brush formation became less pronounced upon crosslinking, brush-induced lubrication was hindered, leading to an increase in
friction coefficient. A similar contrast in macroscopic lubrication behavior for gels with and without brush termination, has been reported by Gong.\textsuperscript{29,30}

In order to examine the wear behavior of these polymeric films, PAAm films with different crosslink degrees were tested under oscillatory sliding against a glass counter surface under constant load, by means of a nanotribometer. As shown in Figure 3.15, friction coefficients of the PAAm films were recorded with respect to sliding time. In these measurements the sharp increase of the friction coefficient corresponds to the layer wearing through. After the tests, the durability of the films was further examined by means of optical microscopy (Figure 3.16). The durability of homogeneous PAAm films with similar dry thicknesses were compared under 2 mN load in an aqueous environment. We notice that homogeneous PAAm-0 brushes still remained intact after 360s of sliding. In contrast, the crosslinked polymer brushes (PAAm-0.5 and PAAm-1.0) immediately failed soon after the initiation of sliding, as confirmed by immediate increase of friction and wear debris observed by optical microscopy. We thus conclude that the crosslinking in these samples was deleterious to the wear-resistance properties of the films.

By varying the concentration of crosslinks inside PAAm films, we are aiming to understand mechanisms of wear for the surface-tethered films. Generally, the fracture energy required to break the network structure of the PAAm gels near the crack front is mainly due to viscoelastic dissipation within the polymer at the specific testing speed. This contribution is proportional to the viscous resistance at the fracture interface, which scales inversely with the crosslink degree.\textsuperscript{61}

Consistent with this theory, the presence of ‘free’ brush greatly improved the durability during tribological test, while crosslinking in PAAm films led to increased susceptibility to wear. The constrained polymeric chains are less able to participate in viscoelastic dissipation as well as provide a higher bond tension,\textsuperscript{62} allowing fracture at the film-substrate interface to occur at a lower shear stress, as reported by Gent.\textsuperscript{63}
Figure 3.15. Stability of homogeneous PAAm films studied by a nanotribometer under 2 mN load in Milli-Q water (dry thickness: PAAm-0: 110 nm, PAAm-0.5: 120 nm, PAAm-1.0: 130 nm) sliding against a glass pin.

Figure 3.16. Optical images of the homogeneous PAAm films (a. PAAm-0, b. PAAm-0.5, c. PAAm-1.0) studied in Figure 3.15 after 360s, 30s and 50s’ sliding against a glass pin under 2 mN load in Milli-Q water (image sizes: 120 μm × 120 μm, contact pressure: 68 MPa).

3.3 Conclusions

Poly(acrylamide) (PAAm) films with different crosslink degrees were synthesized by UVLED surface-initiated iniferter-mediated photopolymerization (UVLED-SIMP) from SAMs of photoiniferter immobilized on oxidized silicon surfaces. The employment of a UVLED guaranteed that photopolymerization occurs exclusively at the photoiniferter-
modified surfaces. Addition of crosslinker dramatically increased both the film-growth rate and the dry roughness without significantly altering the chemical composition of the hydrogel thin films. Lateral crosslinking of the PAAm brushes was demonstrated to strongly determine the interfacial properties of the fabricated films to an extent that was directly related to the amount of crosslinker in the monomer feed. A marked increase in wettability for covalently crosslinked brushes was attributed to the lateral networking of grafted polymer chains, which eliminated their ‘bridging effect’ at the solvent-vapor interface.

The bulk properties of the PAAm films could also be tailored by varying the amount of crosslinker in the feed. Young’s moduli and swelling ratios of the covalently crosslinked PAAm hydrogel thin films, measured by AFM, varied from the typical values for profusely swollen and compliant brushes to values characteristic of ‘stiff’ bulk gels, as the lateral crosslinks were introduced. Finally, microscale tribological measurements demonstrated that frictional properties of PAAm films were modified by the addition of crosslinker. PAAm brushes behaved as highly effective lubricating films when immersed in an aqueous environment. In contrast, covalently crosslinked brushes showed an increase in the coefficient of friction with increasing amounts of crosslinks, due to the progressive elimination of the lubricious brush structure coupled with the reduction of the water content of the films.

In conclusion, a fine control over wettability, water content, mechanical and tribological properties of PAAm films was demonstrated. A relatively straightforward fabrication method based on UVLED-SIMP provides an attractive polymeric platform displaying the advantages of a polymer brush layer together with the versatility of bulk gel materials.

3.4 References


Chapter 4

Nanotribological Properties of Surface-Grafted Homogeneous Poly(acrylamide) Films in Water-Methanol Mixtures

In this chapter, the adhesive and nanotribological properties of surface-grafted poly(acrylamide) (PAAm) films with various crosslink degrees, and in the presence of solvents over a broad spectrum of quality, were investigated by means of colloidal-probe atomic force microscopy. The solvent consisted of a mixture of water (good solvent for PAAm) and methanol (bad solvent for PAAm). Adhesion measurements carried out on brush (uncrosslinked) structures revealed significant pull-off forces in solvent mixtures that placed the polymer at its glass transition. These pull-off forces, which were orders of magnitude higher than those measured in either pure solvent, were significantly reduced in the presence of crosslinking. The nanostructures of PAAm films with different crosslink degrees were elucidated in their maximum collapsed state by means of atomic force microscopy, and the parameters influencing adhesive properties of films with brush structures at their glass transition were investigated. Complex nanotribological behavior of PAAm films was observed, and found to result from the interplay of film structure and adhesion forces, which were influenced by both crosslink degree and solvent quality.

4.1 Introduction

Mechanical and tribological properties of polymeric thin films and coatings have to be taken into account during their fabrication in order to obtain the desired performance

* Part of this chapter is published in:
Li, A.; Ramakrishna, S. N.; Kooij, E. S.; Espinosa-Marzal, R. M.; Spencer, N. D. Soft Matter 2012, 8, 9092-9100.
The major part of this work was done by Ang Li, including all experiments and writing of the manuscript. ShivaPrakash N. Ramakrishna conducted Cypher™ AFM imaging as well as CPM force calibration. E. Stefan Kooij carried out the ellipsometry measurements. Rosa M. Espinosa-Marzal and Nicholas D. Spencer contributed in discussions and further correcting the paper.
throughout the lifetime of these materials. Surface-tethered polymer brushes/gels\(^1^3\) have been extensively studied during the last decade and increasingly applied for the preparation of ultra-thin films with tunable and versatile properties. These are of great interest for applications in colloidal stabilization,\(^4^8\) lubrication,\(^9^18\) antifouling surfaces,\(^19,20\) controlled cell adhesion,\(^21,22\) biomedical devices\(^23\) and chromatographic technology.\(^24,25\) It is a challenging but fruitful task to bring highly developed macromolecular chemistry and surface science together, in order to tailor and engineer polymeric thin films with complex, hierarchical architectures leading to useful characteristics such as tribological stability, adaptability and functionality.

Polymer brushes have shown complex tribological behavior in a mixed-solvent environment, thanks to their remarkable co-(non)solvency properties. Tsujii studied the lubrication mechanism of high-grafting-density polystyrene (PS) brushes in a mixture of toluene and 2-propanol.\(^26\) Upon decreasing the solvent quality, the brushes were found to collapse monotonically, resulting in a high coefficient of friction due to the failure of brush-assisted lubrication. In addition, large adhesive forces were observed as the films experienced the glass transition, significantly increasing the frictional force. The frictional properties of a surface-bound brush-forming graft copolymer (PLL-\(g\)-PEG) in an aqueous binary solvent mixture were also studied by our group; similarly, the coefficient of friction between the polymeric films and the counter-surface increased upon decreasing the solvent quality.\(^27\) Besides these co-solvency studies, the nanotribological behaviors of the poly(\(N\)-isopropylacrylamide) (PNIPAM) brushes and the poly(2-(methacryloyloxy)ethylphosphorylcholine) (PMPC) brushes in co-nonsolvency environments have been studied by Vancso\(^28\) and Leggett,\(^29\) respectively. Both research groups reported substantially increased adhesion and reduced lubrication at an intermediate co-solvent concentration, which was attributed to the decreased hydration of the brush chains due to co-nonsolvency, i.e. when a mixture of two good solvents becomes a poor solvent for the polymer, resulting in brush collapse.

Large numbers of experimental and theoretical studies on the equilibrium configuration of polymer brushes in solvent mixtures have been reported.\(^30^36\) However, the swelling properties and tribological performance of irreversibly covalently crosslinked polymer
brushes, i.e. 2D-gels, in co-solvent systems have not, to our knowledge, been investigated. Furthermore, crosslink-degree-dependent responses to external stimuli are little-researched issues.\textsuperscript{37-41} Using polymer films with a previously reported, well-defined microstructure,\textsuperscript{42,43} we show here that the equilibrium configuration and swelling behavior of tethered films are not only strongly affected by the solvent quality, but also by the film structure, i.e. by the crosslink degree. The pull-off forces between polymer brushes and a silica counter surface measured by colloidal probe microscopy (CPM) increased with decreasing solvent quality, while the crosslinked structure of the polymeric films maintained low pull-off force over a wide range of solvent quality. Polymer films with brush structures were shown to exhibit a glass transition at a methanol volume fraction of 75\%, at which point the pull-off force reached a maximum value (orders of magnitude greater than the values measured under the pure solvents) and the collapsed brushes showed a dimpled structure (evidencing instabilities). In contrast, these characteristics of the glass transition were not observed for the crosslinked films. In order to further explore the effects of the solvent-induced glass transition of the polymer brushes, pull-off force measurements were performed as a function of applied load, testing speed and methanol volume fraction. The nanotribological performance of the polymer films was also investigated by CPM, which showed that the combined effects of solvent quality and crosslink degree enable the tuning of adhesion and friction of surface-tethered polymer films, while the chemical composition of the polymers remains nearly constant.

These findings are of practical importance for the design of polymer coatings with controlled lubricating/adhesion characteristics in complex solvent mixtures, with applications that include aqueous lubrication and colloidal-particle stabilization.

4.2 Results and Discussion

4.2.1 Synthesis of Surface-Tethered PAAm Thin Films with Defined Crosslink Degrees

Surface-grafted PAAm films with virtually identical chemical compositions were fabricated by UVLED surface-initiated polymerization (UVLED-SIP) following the same technique introduced in the previous chapter. Polymer films with different crosslink
degrees were synthesized in a monomer (AAm) solution containing a range of different relative concentrations of crosslinker ($W_{\text{bisAAm}}\%$: 0, 0.5 and 1.0 in feed), as summarized in Figure 4.1. The polymer films are denoted as PAAm-X, where the numbers (X) indicate the crosslinker weight percentage in the feed. The thickness of grafted polymeric films could be easily tailored by controlling the polymerization time at a given crosslinker concentration in the feed. FT-IR measurement was employed to confirm the incorporation of crosslinker in PAAm films as well as to quantitatively determine the crosslink degree of the PAAm films prior to adhesion and friction studies (Figure 4.2). All FT-IR spectra of the PAAm films with different crosslink degrees show an almost identical profile, similar to previous results indicating an approximately constant chemical composition throughout the films.\textsuperscript{42,44} The strong bands at 3338 and 3200 cm\textsuperscript{-1} are related to N–H asymmetric and symmetric stretching of the NH\textsubscript{2} repeat unit, respectively. Both amide I and amide II bands from monomer and crosslinker can be found between 1480 and 1800 cm\textsuperscript{-1}. The only difference among these spectra is the peak at 1520 cm\textsuperscript{-1} (amide II band), characteristic of the crosslinker. The more crosslinker employed during the polymerization, the higher the intensity at this specific wavelength.

The crosslinker amount (molar fraction) in the PAAm films was determined to be 0%, 2.3% and 4.8% for PAAm-0, PAAm-0.5 and PAAm-1.0, respectively, according to the previously reported method (Chapter 3).

\textbf{Figure 4.1.} General scheme for fabrication of surface-tethered poly(acrylamide) thin films with tunable crosslink degrees.
Figure 4.2. FT-IR spectra of surface-tethered poly(acrylamide) thin films with different crosslink degrees. Dry thickness of PAAm-0, PAAm-0.5 and PAAm-1.0 are 189 nm, 173 nm and 217 nm, respectively.

4.2.2 Swelling Behavior of Surface-Grafted PAAm Thin Films upon Varying Solvent Quality

We have evaluated the influence of both the crosslink degree of the films and solvent quality of binary mixtures on swelling behavior by means of ellipsometry. Due to the interfacial confinement, surface-tethered PAAm films are only allowed to respond perpendicularly to the substrate (1-D swelling). Thus, the swelling ratio ($Q$) was defined according to equation (3.4) as described in the previous chapter:\textsuperscript{41,42}

Figure 4.3 shows the swelling ratio of PAAm films with different crosslink degrees in a series of aqueous methanol mixtures (methanol volume fraction: 0%, 25%, 50%, 75% and 100%). It is concluded that the swelling ratio of PAAm films is enhanced both by increasing solvent quality and by decreasing the crosslink degree.

