

HOW BULK CHEMISTRY AFFECTS SURFACE ADAPTATION

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1.1 Acknowledgment

1.2 Abstract

The wetting properties of materials play a crucial role for example in biology or industrial processes and applications. While the surface is in contact with the liquid, the wetting properties can change. The change of the wetting properties in contact with a liquid is known as surface adaptation. To understand surface adaptation is important, to improve new coatings, optimize industrial processes such as the fabrication of materials or printing.

For polymer surfaces, swelling or reorientation of the polymer surface results in surface adaptation. In this thesis I synthesized grafted hydrophilic-*b*-hydrophobic diblock copolymer brush surfaces. Two parameters were used to study the surface adaptation behavior in contact with water. One parameter was the thickness of the hydrophobic and hydrophilic block, respectively. The second parameter was the ratio between the grafting density of the hydrophilic and hydrophobic block. It was shown that both parameters affect the wetting behavior. For diblock copolymer surfaces, with a hydrophobic layer above ≈ 25 nm, no surface adaptation was observed. The thickness of the hydrophobic block is the dominating parameter for the wetting properties. Below the thickness of ≈ 25 nm of the hydrophobic block, the ratio between the grafting density of the hydrophilic and hydrophobic block determines the wetting behavior. With decreasing ratio of the grafting density between the hydrophobic and hydrophilic block, the diblock copolymer surface adapts to water. Increasing the ratio of the grafting density between the hydrophobic and hydrophilic block, no surface adaptation was observed, even for hydrophobic layers with a thickness of ≈ 6 nm.

Next to the influence of swelling and reorientation, the influence of crosslinking of grafted polymer brushes on the wetting properties was investigated. Here a grafted hydrophobic, coumarin containing copolymer was synthesized. Under long-wave UV irradiation, crosslinking of the polymer brushes was observed. Under short-wave UV irradiation, cleavage in the monomeric state of the polymer brushes was observed. It could be shown that the friction force of sliding water drop was influenced by the crosslinking.

It is known that sliding drops over a hydrophobic surface get charged. The counter charges stay on the surface and the surface gets charged. This phenomenon is called slide electrification. However, the role of surface adaptation in slide electrification on fluorinated monolayers has not been investigated yet. In this thesis, different silicate glasses were fluorinated with a trichlorosilane and monochlorosilane layer. The fluorinated surfaces were analyzed by measuring the charge of sliding drops and modified contact angle measurements. Compared to the monochlorosilane coated surface, the drop charge on the trichlorosilane coated surfaces correlated to the substrate properties. The modified contact angle measurements showed that the trichlorosilane surfaces adapt to water.

1.3 Zusammenfassung

Die Benetzungseigenschaften von Oberflächen spielen unter anderem in der Natur und bei industriellen Prozessen eine wichtige Rolle. Durch den Kontakt mit Flüssigkeiten können sich die Eigenschaften von Oberflächen verändern. Dieser Effekt wird als Oberflächenadaptation bezeichnet. Um z.B. schützende Beschichtungen herzustellen oder zu optimieren, ist es wichtig, den Einfluss der Oberflächenadaptation zu verstehen.

Bei Polymeroberflächen können das Quellen oder die Umorientierung der Polymerketten zur Oberflächenadaptation führen. In meiner Dissertation habe ich hydrophile-*b*-hydrophobe Diblock Copolymer Bürsten synthetisiert. Ich habe die folgenden zwei Parameter variiert, um das Adaptationsverhalten der Polymeroberflächen in Gegenwart von Wasser zu erforschen. Zum einen wurden die Schichtdicken des hydrophilen und des hydrophoben Blocks variiert. Zum anderen wurde das Verhältnis der Polymerketten-Dichte zwischen hydrophobem und hydrophilem Block verwendet. Ab einer Schichtdicke des hydrophoben Blocks von ≈ 25 nm, konnte keine Oberflächenadaptation beobachtet werden konnte. Hierbei war die Schichtdicke des hydrophoben Blocks der entscheidende Parameter für das Benetzungsverhalten der Oberfläche. Mit abnehmender Schichtdicke, wurde das Verhältnis der Polymerketten-Dichte zwischen hydrophobem und hydrophilem Block für das Benetzungsverhalten relevant. Mit abnehmendem Verhältnis der Polymerketten-Dichte zwischen hydrophobem und hydrophilem Block konnte Oberflächenadaptation beobachtet werden. Mit zunehmendem Verhältnis der Polymerketten-Dichte zwischen hydrophobem und hydrophilem Block, wurde der hydrophile Block abgeschirmt. Selbst bei einer Schichtdicke von ≈ 6 nm, konnte kein adaptives Verhalten beobachtet werden.

Weiterhin wurde untersucht, wie die Vernetzung von Polymerketten das Benetzungsverhalten von Copolymeroberflächen beeinflusst. Dazu wurde ein Coumarin-haltiges Copolymer synthetisiert. Unter langwelliger UV-Bestrahlung konnte die Vernetzung der Polymerketten beobachtet werden. Unter kurzwelliger UV-Bestrahlung wurden die Bindungen zwischen den Polymerketten wieder gespalten. Es konnte gezeigt werden, dass die Reibungskraft eines Wassertropfens auf der Oberfläche durch die Vernetzung der Polymerbürsten beeinflusst wird.

Bei der Benetzung einer Oberfläche kann auch die Ausbildung einer elektronischen Doppelschicht zur Oberflächenadaptation führen. Gleitet beispielsweise ein Wassertropfen über eine hydrophobe Oberfläche herunter, so lädt sich der Tropfen elektrisch auf. Die Gegenladung verbleibt an der Oberfläche. Dieses Phänomen wird als "slide electrification" bezeichnet. Die Rolle der Oberflächenadaptation in slide electrification auf fluorierten monomolekularen Schichten ist nicht bekannt. In meiner Dissertation habe ich verschiedene Gläser mit einem Monochlorosilan und einem Trichlorosilan fluoriert. Anschließend wurden die Tropfenladung und der Kontaktwinkel auf der fluorierten Oberflächen gemessen. Der Kontaktwinkel wurde mit einem modifizierten Goniometer gemessen. Im Vergleich zum Monochlorosilan war die Tropfenladung auf der Trichlorosilanoberfläche hoch und abhängig von den chemischen und physikalischen Eigenschaften des Substrates. Mit Hilfe der modifizierten Kontaktwinkelmessung konnte gezeigt werden, dass die hohe Tropfenladung zur Oberflächenadaptation führt.

2 Introduction & Theoretical Background

2.1 Contact Angle

Wetting of surfaces is an omnipresent phenomenon that plays a critical role in many aspects of life. The wetting properties of plants for example protect them for uncontrolled water loss,^[3] wetting properties of materials are used for water repellent outdoor clothing,^[4] self-cleaning surfaces^[5,6] or plays a crucial role in industrial application such as printing.^[7-9]

The most common technique to characterize the wetting properties of surfaces is measuring the contact angle.^[8] Here a drop is placed on a surface. Depend on the surface properties the liquid spreads over the surface and forms a film or the drop spreads until a equilibrium drop diameter is reached.^[7] Figure 2.1 shows the situation of drop on an ideal solid surface, which reached the equilibrium diameter.

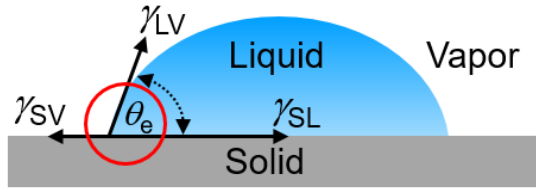


Figure 2.1: Schematic of a sessile drop on ideal solid substrate. The red cycle marks the slope between the contact line of the solid-liquid interface and the solid, liquid, vapor interface. The slope is define as Young contact angle θ_e . θ_e is related to the interfacial energy γ of the solid-liquid (SL) interface, the solid-vapor (SV) interface and liquid-vapor (SV) interface.^[7] The figure was made after Ref.^[10,11]

In 1805, Thomas Young observed and described the situation of the drop in the equilibrium state (Figure 2.1).^[12] At the interphase between the air, solid and liquid (red cycle in Figure 2.1) the drop front has a slope. The slope is define as the contact angle θ_e . The Young equation (2.1) describes that the equilibrium contact angle θ_e is related to the interfacial energy of the solid-liquid interface (γ_{SL}), the solid-vapor (γ_{SV}) interphase and liquid-vapor(γ_{LV}) interface.^[7,10] θ is used to classify the surfaces into the categories hydrophilic ($\theta < 90^\circ$), hydrophobic ($\theta > 90^\circ$) and superhydrophobic ($\theta > 150^\circ$).^[9]

$$\cos\theta_e = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} \quad (2.1)$$

A drop on an ideal, flat and inert surface would be in the energetic global minimum state, that correspond to the θ_e (Figure 2.2a).^[11,13] However, real surfaces are chemically heterogeneous and have physical defects.^[8] The surface inhomogeneity means that the drop can be in any local energetic minimum (Figure 2.2b).^[11] Therefore θ_e can differ from position to position. A measurement technique to overcoming the local energetic minimum and measure the most stable θ , is to measure the advancing θ_{ACA} and receding contact angle θ_{RCA} . To measure the θ_{ACA} and θ_{RCA} a drop is deposited on the surface and the drop volume increases and decreases. While increasing the drop volume, θ increased till the drop front is

moving with a constant θ . The constant θ of the moving drop front is defined as θ_{ACA} . While decreasing the drop volume θ decreases until the drop front recedes with a constant θ . The constant θ of the receding drop front is defined as θ_{RCA} .^[11] The difference between θ_{ACA} and θ_{RCA} is defined as contact angle hysteresis (CAH). For an ideal surface the CAH would be zero and the drop would slide off the surface even at low tilt angles.^[14]

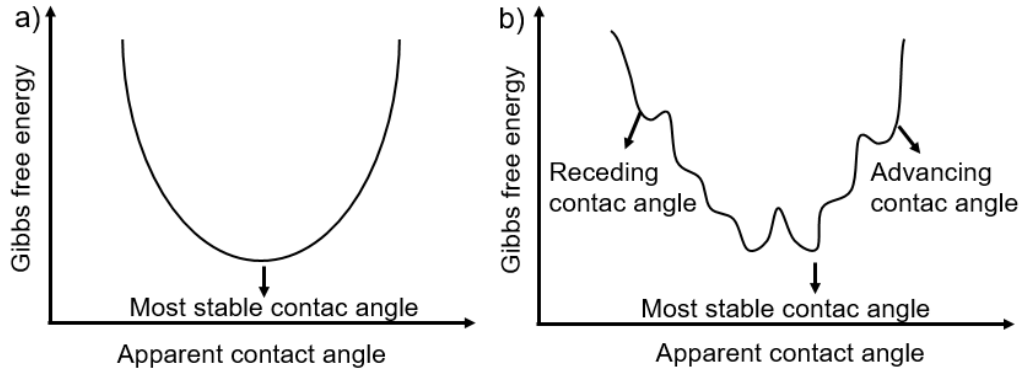


Figure 2.2: The Gibbs free energy plotted against the apparent contact angle. a) Gibbs free energy of a drop on ideal surface. The system has only one Gibbs free energetic minimum. The energetic minimum corresponds to most stable contact angle (Youngs contact angle). b) Gibbs free energy of a real surface. The most stable contact angle corresponds to the Gibbs free energetic global minimum. The system shows also many metastable Gibbs free energetic local minima. The measured static contact angle of a deposited drop could corresponds to any energetic minima. The measurement would be not reproducible for the whole surface. The only reproducible characterization is to measure the advancing and receding contact angles.^[11] The figure was made after Ref.^[11]

2.2 Surface Adaptation & Aim of the Thesis

The contact of a surface with a liquid can lead to a change in the surface properties, such as the surface structure. An example from everyday life would be a paper straw in a glass of water. As shown in Figure 2.3, over time the paper straw swells and changes its structure. The change of the surface structure leads to a change in the surface energy. The change in surface energy of a surface, when it comes into contact with a liquid, is known as surface adaptation.^[14–16] Examples for processes which lead to surface adaptation are polymer reconstruction, swelling, diffusion, adsorption of surfactants or the formation of an electric double layer.^[14] Understanding the effect of surface adaptation of polymer or organic monolayer surfaces is necessary to optimize coatings in many applications such as anti-icing,^[17,18] printing^[7,9] or protect surfaces for corrosion.^[19]

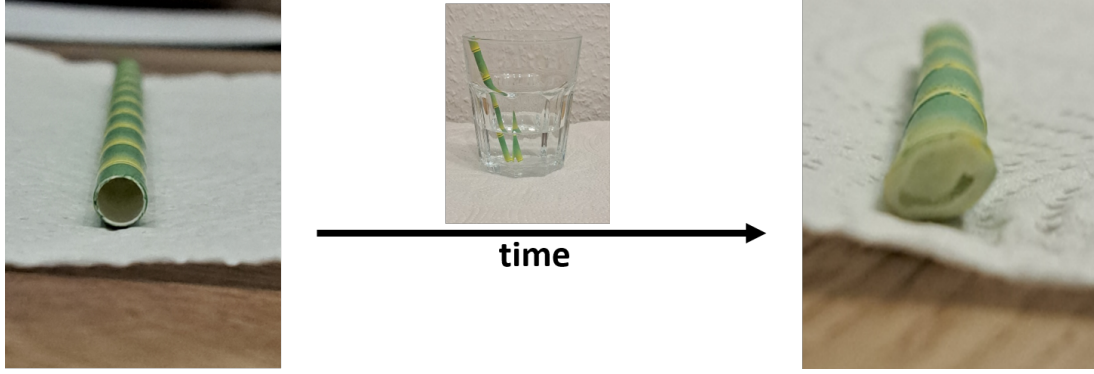


Figure 2.3: On the left side is a new paper straw. The paper straw was put in a glass of water. On the right side is the paper straw after exposing to water for ≈ 1 h. The surface of the paper straw changed and the opening was no longer clearly recognizable. With the time the surface of the paper straw adapt to water and changed the surface energy. The pictures were recorded by Benjamin Leibauer.

Contact angle measurements can be used to study surface adaptation. With regard to equation 2.1, a change of the surface energy leads to a change of the term γ_{SV} . The surface energy will change until it reaches a new energetic minimum. Thus the term γ_{SV} becomes time-dependent and the equation 2.1 transformed to equation 2.2. The exponential term comes from the assumption that the change of the surface energy follows a first order kinetic. l_{SL} is the peripheral thickness, which is the width of the contact region, which affects θ . v is the velocity of the drop front. ∞ describes the equilibrium state of the parameter, respectively.^[14]

$$\cos\theta = \frac{\gamma_{SV}^{\infty} - \gamma_{SL}(t = l_{SL}/v)}{\gamma_{LV}} = \cos\theta^{\infty} - \frac{\Delta\gamma_{SL}}{\gamma_{SV}^{\infty}} e^{-l_{SL}/v\tau_{SL}} \quad (2.2)$$

The adaptation model of equation 2.2 was successfully applied to describe the wetting behavior of a non-grafted PS-co-PAA copolymer surfaces^[20] and non-grafted PMMA-co-PHQSEA copolymer surfaces.^[21] However, to analyze the adaptation process of a non grafted polymer surface is a challenge.^[20] The challenge is that non grafted polymers can dissolved in the drop and the non defined structure makes it difficult to analyze the change in the surface structure in more detail.

The research goal of my thesis is to solve the challenge and design well defined surface grafted polymer surfaces. Surface grafted polymer chains are covalently bonded to the substrate. The covalent bond allows to expose the polymer surface several times to good solvents, without being concerned that the polymer will be dissolved.^[22] Furthermore, the structure of the grafted polymer chains is known,^[23] which allows to analyze the change of the surface structure after the contact with the liquid. The idea is to use two different approaches to tune the wetting behavior. One concept is to use hydrophilic-*b*-hydrophobic diblock copolymer brush surfaces, to tune the wetting behavior by reorientation, swelling or phase separation of the polymer brushes. The second idea is to influence the wetting properties by photo induced crosslinking of the polymer brushes.

With regard to the relation between formation of an electric double layer and surface adaptation, I want to study the role of adaptation in the charge separation between a sliding drop and a hydrophobic surface (slide electrification).

2.3 Slide Electrification

Formation of charges at solid-liquid interfaces is an omnipresent phenomena, which is still not well understand.^[24] It was already discovered in the 19th century that all surfaces are negatively charged in contact with pure water and the charge effect was strong on hydrophobic materials.^[25] Starting from the end of the 19th century, it was shown that rain drops^[26] can be positively or negatively charged, single water drops becomes charged when the drops splash onto solid^[27] or liquid^[28] surfaces or liquids flows through a dropper. The sign of charge was affected by the material of the dropper.^[29] In the end of the 20th century it was shown that a sliding water drop on a polytetrafluoroethylene (PTFE) surface gets positively charged. The PTFE surface gets negatively charged after the drop slides down the surface.^[30,31] The effect was called slide electrification.^[32] 2020 it was shown that sliding water drops can be used to power LEDs.^[33]

However, the origin of the drop and surface charge is still not clear and discussed in the community. For some surfaces it was reported that charge results from electron transfer between the surface and the drop.^[34,35] The more common description is that an electric double layer (EDL) forms at the solid-liquid interface and that interfacial charge remains behind the sliding drop.^[24,36–41] The process is schematically shown in three steps in Figure 2.4.^[32] Spontaneous charging occurs at the solid-liquid interface (Figure 2.4(1)).^[32] On the back side of the sliding drop the charge separation happens and charges stay or transfer to the surface (Figure 2.4(2)).^[32,40] Recently, the acid-base model was used to described the charge separation, in which the PTFE surface interacts as proton donor or acceptor.^[36] It was shown that surface bonded amine groups can be protonated as Brönsted bases, so that the surface becomes positively and the drop negatively charged ($\text{surface-NH}_2 + \text{H}_2\text{O} \longrightarrow \text{surface-NH}_3^+ + \text{OH}^-$).^[37] The effect of pH^[36,42] and various dissolved ions^[43–45] on the drop and surface charge have been investigated.

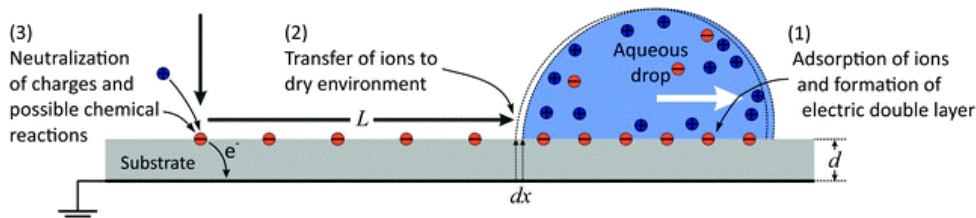


Figure 2.4: Schematic of charge separation between a sliding drop and a hydrophobic surface. The charge deposition of the drop on the surface can be described in three steps. (1) The formation of an electric double layer at the solid-liquid interphase.^[32] (2) Ions in the drop are transferred or removed behind the sliding drop.^[32,40] (3) The remaining charges on the surfaces are neutralized by interaction with the environment.^[32] Reproduced from Ref.^[32] with permission from the Royal Society of Chemistry.

However, in all publications, the phenomenon of slide electrification was described at different hydrophobic surfaces such as PTFE,^[30,31,36,44] fluorinated ethylene propylene^[39,46,47] or fluorinated glass.^[32,43,48,49] This poses the question: can the respective models be applied to other fluorinated surfaces or is the charge separation also influenced by the properties such as the bulk chemistry? To answer the question is important for the community, to find a general description of slide electrification in the future. In my thesis I want to answer the question by using fluoro-organic monolayers on different silicate glasses.

Silicate glass consists of a network of corner-linked SiO_4 tetrahedra (silicate matrix). Figure 2.5 shows schematically the silicate matrix of pure silicate glass (Figure 2.5a) and sodium silicate glass (Figure 2.5b). Pure silicate glass is defined as quartz glass. During the fabrication process, different metal oxides can be added to the SiO_2 melt and the metal ions can be inserted to the silicate matrix. The adding of metal ions allows to tune the physical and chemical properties of the silicate glass. By adding a specific

quantity of metal ions for example, the polarizability of the silicate glass can be tuned. By adding specific metal ions the chemical properties of the silicate glass can be tuned.^[50,51] By adding for example alumina ions to the silicate matrix, the Pearson hardness can be tuned.

The Pearson hardness is a fundamental parameter of the *Hard and Soft Acids and Bases* (HSAB) concept. The HSAB model is a general acid-base model, which involved the orbital energy of chemical species. The HSAB concept allows to predict the stability of compounds and the outcome of chemical reactions. The Pearson hardness of the respective species is used for the prediction. In general the model shows, that the orbital interaction between soft acids and soft bases and hard acids and hard bases is preferred.^[52]

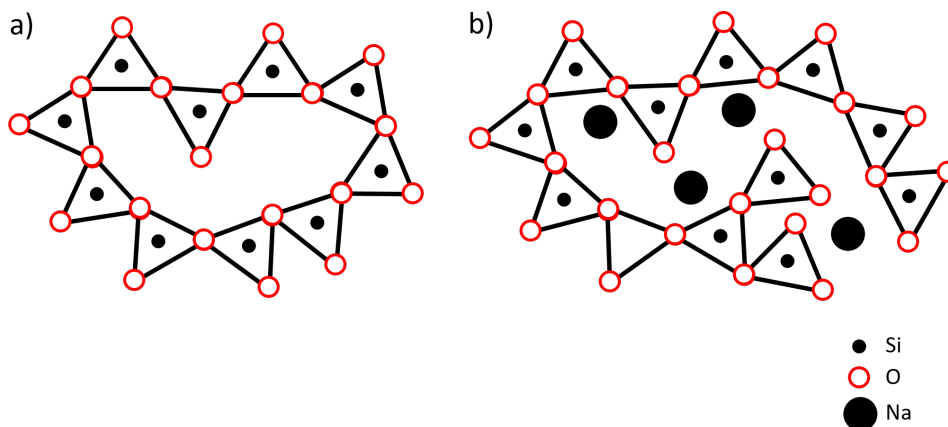


Figure 2.5: Schematic two-dimensional illustration of the arrangement of SiO_4 tetrahedra. The SiO_4 tetrahedra are corner linked and form a network. a) The network consists only SiO_4 tetrahedra (network former). Pure SiO_2 glass is define as quartz glass. b) Sodium silicate glass. Sodium ions are incorporated in the SiO_4 network. The added basic sodium oxide (network changer) separates $\text{Si}-\text{O}-\text{Si}$ bindings.^[50,53] The figure was made after Ref.^[53]

2.4 Surface Modification

There are many different methods to coat a surface such as spin coating, dip coating or spray coating.^[54] The focus of this thesis is to modify SiO_2 surfaces of a silicon substrate or silicate glasses with a covalent bonded (grafted) monolayer or polymer layer.

2.4.1 Self-Assembly Monolayer

A widely used group of compounds are organosilanes to modify SiO_2 surfaces in research and technology.^[55] In addition to the covalent bond to the substrate, organosilanes have the advantage, that they can be synthesized under standard laboratory conditions.^[56] As a result, there is a variety of different organosilanes with different functional groups and chain lengths. The organosilanes have an anchoring group, which reacts with the silanol group ($\text{Si}-\text{OH}$) of the activated SiO_2 surface. After the reaction, the organosilane is covalently bound to the SiO_2 surface. The reaction mechanism is called *grafted to the surface*.^[22] Common grafting reagents are organosilanes with 1,2 or 3 halide or alkoxy groups as anchoring groups.^[23] For my thesis 1 and 3 chlorosilanes ($\text{ClSiR}_3/\text{Cl}_3\text{SiR}$) are relevant. Figure 2.6 shows the reaction scheme of the chlorosilanes with the activated SiO_2 surface.^[55] The anchoring group reacts with the silanol group of the surface ($\text{R}_3\text{Si}-\text{Cl} + \text{SiOH} \longrightarrow \text{R}_3\text{Si}-\text{O}-\text{Si} + \text{HCl}$). The monochlorosilanes have only one anchoring group, which can grafted to the surface. The result of the reaction is a *self-assembly monolayer* (SAM) of the organosilane on the SiO_2 surface. The SAM with the monochlorosilane

has a high reproducibility.^[55,57] Due to the three anchoring groups, the trichlorosilane can undergo different reactions (Figure 2.6). One anchoring group can be grafted to the surface and the other anchoring groups can be hydrolyzed ($\text{R}_3\text{SiCl} + \text{H}_2\text{O} \longrightarrow \text{R}_3\text{SiOH} + \text{HCl}$) and polymerized with adjacent molecules ($\text{R}_3\text{SiOH} + \text{R}_3\text{SiOH} \longrightarrow \text{R}_3\text{Si-O-SiR}_3 + \text{H}_2\text{O}$). The horizontal polymerization to a monolayer is defined as SAM.^[55,57] The other possibility of the reaction is the covalent attachment. Here one or more anchoring groups are grafted to the surface and the non-grafted anchoring group can polymerize horizontally with adjacent molecules. A further possibility is that at least one anchoring group is grafted to the surface and free silanol groups can polymerize vertically. The possibility of the polymerization of the silanol groups, using a trichlorosilane, complicates the reproducibility of the silane surface.^[55] The packing density is different between the monochlorosilane and trichlorosilane SAM. The packing density of the trichlorosilane is higher than the packaging density of the monochlorosilane (same carbon chain length). For the monochlorosilane the packing density is limited by the steric hindrance of the bulky methyl groups of the siloxane.^[55,57]

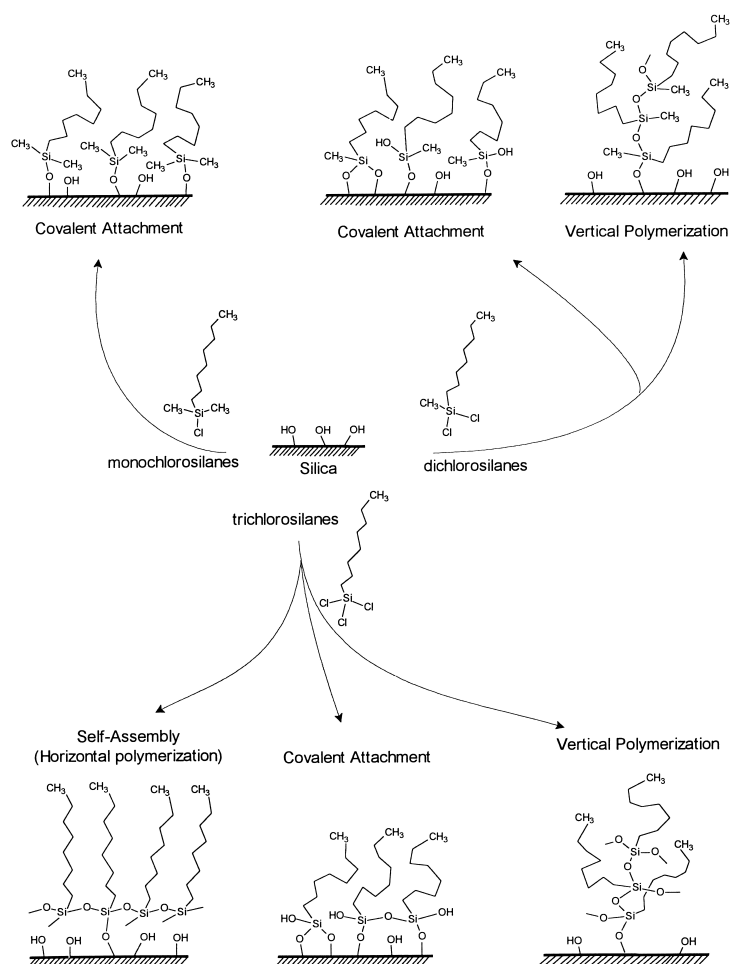


Figure 2.6: Possible products of the reaction of alkylchlorosilanes with an activate silicon dioxide surface. For my thesis, the reaction between the monochlorosilane and trichlorosilane with the silicon dioxide surface are relevant. The product of the reaction between the monochlorosilane and the silicon dioxide surface are shown on the top left side. Only the formation of a monolayer is possible. The possible products of the reaction of the trichlorosilane and the silicon dioxide surface are shown on the bottom part of the figure. Left: Horizontal polymerization of the trichlorosilane. Middle: Covalent attachment of the trichlorosilane to the silicon dioxide surface. Right: Vertical polymerization of the trichlorosilanes. Reprinted with permission from Ref.^[55] Copyright 2025 American Chemical Society.

2.4.2 Surface Polymerization

Polymers can be grafted to a surface by different methods. According the previous chapter a polymer with an anchoring group can be grafted to the activated SiO_2 surface.^[22] The advantage of the *grafting to* method is that the polymer properties such as the molecular weight are known or can be measured before grafting. If the molecular weight is known, the thickness of the polymer layer can be measured and the grafting density σ can be calculated with equation 2.3. h is the thickness of the polymer coating, ρ_{polymer} the density of the polymer, M_{polymer} the molecular weight of the polymer and N_A the Avogadro constant.^[58]

$$\sigma = \frac{h\rho_{\text{polymer}}N_A}{M_{\text{polymer}}} \quad (2.3)$$

However, a challenge of the *grafting to* method is to control the resulting polymer structure on the surface. Figure 2.7 schematically summarizes different surface grafted polymer structures. If the polymer-surface interaction is weak or repulsive, the polymer chains can form a random coil. The resulting polymer conformation is called as "mushroom" like structure (Figure 2.7a). If the polymer-surface interaction is strong, the polymer chains get adsorbed on the surface and form a flat conformation. The resulting polymer conformation is called "pancake" like structure (Figure 2.7b). If the polymer chains are grafted to the surface at short distances between each other, the polymer chains overlap. In this situation the polymer chains try to avoid each other as much as possible. The result is a conformation of stretched polymer chains, which is called "brush" like structure (Figure 2.7c).^[22] In my thesis the focus will be on polymer brush surfaces.



Figure 2.7: Schematic of the possible conformation of surface grafted polymer chains. a) The weak or repulsive polymer-surface interaction results in a polymer coil. The conformation is referred as "mushroom" like structure. b) The strong surface-polymer interaction leads to adsorption of the polymer chain on the surface. The resulting conformation is referred as "pancake" conformation. c) The density of the grafted polymer chain is high. The overlap of the polymer chains results in stretched polymer chains. The resulting conformation is referred as "brush" like structure.^[22] The figure was made after Ref.^[22,59]

Alternative to the *grafting to* method, polymers can be grafted from the surface. The method is called *grafted from*. Here the polymer chains are grown from the surface. The grafted from method results in a polymer surface with a high grafting density. The polymer chains become crowded and stretched away from the surface. The resulting polymer conformation is referred to the term polymer "brush" like structure.^[22] In the 1970s, the grafting from method was introduced by growing polystyrene (PS) from a SiO_2 surface^[60] and a reaction mechanism^[61] was proposed. Since that time, many techniques have been introduced for *surface initiated* (SI) polymerization. Examples for SI polymerization techniques are SI-RAFT (reversible addition-fragmentation chain transfer) polymerization,^[62] SI-ARGET (activator regeneration by electron transfer) polymerization^[23] or SI-ATRP (atom transfer radical polymerization).^[63,64] The SI-ATRP synthesis is of interest for my thesis. In general the ATRP synthesis^[65,66] allows to control the polymerization well, because the termination reactions are minimized by reducing the concentration of active radicals. The controlled polymerization results in polymers with a low molar weight distribution.^[67] The controlled polymerization and the applicability of a huge range of monomers make the SI-ATRP synthesis a powerful tool to design well defined polymer surfaces such as random copolymer

brushes or multiblock copolymer brushes.^[62] The reaction mechanism of the SI-ATRP synthesis is shown in Figure 2.8. In general, a copper(I) complex is used as catalyst. The copper(I) complex can react reversibly with the alkyl-halide group of the initiator layer and capping polymers in the dormant state (k_a). During the reaction the copper(I) complex is oxidized to a copper(II) species. Polymer chains can grow from the active polymerization center by adding monomer units in the propagation state (k_p). By reducing the copper(II) complex to the copper(I) complex, the radicals get deactivated back to the dormant state (k_d). Termination reactions by recombination can be neglected (k_t). The polymerization kinetic can be tuned by the variation of the ligand, catalyst, initiator layer and solvent.^[68]

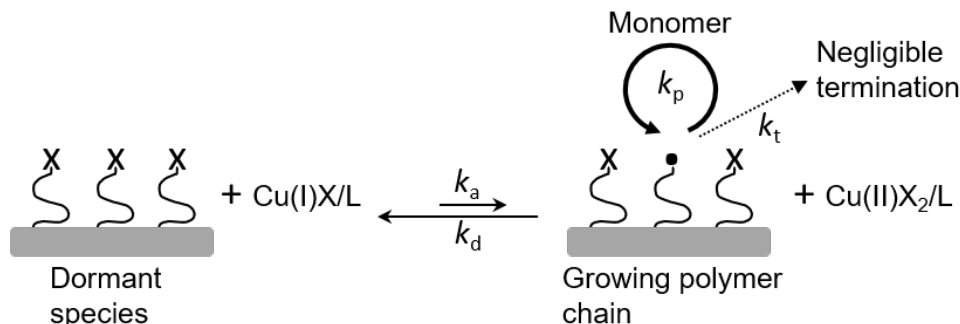


Figure 2.8: Reaction mechanism of the *surface-initiated atom transfer radical polymerization* (SI-ATRP). On the left side is the system in the dormant state. The dormant species can be the surface initiator or capping polymer. The dormant species can react reversibly with the copper(I) complex. On the right side are the products of the reaction. Products are a copper(II) complex and the active (k_a) polymerization center. From the active polymerization center, the polymer chains can grow by adding monomer units in the propagation (k_p) state. By the reaction of the copper(II) complex with the active polymerization center to the copper(I) complex the active polymerization gets deactivated (k_d) and back to the dormant state. The termination (k_t) reaction by recombination can be neglected.^[67,68] The figure was made with changes after Ref.^[59]

2.5 Photo Switchable Surfaces

Light responsive coatings allow to reversibly switch the wetting properties of surfaces.^[69–71] Polymers can be functionalized with photo reactive side groups. Common photo reactive functional groups in applications and research are azobenzenes,^[72,73] spiropyranes,^[70,73] diarylethernes^[70,73] and arylazopyrazoles.^[70,74] Photo-switchable surfaces change their structure by irradiation with light of a specific wavelength. A change in the surface structure results in a change in the surface energy, which results in a change in wetting properties. Azobenzenes or arylazopyrazoles functional groups for example, undergoes a transition from the cis-state to the trans state, under irradiation at a wavelength of 365 nm. The photo switch is reversible by irradiation of a wavelength of 520 nm.^[70,71] This kind of photo switch is called photo isomerization. It was shown that polymer surfaces can reversibly switch from hydrophobic to hydrophilic by photo isomerization.^[70,71]

A further possibility to change the polymer structure by irradiation is photo induced crosslinking of polymer chains to a polymer network. Photo induced crosslinking of polymer chains is widely used in fabrication process of dynamic and adaptable materials such as elastomers.^[75–77] Photo active functional groups such as coumarin/ coumarin derivatives^[75–77] or anthracene/ anthracene derivatives^[78–80] undergo reversible dimerization or cleavage reactions under irradiation. This kind of photo induced reactions is referred to as photodimerization or photocleavage.

Relevant for my thesis is the [2+2] photoinduced cycloaddition of coumarin. The photodimerization of coumarin containing polymer brushes is showed in the Figure 2.9. Under long-wave ($\lambda = 365$ nm) UV irradiation, the coumarin groups undergo a photodimerization. The result of the photodimerization is the crosslinking of the coumarin containing polymer chains. Short-wave ($\lambda = 254$ nm) UV irradiation induces a photocleavage reaction, restoring the crosslinked polymer chains in their monomer state.^[75] The photodimerization of non-grafted coumarin containing polymer brush surfaces as used to change the softness of polymers,^[77] designing polymer surfaces^[75] or in self-healing polymer surfaces.^[81] However, the influence of the photodimerization of coumarin containing grafted polymer brushes on the wetting behavior is not described in the literature. Furthermore it is not known, how the photodimerization of coumarin containing grafted polymer brushes affect the friction force of sliding water drop. In my thesis I want to answer the question, if photodimerization of grafted polymer brushes can be used to tune the surface adaptation behavior of a polymer surface.

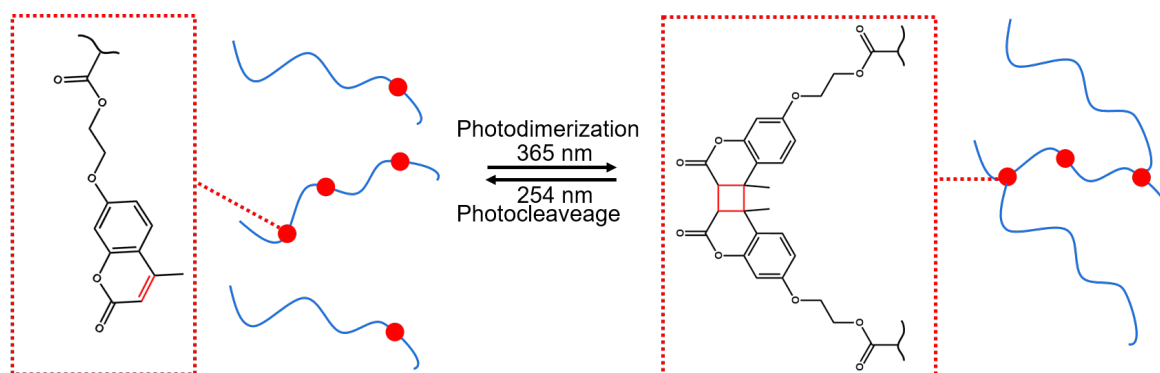


Figure 2.9: Schematic of the photodimerization of coumarin copolymer chains. On the left side are the copolymer chains in the monomeric state. Under UV irradiation with light with a wavelength of 365 nm, a [2+2] cycloaddition of the coumarins occurs. Result of the cycloaddition is the crosslinking of the copolymer chains. The crosslinking is shown on the right side. Under UV irradiation with light with a wavelength of 254 nm, photocleavage occurs. The polymer chains get back in the monomeric state.^[75,76] The figure was made with changes after Ref.^[76]

2.6 Motivation & Goals

Surface adaptation plays an important role for the wetting properties of materials and coatings in many technical and industrial applications. To optimize coatings for surface protection for example, it is important to understand how the bulk material affects the wetting properties.

The aim of my thesis is to contribute to a better understanding on surface adaptation. The thesis is divided in three following chapters (3-5). In each chapter, I will answer a research question to expand the knowledge of the wetting properties of hydrophobic surfaces. In the third chapter, I will answer the research question, how surface adaptation affects slide electrification. The research question of the fourth chapter is, how thick does a hydrophobic polymer layer have to be, to shield a hydrophilic polymer layer underneath? Can diblock copolymer surfaces used to tune the surface adaptation behavior? In the fifth chapter I want to answer the question, how photodimerization of a polymer surface affect the friction force of sliding drop.

3 The Role of Surface Adaptation in Slide Electrification

3.1 Author Contributions

3.2 Summary

In this chapter I showed on the one hand the role of adaptation in slide electrification. On the other hand I was able to extend the model of acid-base reaction in slide electrification by exploiting the Pearson concept.

