Neutron Reflectometry Studies of the Hydrated Structure of Polymer Thin Films

Béla Nagy
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Béla Nagy

Department of Physics, Chemistry and Biology (IFM)
Division of Biophysics and bioengineering (BBIOBIO)
Faculty of Science and Engineering
Linköpings universitet, SE-581 83 Linköping, Sweden
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Abstract

Polymer coatings are inexpensive surface modifications providing a wide variety of functions. There is an ever-present motivation to improve the films’ performance and to decrease the cost and the environmental footprint of their production. This thesis includes the study of the structural and functional parameters of polymer coatings that are aimed at preventing biological fouling, the unwanted attachment of organic molecules and organisms on surfaces. The focus was on thin films prepared by the self-initiated photografting and photopolymerization method. This is a UV-initiated polymerization reaction that does not require additional chemicals beyond the monomers and the solvent. Since biofouling is a prominent problem in wet environments, the emphasis was placed on the hydrated structure of the films. Neutron reflectometry was selected as a primary method for these studies, since it is a powerful method for investigating the structure of polymer thin films, especially in the hydrated state due to the labelling offered by isotope substitution. This allows the determination of the solvent volume fraction depth profile, which reveals the chain segment density profile in the hydrated film. To resolve fast changes in the film structure and to study the chemical composition, spectroscopic ellipsometry and infrared absorption spectroscopy was implemented in a setup for in-situ measurements in parallel with neutron reflectometry.

This thesis contains an introduction and five research articles, and it can be divided into two main parts: the first focusing on the polymerization reaction and the resulting polymer films and the second on the reflectivity method and instrumentation development. Firstly, uncharged hydrophilic polymer layers were prepared by self-initiated photografting and photopolymerization and the hydrated structure of these was investigated. It was found that the films follow a stretched profile indicating negligible crosslinking, and that the growth dynamics is determined by the balance of grafting and removal through radiation damage. Studying sequential grafting of oppositely charged polyelectrolytes confirmed the results on growth dynamics and showed the effects of electrostatic interactions between the monomers. This also demonstrated that the polymerization method is ill suited for preparing block co-polymers due to the removal of material from the previous layer. However, these studies also show that the growth of the second layer tends to proceed from the substrate, forming a system where the two kinds of chains co-exist and interact in the same layer. The grafting of random co-polymers was also investigated by comparing the anti-fouling performance of layers made from a mixture of oppositely charged monomers to layers made using zwitterionic polymers, resulting in no significant difference. This was attributed to the pairwise deposition of oppositely charged monomers, further emphasizing the importance of the Coulomb force in defining the structure of the charged films. The second part of this work focuses on instrument development. Here the building and testing of an angle-dispersive reflectometer is presented, and the design and first applications of an in-situ setup for measuring spectroscopic ellipsometry and infrared spectroscopy along with neutron reflectometry is described.
By investigating the structure of the polymer films prepared by self-initiated photografting and photopolymerization, this work improved the understanding of this method, facilitating the development of new applications in the future. By combining additional methods with neutron reflectometry, both fast changes in the structure and the chemical evolution of the samples can be investigated. However, the differences in the sensitivities and the structural models required by the probes present new challenges in modelling.
Populärvetenskaplig sammanfattning


Polymerer är jättemolekyler som består av en kedja av ett stort antal små upprepade enheter (monomerer). En polymerborste är en matta av polymerer där ena änden av varje molekyl är förankrad på ytan i ett tätt mönster, och där kedjorna tvingas att sträcka ut sig på grund av att molekylerna sitter så tätt på ytan. Generellt sett kräver tillverkningen av polymerer inga stora ansträngningar, men vid tillverkning av polymerborstar är det svårt att se till att kedjorna är raka och utan förgreningar eller kopplingar till varandra, liksom att uppnå den önskade packningstätheten för att effektivt täcka hela ytan. De vanliga metoderna för att framställa polymerer med sådan struktur kräver dyra skräddarsydda kemikalier eller kemikalier som är skadliga för miljön. De kan också kräva särskilda förhållanden, som syrefri atmosfär, vilket kräver dyr utrustning och komplicerar tillverkningen. Ett av syftena med detta arbete var att undersöka en alternativ framställningsmetod som gör det möjligt att producera polymerborstar utan att kräva något annat än en blandning av monomerer och ett lösningsmedel, som vanligtvis är vatten, för att minska de ekonomiska och miljömässiga kostnaderna. Vid denna metod används ultraviolett (UV) strålning med hög energi för att klyva bindningar i monomererna så att de blir reaktiva. De kan då binda till varandra eller till ytan genom att de klyvda bindingarna reagerar och bildar nya kemiska bindingar.

Vårt mål är att förstå hur strukturen hos polymerborstar påverkar deras förmåga att förhindra biologisk påväxt, och en förutsättning för detta är att känna till strukturen hos de polymerer som skapas med hjälp av detta förfarande. För detta har vi använt en metod som kallas neutronreflektometri, som registrerar ett interferensmönster genom att mätta intensiteten hos en neutronstråle som reflekteras från en yta samtidigt som neutronernas infallsvinkel eller energi ändras. Utifrån detta mönster kan ytstrikterna struktur, till exempel hur polymerborstens densitet varierar med avståndet från ytan, bestämmas genom modellering. Denna metod är väl lämpad för att undersöka tunna

I den här avhandlingen har vi fokuserat på att undersöka polymerfilmer avsedda att förhindra biologisk påväxt, som framställts med den ovan beskrivna UV-polymeriseringsmetoden. Vi har visat deras förmåga att förhindra påväxt, och undersökt deras struktur med neutronreflektometri. Vi har fastställt hur polymerkedjorna bildar filmer på ytan, och att de i vatten bildar de ett skikt som har en struktur som liknar en polymerborste med sträckta kedjor. Vi har också undersökt polymeriseringsprocessen genom att låta en annan monomer bilda polymerer ovanpå ett befintligt polymerskikt. Där har vi funnit att UV-strålningen långsamt bryter ned båda lagren, samtidigt som nya monomerer binds till ytan med högre hastighet, och att de nya monomererna tenderar att starta nya kedjor från ytan (och inte ovanpå befintliga skiktet). Detta har också funnit indikationer på att mängden UV-ljus som reflekteras från provets yta i hög grad påverkar både tillväxt- och nedbrytningshastigheten. Vi har bekräftat betydelsen av elektriska laddningar på polymererna, och växelverkan mellan dessa, som formar strukturen genom att tillverka prover med motsatt laddade monomerer, och undersökt deras beteende i olika laddade tillstånd vid olika pH-värden. För att underlätta studiet av sådana system har vi också konstruerat och testat en uppställning där neutronreflektometri kan kombineras med metoder som kan studera snabba förändringar i provets tjocklek och ge information om tillståndet hos de kemiska bindingarna i provet.
Tudományos-ismeretterjesztő összefoglaló

A felületmódosító eljárások fontos szerepet játszanak napjaink technológiai fejlődésében. Alkalmazási területeik magukba foglalják a kenőanyagokat, a kémiai ellenállást növelő rétegeket, a felületkeményítő eljárásokat, illetve a korrózió vagy másfajta szennyeződések elleni védelmet. Az egyik a felületekkel kapcsolatos probléma a biológiai szennyezés, amely a biológiai anyagok nemkívánatos felhalmozódását jelenti a különféle felületeken. Ez számos területen okoz problémát, például a hajókon az algák növekedése megőrzi a közegellenállást, a papír- és élelmiszeriparban az eltömődött szűrők és a nedves felületeken tenyésző baktériumok jelentenek veszélyt, az orvosi implantátumokra tapadó és ott gyulladást okozó szerves törmelék pedig egészségügyi kockázatot jelentenek. Az organizmusok és szerves molekulák lerakódásából eredő problémák elleni védekezés egyik módja annak megakadályozása, hogy eleve megtapadjának a felületen. Ezt a felülethez erősen kötődő vízmolekulák megjelenését lehet elkerülni. Így a szennyező molekuláknak vagy organizmusoknak először el kell távolítaniuk a megköthött vízmolekulákat, hogy hozzáférhessenek a felülethez, mielőtt azon megtapadnának. A poláros molekulák hidrogénköttel, a töltött részek pedig elektrosztatikus kölcsönhatással kötik meg a vízmolekulákat. A polimerek kis ismétlődő egységekből, ügynevezett monomerekből álló óriásmolekulák. Azokat a polimerstruktúrákat, ahol elágazásmentes polimerláncok olyan sűrűn vannak az egyik végükkel egy felülethez rögzítve, hogy a láncok átlapolnak, polimerkeféknek nevezzük. A hidrofil polimerkefe vékony rétegek biológiai szennyezés elleni védelemként való alkalmazása jelenleg is kutatások tárgyát képezi. A hidrofil jelleg azt jelenti, hogy erősen kölcsönhat a vízzel. Ezek a vizsgálatok azonban egyelőre nem jártak átúti sikerrel. Általában a polimerek előállítása nem igényel bonyolult eljárásokat, azonban nehézséget jelent annak biztosítása, hogy a láncok egyenesek legyenek, azaz ne ágazzanak el vagy kapcsolódjanak egymásba, valamint a kívánt felületi sűrűség elérése is problémát okozhat, azaz a teljes felület lefedeése. Az ilyen szerkezetű polimerbevonatok előállítása költséges, valamint monomerenként egyedi, esetleg a környezetre káros halogéntartalmú vegyszereket igényelnek. Továbbá speciális körülményekre, például oxigénementes atmosférára is szükség lehet a szintézishez. Az itt bemutatott munka egyik célja egy olyan alternatív előállítási módszer vizsgálata volt, amely képes polimerkefet előállítani úgy, hogy a monomerek és az oldószer – ami általában víz – kívül más anyagra nincs szükség, így csökkenthetőek a pénzügyi költségek és környezeti terhelés. Ez a módszer nagy energiájú UV-sugárzás használatával szabadgyököket hoz létre a monomerek kötéseinek felbontásával. Ezek a szabadgyökök lehetővé teszik, hogy a monomerek egymáshoz és a felülethez kapcsolódjanak. A tanulmány célja ezzel az UV-polimerizációs eljárással létrehozott polimerbevonatok szerkezetének leírása. Erre egy neutron-reflektometriának nevezett módszert használtunk, amely egy felületről visszavert neutron sugár intenzitását mérve, valamint a neutronok beesési sűrűségét vagy energiáját változtatva egy interferencia-mintázatot kapunk. Ebből a mintázatból modellizációval azután meghatározható a felületi rétegek szerkezete. Ez a módszer különösen hasznos a vizet tartalmazó vékonyrétegek, így például a hidratált polimerkefék vizsgálata során. A neutronok az atommaggal lépnek kölcsönhatásba. Így a módszer alkalmazásával
megkülönböztethetők a különböző számú neutron, de azonos számú protont tartalmazó atommagok, az ügynevezett izotópok. Mivel elektronjaik száma megegyezik, az izotópok csak nagyon kis mértékben különböznének kémiai viselkedésükben. A filmek víztartalmának mélységprofilja meghatározható, ha ugyanazt a mintát először nehézvízben, majd sima vízben mérjük meg. Mivel a nehézvíz a hidrogén egy nehezebb izotópját tartalmazza, a mért szerkezetek különböznek, és a különbséget a víztartalom okozza. Ez az izotóphelyettesítés módszer arra is használható, hogy megkülönböztessünk két különböző izotópot tartalmazó monomert ugyanabban a mintában. A neutronreflektometriának azonban vannak hátrányaik. A módszer lassú, egy mérés órákig tart, és költséges, mivel a neutronok előállításához atomreaktorra vagy részecskegyorsítóra van szükség. Ezenkívül csak a minta szerkezetéről ad információt, a kémiai kötésekéről és a szerkezet gyors változásairól nem ad felvilágosítást. Ezekre a gyors változásokra és a kémiai kötésekre vonatkozó információk más módszerekkel összegyűjthetők, így előnyös, hogyha ezeket egyszerre, kombináltan mérjük.

Ebben a szakdolgozatban a fent leírt UV-polimerizációs módszerrel előállított szennyeződésálló polímerfilmek vizsgálatára összpontosítottunk. Igazoltuk szennyeződésálló képességüket, és neutronreflektometriálval vizsgáltuk a szerkezetüket. Megállapítottuk, hogy a polímerláncok a felületre oltódnak, és vízbe merítve egy olyan réteget képeznek, amely a polímerkeféhez hasonló szerkezetű. Vizsgáltuk a polimerizációs folyamatot is, amikor egy meglévő polímerréteg tetejére egy másik monomert oltottunk. Itt azt tapasztaltuk, hogy bár az UV-sugárzás lassan lebontja mindkét réteget, az új monomerek gyorsabb útemben rakódnak le a felületre; továbbá azt, hogy az új monomerek új láncokat ősként a felületen indítanak. Arra utaló jelentést találtunk, hogy a minta felületéről visszaverődő UV-fény mennyisége nagyban befolyásolja mind a növekedést, mind az eltávolítási sebességet. A szerkezetet alakító elektrosztatikus kölcsönhatások fontosságát ellenkező töltésű monomerkeket tartalmazó minták növekedésével vizsgáltuk meg, és a rétegek különböző töltő állapotokban való viselkedését különböző pH-értékek mellett tanulmányoztuk. Az ilyen típusú rendszerek vizsgálatának elősegítésére olyan mintatartó elrendezést építettünk és teszteltünk, amelyben a neutronreflektometria kombinálható olyan módszerekkel, amelyek képesek a minta gyors változásainak vizsgálatára, és emellett információt szolgáltatnak a mintában lévő kémiai kötések állapotáról.
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Included works

I. Structure and pH-Induced Swelling of Polymer Films Prepared from Sequentially Grafted Polyelectrolytes

B. Nagy, M. Campana, Y. N. Khaydukov and T. Ederth

*Langmuir* 2022, *38*(5), 1725–1737

Contribution: Participated in the planning of the experiments. Prepared the samples. Conducted the experiments. Performed the fitting and modelling. Written the main part of the manuscript.