Due to the extraordinary swelling characteristics of PAAm-0 brushes in water ($Q = 25.9 \pm 1.0$ according to AFM indentation measurements),\textsuperscript{42} solvent molecules were present in high concentrations in highly swollen PAAm-0 films, which decreased the refractive
index contrast between polymer and solvent. Consequently, the swelling thickness of PAAm-0 brushes could not be precisely determined by ellipsometry at methanol volume fractions smaller than 50%. For PAAm-0 brushes, the decrease of solvent quality between 0% and 75% of methanol volume fraction resulted in a substantial fall in the swelling ratio (i.e. collapse of the brushes). Thus, polymer chains collapsed with decreasing solvent quality, a maximum collapsed conformation being achieved at a methanol volume fraction of 75%. Upon further increase in the methanol volume fraction, the PAAm-0 brushes started to stretch again, as shown by the slight increase of swelling ratio in pure methanol, although it is well known that water and methanol are good and bad solvents for poly(acrylamide), respectively. Thus, PAAm films achieved maximum collapse at an intermediate methanol volume fraction (75%), which corresponded to the worst solvent quality for the PAAm films. We presume that this maximum collapse of polymer chains was due to the so-called ‘solvent-exchange effect’ described by Birshtein: at a low (volume fraction of 25%) content of water (the good solvent) in the solution, collapse of polymer brushes is energetically required in order to equalize the chemical potentials of water between the value within the brushes and that in the bulk solution. With decreasing solvent quality, the swelling ratio of crosslinked films (PAAm-0.5 and PAAm-1.0) also decreased, achieving a minimum at methanol volume fraction of 75%.

By increasing the crosslink degree of PAAm films at a specific solvent quality, the swelling ratio decreased. PAAm-0.5 and PAAm-1.0 films in pure water exhibited a swelling ratio of 4.3 and 2.2, respectively, which were comparable to previously reported values obtained by indentation (4.3 and 2.9). This shows that interfacial constraint of polymer chains, by irreversible covalent crosslinking, was able to effectively restrict the swelling/collapse response upon varying the solvent quality.

In addition to ellipsometry measurements, analogous swelling/collapse behaviors for PAAm films with different crosslink degrees were also verified qualitatively, by conducting AFM force measurements while varying solvent quality (Figure 4.4).
Figure 4.3. Swelling ratios of poly(acrylamide) films with different crosslink degrees measured by ellipsometry in aqueous methanol mixtures with varying solvent quality (dry thickness of PAAm-0: 189 nm, dry thickness of PAAm-0.5: 173 nm, dry thickness of PAAm-1.0: 217 nm). The swelling ratio of PAAm-0 brushes in water (indicated by the black solid circle) was obtained from AFM indentation. Lines are shown as a guide to the eye.
Figure 4.4. Force-distance curves of PAAm films with different crosslink degrees measured by colloidal-probe atomic force microscopy (CPM) (spring constant: 0.511 N/m, radius of silica probe: 14 μm, applied load: 21.4 nN, testing speed: 3.97 μm/s) in aqueous methanol mixtures with various solvent qualities (only approach curves are shown). (a) PAAm-0 films (dry thickness: 189 nm). (b) PAAm-0.5 films (dry thickness: 173 nm). (c) PAAm-1.0 films (dry thickness: 217 nm).
4.2.3 Pull-off Force of Surface-Tethered PAAm Films in Aqueous Methanol Mixtures

Figure 4.5 shows a 3-D plot of the measured pull-off force between a silica probe and the PAAm films as a function of solvent quality and crosslink degree. A notable dependency of the pull-off force on both crosslink degree and solvent quality is observed. Decreasing the crosslink degree of PAAm films or worsening the solvent quality leads to a dramatic increase in pull-off force.

![Figure 4.5](image)

**Figure 4.5.** Pull-off force (standard deviation is < 5%) of PAAm films (dry thickness of PAAm-0: 189 nm, dry thickness of PAAm-0.5: 173 nm, dry thickness of PAAm-1.0: 217 nm) measured by CPM (spring constant: 0.511 N/m, radius of silica probe: 14 μm, applied load: 21.4 nN, testing speed: 3.97 μm/s) in aqueous methanol mixtures of varying composition.

For PAAm-0 brushes, the pull-off force increased upon decreasing the solvent quality and reached a maximum at a methanol volume fraction of 75% (215 ± 10 nN), where, according to ellipsometry, maximum brush collapse occurred. Upon further increasing the methanol volume fraction up to 100%, the pull-off force decreased to 4.8 ± 0.3 nN. Crosslink degree also played a significant role in modifying the pull-off force of PAAm films. As shown in Figure 4.5, the pull-off force decreased rapidly by increasing the
amount of crosslinker in PAAm films for a given solvent quality, analogously to the macroscopic adhesion behavior of polymer gels/coatings. Prior to the study of the pull-off force of PAAm-0 brushes conducted by means of CPM in an open fluid cell, the variation of the methanol volume fraction in water-methanol mixtures upon continuous evaporation of the mixture was examined.

Aqueous methanol solutions are known to be non-azeotropic mixtures, the evaporation rate of methanol being faster than that of water due to their different vapor pressures (vapor pressure of water and methanol at 20 °C are 2.30 kPa and 13.02 kPa, respectively). Constant evaporation rates (0 – 100 min) of pure water (0.7 mg/min), pure methanol (8.0 mg/min) and 75% (volume fraction) aqueous methanol solutions (7.0 mg/min) were measured by using an analytical balance (METTLER TOLEDO® XS105) in accompanying experiments under the same conditions as later used for pull-off force measurements (sample volume: 3.0 ml). According to the vapor-liquid coexistence line for the water-methanol system at standard atmospheric pressure, the molar fractions of methanol \( y_1 \) and water \( y_2 \) in the vapor phase during the evaporation process can be estimated making the assumption that the evaporation rate of the two components results from the individual evaporation rate of each component. Thus, for the 75 vol.% mixture:

\[
8.0 \times y_1 + 0.7 \times y_2 = 7.0 \tag{4.1}
\]

\[
y_1 + y_2 = 1.0 \tag{4.2}
\]

It follows that \( y_1 = 0.863, \) and \( y_2 = 0.137. \)

Furthermore, the evaporation rates of methanol \( k_1 \) and water \( k_2 \) in aqueous methanol mixtures with an initial methanol volume fraction of 75% within the experimental time scale can be calculated from:

\[
k_1 = 8.0 \times y_1 \tag{4.3}
\]

\[
k_2 = 0.7 \times y_2 \tag{4.4}
\]
Hence, \( k_1 = 6.904 \text{ mg/min} \), and \( k_2 = 0.096 \text{ mg/min} \).

The time-dependent volume of methanol \((V_{\text{methanol}})\) and water \((V_{\text{water}})\) can be determined accordingly:

\[
V_{\text{methanol}}(t) = 3.0 \times 0.75 - k_1 \times t / \rho_{\text{methanol}} = 2.25 - 0.00863 \times t \quad (4.5)
\]

\[
V_{\text{water}}(t) = 3.0 \times 0.25 - k_2 \times t / \rho_{\text{water}} = 0.75 - 0.000096 \times t \quad (4.6)
\]

since \( \rho_{\text{methanol}} \) and \( \rho_{\text{water}} \) are 0.8 g/ml and 1.0 g/ml, respectively.

Finally, the methanol volume fraction during evaporation in mixed solutions with an initial methanol volume fraction of 75\% within the experimental time scale (0 – 100 min) results from:

\[
V_{\text{methanol}}(\%) = 100 \times \frac{V_{\text{methanol}}}{V_{\text{methanol}} + V_{\text{water}}} = 100 \times \frac{2.25 - 0.00863 \times t}{3 - 0.008726 \times t} \quad (4.7)
\]

The methanol volume percentage in the binary solution decreases with respect to time, as shown in Figure 4.6.

**Figure 4.6.** Methanol volume percentage in mixed water-methanol solutions, changing upon evaporation with respect to time.
After establishing the time-dependent variation of methanol volume fraction in solution, we further investigated the variation of pull-off force of PAAm-0 brushes in mixed solutions by monitoring pull-off force upon continuous evaporation of methanol. Figure 4.7 (a) shows the time-dependent pull-off force (obtained at intervals of five minutes) of PAAm-0 brushes in an open liquid cell containing an aqueous methanol solution with an initial methanol volume fraction of 75%. The pull-off force decreased moderately at the beginning of the evaporation process (0 – 20 min); a sharp decrease of pull-off force being observed upon further evaporation of water and methanol (20 min – 80 min); finally, pull-off force reached a steady value. Three representative retraction force curves are taken from the data shown in Figure 4.7 (a), shown in Figure 4.7 (b), corresponding to initial (1), intermediate (2) and final (3) states of PAAm-0 brushes during the evaporation process. As described above, the methanol volume fraction in the solution varied roughly from 75% to 65% (mole fraction: 57.5% – 45.5%) over the experimental time scale (Figure 4.6).

In the initial phase, the volume fraction of methanol in solution decreased gradually from 75% to 73% over 20 min, which did not lead to a significant decrease in pull-off force, indicating that PAAm-0 brushes were still at the (solvent-induced) glass transition. Upon further evaporation, the decreasing methanol volume fraction in solution (73% – 67%) led to a shift of the glass transition to values below room temperature and a consequent decrease in pull-off force, as the brushes began to become more mobile (and to swell). In the final stage of the experiment (below 67% methanol vol.%), the residual methanol volume fraction was too low to influence the pull-off force significantly; therefore, a plateau in pull-off force was obtained for the swollen PAAm-0 brushes.
Figure 4.7. Variation of pull-off force of PAAm-0 Brushes (dry thickness: 133 nm) measured by CPM (spring constant: 3.02 N/m, radius of silica probe: 12.5 μm, applied load: 123.9 nN, testing speed: 3.97 μm/s): (a) Variation of pull-off force of PAAm-0 brushes exposed to ambient environment in aqueous methanol mixtures with an initial methanol volume fraction of 75%. (b) Exemplary retraction force curves of polymer brushes at different time indicated by (1), (2) and (3).

4.2.4 Pull-off Force of PAAm Films at The Glass Transition

Tsujii et al. carefully examined the lubrication mechanism of polystyrene brushes in organic mixed solvents and showed that the polymer chains experienced a glass transition under the same conditions as the adhesion force achieved a maximum. In general, the presence of solvent (plasticizer effect) decreases the glass-transition temperature ($T_g$) of the polymer by reducing the barriers for rotational and transitional motion of the chain segments—resembling the mechanism of solvent-driven glass transition reported by Johannsmann. We could estimate the glass-transition temperature ($T_{g,mix}$) of PAAm-0 brushes in their maximum collapsed state (methanol volume fraction of 75%) by applying the classical Gordon-Taylor equation based on a simple mixing rule given by:

$$T_{g,mix} = \phi_1 T_{g1} + \phi_2 T_{g2} + \phi_3 T_{g3}$$  \hspace{1cm} (4.8)

where $T_{g1}$, $T_{g2}$ and $T_{g3}$ are the inherent glass-transition temperatures of poly(acrylamide), water and methanol ($T_{g1} = 438$ k, $T_{g2} = 136$ k and $T_{g3} = 102$ k), $\phi_1 = (1/Q_1)$, $\phi_2 = ((1-...
$1/Q_1 \times 25\%$) and $\phi_3 = (1 - 1/Q_1 \times 75\%)$ are the corresponding volume fraction of each component, which were calculated according to the swelling ratio ($Q_1$) determined by ellipsometry ($\phi_1 = 0.573$, $\phi_2 = 0.107$ and $\phi_3 = 0.320$). The glass-transition temperature ($T_{g,mix}$) of PAAm-0 brushes reaches a maximum of around 25 °C in 75% methanol, corresponding to the temperature at which the pull-off force measurements were carried out. The glass-transition temperature of PAAm-0 brushes in aqueous methanol mixtures with other solvent qualities was also calculated, and all showed much lower values (Figure 4.8), in accordance with their swelling behavior (Figure 4.3).

**Figure 4.8.** Glass-transition temperatures of PAAm-0 brushes in aqueous methanol solutions with different qualities, calculated using swelling-ratio data from ellipsometry, according to the Gordon-Taylor equation (Lines are shown as a guide to the eye).

In general, the adhesion of polymeric materials can be triggered upon varying chemical functionality or topography. In the former case, an order-disorder transition in macromolecules is generally responsible for their adhesive behavior, which includes melting, crystallization and phase transitions. In this study, we conclude that this marked adhesive behavior of polymer brushes occurred as the PAAm chains experienced a glass transition. As water is progressively mixed with methanol, the tendency of the polymer chains to interact with each other, rather than with water, increases, and this
undoubtedly influences the mobility of the polymer chains and therefore also influences the \( T_g \).

As for the mechanism by which pull-off force increases at the glass-transition temperature, two possibilities were considered. In the first case this phenomenon could be due to hydrogen bonding between the silica probe and the chains. Alternatively this was related the competing bond-forming and separation processes at the interface,\(^{48,61}\) bond being interpreted as a physical interaction between surfaces during the pull-off-force measurements. Efficient bond formation requires fast transport of polymer chains toward adhering surfaces to form a robust connection and a high effective area of interacting molecules at the interface. A key factor of the bond formation is the mobility of the polymer chains, which can be expected to be more efficient in highly swollen brushes. In contrast, in the bond-separation process, the adhesion is strengthened by small degrees of resistance to internal motion, which occur during the polymer’s glass transition. According to our measurements, the loss of chain mobility at the glass transition is responsible for the increasing pull-off force. By conducting the pull-off force measurements with a gold-coated silica probe (Figure 4.9), very similar behavior was observed to that observed with the uncoated silica probe, which excludes the possibility that the adhesion-enhancement effect is due to hydrogen bonding to silica, and points to the chain-mobility explanation.
Figure 4.9. Pull-off force of PAAm films (dry thickness of PAAm-0: 189 nm, dry thickness of PAAm-1.0: 217 nm) measured by CPM (spring constant: 0.508 N/m, radius of gold-coated silica probe: 8.66 μm, applied load: 35.2 nN, testing speed: 3.97 μm/s) in aqueous methanol mixtures of varying composition (Lines are shown as a guide to the eye).