Based on the hypothesis that the drop charge of a sliding drop on a fluorinated surface is independent of the bulk chemistry, the surfaces of different silicate glasses were coated with two different fluorosilanes. 1H, 1H, 2H, 2H-perfluorooctyltrichlorosilane (PFOTS) and chloro(dimethyl)(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silane (PFOMS). Commercial silicate glasses were used as substrates, which differ in the quantity of SiO₂ and the quantity and type of ionic components. It was possible to vary the polarizability and the Pearson hardness of the substrate. As reference for a sample where the chemical composition of the bulk and surface chemistry did not differ PTFE foil was used. The drop charge of each drop of a series of 500 sliding water drops were recorded, respectively. The drop charge of the first drop Q_1 showed the maximum charge. With increasing drop number the drop charge decreased until the drop charge reached a constant value Q_∞ . According to the initial hypothesis Q_1 and Q_∞ of the PFOMS coated substrates and the PTFE foil were in the same range of magnitude. However, Q_1 and Q_∞ of the PFOTS coated substrates differ from the drop charge behavior of the PTFE foil. Q_1 of the PFOTS coated substrates decreased with increasing polarizability of the substrate. Q_∞ increased with increasing Pearson hardness of the substrate, respectively.

To understand the difference in the drop charge behavior between the PFOTS and PFOMS coated substrates, the surface layer was characterized by SFM, spectroscopic ellipsometry, XPS. The surface analysis showed that in the case of the PFOTS surfaces, the coverage of the coating differs from substrate to substrate. It was assumed that the difference and quality of the coverage leads to water or water ions penetration through the surface layer to the substrate. However, it was not possible to measure the grafting density or the quality of the surface layer spectroscopically.

As an alternative to the spectroscopic methods, surface characterization using contact angle measurements is a sensitive and established method to study the quality of a coating. To analyze the coating and the influence of surface charge on the wetting properties the contact angle measurements were modified by grounding the needle and an ionic air blower (IAB). For the PFOTS coated quartz glass, no constant θ_{RCA} was observed under standard contact angle measurements. By grounding the needle during the measurements, a constant θ_{RCA} was observed. The remaining surface charges affected the advancing contact angle (θ_{ACA}) of the following measurement cycle. The θ_{ACA} of the 2nd and 3rd cycle did not reach the value of the θ_{ACA} of the 1st cycle. By neutralizing the surface with the IAB during the measurement, a constant θ_{ACA} was measured for all measurement cycles. For the PFOMS surface a constant θ_{ACA} and θ_{RCA} were observed in all cycles with and without grounded needle, which agrees with the contact angle measurements for a fully fluorinated surface. The combination of the grounded needle and the IAB showed the influence of drop and surface charge on the contact angles. The influence of drop charge on θ_{ACA} and θ_{RCA} correlated with the high Q_1 of the PFOTS coated quartz glass and low Q_1 of the PFOMS coated quartz glass surface, respectively.

3.3 Abstract

In my first author publication "How Surface and Substrate Chemistry Affect Slide Electrification", *J. Am. Chem. Soc.* 2024, 146, 10073-10083 the influence of the physico chemical properties of the substrate and the influence of the coating on slide electrification was investigated. The main finding of the publication was, that for the first drop sliding on a hydrophobic surface the properties of the coating and the permittivity of the substrate are the dominant parameter to explain the charge separation between drop and surface. However, in the saturated state the substrate chemistry is the dominant parameter to explain the charge separation between drop and surface. The correlation between the drop charge and the Pearson hardness of the substrate showed that in the saturated state, slide electrification can be described as acid-base reaction. All results that are based on this publication will be cited.

However, the publication left open the question why the drop charge of PFOTS coated glass surfaces differs from that of PTFE. I assumed, that the drop charge on different fully fluorinated surfaces should be in the same order of magnitude. The research goal of this chapter is to check how far slide electrification on different fully fluorinated surfaces are comparable with each other. Furthermore I want to answer the question how far surface adaptation plays a role in slide electrification on fluorinated surfaces.

3.4 Drop Charge on Fluorinated Surfaces

If slide electrification can be described as an acid-base reaction between a sliding water drop and a hydrophobic surface,^[36,37] the drop and surface charge on hydrophobic surfaces with similar surface roughness^[46] and comparable surface chemistry should be in the same order of magnitude. To check the hypothesis the drop charge on different fluorinated surfaces; 1H, 1H, 2H, 2H-perfluorooctyltrichlorosilane (PFOTS) coated sodium silicate glass, chloro(dimethyl)(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silane (PFOMS) coated sodium silicate glass and polytetrafluoroethylene (PTFE) foil was measured. It was assumed that on all surfaces CF_3 groups are present at the air-solid interface. The drop charge was measured by a house made experimental setup^[32] and is shown schematically in Figure 3.1a.

In Figure 3.1b the measured drop charge is plotted against the drop number for PFOTS,^[1] PFOMS coated sodium silicate glass and PTFE foil,^[1] respectively. In general, it was observed that for a series of sliding drops at a fixed drop rate the drop charge decreases with increasing drop number, which agrees with previous work.^[32] Q_1 always had the maximum charge and between 100 and 200 drops, the drop charge reach a saturated state Q_∞ . The drop charge of the first drop, Q_1 and the averaged drop charge Q_∞ between the drop 200 and 500 were used for the evaluation.

A comparison of the drop charge of the PFOMS coated sodium silicate glass and the PTFE surface confirmed that the hypothesis of similar surface chemistry has similar influence on slide electrification applies here. Both Q_1 and Q_∞ are in the same order of magnitude (Table 3.1). However Q_1 and Q_∞ of the PFOTS coated sodium silicate glass differ from the PFOMS coated silicate glass and the PTFE foil. Q_1 of the PFOTS coated sodium silicate glass was 300% larger than Q_1 of the PFOMS coated sodium silicate glass and PTFE foil. Q_∞ of the PFOTS coated sodium silicate glass was in the range of Q_1 of the PFOMS coated sodium silicate glass and PTFE foil.

Here first the question arose how far surface chemistry of the PFOMS and PFOTS surfaces differ. Also the question arose how far the bulk properties of the substrate affect the acid-base reaction in slide electrification. To answer the questions next to the sodium silicate glass, quartz glass, aluminosilicate glass and lanthanum silicate glasses were coated with PFOTS and PFOMS, respectively. In the following the silicate glasses will be refer as substrate. All measured drop charges with the corresponding drop number are summarized in Figure 8.1. In the first part I will analyze the influence of the coating. In the second

part I will analyze the influence of the bulk properties on slide electrification.

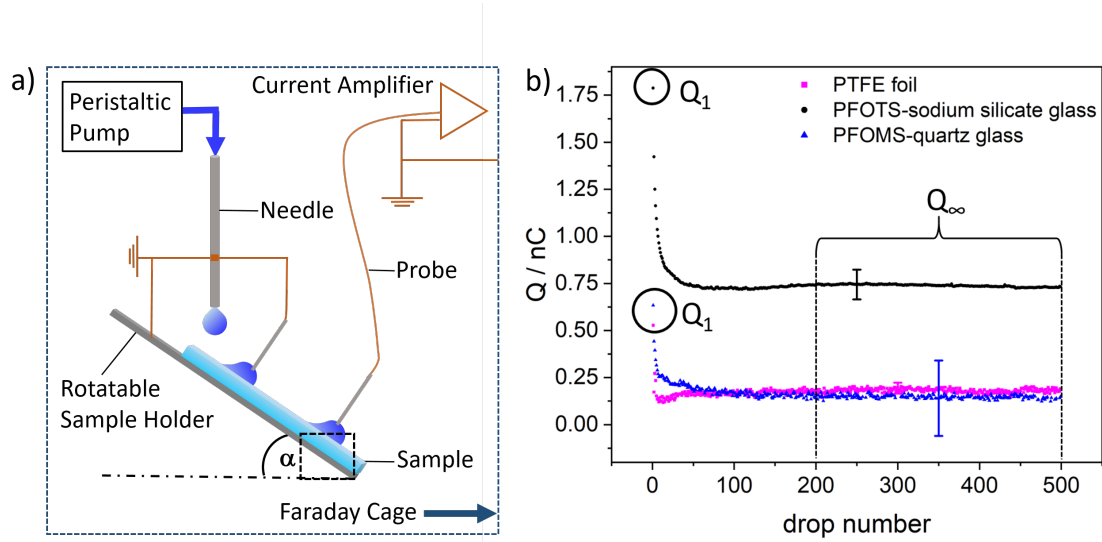


Figure 3.1: a) The experimental setup to measure the drop charge. The setup is located in a Faraday cage. The tilt angle can be varied. A peristaltic pump is connected to a grounded needle. The deposited drop starts to slide and touch a grounded wire. After a fixed sliding length the drop touches a probe. The probe is connecting to a current amplifier and a current signal gets recorded. a) was taken with changes from my first author publication and reprinted with permission from Ref.^[1] Copyright [2025] American Chemical Society. b) The charge of the drop is plotted the corresponding drop number in a series of 500 drops. Magenta shows the drop charge on a PTFE foil. Black shows the drop charge on a PFOTS coated sodium silicate glass surface. Blue shows the drop charge of a PFOMS coated quartz glass. It was noted, that the charge behavior on the PFOTS surface, differ from the charge behavior of the PFOMS surface and PTFE surface.

3.4.1 PFOTS Surfaces

3.4.1.1 Drop Charge

It was observed that Q_1 of the PFOTS coated quartz glass, aluminosilicate glass and sodium silicate glass was in the order of 1.8 ± 0.2 nC. However for Q_1 of the lanthanum silicate glass no drop charge was measured. Q_∞ for the PFOTS coated sodium silicate glass and aluminosilicate glass was in the order of 0.8 ± 0.1 nC. Q_∞ of the PFOTS coated quartz glass and lanthanum silicate glass was in order of -0.1 ± 0.1 nC. Both Q_1 and Q_∞ of all PFOTS coated substrates differed significantly from Q_1 and Q_∞ of the PTFE foil. All measured Q_1 and Q_∞ are summarized in Table 3.1. To check if the differed of Q_1 and Q_∞ is related to the PFOTS surfaces or bulk properties of the coated substrates, respectively, the PFOTS surfaces needed to be analyzed in more detail.

Table 3.1: Advancing contact angle θ_{ACA} , receding contact angle θ_{RCA} , contact angle hysteresis (CAH), the thickness (d) of the coating, the drop charge of the first drop (Q_1) and the drop charge in the saturated state (Q_∞) of the PFOTS and PFOMS coated silicate glasses and PTFE foil. The measurements uncertainty of θ_{ACA} , θ_{RCA} , d , Q_1 , Q_∞ were calculated by the standard deviation. The measurement uncertainty of the CAH was calculated using Gaussian error propagation. The values of all PFOTS coated silicate glasses and the PTFE foil were taken from my publication.^[1]

Sample	$\theta_{ACA}/^\circ$	$\theta_{RCA}/^\circ$	CAH/ $^\circ$	d/nm	Q_1/nC	Q_∞/nC
PFOTS-quartz glass ^[1]	116 $\pm$ 2	83 $\pm$ 2	33 $\pm$ 3	1.3 $\pm$ 0.1	2.08 $\pm$ 0.28	-0.21 $\pm$ 0.07
PFOTS-sodium silicate glass ^[1]	119 $\pm$ 1	101 $\pm$ 3	18 $\pm$ 3	4.9 $\pm$ 1.8	1.78 $\pm$ 0.08	0.76 $\pm$ 0.01
PFOTS-aluminosilicate glass ^[1]	111 $\pm$ 2	88 $\pm$ 2	23 $\pm$ 2	1.0 $\pm$ 0.1	1.66 $\pm$ 0.30	0.85 $\pm$ 0.30
PFOTS-lanthanum silicate glass ^[1]	106 $\pm$ 1	80 $\pm$ 1	26 $\pm$ 1	5.6 $\pm$ 0.5	$\approx$ 0 $\pm$ 0.1	-0.17 $\pm$ 0.1
PFOMS-quartz glass	100 $\pm$ 2	85 $\pm$ 2	15 $\pm$ 3	1.8 $\pm$ 0.3	0.35 $\pm$ 0.10	$\approx$ 0 $\pm$ 0.1
PFOMS-sodium silicate glass	95 $\pm$ 2	82 $\pm$ 2	13 $\pm$ 3	1.8 $\pm$ 0.3	0.75 $\pm$ 0.05	0.23 $\pm$ 0.09
PFOMS-aluminosilicate glass	92 $\pm$ 3	81 $\pm$ 2	11 $\pm$ 4	1.8 $\pm$ 0.3	0.76 $\pm$ 0.06	0.24 $\pm$ 0.07
PFOMS-lanthanum silicate glass	97 $\pm$ 3	80 $\pm$ 3	17 $\pm$ 4	1.8 $\pm$ 0.3	0.57 $\pm$ 0.10	0.07 $\pm$ 0.01
PTFE foil ^[1]	109 $\pm$ 2	88 $\pm$ 1	21 $\pm$ 2	50 $\times$ 10 ³	0.57 $\pm$ 0.05	0.19 $\pm$ 0.03

3.4.1.2 Thickness of the PFOTS Surface

In general the Si-Cl bond of a chlorosilane molecule can hydrolyze in the presence of water. Product of the hydrolysis is the formation of a silanol group and hydrochloric acid ($\text{Si-Cl} + \text{H}_2\text{O} \longrightarrow \text{Si-OH} + \text{HCl}$). In the case of trichlorosilanes, the silanol group can react with adjacent silanol group and polymerize to a multi siloxane network ($\text{Si-OH} + \text{Si-OH} \longrightarrow \text{Si-O-Si} + \text{H}_2\text{O}$).^[82] With regard to a SiO_2 surface the reaction between the surface and trichlorosilanes can lead to the formation of different silane surfaces. The trichlorosilanes can react with the surface and polymerize in the horizontal direction (self-Assembly). The trichlorosilanes can react with the surface and polymerize in the vertical direction or the trichlorosilanes can polymerize in the vertical and horizontal direction. Furthermore the trichlorosilanes can covalently be attached to the substrate.^[55]

The question that arose was whether the PFOTS surfaces were a monolayer or multi siloxane layer and if the surface structure is related to Q_1 and Q_∞ . It was assumed that the thickness of a monolayer should be of the same order of magnitude as the length of a PFOTS molecule. For a PFOTS molecule the length of 1 nm was calculated.^[1] The calculation was performed with the open source software Avogadro, using universal force field mode with geometry optimizing.^[83] The simulated chemical structure of a PFOTS molecule is shown in Figure 3.2a. To simulate the bonded PFOTS molecule on the SiO_2 surface, the Cl atoms were substituted by O atoms. The thickness of the PFOTS surfaces was measured by spectroscopic ellipsometry. The measured thicknesses of the PFOTS surfaces^[1] are summarized in Table 3.1, respectively. In general it was noted that the thickness of the PFOTS surface differs from glass substrate to glass substrate, which agrees with the literature.^[84] For the PFOTS coated quartz glass and aluminosilicate glass a thickness of 1.3 ± 0.1 nm and 1.0 ± 0.1 nm were measured. Comparing this value with the calculated value of 1 nm for a PFOTS molecule, indicates that a monolayer was present. However the thickness of the PFOTS coated sodium silicate and lanthanum silicate glass was 4.9 ± 1.8 nm and 5.6 ± 0.5 nm. This value indicates the presence of a multi siloxane layer.

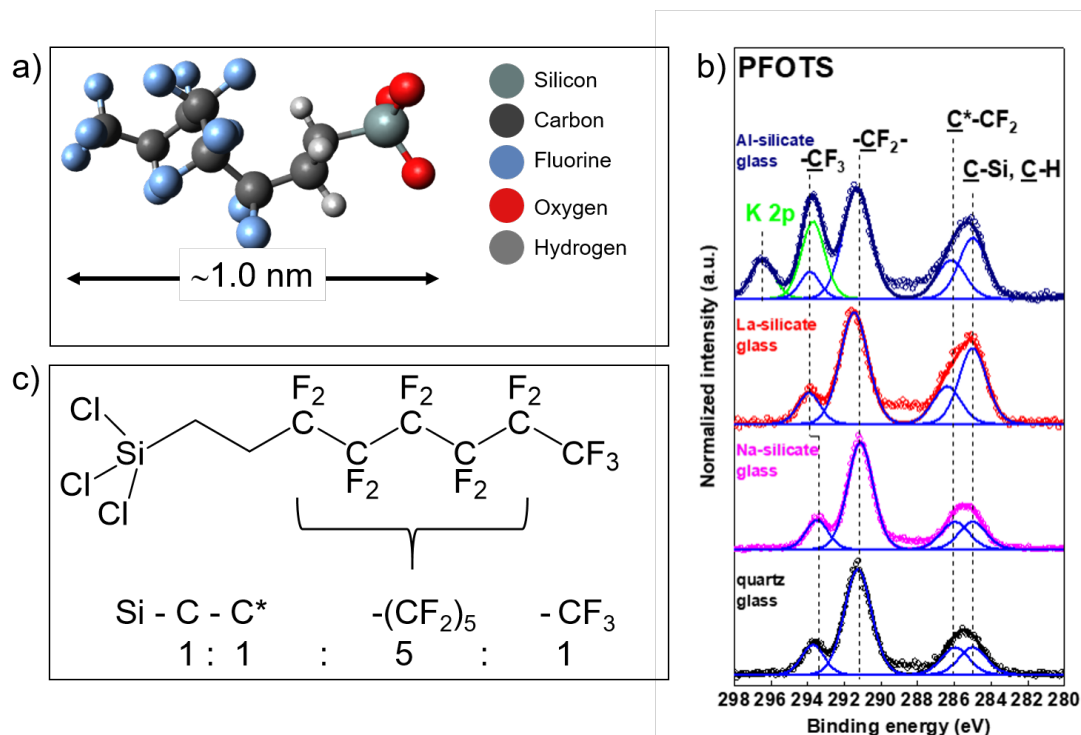


Figure 3.2: a) Chemical structure of the 1H, 2H, 2H-perfluorooctyltrichlorosilane (PFOTS) molecule. The chemical structure was simulated with the software Avogadro, using universal force field mode with geometry optimizing.^[83] For the PFOTS molecule a length of ≈ 1 nm was calculated. To simulate the covalent bond between the PFOTS molecule and the SiO_2 surface, the 3 chlorine atoms were substitute by oxygen atoms, respectively. b) Normalized intensity of the x-ray photoelectron spectra (XPS) is plotted against the binding energy of the corresponding chemical species. From top to bottom: XPS spectra of the PFOTS coated aluminasilicate glass, PFOTS coated lanthanum silicate glass, PFOTS coated sodium silicate glass and FOTS coated quartz glass. b) was taken from my first author publication and reprinted with permission from Ref.^[1] Copyright [2025] American Chemical Society. c) Chemical structure of the PFOTS molecule. The ratio between carbon atoms with the corresponding functional group. The ration between the carbon atoms with functional group was used for the XPS analysis. The XPS characterization confirmed the PFOTS surface on all coated substrates.

3.4.1.3 Surface Topography

To check if the different thickness of the coating affect the surface topography, the surfaces were analyzed by scanning force microscopy (SFM) in tapping mode.^[1] Figure 3.3 show the surface topography of the PFOTS coated substrates. For all coated substrates it could not be distinguish between the coated and non coated glass surfaces. The root mean square roughness (rms) of all substrate surfaces was between 0 and 1 nm. By using a flat substrate, the influence of surface roughness on the wetting properties^[85] and slide electrification^[46,86] can be neglected. However, it was noted that the surface of the pristine sodium silicate glass and aluminosilicate glass showed irregular structure. This structure could be the result of phase separation of the chemical species in the melt during the cooling process.^[50] It was concluded that at the pristine silicate glass surfaces was chemical inhomogeneous.

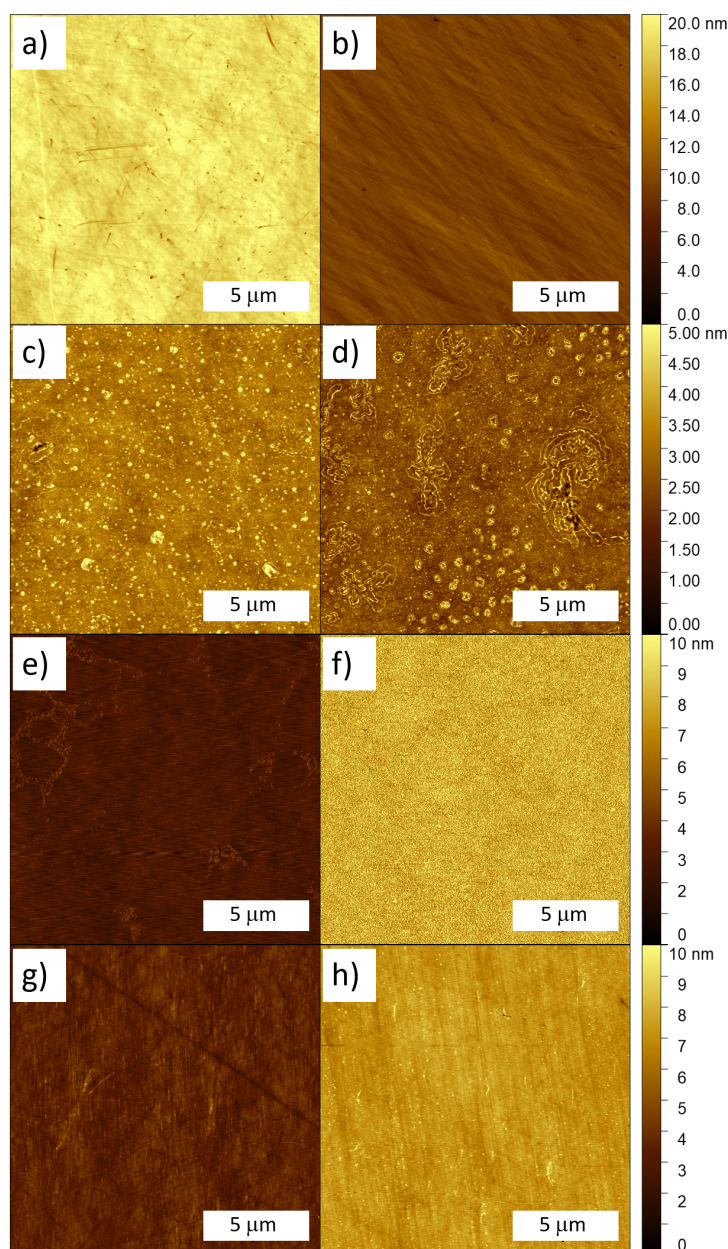


Figure 3.3: The surface topography was measured by scanning force microscopy measurements, respectively. The measurements were performed in tapping mode, with a scan size of $15 \times 15 \mu\text{m}^2$. a) Pristine quartz glass. b) PFOTS coated quartz glass. c) Pristine sodium silicate glass. d) PFOTS coated silicate glass. e) Pristine aluminosilicate glass. f) PFOTS coated aluminosilicate glass. g) Pristine lanthanum silicate glass. h) PFOTS coated lanthanum silicate glass. It was noted, that the surface topography of the coated and non coated silicate glass did not distinguish, respectively. b), d), f) and h) were taken with changes from the SI of my first author publication and reprinted with permission from Ref.^[1] Copyright [2025] American Chemical Society.

3.4.1.4 XPS Characterization

The PFOTS surfaces were analyzed by X-ray photoelectron spectroscopy (XPS). The XPS spectra of the PFOTS coated substrates^[1] are plotted in Figure 3.2b. The C 1s XPS spectra of the PFOTS surfaces have been deconvoluted with a C-Si contribution at 285 eV. The C-Si signal overlapped with C-C contributions of adventitious carbon contamination. The C* – CF₂ peak appears at 286 eV, the

dominating CF_2 peak appears at 291 eV and the CF_3 peak appears at 293 eV. Based on the molecular structure of a PFOTS molecule in Figure 3.2c, a chemically bounded PFOTS molecule on the substrate would lead to the expected peak ratio of $\text{C} - \text{Si} : \text{C}^* - \text{CF}_2 : \text{CF}_2 - \text{CF}_2 : \text{CF}_2 - \text{CF}_3 = 1 : 1 : 5 : 1$. The determined ratio of the $\text{C} - \text{Si} : \text{C}^* - \text{CF}_2 : \text{CF}_2 - \text{CF}_2 : \text{CF}_2 - \text{CF}_3$ peaks of the PFOTS coated quartz glass, aluminosilicate glass, lanthanum silicate glass and sodium silicate glass were $1.2 : 1.1 : 4.4 : 1.0$, $3.5 : 2.3 : 6.3 : 1.0$, $3.0 : 1.5 : 4.5 : 1.0$, $1.2 : 1.1 : 4.4 : 1.0$ respectively. Neglecting the carbon contamination contribution at 285 eV, the C 1s XPS spectra confirm the chemical structure of a PFOTS surface.

All XPS spectra showed no Cl 2p contribution arising from Si-Cl. This proves the complete reaction of the used PFOTS precursor to a mono or multi siloxane layer. The quantity in atom % of carbon and organic fluorine contribution in the XPS spectra differ from substrate to substrate, which indicates different thicknesses or grafting densities of the PFOTS surfaces. Higher quantity of PFOTS were observed on sodium silicate glass and lanthanum silicate glass than on quartz glass or aluminosilicate glass, which agrees with the measured thicknesses by spectroscopic ellipsometry.

3.4.1.5 Wetting Properties

The advancing (θ_{ACA}) and receding (θ_{RCA}) contact angles were measured to characterize wetting properties of the surfaces.^[1] The results are summarized in Table 3.1.

For the PFOTS coated quartz glass and sodium silicate glass the θ_{ACA} were in the range of $117 \pm 2^\circ$. However the θ_{RCA} of this both sample differs. For the PFOTS coated quartz glass the θ_{RCA} was $88 \pm 2^\circ$ and for the PFOTS coated sodium silicate glass $101 \pm 3^\circ$. For the aluminosilicate glass a θ_{ACA} of $111 \pm 2^\circ$ and θ_{RCA} $88 \pm 2^\circ$ were measured. For the lanthanum silicate glass a θ_{ACA} of $106 \pm 1^\circ$ and a θ_{RCA} of $80 \pm 1^\circ$ was measured. It was noted that θ_{ACA} differ by a maximum of 13° between the PFOTS coated sodium silicate glass and the PFOTS coated aluminosilicate glass. The θ_{RCA} differed by up to 26° between the PFOTS coated quartz glass and the PFOTS coated sodium silicate glass. The differ in the contact angles showed that the PFOTS surface properties difference from each other.

To check how far the differ in the wetting properties affect the drop charge, Q_1 and Q_∞ were plotted against θ_{ACA} and θ_{RCA} in Figure 3.4, respectively. The plotted Q_1 and Q_∞ of the PFOTS coated substrates against the θ_{ACA} and receding θ_{RCA} in Figure 3.4 showed no correlation between the drop charge and the wetting properties.

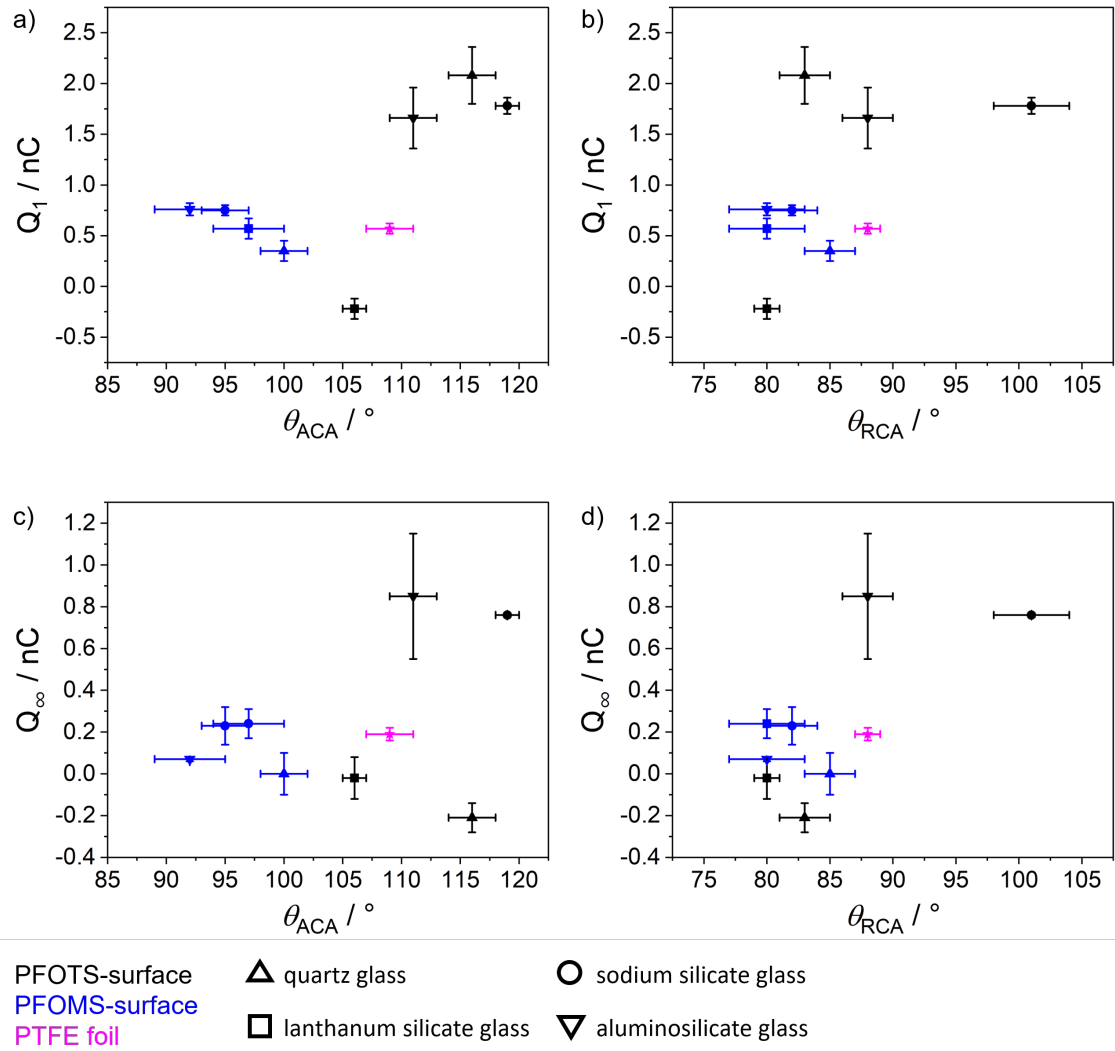


Figure 3.4: a) The drop charge of the first drop (Q_1) is plotted against the advancing contact angle (θ_{ACA}). b) Q_1 is plotted against the receding contact angle (θ_{RCA}). c) The saturated drop charge (Q_∞) is plotted against the θ_{ACA} . d) Q_∞ is plotted against the θ_{RCA} . No correlation between the drop charge and the wetting properties were observed.

3.4.1.6 Quality of the PFOTS Surface

The PFOTS coating were done by chemical vapor deposition (CVD) under reduced pressure, which allows to control the reaction environment during the reaction. To increase the quantity of hydroxyl groups of the substrate, the substrates were treated by oxygen plasma before the reaction.^[87] After the plasma treatment the substrates were exposed to the laboratory environment till the substrates were placed in the desiccator. During the year it was observed that the humidity in the laboratory varied between 15% and 80%. This means the quantities of adsorbed water on the substrate differ from day to day, could result in different siloxane surfaces structure^[82,88,89] and different contact angle hysteresis (CAH)^[55,90] even for the same substrate.

However, the samples for the XPS and spectroscopic ellipsometry analysis were done at the same batch. The previous discussed XPS and spectroscopic ellipsometry experiments shown that the PFOTS surface also differ from substrate to substrate within a batch. This means the difference in the coating could be affected also from the substrate properties. The surface topography of the non coated substrates in

Figure 3.3 showed that the surface of silicate glass can be inhomogeneous through phase separation in the manufacturing process.^[50] This arose the question how far the inhomogeneity of the substrate affect the coating.

However, the chemical identification of the inhomogeneity of the coating on a microscopic level remains a challenge. One option could be the analysis by KPFM. KPFM measurements were not done, because of the thickness of 1mm of the substrates and the low conductivity of the substrates. Another option is the use of Raman spectroscopy with a lateral resolution of 1 μm . Before using Raman spectroscopy, the PFOTS coated sodium silicate glass was scanned by scanning force microscopy in peak force mode at scan size of 1 μm^2 .^[1] The result are summarized in Figure 3.5. Even at the scan size below the resolution limit of the Raman spectroscopy the surface topography showed inhomogeneities. Therefore no Raman spectroscopy was measured and it was not possible to characterize the homogeneity of the PFOTS surface in more detail.

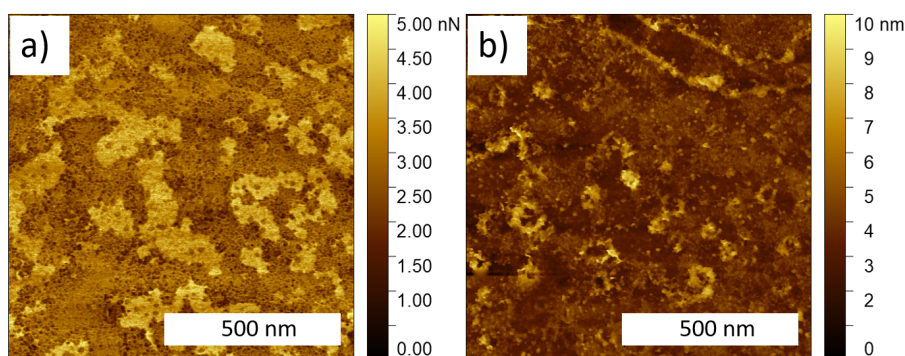


Figure 3.5: The PFOTS coated sodium silicate glass surface was measured by scanning force microscopy measurements (SFM). The SFM measurements were performed in peak force mode, with a scan size of 1 x 1 μm^2 . a) Adhesion force. b) Surface topography. The SFM analysis showed, that even at scan size of 1 x 1 μm^2 , the substrate surface was inhomogeneous. From the SFM measurements I concluded that Raman spectroscopy (lateral resolution limit of 1 μm^2) can not detect, to which degree the coating is inhomogeneous. The SFM images were taken with changes from the SI of my first author publication and reprinted with permission from Ref.^[1] Copyright [2025] American Chemical Society.

The PFOTS surface analysis revealed the following. The XPS characterization has shown that all substrates had a PFOTS surface with comparable chemical anchoring. It was concluded, that the PFOTS surface differ in their coverage. No correlation between the wetting properties and the drop charge was found.

3.4.2 PFOMS Surface

3.4.2.1 Drop Charge

It was observed that Q_1 of the PFOMS coated sodium silicate glass and aluminosilicate glass was ≈ 0.7 nC. For the PFOMS coated lanthanum silicate glass a Q_1 of ≈ 0.5 nC was measured. For the PFOMS coated quartz glass a Q_1 of ≈ 0.3 nC was measured. Q_∞ of the PFOMS coated sodium silicate glass and aluminosilicate glass was ≈ 0.2 nC. Q_∞ of the PFOMS coated quartz glass and lanthanum silicate glass was ≈ 0 nC. It was noted that both Q_1 and Q_∞ of all PFOMS coated substrates have differed by a maximum of 0.2 nC of Q_1 and Q_∞ of the PTFE foil. All measured Q_1 and Q_∞ are summarized in Table 3.1. It was noted that the drop charge on all PFOMS coated silicate glasses were in the same

range.

3.4.2.2 Thickness of the PFOMS Surface

To analyze the PFOMS surface the length of 1.5 nm for a free PFOMS molecule was calculated. The calculation was done with the open source software Avogadro, using universal force field mode with geometry optimizing.^[83] The simulated chemical structure of a PFOMS molecule is shown in Figure 3.6. To simulate the bonded PFOMS molecule on the SiO₂ surface, the Cl atoms were substitute by O atoms. The surface of a PFOMS coated silicon wafer was used to measure the PFOMS surface thickness to increase the accuracy of the measurement by spectroscopic ellipsometry. A PFOMS surface thickness of 1.8 ± 0.3 nm was measured by spectroscopic ellipsometry. With regard to the measurement uncertainty and the assumption for the calculation the experimental value of 1.8 ± 0.3 nm and theoretical calculated value of 1.5 nm agree with each other.

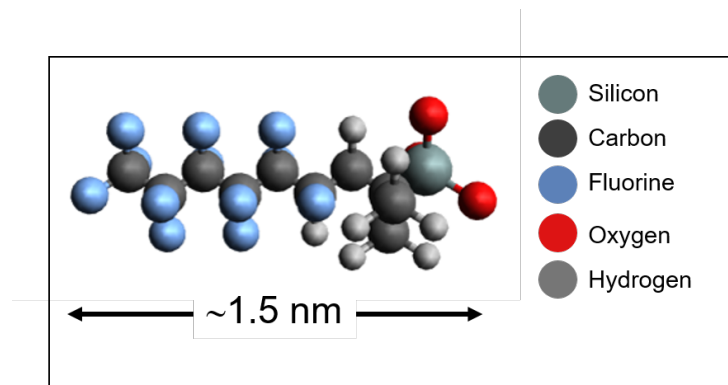


Figure 3.6: Chemical structure of the chloro(dimethyl)(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silane) (PFOMS) molecule. The chemical structure was simulated with the software Avogadro, using universal force field mode with geometry optimizing.^[83] For the PFOMS molecule a length of ≈ 1.5 nm was calculated. To simulate the covalent bond between the PFOMS molecule and the SiO₂ surface, the chlorine atom was substitute by an oxygen atom. The calculated length of the PFOMS, matched with the measured thickness of the PFOMS surface.

Since the formation of multi siloxane structure was excluded by the use of the monochlorosilane^[55,91] it was assumed that the thickness of 1.8 ± 0.3 nm applies to all PFOMS coated substrates.

3.4.2.3 SFM Characterization

To check if the PFOMS surface on silicon wafer is comparable with PFOMS surface on quartz glass, the surfaces were analyzed by SFM. The SFM analysis was done in peak force mode and is summarized in Figure 3.7. The samples were always measured alternately with the same cantilever twice with a scan size of $1 \mu\text{m}^2$, then with a scan size of $20 \mu\text{m}^2$ and again with with a scan size of $1 \mu\text{m}^2$. The adhesion force was averaged, respectively. The measurement uncertainty was obtained by forming the standard deviation. For the PFOMS quartz glass surface a adhesion force of 1.8 ± 1.3 nN was measured. For the the PFOMS silicon wafer surface a adhesion force of 1.3 ± 0.3 nN was measured. Since the adhesion forces were in the same order of magnitude, the assumption that the PFOMS surfaces on the glass substrates and silicon wafer were comparable was confirmed. With regard to the surface topography, it could not be distinguish between the coated and non coated quartz glass surface.