II. The structure of self-initiated photopolymerized films: A comparison of models

B. Nagy, T. Ekblad, G. Fragneto and T. Ederth

Submitted for publication

Contribution: Performed the fitting and modelling. Written the main part of the manuscript.

III. Polyampholytic Poly(AEMA-co-SPMA) Thin Films and Their Potential for Antifouling Applications

W. Yandi, B. Nagy, A. Skallberg, K. Uvdal, R. Zimmermann, B. Liedberg and T. Ederth


Contribution: Prepared all samples for streaming current measurements and contributed to sample preparation for all other characterization except the algal assays and XPS. Carried out additional measurements during the review process and contributed to writing and review.

IV. A mobile set-up for simultaneous and in situ neutron reflectivity, infrared spectroscopy, and ellipsometry studies

C. Bush, B. Nagy, A. Stöcklin, P. Gutfreund, R. Dahint and T. Ederth

*Review of Scientific Instruments*, accepted for publication.

DOI: 10.1063/5.0118329

Contribution: Tested the ellipsometer setup. Prepared the polyelectrolyte samples. Was part of the experimental team investigating the polyelectrolyte samples. Performed the modelling and fitting of the data recorded on the polyelectrolyte samples. Took part in writing the manuscript.

V. GINA—A polarized neutron reflectometer at the Budapest Neutron Centre


Contribution: Participated in building the instrument. Performed and evaluated the test measurements. Took part in writing the manuscript.
Not included publications

VI.  **Note: 4-bounce neutron polarizer for reflectometry applications**  
*Review of Scientific Instruments*, 2018, **89** (5) 056105

VII. **Fe/FeO/Fe/FeV multilayers characterized by magnetometry and polarized neutron reflectometry**  
*IEEE Magnetics Letters*, 2017, **8**, 1-5

VIII. **Nano-metric self-diffusion of Fe: effect of grain size**  
J. Gong, N. Paul, **B. Nagy**, M. Dolgos, L. Bottyán, P. Böni and A. Paul  
*RSC Advances*, 2017,7 (16) 9573-9578

IX. **Morphology of Fe nanolayers with Pt overlayers on low-temperature annealing**  
*Journal of Applied Crystallography*, 2016, **49** (5) 1682-1692

X. **On the explanation of the paramagnetic Meissner effect in superconductor/ferromagnet heterostructures**  
*Europhysics Letters*, 2016, **116** (1) 17005

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XIII. **Investigation of periodic Ni–Ti multilayers**  
T. Veres, L. Cser, V. Bodnarchuck, V. Ignatovich, Z. E. Horváth and B. Nagy  
*Thin Solid Films*, 2013, **540**, 69-72

XIV. **On the feasibility to study inverse proximity effect in a single S/F bilayer by Polarized Neutron Reflectometry**  
*JETP Letters*, 2013, **98** (2) 107–110

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L. Bottyán, D. G. Merkel, B. Nagy and J. Major  
*Neutron News*, 2012, **23** (1) 21-24

XVI. **Magnetic proximity effects in V/Fe superconductor/ferromagnet single bilayer revealed by waveguide-enhanced polarized neutron reflectometry**  
*Journal of Superconductivity and Novel Magnetism*, 2011, **24** (1) 961–968
Introduction

The interface is defined as the area where two systems, subjects, organizations, etc. meet and interact. The most abundant type of physical interface is that between objects and their environments. The properties of these regions define the friction, corrosion resistance, biocompatibility of the objects. By using surface modifications these interactions can be controlled without influencing the bulk system. Common examples are oil films for lubrication, paint for corrosion resistance or surface hardened metal tools. Polymer coatings are widely used treatments on surfaces due to their versatility, low price and easy application. Polymer brushes are special cases of polymer coatings where polymer chains are grafted to the surface by one end so densely that the chains are forced to interact. One type of application of these polymer brushes is anti-biofouling, which deals with the prevention of organisms and organic materials from adhering onto surfaces in both marine and freshwater environments. The important characteristic of the coatings, in this case, is their hydration, which is determined by a complicated interplay between the structure of the polymer film, the functional groups of the monomers and their interaction with the water molecules. One important tool for investigating the hydration of thin organic film is neutron reflectometry. Since the neutrons interact with the nucleus the contrast between organic molecules may be increased by labelling them using different isotopes providing a unique precision to the method. Since the efficiency of these anti-fouling coatings depends on hydration, understanding how the structural properties influence the hydration helps in development of the applications. However, neutron reflectometry, as useful as is, is a very expensive method due to the need for a neutron source, like a nuclear reactor or a spallation source with a large particle accelerator. The method also requires extensive modelling since the phase of the reflected beam cannot be determined by measuring the intensity of the reflected beam. Developing combined setups where neutron reflectometry is measured simultaneously with common bench-top methods, like spectroscopic ellipsometry, may lead to refinements in the models used to interpret the data. Furthermore, in soft condensed matter, reproducing the exact state of the sample for consecutive measurements is challenging. Measuring the sample with multiple techniques that probe different characteristics of the sample at the same time is thus beneficial for the understanding of the ongoing processes.

In the following I will briefly introduce the problem of biofouling and the solutions that were investigated in the included papers. Then I will present the deposition techniques used to prepare the investigated samples. After an overview of the basics of neutron reflectometry, I will discuss the modelling aspects related to polymer brushes. Thereafter, I will briefly introduce the methods used for characterising the samples and used for the in-situ reflectometry setup, that was developed during the project, and finally discuss the polymer brushes, and the preparation of these brushes.
Motivation

Biofouling

Biofouling is the unfavourable accumulation of biological material on surfaces. It is a concern both in marine and freshwater environments, many industrial and medical applications. In shipping the algal growth and settled animals on ships greatly increases the drag and with it the fuel and maintenance costs. Oceanographic equipment has their efficiency lowered by the settlement of marine organisms, for example, the sensitivity of sound recording equipment is lowered by fouling. Also, biofouling causes problems in the fish farming industry and sea-based power generation. The problem is not limited to natural waters. In other aqueous environments biofouling issues are mostly caused by bacterial biofilms. In food and paper industry it affects the product quality and increases the maintenance costs. Filters are especially prone to failure due to fouling. Similarly, the attachment of proteins and organic fragments onto medical implants increase the risk of inflammation and rejection, and provides an environment for bacterial infection.

To understand the connection between these different cases of biofouling, the time and size scales of marine biofouling are displayed in Figure 1. When immersed in water most surfaces immediately become negatively charged. This charge is in turn screened by counterions from the solution forming a double layer of charges with a characteristic thickness, called the Debye length. It is onto this charged surface that nonpolar and oppositely charged molecules physiosorb. This adsorbed layer, that is called the conditioning film, presents an ideal environment for bacteria to settle. The settled bacteria then continue to thrive, slowly covering the surface with a bacterial biofilm. The organic molecules and bacteria that cover the surface are called microfoulers, based on their size. It is after this that algal spores or barnacle larvae settle and develop into the macrofouling that is visible by eye. It is also evident that each of the examples of problems caused by biofouling discussed above can be associated with mainly one of the stages in the growth chart. Issues with medical implants are mostly caused by the first stages of fouling, while other medical devices and certain industrial applications suffer mostly from the bacterial biofilms. Finally, macrofouling causes problems with industrial cooling towers, shipping, sea bases power generation equipment, and aquaculture. The dependence of the different stages on each other means that preventing the attachment of the smaller foulants could prevent also additional fouling problems.

There are three main strategies in marine anti-fouling measures. First and oldest is the use of biocides and biocide-releasing coatings. The prime example of a harmful biocide used for anti-fouling is tributyltin, that has now been banned due to environmental concerns. Also, copper-based paints have been widely used, but environmental concerns caused legislation to ban them in certain regions. Current technologies are aiming to develop coatings with controlled release of anti-microbial agents and films that kill bacteria on contact without release, or which degrade quickly after release. These solutions are efficient against bacteria and macrofoulers.
The second type of preventive strategy is the use of silicone-based self-cleaning films. Today most of the non-biocide based anti-fouling products for shipping are in this group. The coating itself does not prevent attachment of macrofoulers, instead it presents a surface that allows only weak attachment. This means that at sufficiently high shear rates the larger organisms detach from the surface. This effect is caused by the combination of low roughness, low surface energy and mechanical softness. The fast flow requirement in turn limits the range of useful applications, and these coatings are only effective against larger organisms, thus most treated surfaces are covered in diatom slime. Also, the softness of these films makes them sensitive to mechanical degradation.

The third strategy, investigated in this work, involves the prevention of the settlement of the foulant, by inhibiting the formation of the conditioning film through hindering the attachment of any kind of organic molecule. By preventing the build-up of the conditioning film, the subsequent attachment of larger organisms could be prevented. For this it is necessary to 1) isolate the surface from the water, 2) minimise the participation in electrostatic interactions with the foulant, and 3) bind the water molecules strongly to the surface, increasing the energy cost for the displacing the water before adsorption. All three of these criteria can be met using strongly hydrophilic polymer coatings.

The efficiency of an anti-fouling coating is determined with a regime of immersion tests measuring the amount of settled biomass on the surface. However, such tests do not reveal the causes determining the performance of the coating. In case of strongly hydrophilic coatings the water content and the segment density profile of the film is a good indicator of the hydration, which influences the performance of the film. Researching the details of the interaction between the brush and the solvent may lead to improvements in the applications.

Responsive coatings

There is an ever-present interest in coatings, where the properties of the surface treatment can be controlled by external factors. Diblock copolymer brushes, consisting of two blocks of different monomers, are typical examples of these responsive coatings that can change a physical property (hydrophilicity, bio-compatibility) upon an external trigger, such as heat (in the case of materials with a lower critical solution state).
temperature, LCST), pH, or salt concentration (polyelectrolytes). The zwitterionic types of anti-fouling coatings are typically made using strong electrolytes to broaden the pH and salinity ranges of their application. Coatings made from weak polyelectrolytes lose these wide ranges but may instead become switchable by controlling the number of charges in the layer.
Polymer brushes

Polymer brushes are made when polymer chains are anchored to the surface such that the average distance between two chains is smaller than sum of the radii of gyration for the two chains. This means that the chains interact with each other. This interaction is repulsion, if the solvent-chain interactions are favoured, that makes the chains stretched, swelling the layer, or collapse if the inter- or intra-chain interactions are favoured. An essential property of the brushes is their high grafting density, which allows them to completely isolate the surface from the environment, making them effective as surface modifications.

Strongly hydrophilic polymer brushes
A well-known strongly hydrophilic polymer is poly(ethylene glycol) (PEG). Due to the abundance of ether groups in its structure (Figure 2), it engages in hydrogen bonding with water, making it energetically unfavourable to remove the water, which thus prevents the foulants from absorbing to the polymer. Its zero net charge minimises its participation in electrostatic interactions, further decreasing the probability of attachment. Long PEG chains also benefit from isolation effects which are combined from two terms. Firstly, the attachment of an organic molecule decreases the possible conformations that is available for the PEG chain. This lowers the conformational entropy hindering the adsorption. The second term is associated with the increase of PEG concentration when the chain is compressed due to attachment. This increase will create an osmotic pressure that counteracts the adsorption.

However, PEG is not the optimal solution for anti-fouling. It has been shown that oxidative damage of the polymer chain results in loss of functionality within weeks of application. Reports on complement activation caused by PEG in medical applications have also been published, limiting the biocompatibility of such coatings. The loss of anti-fouling functionality is a direct result of the removal of material through oxidation. To prolong the decay of the PEG chains, the use of PEG derivative methacrylate monomers was investigated. 2-Hydroxethyl methacrylate (HEMA) and poly(ethylene glycol) methacrylates (PEGnMA, where n is the number of EG units) are widely used monomers (Figure 2). These monomers combine the resistance to environmental damage of poly(methyl methacrylate) and the anti-fouling functionality of PEG. The methacrylate backbone forms a bottlebrush-like structure with the ethylene oxide units forming the sidechains (Figure 3). The idea is that the oxidation would only cleave one sidechain at a time, instead of removing the whole chain, thus increasing the time the surface is resistant to fouling. Different mixtures of the two monomers have been investigated for optimising the deposition, and the thickness dependence of the anti-fouling parameters have been investigated. This study has showed that an optimal dry thickness exists and have linked the cause of the deterioration of the performance to insufficient hydration due to crowding of the brush.

Another type of strongly hydrophilic polymer is based on zwitterionic molecules. These molecules have both a positively and a negatively charged group. Utilizing charged
groups may seem counterintuitive, as they may promote fouling through long range electrostatic interactions, but the opposite charges cancel each other out at long distances and act as a dipole at short range, binding water through dipole-dipole interactions similarly to hydrogen bonds. These properties make them ideal for anti-fouling applications. The most widely used zwitterionic monomers for preparing anti-fouling coatings are all acrylic or methacrylic monomers containing quaternary amines, and come in three main categories depending on the anionic group in the molecule. Betaines with a carboxylic group, sulfobetaines with a sulfonate group and phosphatidylcholines that have a phosphate group linked to a choline group. Since these moieties are charged in a wide pH range, these materials perform well as anti-fouling coatings in most applications, independent of pH and salinity. This robustness comes with inflexibility. It is proven that minor details in the structure of the zwitterionic monomers, such as the number of carbons between the two charged groups, lead to differences in the strength of binding water (and hence anti-fouling performance). Recent works investigated alternative zwitterionic chemical structures, but the problem of non-trivial monomer synthesis was not solved.