Covalent crosslinking significantly reduces the chain-segment mobility on a molecular level,\(^{62-65}\) and influences the glass-transition temperature in ultrathin polymer films, if either the crosslink density is high or crosslinking modifies the free volume of the polymers.\(^{66-68}\) In the present case, crosslinked PAAm films with low crosslink density (crosslinker amount in films < 4.8%) most probably also experienced the glass transition at their most collapsed state (methanol volume fraction of 75%) at ambient temperature, which is in accordance with the observable low pull-off force of PAAm-0.5 and PAAm-1.0 in Figure 4.5. The less-adhesive behavior of crosslinked brushes can, however, also be related to their 2-D network structure. In irreversibly crosslinked polymer brushes in 75% methanol (PAAm-0.5 and PAAm-1.0), the surface-tethered macromolecule segments were covalently linked to each other in a multiple fashion, and thus a substantial loss of conformation freedom occurred. The silica probe was not able to penetrate into the rigid films during the pull-off force measurement, and the decreased contact area led to a dramatically reduced adhesion force. Therefore, these results demonstrate that interfacial adhesion force of polymeric films at the nanoscale can be effectively reduced by irreversibly covalently crosslinking dangling polymer chains, irrespective of the external solvent quality.

4.2.5 AFM Morphological Study of Surface-Tethered PAAm Films in 75% Methanol

In order to further reveal the properties of polymer films at their maximum collapsed state, morphologies of PAAm films with different crosslink degrees were determined by AFM under 75% methanol (Figure 4.10). Uncrosslinked PAAm films (a) showed a relative smooth surface with some ‘dimpled’ features. In contrast to the brushes’ structures, PAAm-0.5 (b) and PAAm-1.0 (c) films presented fairly rough surfaces resembling their morphologies in a dry state.\(^{42}\)
The ‘dimple’ features (depth: 8 ± 2 nm and width: 380 ± 20 nm) appeared for PAAm-0 brushes at the glass transition, indicating the lateral instability of the grafted layer in a poor solvent. Both theoretical predictions and experimental studies have previously identified this feature and the influencing parameters, e.g. chain length, solvent quality and grafting density.\textsuperscript{69-72} Swollen polymer brushes exhibit a smooth morphology with small RMS value in a good solvent.\textsuperscript{73} As the solvent quality decreases, the grafted films develop instabilities tangential to the substrate. In the normal direction, the spatial inhomogeneity occurs throughout the entire tethered films and a ‘dimpled’ structure (local clumping of the polymer chains) appeared. This was the region near to the top of the polymer films, provided the chain length is sufficiently large.\textsuperscript{70} Furthermore, the lateral instabilities of the polymer chains imply that the response of the tethered film is not strictly one-dimensional (perpendicular to the substrate), and therefore equation (3.4) is not strictly valid in determining the swelling ratio at the glass transition. Nevertheless, considering the small height of the dimples compared to the dry film thickness the calculated swelling ratio can be regarded as a very good approximation.

Upon covalently crosslinking the PAAm-0 brushes, clustering domains appeared and became more densely packed with increasing crosslink degree (Figure 4.10). The morphologies of PAAm-0.5 and PAAm-1.0 films in a methanol volume fraction of 75% retained the clustering features that they also displayed in a dry state and also in pure water,\textsuperscript{42} indicating that the lateral constraints of the grafted chains can maintain the films’ original structures even upon exposure to poor solvents. This nanoscale, crosslinked structure of hydrogels greatly hinders the penetration of the colloidal probe into the polymeric films, resulting in a substantially reduced contact area and pull-off force, as discussed above. Although the effect of surface roughness on adhesion force is well known,\textsuperscript{74-77} it has to be mentioned that no correlation between surface roughness (RMS roughness: 2.6 nm – 13.7 nm) and pull-off force was found in our systems.
Figure 4.10. Morphologies of PAAm films with different crosslink degrees measured by a Cypher™ (Asylum Research) AFM in aqueous methanol mixtures (75% methanol) at a scanning rate of 1.0 Hz. (a) – (c) are the height images for PAAm-0 (RMS roughness: 2.6 nm), PAAm-0.5 (RMS roughness: 8.7 nm) and PAAm-1.0 (RMS roughness: 13.7 nm), sharing the same height scale bar; the roughness was calculated over an area of 5 μm × 5 μm. (d) – (f) are their respective phase images, sharing same phase scale bar (white scale bar in these images indicates 1 μm).

The swelling behaviors of surface-grafted films are strongly determined by the solvent quality; thus, it is of great interest to probe the average mesh sizes (ξ) of PAAm gel films presenting different swelling states according to equation (3.5).

As shown in Table 4.1 and Figure 4.11, the average mesh size of PAAm films is enhanced both by increasing solvent quality and by decreasing the crosslink degree. The average mesh size of surface-grafted PAAm-0.5 gel films increases from 4.7 nm to 6.3 nm upon decreasing methanol volume fraction from 100% to 0%. In contrast, the average mesh size of PAAm-1.0 gel films is less sensitive to the variation of solvent quality: ξ only varies from 3.2 to 3.4 upon increasing the solvent quality.

<table>
<thead>
<tr>
<th>( V_{\text{methanol}} )</th>
<th>0%</th>
<th>( C_n )</th>
<th>( n )</th>
<th>( l ) (nm)</th>
<th>( Q )</th>
<th>( \xi ) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAAm-0.5</td>
<td></td>
<td>14.8</td>
<td>42.9</td>
<td>0.154</td>
<td>4.25</td>
<td>6.3</td>
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</tbody>
</table>
Table 4.1. Molecular parameters for calculating average mesh size of PAAm gel films in aqueous methanol solution with different solvent quality.

<table>
<thead>
<tr>
<th></th>
<th>$C_n$</th>
<th>$n$</th>
<th>$l$ (nm)</th>
<th>$Q$</th>
<th>$\xi$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAAm-1.0</td>
<td>14.8</td>
<td>19.8</td>
<td>0.154</td>
<td>2.21</td>
<td>3.4</td>
</tr>
<tr>
<td>$V_{methanol}$: 25%</td>
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<td></td>
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<tr>
<td>PAAm-0.5</td>
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<td>42.9</td>
<td>0.154</td>
<td>3.83</td>
<td>6.1</td>
</tr>
<tr>
<td>PAAm-1.0</td>
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<td>19.8</td>
<td>0.154</td>
<td>2.09</td>
<td>3.4</td>
</tr>
<tr>
<td>$V_{methanol}$: 50%</td>
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<tr>
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<td>42.9</td>
<td>0.154</td>
<td>2.97</td>
<td>5.6</td>
</tr>
<tr>
<td>PAAm-1.0</td>
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<td>19.8</td>
<td>0.154</td>
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<td>3.3</td>
</tr>
<tr>
<td>$V_{methanol}$: 75%</td>
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<td></td>
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<tr>
<td>PAAm-0.5</td>
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<td>42.9</td>
<td>0.154</td>
<td>1.77</td>
<td>4.7</td>
</tr>
<tr>
<td>PAAm-1.0</td>
<td>14.8</td>
<td>19.8</td>
<td>0.154</td>
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<td>3.2</td>
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<td>$V_{methanol}$: 100%</td>
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</tr>
<tr>
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<td>14.8</td>
<td>19.8</td>
<td>0.154</td>
<td>1.79</td>
<td>3.2</td>
</tr>
</tbody>
</table>

Figure 4.11. Average mesh size of PAAm gel films in aqueous methanol solution with different solvent quality.

4.2.6 Load-Dependent Pull-off Force of PAAm Brushes at The Glass Transition
Load-dependent adhesion measurements were carried out on PAAm-0 brushes with three different dry thicknesses (40 nm, 133 nm and 276 nm) in aqueous mixtures with a methanol volume fraction of 75%, i.e. at the glass transition. As shown in Figure 4.12 (a), the acquired pull-off force increases with both dry thickness and applied load.

The relatively low pull-off force of the thinnest (40 nm) PAAm brushes suggests that the deformation of the polymeric films is being impeded by the substrate. Consequently, the contact area between the silica probe and PAAm brushes did not notably increase upon increasing applied load. A similar, but less pronounced substrate effect was also observed for polymer brushes with a dry thickness of 133 nm; however, it was not appreciable for the thickest brushes (276 nm) up to a load of 870 nN.

Figure 4.12 (b) shows a cartoon illustrating the contact-area-dependent adhesive behavior of PAAm-0 brushes at the glass transition. The silica probe can penetrate into the collapsed polymer brushes; the deformed volume increases with applied load (in the absence of a substrate effect), resulting in a concomitant increase of contact area during probe-polymer interaction. An analogous contact-area-dependent adhesive behavior was reported by Cho\textsuperscript{78,79} for self-assembled monolayers in a phase-transition state: the chain mobility of monolayers increased with structural disorder, resulting in increased mechanical deformation and larger contact area at a determined load. By fitting the measured adhesion force with respect to different applied loads, the pull-off force is found to be proportional to (applied load)\textsuperscript{2/3}, as shown in Figure 4.12 (a) by the dotted line, which is consistent with the well-known relation between the contact area and applied load according to the contact mechanics theories.\textsuperscript{80} We thus conclude that, in the absence of substrate effects, the pull-off force between a silica microsphere and PAAm-0 brushes at the glass transition with a given grafting density is proportional to the contact area, which increased with increased applied load in pull-off force measurements. However, we cannot determine which regime (JKR or DMT model) applies to this particular system, due to the inaccessibility of the interfacial work of adhesion.
Figure 4.12. (a) Pull-off force of PAAm-0 films as a function of the applied load in aqueous methanol mixtures with 75% methanol measured by CPM (spring constant: 3.02 N/m, radius of silica probe: 12.5 μm, testing speed: 3.97 μm/s). The fitting line represents the relation: $F_{\text{pull-off}} \propto \text{Load}^{2/3}$. (b) Illustration of contact area-dependent pull-off force of PAAm-0 brushes at the glass transition: contact area (green section) increases with the applied load.

4.2.7 Relaxation Behavior of PAAm Brushes at The Glass Transition

Owing to the viscoelastic nature of polymer chains at the glass transition, relaxation of macromolecular chains upon deformation should be time dependent. Thus, we examined the pull-off force of PAAm-0 brushes in 75% methanol by using various indenting speeds. As shown in Figure 4.13, the pull-off force decreases upon increasing the indenting speed for all studied brushes with different thicknesses; especially at high indenting speeds, the pull-off force drops significantly.

At low indenting speeds, the polymer chains had enough time to interact with the silica probe during the loading/unloading process, leading to a small variation of pull-off force upon varying indenting rate. However, as soon as the indenting speed exceeded the relaxation rate of the polymer chains, the tethered PAAm chains were not able to sufficiently interact with the silica probe within the experimental time scale; therefore, a decreased pull-off force was observed (e.g. 133 nm PAAm-0 brushes showed a pull-off
force that decreased from 360 nN to 110 nN upon increasing the testing speed from 0.4 \( \mu \text{m/s} \) to 41.7 \( \mu \text{m/s} \). Similar relaxation-time-dependent adhesion behavior was observed in polystyrene brushes and octadecyltrichlorosilane-based SAMs at the phase-transition state, as reported by Tsujii and Cho, respectively.\textsuperscript{26,78}

![Graph showing pull-off force vs. indenting speed](image)

**Figure 4.13.** Pull-off force of PAAm-0 films measured at different indenting speeds by CPM (spring constant: 3.02 N/m, radius of silica probe: 12.5 \( \mu \text{m} \), applied load: 123.9 nN) in 75\% methanol.

4.2.8 Nanotribological Properties of PAAm Thin Films with Defined Crosslink Degrees in Aqueous Methanol Mixtures

Frictional properties of the tethered PAAm films were measured as a function of crosslink degree and solvent quality by means of colloidal-probe AFM (Figure 4.14). Friction-load plots of all the studied PAAm films in aqueous methanol mixtures showed two main features: (1) friction force is directly proportional to the applied load for the PAAm films in the absence of a glass transition and (2) friction is notably enhanced by the pull-off force of films with brush structures at the glass transition, which is consistent with the well-known relation between friction and adhesion on the nanoscale.\textsuperscript{81-83}
The friction force of PAAm films strongly depends on both crosslink degree and solvent quality. At a given applied load, the friction force of all studied PAAm films increases steadily upon decreasing solvent quality up to a methanol volume fraction of 50%. Then, the friction force increases significantly up to a maximum value at a methanol volume fraction of 75%; finally, it decreases upon further increasing methanol volume fraction (Figure 4.15).
Figure 4.14. Friction-load plots of PAAm films with different crosslink degrees, measured by CPM (spring constant: 0.511 N/m, radius of silica probe: 14 μm, sliding speed: 10 μm/s, stroke length: 5.0 μm) in aqueous methanol mixtures with varying solvent quality. (a) PAAm-0 films (dry thickness: 189 nm). (b) PAAm-0.5 films (dry thickness: 173 nm). (c) PAAm-1.0 films (dry thickness: 217 nm).

In the region where the methanol volume fraction was less than 50%, the friction force is mainly determined by the degree of swelling of the polymer layer. It has been previously shown that the effectiveness of lubrication decreases as the solvent quality decreases, which leads to a collapse of brush. Similarly, crosslinking, which leads to a less extended brush system, also reduces the lubricity of the system.

At volume fractions of methanol between 50% and 75%, the PAAm brushes and gels collapsed further. As shown in Figure 4.15, the friction force of brushes and gels sliding against a silica microsphere increased dramatically with the worsening solvent quality in this region, correlating with the collapse of the PAAm films. In particular, a large pull-off force was observed for brushes reaching the glass transition, which significantly impacts their frictional behavior. The large friction force between a silica probe and PAAm-0 at the glass transition, as observed in Figure 4.14 (a), was primarily due to the contribution from both adhesion and increased energy dissipation as the chains collapsed. However, compared to brushes, gels did not show such a prominent pull-off force owing to their
crosslinked structure; therefore, the large friction force between silica probe and PAAm-1.0 in 75% methanol was determined by sliding friction. It has to be pointed out that the energy dissipation due to sliding friction should be similar for brushes and gels in 75% methanol since all these films collapsed, reaching similar wet thicknesses (Figure 4.3); consequently, the larger friction force between silica probe and PAAm-0 brushes compared to the gels was primarily regarded as the result of strong adhesion.