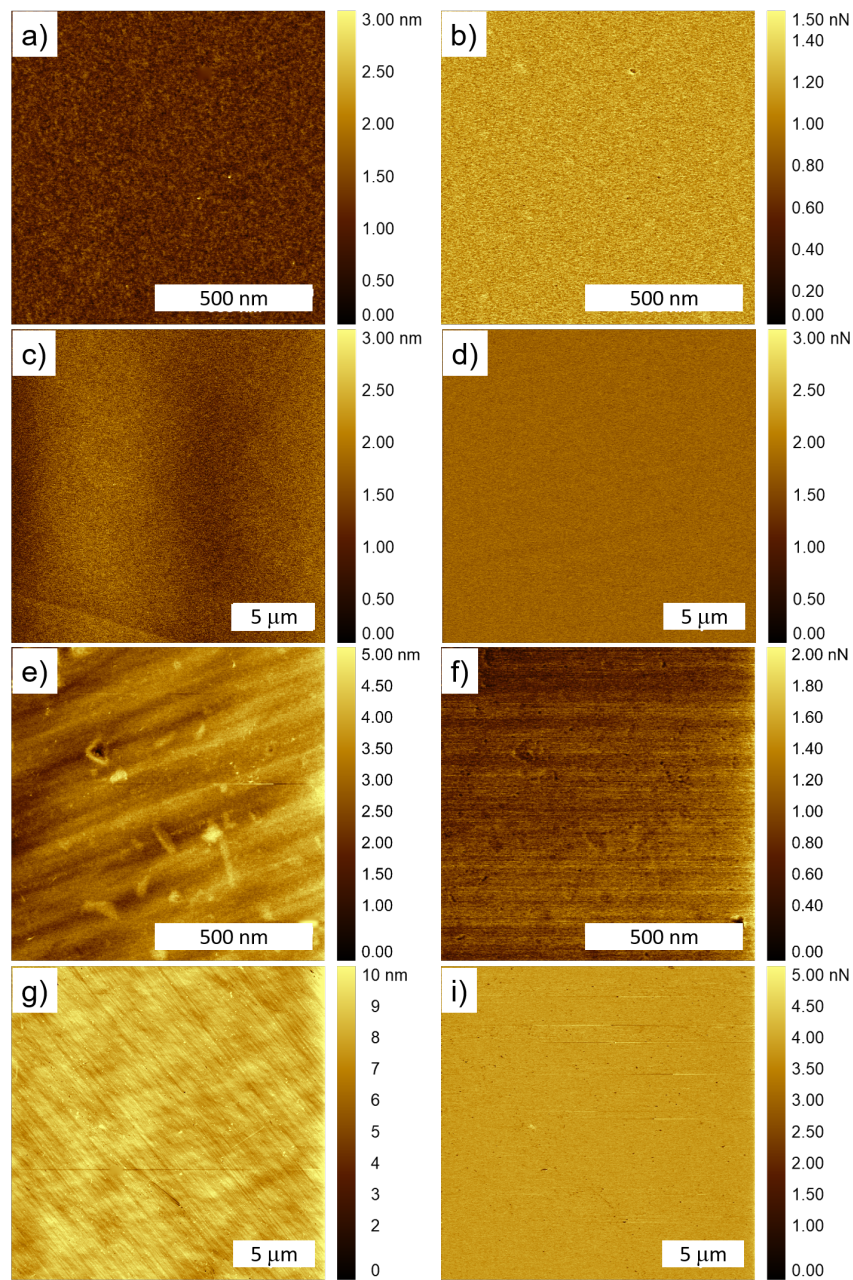


Figure 3.7: PFOMS coated silicon wafer and PFOMS coated quartz glass surfaces were analyzed by scanning force microscopy. The measurements were done in peak force mode at different scan sizes. The aim was to compare the adhesion force on the PFOMS coated quartz glass and silicon wafer. The surfaces were always measured alternately with the same cantilever. a) Surface topography of PFOMS coated silicon wafer, scan size was $1 \times 1 \mu\text{m}^2$. b) Adhesion force of PFOMS coated silicon wafer, scan size was $1 \times 1 \mu\text{m}^2$. c) Surface topography of PFOMS coated silicon wafer, scan size was $20 \times 20 \mu\text{m}^2$. d) Adhesion force of PFOMS coated silicon wafer, scan size was $20 \times 20 \mu\text{m}^2$. e) Surface topography of PFOMS coated quartz glass, scan size was $1 \times 1 \mu\text{m}^2$. f) Adhesion force of PFOMS coated quartz glass, scan size was $1 \times 1 \mu\text{m}^2$. g) Surface topography of PFOMS coated quartz glass, scan size was $20 \times 20 \mu\text{m}^2$. h) Adhesion force of PFOMS coated quartz glass, scan size was $20 \times 20 \mu\text{m}^2$. i) Adhesion force of PFOMS coated quartz glass, scan size was $20 \times 20 \mu\text{m}^2$. The PFOMS surfaces on quartz glass and silicon wafer were comparable.

3.4.2.4 Wetting Properties

The wetting properties were characterized by the θ_{ACA} and θ_{RCA} . The measured contact angles are summarized in Table 3.1. A θ_{ACA} of $95 \pm 5^\circ$ and θ_{RCA} of $82 \pm 3^\circ$ was observed for all PFOMS coated substrates, which showed that the surface properties of all PFOMS coated substrates are comparable. Q_1 and Q_∞ were plotted against θ_{ACA} and θ_{RCA} in Figure 3.4, respectively to check how far the drop charge is affected by the wetting properties. It was noted that both the contact angles and Q_1 and Q_∞ were in the same range.

In conclusion, the surface analysis of the PFOMS coated substrates showed, that the PFOMS surfaces on the different substrates were comparable in coverage and surface properties.

3.4.3 Pearson Hardness of the Substrate

To investigate the influence of the substrate on Q_1 and Q_∞ the *Hard and Soft Acids and Bases* (HSAB) concept was used.

The HSAB concept involves the orbital energy of a chemical species and allows to predict the stability of compounds, the outcome of chemical reactions such as an acid-base reaction and the formation of compounds by associating hard acids with hard bases and soft acids with soft bases. The absolute Pearson hardness η is a fundamental parameter of the HSAB concept and is defined as the half of the second derivation of a species energy E to the changes of the total number of electrons N_{e-} (equation 3.1).^[52] Since the hydroxide ion or the water molecule are hard bases,^[92] the idea was to increase the absolute Pearson hardness of the substrate (acid) to check the influence of the substrate chemistry on the acid-base reaction in slide electrification.

The chemical composition of the used quartz glass (99.99% SiO₂), sodium silicate glass (72.9% SiO₂), aluminosilicate glass (60% SiO₂) and lanthanum silicate glass (24.9% SiO₂) are summarized in Table 3.2.^[1]

Table 3.2: List of the chemical species, their quantities and molar weight M , respectively. Absolute Pearson hardness η of the cation of the chemical species, respectively. The values were taken from my first author publication.^[1] M_{mean} is the calculated mean molar weight of each substrate. The chemical species and the corresponding quantity were measured by the IGR Institut für Glas- und Rohstofftechnologie GmbH, Göttingen, Germany via ICP-OES. η was taken from the work of R. Pearson.^[93]

Substrate	Species	M / gmol^{-1}	fraction %	$\eta(\text{M}^{x+})/\text{eV}$	$M_{\text{mean}}/\text{gmol}^{-1}$
quartz glass	SiO_2	60.08	99.9	-	60.08
sodium silicate glass	SiO_2	60.08	72.9	-	60.09
	MgO	40.3	4.32	33	
	Na_2O	61.98	13.99	21	
	Al_2O_3	101.96	1.25	46	
	K_2O	94.2	0.93	<20	
	CaO	56.08	6.26	<20	
	SO_3	80.06	0.28	<20	
aluminosilicate glass	SiO_2	60.08	60	-	70.21
	MgO	40.3	3.73	33	
	Na_2O	61.98	12.32	21	
	Al_2O_3	101.96	16.24	46	
	K_2O	94.2	4.02	<20	
	CaO	56.08	0.13	<20	
	SO_3	80.06	0.28	<20	
	ZrO_2	123.22	0.87	<20	
	TiO_2	79.86	0.02	<20	
	SnO_2	150.71	0.07	<20	
	Fe_2O_3	159.69	0.02	<20	
lanthanum silicate glass	SiO_2	60.08	24.9	-	107.02
	ZnO	81.38	5.8	<20	
	La_2O_3	325.81	14.2	<20	
	Al_2O_3	101.96	0.38	46	
	Nb_2O_3	108.9	16.1	<20	
	TiO_2	79.86	9.3	<20	
	CaO	56.08	24.6	<20	
	SrO	103.62	0.16	<20	
	ZrO_2	123.22	4.5	<20	

The total $\eta_{\text{substrate}}$ of each substrate was calculated with equation 3.2.^[1]

$$\eta = \frac{1}{2} \frac{d^2 E}{d^2 N_{e-}^2} \quad (3.1)$$

In equation 3.2 is χ the quantity and η the absolute Pearson hardness of the chemical species i , respectively. η were taken from Table 3.2. As the hydroxide ion (5.7eV)^[52] and the water molecule (7.0eV)^[52] are hard bases, only hard acids with a $\eta > 20\text{eV}$ were taken into consideration. It was assumed that this is the hardness factor which is important for the acid-base reaction between the water drop and the surface.

The calculated $\eta_{\text{substrate}}$ of all substrates are summarized in Table 3.3

$$\eta_{\text{substrate}} = \sum \chi_i \cdot \eta_i \quad (3.2)$$

Table 3.3: Compilation of all calculated and measured parameters of the substrates. The values were taken from my first author publication.^[1] Absolute Pearson hardness $\eta_{\text{substrate}}$, density ρ , dielectric permittivity ϵ and polarizability α . The measurements uncertainty of ϵ_r was calculated by the standard deviation. The measurements uncertainty of α and ρ were calculated using Gaussian error propagation. a: parameter was taken from the data sheet of the supplier Schott AG Mainz.

Substrate	$\eta_{\text{substrate}}/\text{eV}$	ρ/gcm^{-3}	$\epsilon_r/\text{As}^{-1}\text{Vm}^{-1}$	$\alpha N_A \epsilon_0/\text{cm}^3$
quartz glass	0	2 ± 0.5	3.65 ± 0.01	354 ± 1
sodium silicate glass	493	2 ± 0.5	6.53 ± 0.06	641 ± 1
aluminum silicate glass	1128	2.5^a	7.7^a	819 ± 1
lanthanum silicate glass	17	3 ± 0.5	10.95 ± 0.5	1106 ± 1

In Figure 3.8 Q_1 and Q_∞ of the PFOTS and PFOMS coated substrates and the PTFE foil were plotted against the $\eta_{\text{substrate}}$ of the substrates, respectively. For Q_1 it was noted that drop charge on all PFOMS coated surfaces were between ≈ 0.4 nC and ≈ 0.7 nC. Q_1 of the PTFE foil was ≈ 0.5 nC. Q_1 of the PFOTS coated quartz glass, sodium silicate glass and aluminosilicate glass was between ≈ 1.5 nC and ≈ 2.0 nC. However Q_1 of the lanthanum silicate glass was in the range of ≈ 0 nC.

Q_∞ of all PFOMS coated substrates were between ≈ 0 nC and ≈ 0.2 nC. Q_∞ of the PTFE foil was ≈ 0.2 nC. Q_∞ of the PFOTS coated quartz glass and lanthanum silicate glass was between ≈ -0.2 nC. Q_∞ of the PFOTS coated sodium silicate glass, aluminosilicate glass was in the range of 0.7 nC.

From the experiments it was concluded that Q_1 did not correlate with $\eta_{\text{substrate}}$, which indicated that for Q_1 the substrate chemistry is negligible. Furthermore it was noted that Q_1 of all PFOMS surfaces was in the same range such as Q_1 of the PTFE foil. In the case of Q_∞ it was shown that Q_∞ increased with increasing $\eta_{\text{substrate}}$. Compared to the PFOTS coated substrates the influence of $\eta_{\text{substrate}}$ on Q_∞ was small for the PFOMS coated substrates. The results are in line with the results of the last paragraph, that the PFOMS surfaces are comparable with the surface of the PTFE foil and that the influence of the substrate chemistry on Q_∞ is negligible. In the case of the PFOTS coated substrates the correlation between Q_∞ and $\eta_{\text{substrate}}$ confirmed that water ions or water molecules penetrates through the surface layer and therefore the $\eta_{\text{substrate}}$ of the substrates affect the acid-base reaction^[36] between drop and surface in the saturated state.

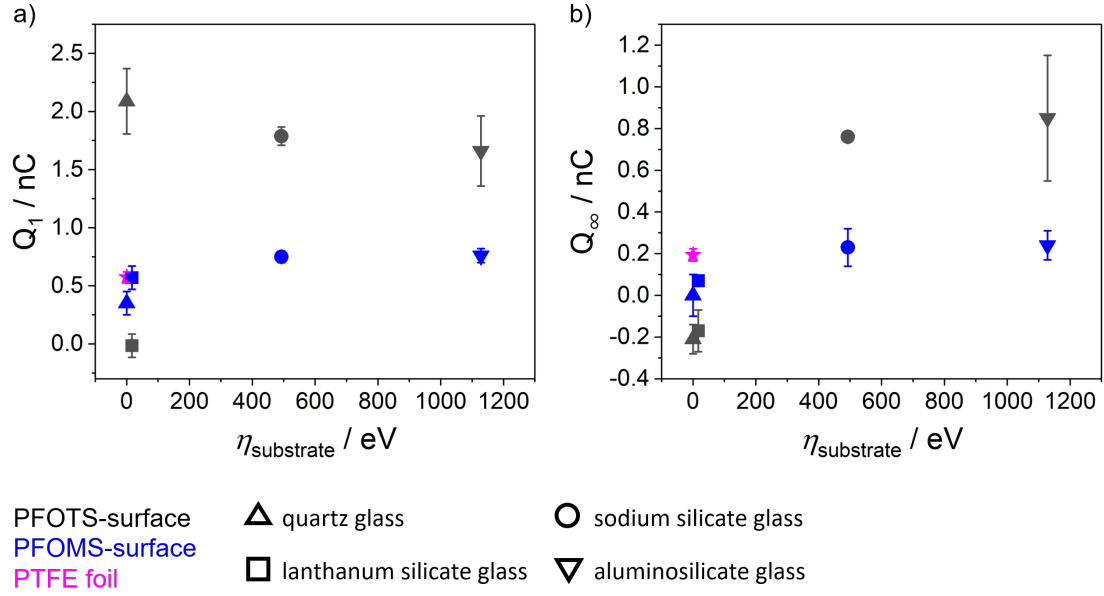


Figure 3.8: a) The drop charge of the first drop (Q_1) is plotted against the Pearson hardness $\eta_{\text{substrate}}$ of the substrate, respectively. b) The saturated drop charge (Q_∞) is plotted against the Pearson hardness $\eta_{\text{substrate}}$ of the substrate, respectively. No correlation was observed between Q_1 and $\eta_{\text{substrate}}$. It was noted that Q_∞ correlated with $\eta_{\text{substrate}}$. With increasing $\eta_{\text{substrate}}$, Q_∞ increased. Q_∞ was influenced by the substrate chemistry.

3.4.4 Polarizability of the Substrate

It has been shown that the dielectric permittivity ϵ_r of the substrate influences the drop motion.^[38] Since the measured drop charge was in the range of nano Coloumb,^[32,37,38] it was preferred to use the microscopic parameter of polarizability α instead of the macroscopic parameter ϵ_r to check how far the electronic properties of the substrate affect the drop charge. α describes how easily the charges within a molecule can be shifted under the influence of an electric field. α can be determined by the Clausius-Mosotti relation (equation 3.3).^[94]

$$\alpha \frac{N_A}{\epsilon_0} = 3 \frac{\epsilon_r - 1}{\epsilon_r + 2} \frac{M_{\text{mean}}}{\rho} \quad (3.3)$$

This equation links the macroscopically measurable ϵ_r with the electric microscopic α .^[94] In equation 3.3 is ρ the density of the medium, M_{mean} is the mean molecular weight of the medium, N_A is the Avogadro constant, ϵ_r is the dielectric permittivity of the medium and ϵ_0 is the dielectric permittivity of the vacuum.^[94] The calculated α of each substrate are summarized in Table 3.3.

The uncertainty $\Delta\alpha$ was calculated by the propagation of uncertainty of the measured parameter ϵ_r and ρ .

$$\Delta\alpha = \sqrt{\left(\frac{\partial\alpha}{\partial\epsilon_r}\Delta\epsilon_r\right)^2 + \left(\frac{\partial\alpha}{\partial\rho}\Delta\rho\right)^2} \quad (3.4)$$

ρ of the substrates was determined as follows. The dimension of the quartz glass, sodium silicate glass and lanthanum silicate glass were measured by caliper with a $\Delta d = \pm 0.01\text{mm}$. After weighing, ρ could be determined by dividing m by V (experimental part). $\Delta m = \pm 0.1\text{mg}$ was taken from the scale METTLER TOLEDO AB204. The uncertainty $\Delta\rho$ was calculated by the propagation of uncertainty of

m and V according equation 3.5.

$$\Delta\rho = \sqrt{\left(\frac{\partial\rho}{\partial m}\Delta m\right)^2 + \left(\frac{\partial\rho}{\partial V}\Delta V\right)^2} \quad (3.5)$$

ΔV was calculated by the propagation of uncertainty of d according equation 3.6 .

$$\Delta V = \sqrt{\left(\frac{\partial V}{\partial x}\Delta d\right)^2 + \left(\frac{\partial V}{\partial y}\Delta d\right)^2 + \left(\frac{\partial V}{\partial z}\Delta d\right)^2} \quad (3.6)$$

The aluminosilicate glass was cut by myself. Due to the thickness of 0.330 mm, it was not possible to cut an exact 90° angle and measure the exact volume. Therefore ρ was taken from the supplier and no uncertainty was determined. ρ of all substrates are summarized in Table 3.3.

M_{mean} was calculated by sum the product of the quantity and molecular weight of each chemical species of the substrates and is listed in Table 3.2. No uncertainty of M_{mean} was calculated.

ϵ_r of the quartz glass, sodium silicate glass and lanthanum silicate glass were measured by dielectric spectroscopy and summarized in Figure 3.9. $\Delta\epsilon_r$ was calculated by the standard derivation of three measurements, respectively. The aluminosilicate glass is used for electric devices and ϵ_r of the aluminum silicate glass was taken from the supplier. ϵ_r are summarized in Table 3.3.

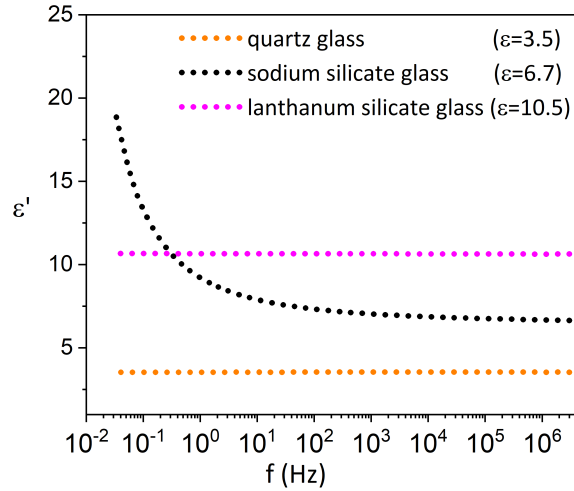


Figure 3.9: Dielectric spectra of quartz glass (orange), sodium silicate glass (black) and lanthanum silicate glass (magenta). The real part ϵ' of permittivity ($\epsilon = \epsilon' + i\epsilon''$) is plotted against the frequency. The spectra was taken with changes from the SI of my first author publication and reprinted with permission from Ref.^[1] Copyright [2025] American Chemical Society.^[1]

In Figure 3.10 Q_1 and Q_∞ of the PTFE foil, the PFOTS and PFOMS coated substrates are plotted against α of the substrates, respectively. Q_1 of the PFOMS coated substrates and the PTFE foil was between ≈ 0.4 nC and ≈ 0.7 nC. No correlation between Q_1 of the PFOMS coated substrates and α were observed. Q_1 of the PFOTS coated quartz glass, sodium silicate glass and aluminosilicate glass was between ≈ 1.5 nC and ≈ 2.0 nC. Q_1 of the PFOTS coated lanthanum silicate glass was ≈ 0 nC. Here a correlation between Q_1 and α were observed. With increasing α , Q_1 decreased.

Q_∞ of the PFOMS coated substrates were ≈ 0 nC and ≈ 0.2 nC. Q_∞ of the PTFE foil was ≈ 0.2 nC. Q_∞ of the PFOTS coated substrates were scattering between ≈ -0.2 nC for the PFOTS coated quartz glass and lanthanum silicate glass and ≈ 0.8 nC for the PFOTS coated sodium silicate glass and aluminosilicate

glass. No correlation was observed between Q_∞ and α .

From the discussed results in Figure 3.10 it was concluded that for the PFOMS coated substrates and the PTFE foil Q_1 and Q_∞ were in the same range of magnitude and not affected by the α of the substrate. However Q_1 of the PFOTS coated substrates correlated with α . With increasing α , Q_1 decreased, which agrees with previous reported work^[38] and the results of the previous paragraphs that the coverage of the PFOTS surfaces is the reason for the strong influence of the substrate properties on slide electrification. From the results it was concluded on the one hand, that in the saturated state, slide electrification can be described at acid base reaction. On the other hand, it was concluded that for the first drops, the influence of α is the dominating parameter to describe the drop charge.

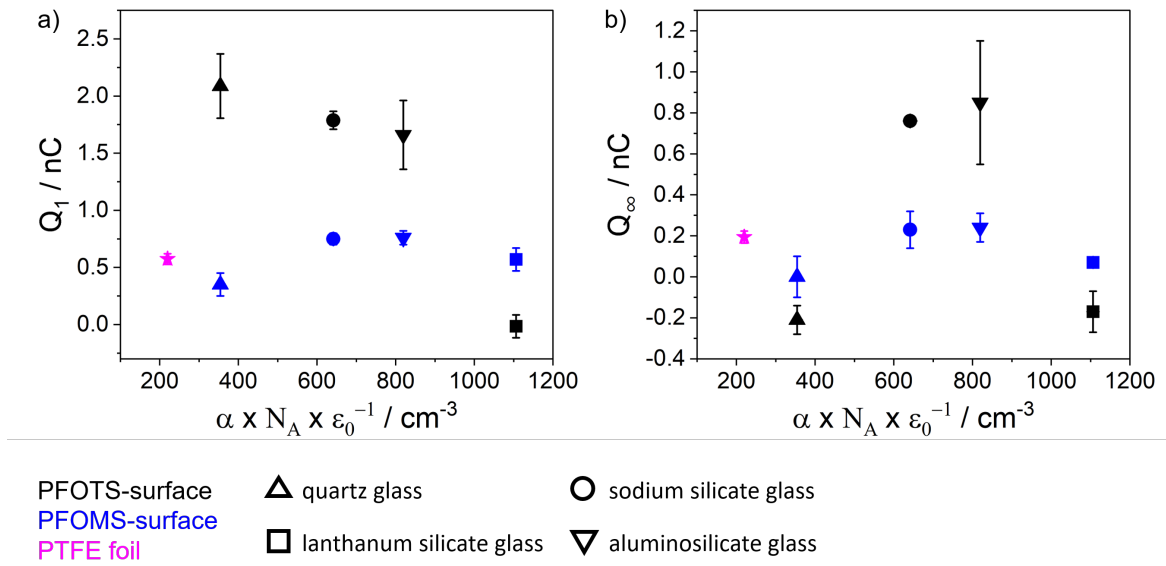


Figure 3.10: a) The drop charge of the first drop (Q_1) is plotted against the polarizability α of the substrate, respectively. It was noted that for the PFOTS coated surfaces, Q_1 decreased with increasing α . For the PFOMS surfaces no correlation between Q_1 and α was observed. b) The saturated drop charge (Q_∞) is plotted against α of the substrate, respectively. No correlation between Q_1 or Q_∞ and α was observed.

3.5 Surface Adaptation

Comparing the drop charge and the wetting properties of the PFOTS and PFOMS surfaces the question arose how far the contact angle θ is influenced by the drop charge or surface charge. To answer the question the goniometer was modified by grounding the needle and installing an ionic air blower (IAB) above the sample holder. θ of PFOMS and PFOTS coated quartz glass were measured by 3 cycles of increasing and decreasing the drop volume from 6 μL to 41 μL . θ was plotted against the measuring time, respectively. The measurement are summarized in Figure 3.11.

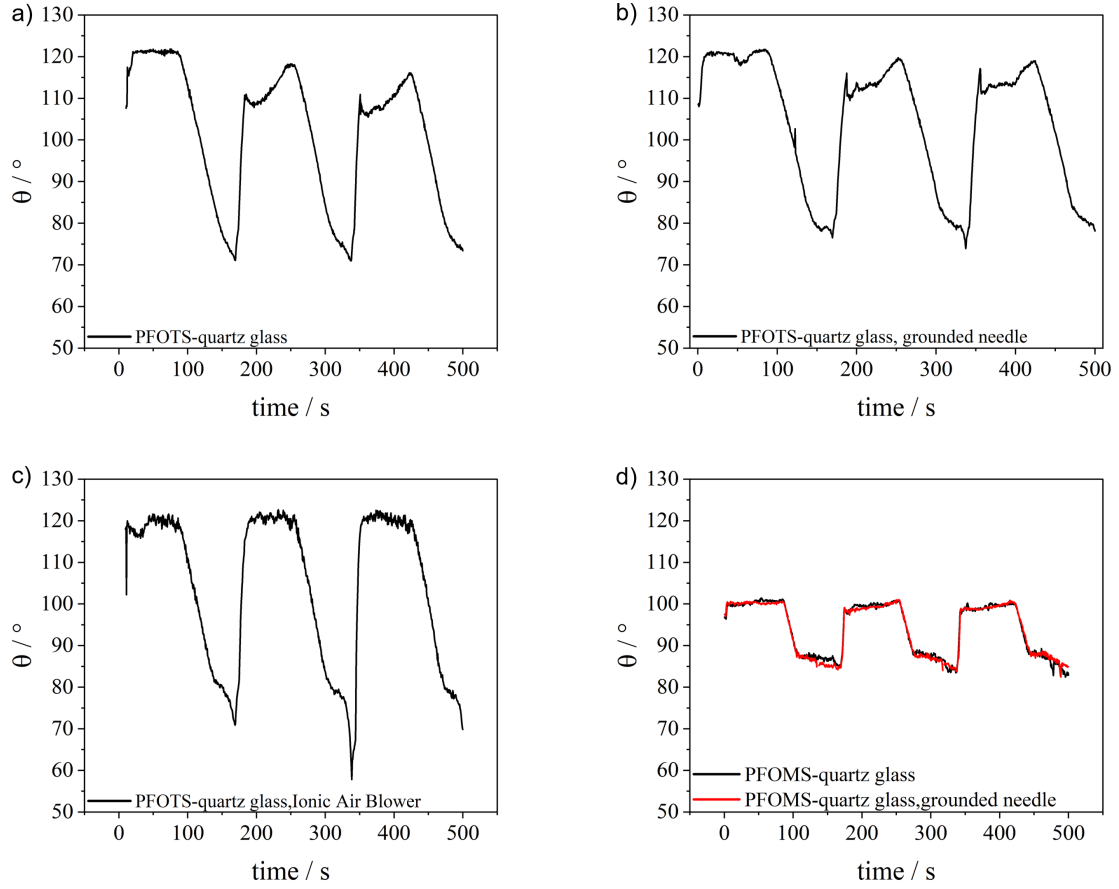


Figure 3.11: A drop with a volume of $6 \mu\text{L}$ was deposited on the surface. The drop volume was increased and decreased by $35 \mu\text{L}$. During the variation of the drop volume, θ was measured. θ is plotted against the measurement time, respectively. a) PFOTS coated quartz glass. The measurement was done under standard conditions. The θ_{RCA} did not reached a constant value. The θ_{ACA} of the second and third measurement cycle was lower than the θ_{ACA} of the first measurement cycle. b) PFOTS coated quartz glass. During the measurement the needle was grounded to neutralize the drop, during receding of the drop front. The θ_{RCA} reached a constant value. The θ_{ACA} of the second and third measurement cycle was lower than the θ_{ACA} of the first measurement cycle. c) PFOTS coated quartz glass. During the measurement a Ionic Air Blower was running, to neutralize the remaining surface charges behind the receding drop front. The θ_{RCA} did not reached a constant value. The θ_{ACA} of all three measurement cycles were similar. The measurement with the grounded needle and the Ion Air Blower showed that the drop charge lead to surface adaptation. d) PFOMS coated quartz glass. Black: Under standard condition. Red: Grounded needle during the measurement. No influence of drop and surface charge was observed at the PFOMS coated quartz glass.

For the θ of the PFOTS coated quartz glass in Figure 3.11a, it was observed that the θ_{RCA} did not reach a constant value during receding of the drop front. With regard to the model of slide electrification, it was assumed that charges remain on the surface behind the receding drop front.^[40] As shown schematically in Figure 3.12a, the remaining surface charges can interact with the charged drop. The change in surface energy due to the remaining charges leads to surface adaptation,^[14] which affects the θ .^[16] θ of the PFOTS coated quartz glass with the grounded needle in Figure 3.11b reached a constant value during the receding of the drop front and demonstrated the influence of the drop and surface charge on θ_{RCA} . The influence of the grounded needle on the receding drop front is schematically shown in 3.12b.

After receding of the drop front of the 1st measurement cycle, the surface is charged. The remaining surface charges can interact with the advancing drop front of the 2nd and 3rd measurement cycle, respectively. Therefore the θ_{ACA} of the 2nd and 3rd cycle of the PFOTS coated quartz glass in Figure 3.11a and b differ from the θ_{ACA} of the 1st cycle and did not reached a constant value. The influence of surface charge on the θ_{ACA} is shown schematically in Figure 3.12c. To show that the difference of θ_{ACA} of the 2nd and 3rd cycle is the result of the surface charge, an IAB was running during the measurement to neutralize the surface. The measurement θ of the PFOTS coated quartz glass with IAB is summarized in Figure 3.11c. The influence of the IAB on the θ measurement is schematically shown in Figure 3.12d. The measurement shows that the θ_{ACA} of all three cycles were in the same order of magnitude. However it was observed that the drop shape was fluttered by the use of the IAB. The fluttering of the drop shape lead to a scattering of the θ_{ACA} . Furthermore the fluttering of the drop shape meant that the θ_{RCA} did not reach a constant value.

The measurement of θ of the PFOMS coated quartz glass is summarized in Figure 3.11d. In contrast to the PFOTS surface the influence of charge on θ of the PFOMS coated quartz glass was negligibly small, which agrees with the low Q_1 of the PFOMS coated quartz glass. For the measurement with and without grounded needle the θ_{RCA} and θ_{ACA} in all three cycle reached a constant value and were in the same order of magnitude. It was observed, that the drop shape was fluttered by the use of the IAB. With regard to the θ_{ACA} , the fluttering of the drop shape lead to scattering in the θ_{ACA} . Since the θ_{ACA} in all three measurement cycles were in the same range, no IAB was used.

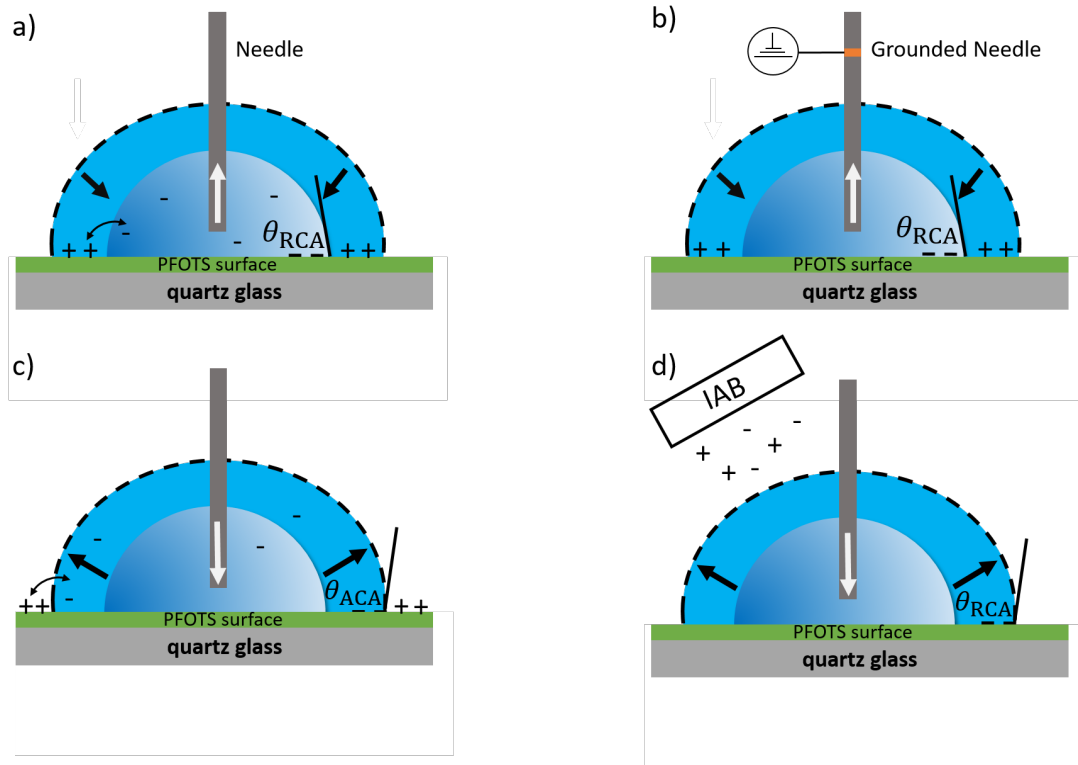


Figure 3.12: Schematic of the modified contact angle measurements on the PFOTS coated quartz glass surface. a) Standard condition. During the receding of the drop front, charges remaining behind the receding drop front. The drop and the surface are charged. b) The needle is grounded during the measurement. During the receding of the drop front, charges remaining on the surface. The drop are neutralized by the grounding needle. c) Standard condition. The advancing drop front of the charged drop can interact with the remaining charges on the surface. d) Running an ion air blower (IAB) during the measurement. The remaining surface charges and the drop charge are neutralized by the Ion Air Blower. The schematic showed how the drop and surface charge influenced the contact angle measurements.

3.6 Conclusion

From the results it was demonstrated, that the initial hypothesis that drop charge of a sliding water drop on a fluorinated surface is in the same order of magnitude applies for the PFOMS coated substrates and PTFE foil. The hypothesis did not apply to the PFOTS coated substrate. For the PFOTS coated substrates it was observed that Q_1 correlates with α of the substrates. Q_∞ correlated with $\eta_{\text{substrate}}$ of the substrate. The finding of the correlation between the drop charge and the substrate properties indicated that despite the PFOTS surface the water drop interact with the substrate.

It was concluded, that surface adaptation plays a role for the PFOTS coated substrate. From the modified contact angle measurements, it was concluded that slide electrification can affect contact angle measurements.

3.7 Experimental part

3.7.1 Substrates

Aluminosilicate glass ($25 \times 76 \times 0.330 \text{ mm}^3$, Schott AG, Germany), quartz glass slides ($25 \times 76 \times 1 \text{ mm}^3$, fused silica, Thermo Fisher Scientific, USA), sodium silicate glass ($26 \times 76 \times 1 \text{ mm}^3$, Thermo Fisher Scientific Gerhard Menzel B.V. & Co. KG, Germany), lanthanum silicate glass slides ($25 \times 76 \times 1.5 \text{ mm}^3$, Schott AG, Germany), and polytetrafluoroethylene foil (PTFE, thickness 0.05 mm, REIFF Technische Produkte GmbH, Germany) were used as substrates. The chemical composition and physical properties of the substrate are summarized in Table 3.2 and Table 3.3, respectively.

3.7.2 Coating^[1]

The substrates were rinsed with ethanol, cleaned with 2-propanol (both absolute, Honeywell, Germany) in an ultrasonic bath (30 min) and then treated with hydrochloric acid (37%, Sigma-Aldrich, Germany) in methanol (VWR chemicals, France) (ratio 1:1) for 30 min.^[95] After the treatment, the glass slides were rinsed three times with methanol and deionized and filtered water (DI water, 18 MΩ cm, obtained from an Arium Pro, Sartorius, Germany), respectively. Finally the substrates were dried with nitrogen gas. No treatment with hydrochloride acid was carried out for the lanthanum silicate glass.^[1] After the cleaning the surface was treated with an oxygen plasma (Diener electronic Femto, Plasma-Surface-Technology, Germany, $6 \text{ cm}^3 \text{ min}^{-1}$ oxygen flow rate, 300 W) for 5 min. The substrates were transferred directly to a desiccator. For CVD, 1 mL of 1H, 1H, 2H, 2H-perfluorooctyltrichlorosilane (PFOTS, 97% Alfa Aesar) or Chloro(dimethyl)(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silane (PFOMS), 97% TCI) was placed in a glass Petri dish in the middle of the desiccator. The CVD reaction was carried out at a pressure of less than 200 mbar^[87] for 1 h at room temperature. After the reaction, the samples were rinsed three times with ethanol and DI water (to remove side products^[1,87]), dried with nitrogen gas, and subsequently dried in a desiccator at less than 100 mbar for at least 2 h.

3.7.3 Scanning Force Microscopy^[1]

The surfaces were measured in tapping mode (JPK NanoWizard 4, Bruker Nano GmbH, USA) with a cantilever (type OPUS, 160-AC-NA, back side coating with reflective aluminum), 300 kHz resonance frequency, a spring constant of 26 Nm^{-1} and a nominal tip radius $< 7 \text{ nm}$. The adhesion force were measured in peak force mode, non contact mode (Dimension Icon, Bruker Nano GmbH, USA) with a cantilever (type OLTESPA, back side coating with reflective aluminum), 70 kHz resonance frequency and a spring constant of Nm^{-1} . The root mean square roughness (RMS) roughness and averaged adhesion force was calculated with the software Gwyddion 2.67. The images were leveled using a polynomial background of first degree (offset and plane). Each sample was measured in at least two different positions. Each process was repeated with three independent samples. The measurement uncertainty was calculated by the standard deviation, respectively.

3.7.4 Contact Angle Measurements^[1]

The θ_{ACA} and θ_{RCA} were measured to analyze the wetting properties of the surfaces, respectively. Measurements were performed with a goniometer (OCA35, DataPhysics Instrument GmbH, Germany). A DI water drop with a volume of $6 \mu\text{L}$ was placed with a Hamilton syringe (needle: blunt end, coated with PTFE, 51 mm length, 0.4 mm inner diameter) onto the horizontal surface. Side view videos were recorded

and analyzed with the help of software SCA20 provided by DataPhysics Instrument GmbH. After placing the drop, the drop volume was increased and decreased by 40 or 50 μL (dependent on the surface) with a rate of 0.5 $\mu\text{L s}^{-1}$ and 2 repeats. For each surface three different samples were analyzed and least at three different surface areas was measured, respectively. Measurements uncertainty were calculated by using standard deviation. The error in the contact angle hysteresis was calculated by Gaussian error propagation.

3.7.5 Modified Contact Angle Measurements

The modified contact angle measurements were performed at the goniometer (Krüss DSA100, Krüss GmbH Germany). A DI water drop with a volume of 6 μL was placed with a Hamilton syringe (needle: blunt end, coated with PTFE, 51 mm length, 0.4 mm inner diameter) onto the horizontal surface. After placing the drop, the drop volume was increased and decreased by 35 μL with a rate of 0.5 μLs^{-1} . The videos were recorded from side view with 2 frames per second. Video recording and analysis were performed by the *Advance software* (Krüss GmbH, Germany). To ground the needle a metal wire was connected the top of the needle to the potential equalization of the laboratory. The Ion air blower (Simco-Ion, Aerostat PC Ionizing Air Blower, USA) was placed below the state.