One alternative to the zwitterionic polymers is polyelectrolytes made from a mixture of oppositely charged monomers, that have equal amounts of both charges. These are called pseudo-zwitterionic polymers. In Paper III we have investigated the anti-fouling performance of random co-polymers of oppositely charged monomers (2-aminopropyl methacrylate (AEMA) and 3-Sulfopropyl methacrylate (SPMA), [(2-(Methacryloyloxy)ethyl)dimethyl-(3-sulfopropyl)ammonium hydroxide (SBMA), and 2-(Dimethylamino)ethyl methacrylate (DMAEMA)).

Figure 2: Chemical structure of poly(ethylene glycol) (PEG), 2-Hydroxethyl methacrylate (HEMA), poly(ethylene glycol) methacrylate (PEGnMA), Methacrylic acid (MAA), 2-aminoethyl methacrylate (AEMA), 3-Sulfopropyl methacrylate (SPMA), 2-(Methacryloyloxy)ethyl(dimethyl-(3-sulfopropyl)ammonium hydroxide (SBMA), and 2-(Dimethylamino)ethyl methacrylate (DMAEMA).
zwitterionic monomers ([2-(Methacryloyloxy)ethyl]dimethyl-(3-sulfopropyl)ammonium hydroxide (SBMA), see Figure 2). Apart from solving problems with the complicated monomer synthesis this pseudo-zwitterionic films allows the use of, for example, primary amines as the positively charged group, allowing the charges in the film to change depending on the pH of the solvent. Investigations on composition gradients\textsuperscript{32,33} linked the optimal fouling resistance to the charge equilibrium of the films and showed that this optimum is moving along the gradient depending on the pH of the solvent. This opens the possibility of a switchable anti-fouling coating. In Paper I the influence of the composition and the solvent pH on the hydration of a series of polyampholytic films were studied. We concluded that the changes in hydration, linked to the charging of the monomers, are independent of the composition of the film and are corresponding to the pK\textsubscript{a} values of the two functional groups, confirming that the interactions of the charged groups are determining the hydrated structure of the film.

![Figure 3: Schematic drawing of a pHEMA chain.](image)

**Figure 3: Schematic drawing of a pHEMA chain.**

**Grafting methods**
Polymer brush grafting follows two main strategies. First is the “grafting to” route\textsuperscript{34} where previously synthesized polymer chains are anchored onto the surface through physical or chemical methods from a solution or melt, and the second is the “grafting from” route\textsuperscript{35}, often called surface-initiated polymerization, where the polymer chains are grown from the surface bound initiator molecules. The advantage of the “grafting to” method is that the polymer chain which is grafted to the surface can be well characterised and processed to have a narrow weight distribution, resulting in a well-defined brush. The disadvantage is that the grafting densities of the brushes are typically lower than that for the surface-initiated brushes, since there is an increasing diffusion barrier limiting the number of chains that can reach and attach to the surface with increasing density. This may be mitigated by depositing the polymer from a melt to bypass the excluded volume interactions. The attachment methods can be
physisorption or chemisorption. Physisorption uses electrostatic forces or the hydrophobic interactions by anchoring a block co-polymer with a hydrophobic anchor to the oil-water interface or some other hydrophobic surface. Here we present two chemisorption methods, thiol chemistry for metal surfaces and silane chemistry for oxides. These are procedures utilized in this work and their description will follow below. Polymer surfaces can be modified using reactive groups if they are present on the surface, otherwise extra steps are needed for functionalization of the surface\textsuperscript{36,37}. Lithographically patterned surfaces can be fabricated using these methods\textsuperscript{38,39}, and gradient surfaces may also be produced by either temperature dependent kinetics and temperature gradients\textsuperscript{40}, or by controlling the immersion time of the substrate into the polymer melt or solution\textsuperscript{41}.

The “grafting from” strategy, as its alternative name surface-initiated polymerization suggests, involves a layer of initiator molecules bound to the interface that acts as seeds for the polymerization process, anchoring the polymer brush to the surface. With the addition of monomers, catalysts and solvent the polymer films grow onto the substrate. The initiator layer is usually deposited with the chemisorption methods mentioned in the previous paragraph. The reactions used for the grafting are almost always controlled polymerization reactions to maximize the control over the density, polydispersity and composition within the film. The two most commonly used polymerization methods are atom transfer radical polymerization (ATRP) and reversible addition–fragmentation chain transfer polymerization, although more methods exist. Such films can be denser and thicker than films deposited with the “grafting to” method since the diffusion of monomers is much faster than the diffusion of complete polymer chains, but the polydispersity and composition can only be determined after the termination of the reaction. Patterning of such films can be achieved by patterning the initiator monolayers but the preparation of gradient samples is hindered by the non-linear time dependence of the layer thickness during the reaction. In this thesis the ATRP and the self-initiated photopolymerization and photografting (SI-PGP) methods were used for preparing samples. SI-PGP is also considered to be a “grafting from” method, however the details of the polymerization and the resulting structure is still investigated. Both methods are further discussed below.

Initiator deposition
In this work gold and silicon dioxide surfaces were used as a substrate for surface-initiated polymerization to prepare the samples. For the gold surfaces the initiator monolayer was deposited using thiol chemistry and silane chemistry was used for the silicon surfaces with native oxide layers.

Thiol chemistry
Organosulfur molecules bind covalently to a range of metal surfaces, forming well-ordered dense monolayers\textsuperscript{42}. The typical molecule used for such layers is made up of a thiol group, an alkyl chain consisting of 10-20 methylene units and an end group that determines the functionality of the surface. The usual layer preparation procedure involves the immersion of the surface in a dilute (50-100 μM) loading solution until the layer had time to order and then removing any physisorbed molecules with sonication. The deposition process starts with the attachment to the surface by the thiol groups, and it is followed by an ordering phase where the layer arranges itself into a
two-dimensional lattice. The ordering of these molecules is driven by the van der Waals interactions between the alkyl chains. This is a slow process that takes several hours, with the speed depending on the lengths of the chains. On gold surfaces the mismatch in the distance of the sulphur binding sites and the van der Waals radius of the alkyl chain introduces a chain tilt of 26°-28°. Layers containing more than one molecule can be prepared from mixtures, although the ratio of the molecules may not reflect that of the preparation solution. Furthermore, patterned films may be prepared by micropattern printing.

Silane chemistry
Silanization of semiconductor surfaces was reported in 1978. This method is suitable for functionalizing hydroxylated surfaces such as metal oxides. The molecules used for this purpose have the RSiX₃-H₂ structure, where X is either a chloride or an alkoxy group and R is some organic group determined by the intended surface modification. Silane monolayers are typically deposited using chemical vapour deposition or wet chemistry. The silane molecule binds to the surface by condensation. Chlorosilanes are generally more reactive than alkoxy silanes which require heat to bond to the surface. During the process the molecules form a durable network by forming bonds between themselves. Silane layers are not as dense or well-ordered as thiol layers, and multilayer formation is possible especially in situations where water is present during the procedure. Microcontact printing is also a possibility to prepare patterns on silanized surfaces.

Polymerization reactions
The main polymerization method used to produce the films studied in this thesis was self-initiated photografting and photopolymerization (SI-PGP) which is not a widely used process. Our investigations in Papers I and III revealed correlations regarding the anti-fouling performance of pseudo-zwitterionic films made using the method, and results presented in Paper II lead to a better understanding of the SI-PGP polymerization process in general.

Surface-initiated atom transfer radical polymerization
This method was first used to prepare surface bound polymers in 1997. ATRP is a commonly used procedure to prepare polymer brushes, because its superb control of the molecular weight and the possibility to create block co-polymers using the same reaction. A typical reaction requires a halogen initiator, usually Br or Cl, a transition metal catalyst, commonly Cu, and an N-containing ligand to form a complex with the catalyst allowing for the transfer of the halogen atom to and from the chain. The key aspect of the reaction is the reversibility. Unlike other free-radical polymerizations, the termination of the chain is reversible and dormant chains may be reactivated. Since only a fraction of the chains are living at a time, the termination of the reaction is simultaneous for the whole sample, also the chance of radical coupling is minimised. The process typically takes hours, allowing the possibility of adding additional monomers of the same type, or other monomers to form block copolymers. The method is mostly used with acrylates, methacrylates and methacrylamides, usually with their sidechains having the functional component of the polymer. Disadvantages of the process are that oxygen-free atmosphere is required for the reaction, and that monomers containing carboxylic acid poison the reaction. Films prepared with this
procedure may be incompatible with biomedical and marine applications, due to the cytotoxicity of the copper catalyst.

Self-initiated Photografting and Photopolymerization

This method was first reported using styrene\textsuperscript{51} and later with acrylic and methacrylic monomers\textsuperscript{52-53}. The self-initiation is achieved by shining short wavelength UV-light (in our case mainly 254 nm) on the monomer solution, forming radicals on the monomers themselves. The details of the polymerization reaction are not well known, but results on 1,4-bunasediol diacrylate suggest\textsuperscript{54} that the UV radiation excites the C=C bonds to their triplet state through intersystem crossing, which then form bi-radicals. However, studies on acrylic acid\textsuperscript{55,56} also found that C-C and C-O can be cleaved by the UV-radiation to form radicals. These free radicals can initiate the polymerization reaction. The grafting of the polymer happens when a hydrogen atom is abstracted from the surface by the radical at the end of the chain. This process is possible on any kind of organic surface having available hydrogens for abstraction, including the already grafted chains, allowing for branched or even crosslinked polymer films. The method can be used for grafting polymers onto surfaces that are relatively inert, or otherwise hard to functionalize, such as polyethylene\textsuperscript{57,58}, carbon nanotubes\textsuperscript{59,60}, hexagonal boron nitride\textsuperscript{61}, or graphene\textsuperscript{62}. The technique was recently used to graft onto cellulose nanocrystals\textsuperscript{63}, to improve the device capabilities of perovskite quantum wells\textsuperscript{64}, and during the synthesis of metal–organic frameworks\textsuperscript{65,66}. The preparation of patterned films\textsuperscript{67-70} and gradients\textsuperscript{32,71,72} is straightforward by spatial and temporal control of the irradiation. Further applications of the method can be found in the recent review by Jagtap and More\textsuperscript{73}.

We have attempted to determine the chain segment density profile of hydrated poly(HEMA-co-PEG$_{10}$MA) films prepared with SI-PGP in \textbf{Paper II} using neutron reflectometry, where the results suggested that the volume fraction profiles of the films are more stretched than the regular brush profile. We attributed this to the increase of repulsion between the chain units caused by the excluded volume due to the long sidechains. The effect of sequential grafting of monomers were also investigated in \textbf{Papers I and II}, where we have found that the grafting mainly occurs to the surface
of the substrate, and that the speed of grafting is influenced by the removal of material from the surface by the UV radiation, impeding the control over the composition and the layer thickness. This has already been demonstrated by Larsson et al\textsuperscript{26}. The schematic drawing of the grafting setup used in this project is shown in Figure 4. Since the monomer solution absorbs the UV radiation, a thin (20-40 μm) even coverage is provided by suspending the substrate from the quartz disk via capillary forces, or gently placing the disk on top of the monomer solution in case of larger substrates such as the Si block used for neutron reflectometry. The homogeneity of the illumination is ensured by placing the sample under a light source with a large area (195×139 mm\textsuperscript{2}) at a medium distance (45 mm). The typical irradiation times depend on the reflectivity of the substrates (usually 2-5 min for Si and 1-3 min for Au) and the monomer. Despite the poor control and understanding of the reaction, the method has many advantages. The lack of initiator and other necessary chemicals make it an inexpensive and robust method for practical applications, and its insensitivity to the substrate material allows a wide range of uses, like functionalising substrates with low reactivity. Compared to other surface-initiated polymerization methods SI-PGP could be a more cost-efficient and environmentally friendly alternative.
Neutron reflectometry

Thermal and cold neutrons are excellent probes of condensed matter since their energy is of the same order as the kinetic energies of the atoms in condensed matter, and their wavelengths are of the same order of length as the atomic distances. Their low absorption in structural materials mitigates the use of complicated sample environments, while their magnetic moment allows to investigate magnetism in the samples. On the other hand, neutron sources have low intensity, and they are very expensive to build and maintain. For this reason, neutron instruments are highly specialised for optimal collection of neutrons for a given type of experiment. Neutron reflectometry (NR) is used in investigating layered structures in the 10 Å - 4×10⁴ Å thickness range. The method utilizes the interference of the reflected neutron beam impinging on the surface at a shallow angle. Measuring the reflected intensity as the function of the incident angle and the neutron wavelength allows the determination of the depth profile of the isotope composition using modelling.