Figure 4.15. 3-D Friction plot of PAAm films with different crosslink degrees at a given applied load of 84.5 nN, measured by CPM, data extracted from plots shown in Figure 4.14.

Upon increasing the methanol volume fraction from 75% to 100%, the PAAm films swell to a small extent, and a minor drop in the friction force is measured. As shown in Figure 4.5, the pull-off force between the brushes and the silica probe was greatly reduced. Hence, in this case, it is purely the frictional dissipation process that determines the friction force between the silica counter-surface and the PAAm films as shown in Figure 4.15.

4.3 Conclusions

Surface-tethered PAAm films with nearly identical chemical compositions and various crosslink degrees were fabricated and characterized; their swelling behavior in a series of
aqueous methanol mixtures were studied by means of ellipsometry and AFM indentation. Adhesion properties of the polymeric films were examined as a function of solvent quality and crosslink degree by means of colloidal probe microscopy. Crosslinked films efficiently prevented adhesion in water-methanol mixtures over the entire composition range studied. However, for films with brush structures, large pull-off forces were observed in their most collapsed state, owing to the films undergoing a glass transition. Morphologies of PAAm films with different crosslink degrees in their most collapsed state were explored, in order to clarify the influence of nano-structure on adhesion behavior; the network structure at the molecular level greatly reduced the contact area during adhesion measurements, resulting in a significantly decreased pull-off force. Investigation of adhesive behavior of brushes at the solvent-induced glass transition also showed that that the pull-off force was significantly affected by contact area and testing speed during pull-off force measurement. Finally, nanotribological measurements of PAAm films with different crosslink degrees were carried out in aqueous methanol mixtures. The tribological behavior of these films was determined by the complex interplay between adhesion and film structure, which were both modified by solvent quality and crosslink degree.

4.4 References

84. Nalam, P. C. Ph.D. Thesis; Department of Materials, ETH Zurich, Switzerland, 2012.
Chapter 5*

Nanotribological Implications of Surface-Grafted Stratified Poly(acrylamide) Films

Surface-grafted stratified PAAm films have been synthesized by reinitiating polymerization on homogeneous films encompassing brush or gel structures, resulting in layered structures such as brush-gel or gel-brush. FT-IR and ellipsometry measurements have been carried out, in order to verify the overall composition and thickness variation upon reinitiation. Measurements of the mechanical, adhesive and frictional properties assisted in qualitative estimation of the structure of the resultant film in the direction perpendicular to the surface. In particular, it was observed that the reinitiation location as well as the real structure of stratified films strongly depend on the synthetic conditions, e.g. solvent quality and the films’ structure prior to reinitiating polymerization. Nanotribological properties of the stratified PAAm films in water were studied by means of colloidal-probe microscopy. It is shown that the structure of the top layer of the grafted films strongly influences the friction properties of the stratified films. Effects due to hydrodynamic forces during sliding were also observed.

5.1 Introduction

Surface coatings with heterogeneous structures are of particular interest in tribology and biomechanics, owing to their graded mechanical responses during normal or sliding contact. Many efforts have been made to fabricate structural (composite) materials with a

* This chapter has been submitted as a paper:
The major part of this work was done by Ang Li, including all experiments and writing of this chapter. Shivaprkash N. Ramakrishna conducted CPM-based measurements. Prathima C. Nalam, Edmondo M. Benetti and Nicholas D. Spencer contributed in discussions and further correcting the chapter.
(sub-) micrometer gradient periodicity in length, in order to resist contact deformation as well as damage by reducing stress concentration at the contact location.$^{1,2}$

Stratification is the building up of layers in the vertical direction, and it is widely adopted in many biological systems, being one of the important components in the family of graded structures. For instance, human skin consists of an epidermis layer built upon the dermis and foundation layers (hypodermis). Keratinizing epithelial cells representing an elastic layer with low modulus are located at the bottom of the epidermis layer. A dead cell layer with higher modulus, the *stratum corneum*, resides on the outermost layer of the epidermis (skin) and the inner lining of the mouth, where saliva-based aqueous lubrication is active.$^3$ This stiff layer is well suited to areas on the skin that are subject to constant abrasion, as it can be sequentially sloughed off and replaced by regenerative mechanisms, before the inner layer is exposed. The stratified epithelium acts as the body’s major barrier against an inhospitable environment, by preventing pathogens from entering, making the skin a natural barrier to infection.$^4$

The synthesis of soft-matter-based films mimicking the nano-graded structures found in nature still represents a challenging task. To the best of our knowledge, such investigations have barely been documented. The work conducted by Tsukruk briefly discuss a prototype for stratified films.$^5,6$

The characterization of stratified films, especially when focusing on buried structures of polymeric films on a supported substrate is a challenging problem. Although real-space analytical techniques such as atomic force microscopy (AFM) enable straightforward access to surface properties in two dimensions, analysis of physical properties in the third dimension can more readily be achieved by reciprocal-space analysis techniques such as grazing incidence small-angle scattering (GISAS), or X-ray and neutron reflectivity, which determine the density profile of materials perpendicular to the sample surface. However, probing the vertical architecture of polymer nano-films with such techniques normally requires complex contrast-enhancing methods (isotopic labelling), which restricts their feasibility in the structural characterization of thin polymeric films.$^7$
In this chapter, we describe the fabrication of stratified PAAm films by reinitiating pre-synthesized homogeneous PAAm films with a defined crosslink degree. Two types of stratified films comprising a polymer brush on top of a gel structure or a gel on top of a polymer brush were synthesized. These structures represent a two-layered graded film. FT-IR in transmission mode was conducted to confirm the inclusion of crosslinker into polymer layers upon reinitiation. Furthermore, AFM imaging of these films in water was carried out, in order to understand their interfacial structure in a good solvent. In addition, we introduced a methodology for rapidly characterizing the structure of the stratified films by investigating both pull-off force and frictional behavior in solvents of different qualities. The pull-off-force measurement of PAAm films in a bad solvent provides direct evidence about the interfacial structure of the films, as already discussed in Chapter 4. The measurement of friction forces, as well as the shape of the friction loop, can provide additional insights as to the interior structure of the stratified films. In particular, we have successfully distinguished the different structures of PAAm films upon fabricating a gel layer on top of brush layers in solvents of different qualities, which in turn determines their distinct mechanical/tribological behaviors. Finally, frictional forces of the stratified PAAm films were measured as a function of sliding velocity and applied load, using colloidal probe microscopy (CPM). These measurements have yielded fundamental knowledge concerning the structure-dependent frictional response of stratified polymer films on the nanoscale.

5.2 Results and Discussion

5.2.1 Synthesis of PAAm Films with Stratified Structures

The homogeneous PAAm films were prepared by using a ‘grafting-from’ strategy on an iniferter-modified silicon substrate, as described in Chapter 3. Stratified PAAm films were fabricated with UVLED SIP, by reinitiating the dormant species (dithiocarbamate moieties) at the chain ends of pre-synthesized homogeneous tethered brushes (PAAm-0) or gels (PAAm-1) either in an aqueous methanol (volume fraction: 75%) solution containing monomer/crosslinker, or in a methanol-free aqueous monomer solution,
respectively. The resulting stratified PAAm films have a brush-gel (PAAm-0-1_{methanol}) or
gel-brush (PAAm-1-0) structure, which are shown in Figure 5.1.†

The stratified films in the text are represented as PAAm-a-b, where the total number of
letters indicate the number of layers; the value of ‘a’ or ‘b’ indicates the wt% of
crosslinker in the feed used during synthesis of the corresponding layer.

![Figure 5.1. Surface-grafted PAAm films with homogeneous and stratified structure. (a) PAAm-1, (b) PAAm-1-0 (reinitiated in water), (c) PAAm-0, (d) PAAm-0-1_{methanol} (reinitiated in 75% aqueous methanol solution).](image)

Due to our inadequate knowledge of the location of reinitiating SIP within the initial
polymeric layer, both the thickness of homogeneous PAAm films and the stratified film
thickness following the sequential photografting step in this study are converted to the
mass gained ($\Delta \delta$) according to the equation below:

$$\Delta \delta = \rho \times \Delta d$$  \hspace{1cm} (5.1)

where $\rho$ is the poly(acrylamide) density (0.8 g/cm³) and $\Delta d$ is the change of thickness.

5.2.2 Characterization of PAAm Films with Stratified Structures

FT-IR measurements were performed to chemically characterize the stratified films and
to confirm the incorporation of crosslinker in the PAAm films. As shown in Figure 5.2,
all FT-IR spectra of the PAAm films with different architectures show a similar profile

† The structure analysis of stratified films upon reinitiating brush films in water (PAAm-0-1_{water}) is
discussed in section 5.2.6.
comparable with the previous results and indicate an overall constant chemical composition throughout the films. The strong bands at 3338 and 3200 cm\(^{-1}\) are related to N–H asymmetric and symmetric stretching of the NH\(_2\) repeat unit, respectively. Both amide I and amide II bands from monomer and crosslinker can be found between 1480 and 1800 cm\(^{-1}\). The only difference among these spectra is the peak at 1520 cm\(^{-1}\) (amide II band), characteristic of the crosslinker (indicated by arrows). The characteristic peak of crosslinker is observed for the homogeneous PAAm-1 gels (a). The intensity of this signal decreased upon grafting brushes on top of gel layers (b), which indicates the consecutive grafting of a free PAAm brush upon reinitiation. The characteristic peak of crosslinker was not detected for homogeneous PAAm-0 brushes (c), but the intensity of the characteristic crosslinker peak increases for PAAm-0-1\(_{\text{methanol}}\) films (d) upon sequential photografting in the presence of bisAAm. This last finding indicated the inclusion of crosslinked structure upon reinitiation.

**Figure 5.2.** FT-IR spectra of homogeneous and stratified PAAm films in dry state (absorbance is normalized according to the maximum intensity at 1658 cm\(^{-1}\), inset is the zoomed absorbance peak indicated by the arrows and y-axis in inset is shifted for clarity).

(a) PAAm-1, (b) PAAm-1-0, (c) PAAm-0, (d) PAAm-0-1\(_{\text{methanol}}\).

Surface morphologies of the homogeneous and stratified PAAm films in water were obtained using AFM. Tapping-mode images depict the interfacial morphology that is
later subjected to mechanical/tribological measurements (Figure 5.3). The homogeneous PAAm-1 (a) shows large roughness (RMS: 5.5 nm) due to clustering of crosslinked chains. The roughness of the stratified PAAm-1-0 (b) decreases by 91% (RMS: 0.5 nm) due to the presence of the brush layer on top of the grafted gel. The PAAm-0 (c), homogeneous brushes, present a low value of roughness (RMS: 0.8 nm). The exposed interface of stratified PAAm-0-1_methanol shows an increased RMS value if compared to PMAA-0 approximately reaching 4.6 nm, due to the growth of crosslinked gel on top of the polymer brushes. In addition, it is worth noting that the exposed surface of PAAm-0-1_methanol (d) shows lower RMS values when compared to homogeneous PAAm-1 (a). It is likely that the larger network size of PAAm-0-1_methanol compared to PAAm-1, which was caused by the decrease in the amount of crosslinks upon reinitiation (low reinitiation efficiency), influenced the measured RMS roughness.

**Figure 5.3.** Morphologies of homogeneous and stratified PAAm films were imaged in a closed liquid cell with a Cypher™ AFM (Asylum Research, Santa Barbara, USA) in water. A triangular-shaped cantilever with a silicon nitride tip (spring constant: 0.32 N m⁻¹, model: DNP-S, Veeco, USA) was used in fluid AC mode to acquire height images over the scanning area (5 μm × 5 μm) (scale bar: 1 μm). (a) PAAm-1, (b) PAAm-1-0, (c) PAAm-0, (d) PAAm-0-1_methanol.
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It is important to verify the structures of the synthesized films, prior to investigation of the influence of film structure on mechanical properties. Therefore, we conducted measurements on PAAm films with four representative structures, i.e. homogeneous brush PAAm-0, homogeneous gel PAAm-1, stratified brush-gel PAAm-0-1\textsubscript{methanol} and stratified gel-brush PAAm-1-0, in order to distinguish their rigidity (modulus), adhesion and frictional response on application of external load.