3.7.6 Drop Charge^[1]

A custom-made experimental setup described previously was used.^[32] The whole device was placed in a Faraday cage (Figure 3.1). All metallic components were grounded. The sample was placed on a tilted sample holder. The tilt angle was adjusted to 50°. With a peristaltic pump (Gilson, MINIPULS 3, Wisconsin, USA), a series of water droplets were placed on top of the surface at a rate of 30 drops per minute. The needle used had an inner diameter of 2 mm, resulting in a drop size of $45 \pm 2 \mu\text{L}$. The needle was positioned 0.5 cm above the sample surface. To discharge the drop, the sliding drop first touched a ground wire. The distance between the ground wire and the electrode was 4 cm. The probe was connected to a current amplifier (DDPCA-300, FEMTO, Germany, gain of 106 V/A with a raise time of 0.8 ms). The probe was used to measure the discharge current of the drops, respectively. The current signal was integrated over the discharging time to calculate the drop charge of each drop. The data were recorded using a multifunction box (National instruments, NI USB-6366, Hungary) connected to a computer. To neutralize the sample surface before every drop charge measurement, an ion air blower (Simco-Ion, Aerostat PC Ionizing Air Blower, USA) was used (5 min). For the evaluation, the drop charge of the first droplet (Q_1) and the the saturated drop charge (Q_∞) was used. A serie of 500 drops were measured, respectively. Every surface was messured at least three times. The standard deviation was then used to determine the measurement uncertainty. We used fresh DI water for each experiment. At the time of use, the DI water had a pH of 5.5 due to the ubiquitous uptake of CO_2 from the surrounding air. The plot of the drop charge against the drop number for all surfaces is summarized in Figure 8.1.

3.7.7 Dielectric Spectroscopy^[1]

For the measurement Novocontrol Alpha frequency analyzer consisting of a broadband dielectric converter and an active sample head was used. The substrates were measured with two stainless steel electrodes. The diameter of the electrodes was 20 mm, respectively. A broad frequency range from 10^{-2} to 10^7 Hz was applied. The measurements were performed at an ambient temperature. The applied voltage had an amplitude of 1 V. Each substrate were measured in five different areas. The average of five measurements was use to calculate the permittivity. The measurement uncertainty was determined by forming the

standard deviation of the five measurements. The dielectric spectra of the substrates are summarized in Figure 3.9.

3.7.8 Spectroscopic Ellipsometry on Silicate Glass^[1]

The measurements were done on a J.A. Woollam M-2000X spectroscopic ellipsometer. A rotating compensator mode at an angle of incidence range of 60–80° and spectral range of 250 – 1000nm was used. The angle was changed with a step of 2.5°, respectively. The obtained data was evaluated by the CompleteEASE software (J.A.Woollam, USA). A multilayer model was used. Back side reflections were canceled by scratching the substrate backside. The complex refractive indices of all substrates were calculated after their activation using a superposition of Cauchy dispersion ($n(\lambda) = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4}$) and Urbach absorption tail ($k(\lambda) = k_1 \cdot e^{k_2(\frac{1240}{\lambda} - \frac{1240}{\lambda_b})}$) functions. The PFOTS thickness values are averages obtained from six independent measurements. The measurement uncertainty was calculated using standard deviation of the six measurements, respectively.

3.7.9 Spectroscopic Ellipsometry on Silicon Wafer

The measurements were performed on an ellipsometer (alpha 2.0 SE, Quantum Design, Germany) at an angle of incidence in the range of 65–75°, with a step of 5°. For the measurements a spectral range of 400–1000 nm was used. The data were analyzed with the software CompleteEASE 6.5 (J.A. Woollam, USA). For the multilayer fit model silicon as substrate, with a native oxide SiO₂ layer and on top a Cauchy. The optical parameter of silicon were used from J.A.Woolam (Si.JAW). A thickness of 1.6 nm was measured for the SiO₂ layer. The value for the SiO₂ layer was kept constant all measurements. For the silane layer the Cauchy dispersion relation was used to parametrize the refractive index (J.A.Woolam). By fitting the measured data the thickness of the silane layer was obtained. Every sample was analyzed at three different areas. The average value of the three measurements was used to calculate the thickness of the silane layer. The measurement uncertainty was obtained from the standard deviation of the three measurements.

3.7.10 X-ray Photoelectron Spectroscopy - XPS^[1]

XPS measurements were performed with a K-Alpha+ spectrometer (ThermoFisher Scientific, East Grinstead, UK). A microfocused, monochromated Al *Kα* X-ray source at an angle of incidence of 30° and an emission angle normal to the surface was used to characterize the samples. The kinetic energy of the electrons was measured by a 180° hemispherical energy analyzer. The constant analyzer energy mode at 200 and 50 eV pass energy for the survey and high-resolution spectra was used, respectively. To limit the X-ray-induced destruction of the thin polymer films and to maximize the signal-to-noise ratio, 20 individual points were measured (4 × 8 mm²). At each spot, survey and high-resolution core-level spectra were measured. Spectral resolutions of 1.0 and 0.1 eV were used for the survey and high-resolution spectra. All showed XPS spectra are averages of the 20 individual measurements. The C1s peak of hydrocarbons at 285.0 eV was used as reference. Data evaluation and processing were done by using the Thermo Advantage software. For the fitting of the XPS spectra a Voigt profiles was used. Voigt profile was obtained by convolving Lorentzian and Gaussian functions to determine the amounts in atomic % of the individual chemical species of the sample. For the analysis the ratios of the chemical species in the high-resolution spectra were taken in the C 1s region. The analyzer transmission function, Scofield sensitivity factors, and effective attenuation lengths (EALs) for photoelectrons were used for quantification. EALs were determined using the standard TPP-2 M formalism. The BE scale was controlled by the position of the

photoelectron C-C and C-H, C-O and C(=O)-O C 1s peaks of poly(ethylene terephthalate), and Cu 2p, Ag 3d, and Au 4f peaks of metallic Cu, Ag, and Au, respectively. The BE uncertainty of the reported measurements and analysis is in the range of $\pm 0.1\text{eV}$.

4 Surface Adaptation on Grafted Diblock Copolymer Brushes

4.1 Author Contributions

4.2 Summary

In this chapter the influence of the silane initiator on the surface properties of grafted diblock copolymer brush surfaces was studied. Poly(2-hydroxyethyl methacrylate) (PHEMA) was used as hydrophilic polymer. Polystyrene (PS) was used as hydrophobic copolymer.

PHEMA-*b*-PS diblock copolymer brush surfaces were synthesized with two different silane initiators. In the first synthesis method a monochlorosilane initiator was used for the synthesis of the diblock copolymer brush surfaces. The thickness of the PHEMA and PS block was varied, respectively. For all diblock copolymer brush surfaces the advancing and receding contact angle corresponds to the wetting properties of the PS block. For all diblock copolymer brush surfaces a root mean square (rms) roughness of ≈ 1 nm was observed. Furthermore, the influence of the grafting density of the PS block on the surface properties were studied. To decrease the grafting density of the PS block in relation to the PHEMA block, the active C-Br groups of the PHEMA block were reduced by azidation, before the synthesis of the PS block. The azidation of the PHEMA layer affects the wetting properties and surface topography of the diblock copolymer brush surface. An increase of the rms surface roughness up to ≈ 2.5 nm and a change of the wetting properties were observed on the diblock copolymer brush surfaces. After azidation of the PHEMA block, the diblock copolymer surfaces adapt to water.

In the second synthesis method, a trichlorosilane initiator was used for the synthesis of the diblock copolymer brush surfaces. The trichlorosilane initiator was used to increase the density of the C-Br groups of the initiator layer. For the diblock copolymer brush surfaces synthesized with the trichlorosilane initiator, it was found that the thickness of the PHEMA and PS block influenced the surface properties. With regard to the thickness, it was observed that for a thickness of the PS block below ≈ 25 nm the diblock copolymer brush surface adapt to water. The diblock copolymer surfaces synthesized with the trichlorosilane differ in the surface topography roughness from the diblock copolymer brush surfaces synthesized with the monochlorosilane initiator. However, no correlation between the surface topography and the wetting properties was observed. It was noted that the diblock copolymer brush surfaces grafted from the trichlorosilane initiator had similar surface properties to the diblock copolymer brush surfaces treated with NaN_3 for the azidation. Therefore it was assumed that the grafting density of the PS block in relation to the grafting density to the PHEMA block is lower by using the trichlorosilane initiator for the diblock copolymer brush synthesis.

A diblock copolymer brush surface synthesized with the monochlorosilane and trichlorosilane was exposed to warm water. No influence of the warm water treatment was observed on the diblock copolymer brush surfaces grafted from the monochlorosilane initiator. However a switch from hydrophobic to hydrophilic was observed for the diblock copolymer brush surfaces grafted from the trichlorosilane initiator. After annealing the wetting properties of the diblock copolymer brush surface switched from hydrophilic to hydrophobic. The switch between the hydrophilic and hydrophobic state after warm water or toluene treatment was reversible.

From the results, I concluded that the initiator of the SI-ATRP synthesis affects the ratio between the grafting density of the PS and PHEMA block. The ratio between the grafting density of the PS and PHEMA block is an important parameter to understand the wetting behavior of grafted diblock copolymer brush surfaces. For a lower grafting density ratio between the PS and PHEMA block, the thickness of the PS block can be used as a parameter to tune the wetting behavior. For a larger grafting density ratio between the PS block and PHEMA block even a thickness of a few nanometer of PS is enough to shield the PHEMA block from contact with water.

4.3 Abstract

This chapter is partly based on my first author publication "Wetting of Surface Grafted Hydrophilic-*b*-Hydrophobic Block Copolymer Brushes", *Advanced Functional Materials*, page 2419443, 2025. The main finding reported in the publication was, that the wetting properties can be tuned by variation of the thickness of the PHEMA block or PS/PETHexMA block. Below a thickness of the hydrophobic block of ≈ 25 nm the receding contact angle was influenced by the hydrophilic block and surface adaptation was observed. The advancing contact angle showed always the wetting properties of the hydrophobic block. Furthermore the results of the publication showed, that the PHEMA-*b*-PS copolymer brush surfaces can switch between a hydrophobic and hydrophilic state by exposing the diblock copolymer brush surface to warm water or toluene. The switch between the hydrophobic and hydrophilic state was reversible. All results that are based on the publication will be cited.

From an ideal diblock copolymer brush surface, I would expect a flat surface and that a thickness of the hydrophobic block up to ≈ 5 nm is thick enough to shield the hydrophilic block from water contact. However, the diblock copolymer brush surfaces in the publication were unexpectedly rough and showed that the wetting properties were depending on the thickness of the hydrophobic block. The reason for the surface roughness was unclear. I assumed, that the surface roughness was due to the polymerization of the trichlorosilane initiator or due to the ratio between the grafting density of the PHEMA and PS blocks. The grafting density of the PHEMA block is determined by the grafting density of the initiator layer. This raises the question of the extend to which the silane initiator layer influences the surface properties of the diblock copolymer brush surfaces. Hypothesis is, that using a silane initiator with a lower grafting density should lead to lower grafting density of the PHEMA block. Therefore the ratio between the grafting density of the PHEMA block and PS should differ from the previous used diblock copolymer brush surfaces. The research goal of this chapter is to answer the research question how the initiator layer affect the wetting properties and surface topography of the PHEMA-*b*-PS diblock copolymer brush surfaces.

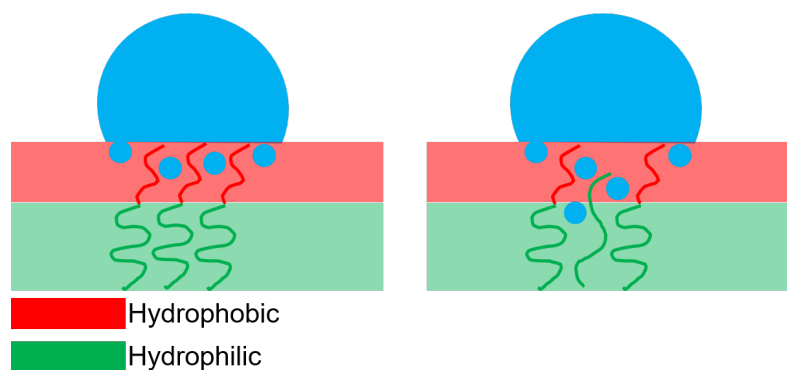


Figure 4.1: Schematic wetting of hydrophilic-*b*-hydrophobic diblock copolymer brushes. Left: Ideal diblock copolymer brush surfaces. The ratio between the grafting density of the hydrophobic and hydrophilic block is ≈ 1 . The hydrophobic block shield the hydrophilic block. Water can not penetrate through the hydrophobic block. The surface topography of the diblock copolymer brushes is flat. Right: Diblock copolymer brush surfaces, where the ratio between the grafting density of the hydrophobic and hydrophilic block is < 1 . Water can penetrate through the hydrophobic block and interact with the hydrophilic block. The surface topography of the diblock copolymer brushes is rough.

4.4 Diblock Copolymer Brushes

To study the effect of surface adaptation in contact with water, surface grafted hydrophilic-*b*-hydrophobic diblock copolymer brush surfaces were selected. On the one hand surface grafted polymer brush surfaces were used, because the polymer brushes are covalently bonded to the substrate. On the other hand because the structure of polymer brushes is well defined. The covalently grafted polymer brushes can be exposed to solvents several times without concern that the polymer brushes will be displaced, dissolved or removed from the substrate.^[22] To synthesize well define diblock copolymer surfaces the established *Surface-Initiated Atom Transfer Radical Polymerization* (SI-ATRP) technique was selected.^[58,63,64,84,96–98] In general the first step of the SI-ATRP synthesis is to graft an initiator layer to the substrate. In this chapter silicon was used as substrate, because the influence of surface and drop charge on the wetting properties can be neglected on silicon substrates.^[38] There is a large selection of surface initiators for silicon substrates such as tri- or mono halo/alkoxysilanes.^[23] I decided to use a monochlorosilane and a trichlorosilane initiator for the synthesis of the diblock copolymer brush surfaces. Reason for selecting the chlorosilane initiators was that the chlorosilanes can be grafted to the substrates in one step. For trialkoxysilanes it needs up to two reaction steps to synthesize the initiator silane layer.^[99] Furthermore, chlorosilane initiators were selected, because the synthesis of different silanes are well described.^[56,100–102] The idea to use a monochlorosilane and a trichlorosilane was to vary the grafting density of the initiator layer^[57,103,104] to affect the grafting density of the diblock copolymer brush surfaces.

For the hydrophilic bottom block PHEMA was selected. PHEMA was used, because of its hydrophilic wetting properties and because PHEMA brushes swells in contact with water. The swelling of the PHEMA brushes lead to surface adaptation.^[15,16] For the hydrophobic top block PS was used. PS was selected because of its hydrophobic wetting properties. Furthermore, the chemical structure allows PS to be distinguished spectroscopically from PHEMA by the absence of the carbonyl and C-O groups.

This chapter is split in two parts. In the first part the results of the diblock copolymer brush surfaces using a monochlorosilane initiator are shown and discussed. In the second part the results of the diblock copolymer brush surfaces using a trinochlorosilane initiator are shown and discussed.

4.4.1 PHEMA-*b*-PS Diblock Copolymer Brushes I

4.4.1.1 Synthesis of the Monochlorosilane Initiator

Monochlorosilane (3-(Bromoisobutyl)propyl)dimethylchlorosilane (Br-SAM I) was synthesized and used as initiator for the SI-ATRP synthesis. The synthesis^[56,100] is summarized in Figure 4.2. 2-Bromo-2-methylpropionyl bromide (1) was esterified with allyl alcohol (2) to allyl 2-bromo-2-methylpropionate (3). (3) was confirmed by ¹H-NMR (Figure 8.2). In a further reaction step the Br-SAM I (5) was obtained by hydrosilation of (3) with dimethylchlorosilane (4). The Br-SAM I was confirmed by ¹H-NMR (Figure 8.3).

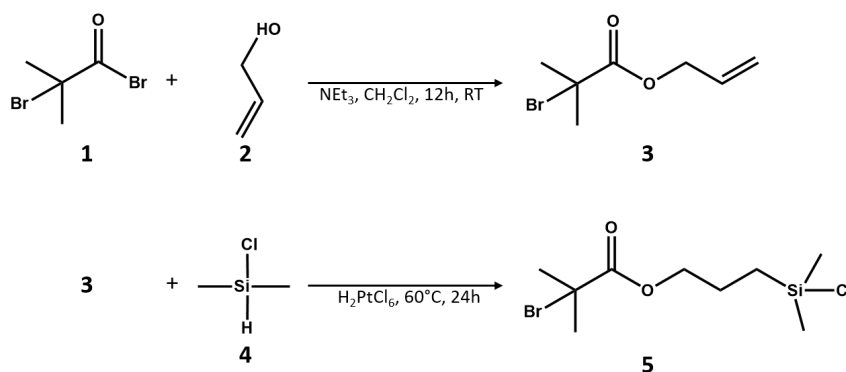


Figure 4.2: Synthesis of (3-(bromoisobutyryl)propyl)dimethylchlorosilane. Top: 2-bromo-2-methylpropionyl bromide (1) is esterified with allyl alcohol (2) to allyl 2-bromo-2-methylpropionate (3). Dichloromethane (CH_2Cl_2) is the solvent. Triethylamine (NEt_3) is an acid-capturing agent. The reaction time is 12h at room temperature (RT). Bottom: Hydrosilylation of (3) with dimethylchlorosilane (4) to (3-(bromoisobutyryl)propyl)dimethylchlorosilane. (4) is the solvent as well. Hexachloroplatinate (H_2PtCl_6) is the catalyst. The reaction is performed at 60°C . The reaction time is 24 h.

4.4.1.2 Synthesis of PHEMA-*b*-PS Diblock Copolymer Brush Surfaces I

The synthesis path of the PHEMA-*b*-PS diblock copolymer brushes is shown in Figure 4.3. In a first step the Br-SAM was grafted to the O_2 plasma activated silicon surface (Figure 4.3a). A thickness of 2.5 ± 0.5 nm was measured for the Br-SAM I layer by spectroscopic ellipsometry. From the Br-SAM I the hydrophilic PHEMA block was grafted (Figure 4.3b).

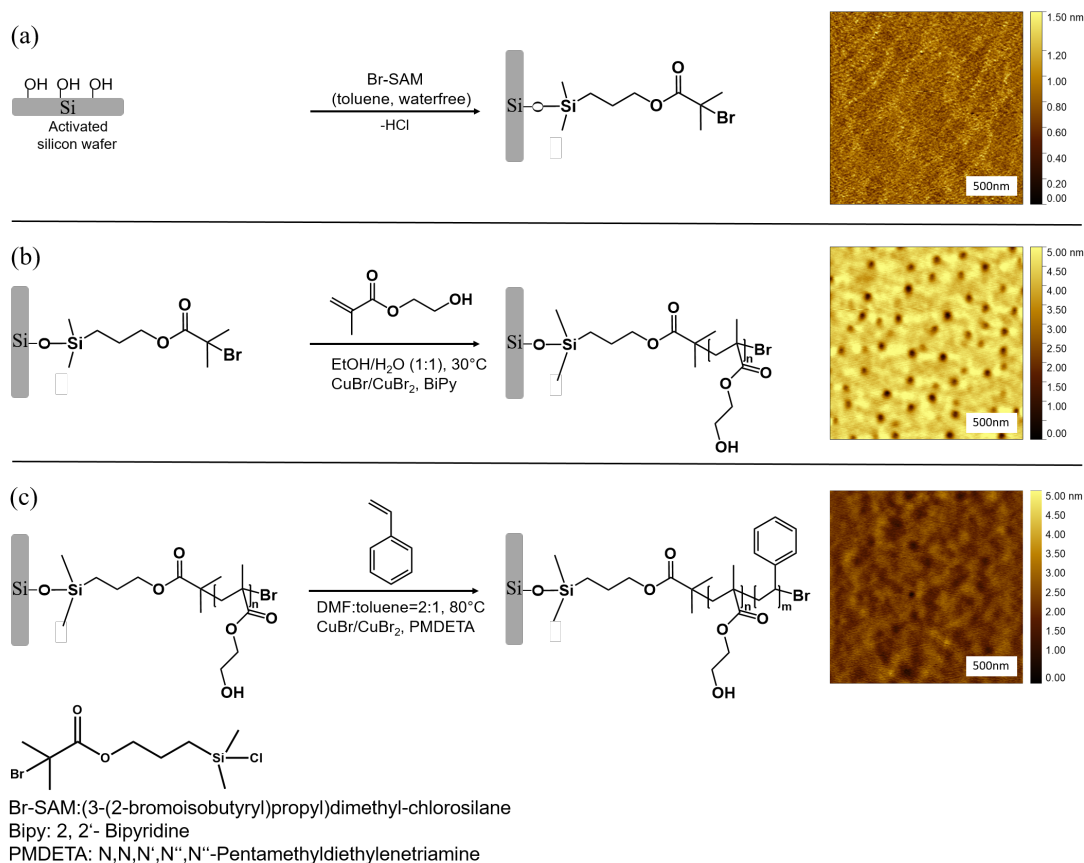


Figure 4.3: Synthesis of the PHEMA-*b*-PS diblock copolymer brush surfaces, using *surface-initiated atom transfer radical polymerization* (SI-ATRP). The synthesis consists of three steps (a-c). The surface topography is shown on the right side, respectively. The measurement of the surface topography was done by scanning force microscopy in tapping mode, with a scan size of $2 \times 2 \mu\text{m}^2$. a) The silicon wafer surface gets activated via O_2 plasma. The SI (bromoisobutyl)propyl)dimethylchlorosilane) (Br-SAM) is grafted to the activated SiO_2 surface in water free toluene. b) The PHEMA layer gets grafted from the Br-SAM surface. Solvent is a mixture of ethanol (EtOH) and water in the ratio 1:1. The polymerization is performed at 30°C . Catalyst is copper(I) bromide (CuBr). Copper(II) bromide (CuBr_2) is added to control the polymerization. Ligand is bipyridine (Bipy). c) PS is grafted from the PHEMA layer. Solvent is a mixture from dimethylformamide (DMF) and toluene in the ratio 2:1. The polymerization gets performed at 80°C . Catalyst is copper(I) bromide (CuBr). Copper(II) bromide (CuBr_2) is added to control the polymerization. Ligand is Pentamethyldiethylenetriamine (PMDETA).

To check the reinitiation of the PHEMA surface, PHEMA (α -PHEMA) surfaces were used as macro initiator for a second PHEMA block (β -PHEMA). The thickness of the α -PHEMA were 18 ± 1 nm, respectively. For both the α -PHEMA and β -PHEMA surfaces the polymerization time was 5, 15, 25 and 35 minutes, respectively. The thickness of each PHEMA surface was measured by spectroscopic ellipsometry and plotted against the polymerization time (Figure 4.4). A linear fit ($y=mx+b$) was placed through each plot. The growing rate of the α -PHEMA and β -PHEMA surface was calculated using the slope m of the linear fit, respectively. For the α -PHEMA surface a slope of $0.69 \pm 0.06 \text{ nm min}^{-1}$ was calculated. For the β -PHEMA surface a slope of $0.62 \pm 0.02 \text{ nm min}^{-1}$ was calculated. The ratio between the growing rates of the β -PHEMA block and the α -PHEMA block corresponds to ≈ 0.89 . The reinitiation of the PHEMA block was $\approx 89\%$. It was concluded, that the PHEMA block can be used as macro initiator for a further copolymer block. The PHEMA block is refereed as the bottom block in the following.

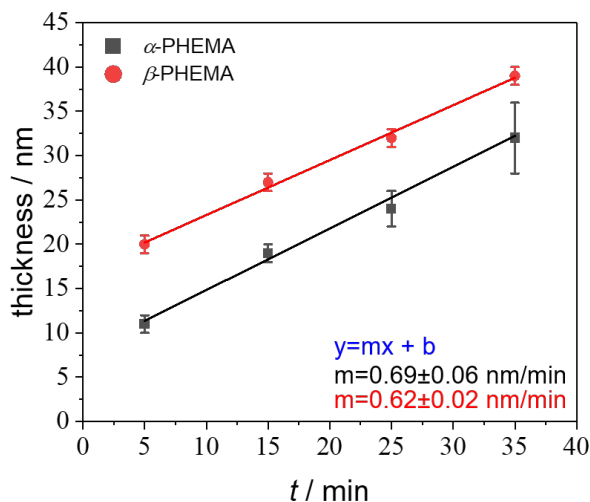


Figure 4.4: The thickness of the PHEMA surface was plotted against the polymerization time of the PHEMA. α -PHEMA described the PHEMA layer grafted from the surface initiator. β -PHEMA described the PHEMA layer grafted from the α -PHEMA surface. A linear fit ($y = mx + b$) was used to calculate the growing rate, respectively. For α -PHEMA a growing rate of 0.069 ± 0.06 nm/min was obtained. For β -PHEMA a growing rate of 0.062 ± 0.02 nm/min was obtained. The growing rate showed, that the α -PHEMA layer can be used as macro initiator for diblock copolymer brush surfaces.

In a second reaction step the PS was grafted from the PHEMA block (Figure 4.3c). The PS synthesis was carried out in a solvent mixture of toluene and dimethylformamide (DMF) in a volume ratio of 1:2. This ratio of 1:2 was used because the copper(I) bromide was well solved and it was assumed that the PHEMA brushes swell. The idea was that the swelling of the PHEMA increased the grafting density of the PS block. Figure 4.5 showed, that the growing rate of the PS block differs from batch to batch. I assumed, that the growing rate of the PS block depends on the quantity of the active C-Br groups^[97] and the thickness of the bottom block. The PS block is referred to as the top block in the following.

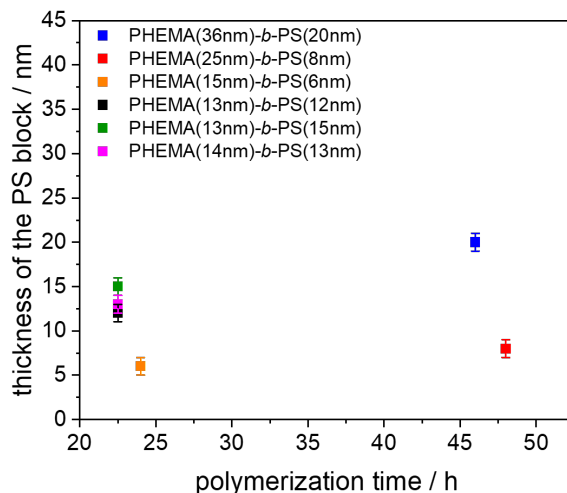


Figure 4.5: The thickness of the PS block, of the PHEMA-*b*-PS diblock copolymer brush surfaces was plotted against the polymerization time of the PS block, respectively. No correlation between the thickness of the PS block and the reaction time was observed. This showed, that the polymerization of the PS block differ from batch to batch.

4.4.1.3 Thickness of the Polymer Surface

To check if the diblock copolymer structure was present, the surfaces were analysed by spectroscopic ellipsometry and θ measurements. All measurements are summarized in the Table 4.1.

After every synthesis step the thickness of the surface was measured. By forming the difference between the total thickness of the surface and the thickness of the bottom block, the thickness of the top block was calculated. For all diblock copolymer surfaces, an increase of the thickness was observed after each polymerization step, which showed that the polymer layer was growing.

4.4.1.4 Wetting Properties

Additionally, the wetting properties of the polymer surfaces were characterized after synthesis steps by measuring the advancing (θ_{ACA}) and receding (θ_{RCA}) contact angle. For the evaluation, the θ was plotted against the measurement time. Figure 4.6a summarized the θ measurements of the Br-SAM I layer (light blue data points), the PHEMA (green data points) homopolymer surface, PS (red data points) homopolymer surface and the PHEMA(36nm)-*b*-PS(20nm) diblock copolymer surface (black data points) summarized. On the Br-SAM I surface, a constant θ_{ACA} of $\approx 80^\circ$ and constant θ_{RCA} of $\approx 60^\circ$ in all 3 cycles was measured. In the case of the PHEMA homopolymer surface the θ_{ACA} reached a constant value during increasing the drop volume, respectively. The θ_{ACA} of the 1st cycle was $\approx 65^\circ$. The θ_{ACA} of the 2nd and 3rd cycle was $\approx 60^\circ$. The lower θ_{ACA} of the 2nd and 3rd cycle is the result of surface adaptation.^[14] In the 1st cycle the advancing drop front is always in contact with a fresh surface. In contrast to the 1st cycle, the advancing drop front of the 2nd and 3rd cycle is always in contact with an already wetted surface. The contact with water leads to swelling of the PHEMA brushes and changes the surface energy.^[16] Therefore the θ_{ACA} of the 1st and the 2nd and 3rd cycle differ. The change in θ during receding of the drop front showed the surface adaptation or swelling of the PHEMA brushes clearly. Only after a contact time of ≈ 100 s did the θ_{RCA} reach a constant value of $\approx 15^\circ$ in all 3 cycles, which showed that the PHEMA block swells completely and the surface energy reached a constant value at this point. For the PS homopolymer surface no surface adaptation was observed. The θ_{ACA} was $\approx 93^\circ$ in all 3 cycles.

Also the θ_{RCA} reached a constant value of $\approx 80^\circ$ in all 3 cycles. For the PHEMA(36nm)-*b*-PS(20nm) diblock copolymer surface, θ_{ACA} of $\approx 90^\circ$ and a θ_{RCA} of $\approx 79^\circ$ was measured. Both the θ_{ACA} and θ_{RCA} correspond to the wetting properties of the top block. Analogous to the PS homopolymer surface, no surface adaptation was observed.

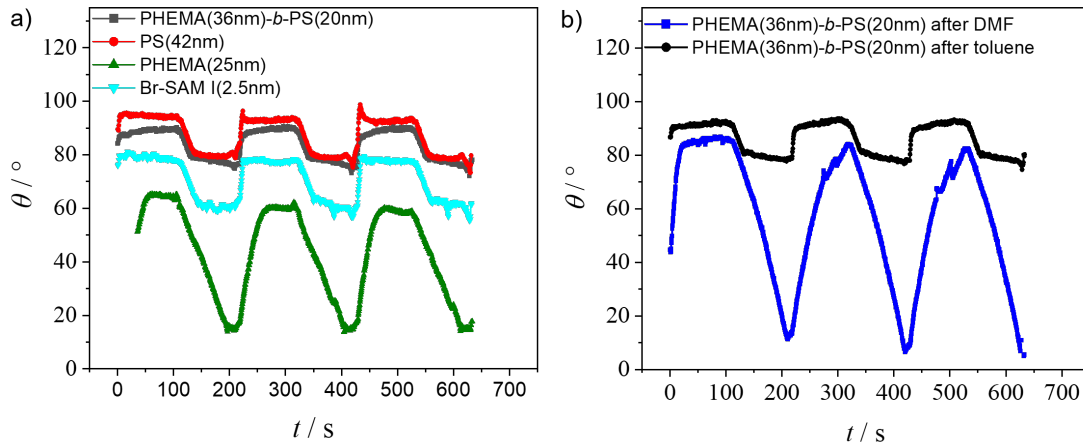


Figure 4.6: A drop with a volume of $6 \mu\text{L}$ was placed on the surface. The drop volume was increased and decreased by $30 \mu\text{L}$. During the variation of the drop volume, θ was measured. θ is plotted against the measurement time, respectively. a) PHEMA-*b*-PS diblock copolymer surface after the synthesis, PHEMA and PS homopolymer brush surface, Br-SAM surface. For the PHEMA homopolymer brush surface, surface adaptation was observed. While receding of the drop front, the θ_{RCA} is reached after ≈ 100 s. b) PHEMA-*b*-PS diblock copolymer surface after exposing to toluene and dimethylformamide (DMF). Exposing to the diblock copolymer brush surface to DMF changed the wetting behavior. After the DMF treatment, the surface adapted to water. The wetting behavior of the diblock copolymer surface is influenced by the PHEMA block. After the toluene treatment, no surface adaptation was observed. The wetting behavior of the diblock copolymer brush was comparable with the wetting properties of the PS homopolymer brush surface. b) showed that the diblock copolymer brush surface can reversibly switch the wetting behavior from hydrophobic to hydrophilic.

For all diblock copolymer surfaces a change from hydrophobic (Br-SAM I surface) to hydrophilic wetting properties were observed after the PHEMA synthesis. Furthermore a change from hydrophilic to hydrophobic wetting properties were observed after the PS synthesis, respectively. The change of the wetting properties and the increase of the surface thickness after each polymerization step indicated that a diblock copolymer structure was present.

From the results in Table 4.1, it was noted that the θ_{ACA} and θ_{RCA} of all diblock copolymer surfaces corresponds to the wetting properties of the top block. Furthermore, the results in Table 4.1 showed, that the thickness of the bottom or top block did not affect the wetting properties of the diblock copolymer brush surfaces. From the results, it was concluded that the thickness and grafting density of the top block was sufficient to shield the bottom block from water contact or water penetration. Therefore no surface adaptation on the diblock copolymer surfaces were observed.

Table 4.1: Summary of the surface characterization. d is the thickness of the PHEMA and PS block, respectively. The advancing contact angle θ_{ACA} , receding contact angle θ_{RCA} and contact angle hysteresis (CAH). The root mean square roughness (rms). The rms roughness was calculated from the surface topography. The surface topography was measured with scanning force microscopy in tapping mode, with a scan size of $2 \times 2 \mu\text{m}^2$. The azidation time described the exposition time of the PHEMA layer, after the synthesis, with sodium azide (NaN_3) in dimethylformamide. The measurements uncertainty of θ_{ACA} , θ_{RCA} , d , Q_1 , Q_∞ and the *rms* roughness was calculated by the standard deviation, respectively. The measurement uncertainty of the CAH was calculated using Gaussian error propagation.

Surface	d PHEMA/nm	d PS/nm	$\theta_{ACA}/^\circ$	$\theta_{RCA}/^\circ$	CAH/ $^\circ$	rms/nm	NaN_3/h
Br-SAM	-	-	80 ± 3	60 ± 3	13 ± 2	0.2 ± 0.1	-
PHEMA	25 ± 1	-	65 ± 5	15 ± 2	50 ± 6	0.6 ± 0.1	-
PS	-	42 ± 1	93 ± 2	80 ± 2	13 ± 3	0.7 ± 0.1	-
PHEMA- <i>b</i> -PS	36 ± 1	20 ± 1	90 ± 2	79 ± 2	11 ± 3	-	-
PHEMA- <i>b</i> -PS	25 ± 1	8 ± 1	90 ± 1	79 ± 2	11 ± 2	0.7 ± 0.1	-
PHEMA- <i>b</i> -PS	15 ± 1	6 ± 1	95 ± 3	80 ± 2	15 ± 4	0.4 ± 0.1	-
PHEMA- <i>b</i> -PS	13 ± 1	12 ± 1	92 ± 2	80 ± 2	12 ± 3	0.7 ± 0.3	-
PHEMA- <i>b</i> -PS	13 ± 1	15 ± 1	89 ± 3	52 ± 2	37 ± 3	1.7 ± 0.2	1
PHEMA- <i>b</i> -PS	14 ± 1	13 ± 1	88 ± 3	52 ± 8	37 ± 8	2.8 ± 0.6	3

4.4.1.5 Surface Topography

To check how far the synthesis affected the surface topography, the diblock copolymer surfaces were characterized by scanning force microscopy (SFM). The SFM measurements were performed in tapping mode. Figure 4.7 shows the surface topography of the diblock copolymer brush surface, respectively. For all diblock copolymer surfaces a flat topography with root mean square (rms) roughness between 0-1 nm was observed. The measured rms values are summarized in Table 4.1. From the flat surfaces it was concluded, that the surface topography was not influenced by the ratio of thickness^[58] between the bottom or top block.

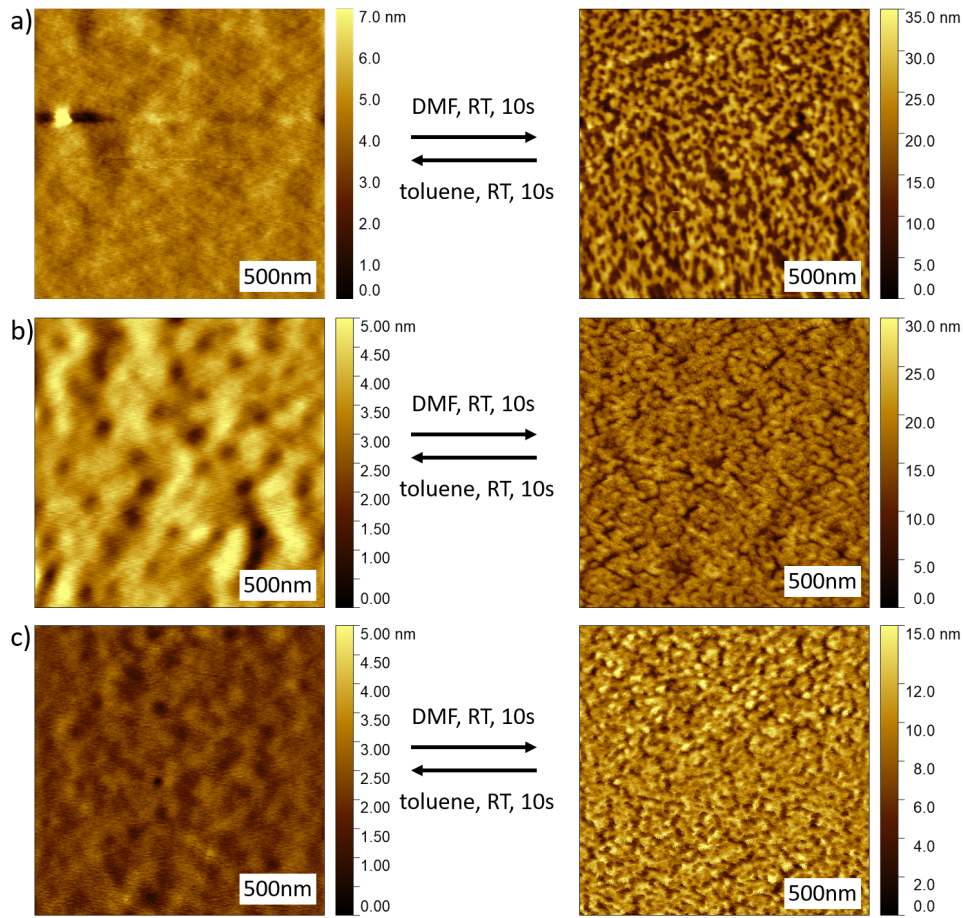


Figure 4.7: The PHEMA-*b*-PS diblock copolymer brush surface topographies were measured by scanning force microscopy measurements. The measurements were performed in tapping force mode, with a scan size of $2 \times 2 \mu\text{m}^2$. The surface topography reversibly switched, exposing the surface to dimethylformamide (DMF) and toluene for 10 s at room temperature (RT). On the left side, the surface topography after exposing to toluene for 10 s. Toluene is a good solvent for the PS and the PS brushes are stretched. A flat surface topography is observed. On the right side, the surface topography after exposing the surface to DMF. DMF is good solvent for the PHEMA block and a non so good solvent for the PS block. The diblock copolymer brushes collapse. Result of the collapse in an a change in the surface topography and an increase in the rms roughness. a) PHEMA(25nm)-*b*-PS(8nm) diblock copolymer brush surfaces. b) PHEMA(15nm)-*b*-PS(6nm) diblock copolymer brush surfaces. c) PHEMA(13nm)-*b*-PS(12nm) diblock copolymer brush surfaces. It was noted that the topographies were independent of the thickness of the PHEMA or PS block.