Properties of neutrons
Neutrons are subatomic particles that constitute nuclei along with protons. They are consisting of two up and one down quarks. They have no electric charge, but they have ½ spin. Their properties are summarized in Table 1. Neutrons are only stable in the nuclei. In free form they decay according to the following reaction

\[ n^0 \rightarrow p^+ + e^- + \bar{\nu}_e \]

where \( n^0, p^+, e^- \) and \( \bar{\nu}_e \) denote the neutron, proton, electron and electron antineutrino, respectively.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass</td>
<td>( 1.674 \times 10^{-27}\text{kg} )</td>
</tr>
<tr>
<td>Charge</td>
<td>( 0 (\pm 2 \times 10^{-12})\text{e} )</td>
</tr>
<tr>
<td>Magnetic moment</td>
<td>( -1.041 \times 10^{-5}\text{\mu}_B )</td>
</tr>
<tr>
<td>Mean free lifetime</td>
<td>( 879.4 \pm 0.6\text{ s} )</td>
</tr>
</tbody>
</table>

The wavelength of the neutrons is dependent on their kinetic energy. This is described by the following equation

\[ E = \frac{2\pi^2 \hbar^2}{m\lambda^2} \]

where \( E \) is the energy, \( m \) and \( \lambda \), denote the mass and the wavelength of the neutron, respectively. Another important quantity is the wave vector, which points in the direction in which the wave is travelling, and has a magnitude inversely proportional to the wavelength. The wavevector of a planar wave is defined as
where $k$ is the wavevector, $k$ is called wavenumber and $\hat{k}$ is the unit vector pointing in the direction of the wave propagation. Neutrons, used for condensed matter research, are predominantly generated through nuclear fission in research reactors and through nuclear spallation in spallation sources where a target is bombarded with a high-energy proton beam to create the neutrons. Neutrons produced in these processes have kinetic energies of the order of MeV, and are called fast neutrons, which makes them unsuitable for investigating condensed matter because of their short wavelengths. The energy of the neutron is decreased via collisions with other nuclei in the medium surrounding the source. This medium is called the moderator. Since the energy transfer in a collision is the largest when the colliding objects have the same mass, the most common elements used as moderators are hydrogen, in the form of water, and carbon, in the form of graphite. Paraffin wax is also used as a moderator where heating is not an issue. In a moderator medium the neutrons rapidly lose most of their energy, after only a few collisions the remaining energy is of the order of the thermal energy $(k_B T)$ in the moderator. This is the reason why the energy of the neutron is categorized in a heat scale, and that the energy spectrum of the moderated neutrons resembles the Maxwell–Boltzmann distribution. Cold neutrons have an average energy less than 25 meV ($\lambda \approx 1.78 \text{ Å}$). They are produced with the help of a cold source, which is a vessel containing liquid H$_2$ $(T \approx 20\text{ K})$ near the reactor core or the spallation target.

Neutrons interacting with matter

Let us now consider the interactions of neutrons with matter. One of the possible interactions is the absorption of the neutron as part of a nuclear reaction. Products of these reaction are gamma rays with characteristic energies, used in the activation analysis method, that reveal the isotope composition of the target. Another interaction is scattering. If the energy on the neutron is changed during the collision the process is called inelastic scattering. This change in the energy relays information about the motion of atoms and molecules as well as the excitations of the magnetic field and the crystal structure. Neutron reflectometry measures elastic scattering that is determined by the structure of the sample. During elastic scattering the magnitude of the wavevector is constant, only its direction is changed. This change is characterized by the momentum transfer vector $Q$ that is defined as $Q = k_f - k_i$, where $k_f$ and $k_i$ are the final and initial wavevectors, respectively.

Let us consider the case where a nucleus is fixed at the origin of our system and there is an incoming neutron plane wave, and its wavefunction is described by the $\Psi(r) = e^{ikr}$ equation. Then, the wavefunction of the scattered wave can be calculated by solving the Schrödinger equation

$$\left( k^2 + \nabla^2 - \frac{2m}{\hbar^2} V(r) \right) \Psi(r) = 0$$

where $V(r)$ is the scattering potential. In case of a fixed nucleus the scattering potential can be considered as a point scatterer, that is described using the Dirac delta distribution, $\delta(r)$, and the parameter $b = b' + ib''$, called the bound scattering length, in the following equation
Using the Dirac delta distribution may be problematic when applying the Born approximation, which supposes that the wavefunction is only negligibly perturbed by the scattering and the scattering potential is, by definition, infinite when \( r = 0 \). However, calculations regarding the scattering of low energy particles on a rigid sphere using the method of partial waves show that the phase shift caused by the scattering is of the order of the scattering length. Since the scattering length of the nuclei are typically four orders of magnitude smaller than the wavelength of the neutrons, this phase shift can be neglected. The solution of the Schrödinger equation is made up of an incoming plane wave and an outgoing spherical wave as

\[
\Psi(r) = e^{ikr} + f(q) \frac{e^{ikr}}{r}
\]

where \( f(q) \) is called the scattering amplitude. In the Born approximation as \( r \to \infty \), \( f(q) \) can be written as

\[
f(q) = -\frac{m}{2\pi \hbar^2} \int e^{-iqr} V(r) dr = -b
\]

An important quantity that describes the scattering process is the cross section \( (\sigma) \). Considering a neutron beam with well-defined energy impacting an object placed at the centre of the coordinate system. The differential cross section is defined as the number of particles \( (n) \) scattered in a direction given by the angles \( \theta \) and \( \phi \), going through solid angle of \( d\Omega \) per second, divided by the incoming flux \( (\Phi) \).

\[
\frac{d\sigma}{d\Omega} = \frac{\eta(\theta, \phi, d\Omega)}{\Phi}
\]

Using this expression, we can calculate the total scattering cross section \( (\sigma_{tot}) \) integrating over the whole sphere.

\[
\sigma_{tot} = \eta_{scattered} = \int \frac{d\sigma}{d\Omega} d\Omega
\]

Calculating the \( \eta_{scattered} \) and the \( \Phi \) values using the velocity of the neutrons \( v \) and \( \Psi(r) \) and substituting this into the expression above we get that

\[
\sigma_{tot} = \frac{4\pi r^2 v \left| b \right|^2}{\left| \frac{\hbar}{r} e^{ikr} \right|^2} = 4\pi |b|^2
\]

Through more rigorous quantum mechanical calculations regarding absorption and a distribution of different nuclei in a system, it was shown that the scattering can be decomposed into three parts \( b = b_{coh} + b_{inc} + b_{abs} \) the coherent, incoherent and absorption scattering length, respectively. From these \( b_{abs} = ib'' \) deals with the absorption of the materials in the system. This value is not significant for most materials, however, elements with low-energy resonant absorption such as Cd, Gd have significant absorption. Incoherent scattering does not preserve the phase of the
neutrons and thus do not lead to interference; however, it does increase the background for the measurements as it scatters in all directions.

Neutron optics
Let us now consider a monochromatic neutron beam impinging on a surface at a shallow angle \( \vartheta \) described by the wavevector \( k_0 \). If the direction of the incoming beam does not coincide with any Bragg directions in the sample, the sample can be described by a homogeneous potential \( V_0 \) derived from the average scattering length

\[
V_0 = \frac{2\pi \hbar^2}{m} \sum_i b_i \delta_i(r) d^3r = \frac{2\pi \hbar^2}{m} \rho
\]

so that

\[
V(z) = \begin{cases} 
0, & \text{if } z < 0 \\
V_0, & \text{if } z \geq 0
\end{cases}
\]

where \( b_i \) and \( \delta_i(r) \) are the scattering length and the position of the \( i \)th nucleus in the sample, respectively. The value \( \rho \) is called the scattering length density (SLD) of the sample.

If the surface of the sample is smooth, a planar symmetry exists, and the gradient of the potential, also the force acting on the neutrons, is perpendicular to the surface. This case is called the specular reflection, and it is illustrated in Figure 5, and the reflected wave is defined by the wavevector \( k_r \). The momentum transfer vector \( \{Q\} \) is also perpendicular to the surface. Its magnitude can be calculated as

\[
Q_x = 2k_{0,x} = 2k_0 \sin(\vartheta) = \frac{4\pi}{\lambda} \sin(\vartheta)
\]

![Figure 5: Schematic illustration of the specular scattering geometry on a semi-infinite surface.](image)

The energy corresponding to the perpendicular component of the incident wavevector \( E_{0,x} \) can be written as

\[
E_{0,x} = \frac{\hbar^2}{2m} (k_0 \sin(\vartheta))^2 = \frac{2\pi^2 \hbar^2}{m \lambda^2} \sin^2(\vartheta) = \frac{\hbar^2 Q_x^2}{8m}
\]

If \( E_{0,x} \leq V_0 \) then the neutrons undergo total reflection. The critical value of the momentum transfer vector can be calculated from \( E_{0,x} = V_0 \) as \( Q_c = \sqrt{16\pi \rho} \). Since \( \rho \) is
of the order of $10^{-5}$-$10^{-7}$ for thermal neutrons ($\lambda \sim 1.78\text{Å}$), the angle of incidence corresponding to $Q_c$ is always less than 0.5°.

If $E_{0z} > V_0$ then some of the neutrons enter the sample while the rest are reflected. The beam entering the sample is refracted and it is described by the refracted wavenumber vector ($k_\beta$), which can be calculated using the wave equation, resulting in

$$k_\beta^2 = \frac{2m}{\hbar^2} (E - V) = k_0^2 - 4\pi\rho$$

This calculation leads to the definition of a refractive index for neutrons, which allows us to treat neutron reflectometry as optics instead of scattering.

$$n^2 = \frac{k_\beta^2}{k_0^2} = \frac{k_0^2 - 4\pi\rho}{k_0^2} = 1 - \frac{\lambda^2\rho}{\pi}$$

Since $\rho$ is of the order of $10^{-5}$-$10^{-7}$ the refractive index can be estimated as

$$n \approx 1 - \frac{\lambda^2\rho}{2\pi}$$

For most materials the refractive index will be smaller than the refractive index of vacuum. This verifies the statement that in the $E_{0z} < V_0$ case, for surfaces with a positive scattering length density, all of the impinging neutron beam will be reflected.

The measured quantity in neutron reflectometry is the intensity of the reflected beam. This can be calculated by squaring the amplitude of the reflected wavefunction. The solution of the Schrödinger equation in this case can be written as

$$\Psi(z) = \begin{cases} e^{ik_0xz} + re^{-ik_0xz}, & \text{if } z < 0 \\ te^{ik_tzz}, & \text{if } z > 0 \end{cases}$$

where $r$ and $t$ are the reflection and transmission probability amplitudes, and $k_{0z}$ and $k_{tz}$ are the $z$ components of the incoming and transmitted wavevectors, respectively. From the criteria that the wavefunction and its first derivate have to be continuous, we get the following equations

$$1 + r = t \text{ and } k_{0z}(1 - r) = k_{tz}t$$

Expressing $r$ and $t$ from these equations we get the well-known Fresnel coefficients.

$$r = \frac{k_{0z} - k_{tz}}{k_{0z} + k_{tz}} \text{ and } t = \frac{2k_{0z}}{k_{0z} + k_{tz}}$$

The reflected intensity $R$ can be expressed using $Q$ and $Q_c$ as

$$R = r^2 = \frac{Q_x - \sqrt{Q_x^2 - Q_z^2}^2}{Q_x + \sqrt{Q_x^2 - Q_z^2}}$$

If $Q \gg Q_c$ this equation can be further simplified as

$$R_p \approx \frac{16\pi^2\rho^2}{Q_x^4}$$
which is the Fresnel reflectivity of a semi-infinite layer. A simulated neutron reflectogram, calculated for a semi-infinite sapphire surface, and its relation to the Fresnel reflectivity, is shown in Figure 6.

Figure 6: A simulated neutron reflectogram (black) and the Fresnel reflectivity (red) calculated for a semi-infinite sapphire surface with \( \rho_{Al_2O_3} = 5.74 \times 10^{-6} \text{Å}^{-2} \).

Let us now return to the case where \( E_{0,x} < V_0 \) and examine the refracted wave. In this case, when \( Q_x < Q_c \) there is a non-imaginary solution to the wavefunction written as

\[
\Psi(x < 0) = t e^{-\frac{x}{2 \sqrt{Q_x^2 - Q_0^2}}}.
\]

This solution describes an exponentially decaying wave in the sample with a characteristic penetration length of \( \sqrt{Q_x^2 - Q_0^2} \), despite the perpendicular energy of the particle being smaller than the potential barrier. This is the evanescent wave solution where the neutrons enter the sample and travel briefly in the direction of \( k_1 \) before exiting the sample. The lateral travel of the beam is called the Goos–Hänchen-shift. If the penetration depth is larger than the thickness of the top layer of the sample, then a more sophisticated approach is required to determine the reflectivity.

Reflectivity of a Multilayer Sample
Let us consider the reflectivity of a sample with a surface layer on a semi-infinite substrate. The surface layer has a thickness \( d \) and an SLD value \( \rho_1 \) and the substrate has an SLD of \( \rho_2 \). The solution of the Schrödinger equation in this case can be written as
\[ \Psi(z) = \begin{cases} 
e^{-ik_0xz}, & \text{if } z < 0 \\
A_1 e^{ik_{1x}z} + B_1 e^{-ik_{1x}z}, & \text{if } 0 < z \leq d \\
& te^{ik_{x}z}, \quad \text{if } z > d 
\end{cases} \]

where \( A_1 \) and \( B_1 \) are the reflection and transmission probability amplitudes in the layer and \( k_{jx} = \sqrt{k_{0x}^2 - 4\pi \rho_j} \) is the \( z \) component of the wavenumber vector in the \( j \)th layer. The continuity conditions for the wavefunction gives a system of equations that if solved for \( r \) results in

\[ r = \frac{r_{0,1} + r_{1,2}e^{2ik_{1x}d}}{1 + r_{0,1}r_{1,2}e^{2ik_{x}d}} \]

where \( r_{j,j+1} = \frac{k_{j+1} - k_j}{k_j + k_{j+1}} \) are the Fresnel coefficients for the \( i \)th interface. Calculating the reflected intensity

\[ R = rr^* = \frac{r_{0,1}^2 + r_{1,2}^2 + 2r_{0,1}r_{1,2}\cos(2k_{1x}d)}{1 + r_{0,1}^2r_{1,2}^2 + 2r_{0,1}r_{1,2}\cos(2k_{1x}d)} \]

the cosine term indicates that there is a periodicity in the function with a period (p)

\[ 2k_{1x}d = Q_{x}d = 2\pi p \]

This periodicity is caused by the interference of the reflected beams from the two interfaces. The same results can be obtained by calculating the path length difference between the two beams and applying the interference condition, resulting in \( 2dsin(\bar{\theta}) = p\lambda \). Substituting \( Q_x = 4\pi sin(\bar{\theta})/\lambda \) we get the expression from above. This periodicity manifests itself in the so called Kiessig fringes\(^{79} \) in the reflectogram shown in Figure 7.