5.2.3 Nanoindentation Studies of PAAm Films with Stratified Structures

Colloidal probe microscopy (CPM) was employed in an aqueous environment to investigate the mechanical properties of the stratified films. Figure 5.4 shows force vs. indentation depth plots for homogeneous and stratified films after each photografting step, i.e. gel and gel-brush in (a); brush and brush-gel in (b). Due to the presence of crosslinker (bisAAm), PAAm-1 gels have higher modulus (the slope of force and penetration depth during the first 10\% curve after the contact) in comparison to the corresponding grafted polymer brushes (PAAm-0).\textsuperscript{9} Also, the slope after initial indentation for grafted PAAm-1 films increases sharply for the measured force-penetration curves, indicating the lower swelling ratio of the gels in aqueous environment in comparison to brushes (PAAm-0). The steep increase in the force with increase in penetration depth indicates the influence of the underlying substrate. Upon grafting a brush layer on top of the PAAm-1 films, the indentation curve of PAAm-1-0 significantly shifts to the right, revealing the increased wet thickness due to the presence of a highly compliant and swollen brush layer, as shown in Figure 5.4 (a). In contrast, upon grafting a gel layer after the brush films, the indentation curve of PAAm-0-1\textsubscript{methanol} shows a large shift of the curve towards lower indentation depths implying a reduced overall swelling of the stratified films, as indicated in Figure 5.4 (b). The relative shrinking of PAAm-0-1\textsubscript{methanol} films is presumably caused by the crosslinking between grafted chains on top of the underlying brush layer, during the reinitiation process in 75\% aqueous methanol solution.
Figure 5.4. Indentation force curves of homogeneous and stratified PAAm films measured by CPM (spring constant: 1.28 N/m, radius of silica probe: 9.1 \( \mu \)m) in water. Dry mass of polymer films on silicon substrate: (a) PAAm-1: 148 mg/m\(^2\), PAAm-1-0: 148-30 mg/m\(^2\), (b) PAAm-0: 52 mg/m\(^2\), PAAm-0-1_{methanol}: 52-108 mg/m\(^2\).

5.2.4 Interfacial Structure Analysis of Stratified PAAm Films by Conducting Pull-off Force Measurements at the Solvent-Induced Glass Transition

As demonstrated in the previous chapter, pull-off measurements were used to investigate adhesion of PAAm brushes at their glass transition. The adhesion characteristics can be further used to study the interfacial grafted architecture, i.e. brush layers show a significant adhesion and crosslinked films show a negligible adhesion in 75% aqueous methanol solution. In Figure 5.5 (a), a pull-off force of PAAm-1 films in 75% aqueous methanol solution shows a very small value (0.5 nN), indicating the presence of crosslinked interfacial structure. Additional grafting of brush layer on top of the gel films resulted in an increase of pull-off force up to 40 nN as indicated in Figure 5.5 (a), confirming the existing of the dangling chains (brushes) at the interface of these stratified films. In contrast, according to Figure 5.5 (b), starting PAAm-0 films show a pull-off force of 85 nN, indicating the strong interaction between colloidal probe and free brush chains at their glass transition. However, the pull-off force of PAAm-0-1_{methanol} films in 75% aqueous methanol solution reduces to a negligible value (0.3 nN), which suggests the stratified PAAm-0-1_{methanol} films have a well-defined interfacial crosslinked structure.
Figure 5.5. Pull-off forces of homogeneous and stratified PAAm films measured by CPM (spring constant: 1.28 N/m, radius of silica probe: 9.1 μm) in 75% aqueous methanol solution (only retracting curves are shown). Dry mass of polymer films on silicon substrate: (a) PAAm-1: 148 mg/m², PAAm-1-0: 148-30 mg/m², (b) PAAm-0: 52 mg/m², PAAm-0-1\textsubscript{methanol}: 52-108 mg/m².

The initiation efficiency, initiator residue (unreacted initiator) at substrate surface, and the presence of dormant species at chain ends within the first layer of polymer films are all decisive parameters for the reinitiation of UV-LED SIP. The first two factors rely on the chemical nature of the iniferter and the irradiation intensity, respectively, which are considered to be approximately constant during the reinitiating process for this study.

For the purposes of grafting polymer brushes by reinitiation of UVLED-SIP on top of highly crosslinked gels, the average mesh size of the gels (insensitive to the variation of solvent quality, according to Chapter 4) is 3.3 ± 0.1 nm, which does not provide a significant steric barrier for the monomer diffusion (Kuhn length of acrylamide: 0.3 nm). This stiff network cannot prevent monomers from accessing the residual iniferter on substrate; therefore, the reinitiation occurs also at the substrate. Highly swollen brush chains interpenetrate and further stretch away from the starting gel layers upon reinitiation, resulting a gel-brush structure.

In contrast, grafting a crosslinked layer on top of a polymer brush via reinitiation is a challenging fabrication strategy. Theoretical and experimental studies on polymer
brushes have shown that the distribution of free end groups in the polymer brushes covers the entire layer. This has been found to be dependent on solvent quality, under equilibrium conditions. The chain-end distribution for a polymer brush shows a maximum located within the films in a good solvent; however, in a solvent with poor quality the maximum probability to find the chain ends lies at the outer surface of the films. Apart from the solvent-quality-dependent chain-end distributions, the degree of swelling of a brush film is also strongly influenced by the solvent quality, which also influences the reinitiation process.

When the reinitiation is carried out in a bad solvent, the bottom, substrate-bonded brush layers strongly collapse, exposing the reinitiable end groups at the outmost layer of the collapsed films for further polymerization. Following this particular strategy, stratified films with a brush-gel structure are thus obtained. One might expect no explicit horizontal interface between two layers in stratified films, since the dormant species could be reinitiated in the monomer (crosslinker) solutions throughout the entire pre-synthesized films. On the other hand, the feed of monomer (crosslinker) approaches from the solution above, and those chain-ends closest to the top will promptly react first. The balance between these two effects is kinetically determined, and will influence the sharpness of the composition changes between brush and gel within the film architecture.

5.2.5 Aqueous Tribology of Stratified PAAm Films on the Nanoscale

In addition to the characterization of interfacial structure of stratified films by investigating the pull-off force at the glass transition, the inner structure of these films can be studied by examining the static and kinetic friction regions in their friction loops. Figure 5.6 depicts the friction loops acquired for PAAm films with different architectures (sliding distance: 1 μm, sliding speed: 2 μm/s). Both PAAm-0 (green curve) and PAAm-1-0 (blue curve) films present free chains at the interfacial layer where contact occurs and show tilted friction loops with a small hysteresis, reflecting their highly lubricious nature. When the colloid probe is sliding against soft polymer brushes, it appears that the brushes tilt as the cantilever moves laterally giving rise to tilted friction loops. On the other hand, the rigid PAAm-1 (red curve) gel films show a friction loop with a stable sliding friction
(horizontal part in friction loop) after overcoming an initial static friction (vertical part in friction loop), and their high friction is due to the energy dissipation during tribological test upon crosslinking the whole films. The stratified PAAm-0-1_methanol (black curve) films, however, show a brush-like friction loop according to Figure 5.6. We presume that as long as the colloidal probe rubs on the brush-gel films over a short distance (1 μm), the sliding contact between counter surface and stratified films is not in steady state and thus it is the static friction that dominates the tribological process. Hence, the acquired friction loop of PAAm-0-1_methanol films is exclusively determined by the underlying brush layers and the interfacial architecture (gels) of the stratified films.

**Figure 5.6.** Representative friction loops of homogeneous and stratified PAAm films measured by CPM (spring constant: 1.28 N/m, radius of silica probe: 9.1 μm) in water at a load of 251 nN with a sliding distance of 1 μm (sliding speed: 2 μm/s). Dry mass of polymer films on silicon substrate: PAAm-1: 148 mg/m², PAAm-1-0: 148-30 mg/m², PAAm-0: 52 mg/m², PAAm-0-1_methanol: 52-108 mg/m².

Upon maintaining the identical load and increasing the sliding distance to 5 μm, the PAAm-1, PAAm-0 and PAAm-1-0 films preserve the original shape of the friction loops as recorded at smaller sliding distance (Figure 5.6). However, the stratified PAAm-0-1_methanol shows a significant change in the friction loop from a brush-like shape (Figure 5.6) to a gel-like shape (Figure 5.7). The PAAm-0-1_methanol films present a significant initial
static friction (with a sliding distance of 1.5 μm according to Figure 5.7) before the sliding friction (with a sliding distance of 3.5 μm according to Figure 5.7) sets in. The static friction is presumably overcome by extending effective sliding distance in this case, while the sliding friction of the stratified brush-gel films is considered from the energy dissipation during sliding contact with the interfacial gel layer under steady state. It is presumed that the difference of sliding speeds (2 μm/s and 10 μm/s) in Figure 5.6 and 5.7 is too small to influence the tribological responses of stratified PAAm-0-1 methanol films under given sliding distances.

Figure 5.7. Representative friction loops of homogeneous and stratified PAAm films measured by CPM (spring constant: 1.28 N/m, radius of silica probe: 9.1 μm) in water at a load of 251 nN with a sliding distance of 5 μm (sliding speed: 10 μm/s). Dry mass of polymer films on silicon substrate: PAAm-1: 148 mg/m², PAAm-1-0: 148-30 mg/m², PAAm-0: 52 mg/m², PAAm-0-1 methanol: 52-108 mg/m².

Lateral-force measurements were conducted for stratified PAAm films by means of CPM, in order to investigate the effect of film structure on the nanoscale frictional properties of the films (in the presence of no wear). In Figure 5.8, the load dependence of friction forces is plotted for the four studied structures, the homogeneous PAAm-0 and PAAm-1 films showing the lowest and highest friction values, respectively. PAAm-0 is a low-friction surface due to brush-assisted lubrication (green curve). However, PAAm-1 gels
(red curve) show high frictional force due to the increased dissipation upon crosslinking. As for the PAAm-1-0 films (blue curve), they show a low but slightly increased friction force in comparison to the homogeneous brush films (green curve). In spite of having similar interfacial structure, the decreased grafting density for polymer brushes in PAAm-1-0 upon reinitiation results in higher friction forces.\textsuperscript{17} In contrast, the PAAm-0-1\textsubscript{methanol} films show a frictional property similar to the homogeneous grafted gels however with a slight reduction in the frictional forces (black curve), due to lower crosslink density of gels layer upon reinitiation for stratified brush-gel films.

From the results obtained here, we conclude that the tribological properties of the stratified PAAm films in aqueous environments are mainly determined by their interfacial structure where the contact sliding takes place; the interior build-up of these films, seems to not play a major role on their frictional behaviors at nanoscale.

\textbf{Figure 5.8.} Friction of homogeneous and stratified PAAm films measured by CPM (spring constant: 1.28 N/m, radius of silica probe: 9.1 μm, sliding distance: 5 μm, sliding speed: 10 μm/s) in water. Dry mass of polymer films on silicon substrate: PAAm-1: 148 mg/m\textsuperscript{2}, PAAm-1-0: 148-30 mg/m\textsuperscript{2}, PAAm-0: 52 mg/m\textsuperscript{2}, PAAm-0-1\textsubscript{methanol}: 52-108 mg/m\textsuperscript{2}.

The dependence of frictional force of both homogeneous and stratified PAAm films as a function of shear velocity in aqueous medium is shown in Figure 5.9. Friction force is
seen to increase with the sliding speed for all the investigated films. PAAm films with a gel structure in top interfacial layer (PAAm-1 and PAAm-0-1\textsubscript{methanol}) show high friction at all measured sliding speeds. In contrast, the frictional force of PAAm films with brush structures at the interface (PAAm-0 and PAAm-1-0) is relatively low, due to the effective brush-assisted lubrication. The friction of all studied homogeneous and stratified PAAm films increases upon increasing the sliding speed, which is likely due to hydrodynamic drag of the solvent on the probe. The shear-velocity-dependent frictional behavior of both homogeneous and stratified PAAm films resembles the nanotribological characteristics of other brush systems in various media upon varying sliding speed.\textsuperscript{18,19}

**Figure 5.9.** Dependence of friction of homogeneous and stratified PAAm films on sliding speed measured by CPM (spring constant: 1.28 N/m, radius of silica probe: 9.1 μm) in water at a load of 84 nN with a sliding distance of 5 μm. Dry mass of polymer films on silicon substrate: PAAm-1: 148 mg/m\textsuperscript{2}, PAAm-1-0: 148-30 mg/m\textsuperscript{2}, PAAm-0: 52 mg/m\textsuperscript{2}, PAAm-0-1\textsubscript{methanol}: 52-108 mg/m\textsuperscript{2}.

### 5.2.6 Structural Analysis of Stratified PAAm Films upon Reinitiating Brush Films in A Good Solvent

In this section, we describe the structural characterization of PAAm films that were fabricated by photografting gels layers on brush layers in a good solvent (pure water). In
order to distinguish these from the previously discussed PAAm-0-1\text{methanol} films fabricated by reinitiating in 75\% aqueous methanol solution, we use PAAm-0-1\text{water} here as an acronym to represent films that have been fabricated by reinitiating in pure water. The approaching force curves for homogeneous PAAm-0 and the corresponding stratified PAAm-0-1\text{water} films are shown in Figure 5.10. The force curves for PAAm-0 and PAAm-0-1\text{water} in their swollen state almost overlap, despite the stratified films showing a mass increase of 42 mg/m\(^2\) upon reinitiation, according to ellipsometry. FT-IR spectra of the PAAm-0-1\text{water} films also confirm the successful incorporation of the crosslinker upon reinitiation as shown in Figure 5.11. We therefore presume that the reinitiation process in pure water takes place on the \textit{iniferter}-rich silicon substrate rather than at the interface of the starting PAAm-0 films, as the sparsely grafted brush film in good solvent provides low concentration end groups for further crosslinking reaction. The high degree of swelling of PAAm brushes in pure water (\(Q = 26\)) allows rapid diffusion of monomer species (AAm and bisAAm) through the starting layers during the reinitiation process. This leads to the secondary grafting step occurring chiefly at the locations where the \textit{iniferter} can be found in highest concentration—at the substrate.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{force_curves.png}
\caption{Force approaching curves of PAAm-0 and PAAm-0-1\text{water} films measured by CPM (spring constant: 0.51 N/m, radius of gold-coated silica probe: 8.7 \(\mu\)m) in water. Dry mass of polymer films on silicon substrate: PAAm-0: 31 mg/m\(^2\), PAAm-0-1\text{water}: 31-42 mg/m\(^2\).}
\end{figure}
Figure 5.11. FT-IR spectra of PAAm-0 and PAAm-0-1\textsubscript{water} films in dry state (absorbance is normalized to the maximum intensity peak at 1658 cm\(^{-1}\)).