4.4.1.6 Solvent Effect

It has been reported that grafted diblock copolymer brushes can collapse by exploiting the solvent effect.^[15,96,105] In a good solvent polymer brushes swell, because the polymer-solvent interaction is preferred over the polymer-polymer interaction. In a poor solvent the polymer-polymer is preferred over the polymer-solvent interaction and the polymer brushes collapse and micelle formation occurs.^[106] To check how the collapse of the diblock copolymer brushes can affect the wetting properties, the diblock copolymer brush surfaces were exposed to DMF and toluene. DMF is a good solvent for PHEMA and a poor solvent for PS. Toluene is a good solvent for PS and a poor solvent for PHEMA.

The diblock copolymer surfaces were exposed to DMF for 10 seconds, dried with a stream of nitrogen and the θ_{ACA} and θ_{RCA} were measured. In a further step the diblock copolymer surfaces were exposed

to toluene for 10 seconds, rinsed with DI water and dried with a stream of nitrogen. The θ_{ACA} and θ_{RCA} were measured. The θ measurements after DMF (blue data points) and toluene (black data points) treatment of the PHEMA(36nm)-*b*-PS(20nm) diblock copolymer surface θ are shown in Figure 4.6b. After the DMF treatment the θ_{ACA} of the 1st cycle reached a constant value of $\approx 82^\circ$. It was observed that the θ_{ACA} of the 2nd and 3rd was in the range of $\approx 80^\circ$ and did not reach a constant value, which showed that surface adapt to water. Compared to the PS surface the θ_{ACA} was around 10° lower and the θ_{ACA} showed surface adaptation in the 2nd and 3rd cycle. The θ_{RCA} was in all 3 cycles in the range of $\approx 15^\circ$ and correspond to the wetting properties of the PHEMA surface. After the toluene treatment the wetting behavior of the diblock copolymer surface corresponds to the wetting properties of the top block.

From the experiments it was concluded that the collapse of the diblock copolymer brushes leads to surface adaptation. Both θ_{ACA} and the θ_{RCA} were influenced by the collapse of the diblock copolymer brushes. To check how the collapse of the diblock copolymer brushes affected the surface topography, the diblock copolymer surfaces were analyzed by SFM in tapping mode. The SFM analysis of the PHEMA(36nm)-*b*-PS(20nm) diblock copolymer surface is summarized in Figure 4.7a. After the DMF treatment the rms roughness increased from ≈ 0.5 nm to ≈ 5.6 nm. After the toluene treatment the rms roughness decreased from ≈ 5.6 nm to ≈ 0.5 nm. The switch of the surface topography after DMF and toluene treatment was reversible. With regard to the wetting properties, previous work has shown that a change of the surface roughness on nano scale^[107] or molecular scale^[91] can influence the θ_{ACA} and θ_{RCA} . But since the θ_{RCA} here clearly corresponds to the θ_{RCA} of the PHEMA surface, I assumed that the change in the wetting properties is based on the change in the surface chemistry by the collapse of the diblock copolymer brushes.^[96] The influence of the DMF and toluene treatment on the wetting properties was observed for all diblock copolymer surfaces, From Figure 4.7 it was concluded, that the solvent effect of DMF and toluene on the surface topography was independent of the thickness of the bottom or top block.

4.4.1.7 Grafting Density of the Top Block

Based on the results of the surface adaptation of the collapsed diblock copolymer brush surfaces, the idea came up to reduce the density of the top block. It was assumed that, a decreasing of the grafting density of the top block result in water penetration through the top block and leads to surface adaptation. The reduction of the grafting density of the top was done by azidation^[77] of the PHEMA-Br end groups ($\text{PHEMA-Br} + \text{NaN}_3 \longrightarrow \text{PHEMA-N}_3 + \text{NaBr}$). A fresh batch of PHEMA surfaces were synthesized. One PHEMA surface was used without NaN_3 treatment. One PHEMA surface was treated with a NaN_3 /DMF solution for 1 h and one PHEMA surface was treated with a NaN_3 /DMF solution for 3 h. PS was grafted from the PHEMA surface, respectively. The surfaces were characterized by contact angle, SFM and spectroscopic ellipsometry measurements. The results are summarized in Table 4.1 and Figure 4.8.

From the SFM analysis in Figure 4.8, it was noted that the surface topography was influenced by the azidation. For the non NaN_3 treated diblock copolymer brush surface a flat surface with a rms roughness of ≈ 1 nm was observed. For the 1 h NaN_3 treated diblock copolymer surface a rms roughness of ≈ 1.8 nm was measured. Here a dimple-like structure surface topography^[108] was observed. For the 3 h NaN_3 treated diblock copolymer surface a rms roughness of ≈ 2.8 nm was measured. Here the surface topography showed a mixed ripple and dimple like structure. From the SFM characterization, it was concluded that the grafting density of the top block influenced the surface topography of the diblock copolymer brush surfaces.

The contact angle of the three diblock copolymer surfaces were measured and θ was plotted against the measurement time, respectively. The results are summarized in Figure 4.8. The wetting properties of the

non NaN_3 treated diblock copolymer surface (black data points) corresponds to the wetting properties of the top block. For the 1 h NaN_3 treated diblock copolymer brush surface the θ_{ACA} of the 1st cycle reached a value of $\approx 90^\circ$. The θ_{ACA} of the 2nd and 3rd was $\approx 87^\circ$. The θ_{ACA} of the 2nd and 3rd cycle were lower than the θ_{ACA} of the top block and showed that the surface adapt to water (orange plot in Figure 4.8). The θ_{RCA} was in the range of $\approx 50^\circ$ in all cycles. This value does not correspond to the θ_{RCA} of the bottom or top block. For the 3 h NaN_3 treated diblock copolymer surface a θ_{ACA} of $\approx 87^\circ$ was observed in all three cycles. For the θ_{RCA} a value of $\approx 45^\circ$ was observed in all cycles. This value corresponds either to the θ_{RCA} of the bottom nor to the θ_{RCA} of the top block. The change of the θ during the receding of the drop front showed the swelling of the bottom block. The swelling of the bottom block leads to surface adaptation. However, the θ_{RCA} did not reach the θ_{RCA} of the bottom block. I assumed, that the θ_{RCA} showed mixed wetting character of the top and bottom block. The receding drop front was in contact with the top and the bottom block.

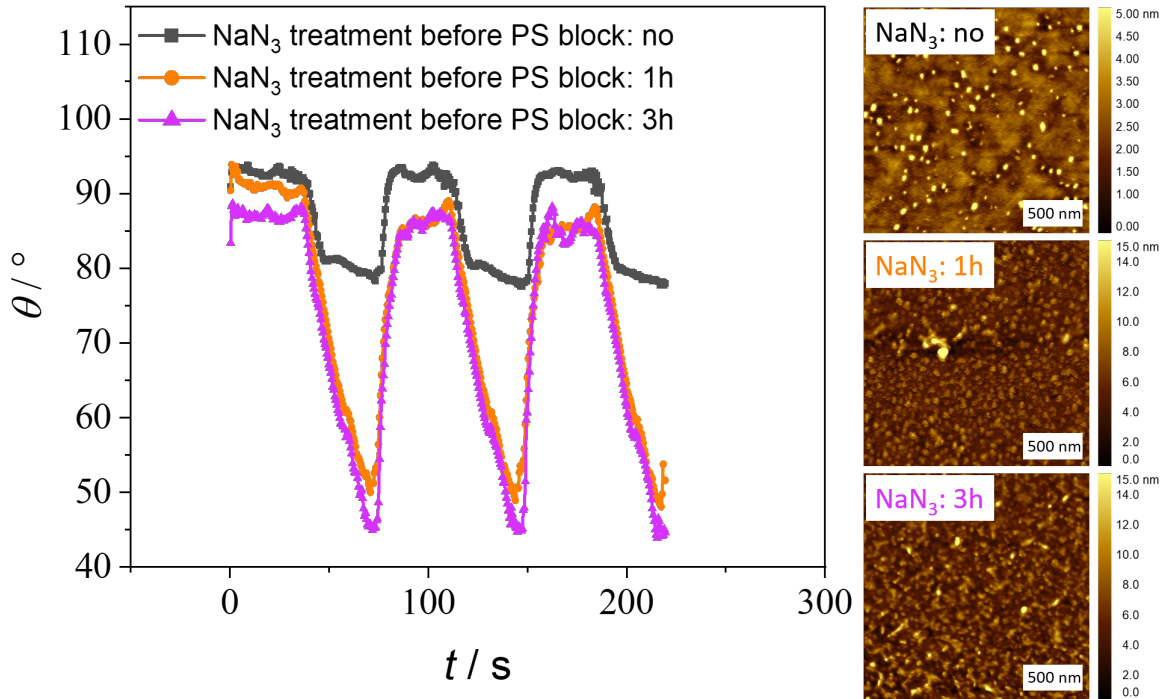


Figure 4.8: A drop with a volume of $6 \mu\text{L}$ was deposited on different PHEMA-*b*-PS diblock copolymer surfaces. The drop volume was increased and decreased by $30 \mu\text{L}$, respectively. While the variation of the drop volume, θ was measured. On the left side is the θ plotted against the measurement time, respectively. On the right side are the surface topography of the corresponding diblock copolymer brush surface summarized. The measurements were performed in tapping mode, with a scan size of $2 \times 2 \mu\text{m}^2$. The difference between the three diblock copolymer brush surfaces was the azidation time of the PHEMA block. For the azidation, the surfaces were exposed to sodium azide (NaN_3) dimethylformamide solution. Black: PHEMA(13nm)-*b*-PS(12nm), rms roughness: $0.7 \pm 0.3 \text{ nm}$. Orange: PHEMA(13nm)-*b*-PS(15nm), rms roughness: $1.7 \pm 0.2 \text{ nm}$. Magenta: PHEMA(14nm)-*b*-PS(13nm), rms roughness: $2.8 \pm 0.6 \text{ nm}$. It was observed that the rms roughness increased with increasing azidation time. The azidation of the PHEMA layer, results in surface adaptation of the PHEMA-*b*-PS diblock copolymer brush surfaces.

Based on the results of the NaN_3 treatment, the question arose, if the contact angles of the NaN_3 treated diblock copolymer surface switch to the θ_{ACA} or θ_{RCA} of the bottom block by increasing the contact

time to water. The 1 h NaN_3 treated diblock copolymer surface were exposed to water at different temperatures. The results are summarized in Figure 4.9. After exposing the surface to water at room temperature (RT), the θ_{ACA} was $\approx 90^\circ$ and corresponds to the θ_{ACA} of the top block. The θ_{RCA} was $\approx 55^\circ$. This value did not correspond to the θ_{RCA} of the bottom or top block. Both, the θ_{ACA} and the θ_{RCA} corresponds to the contact angles after the synthesis (Figure 4.8). After exposing the surface to water at 40° , the θ_{ACA} was $\approx 80^\circ$ and the θ_{RCA} was $\approx 45^\circ$. It was noted, that the θ_{ACA} decreased from the $\approx 90^\circ$ to $\approx 80^\circ$ after warm water treatment. The θ_{RCA} decreased from the $\approx 55^\circ$ to $\approx 45^\circ$ after warm water (40°C) treatment. From the experiment it was concluded, that exposing the NaN_3 treated diblock copolymer surface to water at 40°C affect the wetting properties of the diblock copolymer brush surface.

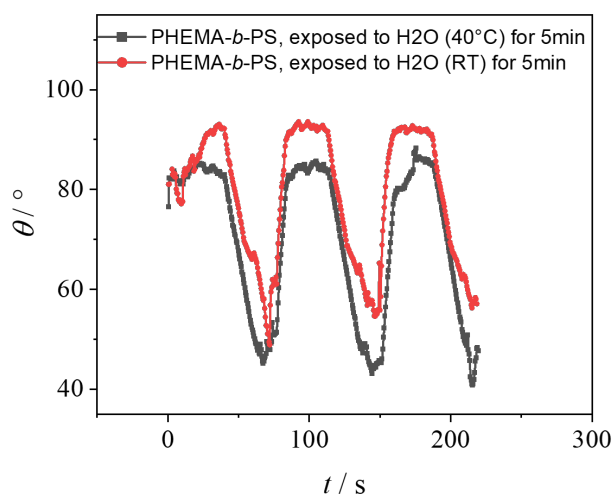


Figure 4.9: The contact angle is plotted against the measurement time. A water drop of $6\mu\text{L}$ was placed on the surface. The drop volume was increased and decreased by $30\mu\text{L}$ and the contact angle was recorded. The 1 h NaN_3 treated PHEMA(13nm)-*b*-PS(15nm) diblock copolymer brush surface was exposed to water at different temperature. After exposing the surface to water, the surface was dried with a stream of nitrogen and the contact angle was measured. After exposing the surface to water at room temperature (RT), the θ_{ACA} was $\approx 90^\circ$ and the θ_{RCA} was $\approx 55^\circ$ (red plot in Figure 4.9). Both, the θ_{ACA} and the θ_{RCA} corresponds to the contact angles after the synthesis. After exposing the surface to water at 40° , the θ_{ACA} was $\approx 80^\circ$ and the θ_{RCA} was $\approx 45^\circ$. It was noted, that the θ_{ACA} decreased from the $\approx 90^\circ$ to $\approx 80^\circ$ after warm water treatment. The θ_{RCA} decreased from the $\approx 55^\circ$ to $\approx 45^\circ$ after warm water treatment. It was concluded that warm water treatment affect the

Conclusion: PHEMA-*b*-PS Diblock Copolymer Brushes I

In this section the synthesis of PHEMA-*b*-PS diblock copolymer surfaces using a monochlorosilane initiator was successfully introduced. For a diblock copolymer brush surface a top block thickness of $\approx 5\text{ nm}$ was enough to shield the bottom block from water contact. The wetting properties of the diblock copolymer brush surfaces correspond to the wetting properties of the top block homopolymer. However, decreasing the grafting density of the top block in relation to the grafting density of the bottom block lead to surface adaptation of diblock copolymer brush surface in contact with water. Even at a thickness of the top block of $\approx 13\text{ nm}$ the bottom block was not shielded.

I concluded from the experiments, that by decreasing the grafting density of the top block, water can penetrate through the top layer and interact with the bottom block. The interaction between water and

the bottom block lead to swelling of the bottom block. From the SFM measurements it was concluded that the surface topography is affected by the ratio between the grafting density of the top block and bottom block. By decreasing the ratio between the grafting density of the top block and bottom block the rms roughness of the surface topography increased and a dimple-like structure surface topography was observed. The conclusion is schematically shown in Figure 4.10.

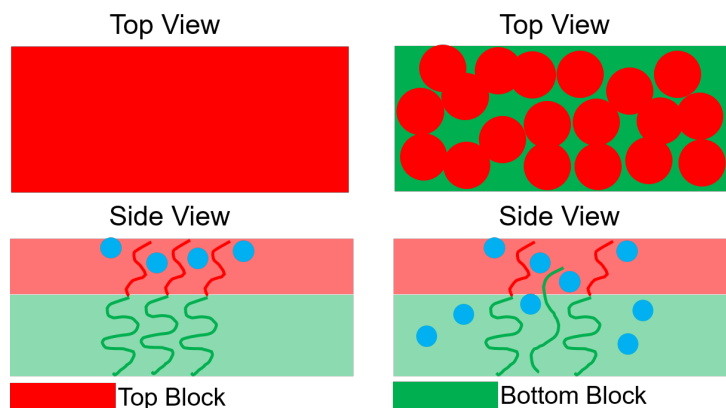


Figure 4.10: Left: Schematically top and side view of the PHEMA-*b*-PS diblock copolymer brush surfaces, where the ratio of the grafting density between the hydrophobic top block (PS) and the hydrophilic bottom block (PHEMA) is ≈ 1 . The top view shows a flat surface topography. The side view shows that water can not penetrate through to the top block. Right: Schematically top and side view of the PHEMA-*b*-PS diblock copolymer brush surfaces, where the ratio of the grafting density between the hydrophobic top block (PS) and the hydrophilic bottom block (PHEMA) block is < 1 . The grafting density of the top block is lower. The top view shows a rough surface topography. The side view shows that water can penetrate through to the top block and interact with the PHEMA block.

4.4.2 PHEMA-*b*-PS diblock Copolymer Brushes II

4.4.2.1 Synthesis of PHEMA-*b*-PS Diblock Copolymer Brush Surfaces II

In the previous section it was shown that the ratio between the grafting density of the top block and bottom block is an important parameter to tune the wetting properties of the PHEMA-*b*-PS diblock copolymer brush surfaces. The idea came up to increase the grafting density of the bottom block by the use of a trichlorosilane initiator. I assumed, that increasing the grafting density of the bottom block lead to a lower ratio of the grafting density between the top block and the bottom block. It was shown that the packing density of trichlorosilanes is larger than the packing density of monochlorosilanes.^[55,57,103,104] Furthermore it was shown that the surface ordering increase with the length of the carbon chain.^[18,103] I assumed that a higher surface ordering and packing density of the initiator layer results in a larger grafting density of the bottom block and can tune the ratio of the grafting density between the top and bottom block. Therefore the (11-(2-Bromo-2-methyl)propionysyloxy)undecyltrichlorosilane (Br-SAM-II) was used as initiator.^[2]

The synthesis path of the diblock copolymer brush surfaces are shown in Figure 4.11.

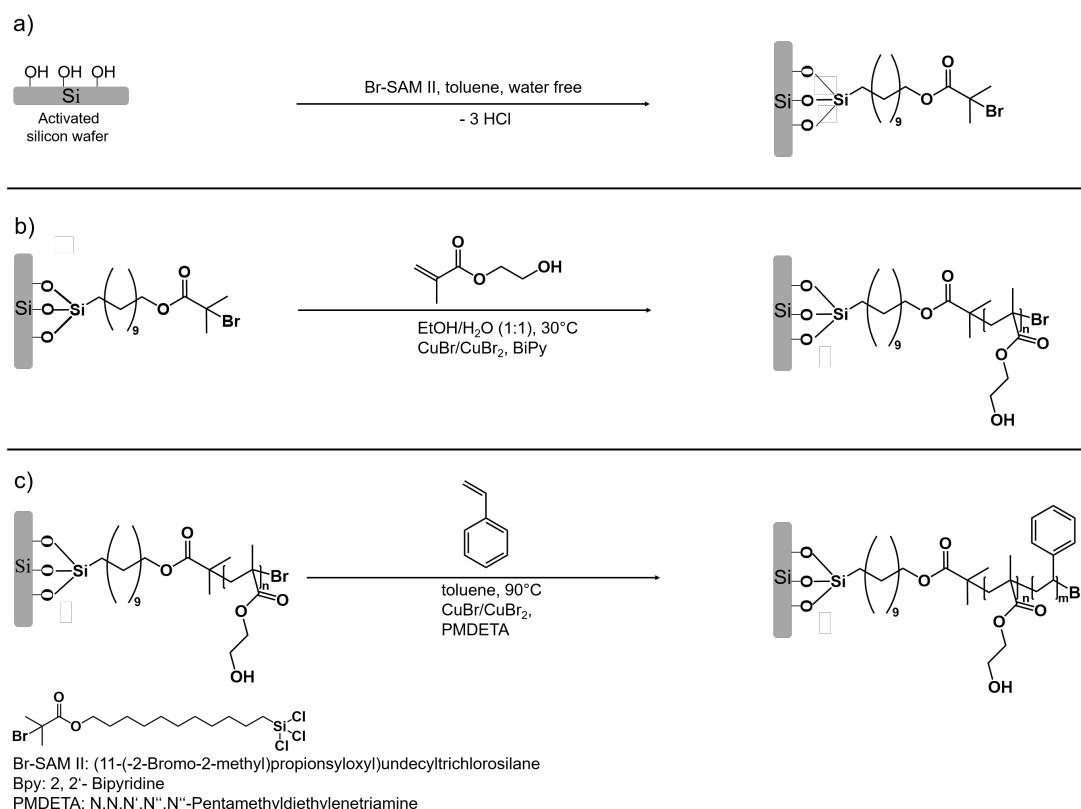


Figure 4.11: The synthesis of the PHEMA-*b*-PS diblock copolymer brush surfaces, using *surface-initiated atom transfer radical polymerization* (SI-ATRP). PHEMA: Poly(2-hydroxyethyl methacrylate). PS: Polystyrene. The synthesis consists of three steps (a-c). a) The silicon wafer surface gets activated via O₂ plasma. The SI (11-(2-bromo-2-methyl)propionsyloxy)undecyltrichlorosilane (Br-SAM II) is grafted to the activated SiO₂ surface in water free toluene. b) The PHEMA layer gets grafted from the Br-SAM surface. Solvent is a mixture of ethanol (EtOH) and water in the ratio 1:1. The polymerization is performed at 30°C. Catalyst is copper(I) bromide (CuBr). Copper(II) bromide (CuBr₂) is added to control the polymerization. Ligand is bipyridine (Bipy). c) PS is grafted from the PHEMA layer. Solvent is toluene. The polymerization gets performed at 90°C. Catalyst is copper(I) bromide (CuBr). Copper(II) bromide (CuBr₂) is added to control the polymerization. Ligand is pentamethyldiethylenetriamine (PMDETA).

In a first reaction step the Br-SAM II was grafted to the O₂ activated silicon substrate (Figure 4.11a). From the Br-SAM the hydrophilic PHEMA block was grafted (Figure 4.11b). To check the reinitiation of the PHEMA surface, PHEMA (α -PHEMA) surfaces were used as macro initiator for a second PHEMA block (β -PHEMA).^[2] The thickness of the α -PHEMA were 33 ± 1 nm, respectively. For both the α -PHEMA and β -PHEMA surfaces the polymerization time was 5, 15, 30 and 45 minutes, respectively. The thickness of each PHEMA surface was measured by spectroscopic ellipsometry and plotted against the polymerization time. The results are summarized in Figure 4.12. A linear fit ($y=mx+b$) was used to calculate the growing rate of the α -PHEMA and β -PHEMA surface. For the α -PHEMA surface a slope of 1.24 ± 0.06 nm min⁻¹ was calculated. Compared to the growing rate of 0.69 ± 0.06 nm min⁻¹ using the monochlorosilane (Figure 4.4), it was noted that the growing rate using the trichlorosilane initiator was $\approx 179\%$ faster. The higher growing rate corresponds to a higher density/packing of the initiator layer.^[109] For the β -PHEMA surface a slope of 0.99 ± 0.01 nm min⁻¹ was calculated. The ratio between the growing rates of the β -PHEMA block and the α -PHEMA block corresponds to ≈ 0.79 . It was concluded that the reinitiation of the PHEMA block was $\approx 79\%$ and that the PHEMA block

can be used as macro initiator for a diblock copolymer brush surface. From the higher growing rate of the PHEMA block using the trichlorosilane initiator it was concluded that the grafting density of the PHEMA block was higher than the grafting density of the PHEMA block using the monochlorosilane initiator. In the following the PHEMA block will be referred to bottom block.

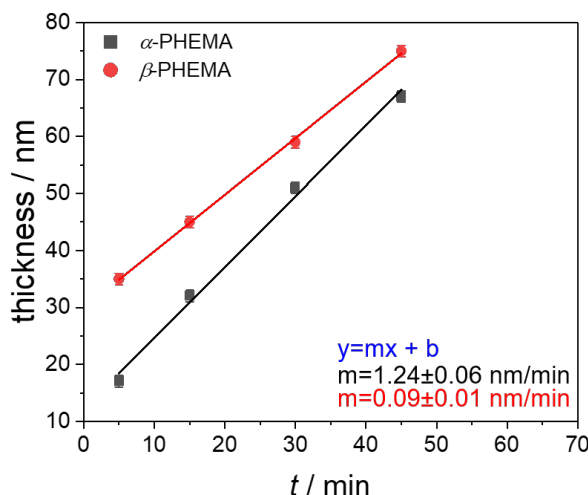


Figure 4.12: The thickness of the PHEMA surface was plotted against the polymerization time of the PHEMA. α -PHEMA described the PHEMA layer grafted from the surface initiator. β -PHEMA described the PHEMA layer grafted from the α -PHEMA surface. A linear fit ($y = mx + b$) was placed thorough the data point, to calculate the growing rate. For α -PHEMA a growing rate of 1.24 ± 0.06 nm/min was obtained. For β -PHEMA a growing rate of 0.99 ± 0.01 nm/min was obtained. The growing rate showed, that the α -PHEMA layer can be used as macro initiator for diblock copolymer brush surfaces. The figure was taken with changes from the SI of my first author publication.^[2]

From the bottom block the PS block was grafted. In contrast to the previous section, the PS polymerization was carried out in toluene.^[2] The idea of using toluene without DMF was to decrease the polarity of the solvent to reduce the swelling of the PHEMA brushes. It was assumed that by reducing the swelling of the PHEMA brushes the grafting density of the PS block decreased. The PS block will be referred to as the top block in the following. Different diblock copolymer brush surfaces were synthesized. The thickness of the top and bottom block was varied. Figure 4.13 showed that the growing rate of the top block differ from batch to batch. On the one hand it was assumed that the differ in the growing rate depend on the quantity of the active C-Br-groups of the bottom block^[97] and the thickness of the bottom block. On the other hand it was observed that the solubility of CuBr in toluene was low. Therefore, it was assumed that the quantity of dissolved CuBr differ from batch to batch and influenced the growing rate.

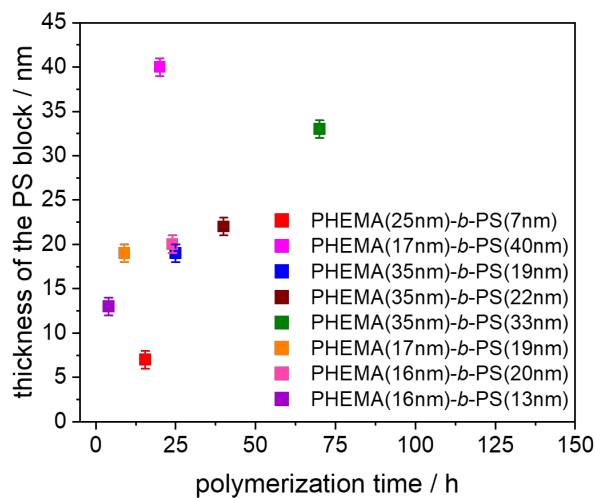


Figure 4.13: The thickness of the PS block, of the PHEMA-*b*-PS diblock copolymer brush surfaces was plotted against the polymerization time of PS, respectively. No correlation between the thickness of the PS block and the reaction time was observed. This showed, that the polymerization of the PS block differ from batch to batch. The figure was taken with changes from the SI of my first author publication.

4.4.2.2 Thickness of the Polymer Surface

The diblock copolymer brush surfaces were analyzed by spectroscopic ellipsometry, contact angle measurements, SFM and XPS measurements.^[2] Results are summarized in the Table 4.2.

Analogous to the previous section the thickness of the bottom block and top block was measured by spectroscopic ellipsometry. After every polymerization step, an increase in the surface thickness was observed. The increasing thickness of the surface showed that the polymer blocks were growing.

Table 4.2: Summary of the surface characterization. d is the thickness of the PHEMA and PS block, respectively. d was measured by spectroscopic ellipsometry. The advancing contact angle θ_{ACA} , receding contact angle θ_{RCA} and contact angle hysteresis (CAH). The root mean square roughness (rms). The rms roughness was calculated from the surface topography. the surface topography was measured with scanning force microscopy in tapping mode, with a scan size of $2 \times 2 \mu\text{m}^2$. The azidation time described the exposition time of the PHEMA layer, after the synthesis, with sodium azide (NaN_3) in dimethylformamide. The measurements uncertainty of θ_{ACA} , θ_{RCA} , d , Q_1 , Q_∞ and the *rms* roughness was calculated by the standard deviation, respectively. The measurement uncertainty of the CAH was calculated using Gaussian error propagation. All values, except the values of the Br-SAM II surfaces, were taken from my first author publication.^[2]

Surface	d PHEMA/nm	d PS/nm	$\theta_{ACA}/^\circ$	$\theta_{RCA}/^\circ$	CAH/ $^\circ$	rms/nm
Br-SAM II	-	-	90 ± 2	80 ± 2	10 ± 3	-
PHEMA ^[2]	16 ± 1	-	65 ± 5	15 ± 5	50 ± 7	-
PS ^[2]	-	19 ± 1	96 ± 2	77 ± 2	19 ± 3	-
PHEMA- <i>b</i> -PS ^[2]	25 ± 1	7 ± 1	89 ± 2	21 ± 1	68 ± 2	0.8 ± 0.3
PHEMA- <i>b</i> -PS ^[2]	16 ± 1	13 ± 1	93 ± 2	21 ± 1	72 ± 2	
PHEMA- <i>b</i> -PS ^[2]	17 ± 1	19 ± 1	93 ± 2	21 ± 3	72 ± 4	5 ± 2
PHEMA- <i>b</i> -PS ^[2]	15 ± 1	20 ± 1	92 ± 3	50 ± 4	42 ± 5	-
PHEMA- <i>b</i> -PS ^[2]	17 ± 1	40 ± 1	98 ± 1	77 ± 1	21 ± 1	7 ± 2
PHEMA- <i>b</i> -PS ^[2]	35 ± 1	19 ± 1	92 ± 3	43 ± 10	49 ± 10	3.7 ± 0.1
PHEMA- <i>b</i> -PS ^[2]	35 ± 1	22 ± 1	93 ± 1	76 ± 5	17 ± 5	-
PHEMA- <i>b</i> -PS ^[2]	35 ± 1	33 ± 1	92 ± 2	74 ± 4	18 ± 5	-

4.4.2.3 Wetting Properties

The diblock copolymer brush surfaces were characterized by the contact angle measurements. In Figure 4.14, θ of the homopolymer brush surfaces is plotted against the measuring time, respectively. The wetting behavior of the PHEMA and PS homopolymer brush surfaces were similar to the homopolymer brush surfaces discussed in the previous section. For the PHEMA homopolymer brush surface, surface adaptation was observed. No surface adaptation was observed for the PS homopolymer brush surface. No difference in the wetting properties of the homopolymer brush surfaces using the monochloro silane or trichloro silane initiator were observed.

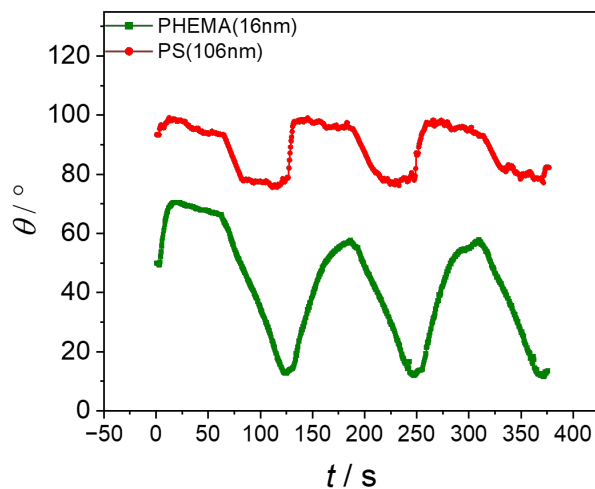


Figure 4.14: The contact angle θ is plotted against the measurement time. A water drop of $6\mu\text{L}$ was deposited on the surface. The drop volume was increased and decreased by $30\mu\text{L}$ and the contact angle was recorded. For the PS homopolymer brush surface, no surface adaptation was observed. For the PHEMA homopolymer brush surfaces surface adaptation was observed. No difference in the wetting behavior between the homopolymer brush surfaces, grafted from the monochlorosilane or trihalorosilane initiator was observed.

The wetting behavior of the diblock copolymer brush surfaces differ from the diblock copolymer brush surfaces presented in the previous section. For a better overview the θ_{ACA} and θ_{RCA} were plotted against the thickness of the top block, respectively.^[2] In Figure 4.15 black data points are used for the diblock copolymer brush surfaces with a thickness of the bottom block between 16 and 25 nm. Blue data points are used for the diblock copolymer brush surfaces with a thickness of the bottom block of ≈ 35 nm.

It was observed that the θ_{ACA} of all diblock copolymer brush surfaces were in the range of the θ_{ACA} of the top block (Figure 4.15a). This results are consistent with the wetting behavior of the diblock copolymer brush surfaces in the previous section, using a monochlorosilane initiator (Table 4.1). However, it was noted that only the θ_{ACA} of the PHEMA(17nm)-*b*-PS(40nm) surface was larger than the θ_{ACA} of the top block. It was assumed that the larger θ_{ACA} results from a larger rms roughness on nano scale^[107] (Table 4.2). The influence of the rms roughness on the wetting properties will be discussed later in this section in more detail. It was noted that the θ_{RCA} depends on the thickness of the top block. For a thickness of the top block between ≈ 7 and ≈ 19 nm the θ_{RCA} corresponds to the θ_{RCA} of the bottom block. For a thickness of the top block of ≈ 20 nm, the θ_{RCA} either corresponds to the θ_{RCA} of the bottom or top block. For a thickness of the top block above ≈ 25 nm the θ_{RCA} corresponds to the θ_{RCA} of the top block. For a thickness of the top block below ≈ 25 nm the diblock copolymer brush surfaces adapt to water. Figure 4.15c show schematically how the swelling of the PHEMA brushes lead to surface adaptation. This dependence of the θ_{RCA} on the thickness of the top block differs from the wetting properties of the diblock copolymer brush surfaces showed in the previous section (Table 4.1). In the previous section, it was shown that the wetting properties were independent of the thickness of the top block.

From the correlation between the θ_{RCA} the thickness of the top block it was concluded that the ratio between the grafting density of the top block and bottom is lower using the trichlorosilane initiator. Water can interact with the bottom block and the diblock copolymer brush surfaces adapt to water by swelling of the bottom block. The influence of the thickness on the wetting properties confirmed the initial idea to tune the wetting properties of the diblock copolymer brush surfaces by using the trichlorosilane initiator and another solvent for the synthesis of the top block.

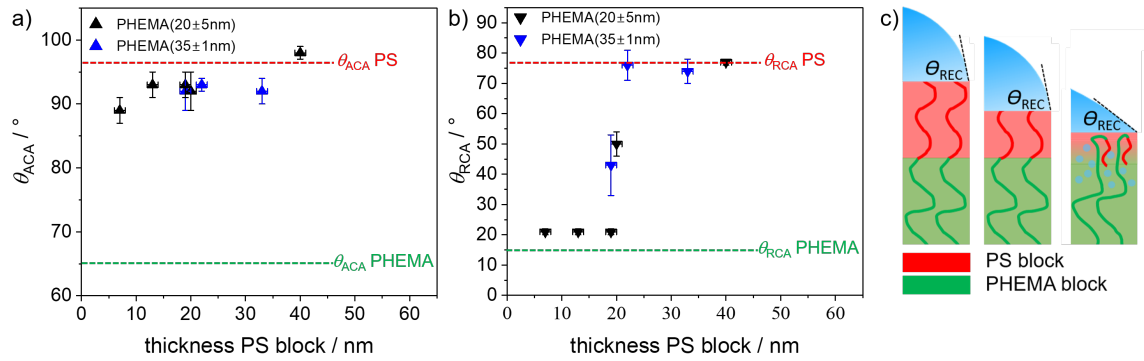


Figure 4.15: The wetting behavior of the PHEMA-*b*-PS diblock copolymer brush surfaces. The thickness of the PHEMA block was varied (black and blue). a) The advancing contact angle θ_{ACA} is plotted against the thickness of the PS block. The θ_{ACA} of the PHEMA homopolymer brush surfaces is showed by the green dashed line. The θ_{ACA} of the PS homopolymer brush surfaces is showed by the red dashed line. It was noted, that the θ_{ACA} of all surfaces corresponds to the θ_{ACA} of the PS surface. b) The receding contact angle θ_{RCA} is plotted against the thickness of the PS block. The θ_{RCA} of the PHEMA homopolymer brush surfaces is showed by the green dashed line. The θ_{RCA} of the PS homopolymer brush surfaces is showed by the red dashed line. It was noted, that the θ_{RCA} correlated with the thickness of the PS block. For a thickness below ≈ 20 nm, the θ_{RCA} corresponds to the θ_{RCA} of the PHEMA block. With a PS thickness of ≈ 20 nm, the θ_{RCA} showed mixed wetting behavior of both blocks. Above a thickness of ≈ 25 nm, the θ_{RCA} corresponds to the wetting behavior of the PS block. The figure showed, that the θ_{RCA} of the diblock copolymer brush surfaces were dependent on the thickness of the PS block. c) Schematic figure of the correlation between the thickness of the top block and the wetting behavior of the diblock copolymer brush surface. With decreasing thickness of the top block, the θ_{RCA} is affected by the bottom block. The interaction between the water and bottom block leads to swelling of the PHEMA brushes. a), b) and c) were taken with changes from my first author publication.^[2]

4.4.2.4 Surface Topography

In the previous section it was shown that after decreasing the ratio between the grafting density of the top block and the bottom block the surface topography showed protrusions (Figure 4.8) and the rms roughness increased. To check if the wetting properties were affected by the surface topography of the diblock copolymer brush surfaces, four diblock copolymer brush surfaces were scanned by SFM. The results are summarized in Figure 4.16. The rms roughness was plotted against the thickness of the top block, respectively (Figure 4.16a). It was observed that the rms roughness increased with increasing thickness of the top block. However, the huge error bars showed that the diblock copolymer brush surfaces were inhomogeneous. In consideration of the error bars the rms roughness of the PHEMA(17nm)-*b*-PS(19nm) (black data point in Figure 4.16a) and PHEMA(17nm)-*b*-PS(40nm) (orange data point in Figure 4.16a) were in the same range. For the PHEMA(17nm)-*b*-PS(19nm) (Figure 4.16d) and PHEMA(25nm)-*b*-PS(7nm) (Figure 4.16b) surface adaptation was observed in the wetting experiments (Table 4.2). For the PHEMA(17nm)-*b*-PS(40nm) (Figure 4.16e) surface no surface adaptation was observed in the wetting experiments (Table 4.2). From the results in Table 4.2, it was concluded that the rms roughness did not correlate with the wetting properties of the diblock copolymer brush surfaces.

Next to the rms roughness the structure in the surface topographies of the diblock copolymer brush surfaces in Figure 4.16 differed. For the PHEMA(25nm)-*b*-PS(7nm) surface a flat surface topography was observed, which was consistent with the diblock copolymer brush surfaces from the previous section. For the PHEMA(17nm)-*b*-PS(19nm) and PHEMA(17nm)-*b*-PS(40nm) surface a dimple-like structure^[108]

was observed. For the PHEMA(35nm)-*b*-PS(19nm) surface a ripple-like structure^[108] was observed. It was assumed that the change in the surface topography results from the variation of the ratio between the thickness of the top block and bottom block^[58] and the ratio between the grafting density between the top block and the bottom block.