In the expression of the amplitude of the reflected beam (\( r, \) above), the term \( e^{i2k_{1x}d} = e^{iQ_zd} = e^{i\theta} \) is corresponding to a phase shift that the wave suffers while traveling through the layer, and the term \( r_{0,1}r_{1,2}e^{i\theta} \) is corresponding to multiple scattering.

Neglecting the term originating from the multiple scattering the expression is greatly simplified. Applying this approximation, one may write the reflection amplitude of \( N \) layers as

\[ r = r_{0,1} + r_{1,2}e^{iQ_zd_1} + r_{1,2}e^{i(Q_zd_1 + Q_zd_2)} + \cdots + r_{j,j+1}e^{i\sum_{l=1}^{j}Q_zd_k} \]
Figure 7: Comparison of simulated reflectograms of a semi-infinite sapphire surface (black) and a 300 Å thick Poly(methyl methacrylate) layer on top of a semi-infinite sapphire surface.

We can now express $r_{j,j+1}$ as

$$r_{i,i+1} = \sqrt{\frac{Q_d^2 - Q_{c,i}^2}{Q_d^2 - Q_{c,i+1}^2}} \sqrt{\frac{Q_d^2 - Q_{c,i+1}^2}{Q_d^2 - Q_{c,i}^2}} \frac{Q_{c,i+1}^2 - Q_{c,i}^2}{4Q_d^2} = \frac{4\pi (\rho_{i+1} - \rho_i)}{Q_d^2}$$

Substituting this into the expression, and introducing $z_j = \sum_i^j d_k$, as the depth of the $j+1^{st}$ interface we get

$$r = 4\pi \sum_0^N \frac{(\rho_{i+1} - \rho_i)}{Q_d^2} e^{iQ_dz_j}$$

One may transition from summation to integration by building up the sample using infinitely thin layers and arrive at this expression, which is the reflection amplitude according to the kinematic theory:

$$r = \frac{4\pi}{Q_d^2} \int \frac{\partial \rho(z)}{\partial z} e^{iQ_dz} dz$$
Calculating the reflected intensity and substituting the Fresnel reflectivity, one arrives to the well-known expression for the Born approximation for an arbitrary SLD profile

$$R = R_f(Q_z) \left| \frac{1}{\rho_{\infty}} \int \frac{\partial \rho(z)}{\partial z} e^{iQ_z z} dz \right|^2$$

Although, this is a very simple expression, it is not exact. Calculating the reflectivity curve is usually done by calculating the probability amplitudes for each layer. A schematic illustration of an N-layer sample is presented in Figure 8. One method for this is the Parratt recursive algorithm\(^{80}\). This exploits the fact that the reflection and
transmission amplitudes in each layer depend on their values in the layer below and the Fresnel coefficient of the lower interface. Thus, starting from the substrate layer one can calculate the reflectivity using the following expression

\[ X_j = \frac{B_j}{A_j} = e^{i2k_jz_j} \frac{r_{j,j+1}}{1 + r_{j,j+1}e^{i2k_{j+1}z_j}} \]

where \( A_j \) and \( B_j \) are the transmission and reflection probability amplitudes in the \( j \)th layer and \( z_j \) is the depth of the \( j \)th interface. To calculate the amplitude of the reflected beam \( B_0 = r \), one must consider that \( A_0 = 1 \), since the incoming plane wave has an amplitude of unity, and that \( B_N = 0 \), as there is no reflection from the back side of the sample.

The other method is called the Abeles matrix formalism. The continuity conditions for the neutron wavefunction at the \( j \)th interface at the depth of \( z_j \) can be written as

\[ A_j e^{ik_j z_j} + B_j e^{-ik_j z_j} = A_{j+1} e^{ik_{j+1} z_j} + B_{j+1} e^{-ik_{j+1} z_j} \]

and

\[ k_{j+1}(A_j e^{ik_j z_j} - B_j e^{-ik_j z_j}) = k_{j+1}(A_{j+1} e^{ik_{j+1} z_j} - B_{j+1} e^{-ik_{j+1} z_j}) \]

These two equations can be summed up using matrix formalism

\[
\begin{bmatrix}
A_j \\
B_j
\end{bmatrix} = \begin{bmatrix}
k_{j+1} + k_j z_j & k_{j+1} - k_j z_j e^{-i(k_{j+1} x_j + k_j x_j)} \\
k_{j+1} - k_j z_j e^{i(k_{j+1} x_j + k_j x_j)} & k_{j+1} + k_j z_j e^{i(k_{j+1} x_j + k_j x_j)}
\end{bmatrix} \begin{bmatrix}
A_{j+1} \\
B_{j+1}
\end{bmatrix}
\]

This matrix is noted \( S_{j,j+1} \). To calculate the reflectivity \( B_0/A_0 \), one must solve the equation

\[
\begin{bmatrix}
A_0 \\
B_0
\end{bmatrix} = S_0 S_1 S_2 ... S_{N-1} S_N \begin{bmatrix}
A_N \\
B_N
\end{bmatrix} = M \begin{bmatrix}
A_N \\
B_N
\end{bmatrix}
\]

Where the matrix \( M \) is called the transfer matrix. Substituting \( B_N = 0 \) since there is no reflection from the back side of the sample, one arrives to the following result

\[
r = \frac{B_0}{A_0} = \frac{M_{21}}{M_{11}}
\]

Being able to calculate the reflectivity of a layer stack, results in the ability to calculate the reflectivity for an arbitrary structure by slicing up the profile into thin slices and calculating the reflectogram of the stacks.
Roughness
Up to this point we have been looking at ideally smooth interfaces. Real interfaces have a finite roughness either because of a jagged interface (Figure 9A) or because of interdiffusion between the layers (Figure 9B). This can be modelled by replacing $z_j$ in the calculations with $z_j + z'_j(x, y)$, where $z'_j(x, y)$ is the distance from the interface depending on the position in the x,y plane. This value is usually considered as having a normal distribution that is characterized by the value $\sigma_j$ (Figure 9D). By averaging over the plane of the sample, the ratio of the matrix components is found to be

$$\frac{R_{j,j+1}}{R_{j,j+1}^{flat}} = e^{-2k_j k_{j+1} z \sigma_j}$$

This exponential expression is called the Névot-Croce factor, which, when the Born approximation holds, simplifies into a Debye-Waller factor.

$$\frac{R_{j,j+1}^{rough}}{R_{j,j+1}^{flat}} = e^{-q^2 \sigma_j^2 / 2}$$

Figure 9A: Illustration of a jagged interface between two layers. B: Illustration of a diffuse interface between two layers. C: Illustration of the SLD profile of a rough interface described with a normal distribution. D: Illustration of the derivative of the SLD profile at a rough interface described with a normal distribution.

The exponent in the expression above is always negative meaning that the reflected intensity is less from a rough interface than from a flat interface. This is illustrated in Figure 10A for a semi-infinite layer. For a finite layer on a semi-infinite substrate roughness presents itself in the decay of the amplitude of the Kiessig fringes, which is illustrated in Figure 10B. This loss of the reflected intensity is caused by two different mechanisms for the two types of rough interfaces. In case of the diffuse interface this can be understood using the kinematic expression of the reflectivity of an arbitrary SLD profile. There the reflectivity is dependent on the derivative of the SLD profile. At sharp
interface this derivative is larger than at a diffuse interface meaning that at a rough interface more intensity is transmitted through the interface. However, this is not the case at a jagged interface. Here our assumption about a structureless surface becomes invalid. The scattering angle will be different from the angle.

![Figure 10A: Comparison of simulated reflectograms for a semi-infinite sapphire surface without (black) and with 10 Å surface roughness (red) B: Comparison of simulated reflectograms for 300 Å thick Poly(methyl methacrylate) layer on a semi-infinite sapphire surface without (black) and with 10 Å surface roughness (red).](image)

between the \( k_i \) and the XY plane. This will result in reflections in directions different from the specular direction, resulting in off-specular scattering.

The calculations presented above are valid in the simple case of a roughness that is independent of the position in the XY-plane and has a Gaussian height probability. This simple model is what is usually implemented in fitting programs. However, this does not mean that real interfaces may always be accurately modelled this way. In **Paper I** we use a double Gaussian model to fit our samples.

**Magnetic Samples**

Since neutrons have a magnetic moment \( \mu_n \), they interact with the magnetic induction vector \( B \) in the sample. This can be used to investigate the magnetization in the samples, using a technique called polarized neutron reflectometry. The interaction of the neutron and the magnetic induction can be described using a magnetic potential \( V_{mag}(r) \) as

\[
V_{mag}(r) = -\mu_n \cdot B(r)
\]

This potential can be expressed analogous to the scattering length for a given element as

\[
b_{mag} = \frac{2.69}{\mu_B \mu} fm
\]

where \( \mu_B \) is the Bohr magneton and \( \mu \) is the magnetic moment of an atom of the element. The potential can also be expressed in a form similar to the SLD as
\[ \rho_{\text{mag}} = 2.3 \times 10^{-6} B \frac{1}{A^{2/T}} \]

where \( B \) is the magnitude of the magnetic induction at the position of the neutron. The scalar product in the expression of the potential means that depending on the orientation of the two vectors the additional scattering term would have a different sign. This parallel or anti-parallel orientation is called the polarization of the neutron.

\[ b = b_{\text{nuc}} \pm b_{\text{mag}} \]

For reflection to happen there must be a jump in the scattering potential. Solving Maxwell’s equations for a planar sample, shows that the perpendicular component of the magnetic induction \( B_{\perp}(r) \) is continuous and that the jump in the component parallel to the sample surface \( B_{\parallel}(r) \) is equal to \( \mu_0 M_{\parallel}(r) \), where \( \mu_0 \) is the permeability of free space and \( M_{\parallel}(r) \) is the component of the magnetization vector parallel to the surface. The polarization of the neutron can only probe one component of \( M_{\parallel}(r) \) depending on the orientation of the sample. However, the other component, perpendicular to the polarization, applies a torque that may result in the change of the polarization direction of the neutron. This is called the spin flip reflection and it is dependent on the component of the in-plane magnetization that is perpendicular to the polarization.

A more detailed discussion of polarized neutron reflectometry is presented in Gibaud\(^{86}\).

Off-specular reflectometry

Specular reflection is the case when the reflected beam is within the plane of incidence, the plane defined by the surface normal and the incident wavevector, and the angle of reflection is equal to the angle of incidence. As mentioned in the paragraph about the roughness, local variations in the angle of the surface will cause the reflected beam to deviate from the specular direction. This is called off-specular scattering. This means that \( \mathbf{Q} \) has other components, illustrated in Figure 11, that can be calculated as

\[
Q_x = k_0 (\cos \theta_i \cos \psi - \cos \theta_f)
\]

\[
Q_y = k_0 (\cos \theta_i \sin \psi)
\]

\[
Q_z = k_0 (\sin \theta_f + \sin \theta_i)
\]

where \( k_0 \) is the magnitude of the incident wavevector, \( \psi \) is the angle between the plane of incidence and the reflected wavevector, \( \theta_i \) and \( \theta_f \) is the angle between the surface of the sample and the incident and reflected wavevector, respectively. The \( Q_y \) component\(^{85–87}\) of the scattering can be studied during a conventional neutron reflectometry experiment by using a 2D neutron detector. The intensity reflected to different \( \theta_f \) angles will appear as lines on both sides of the specular beam. Measuring the \( Q_x \) component of the momentum transfer is done by grazing incidence small angle neutron scattering (GISANS) experiments\(^{88}\). The gathered data in both cases can be analyzed using the distorted wave Born approximation of scattering\(^{89}\). Unlike the Born approximation this formalism is designed to model multiple scattering by treating its effects as perturbations to the average neutron field that is calculated by the Born approximation.
Figure 11: Scattering geometry for off-specular scattering.

Instrumentation

There are two types of instrument setups measuring neutron reflectometry corresponding to the two variables in the expression \( Q = \frac{4\pi \sin \delta}{\lambda} \). Instruments that measure \( Q \) by changing \( \delta \) are called angle dispersive instruments. The other type of instruments, that measure the reflectivity for different wavelengths using a technique called time-of-flight (ToF), are called ToF instruments. A schematic drawing of a neutron reflectometer is displayed in Figure 12.

Changing \( \delta \) is straightforward in case of solid samples, to record the specular reflectogram the sample is rotated with the angle \( \delta \) while the detector is rotated to twice the angle. For liquid surfaces the incoming beam is diverted using a mirror and the sample is lowered while the mirror is rotated to change the angle. The divergence (\( \Delta \delta \)) of the beam is defined by slits made from neutron absorbing material. Older devices use Cd metal as absorber, but new slits use B\(_4\)C ceramics to decrease the energy of emitted gamma rays.

Selecting a wavelength from a white neutron beam is done using a diffraction peak from a crystal. The wavelength of the beam is calculated using Bragg’s law. The use of highly oriented pyrolytic graphite crystals is preferred over single crystal pieces to increase the intensity at the cost of the wavelength resolution (\( \Delta \lambda \)). The \( \Delta \lambda \) can be further decreased using a velocity selector for even higher gains in intensity\(^9^0\). Changing \( \lambda \) is done using a technique called time-of-flight neutron spectroscopy, where the wavelength of the neutron is determined by measuring its speed, more precisely the time it takes to reach the detector. The start signal for the time measurement is determined using one or a pair of beam choppers\(^9^1\), rotating disks of neutron absorbing material with a small opening, depending on if the source is pulsed or not. This technique is inherently used with pulsed sources, as no neutrons are generated between the pulses, giving time for the neutrons to arrive at the detector. A novel technique to measure the wavelength of the neutrons is utilizing the angular deflection of a prism\(^9^2,^9^3\). Converting the wavelength into angle and using a position sensitive
Figure 12: Schematic drawing of a neutron reflectometer. The wavelength is defined by a monochromator or a chopper setup (W), followed by a wavelength filter (F) and a monitor detector (M). This is followed by a polarizer (P) and a spin flipper (S). The angular resolution of the beam is set using slit S1 and S2. S3 is placed after the sample, to decrease the background, and if needed an additional spin flipper and polarizer can analyse the polarization of the reflected beam. The reflected intensity is measured using a detector (D). In case of a point detector an additional slit (S4) is used to select the specular reflection.

detector, a wide Q range can be measured at the same time without chopping the beam, resulting in a major decrease in measurement time.