Pull-off force measurements for PAAm-0 and PAAm-0-1\textsubscript{water} films were conducted in 75% aqueous methanol solution, in order to further examine their interfacial structure. As seen in Figure 5.12, homogeneous PAAm-0 and stratified PAAm-0-1\textsubscript{water} films have similar pull-off forces. These data suggest that reinitiation process occurs on residual \textit{iniferter} on the substrate, which leads to a stratified film with a gel-brush structure instead of a brush-gel structure.
Figure 5.12. Representative force curves of (a) PAAm-0, (b) PAAm-0-1\textsubscript{water} and (c) their statistic pull-off forces measured by CPM (spring constant: 0.51 N/m, radius of gold-coated silica probe: 8.7 μm) in aqueous methanol solution (volume fraction of methanol: 75%). Dry mass of polymer films on silicon substrate: PAAm-0: 31 mg/m\textsuperscript{2}, PAAm-0-1\textsubscript{water}: 31-42 mg/m\textsuperscript{2}.

The frictional properties of PAAm-0 and PAAm-0-1\textsubscript{water} films were also studied by colloidal probe microscopy in water. As shown in Figure 5.13, both films present similar frictional behavior with a low coefficient of friction (0.05). This result further supports the argument of identical interfacial structures of PAAm-0 and PAAm-0-1\textsubscript{water} when sequential polymerization is carried out in a good solvent, such as pure water. Kilbey et al.\textsuperscript{20,21} developed a kinetic model describing the reinitiation ability (in good solvent) of polymer brushes grown by surface-initiated photoiniferter-mediated polymerization. Polymerization kinetics were strongly influenced by the light intensity and concentration of deactivator (dithiocarbamate). Without adding deactivator to the system during reinitiating polymerization in a good solvent, the generation of mixed polymer brushes on a substrate is theoretically predicted. This phenomenon is thus favored compared to the formation of diblock copolymer brushes.
Figure 5.13. Friction of PAAm-0 and PAAm-0-1\textsubscript{water} measured by CPM (spring constant: 0.51 N/m, radius of gold-coated silica probe: 8.7 μm) in water with a sliding distance of 5 μm (sliding speed: 10 μm/s). Dry mass of polymer films on silicon substrate: PAAm-0: 31 mg/m\textsuperscript{2}, PAAm-0-1\textsubscript{water}: 31-42 mg/m\textsuperscript{2}.

In a good solvent, grafting of a crosslinked layer on a polymer brush film substantially takes place on the residual inhibitor on the substrate surface. This is due to the combined effects of low grafting density of the brush layer (and thus facile diffusion of monomers), low initiation efficiency at the chain ends\textsuperscript{22} as well as competition from a large number of available inhibitor-residual sites on the substrate. Therefore, the corresponding brush films upon reinitiation possess a gel-brush structure rather than an expected brush-gel architecture. Analogously, Foster observed the internal structure of the diblock copolymer brushes grown via ATRP upon reinitiation in a good solvent by conducting neutron scattering experiments. The top block was found to be substantially in the region adjacent to the substrate and the resulting polymer films differed from their ideal structures.\textsuperscript{23}

The reinitiation conditions greatly influence the architecture of the resulted polymer films (Figure 5.14). Our results suggest that ellipsometry and FT-IR fail to reveal the true structure of these surface-grafted polymer films. Moreover, this study also suggests that caution should be used in assuming formation of diblock copolymer brushes upon
reinitiating polymerization, unless the appropriate structural characterization is performed. This is especially the case when starting with polymer brushes in a good solvent. This is also valid for other controlled radical polymerization, such as ATRP, which, on a flat surface, has an approximate initiation efficiency of 10%.²⁴

![Proposed grafting mechanism of stratified PAAm films through surface-initiated photoiniferter-mediated polymerization upon reinitiation.](image)

**Figure 5.14.** Proposed grafting mechanism of stratified PAAm films through surface-initiated photoiniferter-mediated polymerization upon reinitiation.

### 5.3 Conclusions

In this chapter, the fabrication of stratified PAAm films with gel-brush and brush-gel structures by sequential SIP was reported. FT-IR measurement and AFM imaging were employed in order to study the chemical composition and the interfacial morphologies of resulted films, respectively. Mechanical properties of these surface-grafted films were further studied by CPM-based nanoindentation in water, which showed the different swelling behaviors upon reinitiating from the corresponding homogeneous films. Pull-off force measurements of the stratified PAAm films were carried out in 75% aqueous methanol solution, in order to explore their interfacial structures. The shape of the friction loops for these polymer films were examined with respect to different sliding distances under identical applied load, so as to distinguish the inner structure of the stratified films from their static and kinetic sliding behavior. It was found that frictional forces of the
stratified PAAm films in an aqueous environment are dominated by their interfacial structure, as well as external shear velocity under steady sliding. Moreover, a novel methodology based on combined nanoindentation, adhesion and friction measurements was used, in order to probe the architecture of tethered polymer films. This strategy successfully distinguishes the structures of stratified films formed upon reinitiating polymerization on brush films in solvents with different quality.

5.4 References

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Chapter 6*

Tuning Surface Mechanical Properties by Amplified Polyelectrolyte Self-Assembly: Where ‘Grafting-From’ Meets ‘Grafting-To’

The interaction has been studied of surface-tethered weak polyacid brushes, poly(methacrylic acid), with a weak polybase poly(l-lysine)-graft-poly(ethylene glycol), in solution. The grafted polyacid brushes, grown directly from the silicon substrate by UVLED surface-initiated polymerization, acts as a nanotemplate for the solution-phase polybase, which penetrates into the brushes, forming a polyelectrolyte complex (PEC), whose mechanical and nanotribological properties are markedly influenced by the electrostatic assembly conditions. The mechanical effects are amplified due to the architecture of the specific polybase used, which contributes approximately 2k Da per unit charge to the overall system, resulting in an efficient filling of the polyacid brushes, which thus acts as a scaffold. The distribution of the adsorbed copolymers in the PEC films has been investigated by means of confocal microscopy. The unique structure of the PEC films provides a system whose mechanical and nanotribological properties can be tuned over a wide range.

6.1 Introduction

* Part of this chapter is published in:

The major part of this work was done by Ang Li, including all experiments and writing of the manuscript. Shivaparakash N. Ramakrishna conducted CPM-based mechanical and frictional measurements. Tobias Schwarz carried out the confocal fluorescence microscopy measurements. Edmondo M. Benetti and Nicholas D. Spencer contributed in discussions and further correcting the paper.
Surface modification (of organics, inorganics and metals) by adhering polymer species with well-defined structures is a highly desirable approach to tailoring interfacial properties for specific applications. In order to realize this goal, different fabrication strategies have been proposed during the last two decades. Both the controlled grafting of polymer chains (either adsorbed from solution or grown from the substrate to form polymer brushes)/gels\textsuperscript{1-6} and the fabrication of polymer multilayers\textsuperscript{7} have been extensively investigated, as two major examples. The former approach involves tethering polymer chain ends at interfaces, while the latter method features the layer-by-layer (LbL) assembly of oppositely charged macromolecules. These fabricated thin films showed well-defined architectures and have been applied to the modification of biomaterials or, alternatively, for the fabrication of three-dimensional nano-objects for drug-delivery or advanced sensing devices (e.g. nanoparticles, quantum dots).\textsuperscript{8-12}

An emerging surface-modification strategy that combines the two approaches of surface grafting and charge-based assembly is the so-called polyelectrolyte self-assembly, where grafted polyelectrolyte act as receptors for oppositely charged polymer chains that adsorb from solution. This approach has been shown to enhance the control over the films’ composition and thickness to nanometer precision. In this context of integrating ‘grafting-from’, ‘grafting-to’ and LbL techniques, Rühe et al. pioneered the methodology by assembling poly(4-vinyl-N-methylpyridinium) iodide on poly(methacrylic acid) (PMAA) brushes. The generated films were thus composed of surface-attached polyelectrolyte complexes (PECs), and displayed film thicknesses ranging from a few to several tens of nanometers, and could act as starting platforms for polyelectrolyte multilayers.\textsuperscript{13}

Moya et al. additionally exploited similar PEC films for templating 3D structures featuring hollow patterns and ledges on the nanoscale, and demonstrated the possibility of fabricating extended architectures, using a grafted polymer layer as a scaffold.\textsuperscript{14} The characteristics of the grafted layer (i.e. grafting density or chain length) have been shown to influence the assembly of polyelectrolyte from solution, which in turn determine the properties of the subsequently fabricated multi-layered films, as reported by Portinha and Charlot.\textsuperscript{15}
Inspired by these preliminary reports, our study focuses on the fabrication of grafted PEC films by the electrostatic-driven assembly of poly(l-lysine)-graft-poly(ethylene glycol) (PLL-g-PEG) into poly(methacrylic acid) (PMAA) brushes, that had been previously grafted from 2D surfaces. Graft copolymers with a positively charged PLL backbone and PEG side chains have been reported to form ultra-thin films and act as widely applicable surface modifiers for a variety of negatively charged surfaces (ranging from glass to titania) and have shown excellent biopassive and lubricating properties.\textsuperscript{16,17} In this study we assembled PLL-g-PEG species into PMAA grafts to form PEC films and this self-assembly mechanism was studied under different conditions. The generated PEC films presented variable thicknesses depending on the assembly conditions, which ranged from a few tens to several hundred nanometers. The mechanical and nanotribological properties varied noticeably from the pristine PMAA brushes to the saturated grafted PEC films. Furthermore, the PEC films demonstrated fully reversible characteristics following salt-driven desorption of PLL-g-PEG adsorbents from the brush scaffolds. The morphologies and structures of these films were further investigated by using atomic force microscopy (AFM) and confocal fluorescence microscopy, in order to gain additional insights into the architecture of the films.

In this work, we propose a general approach to generating grafted PEC films with controlled thickness, presenting variable and reversible interfacial and mechanical properties. These effects can be amplified by the use of polybase architectures that have an intrinsically high mass per unit charge. Grafted PECs show promise for further application in the fabrication of multifunctional, quasi-3D structures that may impact a wide range of technologies ranging from the tailoring of biomaterial interfaces, to the development sensing platforms and the fabrication of intelligent membranes.

### 6.2 Results and Discussion

#### 6.2.1 Adsorption Kinetics of Grafted PEC Films

The adsorption behavior of PLL-g-PEG in PMAA brush platforms of different film thicknesses (chain lengths) was studied by VASE and is compared to the adsorption
behavior of PLL-g-PEG on bare silicon oxide (Scheme 6.1 and Figure 6.1). In the latter case, graft copolymers showed an initial fast adsorption, followed by a slowing down of the film growth rate (inset in Figure 6.1). Fast adsorption kinetics occurs, initially, due to the electrostatic interactions between the positively charged PLL moieties and the negatively charged silicon oxide surface. After attaining an initial coverage, the adsorption rate gradually decreases, owing to the high concentration of polymer chains at the surface leading to steric hindrance that further inhibits assembly. A saturation film thickness of $1.2 \pm 0.1$ nm was finally reached after 30 minutes of incubation.$^{18}$

The mass of PLL-g-PEG adsorbed into the PMAA brush layer was found to be two orders higher in magnitude than that of PLL-g-PEG adsorbed onto bare silicon oxide samples. Yet the adsorption profiles of PLL-g-PEG into PMAA brushes, starting with different PMAA dry thicknesses (namely 7, 13 and 33 nm as shown in Figure 6.1), followed similar kinetics: initial fast adsorption and a subsequent slowing down of adsorption rate until a plateau was reached (Figure 6.1).

A 30 min adsorption of PLL-g-PEG increases the dry thickness of PEC films to 100, 200 and 500 nm (obtaining PEC films-1, PEC films-2 and PEC films-3, respectively) from 7, 13 and 33 nm of PMAA brushes, respectively. Thus the dry height of the PECs is comparable to the wet height of the PMAA brushes,$^{19}$ suggesting that the PLL-g-PEG is essentially filling the space within the brushes.
Scheme 6.1. (a) ‘grafting to’ of PLL-g-PEG on a silicon wafer and (b) ‘grafting to’ of PLL-g-PEG into surface-grafted PMAA brushes (proposed structure for polyelectrolyte complex films).

In addition, it should be mentioned that the saturation time for achieving the maximum thickness of PEC films also increased with the starting thickness of PMAA brushes. This observation suggests an adsorption mechanism involving complexation of the graft copolymers into the brush architecture, which becomes more difficult in longer brushes due to the increased diffusion lengths involved, prior to encountering free charges.

The driving force for fabricating the PEC films is the formation of the water-soluble weak polyelectrolyte complex between oppositely charged PMAA brushes and PLL-g-PEG. As pointed out by de Vos,\textsuperscript{20} anchoring weak polyacids on silicon substrates enables the creation of a significant volumetric charge density. In this case, the thickness of the grafted PEC films is tuneable by either varying the starting thickness of the PMAA brushes or by changing the PLL-g-PEG adsorption time. During the initial (fast) adsorption, PLL-g-PEG with a relatively small molecular size (apparent contour length of 53 nm, apparent persistence length of 19.9 nm and radius of gyration equal to 12.2 nm)\textsuperscript{21} rapidly diffused into the highly swollen PMAA brushes (characterized by an average
swelling ratio of 26)\(^{19}\) and complexed with the PMAA backbones. Further adsorption of PLL-g-PEG was progressively hindered by the physical barrier of the newly formed PEC layer, which slowed down adsorption and complexation of additional PLL-g-PEG. As a result, a thickness saturation was reached (plateaus in the adsorption profiles in Figure 6.1).\(^{22}\)

![Figure 6.1](image.png)

**Figure 6.1.** Adsorption kinetics of PLL-g-PEG (2.5 mg/ml in HEPES buffer with a pH of 7.4) on a silicon wafer (inset) and on PMAA brushes, as a function of adsorption time. Initial dry thicknesses of PMAA brushes for preparing PEC films 1, 2 and 3 are 7 nm, 13 nm and 33 nm, respectively.