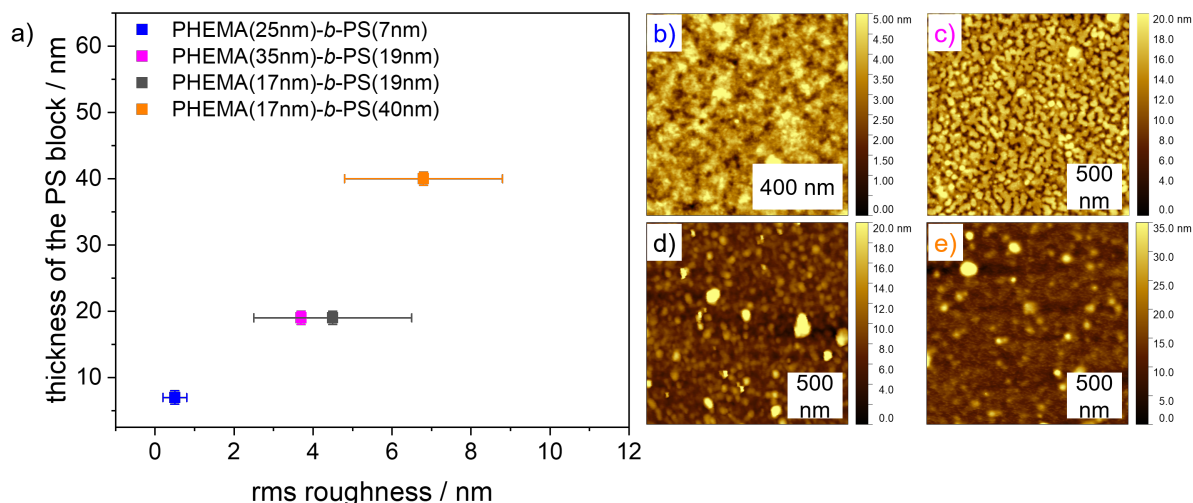


Figure 4.16: Influence of the thickness of the PS block on the surface topography of the PHEMA-*b*-PS diblock copolymer brush surfaces. The surface topography was measured by scanning force microscopy. The measurements were performed in tapping force mode, with a scan size of $1 \times 1 \mu\text{m}^2$ or $2 \times 2 \mu\text{m}^2$. a) The thickness of the polystyrene block is plotted against the rms roughness of the surface topography. With regard to the error bars of the rms roughness, no correlation between the thickness of the top block and the rms roughness was observed. b) Surface topography of the PHEMA(25nm)-*b*-PS(7nm) surface. c) Surface topography of the PHEMA(35nm)-*b*-PS(19nm) surface. d) Surface topography of the PHEMA(17nm)-*b*-PS(19nm) surface. e) Surface topography of the PHEMA(17nm)-*b*-PS(40nm) surface. c), d) and e) was taken from my first author publication.^[2]

4.4.2.5 XPS Depth Profiling

The observed differences and inhomogeneities in the surface topography leads to the question about the homogeneity of the surface chemistry. To answer the question the phase images of the SFM measurements of the PHEMA(17nm)-*b*-PS(19nm) and PHEMA(17nm)-*b*-PS(40nm) surface were analyzed. The phase images are summarized in Figure 4.17a,b. The two diblock copolymer brush surfaces were used, because the rms roughness of both diblock copolymer brush surfaces were in the same range (Figure 4.16a) and PHEMA(17nm)-*b*-PS(19nm) adapted to water and PHEMA(17nm)-*b*-PS(40nm) did not adapt to water (Table 4.2). The phase images showed, that the surface was chemically homogeneous.

To characterize the surface chemistry and the diblock copolymer brush structure spectroscopically, the diblock copolymer brush surface were analyzed by XPS depth profiling.^[2] XPS depth profiling allows to record a XPS spectra through the diblock copolymer brush film. With this method a XPS spectrum is measured of the surface. Then the surface gets etched by sputtering the surface with Ar^+ clusters and a XPS spectra is taken again. By alternating etching and recording a XPS spectra. The chemical structure of PS and PHEMA can be well distinguished spectroscopically. PS contains no C–O and C=O group. PHEMA does not contain an aromatic system. The results of the XPS depth profiling are summarized in Figure 4.17c. The XPS spectra of the PS homopolymer brush surfaces is shown in Figure 4.17c(I). The XPS spectra showed the C–C/C–H peak at ≈ 285 eV. The XPS spectra of the diblock copolymer brush

surface is shown in Figure 4.17c(II). The XPS spectra of the surface showed only the C–C/C–H peak at ≈ 285 eV. After etching the surface (intermediate) the C–O peak at ≈ 286.6 eV and C(=O)–O peak at ≈ 288.9 eV appeared. In the XPS spectra at the substrate interface the C–O peak and C(=O)–O peak increased. A comparison of the C–O peak and C(=O)–O peak with the XPS spectra of the PHEMA homopolymer brush surface in Figure 4.17c(III) showed that these two peaks could be assigned to the PHEMA block. From the XPS depth profiling it was concluded that the PHEMA-*b*-PS diblock copolymer structure were present.

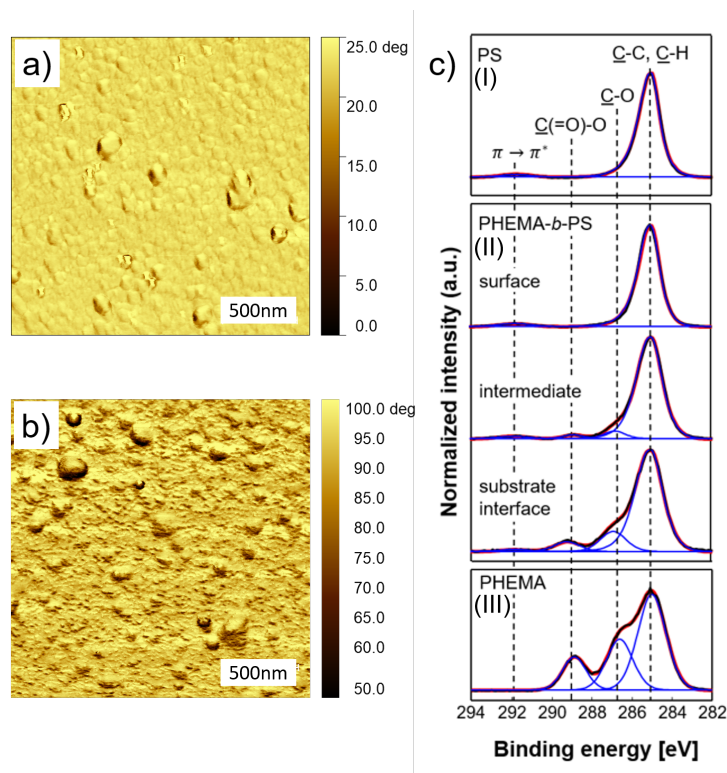


Figure 4.17: a) Phase image of the PHEMA(17nm)-*b*-PS(19nm) diblock copolymer brush surface. The surface was measured by scanning force microscopy. b) Phase image of the PHEMA(17nm)-*b*-PS(40nm) diblock copolymer brush surface. The measurements were performed in tapping mode, with a scan size of $1 \times 1 \mu\text{m}^2$ or $2 \times 2 \mu\text{m}^2$. The phase images indicated, that the surface were rough but chemical homogeneous. c) X-ray photoelectron spectra (XPS) of (I) PS homopolymer brush surface and (III) PHEMA homopolymer brush surface. (II) XPS depth profiling spectra of the PHEMA-*b*-PS diblock copolymer surface. On the solid-air interphase, the XPS spectra corresponds to the PS XPS spectra (surface). After etching, the XPS spectra shows the XPS peaks of the PHEMA XPS spectra (intermediate). The intensity of the PHMEA peaks increased by etching the surface to the substrate (substrate interphase). The XPS depth profiling confirms the PHEMA-*b*-PS diblock copolymer structure. a) and c) were taken from my first author publication.^[2]

4.4.2.6 Switchable Wetting Properties

Figure 4.9 showed, that water treatment at 40°C can affect the wetting behavior of the diblock copolymer brush surface. The diblock copolymer brush surface with a thickness of the bottom block of ≈ 17 nm and a thickness of the top block of ≈ 34 nm grafted from the trichlorosilane initiator was exposed to water (40°C) for 2 h.^[2] The 40°C water will be referred as warm water in the following.

After the synthesis of the diblock copolymer brush surface (pristine), a θ_{ACA} of $\approx 98^\circ$ and a θ_{RCA} of $\approx 77^\circ$ was measured (Table 4.14). The results of the switching experiment are summarized in Figure 4.19a.

Both θ_{ACA} and θ_{RCA} corresponds to the wetting properties of the top block (red dashed line in Figure 4.19a). After exposure the diblock copolymer brush surface to warm water ($H_2O(40^\circ C)$) in Figure 4.19a) the θ_{ACA} decreased to $85 \pm 2^\circ$ and the θ_{RCA} decreased to $26 \pm 3^\circ$. The θ_{ACA} of the warm water treated diblock copolymer brush surface had mixed character of the bottom and the top block. The θ_{RCA} was close to the θ_{RCA} of the bottom block (green dashed line in Figure 4.19a).

From Figure 4.6 it was concluded, that toluene treatment switch the diblock copolymer brushes back from the collapsed state to the state after the synthesis. Therefore the diblock copolymer brush surface was exposed to toluene at $40^\circ C$ for 2 h. After the toluene treatment the diblock copolymer brush surface was annealed at $120^\circ C$ in vacuum for at least 5 h. After annealing (annealed in Figure 4.19a) a θ_{ACA} of $95 \pm 3^\circ$ and θ_{RCA} of $58 \pm 2^\circ$ was measured.

The switching of the θ_{ACA} from $85 \pm 2^\circ$ to $95 \pm 3^\circ$ and the switching of the θ_{RCA} from $26 \pm 3^\circ$ to $58 \pm 2^\circ$ after exposing to warm water and toluene was observed repeatedly in subsequent cycles (Figure 4.19a). It was noted that after the annealing the θ_{ACA} of the diblock copolymer brush surface correspond to the θ_{ACA} after the synthesis.

However, it was observed that the θ_{RCA} was $\approx 20^\circ$ lower than the θ_{RCA} of the diblock copolymer brush surface after the synthesis. It was assumed that during the first exposure to warm water, the bottom block swells and changed the orientation of the entire diblock copolymer brushes. Exposure the diblock copolymer brush surface to toluene and annealing did not fully recover the structure of both polymer blocks in the same way as obtained directly after the synthesis.

4.4.2.7 Surface Topography Switchable Surface

Figure 4.6 showed, that the collapse of the diblock copolymer brushes affected the surface topography. To check how the warm water treatment and annealing of the diblock copolymer brush surface affect the surface topography, the surface was characterized by SFM. The diblock copolymer brush surface was scanned after the synthesis, after the warm water treatment and annealing, respectively. The results of the SFM characterization are summarized in Figure 4.18. No influence of the warm water or annealing on the surface topography was observed. The SFM results were in line with the previous results that the surface topography did not correlate with the wetting behavior of the diblock copolymer brush surfaces. I assumed that a change in the surface chemistry leads to the switch in the wetting behavior.

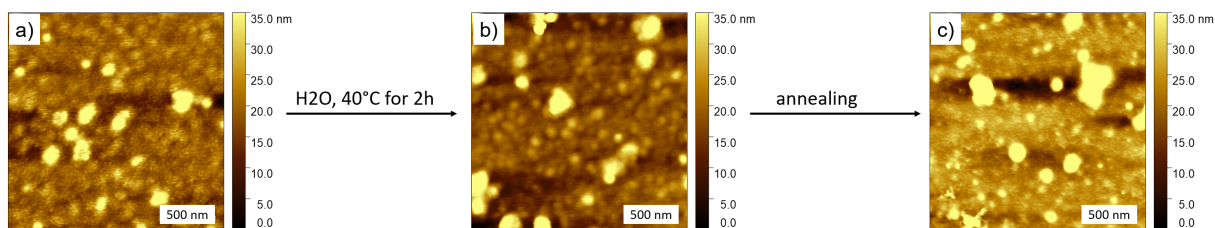


Figure 4.18: The PHEMA(17nm)-*b*-PS(37nm) diblock copolymer brush surface topography were measured by scanning force microscopy. The measurements were performed in tapping force mode, with a scan size of $2 \times 2 \mu m^2$. a) After the synthesis. RMS roughness: 5 nm. b) After exposing the surface to $40^\circ C$ warm water for 2 h. RMS roughness: 7 nm. c) After exposing to $40^\circ C$ warm toluene for 2 h and annealing at $120^\circ C$ for 5 h. RMS roughness: 4 nm. Exposing the surface to warm water or toluene affected the surface topography. The figure was taken with changes from my first author publication.^[2]

4.4.2.8 SFG Characterization

To analyze the surface chemistry in more detail, the diblock copolymer brush surface was analyzed by heterodyne-detected sum frequency generation (HD-SFG) spectroscopy. HD-SFG spectroscopy allows to detect the selective probing of surface-specific vibrational modes at the solid/air interphase without bulk contribution.^[110] Here it was focusing to detect the C–H stretching region at $2850\text{--}3050\text{cm}^{-1}$ of the diblock copolymer brush surface. The HD-SFG spectra was measured after exposing the diblock copolymer brush surface to warm water and annealing, respectively. The results of the HD-SFG measurement are summarized in Figure 4.19b. After warm water (blue spectra in Figure 4.19b) and annealing (black spectra in Figure 4.19b), a prominent positive peak at 3050cm^{-1} was observed. The peak corresponds to the aromatic C–H stretching mode^[111] of the top block. The relative change in the amplitude between the warm water treatment and annealing shows a decrease in out-of-plane molecular alignment after exposing the diblock copolymer brush surface to warm water. The results of the HD-SFG measurements showed that the warm water treatment and annealing of the diblock copolymer brush surface results in a change of the orientation of the top block. The change in the HD-SFG spectra correspond to the change in the wetting properties.

The thickness of the total diblock copolymer brush surface was measured after finishing the switching experiments. No difference in the total thickness of the diblock copolymer brush surface was observed after the synthesis and after the switching experiments. Therefore it was excluded that degrafting^[99] affected the switching experiments. From the HD-SFG measurement it was concluded that the change in the wetting properties results from the change in the surface chemistry.

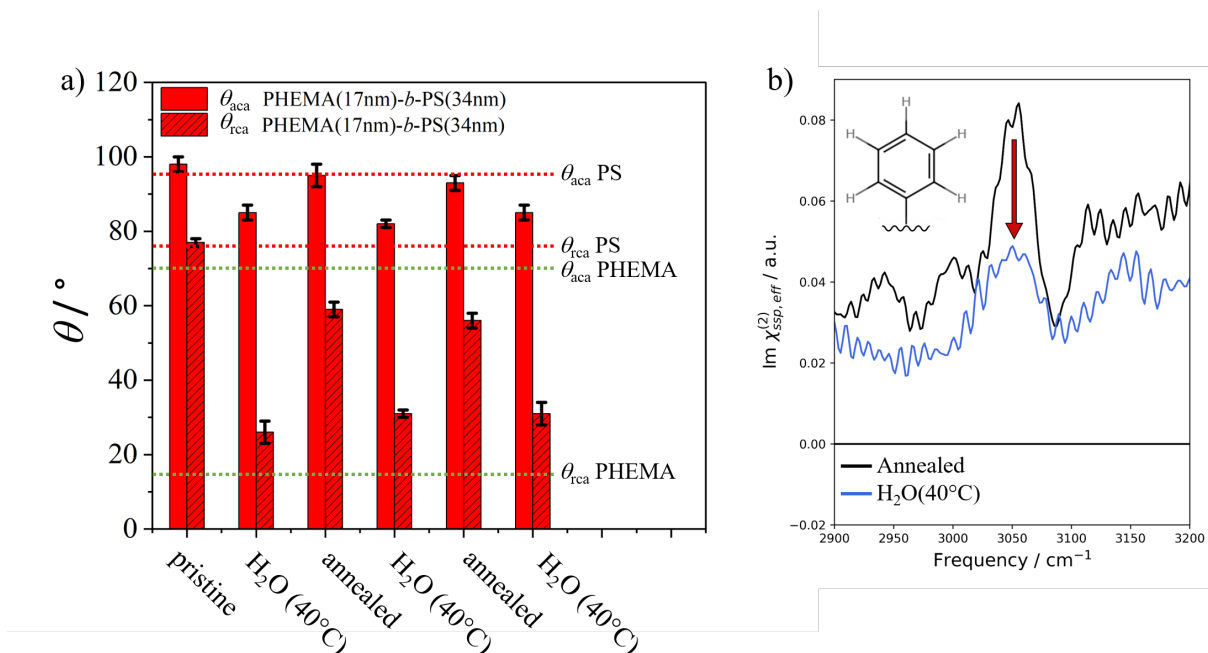


Figure 4.19: a) Advancing contact angle (θ_{ACA}), red columns and receding contact angle (θ_{RCA}), red columns with pattern of the PHEMA(17nm)-*b*-PS(34nm) diblock copolymer surface. θ_{ACA} and θ_{RCA} after the synthesis (pristine). After exposing the surface two hours to 40°C warm water (H₂O(40°C)). After the surface was exposed two hours to 40°C warm toluene, dried with a stream of nitrogen and annealed the surface for at least 5 h in a vacuum oven at 120°C (annealed). By alternating treatment with warm water and annealing, the surface could be reversible switched between a hydrophilic and hydrophobic state. b) Heterodyne-Detected Vibrational Sum Frequency Generation (HD-SFG) spectra of the PHEMA-*b*-PS diblock copolymer brush surface. Black: Annealed surface. Blue: After warm water treatment. The HD-SFG analysis confirmed the change of the surface chemistry by reorientation of the diblock copolymer brushes surface. a) and b) were taken with changes from my first author publication.^[2]

4.5 Conclusion

In the chapter I was able to show, that the ratio between the grafting density of the bottom and the top block determines the surface properties of the diblock copolymer brush surfaces. Surface roughness is not only determined by the ratio of layer thicknesses between the bottom and top block, as is often assumed. Surface roughness is determined by the ratio of the grafting density between the bottom and top block. A crucial role for the surface properties of diblock copolymer brush surfaces plays the initiator. Figure 4.20 shows schematically, how the initiator layer affect the ratio between the grafting density of the top block and bottom block. The grafting density of the bottom block is determined by the order and packing density of the initiator layer. Assuming that 70% of the brushes of the bottom block act as macro initiator for the top block, the higher grafting density of the bottom block results in higher quantity of homopolymer brushes. Therefore the surface roughness increased with decreasing ratio of the grafting density between the top and bottom block.

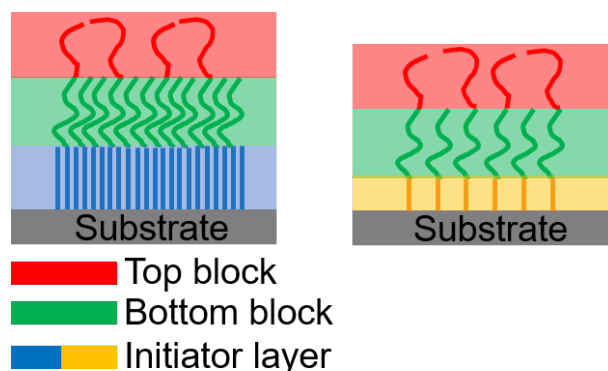


Figure 4.20: From the results I concluded that the grafting density and the order of the silane initiator layer, determined the surfaces properties of grafted diblock copolymer brush surfaces. Left: the initiator layer has a high order and packing density. The bottom block grafted from the initiator layer has a high grafting density. Right: the initiator layer has a lower order and lower packing density, than the initiator layer of the left side. Therefore is the grafting density of the bottom block lower than the grafting density of the bottom block on the left side. Assuming that the same quantity of the bottom block brushes, act as macro initiator for the top block, the higher grafting density of the bottom block results in higher quantity of homopolymer brushes. Therefore the surface roughness increased with decreasing ratio of the grafting density between the top and bottom block.

4.6 Experimental

4.6.1 Substrate and Substrate Treatment^[2]

The silicon substrate (P + +/Boron<100>, thickness $525 \pm 25 \mu\text{m}$) was purchased from Si-Mat silicon Materials, Germany. The silicon substrate (P + +/Boron <100>, thickness $525 \pm 25 \mu\text{m}$) was purchased from Si-Mat silicon Materials, Germany. A thickness of $\approx 1.6 \text{ nm}$ was measured for the native SiO_2 layer by spectroscopic ellipsometry. The silicon substrate was cut in $1.3 \times 1.3 \text{ cm}^2$ or $7.5 \times 7.5 \text{ cm}^2$ chips. The silicon substrates were rinsed with ethanol (absolute, VWR, France) and DI water ($18 \text{ M}\Omega\text{cm}$, Arium Pro system, Satorius, Germany) two times, respectively. After rinsing the silicon substrate was dried with a stream of nitrogen gas. Before the synthesis the silicon substrate was activated by O_2 plasma (Diener electronic Femto, Plasma-Surface-Technology, Germany) using a oxygen flow rate of $6 \text{ cm}^3 \text{ min}^{-1}$ and a power of 300 W for 20 min.

4.6.2 Monochlorosilane Initiator

3-(Bromoisobutyryl)propyl)dimethylchlorosilane was synthesized following the synthesis path in the literature.^[56,100] The synthesis is shown in Figure 4.2. A three-necked flask was fitted with a dropping funnel, an olive connected with argon and a stopper and a stirrer. Dry dichloromethane (DCM, 100 mL, Sigma Aldrich, Germany), triethylamine (TEA, 18 mL, 0.13 mol, Sigma Aldrich, Germany) and allyl alcohol (7.4 mL, 0.108 mol, Sigma Aldrich, Germany) was added to the three-neck flask and the solution was cooled with an ice bath. Under stirring the 2-bromo-2-methylpropionyl bromide (13.42 mL, 0.109 mol, Sigma Aldrich, Germany) was added dropwise. After adding the 2-Bromo-2-methylpropionyl bromide, the solution was stirred at room temperature for 23 h. During adding the 2-Bromo-2-methylpropionyl bromide the colorless solution changed to yellow. DI-water was added to the reaction mixture. The solution was added to a separation funnel. The three-neck flask was rinsed with DCM and the solution

was added to the reaction mixture in the separation funnel. The water and organic phase were separated. The water phase was washed with DCM and added to the organic phase. The organic phase was washed with a 1% HCl-solution. Then the organic phase was washed with a 1% NaHCO₃-solution. In a final step the organic phase was washed with DI water. The organic phase was added to round-neck flask. A distillation (housemade by MPIP) attachment was added to the round-neck flask. The distillation was done under reduced pressure (≈ 20 mbar). At 45°C the non reacted allyl alcohol was distilled. After removing the allyl alcohol the distillation was continued and the allyl 2-bromo-2 methylpropionate was collected (50°C). The allyl 2-bromo-2 methylpropionate was confirmed by ¹H-NMR (Figure 8.2). The yield was 72.5% (16.46g, 0.079 mol). For the hydrosilylation of the allyl 2-bromo-2 methylpropionate a two-neck flask was used. A spatula tip of the hexachloroplatinic acid hexahydrate (catalytic, Sigma Aldrich, Germany) was added to the two-neck flask and heated up with a heat gun to remove water. During heating the hexachloroplatinic acid hexahydrate changed the color from orange to black. The two-neck flask was fitted with a Dimroth condenser and a stopper. A stirrer was added to the flask. The Dimroth condenser was connected with the argon line. Under an argon atmosphere dimethylsilane (58 mL, 0.252 mol, Sigma Aldrich, Germany) was added to the two-neck flask. The reaction mixture was heated up to 60°C and stirred for 24 h. A distillation (housemade by MPIP) attachment was added to the two-neck flask and the non reacted dimethylsilane was distilled. The product was distilled at 120°C under reduced pressure (oil pump, 10⁻² mbar). The 3-(bromoisobutyl)propyl)dimethylchlorosilane was confirmed ¹H-NMR (Figure 8.3). With regard to the previous reaction step the yield was 83% (18.94 g, 0.066 mol). With regard to the 2-bromo-2-methylpropionyl bromide the yield was 60.5%.

4.6.3 Trichlorosilane Initiator

The (11-(2-bromo-2-methyl)propionysyloxy)undecyltrichlorosilane) was synthesized and analyzed by Diego Fernando Dorado Daza at the Institute of Macromolecular Chemistry CAS, Prague, Czech Republic for my first author publication.^[2]

4.6.4 Self-Assembled Monolayer (SAM) on the Silicon Substrate^[2]

To graft the 3-(bromoisobutyl)propyl)dimethylchlorosilane (Br-SAM I) or (11-(2-bromo-2-methyl)propionysyloxy)undecyltrichlorosilane) (Br-SAM II) to the O₂ plasma activate silicon substrate, the silicon substrates were placed in a Petri dish in a solution of anhydrous toluene (extra dry >99.85%, Fisher Scientific, UK) and the Br-SAM I or Br-SAM II for 3 h.^[102] The Petri dish was covered with para film, placed in a desiccator with silica gel. The volume ratio between the Br-SAM I/II and the anhydrous toluene was 1:1000.^[98] After 3 h the coated substrates were rinsed with toluene (>99.8%, Fisher, Netherlands), ethanol and DI water two times, respectively. After rinsing the coated silicon substrates were dried with a stream of nitrogen. The coated silicon substrates were stored in an evacuated desiccator and used for the polymerization step within 7 days.

4.6.5 Purification Copper(I) Bromide

The copper(I) bromide (TCI, Europe) was purified before using. For the purification the copper(I) bromide (yellow-green) was transferred into a beaker containing a mixture from DI water and acetic acid^[112] (100 mL). The volume mixture was 1:1. The solution was stirred and heated up to 65°C for 30 min. The warm solution was filtered through a P2 frit under reduced pressure. The copper(I) bromide (yellow-colorless) was rinsed with DI-water three times. The copper(I) bromide was dried in a

vacuum oven at 80°C. The copper(I) was stored under argon. The copper(I) bromide was purified all 3 months.

4.6.6 Polyhydroxyethylmethacrylate Brushes, PHEMA

2-Hydroxyethylmethacrylate (14.42 g, 0.110 mol, 99%, Sigma Aldrich, Germany), 2,2'-bipyridine (365.9 mg, 93.7 mmol, >99%, TCI, Europe), copper(II) bromide (20.5 mg, 3.7 mmol, 99.999% trace metal basis, Sigma Aldrich, Germany), DI water/ethanol (25 mL, 1:1) were placed in a flask. A stirrer was added to the solution. The flask was provided with a septum and degassed under stirring with argon for 1 h. During the degassing the solution was cooled with an ice bath.^[113] After 1 h the ice bath was removed and under an argon atmosphere purified copper(I) bromide was added to the solution. To solve the copper(I) bromide the monomer solution was treated with ultrasound for 5 min. A syringe was degassed with argon three times. The monomer solution was transferred under argon from the flask into the glass reactors containing the Br-SAM I/II coated silicon substrates. The glass reactors containing the coated Br-SAM I/II coated silicon substrates were degassed with argon for at least 30 minutes before adding the monomer solution. The polymerization was performed at 30°C. After the desired reaction time, the PHEMA coated silicon substrates were treated and stored differently for the PS polymerization. The treatment is listed in the PS synthesis, respectively.

4.6.7 Polystyrene / PHEMA-*b*-PS I

Styrene (Sigma Aldrich, Germany) was purified by distillation before every synthesis.

After the desired PHEMA polymerization time, the PHEMA coated silicon substrates were exposed to a 5 mmol L⁻¹ CuBr₂/bipyridine methanol (ratio 1:1, methanol from VWR, France) solution to bring any active polymer chains in the dormant C-Br state^[97] and were directly stored in the glass reactor under an argon atmosphere.

Purified styrene (18.18 g, 0.174 mol), anhydrous dimethylformamide (DMF, 6.66 mL), toluene (3.33 mL) and N,N',N'',N'''-pentamethyldiethylenetriamine (PMDETA, 3.46 mg, 2 mmol, TCI, Europe) were added to a Schlenk flask, fitted with a septum and degassed by at least three freeze-pump-thaw cycles.^[98] In a second Schlenk flask containing a stirrer, copper(I) bromide (248.2 mg, 1.73 mmol) and copper(II) bromide (20 mg, 0.09 mmol) was oxygenated by three vacuum/argon backfilling cycles. A syringe was three times degassed by argon and the monomer solution was transferred to Schlenk flask containing the copper bromides through a septum. The solution was stirred for 10 minutes. After dissolving the copper(I) and copper(II) bromide, the monomer solution was transferred under an argon atmosphere to the glass reactor containing the PHEMA and/or Br-SAM I coated silicon substrates. The reaction was done at 80°C. After the desired reaction time the reaction was terminated by transferring the monomer solution to a beaker. The PHEMA-*b*-PS or PS coated silicon substrates were rinsed two times with toluene, DMF and water, respectively.

4.6.8 Polystyrene / PHEMA-*b*-PS II^[2]

Styrene (Sigma Aldrich, Germany) was purified by distillation before every synthesis.

After the desired reaction time, the PHEMA reaction was terminated by transferring the monomer solution to a beaker. The PHEMA coated silicon substrates were rinsed two times with water and ethanol, respectively. The PHEMA coated silicon substrates were dried with a stream of nitrogen gas. The PHEMA coated silicon substrates were stored under vacuum in a desiccator or used directly for the PS synthesis.

Purified styrene (18.18 g, 0.174 mol), toluene (10 mL) and PMDETA (3.46 mg, 2 mmol, TCI, Europe) were added to a Schlenk flask, fitted with a septum and degassed by at least three freeze-pump-thaw cycles.^[98] In a second Schlenk flask containing a stirrer, copper(I) bromide (248.2 mg, 1.73 mmol) and copper(II) bromide (20 mg, 0.09 mmol) was oxygenated by three vacuum/argon backfilling cycles. A syringe was three times degassed by argon and the monomer solution was transferred under an argon atmosphere to the Schlenk flask containing the copper bromides through a septum. The solution was stirred and heated up to 90°C for 1 h. It was observed that the solubility of the copper(I) bromide was low in toluene. The oil bath containing the glass reactors was heated up to 90°C and the monomer solution was transferred under an argon atmosphere to the glass reactor containing the PHEMA and/or Br-SAM II coated silicon substrates. The reaction was done at 90°C. After the desired reaction time the reaction was terminated by transferring the monomer solution to a beaker. The PHEMA-*b*-PS or PS coated silicon substrates were rinsed two times with toluene, ethanol and water, respectively.

4.6.9 Contact Angle Measurements

The contact angle θ measurements were performed with a goniometer (OCA35^[2], DataPhysics Instrument GmbH, Germany or Krüss DSA100, Krüss GmbH Germany). A DI water drop with a volume of 6 μL was placed with a Hamilton syringe (needle: blunt end, coated with PTFE, 51 mm length, 0.4 mm inner diameter) onto the horizontal surface. Side view videos were recorded and analyzed with the help of the software *SCA20* provided by DataPhysics Instrument GmbH or the *Advance software* (Krüss GmbH, Germany). After placing the drop, the drop volume was increased and decreased by 30 or 35 μL (dependent on the surface) with a rate of 0.5 $\mu\text{L s}^{-1}$ and 3 repeats. The videos were recorded by 2 frames per second. The measurement time was calculated by dividing the frame number by 2, respectively. For each surface three different spots were measured and analyzed. The measurement uncertainty were calculated by using standard deviation. The error in the contact angle hysteresis was calculated by Gaussian error propagation.

4.6.10 Scanning Force Microscopy^[2]

The surfaces were scanned in tapping mode (JPK, NanoWizard 4, Bruker Nano GmbH, USA) with cantilever (Olympus, OMCL-AC160TS, back side coating with aluminum) having a nominal frequency of 300 kHz, a nominal spring constant of 26 Nm^{-1} and a nominal tip radius < 10 nm. The imaging of the surface topography and the calculation of the root mean square (rms) roughness was done with the software Gwyddion 2.67 for image areas of 2 x 2 μm^2 and 512 x 512 pixels. The images were leveled applying a polynomial background of second degree (offset and plane). Each surface was scanned at least scanned in two different positions. The surfaces taken from my publication were measured at least at three different spots.^[2] The rms roughness was calculated forming the average of the measurements, respectively. The measurement uncertainty was calculated via forming the standard deviation.

4.6.11 Spectroscopic Ellipsometry^[2]

The thickness of the surfaces were performed on an ellipsometer (alpha SE, Quantum Design, Germany). For the measurements were done using an angle of incidence of 65°, 70° and 75° and spectral range of $\lambda = 380 - 980\text{nm}$ was used. The data were analyzed with the software *CompleteEASE* 6.5. For the fit model a three layer model was used. Silicon (Si.JAW) was selected as substrate with a native SiO_2 layer with a fixed thickness of 1.6 nm. For the polymer film a Cauchy dispersion relation was used to parametrize the refractive index (J.A. Woolam). By applying the fit model the thickness of the polymer

film was obtained. Every sample was measured in three different spots. The average value was used for the thickness. The measurement uncertainty was calculated by the standard deviation. To determine the thickness of the top polymer the difference between total polymer brush surface and the thickness of the bottom polymer brush layer was formed.

4.6.12 X-Ray Photoelectron Spectroscopy (XPS), XPS Depth Profiling^[2]

XPS measurements were performed with a K-Alpha+ spectrometer (ThermoFisher Scientific, East Grinstead, UK). A microfocused, monochromated Al $K\alpha$ X-ray source at an angle of incidence of 30° and an emission angle normal to the surface was used to characterize the samples. The kinetic energy of the electrons was measured by a 180° hemispherical energy analyzer. The constant analyzer energy mode at 200 and 50 eV pass energy for the survey and high-resolution spectra was used, respectively. Spectral resolution of 1.0 and 0.1 eV were used for the high resolution spectra and survey. XPS depth profiling was performed using MAGCIS source operated in Ar^+ cluster ion mode with 2000 argon atoms per cluster at 8000 eV. XPS spectra obtained between etching cycles allow the quantitative and qualitative determination of the constituents present in the polymer and diblock copolymer brush surfaces. Here, spectra from three characteristic levels along the layer stacks of the block copolymer brush surfaces are reported: a) the surface of the polymer brushes (depth of 0 nm), b) the intermediate level (depth of 20-30 nm), and c) the level where Si 2p substrate signals were detectable (depth of 40-50 nm). All reported XPS spectra are referenced to the C1s peak of hydrocarbons at 285.0 eV. The analyzer transmission function, Scofield sensitivity factors, and effective attenuation lengths (EALs) for photoelectrons were applied for the purpose of quantification. The BE scale was controlled by the well-known position of the photoelectron C–C, C–H, C–O, and C(=O)–O C 1s peaks of polyethylene terephthalate. The measured XPS spectra were fitted with Voigt profiles obtained by convolving Lorentzian and Gaussian function to calculate the quantity in atomic % of individual chemical species present on the analyzed surfaces.

4.6.13 Heterodyne Detected Vibrational Sum Frequency Generation (HD-SFG) Spectroscopy^[2]

The PHEMA-*b*-PS diblock copolymer brush surface was measured using a HD-SFG spectrometer with a non-collinear beam geometry. A 1 kHz Spitfire Ace Ti:Sapphire regenerative amplifier system from Spectra Physics, centered at 800 nm, was used as the primary light source (5 mJ pulse energy, ≈ 40 fs pulse duration, 1 kHz repetition rate). Subsequently, the output radiation was divided into two branches. One branch was directed as a pulse shaper that used a grating-cylindrical mirror system to generate a narrowband visible pulse (10 cm^{-1}). The other branch was converted into a broadband mid-IR pulse using a combination of an optical parametric amplifier (Light Conversion TOPAS-C, Spectra Physics) and an AgGaS₂ crystal. The infrared (IR) and visible beams were directed onto a 100-nanometer-thick layer of ZnO that had been deposited on a 1-millimeter-thick CaF₂ window. This configuration enabled the generation of a local oscillator (LO) signal. Subsequently, these beams were then re-focused using two off-axis parabolic mirrors, which spatially and temporally overlapped at the polymer surface. A fused silica glass plate with a thickness of 1.5 mm was strategically positioned within the optical path of the LO signal, thereby creating a delay of ≈ 2 ps. The sample SFG signal interfered with the LO signal, creating an SFG interferogram. This interferogram was directed into a spectrometer (Shamrock 303i, Andor Technology) and subsequently captured by an electron-multiplying charge-coupled device (EMCCD) camera (Newton, Andor Technology). The complex $\chi^{(2)}$ spectrum was extracted by Fourier analysis of the SFG interferogram and subsequently normalized using a signal from a z-cut

quartz reference.^[114] Each HD-SFG measurement was performed under a dry air atmosphere using the ssp polarization combination, where ssp denotes s-polarized SFG light, s-polarized visible light, and p-polarized mid-IR light. The spectrum presented in Figure 4.19 was obtained by averaging 15 spectra, with an exposure time of 2 minutes for each spectrum.

4.6.14 ^1H -NMR

The ^1H -NMR measured with a Bruker 200 MHz device. The data were plotted with the software *MestRenova*.

5 Water Adaptation on Photoswitchable Copolymer Brush Surfaces

5.1 Author Contributions

The concept of chapter 5 "Water Adaptation on Photoswitchable Copolymer Brush Surfaces" was created by Benjamin Leibauer, Dr. ... (Max Planck Institute for Polymer Research) and ... (Vidyasirimedhi Institute for Science and Technology, Rayong, Thailand). This chapter is not based on a publication.

Chapter 5 in the form shown was written and designed by Benjamin Leibauer.

The two step synthesis of the 7-(2-acryloyloxyethoxy)-4-methylcoumarin monomer was performed by Benjamin Leibauer. Two batches of the 7-(2-acryloyloxyethoxy)-4-methylcoumarin were synthesized. The $^1\text{H-NMR}$ of the product of the first step 7-(2-hydroxyethoxy)-4-methylcoumarin of both batches was measured by ... (Vidyasirimedhi Institute for Science and Technology, Rayong, Thailand). The $^1\text{H-NMR}$ was analyzed by Benjamin Leibauer and The $^1\text{H-NMR}$ of the product 7-(2-acryloyloxyethoxy)-4-methylcoumarin of both batches was measured by ... and analyzed by Benjamin Leibauer and The $^1\text{H-NMR}$ of the product of the second batch showed impurities. The $^1\text{H-NMR}$ after the purification was measured and analyzed by Benjamin Leibauer.

The synthesis of (3-(2-bromoisobutyl)propyl)dimethyl-chlorosilane was performed by Benjamin Leibauer and ... (Max Planck Institute for Polymer Research, Mainz, Germany). The $^1\text{H-NMR}$ of each reaction step was measured by Benjamin Leibauer and The recorded $^1\text{H-NMR}$ spectrum were analyzed by Benjamin Leibauer.

All polymer or copolymer brush surfaces were synthesized by Benjamin Leibauer.

All scanning force microscopy were performed and analyzed by Benjamin Leibauer.

All spectroscopic ellipsometry measurements were performed and analyzed by Benjamin Leibauer.

All contact angle measurements were performed and analyzed by Benjamin Leibauer.

All UV-VIS measurements were performed and analyzed by Benjamin Leibauer.

All scanning drop friction force microscopy measurements were performed and analyzed by

5.2 Summary

In this chapter, the synthesis of photoswitchable PEHMA-co-CoumAc copolymer brush surfaces is introduced. Poly(2-ethylhexyl methacrylate) (PEHMA) and 7-(2-acryloyloxyethoxy)-4-methylcoumarin (CoumAc) were used as monomers. The synthesis of the PEHMA-co-CoumAc copolymer surface was confirmed by UV-VIS spectroscopy. The wetting properties of the copolymer surface were characterized by contact angle measurements and scanning the friction force of a sliding water drop on the surface. The wetting properties of the PEHMA homopolymer brush surface and the PEHMA-co-CoumAc copolymer brush surface were similar.

The drop friction measurements showed, that the photodimerization of the PEHMA-co-CoumAc copoly-

mer brush surface decreased the friction force between the sliding water drop and the polymer surface.