The resolution of the instrument ($\Delta Q$) can be expressed as a function of $\Delta \theta$ and $\Delta \lambda$ as $(\Delta Q/Q)^2 = (\Delta \theta/\theta)^2 + (\Delta \lambda/\lambda)^2$. The intensity of the beam depends on how wide the acceptance criteria is for the neutrons so that it can be estimated as $\Delta \theta \Delta \lambda$. For a given intensity the minimum of the resolution is given when $\Delta \theta/\theta = \Delta \lambda/\lambda$. Since for angle dispersive systems and ToF systems using double disk choppers\textsuperscript{91} $\Delta \lambda/\lambda$ is constant, as $\theta$ increases the $\Delta \theta$ can be increased by opening the slits, gaining intensity without sacrificing resolution.

Wavelength filters are used to discard unwanted wavelengths. In case of a ToF instrument the filter includes a frame overlap mirror, usually angled so that it diverts neutrons that would reach the detector late and would contaminate the next frame. For single wavelength instruments, only the base harmonic from the solutions of the Bragg equation is used. The rest is discarded by a Be filter or a mirror. Be filters have the advantage that they do not change the beam path, but they require constant LN$_2$ cooling for optimal transmission. Mirrors do not require constant maintenance; however, they usually divert the beam changing the optical axis of the instrument. Mirrors can be made from magnetic material, making them polarizers as well.

To conduct experiments using polarized neutrons one spin state has to be selected. This is done by sending the neutron beam through a magnetic field and discarding one spin state. For this magnetic mirrors\textsuperscript{94-95}, polarized $^3$He filters\textsuperscript{96-97} or Heussler monochromators\textsuperscript{98-99} are used. To avoid the intensity loss during the polarization more complex polarization setups were proposed\textsuperscript{100}. To retain the polarization of the neutrons a magnetic field (~2 mT) with a constant direction, called the guide field, has to be applied throughout the neutron path. Devices, called spin flippers, are used to change the direction of the polarization. Two examples are the Mezei type\textsuperscript{101} and the radio frequency gradient type\textsuperscript{102}. To determine the component of the magnetization that is parallel with the guide field, the setup requires a polarizer and a flipper before
the sample, while the measurement of the spin-flip signal requires an additional spin flipper and polarizer analysing the spin state of the reflected neutrons.

The detection of neutrons is done by detecting the products of nuclear reactions involving neutron absorption. The most common reaction used is the \( \text{n} + ^3\text{He} \rightarrow ^3\text{H} + ^3\text{H} + 0.764 \text{MeV} \), because of the high capture cross section of \(^3\text{He}\) and other favourable properties, such as low gamma sensitivity and chemical inertness. A typical detector is a \(^3\text{He}\) gas filled proportional counter\(^{103}\), but, due to shortages of \(^3\text{He}\) supply\(^{104}\), new boron nitride semiconductors are being developed\(^{105}\). In addition to the main detector, a low efficiency monitor detector is also placed in the beam upstream from the sample to monitor the fluctuations in the source intensity.

In Paper V an angle-dispersive reflectometry setup with a polarized option is presented that was built at the Budapest Research Reactor.

Contrast variation method
The unique advantage of neutron scattering is that no other scattering method used in condensed matter science interacts with the nuclei. This can be exploited by labelling parts of the sample with different isotopes\(^{106,107}\). This is commonly used in soft matter research but has also been implemented in solid films\(^{108,109}\). In Paper I and Paper II we have utilized deuterated methacrylic acid monomers to differentiate them from the other monomers in the films. Another essential use of isotope substitution is determining the solvent volume fraction profile in the system. The SLD of a hydrated polymer layer (\(\rho_{\text{layer}}\)) can be written as

\[
\rho_{\text{layer}} = \rho_{\text{poly}} \phi_{\text{poly}} + (1 - \phi_{\text{poly}}) \rho_{\text{solvent}}
\]

where \(\rho_{\text{poly}}\) is the SLD of polymer in the layer, \(\phi_{\text{poly}}\) is the volume fraction of the polymer in the layer, and \(\rho_{\text{solvent}}\) is the SLD of the solvent. By measuring the same sample with different ratios of deuterated and hydrogenated solvent, most commonly with \(\text{H}_2\text{O}\) and \(\text{D}_2\text{O}\), and simultaneously fitting the datasets, constraining the SLD of the polymer layer according to the equation above, \(\rho_{\text{poly}}\) and \(\phi_{\text{poly}}\) can be determined. Although, measuring with two solvents would provide enough information to solve the equation, measuring a third contrast increases the precision of the modelling\(^{110}\). In Paper II and Paper IV this method was used to determine the volume fraction depth profiles of the polymer in the hydrated layers. Isotope variation of the substrate may also be used to determine the phase of the reflected beam\(^{111}\). However, the method only works if only the substrate layer is affected by the variation.

Polymer models
Polymer brushes are densely packed polymer chains with one end grafted to a surface. Their structure has been modelled using scaling\(^{112}\) and self-consistent\(^{113,114}\) field theory. It was determined that the chains do not stretch uniformly, and they adopt a parabolic volume fraction profile

\[
\phi(z) = \phi_0 \left(1 - \left(\frac{z}{h}\right)^2 \right)
\]
where $\phi_0$ is the grafting density and $h$ is the height of the brush. However, through extensive experimental work\textsuperscript{115–117} it was determined that real brushes adopt a stretched polymer volume fraction profile

$$\phi(z) = \phi_0 \left(1 - \left(\frac{z}{h}\right)^2\right)^\alpha$$

where $\alpha$ is the stretching exponent and that the values of $\alpha$ was found to decrease to $\alpha = 2$ from higher values with increasing grafting density\textsuperscript{118}. Similar calculations using self-consistent field theory on charged polyelectrolyte brushes\textsuperscript{119} in the salt free limit resulted in a volume fraction profile

$$\phi(z) = \phi_0 e^{-\left(\frac{z}{g}\right)^2}$$

where $g$ is the characteristic length of the Gaussian profile. In Paper II the volume fraction profile of a polymer layer grafted using the SI-PGP method was studied by comparing parabolic, gaussian, and sigmoidal polymer models.

Modelling neuron reflectometry

An inherent flaw of neutron reflectometry is that only the intensity of the reflected beam can be measured, but its phase cannot. This makes it impossible to directly calculate the SLD profile from the recorded reflectogram, as multiple profiles can result in similar reflectograms. Instead, the profile is determined by modelling the layer structure and fitting the model parameters. The lack of phase information also entails the abundance of local minima in the parameter space hindering the fitting process and increasing the possibility of overfitting\textsuperscript{120}. To facilitate the search for the global minimum, fitting programs implement stochastic optimization methods\textsuperscript{121,122} such as differential evolution, simulated annealing, or stochastic tunnelling, and novel machine learning methods are being investigated for evaluating reflectograms\textsuperscript{123,124}. The recorded reflectivity spans several orders of magnitude in value. This hampers the evaluation of the fit results with conventional $\chi^2$ statistics, since it favours the large values measured at low $Q$ describing the critical edge, and neglects the rest of the data in the process, while the information about the structure is usually found in the higher $Q$ regions of the spectrum. In this work, the chosen figure-of-merit (FoM) for the fitting was the log and logbars FoM featured in the GenX program\textsuperscript{121}, that only allowed for estimations of the uncertainty of the parameters. A recent approach of evaluating the goodness of the fit is based on Bayesian probability theory\textsuperscript{125,126} that is being implemented in all of the fitting software. To avoid overfitting, constraints may be used to decrease the number of parameters in the system. One such constraint is the amount of polymer, determined from measurements under dry conditions. This has been implemented into fitting using the method of Lagrange multipliers\textsuperscript{127}, but we constrained the amount of polymer for the models in Paper II by numerically calculating the relevant parameters of the models.

Further improvements to the method could be achieved by determination of the phase information using magnetic reference layers\textsuperscript{3}. Although these layers improve the precision of the experiment, they are not widely used as current realizations introduce extra scattering that drowns the signal from the investigated system\textsuperscript{128}. To illustrate this, simulations of a magnetic reference system (with the structure Si // SiO$_2$ 5Å //
Permalloy 150Å // Au 150 Å) with and without a polymer layer is presented in Figure 14. In this figure, the simulated reflectograms of the magnetic reference samples with only an alkylthiol monolayer (solid lines) are compared to the uncertainty of the data of the same system having a polymer layer (shaded area), to illustrate the effects of the extra scattering introduced by the magnetic and gold layers. The uncertainty was calculated according to the Poisson statistics supposing 10⁵ counts at the total reflection edge. The Kiessig fringes in the figures are originating from the Permalloy and Au layers, and only in case of the D₂O solvent did the polymer introduce sufficient contrast to influence the reflectogram significantly. It has to be noted though, that NR data is usually measured with a better statistic in the high Q region than the data presented in Figure 14. However, as available neutron time is a limiting factor for the experiments¹¹⁰, reference samples with less added contrast are sought after. Current research in developing magnetic reference layer structures is focusing on SiO₂ cover layers instead of Au. In Figure 13 a polarized neutron reflectogram of a 10 nm Fe magnetic reference layer covered with a 4 nm SiO₂ layer with a 13 nm thick polymer film measured dry with the beam arriving from the Si side is presented. The data was measured on the GINA reflectometer described in Paper V. The R⁺ channel is dominated by the Kiessig oscillations corresponding to the magnetic Fe layer. Unfortunately, the same oscillations can be seen in the R⁻ channel, indicating the contrast introduced with the magnetic reference layers. The current challenge in producing such layers is the deposition of sufficiently smooth SiO₂ layers, that prevent the Fe ions from leaking into the solution, as multivalent ions may interfere with investigations¹²⁹.

Figure 13: Polarized neutron reflectogram of a 10 nm Fe magnetic reference layer covered with a 4 nm SiO₂ layer with a 13 nm thick polymer film measured dry, with the beam arriving from the Si side. R⁺ denotes the parallel, while R⁻ is the antiparallel spin orientation, relative to the magnetization of the Fe layer.
Figure 14: A comparison of simulated polarized neutron reflectograms of the magnetic reference structure Si // SiO2 5Å // Permalloy 150Å // Au 150 Å measured in three solvents D2O (A, B, C), CMSi (D, E, F) and H2O (G, H, I). The shaded area represents the standard deviation of the reflectometry data calculated if the sample had a polymer layer on top of the magnetic structure. The R+ channel is coloured in blue and the R- in red. The corresponding SLD profiles are shown in the right column (C, F, I).
Auxiliary methods

In the course of the work presented here, additional methods were used to characterise the samples, complementing the neutron reflectometry experiments. These methods all utilise electromagnetic radiation as the probe to investigate the samples. In Paper I the thickness and roughness parameters of the dry films were determined using X-ray reflectometry, while the hydration of the films was studied using spectroscopic ellipsometry. In Paper III ellipsometry was utilized to follow the thickness changes caused by fouling and infrared spectroscopy to monitor the vibrations of amide bands appearing due to the adsorption of the model proteins. A mobile setup was developed for combining ellipsometry and infrared spectroscopy with neutron reflectometry in situ measurements that is presented in Paper IV.

Spectroscopic Ellipsometry
Electromagnetic radiation is a propagating transversal oscillation of the electromagnetic field. The propagation direction is perpendicular to the oscillations of both the magnetic and the electric field, while the two fields are also perpendicular to each other. The polarization of the wave describes the behaviour of the electric field in the plane perpendicular to the vector of propagation. The polarization is denoted using Jones vectors, which are two-component complex vectors, and optical elements that change the polarization are described using Jones matrices. Ellipsometry measures the change in the polarization after the light has interacted with the sample. The measurement is usually done in reflection geometry, however for transparent samples transmission ellipsometry is also feasible, and data is recorded at multiple wavelengths and angles of incidence when possible. The component of the electric field that is within the plane of incidence is referred as the “p” component while the component perpendicular to the plane is the “s” component. If the sample is isotropic, the Jones matrix of the sample has only two non-zero components, \( r_s \) and \( r_p \) in the diagonal, that are the reflection amplitudes for the “s” and “p” polarizations, respectively. From these two components one can calculate the reflectance ratio \( \rho \). This can be expressed as \( \rho = \frac{r_p}{r_s} = \frac{\tan \Psi \tan \Delta}{\sin \Psi} \), where \( \Psi \) and \( \Delta \) are the two ellipsometric angles. The complex refractive index \( n(\lambda) \) of sample can be determined by modelling utilizing the Fresnel equations, Snell’s law, and the measured angles, similarly to neutron reflectometry. For multilayer samples the matrix formalism is used to determine the layer structure. To aid in these calculations, databases with tabulated refractive indices exist for the more commonly used materials. However, the polymer films, that were studied in this work have no such data available, so \( n(\lambda) \) of the films were modelled using the Cauchy formula, that is commonly used for transparent layers. To calculate the optical properties of mixtures of the various materials, effective media approximations are employed. The different setups and modelling programs used for the ellipsometry measurements are described in the presented papers. However, in Paper I an advanced form of ellipsometry based on Mueller calculus was used on the dry films for increased precision. Since this method requires specialized instrumentation, it was not utilized for the rest of the experiments.
Spectroscopic ellipsometry has some significant advantages over neutron reflectometry. Being a desktop method, it is relatively inexpensive, and the intensity of the common light sources allow for measurement times of the order of seconds. Due to the accessibility of phase information, the precision of ellipsometry is of the order of 0.1 nm, despite using the visible light wavelength range (300-1000 nm). The method is also capable of investigating films in the µm thickness range that are unavailable for neutron reflectometry. Due to the minimal differences in electron densities of organic matter, differentiating between components of an organic layer is demanding, however, because of the very similar refractive indices.