PLL-g-PEG loading within the PMAA brush structure was also studied by FT-IR composition analysis (Figure 6.2). Prior to adsorption of the graft copolymers, O-H (3200 cm\(^{-1}\)), C-H (3000 cm\(^{-1}\)) and C=O stretching (1710 cm\(^{-1}\)) vibrations, representative of PMAA films, could be clearly identified.\(^{23}\) Following the complexation of PLL-g-PEG into the PMAA matrix, these characteristic peaks diminished and were substituted by the characteristic signals of PEG segments i.e. C-H (2890 cm\(^{-1}\)) and C-O stretching (1110 cm\(^{-1}\)).\(^ {24}\)
The amount of complexed PLL-g-PEG and the subsequent thickness of grafted PEC films were also studied as a function of the concentration of adsorbing copolymer. As shown in Figure 6.3, the thickness of the grafted PEC films was found to be linearly proportional to the PLL-g-PEG concentration, given a constant starting PMAA thickness. A similar concentration-dependent adsorption behavior was also reported by Rühe and Penn.

In addition to the PLL-g-PEG concentration during adsorption, the influence of pH on the formation of PEC films was also investigated (Figure 6.4). When the adsorption process...
was carried out at pH values lower than 4.0 or higher than 10, i.e. below and above the \( pK_a \)s of PMAA (4.66) and PLL (9.5),\textsuperscript{26,27} respectively, no grafted PEC films were formed. Outside of the 4 - 10 pH range, either PMAA or PLL possessed no net charge, and thus the driving force leading to the formation of PECs was absent. Hence we believe that the very low residual adsorption observed under these conditions was solely due to the formation of hydrogen bonding between the PLL-g-PEG and PMAA. In contrast, PLL-g-PEG strongly adsorbs when the pH value of the incubation solution was set in between the \( pK_a \)s of these polyacids and polybases, to form PEC films. The adsorbed copolymer mass increased monotonically above a pH value of 4.0 and reached a maximum between 7 and 9, evidencing the formation of PECs, due to electrostatic interactions between the negatively charged PMAA brushes and the positively charged PLL backbones.

![Figure 6.4](image)

**Figure 6.4.** Adsorbed mass of PLL-g-PEG (concentration: 2.5 mg/ml, density: 1.27 g/cm\(^3\)) at different pH values under constant adsorption conditions (incubating time: 240 s, initial thickness of PMAA brushes: 26 nm). Adsorbed amount (\( \delta \)) of PLL-g-PEG is calculated according to the equation (5.1).\textsuperscript{13}

In addition to the influence of pH on the fabrication of PEC films, the ionic strength of the medium was varied, in order to study the influence of salt concentration on polyelectrolyte self-assembly. The presence of dissolved ions can significantly affect the swelling equilibrium of weak polyelectrolyte brushes;\textsuperscript{28-30} therefore, the complexing process was conducted at different NaCl concentrations, as shown in Figure 6.5. When
the concentration of NaCl in the aqueous medium is low, PMAA brushes behave according to the ‘osmotic brush’ regime. In this situation, the presence of salt produce a shift in the dissociation equilibrium, favoring the formation of carboxylate moieties along the PMAA backbones. This phenomenon induced brush stretching and an increase in PLL-\textit{g}-PEG adsorbed mass. The adsorbed mass of copolymer reaches a maximum at a specific NaCl concentration (1 mM) and further increase of salt concentration in the adsorbing solution caused the PMAA brushes to adopt the so-called ‘salted brush’. In this situation, dissolved ions screen the charges along the polyelectrolyte brush chains, inhibiting PMAA dissociation. This phenomenon hindered PLL-\textit{g}-PEG adsorption until no observable PEC films were formed, as in the case of concentrated, 1M NaCl solutions.

![Graph showing the adsorption of PLL-\textit{g}-PEG at different salt concentrations under constant adsorption conditions.](image)

**Figure 6.5.** Adsorption of PLL-\textit{g}-PEG at different salt concentrations under constant adsorption conditions (adsorption time: 240 s, initial thickness of PMAA brushes: 19 nm, PLL-\textit{g}-PEG concentration: 2.5 mg/ml, pH of solution: 7.4).

6.2.2 Interfacial Properties of Grafted PEC Films

The surface morphology of grafted PEC films was studied by tapping mode AFM and the corresponding images are shown in Figures 6.6. PLL-\textit{g}-PEG adsorption in PMAA cause an increase in RMS roughness on the polymer films, from (a) 0.4 ± 0.2 nm to (b) 4 ± 2
nm (measured over 5 μm × 5 μm). The increased roughness is attributed to the formation of PLL-g-PEG/PMAA aggregates in the grafted PEC films.

In order to confirm the reversibility of the complexation process of the copolymers, the PEC films were immersed in 1M NaCl solution for 5 seconds and effective PEC dissolution was confirmed by AFM imaging. Uniformly smooth polymer films were obtained due to the salt-driven dissociation of PLL-g-PEG/PMAA complexes and the recovery of the original PMAA brushes.

![Figure 6.6](image)

**Figure 6.6.** Dry morphology of (a) PMAA brushes with thickness of 33 nm and roughness (rms) of 0.4 nm, (b) PEC films with thickness of 426 nm and roughness (rms) of 4 nm and (c) PMAA brushes with thickness of 31 nm and roughness (rms) of 0.4 nm after the desorption process (scanning size: 5 μm × 5 μm). (1) Adsorption of PLL-g-PEG, (2) desorption of PLL-g-PEG in NaCl solution (1 M).

The morphologies of grafted PEC films containing different masses of PLL-g-PEG with identical starting PMAA thickness are shown in Figure 6.7. Upon increasing the adsorbed amount of PLL-g-PEG, the roughness of the grafted PEC films was found to increase. In particular, oriented morphologies on the surface of the PEC films were observed (Figure 6.7 d) at high concentrations of adsorbed PLL-g-PEG. We believe that the observed morphology of PEC films in dry conditions is directly related to their conformation in swollen state. We thus presume that the oriented assemblies are caused by the adsorption of PLL-g-PEG along the highly extended grafted PMAA chains.
Figure 6.7. Dry morphology of PEC films (scanning size: 10 μm x 10 μm), fabricated by using identical PMAA brushes (initial dry thickness: 22 nm) and loading with PLL-g-PEG at different concentrations (a) C = 0.25 mg/ml (b) C = 1.0 mg/ml (c) C = 2.5 mg/ml and (d) C = 6.0 mg/ml for a constant adsorption time (240 s) (pH of solution: 7.4).

6.2.3 Stability of Grafted PEC Films

We examined the stability of the grafted PEC films in HEPES solution (1 mM) by monitoring the thickness variation as a function of incubation time. As can be seen in the Figure 6.8, the dry thickness of the PMAA brushes decreased by 71% and 82% following 7 and 14 days of incubation, respectively. The dry thickness of the PLL-g-PEG films formed on SiOx surfaces decreased by 32% and 55% over the same incubation times. In contrast, the overall thickness of grafted PEC films was shown to decrease by 15% after 1 week of incubation and by 35% after 2 weeks of incubation (Figure 6.8). Thus the formation of PLL-g-PEG/PMAA complexes at the surface resulted in a significant enhancement of film stability when compared to the either singly (physically or chemically) grafted component.

Polyelectrolyte brushes, such as PMAA, have been observed to detach from the surface in an aqueous environment due to hydrolysis of the anchoring groups, and assisted by the relatively high osmotic pressure inside the brush structure and entropic effects.
Assembly of PECs induced a modification of PMAA conformation (vide infra) and as well a loss of net charge along the grafted backbones. We believe that both phenomena inhibit chain desorption, consequently increasing the film stability. This important finding additionally paves the way for possible future applications of grafted PECs as a platform in biological systems and biomaterials.

6.2.4 Structure of Grafted PEC Films Probed by Confocal Fluorescence Microscopy

In order to gain further insight into the mechanism of PLL-g-PEG adsorption into PMAA brushes and to visualize the structure of the subsequently assembled grafted PECs, samples fabricated with fluorophore-labelled PLL-g-PEG (red or green) were probed with confocal fluorescent microscopy. Fluorescence images recorded at different distances from the underlying silicon substrate were used to reconstruct the 3D distribution of PLL-g-PEG within the grafted PECs.

In Figure 6.9 (a), we show the 3D distribution of red fluorophore within grafted PEC films, swollen in water, following two hours of adsorption of PLL-g-PEG-TRITC. The maximum fluorescence intensity was located at the interface between the films and the surrounding solution, gradually fading away at positions closer to the substrate. This finding demonstrated PLL-g-PEG is intercalated inside the PMAA brushes in a
concentration gradient towards the underlying interface (gradual decrease of concentration).

In Figure 6.9 (b), we show the fluorescence intensity profile of the PMAA scaffolds in water, sequentially treated with PLL-g-PEG-TRITC and then PLL-g-PEG-FITC. Following additional adsorption of PLL-g-PEG-FITC on PLL-g-PEG-TRITC loaded PEC films, the maximum fluorescence intensity of each fluorophore-loaded PEC films was shown to undergo a shift by 800 nm (distance between dashed lines) towards the silicon substrate. The fluorescence distribution results from the adsorption profile, convoluted with the intrinsic profile of the confocal microscope.

The results obtained in these experiments confirmed that PLL-g-PEG adsorption kinetics was determined by the diffusion of the copolymers into the PMAA brushes. The PLL-g-PEG copolymers were concentrated at the brushes surface, since further diffusion inside PMAA scaffolds had to overcome both the steric hindrance by pre-adsorbed copolymers and the loss of net opposite charge due to PEC formation. Additional adsorption of the PLL-g-PEG on pre-formed, grafted PEC films showed a further diffusion of copolymers towards the underlying substrate.

Figure 6.9. (a) Reconstruction of confocal data obtained for fluorescence-labelled PLL-g-PEG in swollen, saturated PEC films with a dry thickness of 592 nm and an initial PMAA dry thickness of 65 nm (scale bar: 10 μm, the silicon substrate lying in the x-y
plane beneath the fluorescence-labelled layer). (b) Normalized fluorescence intensity distribution (y-shifted in inset for clarity) after loading PLL-g-PEG-FITC (green fluorescence, dry thickness: 157 nm) into swollen PEC films, preloaded (not saturated) with PLL-g-PEG-TRITC (red fluorescence, dry thickness: 111 nm) (dashed line indicates the position where maximum fluorescence intensity is reached; silicon substrate is at right side of the plot).

6.2.5 Mechanical Properties of Grafted PEC Films

The mechanical properties of grafted PEC films were studied by AFM indentation under buffer solution and compared to the starting PMAA brushes. Upon adsorption of PLL-g-PEG, the PMAA films were shown to increase their Young’s moduli from $0.4 \pm 0.1$ kPa to $1.3 \pm 0.3$ kPa, as indicated by the steepening of the indentation curve shown in Figure 6.10. Film stiffening upon PEC formation was due to filling of the brush films when oppositely charged PLL segments were complexed along the grafted PMAA chains. This is related to the formation of physical interactions (and potentially crosslinking) between PMAA chains and the PLL segments, leading to film shrinkage. It is worth mentioning that compared to covalently crosslinked films$^{19}$ the weak physical interactions in grafted PECs just induced limited stiffening with respect to the starting PMAA brushes. This is due to the high swelling of PEC films generated from weak polyelectrolyte complexes, distinguishing them from strong PECs.$^{35-37}$

The stiffening effect caused by PEC formation was found to be completely reversible upon salt-induced desorption of PLL-g-PEG adsorbents. As can be seen in Figure 6.10, immersion of grafted PECs in 1M NaCl solution for 5 seconds turned the Young’s modulus (decrease of the indentation curve slope) back to the value of $0.4 \pm 0.1$ kPa, which was characteristic of the starting PMAA brushes.
Figure 6.10. Indentation of PMAA brushes upon loading and unloading in HEPES buffer
(only approaching curves are shown, dry thicknesses of PMAA brushes and PEC films
are 22 nm and 148 nm, respectively, adsorbed mass of PLL-g-PEG: 160.02 mg/m²),
measured by colloidal probe microscopy with a gold-coated silica sphere (spring constant:
0.067 N/m, sphere radius: 10 μm).

The formation of stiffening grafted PECs could be additionally monitored by AFM
indentation as a function of the amount of PLL-g-PEG adsorbed into the PMAA brushes.
Progressive loading of PLL-g-PEG caused a gradual increase of film stiffness, as shown
in the indentation profiles reported in Figure 6.11. Typical Young’s moduli thus ranged
from 0.4 ± 0.1 kPa for the starting PMAA brushes to 0.7 ± 0.2 kPa, 1.3 ± 0.2 kPa and 1.6
± 0.2 kPa following the adsorption of 83.8, 135.9 and 233.7 mg/m² PLL-g-PEG, respectively.
Figure 6.11. Indentation of PMAA brushes upon loading with different amounts of PLL-g-PEG in HEPES buffer (only approaching curves are shown, dry thicknesses of PMAA brushes and PEC films 1, 2, 3 are 18 nm, 84 nm, 125 nm, 202 nm, respectively), measured by colloidal probe microscopy with a gold-coated silica sphere (spring constant: 0.217 N/m, sphere radius: 8.5 μm).