5.3 Abstract

Polymers can be functionalized with photoactive groups. The photoactive groups can undergo chemical reactions, when irradiated with light of specific wavelength. Photo responsive properties of polymers are used to modify the polymer structure,^[69,115,116] polymer properties such as the elasticity of polymer materials^[117] or the surface charge^[75] of polymers. With regard to the wetting behavior of polymer surfaces, it was shown that photoisomerization of polymer surfaces can reversibly tune the wetting behavior of polymer surfaces.^[70,71,118] However, if the photodimerization of grafted polymer brushes changes the surface structure and affect the wetting behavior is not described in the literature.

In this chapter, I want to synthesize grafted photoswitchable hydrophobic copolymer brushes, because grafted polymer surfaces have a higher mechanical stability than non grafted polymer surfaces. The research goal is to answer the question how crosslinking of surface grafted hydrophobic copolymer brushes affect the friction force of a sliding water drop.

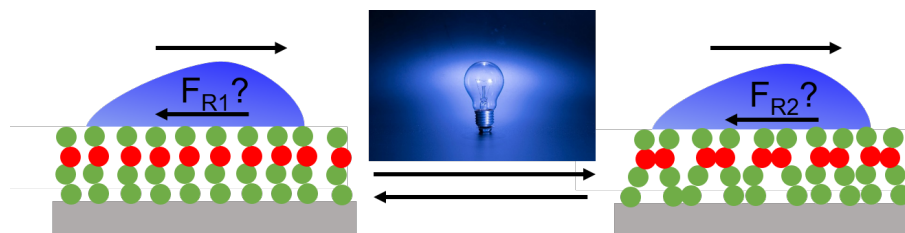


Figure 5.1: Schematic of the photodimerization of the grafted polymer brushes. The green spots represents the hydrophobic monomer units. Red spots represents the photoactive monomer units. Left: The polymer brushes in the monomeric state. A drop slides with the friction force F_{R1} on the surface. Right: The polymer brushes after the photodimerization of the polymer brushes. A drop slides with the friction force F_{R2} on the surface. The hypothesis is, that the photodimerization of the polymer brushes increased the density of the non polar groups. Therefore F_{R2} should be lower than F_{R1} . The goal of this chapter is to check the hypothesis, if the friction force of the sliding drop decreases after the photodimerization.

5.3.1 PEHMA-co-CoumAc Copolymer Brush Surfaces

Grafted PEHMA-co-CoumAc copolymer brush surfaces on quartz glass were synthesized via *surface-initiated atom transfer radical polymerization* (SI-ATRP). The SI-ATRP synthesis was used, because it was shown in chapter 4, that the SI-ATRP technique is a powerful tool to design polymer surfaces. The monomer CoumAc was selected, because the synthesis of the CoumAc monomer is well established in the literature and the photodimerization of the CoumAc is reversible.^[75–77] PEHMA was selected, because PEHMA is hydrophobic and has a T_g of ≈ -10 till -5°C .^[2] The idea was to use a low T_g polymer brushes to increase the flexibility for the photodimerization at room temperature. Quartz glass was selected as substrate, because it is transparent and did not absorb in the spectral range of the UV-VIS measurements. The idea was to use a transparent substrate to illuminate the sample during the measurement of the drop friction force^[119] from the bottom side. The friction force characterization of a sliding drop were selected, because it was shown, that the technique is sensitive to detect changes in the surface chemistry.^[119]

5.3.1.1 Synthesis of CoumAc

The synthesis path of CoumAc is summarized in Figure 5.2. In a first reaction step, 4-Methylumbelliferone (1) was converted with 2-Bromoethanol to 7-(2-Hydroxyethoxy)-4-methylcoumarin (2). (2) was confirmed by $^1\text{H-NMR}$ (Appendix, Figure 8.4). In a second reaction step, (2) was esterified with acryloyl chloride to CoumAc (3). (3) was confirmed by $^1\text{H-NMR}$ (Appendix, Figure 8.5).

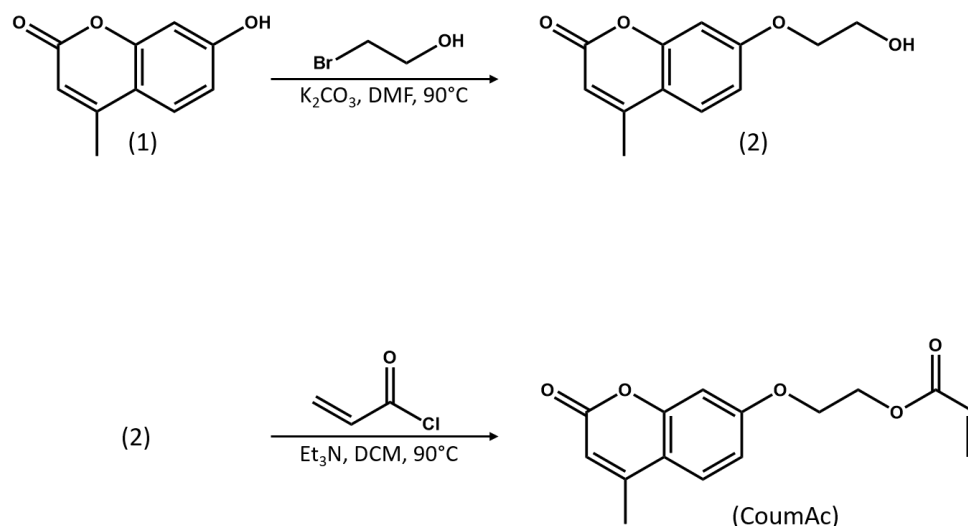


Figure 5.2: Synthesis path of the 7-(2-acryloyloxyethoxy)-4-methylcoumarin (CoumAc). Top: 4-methylumbelliferone (1) reacts with 2-bromoethanol to 7-(2-hydroxyethoxy)-4-methylcoumarin (2). The reaction is carried out in dimethylformamide (DMF). Potassium carbonate is added to the synthesis (K_2CO_3). The reaction temperature is 90°C . Bottom: (2) is esterified with acryloyl chloride to CoumAc. Solvent of the reaction is dichloromethane (DCM). Triethylamine (Et_3N) is added to the reaction as acid-capture reagent. The reaction is carried out at 90°C .

5.3.1.2 Synthesis of PEHMA-co-CoumAc Copolymer Brush Surface

For the SI-ATRP synthesis, the monochlorosilane initiator (3-(Bromoisobutyryl)propyl)dimethylchlorosilane (Br-SAM) from chapter 4 was used. The synthesis is described in chapter 4 (Figure 4.2). The synthesis path of the PEHMA-co-CoumAc copolymer brush surfaces is summarized in Figure 5.3. For my first author publication, the PEHMA synthesis was optimized.^[2] Therefore, the same reaction conditions were used to synthesize the grafted PEHMA-CoumAc copolymer brush and PEHMA homopolymer surfaces. In a first step, the Br-SAM was grafted to the quartz glass and silicon substrate. The silicon substrate was used as reference to measure the thickness of the polymer brush surfaces with a high accuracy by spectroscopic ellipsometry. Figure 3.5 in chapter 3 showed, that a grafted monochlorosilane layer on quartz glass and on silicon substrate are comparable. Therefore it was assumed that the polymerization from the Br-SAM layer on quartz glass and silicon substrates are comparable. The monomer mol ratio between EHMA and CoumAc was 10:1.^[77]

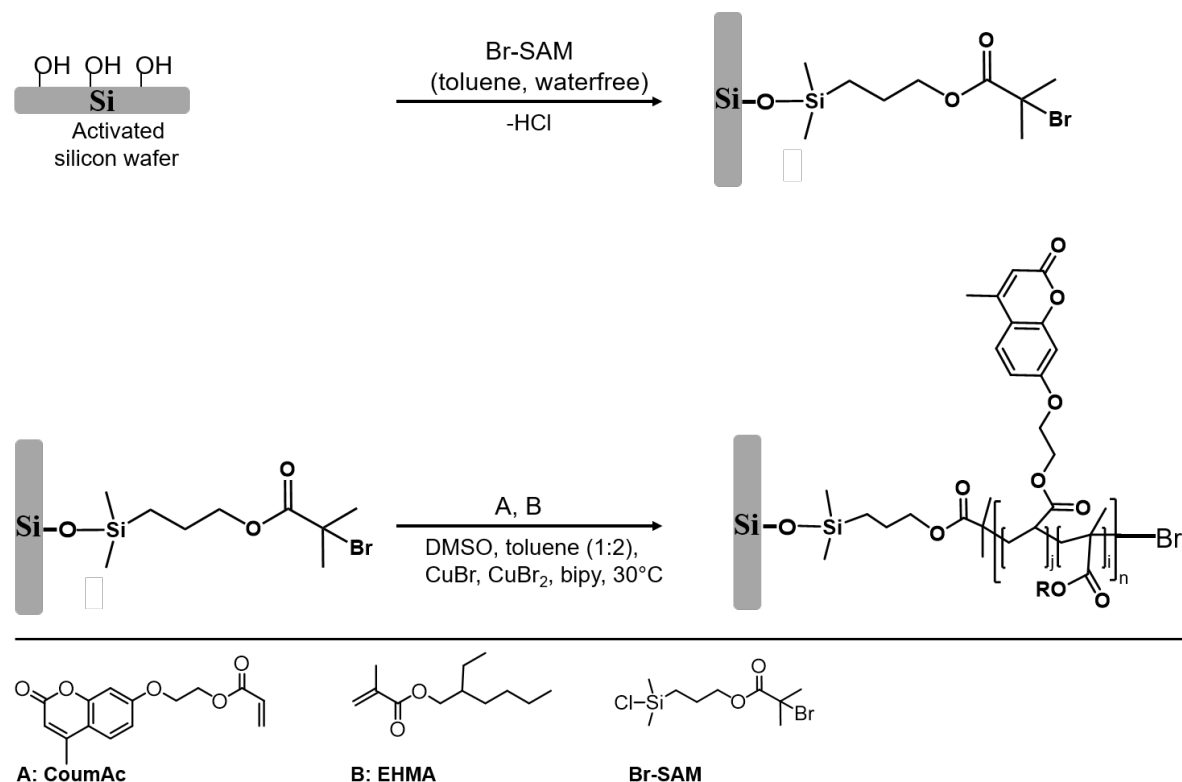


Figure 5.3: The synthesis of the PEHMA-co-CoumAc copolymer brush surface was done, using *surface-initiated atom transfer radical polymerization* (SI-ATRP). PEHMA: Poly(2-ethylhexyl methacrylate). CoumAc: 7-(2-acryloyloxyethoxy)-4-methylcoumarin. The synthesis consists of two steps. Top: The SI (bromoisobutryl)propyl)dimethylchlorosilane) (Br-SAM) is grafted to the activated SiO₂ surface in water free toluene. Bottom: The PEHMA-co-CoumAc copolymer brushes are grafted from the Br-SAM surface. Solvent of the reaction is a mixture of toluene and dimethyl sulfoxide (DMSO) in the ratio 2:1. The polymerization is performed at 30°C. Catalyst is copper(I) bromide (CuBr). Copper(II) bromide (CuBr₂) is added to control the polymerization. Ligand is bipyridine (Bipy).

The homopolymer PEHMA brush surface was synthesized as a reference to the PEHMA-co-CoumAc copolymer brush surface. For the PEHMA homopolymer brush surface a thickness of ≈ 34 nm after 90 minutes polymerization time was obtained. For the PEHMA-co-CoumAc polymer brush a thickness of ≈ 19 nm after a polymerization time of 100 minutes was measured (Figure 5.4). It was assumed that the polarity of the monomer solution decreased by adding the CoumAc monomer. In previous work, it was shown that the solvent influenced the thickness of grafted polymer brushes.^[120] It was concluded that the growing rate decreased by adding the CoumAc monomer to the monomer solution.

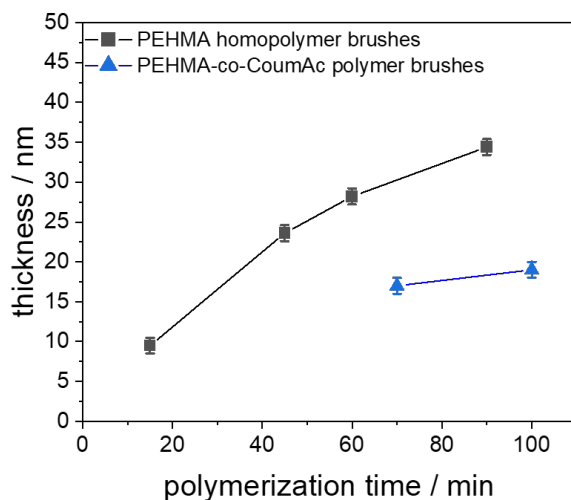


Figure 5.4: The thickness of the homopolymer and copolymer brush surface is plotted against the polymerization time, respectively. It was noted, that the PEHMA polymer brushes grew faster, than the PEHMA-co-CoumAc copolymer brushes.

5.3.1.3 Wetting properties

The polymer brush surfaces were analyzed by SFM, contact angle measurements, UV-VIS spectroscopy and scanning drop friction force microscopy (sDoFFI). The results of the SFM and contact angle measurements are summarized in Figure 5.5.

θ was measured to analyze the wetting properties of the polymer brush surfaces after the synthesis. For the Br-SAM surface, a θ_{ACA} of $84 \pm 2^\circ$ and a θ_{RCA} of $72 \pm 1^\circ$ was measured (Figure 5.5a, black plot). After grafting the PEHMA from the Br-SAM, a θ_{ACA} of $101 \pm 2^\circ$ and a θ_{RCA} of $78 \pm 1^\circ$ was measured (Figure 5.5a, blue plot). For the PEHMA-co-CoumAc copolymer brush surfaces, a θ_{ACA} of $99 \pm 1^\circ$ and a θ_{RCA} of $67 \pm 1^\circ$ was measured (Figure 5.5a, red plot). For both polymer brush surfaces the wetting properties differed from the wetting properties of the Br-SAM surface. The wetting properties of the PEHMA homopolymer brush surfaces were in line with the literature.^[2] For the Br-SAM surface, the PEHMA homopolymer brush surface and the PEHMA-co-CoumAc copolymer brush surface a constant value for the θ_{ACA} and θ_{RCA} in all measurements were observed (Figure 5.5). From the results in Figure 5.5, it was concluded, that the polymer surfaces did not adapt to water.

5.3.1.4 Surface Topography

It was noted that the θ_{RCA} of the PEHMA-co-CoumAc copolymer surface was $\approx 10^\circ$ lower than the θ_{RCA} of the PEHMA homopolymer surface (Figure 5.5c). To check if the difference in the θ_{RCA} between the PEHMA homopolymer brush surface and the PEHMA-co-CoumAc copolymer brush surface were affected by the surface topography, the polymer surfaces were scanned by SFM in tapping mode. For the PEHMA homopolymer surface a flat surface topography was observed (Figure 5.5b). In contrast to the PEHMA homopolymer brush surface, the surface topography of the PEHMA-co-CoumAc copolymer surface showed protrusions (Figure 5.5c). The lower θ_{RCA} of the PEHMA-co-CoumAc copolymer brush surfaces could be the result of pinning effects. The change in the wetting behavior of the surface after the polymerization indicated that the synthesis of the polymer brushes was successful. However, the analysis did not confirm the presence of the PEHMA-co-CoumAc copolymer brush surface.

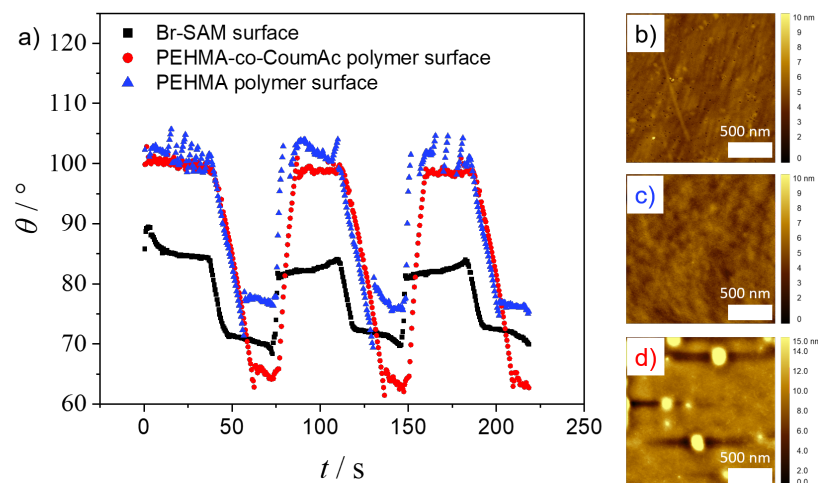


Figure 5.5: a) The contact angle θ is plotted against the measurement time. A water drop of $6\mu\text{L}$ was deposited on the surface. The drop volume was increased and decreased by $30\mu\text{L}$ and the contact angle was recorded. Black: Surface-initiator layer (Br-SAM) surface on quartz glass. Blue: PEHMA homopolymer surface. Red: PEHMA-co-CoumAc polymer surface. It was noted that the θ_{RCA} of the copolymer surface was lower than the θ_{RCA} of the homopolymer surface. b)-d) Showed the surface topography. The surface topography was measured by scanning force microscopy measurements. The measurements were performed in tapping mode, with a scan size of $2 \times 2\mu\text{m}^2$. b) The Br-SAM surface. c) PEHMA homopolymer brush surface. d) PEHMA-co-CoumAc copolymer brush surface. It was noted, that only PEHMA-co-CoumAc surface topography showed protrusions.

5.3.1.5 UV-VIS Spectroscopy

CoumAc undergoes photodimerization (356 nm) or photocleavage (254 nm), when exposed to UV light.^[75–77] Therefore UV-VIS spectroscopy was used to check if the PEHMA-co-CoumAc copolymer brush surface was present. The results are summarized in Figure 5.6. The full UV-VIS spectra is summarized in Figure ??a. Figure ??b showed the UV-VIS adsorption spectra in a spectral range between 250 nm and 400 nm. The spectral range of 250–400 nm was used, because the CoumAc adsorbs at ≈ 320 nm.

The UV-VIS spectrum of the pristine quartz glass and the PEHMA homopolymer brush surface showed no absorbance in the spectral range between 300 and 350 nm. The PEHMA-co-CoumAc copolymer brush surface showed absorbance in the spectral range between 300 and 350 nm, which agrees with the literature.^[75,77] However, comparing the UV-VIS spectra measurements at two different surface areas (M1, M2 in Figure 5.6), showed that the absorbance of the copolymer surface differs. The difference in the absorbance will be discussed in the next paragraph. From the UV-VIS measurements, it was concluded that the PEHMA-co-CoumAc copolymer brush surface was present.

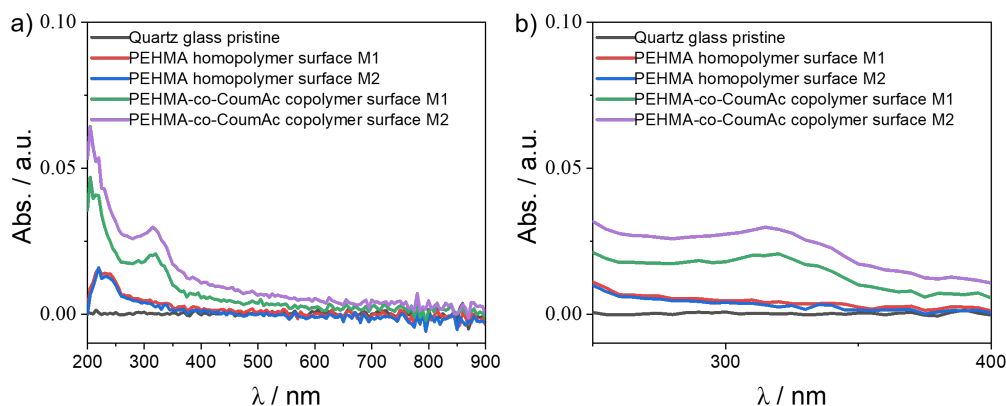


Figure 5.6: UV-VIS absorption spectra of the pristine quartz glass, PEHMA homopolymer brush surface and PEHMA-co-CoumAc copolymer brush surface. The absorption is plotted against the wavelength (λ). a) Complete measured UV-VIS absorption spectra in the spectral range from 200 nm until 900 nm. b) UV-VIS absorption spectra in the spectral range between 250 nm and 400 nm. CoumAc undergoes photodimerization under UV irradiation with a wavelength of 365 nm. The adsorption of the PEHMA-co-CoumAc copolymer brush surface in the spectral range between 300 nm and 350 nm confirms the synthesis of the copolymer brush surfaces.

5.3.2 Photodimerization of PEHMA-co-CoumAc copolymer brushes

The idea was to use the photodimerization of the CoumAc copolymer units to crosslink the PEHMA-co-CoumAc copolymer brushes to tune the wetting behavior of the copolymer brush surfaces. The PEHMA-co-CoumAc copolymer brush surface was illuminated with long-wave UV light (365 nm) for 5, 15, 30, 45 and 60 minutes. After each illumination time the UV-VIS spectra at two different sample positions was recorded. The recorded spectra are summarized in Figure 5.7. Figure 5.7a shows the UV-VIS absorption spectra over the measured spectral range between 200 nm and 900 nm. For a better overview, the UV-VIS absorption spectra was plotted in a spectral range between 250 nm and 400 nm (5.7b). Through the photodimerization, the absorbance of the CoumAc should decrease. Previous work showed, that with increasing irradiation time, the absorbance of CoumAc decreases.^[75,76] However, Figure 5.7 showed, that the absorbance in the UV-VIS spectra did not correlate with the illumination time. It was concluded, that either the distribution of CoumAc differ from position to position or that the UV-VIS measurement is influenced by the substrate.

In chapter 3, I was able to shown that silicate glass is inhomogeneous.^[2] To check how far the inhomogeneity of the quartz glass substrate affected the UV-VIS measurements, the pristine quartz glass was analyzed. Results are summarized in Figure 5.7c and d. Figure 5.7c shows the recorded UV-VIS absorption spectra over the full measured spectral range between 200 nm and 900 nm. For a better overview, the UV-VIS absorption spectra was plotted in a spectral range between 250 nm and 400 nm in Figure 5.7d. In total, the pristine quartz glass was measured at 20 different positions (M1-M20). The spectra of M1 was recorded at the same position such as the baseline was measured. The UV-VIS spectra of M1 showed no absorbance. The UV-VIS spectra of M2 to M20 showed non absorbance peak, but the spectra were shifted up to 0.02 from M1. It was noted that absorbance of the two UV-VIS spectra after a illumination time of 30 minutes differed also in the absorbance of ≈ 0.02 . From the UV-VIS analysis of the pristine quartz glass it was concluded that the inhomogeneity of the quartz glass affected the UV-VIS measurements. The inhomogeneity of the quartz glass shifted the UV-VIS spectra. The shift in the UV-VIS spectra made a quantitative analysis of the photodimerization of PEHMA-co-CoumAc copolymer brush surface difficult. It was not able to show if the photodimerization of the PEHMA-co-CoumAc

copolymer brushes took place. A possible solution of the problem with the shifted UV-VIS spectra will be discussed in the end of the chapter.

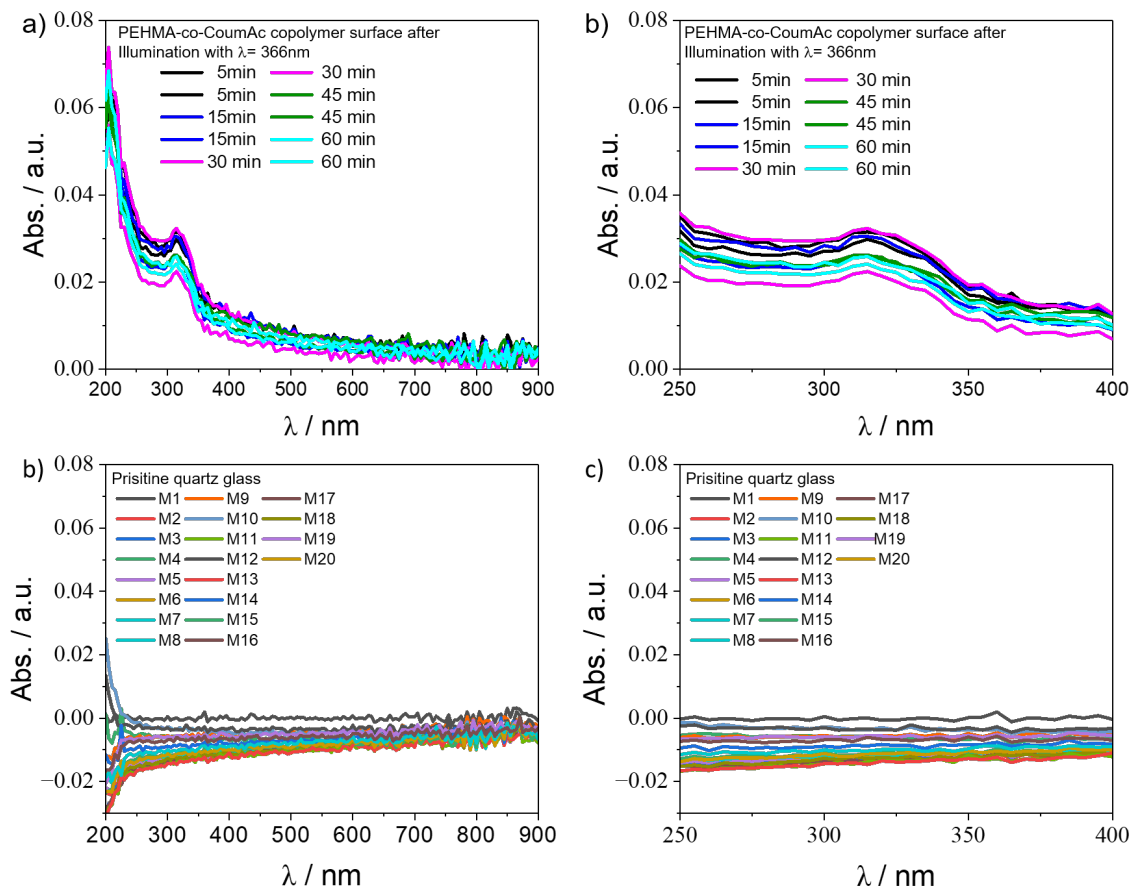


Figure 5.7: UV-VIS absorption spectra: a) PEHMA-co-CoumAc copolymer brush surface. CoumAc undergoes photodimerization under UV irradiation with a wavelength of 365 nm. The copolymer brush surface was irradiated with UV light with a wavelength of 366 nm. The copolymer brush surface was irradiated for 5 min, 15 min, 30 min, 45 min, 60 min. After each irradiation step an UV-VIS spectra was recorded at two different positions (M1 and M2). b) pristine quartz glass. UV-VIS spectra were measured at 20 different positions (M1-M20). The measurements showed, that the pristine quartz glass was inhomogeneous. The inhomogeneity of the substrate made it impossible to quantify the photodimerization of the PEHMA-co-CoumAc copolymer brush surface.

5.3.3 Drop Friction Force on PEHMA-co-CoumAc Brush Surface

A sensitive method to detect changes of a hydrophobic surface is to scan the drop friction force on the surface by sDoFFI.^[119]

For the experiment, the PEHMA-co-CoumAc copolymer brush surface was first illuminated with UV light (254 nm) for 2 h. The 2 h illumination at short-wave UV light was done to bring the PEHMA-co-CoumAc copolymer brushes in their monomeric state by photocleavage. The UV-VIS adsorption spectra are summarized in Figure 5.8. Figure 5.8 a shows the UV-VIS adsorption spectra of the full measured spectra range between 200 nm and 900 nm. For a better overview, the UV-VIS adsorption spectra were plotted against the spectral range between 250 nm and 400 nm (Figure 5.8b).

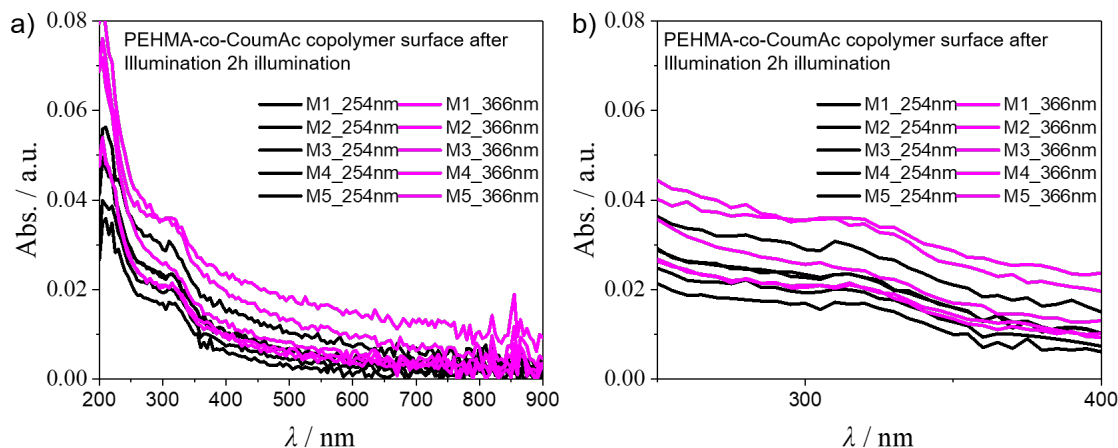


Figure 5.8: UV-VIS absorption spectra of PEHMA-co-CoumAc copolymer brush surface. a) The UV-VIS adsorption spectra of the full measurement. b) For a better overview the UV-VIS adsorption spectra in a spectral range between 200 nm and 400 nm. CoumAc undergoes photodimerization under UV irradiation with a wavelength of 365 nm and the copolymer surface adsorbed in the spectral range between 300 nm and 350 nm. The copolymer brush surface was irradiated with UV light with a wavelength of 366 nm or 254 nm for 2 h, respectively. The surface was measured at 5 different positions (M1, M2, M3, M4, M5), respectively. While the irradiation with UV light with a wavelength of 366 nm, photodimerization of the copolymer brushes occurs. While the irradiation with UV light with a wavelength of 254 nm, photocleavage of the copolymer brushes occurs. I assumed that during the photodimerization the intensity of the adsorption decreased. However, a decrease of the intensity of the adsorption spectra with increasing irradiation time was not observed. The reason is that the inhomogeneity of the quartz glass affect the intensity of the UV-VIS adsorption spectra. The photoswitch can not quantify with the recorded UV-VIS spectra.

After the illumination the drop friction force was scanned at three different sample areas. The friction force was plotted against the slide length. The results are summarized in Figure 5.9a (black line).

After the measurement, the PEHMA-co-CoumAc copolymer brush surface was illuminated with long-wave UV light (366 nm) to induce the photodimerization of the PEHMA-co-CoumAc copolymer brushes. Then the drop friction was measured at three different sample positions.

In Figure 5.9a (purple lines) the friction force is plotted against the slide length. In general the friction force increase till the drop starts to move. When the drop starts to slide, the friction force changes from the static regime^[119] to the kinetic regime. The transition from the static regime to the kinetic regime is marked by the dashed red line in Figure 5.9a. For the evaluation, the friction force in the kinetic regime was used. The kinetic regime was used, because in the kinetic regime the three phase contact line move with constant velocity and drop shape. Therefore, the sliding drop is in an equilibrium state in the kinetic regime. The friction force of the drop on the PEHMA-co-CoumAc copolymer brushes after short-wave UV illumination was $\approx 170 \pm 15 \mu\text{N}$. The friction force of the drop on the PEHMA-co-CoumAc copolymer brushes after long-wave UV illumination was $\approx 140 \pm 20 \mu\text{N}$. The friction force decreased after the illumination with the long-wave UV light. It was assumed, that decrease of the friction force was the results of the photodimerization. It was assumed that the cross linking of the PEHMA-co-CoumAc copolymer brushes result in a higher density on non polar groups (Figure 5.1). The higher density of non polar groups leads to an increase in the hydrophobicity and the drop friction force decreased. The θ_{ACA} and θ_{RCA} were plotted against the slide length in Figure 5.9b. It was observed that the θ_{ACA} of the PEHMA-co-CoumAc copolymer brush surface was in the same range after illumination with long-wave and short-wave UV light. The θ_{RCA} of the PEHMA-co-CoumAc copolymer brush surface differed after

the illumination with long-wave and short-wave UV light. It was noted that the θ_{RCA} decreased from $\approx 57^\circ$ to $\approx 51^\circ$ after the illumination with short-wave UV light in the static regime. The static regime is marked with red dashed line in Figure 5.9b. The difference in the θ_{RCA} corresponds to the higher drop friction force. The lower θ_{RCA} results in an increase in the drop width and decrease in the drop height, which leads to an increase in the drop friction force.^[119,121] The higher θ_{RCA} after the illumination with long-wave UV light indicated that the hydrophobicity of the PEHMA-co-CoumAc copolymer surface increased after the photodimerization of the brushes.

From the drop friction force measurements it was concluded, that the photodimerization of the PEHMA-co-CoumAc copolymer brush surface decreased the friction force of sliding drop.

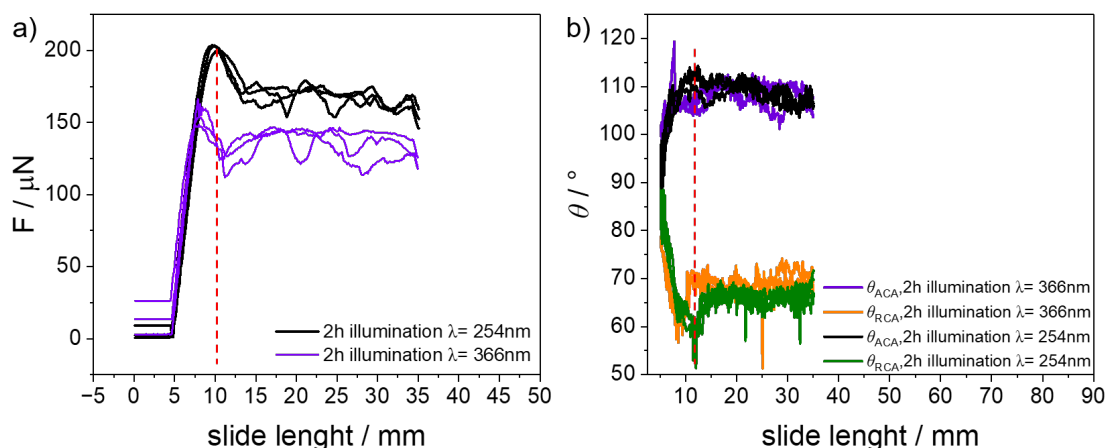


Figure 5.9: a) The measured friction force of a sliding water drop on the PEHMA-co-CoumAc copolymer surface is plotted against the slide length. CoumAc undergoes photodimerization under UV irradiation with a wavelength at 365 nm. Under irradiation of UV light with a wavelength at 254 nm, photocleavage occurs. The regime till the drop start to move is referred as static regime (left side of the dashed red line). At the point where the drop starts to move, the friction force decreases and reached a constant value. This regime is referred as kinetic regime (right side of the red dashed line). The friction force was measured after irradiation with UV light at 366 nm and 254 nm, respectively. It was noted that after the photodimerization the friction force decreased. b) The contact angle is plotted against the sliding length. It was noted that the advancing contact angle after irradiation with UV light at 254 nm and 366 nm was in the same range. However, the receding contact angles θ_{RCA} differ. In the static regime, the θ_{RCA} after the photocleavage (254 nm) was lower than the θ_{RCA} after the photodimerization. Photodimerization affected the friction force of a sliding drop.

5.4 Summary and Outlook

In the chapter, the synthesis of grafted PEHMA-co-CoumAc copolymer brush surfaces was introduced. The characterization with UV-VIS spectroscopy was a challenge. The synthesis of the PEHMA-co-CoumAc copolymer brush surfaces could be confirm by UV-VIS spectroscopy. However, the quartz glass substrate influenced the UV-VIS spectra, by shifting the recorded spectra. The shift in the spectra made it impossible to make a quantitative analysis of the crosslinking of the copolymer brushes.

The problem with the shifted spectra can be solved in the future by marking a quartz glass at some positions. The base line can be measured at the marked positions, respectively. After the polymerization, the sample positions can be analyzed with the corresponding baseline.

From the drop friction measurements, it was concluded that the photodimerization affects the drop

friction force. The finding to tune the drop friction force by the photodimerization of grafted polymer brushes, allows in further experiment to tune the surface properties of polymer surfaces. To measure the change of the friction force of the sliding drop in situ, the friction force of the sliding drop could be varied stepwise. The stepwise tuning of the friction force can help to investigate the adaptation behavior of polymer surfaces.

5.5 Experimental part

5.5.1 CoumAc Synthesis

The synthesis of 7-(2-Acryloyloxyethoxy)-4-methylcoumarin (CoumAc) was adapted from the literature.^[75,122] The reaction path is shown in Figure 5.2. In a first step the 7-(2-hydroxyethoxy)-4-methylcoumarin was synthesized. 4-Methylumbelliferone (45.41 mmol, 8 g, Sigma Aldrich) and DMF (80 mL, anhydrous, Sigma Aldrich)) and potassium carbonate (90.57 mmol, 12.5 g) were added to round-bottom flask with a stirrer. The solution was allowed to stir for 30 minutes under a nitrogen atmosphere. Under nitrogen atmosphere, 2-bromoethanol (67 mmol, 8.37g, 4.84 mL, TCI) were added. The solution was heated up to 90°C for 19 h. The reaction mixture was cooled to room temperature and transferred to ice cold DI-water (400 mL). The flask was rinsed three times with DMF and the solution was transferred to the ice cold water. The colorless precipitate was collected by vacuum filtration and dried in a vacuum oven at 80°C over night. The yield of hydroxyethoxy)-4-methylcoumarin was 61% and the product was confirmed by ¹H-NMR (Figure 8.4). In a second step the 7-(2-hydroxyethoxy)-4-methylcoumarin was esterified with acryloyl chloride to CoumAc. 7-(2-hydroxyethoxy)-4-methylcoumarin (27.23 mmol, 6g) and DCM (100 mL) was added to a three neck flask with a stirrer (Nitrogen, additional funnel and stopper). Under nitrogen atmosphere triethylamine (81.69 mmol, 8.26 g, 11.31 mL) was added dropwise under stirring. After adding the triethylamine the solution was cooled with a ice bath and the acryloyl chloride (81.69 mmol, 6.61g, 5.55 mL) was added dropwise. After adding the acryloyl chloride the ice bath was removed and the reaction mixture was stirred at room temperature for 19 h. The reaction mixture was washed four times with ice cold DI-water, two times with cold saturated sodium bicarbonate solution and two times with ice cold sodium chloride solution. The organic phase was dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel. Eluant was a mixture of DCM/ethyl acetate in the volume ratio 10:1. The yield of CoumAc was 14%. The product was confirmed by ¹H-NMR (Figure 8.5).

5.5.2 Substrate and Substrate Treatment

The substrates were treated with the procedure of chapter 2 and chapter 3.^[1,2] The silicon substrate (P + +/Boron<100>, thickness $525 \pm 25 \mu\text{m}$) was purchased from Si-Mat silicon Materials, Germany. The silicon substrate (P + +/Boron <100>, thickness $525 \pm 25 \mu\text{m}$) was purchased from Si-Mat silicon Materials, Germany. A thickness of $\approx 1.6 \text{ nm}$ was measured for the native SiO₂ layer by spectroscopic ellipsometry. Quartz glass slide ($25 \times 76 \times 1 \text{ mm}^3$, was purchased from Thermo Fisher Scientific, USA. The silicon substrate and quartz glass substrate was cut in $2.5 \times 3.5 \text{ cm}^2$. The silicon substrates were rinsed with ethanol (absolute, VWR, France) and DI water (18 MΩcm, Arium Pro system, Satorius, Germany) two times, respectively. The quartz glass was rinsed two times with ethanol. After rinsing the substrates were dried with a stream of nitrogen gas. Before the synthesis the silicon substrate was activated by O₂ plasma (Diener electronic Femto, Plasma-Surface-Technology, Germany) using a oxygen flow rate of $6 \text{ cm}^3 \text{ min}^{-1}$ and a power of 300 W for 20 min.