X-ray reflectometry

X-ray radiation is electromagnetic radiation with wavelength shorter than 10 nm generated by either by bremsstrahlung or electrons filling vacancies in lower atomic orbitals. Their short wavelength makes it possible to utilize them as probes for atomic structures. High energy photons interact with matter in three ways, by photoelectric absorption, scattering, and pair generation. Here we are only concerned by the elastic scattering of low energy X-rays. In case of reflectometry, X-rays can be treated similarly to neutrons. One can define a refractive index \( n = 1 - \delta - i\beta \). Here

\[
\delta = \frac{\lambda^2}{2\pi r_e \rho_e}
\]

where \( \lambda \) is the wavelength of the X-rays, \( r_e \) is the classical electron radius, and \( \rho_e \) is the electron density. Instead of solving the Schrödinger equation, one solves the Maxwell equations to calculate the reflection amplitudes. Beside the X-rays not probing the magnetic properties of the samples in reflection, the treatment of the data is analogous to the procedure detailed in the neutron reflectometry chapter.

![Figure 15: Attenuation length of X-rays in water (data from database).](image1)

The major advantage of X-rays over neutrons is the commercial availability of instruments that have effective brightness three orders of magnitude higher than that of the brightest neutron sources. However, for light elements X-rays have very similar scattering length densities meaning that it is difficult to differentiate between both the different monomers or the adsorbed water and the polymer in the films. Also,
isotope labelling is not possible, since X-rays interact with the electron cloud. Measurements of the solid /liquid interface are also greatly hindered by the attenuation in water, displayed in Figure 15. Common lab sources, such as Cu K-α tubes, do not have the sufficient energy to penetrate down into the water at grazing incidence, thus higher energy sources, typically Mo K-α tubes, or synchrotron sources, are used for these investigations. Despite all these disadvantages, X-ray reflectometry was routinely used in this work to determine the dry thickness and surface roughness of the samples grafted on Si surfaces. Samples grafted on Au surfaces were not studied, since the large contrast between the air and the Au layer masked the signal from the polymer layer.

Infrared Spectroscopy
Molecules are made up of atoms connected by chemical bonds. The atoms are not fixed but are in constant thermal motion and they vibrate around an equilibrium point. The potential of these vibrations can be approximated using a harmonic potential, and by solving the Schrödinger equation the energy levels can be determined for a given vibration. The energy differences between the levels fall into the frequency range of the infrared (IR) light, so they may be excited by absorbing IR radiation. The absorption frequency depends on the type of bond, its strength, and the masses of the atoms. Infrared absorption spectroscopy measures the frequency of the light absorbed by the bond vibrations in materials, resulting in spectra from which the chemical composition of the sample might be inferred.

IR spectrometers have three main parts: a light source, optics and a detector. Modern spectrometers utilize an interferometer for splitting the energy spectrum, by introducing wavelength dependent radiation modulation. As light sources, silicon carbide heating elements and tungsten-halogen lamps are most commonly used, while detectors are usually pyroelectric sensors made from deuterated L-alanine-doped triglycine sulphate, or semiconductor diodes made from mercury cadmium telluride which are cooled, usually with LN₂, for increased sensitivity and reduced noise. The interferometer is usually a Michelson type interferometer. To obtain an absorption spectrum, a background measurement and a measurement with the sample is needed. In the presented works IR measurements were conducted on thin films, thus instead of transmission geometry either infrared-reflection absorption geometry or attenuated total reflection (ATR) geometry was used. When measuring films with infrared-reflection absorption spectroscopy, the film has to be deposited on a metal surface that has a high reflection in the IR region. In Paper III gold coated glass surfaces were used as substrates for this reason. The light is then reflected at a shallow angle from the surface to increase the beam path through the film. For measurements in ATR geometry the film is placed in contact with a prism with high refractive index and low absorption for IR light. The light is then reflected from the back side of the prism where it undergoes total reflection. However, the evanescent beam will enter the film during reflection making it possible to absorb the light in the film. The prisms can be designed to allow multiple reflections on the surface with the sample, increasing the signal. In the setup presented in Paper IV for the combined neutron, spectroscopic ellipsometry, and IR spectroscopy, the ATR geometry was chosen to enable the investigation of hydrated polymer films, as water is not transparent in the used IR wavelength range. In this case the polymer film was grafted directly on top of the prism.
Understanding the SI-PGP process

The aim of the work described in the thesis was to determine the structural parameters of polymer thin films that were produced using the SI-PGP method from methacrylic monomers, to gather information about the grafting process, to determine key parameters that influence the grafting for a better control of the method, and to develop instrumentation for facilitating the study of hydrated thin films. Essential to reach the aims is the understanding of the molecular mechanisms that are behind the SI-PGP process.

There are multiple processes for acrylic and methacrylic monomers to form radicals due to the interaction with UV-light, and that can cause self-initiation and photografting. One of the main processes involves a UV photon exciting the C=C bond to a triplet state through intersystem crossing, which in turn form bi-radicals. It was also proven that shorter wavelength (< 220 nm) photons can excite the C=O bonds, however this excitation is hypothesized to results in radical recombination and crosslinking after radical transfer reactions. Further studies on pyruvic and acrylic acid claimed that C-C and C-O bonds can be split by UV-radiation (< 249 nm), forming radicals. These free radicals can also initiate the polymerization reaction. Grafting of the polymer happens when a hydrogen atom is abstracted from the surface by the radical at the end of the chain. Calculations of the energy of the excited triplet state resulted in an energy of 471 kJ/mol (corresponding to 254 nm wavelength). This value is larger than the bond strength of the primary, secondary and tertiary hydrogens (418, 402, and 389 kJ/mol, respectively) making the process possible on any kind of organic surface having available hydrogens for abstraction, including the already grafted chains, allowing for branched or even crosslinked polymer films.

The UV-induced free-radical polymerization used in SI-PGP is believed to result in heterogeneous films. In contrast to more well-defined brushes, there are no accepted models for the polymer density profile under hydrated conditions. In Paper II multiple NR measurements were performed on poly(HEMA-co-PEGMA) films utilizing the contrast variation method. Three different samples were studied with different dry thicknesses, two grafted onto Si and one onto Au surfaces. The measured data was analysed using three different models: a sigmoidal model, that has been used to describe the structure of a hydrated hydrogel, a parabolic model, that corresponds to a hydrated brush, and a gaussian model, that corresponds to a stretched brush. To improve the precision of the fitting the amount of polymer has been constrained. The fits resulted in very similar SLD profiles from all models (see Figures S4, S6 and S8 in the support information of Paper II). From the models, the Gaussian model was chosen as the one best suited to represent the structure, because the rest of the models resulted in parameters that contradict the assumptions of the respective models. The selected model describes a swollen brush stretched beyond what is expected from the excluded volume interactions. The origin of this extra stretching is not clear from the neutron experiments. Here it is attributed to the interaction between the PEGoMA sidechains in a bottlebrush-like manner. However, recent results indicate that PEG may bind with hydronium ions, forming a so-called supra-
polyelectrolyte\textsuperscript{150}. If these results are confirmed, that may explain the observed stretched profiles, due to electrostatic repulsion of the PEG-containing sidechains. The comparison of grafting speeds for the two substrates shows that the layers grow faster on the Au surface, which is in accordance with previous results\textsuperscript{151}, and which is discussed further below. The observed structure shows a depth dependence of the polymer density in the films, which is not consistent with the assumptions made in previous works on similar films\textsuperscript{71}.

In previous work in this laboratory, SI-PGP was used to prepare films with composition gradients using sequential grafting of different monomers\textsuperscript{32,152}. The interpretation of the results in these studies were hindered by the lack of structural information, and limited understanding of the grafting and polymerization processes. To answer these questions about the grafting method, an additional polymerization step was performed on top of the existing layers using deuterated methacrylic acid (d-MAA) monomers. This also measures the possibility of the monomers grafting onto existing chains to form sidechains or crosslinks, by tracking the position of the labelled monomers after the sequential grafting. The samples were measured with neutron reflectometry before and after the second grafting step. The resulting SLD profiles indicate that in case of the Si substrates, the new monomers attach to the Si surface and not to the previously grafted chains, while on the Au substrate, there are indications of grafting occurring on top of the existing layer (see Figures 6 and 7 in Paper II). During grafting there is a parallel and continuous degradation of the layer by the UV illumination. There is a large difference in the rate of removal of the previously grafted material from the two different surfaces. The estimated amounts remaining from the initial layers on the Si samples were 10-15\%, while on the Au surface it was close to 100\%. A possible explanation that connects the difference in the grafting speed, the difference in the removal rate, and the preference of grafting from the substrate (as opposed to grafting from the existing polymer) in the second grafting, is that Si has approximately twice the reflectance in the relevant UV wavelength range, as compared to Au\textsuperscript{151}. The increased UV intensity near the surface of the Si substrates increases the removal rate of material from the surface by radiation damage, which slows the grafting process, and prevents the grafting to the existing material by constantly degrading the top layer. Previous investigations into the degradation rates of polymer films made using different monomers show clear differences in their resistance to UV damage\textsuperscript{26}. This aspect of the process was not studied in this work, however these differences in the UV degradation may be correlated to the varying UV absorption characteristics of the different monomers, which is discussed below.

In Paper II the possible grafting models was also considered. The “grafting from”\textsuperscript{35}, the “grafting to”\textsuperscript{34}, and the “grafting through” models were examined. The “grafting through”\textsuperscript{153} model is a variation of the “grafting to” process, where the chains polymerize in the solution, then attach to the surface through a surface-bound monomer without terminating at attachment, and the continues with the polymerization. Previous results on p(HEMA-co-PEG\textsubscript{10}MA) films grafted by SI-PGP showed that there is a maximum in the thickness of the films with increasing grafting time\textsuperscript{26}. This could be attributed to a diffusion barrier that prevents the chains formed in the solution to reach the surface and graft there, suggesting a “grafting to” or a “grafting trough” process. This could also be a result of monomer depletion, which
would be consistent with the “grafting from” model. Another argument for the “grafting from” model can be made by looking at the grafting densities of the layers. From modelling the NR data, the grafting density ($\phi_0$) was determined to be 40-60% for the Si samples and 80-90% for the Au samples, both before and after the second deposition, indicating that these values were determined by the densities of the SAMs on the substrates (see Figure 8 in Paper II). If the thickness was limited by a diffusion barrier there would not be such a difference in the grafting densities. In this case the $\phi_0$ values are probably determined by the density of the silane (65%) and the thiol (95%) layers further supporting the “grafting from” model, but the exact details of the process are still unclear. There is data, measured on a 16-Mercaptohexadecanol (C16OH) SAM to test the stability of the monolayer under UV-irradiation, shown in Figure 16, suggesting that the SAM layer is relatively intact even after a long exposure to the UV radiation, meaning that the degradation mostly affects the polymer layer, and not the SAM. However, initiatorless polymerization of methacrylic and acrylic monomers have been reported in microemulsions, indicating that polymerization may take place in solution. During our investigations, several attempts were made to collect and to analyse the remainder of the grafting solution after grafting, to determine the amount of polymers or oligomers in the solution, but without success.

The SI-PGP method was further investigated using charged monomers in Paper I, where the samples were prepared by sequential grafting in a set of 12 samples with different grafting times. First, a dMAA layer was grown onto silanized wafers, illuminating for 3, 4, 5, and 6 minutes, then an AEMA layer was grafted directly on top of the dMAA layer, illuminating for 3, 4, and 5 minutes. The samples were labelled as $S_{ab}$, where $a$ and $b$ are the dMAA and AEMA grafting times, respectively. The thickness of the initial layer was determined using X-ray

![Figure 16: Infrared reflection-absorption spectra of C16OH SAMs, as prepared (black), and after 3 (red) or 10 min (blue) UV irradiation, respectively. The largely unchanged intensities and peak positions of the CH$_2$-stretching bands centered around 2850 and 2920 cm$^{-1}$ (black arrows) indicate that the hydrocarbon chain region of the SAM is little affected by the irradiation. The emergence of the CH$_3$ band at 2966 cm$^{-1}$ (blue arrow) after 10 min indicates that there is conversion of the chain ends, however](image-url)
reflectometry (XRR). The dMAA layer thicknesses showed little variance, despite the differing grafting times, and were found to be on average $74.0 \pm 1.5$ Å with a maximum deviation of $13.2 \pm 1.7$ Å. This could be caused by quick depletion of available monomers. Because of this result, the samples were regarded as having identical dMAA layers before the sequential grafting, and were grouped according their AEMA grafting times. The dry structure of the samples was then investigated using NR for all the samples. The inferred structures for the samples with the same dMAA grafting times showed great similarities, illustrating the reproducibility of the SI-PGP method, where the standard deviation of the averaged fit parameters is estimated to be 10% (see Figure 3 in Paper I). The modelling revealed a two-layer structure that did not correspond to the order of deposition of the monomers. For 3 and 4 minutes AEMA grafting time, NR revealed a hydrogen-rich bottom layer below a layer close to a 1:1 ratio of the monomers. This ordering was then reversed for the 5 min AEMA grafting time samples (see Figure 4 in Paper I). This behaviour is explained as the interaction of two independent, and oppositely charged polyelectrolyte brushes, grafted to the interface parallel to each other. The positively charged AEMA monomers grafting onto the surface of the Si substrate are bound to the negatively charged p(dMAA) brush by electrostatic forces in a 1:1 ratio. When the amount of the AEMA in the layer exceeds the amount on dMAA, the excess material will be initially buried in the bottom layer. As the AEMA amount increases and the p(dMAA) chains degrade, the uncompensated positive charges will provide the force required to stretch the p(AEMA) chains, that in turn collapse onto the 1:1 ratio layer that is now on the bottom.