6.2.6 Nanotribological Properties of Grafted PEC films

Hydrophilic polymer brushes and polyelectrolyte brushes have been already reported to display highly lubricious behavior in aqueous environments. For this reason, in addition to the mechanical characterization of grafted PEC films, we have also investigated the nanotribological properties of the synthesized films by means of colloidal probe microscopy in an aqueous environment. As shown in Figure 6.12, PMAA brushes showed a very low coefficient of friction (0.01), when slid against a gold-coated silica sphere, indicating very effective lubricating behavior. However, upon formation of the PEC films, the coefficient of friction (COF) increased to a value of 0.04. The fourfold increase in COF was presumably due to the greater number of dissipative pathways upon complexation of PMAA brushes with PLL-g-PEG. A similar phenomenon has been already observed in covalently crosslinked brush systems on the same contact scale.

The lubrication properties of grafted PEC films could also be used to indicate the reversible loading of PLL-g-PEG and thus the restoring of the starting PMAA brush upon
salt treatment. As is shown in Figure 6.12, incubation of grafted PEC films in 1M NaCl led to PLL-g-PEG desorption and the friction behavior of the films showed the regeneration of the original PMAA brushes.

![Figure 6.12](image_url)

**Figure 6.12.** Friction of PMAA brushes as a function of load in HEPES buffer (dry thicknesses of PMAA and PEC films are 22 nm and 148 nm, respectively, adsorbed mass of PLL-g-PEG: 160.02 mg/m²), measured by colloidal probe microscopy with a gold-coated silica sphere (spring constant: 0.067 N/m, sphere radius: 10 μm).

Progressive adsorption of PLL-g-PEG into PMAA brushes is able to gradually increase the stiffening of the swollen brushes and therefore leads to an increase of COF for the generated PEC films, as shown in Figure 6.13. The COF values increased from 0.01 of the starting PMAA brushes to 0.03, 0.04 and 0.06 following the adsorption of 45.7, 140.9 and 820.4 mg/m² PLL-g-PEG, respectively.

Since PLL-g-PEG is known to function as a lubricious coating on flat surfaces, such as silicon oxide, one might expect that the adsorption of these macromolecules into PMAA brushes would lead to low friction. As this is apparently not the case, we can conclude that the PEG moieties of the PLL-g-PEG are held within the PMAA scaffolds, and are not present to a significant extent on the outer, sliding surface of the grafted PECs.
Figure 6.13. Friction of PMAA brushes and PEC films with different uptakes of PLL-g-PEG in HEPES buffer (dry thicknesses of PMAA brushes and PEC films 1, 2, 3 are 40 nm, 76 nm, 151 nm, 686 nm, respectively), measured by colloidal probe microscopy with a gold-coated silica sphere (spring constant: 0.5078 N/m, sphere radius: 8.66 μm).

6.3 Conclusions

We have reported the synthesis and characterization of grafted polyelectrolyte complex films, employing a combination of both ‘grafting-from’ and ‘grafting-to’ strategies, i.e. electrostatically adsorbing copolymers PLL-g-PEG to oppositely charged, surface-tethered PMAA brushes. The grafting kinetics of PEC films could be tailored in a controlled fashion by tuning the adsorption time, starting PMAA brushes thickness, PLL-g-PEG concentration in solution, pH and salt concentration of the solution. The grafted PEC films showed enhanced stability compared to that of each single grafted component. Furthermore, the distribution of copolymers PLL-g-PEG in PEC films was determined optically, in order to understand the structure of the films in their swollen state. The high mass/charge ratio that characterizes PLL-g-PEG leads to an amplification effect when fabricating PECs, which leads to the retention of the swollen dimensions of the PMAA brushes, even in the dry state. Finally, mechanical and nanotribological properties of these PEC films were studied by using colloidal probe microscopy in aqueous phase. The
PEC films presented tuneable mechanical behavior, and provide potential building blocks for application in a wide variety of technologies.

6.4 References

35. Ellipsometry in liquid experiments was also conducted; however, PECs films were strongly swollen in water and no refractive index contrast between polymer films and
water was detected. Therefore, swelling thicknesses of these films were not able to be obtained.

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Chapter 7

Summary

Surface modification by grafting polymer films has been significantly developed in recent years in order to achieve the desired interfacial properties. However, little has been known about how film structure determines the interfacial characteristics. This thesis thus aimed at settling some unresolved issues by the synthesis of a series of end-grafted polymeric models (ultra-thin films, stratified films and electrostatic assemblies), and further study of the structure-property relationships of these surface-tethered polymeric architectures.

Four main investigations were carried out in this thesis. Chapter 3 is dedicated to providing a general insight into the characteristics of tethered poly(acrylamide) films synthesized via surface-initiated photoiniferter-mediated polymerization, such as wettability, morphology, mechanical as well as the frictional properties. These poly(acrylamide) grafts with well-defined crosslink degree serve as a platform-specific model for the homogeneous ultra-thin films in this thesis.

Chapter 4 describes the adhesive and frictional properties of homogeneous poly(acrylamide) films in binary mixed solvents by using colloidal probe microscopy. The nanotribological properties of these films are strongly influenced by the crosslink degree, the solvent quality, as well as practical operating conditions (applied load and testing velocity). In particular, the solvent-induced glass transition of polymer films enhances the adhesion behavior, which is discussed theoretically and experimentally, providing a valuable tool for the characterization of stratified poly(acrylamide) films.

Chapter 5 discusses the synthesis of poly(acrylamide) films encompassing a stratified structure. Surface-grafted gel-brush and brush-gel films with identical chemical
compositions are fabricated, representing two, tiered examples containing different structural sequences in the vertical direction. Moreover, a novel structural characterization method using colloidal probe microscopy is employed to study these stratified films with different interfacial and interior structures. The homogeneous and stratified poly(acrylamide) films show entirely different mechanical responses owing to their distinct overall structures; however, the nanotribological behavior of these grafted films is mainly determined by their interfacial architectures.

Chapter 6 introduces the concept of tethered polyelectrolyte assembled films. These films are inherent in quasi-3D assemblies and show reversible morphological, mechanical as well as nanotribological properties upon loading/unloading the absorbers on a surface-grafted polyacid scaffold. In particular, the electrostatic adsorption process is shown as a function of pH, time, polymer concentration and salt concentration. Upon comprehending the interfacial properties of the assembled films with well-defined architecture, we further broaden our understanding of the structure-property relationships of surface-grafted polymeric films in an aqueous environment.

In conclusion, the interfacial properties of polymeric grafts can be well tailored by controlling their basic nanostructures. The entire study provides fundamental information that assists in understanding the materials’ properties in confined geometries as well as offering the required know-how for designing coatings with novel properties and applications.
Acknowledgements

During my study in Switzerland, I have received numerous helps from people in different countries around the world. It is impossible to finish my PhD study without their kind supports; therefore, I would like to acknowledge those people who made their efforts and contribution to my academic and personal life.

First of all, I would like to thank Prof. Dr. Nicholas Spencer for providing me a precious opportunity to join his group and carry out my PhD study under his supervision. I gratefully appreciate him for lots of brilliant advices and great support throughout my life in Laboratory for Surface Science and Technology.

Second, I would also like to express my great gratitude to another co-examiner of my PhD examination – Prof. Dr. Dieter Schlüter, who founded my master program in Germany and provided prerequisite for my succeeding study in Switzerland.

Furthermore, I would like to sincerely thank Prof. Dr. Julius Vancso, not only for being one of my co-examiners, but also for sharing his profound polymer knowledge with me during my short stay in Netherlands.

In addition, I would like to give my special appreciation to the last co-examiner of my PhD defense – Dr. Edmondo Benetti, who keeps inspiring and motivating me during my PhD life. I very much cherish the great friendship we established together throughout these years.

I would also like to acknowledge Prof. Dr. Walter Steurer, for representing the department of materials at my PhD examination.

European Science Foundation is acknowledged for generously funding my PhD thesis.
I am also grateful to Prof. Dr. Holger Schönherr and Dr. Davide Tranchida, for providing their in-depth AFM knowledge and the fruitful collaboration.

I want to thank Dr. E. Stefan Kooij and Dr. Tobias Schwarz, for their technical supports and professional suggestions during my PhD projects.

I would like to acknowledge my professor and friends in Germany, Prof. Dr. André Laschewsky, Dr. Erik Wischerhoff, Dr. Jan Weiss, Dr. Xin Gong, Dr. Yang Yang, Dr. Yun Chen, Dr. Chunhong Yin, Dr. Huajie Yin, Dr. Shuo Bai, Dr. Wen Li, who have been supporting me apart from my academic life.

I want to especially thank Prof. Dr. Seunghwan Lee, for offering his professional knowledge in aqueous tribology from time to time.

Many thanks to Dr. Shivaprakash Ramakrishna, for being my roommate throughout my life in Switzerland and providing his thorough understanding about AFM. Our great friendship will never be forgotten.

A huge thank to Dr. Prathima Nalam, for helping me dealing with trivial but important issues in my daily life. My gratitude is beyond any word.

My warmest thanks to Dr. Lucy Clasohm and Dr. Jarred Clasohm, for taking care of me and treating me as a family member.

I am also very thankful to Dr. Torben Gillich and Dr. Mathias Rodenstein, for our great friendship and making my life in Zurich unforgettable.

Many thanks to Josephine Baer and Tomas Bartos, for providing the administrative support and the IT support since my first day in Zurich.

A true gratitude to Dr. Vikrant Naik, Dr. Anu Naik, Dr. Mamta Chabria and Prakash Pattisapu for making my personal life in Switzerland so colorful and exotic.
I am also very thankful to Dr. Maura Crobu, Dr. Bidhari Pidhatika and Prof. Dr. Tomoko Hirayama, for providing unlimited wonderful moments together in Zurich.

I would like to give my special thanks to Dr. Sara Morgenthaler and Giovanni Cossu, for translating the abstract of this thesis into German and providing excellent technical supports, respectively.

I would also acknowledge my colleagues and friends in Switzerland throughout these years who helped me in different ways: Dr. Raphael Heeb, Prof. Dr. Lucio Isa, Dr. Kenneth Rosenberg, Dr. Marcella Roba, Dr. Mirren Charnley, Dr. Samuele Tosatti, Dr. Stefan Zürcher, Prof. Dr. Rosa Espinosa-Marzal, Dr. Rowena Crockett, Dr. Eva Beurer, Dr. Doris Spori, Dr. Filippo Mangolini, Dr. Christian Zink, Dr. Jia Pei, Dr. Canet Acikgoz, Dr. Christoph Mayer, Dr. Venkataraman Nagaiyanallur, Dr. Akshata Rao, Prof. Dr. Erik Reimhult, Dr. Robert Bielecki, Clément Cremmel, Dr. Giacomo Fontani, Angela Serrano, Tolga Goren, Olof Sterner, Dr. Ming Li, Jingyi Rao, Yang Zhang, Dr. Zhikun Zheng, Dr. Wei Hu.

I would also like to give my sincere acknowledgement to my aunt and my cousin, for standing by my side through the hardest time.

Last but not least, I want to thank Wei Yao, Yao Fu, Dr. Kai Shi, Dr. Zuojun Guo, Dr. Rui Liu, Jin Fan, Dr. Xuan Li, Jiamin Chen, Baoqiang Shi for their unconditional understanding and support in all aspects of my personal life.
Curriculum Vitae

Personal Information:
Ang Li
Date of Birth: 19, April, 1982
Nationality: Chinese
Address:
Laboratory for Surface Science and Technology
Department of Materials, ETH Zurich
Wolfgang-Pauli-Strasse 10
8093 Zurich Switzerland

Educational Background:
2009 — 2013 Doctor in Surface Science and Technology at ETH Zurich, Switzerland
2007 — 2009 Master in Polymer Science at Free University Berlin, Humboldt University
Berlin, Technical University Berlin and Potsdam University, Germany
2000 — 2004 Bachelor in Polymer Materials and Engineering at Dalian Polytechnic University, P.R.China

Working Experience:
2008.06 — 2008.09 Fraunhofer Institute for Applied Polymer Research, Water-Born Polymer Systems Division, Golm, Germany
2008.02 — 2008.04 Federal Institute for Materials Research and Testing (BAM), Analysis of Nanostructured Polymer Systems Division, Berlin, Germany
2006.05 — 2006.09 R&D Centre, Division of Special Materials, Honeywell, co, ltd, Shanghai, P.R.China
Honors and Awards:

Best Young Researcher Presentation Award

Presentations

2013 NanoEvent 'NextNanoStars', 21 March, Basel, Switzerland. (poster)

2012 244th ACS National Meeting on Chemistry and Physics in Tribology, 19 August – 23 August, Philadelphia, USA. (oral presentation)

2012 MacroGroup UK International Conference on Polymer Synthesis & UKPCF International Conference on Polymer Colloids, 9 July – 12 July, Warwick, UK. (poster presentation)

2011 Materials Research Society Symposium: Dynamics in Confined Systems and Functional Interfaces, 28 November – 2 December, Boston, USA. (oral presentation)

2011 Joint ICTP/FANAS Conference on Trends in Nanotribology, 12 September – 16 September, Trieste, Italy. (poster presentation)

2011 6th MRC Graduate Symposium, 8 June, ETH Zurich, Switzerland. (poster presentation)

2011 Frontiers in Polymer Science, 29 May – 31 May, Lyon, France. (poster presentation)


2011 International Nanotribology Winter School (Organized by European Science Foundation FANAS and the Technical University of Denmark), 17 January – 28 January, Copenhagen, Denmark. (oral presentation)

2010 Material Science Colloquium, 24 November, ETH Zurich, Switzerland. (oral presentation)

2010 Gordon Research Conference on Tribology, 27 June – 2 July, Waterville, Maine, USA. (poster presentation)
List of Publications