The interaction of the charged polyelectrolytes at different pH values were further studied in the hydrated state using spectroscopic ellipsometry in the pH range of 4.2-10.7 pH units. In the intermediate pH range (pH 6-8), when both types of ionizable groups are charged, i.e., both the primary amines and the carboxylic acids, all samples show a collapsed status in accord with the anti-polyelectrolyte behaviour of zwitterionic polyelectrolytes, while at high and low pH the chains are extended due to the electrostatic repulsion, since only one of the two types of ionizable residues is charged (see Figure 5 in Paper I). The transitions corresponding of the deprotonation of the amine groups are relatively narrow and do not fluctuate in pH value, while the transitions corresponding to the deprotonation of the carboxyl groups are wide transitions over a large pH range (see Figure 7 in Paper I). For some samples the carboxyl transition was not observed, possibly because the transition fell outside of the investigated pH range (see Figure 6 in Paper I). A thorough interpretation of the behaviour of the latter transitions is hindered by the lack of information at the lower pH values. The pH values at which both transitions occur, differ from the reported values, both for the monomer and the polyelectrolyte consisting only one of the monomers and are closer in value of the reported pKa and pKb values of the charged groups. This is ascribed to the proximity of the opposing charges in the system.

Undertaking an investigation of the pH-dependence of the hydrated structure of such films requires a large amount of neutron beamtime that is hardly justifiable. However, neutron intensity calculations of reflectometers planned at the new high intensity
neutron sources suggest that the time to record a reflectogram would be comparable to the time needed for a sample change. This may promote more extensive studies that investigate structural changes caused by external parameters. Such studies would greatly benefit from measuring multiple complementary methods on the same sample in parallel with the neutron reflectometry measurement, especially in case of soft matter systems, that are prone to environmental degradation. In Paper IV a setup for in-situ measurement of spectroscopic ellipsometry, infrared absorption spectroscopy and neutron reflectometry is presented. As one of the few available methods to study the hydrated structure of organic thin films, ellipsometry can be used to track fast structural changes with a time resolution of seconds. As shown in Paper IV, the method can be used to monitor, for example, swelling, and to ascertain reaching equilibrium state. Infrared spectroscopy provides information of the chemical evolution of the samples, that is unavailable from neutron reflectometry. This is particularly useful for the type of films investigated in this work, for example, when measuring samples analogous to the ones presented in Paper I, ellipsometry measurements would be used to identify the centre of the transition while infrared spectroscopy would provide information about the state of the ionizable residues.

In Paper III the anti-fouling properties of pseudo-zwitterionic films prepared from the mixture of oppositely charged monomers SPMA and AEMA were compared to films made using the corresponding zwitterionic SBMA monomer and to films of the individual monomers, all grafted using the SI-PGP method onto Au surfaces. The protein and algal assays have proven that the anti-fouling performance of the pseudo-zwitterionic film was similar to that of the zwitterionic film, and better than the individual components alone (see Figures 5, 7, and 8 in Paper III). The composition of the films was also studied with X-ray photoelectron spectroscopy, and it was found that the monomer ratio in the mixture film is 1:0.85 SPMA:AEMA instead of the 1:1 ratio of the grafting solution. The possible explanations for this include the lower solubility of AEMA, the differences in the degree of ionization, or in differences in the resistance to UV degradation. Comparing the thickness of the grafted films there is a clear difference regarding the charged films, the zwitterionic monomer and the mixture (see Table 1 in Paper III). It was shown in Paper I that the electrostatic forces play an important role in determining the structure of the films. Although in the papers presented in this thesis, the pH of the monomer solutions was not adjusted, to investigate the role of charges in the grafting process a study was performed using ionizable monomers, to determine how the pH of the grafting solution influences the thickness of the resulting polymer films. Two negatively charged monomers, SPMA and MAA, and two positively charged monomers, AEMA and DMAEMA were investigated. The samples were grafted onto 20x10 mm² Si (100) pieces using the SI-PGP method. 30 μl solution with a monomer concentration of 0.25 M was used and the illumination time was kept at 5 min. All parameters for the grafting were kept constant except for the monomer and the pH of the grafting solution. The pH was changed by diluting 0.5 M monomer stock solutions with different concentrations of HCl (DMAEMA) or NaOH (other monomers). In Figure 17 the dry thicknesses measured in air with an AutoEl Rudolph Research Auto EL III ellipsometer (He-Ne laser with \( \lambda = 632.8 \) nm and \( \theta = 70° \)) versus the measured pH of the monomer solution is presented. The data shows some variations in the thickness values, however, the fact that the
monomers with the same charge behave differently indicates that other factors also play a role in determining the resulting thicknesses.

Figure 17A: The ellipsometric thickness of the anionic polyelectrolyte films prepared using the SI-PGP method is presented for different pH values of the grafting solution for SPMA (black) and MAA (red) monomers. B: The ellipsometric thickness of the cationic polyelectrolyte films prepared using the SI-PGP method is presented for different pH values of the grafting solution for AEMA (Blue) and DMAEMA (green) monomers. The displayed error bars correspond to the standard deviation of five measurements. The pH of the monomer and water mixture is marked with a MQ label.

To further investigate the difference in the obtained film thickness when grafting with different monomers, UV-VIS spectrophotometry experiments were conducted using a Shimadzu UV-2450 spectrophotometer using a fused quartz cuvette with an optical path length of 4 mm. Three types of monomers, AEMA, SBMA, SPMA, and a 1:1 mixture of AEMA and SPMA (labelled AEMA-co-SPMA), used in Paper III, were studied. The data on SPMA measured at 250 mM concentration, which is a typical grafting concentration, is displayed in Figure 18A.

This data indicates that the monomers are highly absorbing at this concentration and path length. The distance between the bottom surface of the quartz disk, used during grafting, and the surface of the substrate was measured to be of the order of 10 μm for the monomer solutions used throughout this thesis (typically 20-40 μm). This difference was accounted for using the Lambert-Beer law, \[ A = l \sum_{i=1}^{N} \varepsilon_i c_i \], where \( A \) is the absorbance, \( \varepsilon_i \) is the molar attenuation coefficient, \( l \) is the optical path length, and \( c_i \) is the concentration of the attenuating species. The measured absorbance of the monomer solutions with 200 μM concentration is displayed in Figure 18B.

According to the Lambert-Beer law in a homogeneous medium with multiple absorbing species the absorbance of the mixture can be written as
Figure 18A: UV-absorbance of the SPMA monomer at 25 mM (black) and 250 mM (red) concentration. Purple dashed line indicated the main emission peak of the lamp used for SI-PGP grafting. The data is displayed in linear scale in the inset. B: UV-absorbance of 200 μM concentration of AEMA (black), SPMA (red), SBMA (blue), and a 1:1 mixture of AEMA and SPMA (green). The values displayed in the legend correspond to the wavelength of the peak absorbance.

where $N$ is the number of absorbing species and $\epsilon_i$ and $c_i$ are the molar attenuation coefficient and the concentration of the $i$th species, respectively. However, this is only true when the attenuators act independently of each other. Since the absorbance value of the mixture (green curve in Figure 18B) is lower than either of the separate components (black and red curves in Figure 18B), this suggests that the two monomers interact with each other, influencing the grafting. The connection between the charges and the grafting results could be further examined by measuring the absorbance of monomers at different pH values.

The main emission peak of the UV lamp (Philips TUV PL-L 18 W) is at 254 nm, with no or little emission at lower wavelengths159, but the positions of the absorption peaks in the UV-Vis spectra fall in the range 207-210 nm (as shown in Figure 18B). To assess the relevance of this discrepancy, samples were prepared utilizing a high-pass wavelength filter (MKS/Newport 10CGA-225) with a cutoff wavelength of 220 nm (shown in Figure 19). The thickness values measured on films grafted using the AEMA-co-SPMA mixture with $(708 \pm 5 \text{ Å})$ and without $(709 \pm 14 \text{ Å})$ filter show no significant differences, indicating a negligible influence of the shorter wavelengths on the grafting process. However, results on polymers prepared from acrylic monomers using 172 nm wavelength radiation suggests that radicals generated from C=O bonds at shorter wavelengths contribute mainly to crosslinking in the film146. The spectra in Figure 18A suggest that no or very little short-wavelength radiation (< 220 nm) reaches the surface of the substrate, which could explain the absence of crosslinking, as suggested by the Gaussian model used in evaluating the neutron reflectometry results. The plot of the absorbance values at 254 nm for some monomers, as a function of layer thickness grafted onto Si wafers, displayed in Figure 20, indicates a correlation between absorbance and thickness, in accordance with previous works52.
To further investigate the effects of grafting conditions on the thickness, samples were prepared onto Au surfaces (20x15 mm², 10 nm Au evaporated on glass with a 1 nm Ti adhesion layer) with differently terminated thiol SAM layers. This was done to assess the influence of surface groups with different ionizabilities and polarities, and also to test whether different surface chemistries, with variations in the bond strengths of the terminal functional groups, would result in differences in the grafting. The following alkylthiol molecules were used in this study: 11-Aminoundecanethiol (C₁₁NH₂), 11-Mercaptoundecanol (C₁₁OH), 16-Mercaptohexadecane (C₁₆), 11-mercaptoundecanesulfonate (C₁₁SO₃), and N,N,N-Trimethyl-(11-mercaptoundecyl) ammonium (C₁₁NMe₃). The structures of the molecules are displayed in Figure 21.

Figure 20: Absorbance values measured at 254 nm as a function of the grafted thickness for the different monomers.

The layers were grafted using AEMA, SBMA, and SPMA monomers. The samples were made using 15 µl of 0.2 M concentration solutions, while the irradiation times were 3 min. The layer thicknesses were measured with ellipsometry using a Rudolph Research AutoEl III ellipsometer (He-Ne laser with λ = 632.8 nm and θ = 70°). The values are displayed in
Figure 21: The structure of the alkylthiols used to functionalize the Au surfaces for the grafting study.

Figure 22A. To help assess the influence of the surface group, the results were also normalized to the values measured on the C11OH SAM, see Figure 22B. The data merely corroborates the results of the previous absorbance measurements, in that grafting rate is inversely proportional to the absorbance of the monomers, for all surface types. However, the normalized data does not reveal any clear dependence on the ionizability or the polarity of the surfaces.

In Figure 23 the thickness values as a function of the wettability of the surfaces is presented. Other than the effect of the UV absorbance, detailed above, with SBMA polymerizing faster than SPMA and AEMA, no clear dependence on the water contact angle is observed.
Figure 23: Polymer layer thickness as a function of water contact angle measured on the different SAMs in Figure 21. Contact angles for the SAMs were taken from previously published data from our laboratory\textsuperscript{156}. 
Conclusion and outlook

In this thesis, the basics of neutron reflectometry and its application to investigating polymer thin films are presented. It is an essential method for investigating the structure of polymer thin films. The method suffers from low luminosity and the high cost of neutron sources, loss of phase information, and the excessive need for modelling, but presents unique information about the samples due to the possibility of isotope labelling. With the commissioning of new neutrons sources with greatly improved brightness and the development of magnetic reference layers, providing access to the lost phase information, the emphasis of polymer thin film research will shift to the study of dynamic changes in their structure. The in-situ monitoring of these changes with complementary methods will help in verifying the causes, strengthening the link between the offline measurements and the neutron experiments.

Here, neutron reflectometry was used to study the structural properties of functional polymer thin films prepared by self-initiated photografting and photo-polymerization (SI-PGP). Despite its many advantages, this polymerization procedure is seldom utilized, partly due to the lack of understanding of the resulting structure. We confirm that the films polymerized with the SI-PGP method show negligible crosslinking, and that grafting does not only proceed at different rates, but is also qualitatively different on the two substrate types used in this study, i.e., gold and silicon. We showed the importance of the continuous UV-induced degradation on the resulting film structure and composition in case of sequentially grafted films. Despite the significant degradation, the remaining polymer films retain their chemical structure, suggesting that the UV-light removes entire chains or chain segments, rather than affecting the chemistry or the structure of the functional groups. Regarding differences in polymerization rates for different monomers, data suggests a correlation between the UV-absorbance of the monomers and the grafting rate.

Although the current work was largely motivated by an interest in using SI-PGP-prepared films for anti-fouling purposes, we did not reach a stage where we were able to correlate the gained knowledge about structural parameters and polymerization mechanisms to the anti-fouling properties of the films, or to use these insights to improve their anti-fouling properties. However, the investigations have provided answers to issues raised regarding the surface charges$^{55}$ and density profiles of the polymer films$^{71}$ in previous works, and have provided valuable insights for future investigations into developing anti-fouling polymer coatings. The robustness and versatility of the method allow for polymerization of a wide range of monomers on any organic substrate, and its simplicity, especially eliminating the need for additional chemicals, makes it an ideal candidate for use in sustainable technologies. To further improve the understanding of the process, studies could focus on, for example, the recently proposed connections between the UV reflection of the substrate and the polymerization speed, the differences in monomer sensitivity to UV radiation, or the rate differences between monomers.
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References


Papers

The papers associated with this thesis have been removed for copyright reasons. For more details about these see:

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