The 3-(Bromoisobutryl)propyl)dimethylchlorosilane (Br-SAM) was grafted to the substrates as described in chapter 3.

5.5.3 PEHMA / PEHMA-co-CoumAc Synthesis

The PEHMA synthesis was adapted from my first author publication.^[2] 2-Ethyl methacrylate (EHMA, 7.04g, 35.51 mmol, Sigma Aldrich), 4,4'-dinonyl-2,2'-dipyridyl (58.6 mg, 0.143 mmol, TCI), copper(II) bromide (6.6 mg, 0.029 mmol, Sigma Aldrich) and toluene/DMSO (5.3 mL: 2.6 mL) were added to a flask, provided with a septum and degassed with argon for 1 h. For the PEHMA-co-CoumAc copolymer brushes, Coum Ac (1.023 g, 3.55 mmol) was added to the monomer solution. Under argon purified copper(I) bromide (43.6 mg, 0.304 mmol) was added to the monomer solution. After dissolving the copper(I) bromide the monomer solution was transferred with a syringe to the degassed (30 minutes) reaction reactors, containing the Br-SAM grafted substrate. The syringe was degassed with argon three times before using. The polymerization was performed at 30°C. After the desired reaction time, the reaction was terminated by rinsing the polymer brush surfaces two times with toluene, ethanol and DI-water.

5.5.4 UV-VIS Spectroscopy

The UV-VIS spectra were recorded on the Agilent Technologies, Cary 60 UV-VIS. For the measurements the quartz glass sample were fixed at the holder for solid substrates. The measurements were performed in the absorbance mode with the software *scan*. Pristine quartz was used to record the baseline respectively. The UV-VIS spectra were recorded in a spectral range from 200 nm to 900 nm.

5.5.5 Scanning Drop Friction Force

The friction force and dynamic contact angles of sliding droplets were measured using a scanning droplet setup equipped with a motorized XY stage (DAS100, Krüss GmbH, Germany). The stage movement (240 mm/min over a 3 cm path) and video recording were synchronized via Advance software (Krüss GmbH, Germany). A 20 μ L DI water drop was anchored to the metal ring attached glass capillary (CM Scientific Ltd., dimensions: 0.05 mm $\times$ 0.5 mm $\times$ 50 mm) with a spring constant of $K = 101.5 \mu\text{N/mm}$. The spring constant was determined by analyzing the capillary's free oscillations after a small initial displacement, recorded using a CMOS camera. During scanning, interactions between the droplet and surface were captured with an image resolution of 100 pixels/mm and at frame rate of 30 fps. A MATLAB code was used to analyze the videos, extracting friction forces (from capillary deflection) and dynamic contact angles (by tracking contact line movement frame by frame).

5.5.6 Contact Angle Measurements

The measurement procedure of the contact angle is described in chapter 3.

5.5.7 Scanning Force Microscopy

The SFM measurement procedure is described in chapter 3.

5.5.8 Spectroscopic Ellipsometry

The spectroscopic ellipsometry measurement procedure is described in chapter 3.

5.5.9 ^1H -NMR

The ^1H -NMR was measured with a Bruker 200 MHz (MIP) or 300 MHz (VISTEC) device. The data were plotted with the software *MestRenova*.

6 Conclusion & Outlook

My thesis demonstrated the influence of surface adaptation on different surface effects.

In the first part, I showed that surface adaptation and the substrate chemistry plays a role in slide electrification. In future applications, example for harvesting energy for nanosensors, the efficiency of slide electrification can be increased through targeted doping of chemical species with a high Pearson hardness and a permeable hydrophobic layer. One option would be to functionalized nanoparticles with hydrophobic polymer brushes and deposit on a substrate. Coverage with a permeable hydrophobic layer, would lead to surface adaptation and should increase the drop charge. Depending on the surface and substrate, slide electrification can significantly affect the contact angle measurements.

The goal of the second part was to synthesize grafted polymer brush surfaces that specifically adapt to water. The synthesis of grafted hydrophilic-*b*-hydrophobic diblock copolymer brush surfaces and grafted photo reactive copolymer brush surfaces was introduced. In the community of grafted diblock copolymer brushes, it was previously assumed that the ratio of the thicknesses between the top and bottom blocks determined the surface properties such as the surface roughness. My results showed that this is not the case in general. The packing density and order of the silane initiator determines the grafting density of the bottom block. Variation of the active C-Br groups of the bottom block allows to design the surface properties of grafted diblock copolymer surfaces. The surface topography structure and the wetting properties can be described as function of the grafting density between the top and bottom block. The possibility to tune the porosity of the grafted diblock copolymer brush surfaces, can used in future surfaces to control the specific adsorption of chemical species.

Furthermore I showed, that the photodimerization of grafted copolymer brushes affect the friction force of sliding drop. The change in the friction force was to less, to use the introduced copolymer surface for a sensor. However, the substitution of the used monomer with a monomer with a lower T_g could increase the flexibility of the polymer brushes. Furthermore, the decrease in the grafting density of the polymer brushes, could also increased the flexibility of the polymer brushes. A higher flexibility of the polymer brushes, should increased the influence of the photodimerization of the polymer brushes and make the photodimerization of grafted polymer brushes interesting for smart surfaces.

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8 Appendix

8.1 Supporting Information

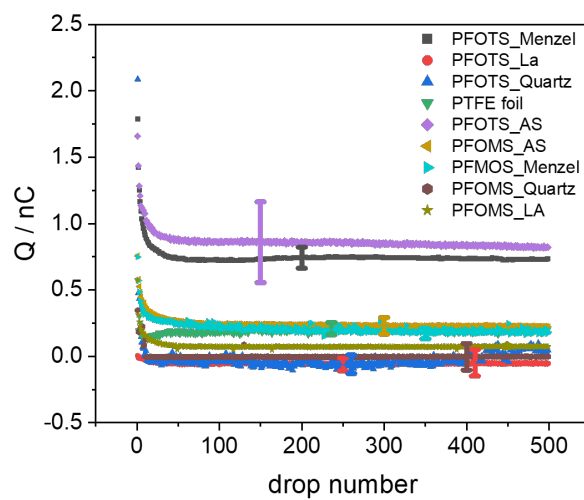


Figure 8.1: All drop charge measurements. The drop charge is plotted against the corresponding drop number. A series of at least 500 drops was measured, respectively. The measurements uncertainty was calculated via the standard deviation of three measurements at three different sample positions.

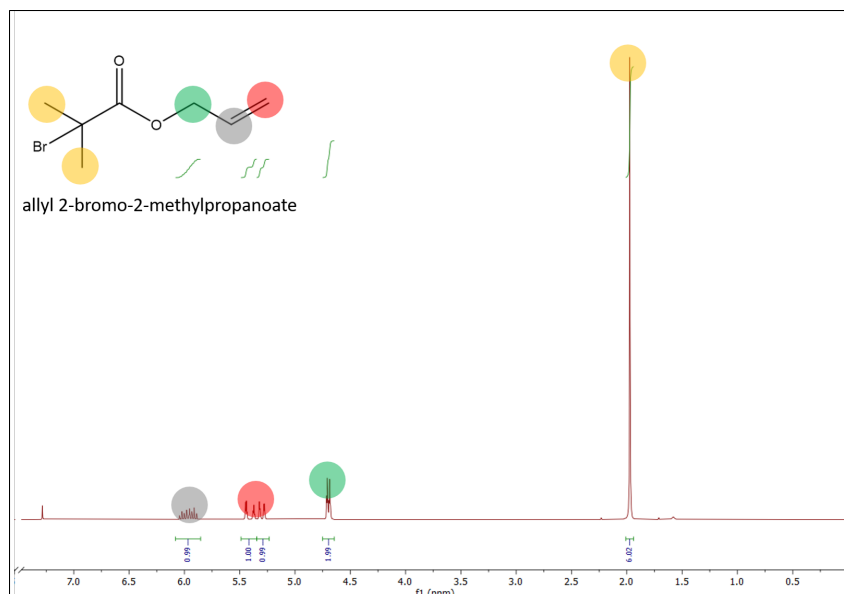


Figure 8.2: ^1H -NMR of the synthesized allyl-2-bromo-2-methylpropanoate. CDCl_3 was used as solvent. All peaks are assigned to the corresponding protons by color, respectively.

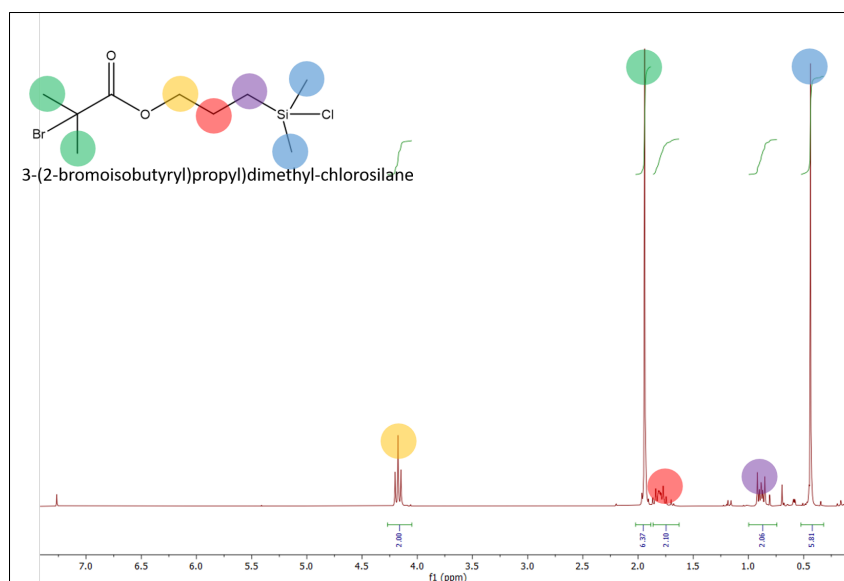


Figure 8.3: ^1H -NMR of the synthesized 3-(Bromoisobutyryl)propyl)dimethylchlorosilane. CDCl_3 was used as solvent. All peaks are assigned to the corresponding protons by color, respectively.

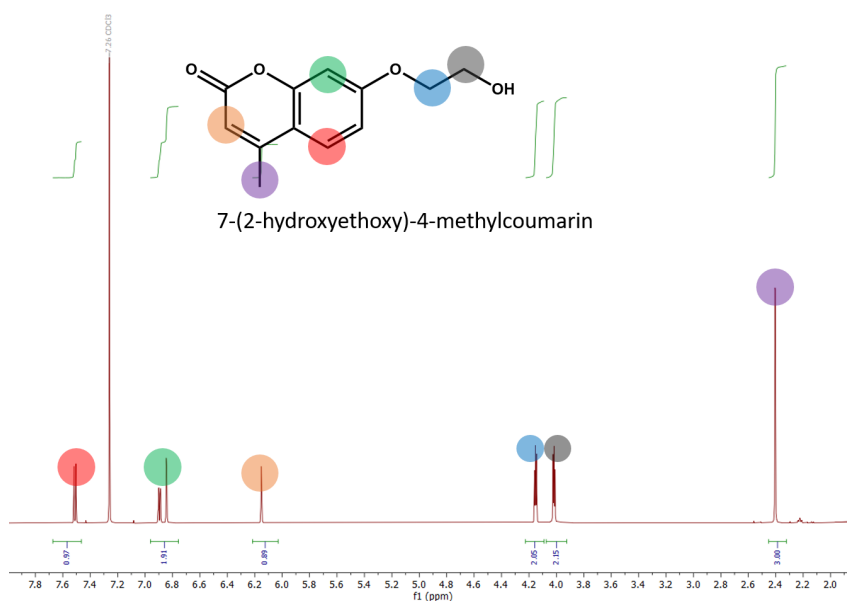


Figure 8.4: ^1H -NMR of the synthesized 7-(2-hydroxyethoxy)-4-methylcoumarin. All peaks are assigned to the corresponding protons by colour, respectively.

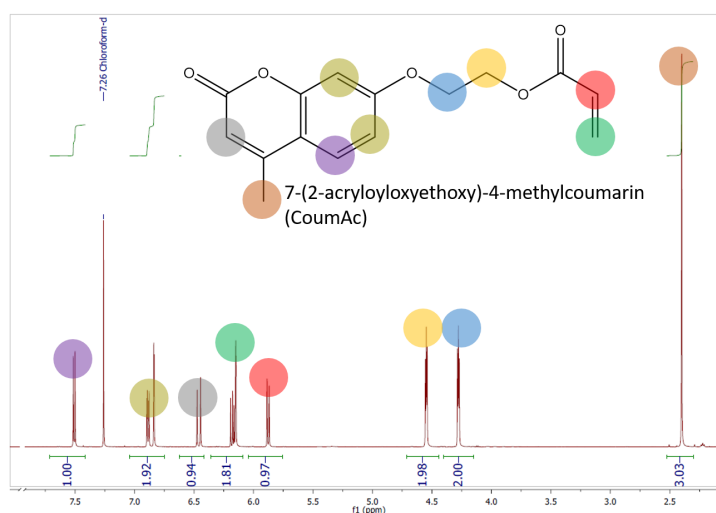


Figure 8.5: ^1H -NMR of the synthesized 7-(2-acryloyloxyethoxy)-4-methylcoumarinmethylecoumarin. All peaks are assigned to the corresponding protons by colour, respectively.

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Issue 43, 2019

From the journal:
Soft Matter

Slide electrification: charging of surfaces by moving water drops

Amy Z. Stetten,^a Dmytro S. Golovko,^a Stefan A. L. Weber^{ib} and Hans-Jürgen Butt^{ib} ^{*a}

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Abstract

We investigate the charge separation caused by the motion of a water drop across a hydrophobic, insulating solid surface. Although the phenomenon of liquid charging has been consistently reported, these reports are primarily observational, results are difficult to reproduce, and no quantitative theory has been developed. In this work, we address both the experimental and theoretical sides of this problem. We reproducibly measure the charge gained by water drops sliding down a substrate, and we outline an analytical theory to describe this charging process. As an experimental system, we choose water drops moving down an inclined plane of glass hydrophobized with perfluoro octadecyltrichlorosilane (PFOTS). On this surface, sliding drops gain a positive charge. We observe charge saturation in three variables: increasing drop number, increasing interval between drops, and increasing drop-sliding length. These charge saturations indicate a limited "storage capacity" of the system, as well as a gradual discharging of the surface. To explain these results, we theorize that some fraction of the charge in the Debye layer is transferred to the surface rather than being neutralized as the drop passes. This fraction, or "transfer coefficient", is dependent on the electric potentials of surface and drop. All of our experimental charge saturation results can be interpreted based on the proposed theory. Given that nearly every surface in our lives comes in contact with water, this water-dependent surface charging may be a ubiquitous process that we can begin to understand through the proposed theory.

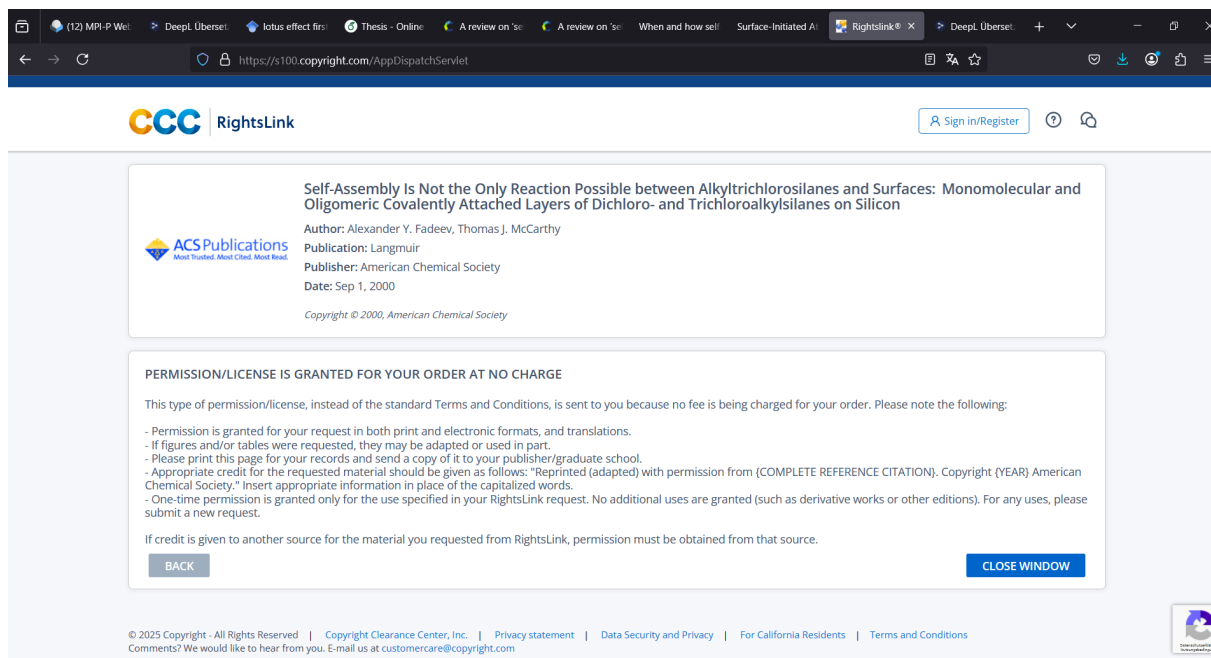
Slide electrification: charging of surfaces by moving water drops

A. Z. Stetten, D. S. Golovko, S. A. L. Weber and H. Butt, *Soft Matter*, 2019, **15**, 8667 DOI: 10.1039/C9SM01348B

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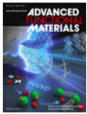
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Wetting of Surface Grafted Hydrophilic-b-Hydrophobic Block Copolymer Brushes

Author: Benjamin Leibauer, Y. Wang, Hans-Jürgen Butt, et al
Publication: Advanced Functional Materials
Publisher: John Wiley and Sons
Date: Mar 10, 2025

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8.3 Tabelle Eigenständigkeitserklärung KI-Tools

Table 8.1: Nutzung KI-Tools

KI-Tool	Genutzt für	Warum	Wann
DeepL Übersetzer	Übersetzung	unbekannte Wörter	einzelne Wörter in jedem Kapitel
DeepL Write	Umformulierung	Grammatik/bessere Lesbarkeit	einzelne Sätze in jedem Kapitel
ChatGPT	Latech Code	Fehlersuche im Code	in jedem Kapitel

8.4 Publications

How Surface and Substrate Chemistry Affect Slide Electrification

Benjamin Leibauer, Ognen Pop-Georgievski, Mariana D. Sosa, Yun Dong, Wolfgang Tremel, Hans-Jürgen Butt, and Werner Steffen*



Cite This: *J. Am. Chem. Soc.* 2024, 146, 10073–10083



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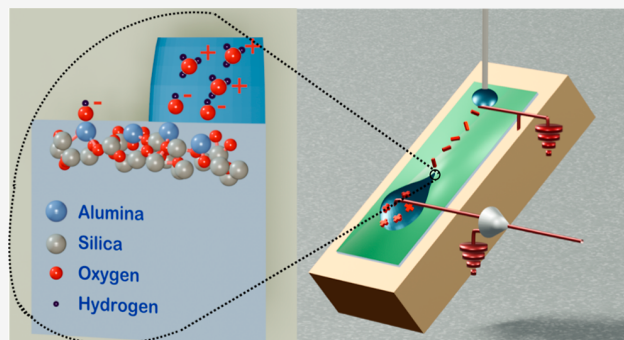


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Supporting Information

ABSTRACT: When water droplets move over a hydrophobic surface, they and the surface become oppositely charged by what is known as slide electrification. This effect can be used to generate electricity, but the physical and especially the chemical processes that cause droplet charging are still poorly understood. The most likely process is that at the base of the droplet, an electric double layer forms, and the interfacial charge remains on the surface behind the three-phase contact line. Here, we investigate the influence of the chemistry of surface (coating) and bulk (substrate) on the slide electrification. We measured the charge of a series of droplets sliding over hydrophobically coated (1–5 nm thickness) glass substrates. Within a series, the charge of the droplet decreases with the increasing droplet number and reaches a constant value after about 50 droplets (saturated state). We show that the charge of the first droplet depends on both coating and substrate chemistry. For a fully fluorinated or fully hydrogenated monolayer on glass, the influence of the substrate on the charge of the first droplet is negligible. In the saturated state, the chemistry of the substrate dominates. Charge separation can be considered as an acid base reaction between the ions of water and the surface. By exploiting the acidity (Pearson hardness) of elements such as aluminum, magnesium, or sodium, a positive saturated charge can be obtained by the counter charge remaining on the surface. With this knowledge, the droplet charge can be manipulated by the chemistry of the substrate.



INTRODUCTION

The formation of charges at solid–gas interfaces after contact with liquids (i.e., charge separation¹) is an universal problem, but it is still not well understood.² There are several channels through which water droplets can spontaneously acquire a charge. At the end of the 19th century, raindrops were shown to be either positively or negatively charged.³ Further experiments demonstrated that a single water droplet becomes charged when it splashes onto a solid or liquid surface or flows through a tube.^{1,4–6} The sign of the charge can vary and be affected, for example, by the application of an electric field or the material of the tube.^{1,5,6} On this basis, it was found that a water droplet sliding over a polytetrafluoroethylene (PTFE) surface becomes charged. This effect became known as slide electrification.^{7,8} It is even possible to generate electrical energy from individual water droplets^{9–12} to power LEDs.¹³ Recently, it was found that the charging due to slide electrification can lead to electric potentials of up to 1 kilovolt.¹⁴

Slide electrification has been observed on many hydrophobic surfaces such as PTFE,^{7,10,11,13} fluorinated ethylene propylene,^{9,15,16} and fluorinated glass.^{8,17,18} In all these cases, the surface behind a sliding drop of water with a pH of around 5.5 (pH of DI water in equilibrium with air) becomes negatively charged.^{19,20} The droplet is positively charged by the

remaining countercharges. The most likely process is that an electric double layer forms at the base of the droplet and that the interfacial charge remains on the surface.^{2,11,17,20,21} In the case of water, it is assumed that hydroxide anions (HO^-) are formed by the autoprotolysis of water ($2\text{H}_2\text{O} \leftrightarrow \text{H}_3\text{O}^+ + \text{HO}^-$) or are the product of an acid base reaction between the hydrophobic surface and the water.^{11,15,19,21,22} It is reported that the charge separation happens at the back of the droplet at the three-phase contactline.²³ For some type of surfaces, the charging effects were explained in terms of an electron transfer between substrate and water droplet and models have been proposed.²⁴

For slide electrification, only surfaces with receding contact angles (RCA) $> 50^\circ$ have been used. One reason is that droplets with smaller RCA no longer slide as easily. In addition, high RCAs appear to lead to higher droplet charges. One recently proposed charging mechanism attributes charge separation to the upward convective flow at the rear of the

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contact line. It leads to an increase in the screening length and, as long as the convection is stronger than the diffusion of counterions, the separation takes place at the rear contact line.²³ It has been shown that the adsorption of protons or hydroxide ions can be influenced by surface modification. Surface-bound amine groups can be protonated as Brønsted bases so that the solid surface becomes positively charged and the droplet negatively charged ($\text{surface-NH}_2 + \text{H}_2\text{O} \rightarrow \text{surface-NH}_3^+ + \text{HO}^-$).¹⁷

Recently, the acid–base model (proton donor–acceptor) was used to describe the charge separation in slide electrification, in which a PTFE surface interacts as a proton acceptor or donor.¹¹ In this context, the effect of pH^{10,11,25} and various dissolved ions^{11,15,21,25} on the droplet charge has been investigated. It has been proposed that the surface charge acquired by the sliding droplet and the ζ potential in the PTFE–water interface have the same physical basis. Therefore, under certain conditions, the same model can capture both charge in sliding droplets and ζ potentials.¹¹

In contrast to PTFE, fluorinated glass has different substrate (bulk) and surface (coating) chemistry. For fluorinated glass, we have a hydrophobic surface bonded to a hydrophilic substrate. This system allows us to vary the substrate and surface chemistry.

In this work, we use different glass substrates and coatings to investigate the influence of surface and substrate chemistry on slide electrification. In general, glass consists of a network builder such as silicon dioxide (SiO_2). By adding other metal oxides to the melt, other cations can be introduced into the network, thereby changing the physical (e.g., the dielectric permittivity ϵ_r) and chemical properties of the glass.^{26,27} We demonstrated on flat hydrophobic surfaces that the dielectric properties influence the droplet motion by its dielectric permittivity ϵ_r and thickness d (Figure 1). The permittivity ϵ_r indicates how easily a material can be polarized in an electric

field. The higher the dielectric permittivity, the better the surface charges are screened. The field strength of the deposited charge decreases and drop motion is less influenced by slide electrification.²⁰ Since we measured a droplet charge in the order of nano-Coulomb and assumed that the droplet charge is generated by the adsorption of ions, we used the polarizability α to investigate the influence of the substrate chemistry.^{8,11,17} The polarizability can be determined by the Clausius–Mossotti relation. This equation links the permittivity ϵ_r , a macroscopically measurable quantity, with the electric polarizability α a microscopic (molecular) quantity.²⁸

In this work, we show that the substrate and the coating can change slide electrification in a more complex way. The glass was coated by chemical vapor deposition (CVD) with perfluorooctyltrichlorosilane (PFOTS)^{8,17,20,29} or octyltrichlorosilane (OTS)^{30,31} to generate a hydrophobic layer. To analyze the influence of both the substrate chemistry and the coating, we measured droplet charging for different substrates and different coatings. In addition, we tested the influence of the surface roughness. Our results can be used in future applications to increase the droplet charge.

EXPERIMENTAL SECTION

Substrates and Coating. Aluminosilicate glass ($25 \times 76 \times 0.330$ mm³, Schott AG, Germany), quartz glass slides ($25 \times 76 \times 1$ mm³, fused silica, Thermo Fisher Scientific, USA), sodium silicate glass ($26 \times 76 \times 1$ mm³, Thermo Fisher Scientific Gerhard Menzel B.V. & Co. KG, Germany), lanthanum silicate glass slides ($25 \times 76 \times 1.5$ mm³, Schott AG, Germany), and polytetrafluoroethylene foil (PTFE, thickness 0.05 mm, REIFF Technische Produkte GmbH, Germany) were used as substrates. The main difference in the chemistry of the glasses is the amount and type of their ionic components. Quartz glass contains only 0.01% of ionic components, sodium silicate glass 27.1%, aluminosilicate glass 40%, and lanthanum glass 75.1% (for details, see Supporting Information, Tables S1–S4).

Before applying the surface coating, the glass slides were rinsed with ethanol, cleaned with 2-propanol (both absolute, Honeywell, Germany) in an ultrasonic bath for 30 min, and then treated with hydrochloric acid (37%, Sigma-Aldrich, Germany) in methanol (VWR chemicals, France) (ratio 1:1) for 30 min.³² Since a change in the chemical surface composition and the surface roughness (etching) of the lanthanum silicate glass was observed in the last step, no treatment with hydrochloric acid was carried out for the lanthanum silicate glass (Figure S1, Tables S5 and S6). After activation, the glass slides were rinsed three times with methanol and then with deionized and filtered water (DI water, 18 M Ω cm, obtained from an Arium Pro, Sartorius, Germany) and then dried with nitrogen gas. Subsequently, the surface was treated with an oxygen plasma (Diener electronic Femto, Plasma-Surface-Technology, Germany, 6 cm³ min^{−1} oxygen flow rate, 300 W) for 5 min. The glass slides were transferred directly to a desiccator. For CVD, 1 mL of 1H, 1H, 2H, 2H-perfluorooctyltrichlorosilane (PFOTS, 97% Alfa Aesar) or octyltrichlorosilane (OTS, 97% Sigma-Aldrich, Germany) was placed in a glass Petri dish in the middle of the desiccator. The CVD reaction was carried out at a pressure of less than 200 mbar for 1 h at room temperature. After the reaction, the samples were rinsed three times with ethanol and DI water (to remove side products, see Figure S2), dried with nitrogen gas, and subsequently dried in a desiccator at less than 100 mbar for at least 2 h.³³ Throughout the paper, we use the nomenclature for samples Coating@substrate.

Atomic Force Microscopy. Surfaces were imaged in tapping mode (JPK NanoWizard 4, Bruker Nano GmbH, USA) with a cantilever (type OPUS, 160-AC-NA, back side coating with reflective aluminum) with 300 kHz resonance frequency, a spring constant of 26 N m^{−1} and a nominal tip radius <7 nm (Figure S3). The calculation of the root mean square roughness (RMS) roughness was done with the software Gwyddion on part of the images of 15 $\times$ 15 μm^2 . The

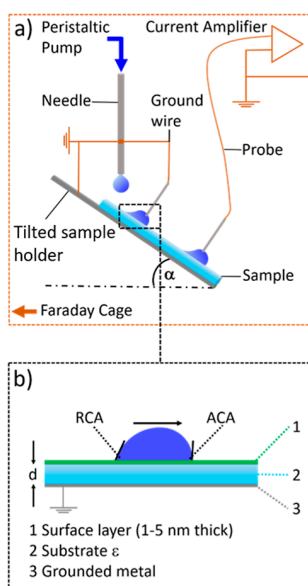


Figure 1. (a) Schematic of the experimental set up. (b) Relation between droplet, coating, and substrate. The thickness of the coating varies among the individual substrates. ϵ is the dielectric permittivity of the substrate and its thickness. ACA is the advancing contact angle and RCA the receding contact angle of the droplet.

Table 1. Measured Surface Roughness [RMS Over $15 \times 15 \mu\text{m}^2$], Static Advancing (ACA) and Receding (RCA) Contact Angles and the Difference Between ACA and RCA (Hysteresis), Thickness of the Coating, the ζ Potential of the Coated Substrates $\zeta_{\text{c&s}}$, and Calculated ζ Potential of the Coating (ζ_{c}). The ζ Potential Value Corresponds to the Measured ζ Potential at pH of 5.5

sample	RMS/nm	ACA/°	RCA/°	hysteresis/°	thickness coating/nm	$\zeta_{\text{c&s}}$ /mV	ζ_{c} /mV
PFOTS@sodium silicate glass	0.5 ± 0.1	119 ± 1	101 ± 3	18 ± 3	4.9 ± 1.8	-14 ± 2	12 ± 3
PFOTS@sodium silicate glass (sandblasted/1.5 bar)	9 ± 6	112 ± 2	80 ± 3	32 ± 2			
PFOTS@sodium silicate glass (sandblasted/2 bar)	104 ± 39	129 ± 1	98 ± 2	31 ± 2			
PFOTS@quartz glass	0.5 ± 0.1	116 ± 2	83 ± 2	33 ± 3	1.3 ± 0.1	-16 ± 2	1 ± 3
PFOTS@lanthanum silicate glass	0.5 ± 0.1	106 ± 1	80 ± 1	26 ± 1	5.6 ± 0.5	-23 ± 2	-6 ± 3
PFOTS@aluminosilicate glass	0.8 ± 0.1	111 ± 1	88 ± 2	23 ± 2	1.0 ± 0.1	-18 ± 2	9 ± 3
OTS@sodium silicate glass	0.7 ± 0.1	111 ± 2	97 ± 2	14 ± 3	1.5 ± 0.3	-4 ± 2	22 ± 3
OTS@quartz glass	0.5 ± 0.1	109 ± 1	89 ± 1	20 ± 1	1.3 ± 0.7	-20 ± 2	-4 ± 3
OTS@lanthanum silicate glass	0.5 ± 0.1	106 ± 2	90 ± 2	16 ± 3	0.8 ± 0.1	-13 ± 2	4 ± 3
OTS@aluminosilicate glass	1.6 ± 0.1	101 ± 1	89 ± 3	12 ± 3	1.1 ± 0.4	-19 ± 2	8 ± 3
PTFE foil ($d = 0.05 \text{ mm}$)	116 ± 9	109 ± 2	88 ± 1	21 ± 2			

images were leveled using a polynomial background of first degree (offset and plane). Each process was repeated with three independent samples. Each sample was measured in at least two different positions. The standard error was calculated using the formula $SE = \sigma \times n^{-1/2}$, where σ represents the standard deviation and n represents the sample size. The measured root-mean-square roughness of the surfaces is summarized in Table 1.

Contact Angle Measurements. To characterize the wetting properties of the surfaces, ACA and RCA were measured with a goniometer (OCA35, DataPhysics Instrument GmbH, Germany). A DI water drop ($6 \mu\text{L}$) was placed with a Hamilton syringe (needle: blunt end, coated with PTFE, 51 mm length, 0.4 mm inner diameter) onto the horizontal surface. Side view videos were recorded and analyzed with the help of software SCA20 provided by DataPhysics Instrument GmbH. An LED (3000 K) was used as the light source. After placing a drop, its volume was increased and decreased by 40 or $50 \mu\text{L}$ (dependent on the surface) with a rate of $0.5 \mu\text{L s}^{-1}$ and 2 repeats. The measured ACAs, RCAs, and calculated contact angle hysteresis are summarized in Table 1. Errors were calculated by using standard deviation; each experiment was done with three different samples and three measurements at three different surface areas. The error in the contact angle hysteresis was calculated by Gaussian error propagation. We point out that the ACA and RCA for sliding drops can be different because they change with velocity, the degree of charge deposition, and the electric potential of the droplet. Only at the onset of sliding should both should match.

Drop Charge Experiments. A custom-made experimental setup described previously was used (Figure 1a).⁸ The whole setup was placed in a Faraday cage. All metallic components were grounded (same ground). The sample was placed in a sample holder, and the tilt angle was adjusted to 50° . With a peristaltic pump (Gilson, MINIPULS 3, Wisconsin, USA), a series of water droplets were placed on top of the surface at a rate of 30 drops per minute. The needle used had an inner diameter of 2 mm, resulting in a drop size of $45 \pm 2 \mu\text{L}$. The needle was positioned 0.5 cm above the sample surface. To discharge possible charges in the droplet, the droplet first slides through a ground wire (Figure 1a). The distance between the ground wire and the electrode was 4 cm (sliding distance). A probe, connected to a current amplifier (DDPCA-300, FEMTO, Germany, gain of 10^6 V/A with a raise time of 0.8 ms), was used to measure the discharge current of the droplets. By integration of the current signal over the discharging time, we calculated the drop charge of each droplet (Figure S4). The data were recorded using a multifunction box (National instruments, NI USB-6366, Hungary) connected to a computer. To electrically neutralize the surface of the sample prior to every drop charge measurement, an ion air blower (Simco-Ion, Aerostat PC Ionizing Air Blower, USA) was applied for 5 min. For the evaluation, we used the drop charge of the first droplet and the saturated drop charge. For this, we measured the charge of 500 droplets. The drop charge decreases with the increasing drop number.

From the point where the drop charge reached a constant value, we averaged it to obtain the saturated drop charge (Figure S4). We measured three different samples three times at three different places. For the evaluation, we calculated the average value from these nine drop charges with the corresponding drop number of each sample. The standard deviation was then used to determine the measurement uncertainty of the droplet charge for each drop number, with the measurement uncertainty of the dropl charge at dropl number 250 being used for the measurement uncertainty in the saturated state (Figure S5). The averaged drop charges of all samples are compiled in Figure S6. We used fresh DI water for each experiment. At the time of use, the DI water had a pH of 5.5 due to the ubiquitous uptake of CO_2 from the surrounding air.

Spectroscopic Ellipsometry. Measurements were performed on a J.A. Woollam M-2000X spectroscopic ellipsometer operating in rotating compensator mode at an angle of incidence range of $60\text{--}80^\circ$ (with a step of 2.5°) and spectral range of $\lambda = 250\text{--}1000 \text{ nm}$. The data obtained was fitted with the CompleteEASE software using a multilayer model. Back side reflections (which limit the analytical performance when measuring on transparent substrates) were avoided by scratching the substrate backside. The complex refractive indices of all substrates were determined immediately after their activation using a superposition of Cauchy dispersion ($n(\lambda) = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4}$) and Urbach absorption tail ($k(\lambda) = k_1 \cdot e^{k_2 \cdot (1240/\lambda - 1240/\lambda_b)}$) functions, where A , B , C , k_1 , k_2 , and λ_b are adjustable parameters (Table S7). All reported thickness values are averages obtained from six independent measurements, expressed as mean $\pm$ standard deviation.

X-ray Photoelectron Spectroscopy. X-ray photoelectron spectroscopy (XPS) measurements were carried out with a K-Alpha⁺ spectrometer (ThermoFisher Scientific, East Grinstead, UK). The samples were analyzed using a microfocused, monochromated Al K α X-ray source at an angle of incidence of 30° (measured from the surface) and an emission angle normal to the surface. The kinetic energy of the electrons was measured using a 180° hemispherical energy analyzer operated in the constant analyzer energy mode at 200 and 50 eV pass energy for the survey and high-resolution spectra, respectively. To limit the X-ray-induced destruction of the thin polymer films and to maximize the signal-to-noise ratio, 20 individual points were measured within areas of $4 \times 8 \text{ mm}^2$. At each point, survey and high-resolution core-level spectra were measured. Spectral resolutions of 1.0 and 0.1 eV were used for the survey and high-resolution spectra, respectively. All reported XPS spectra are averages of the 20 individual measurements referenced to the C1s peak of hydrocarbons at 285.0 eV. Data acquisition and processing were performed using the Thermo Advantage software. The XPS spectra were fitted with Voigt profiles obtained by convolving Lorentzian and Gaussian functions to determine the amounts in atomic % of the individual chemical species present on the analyzed surfaces. For the analysis of the OTS and PFOTS layers, the ratios of the chemical species in the high-resolution spectra taken in the C 1s region were

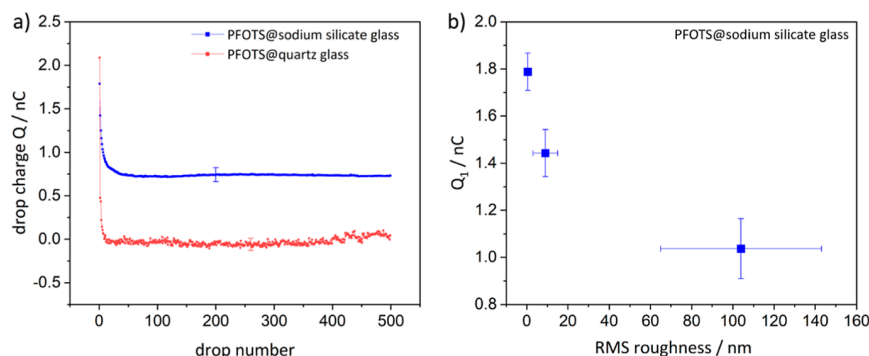


Figure 2. We measured the drop charge and assumed the counter charge to be on the surface. (a) Drop charge versus drop number for a series of 500 water drops of 45 μL moving down a surface at 50° tilt at a rate of one drop every 2 s. For the saturated drop charge, the average value of the drop charge of drop 200 until 500 was taken. The error bar indicates a typical variation from one sample to the next. (b) Drop charge of the first drop of the PFOTS@silicate substrates is plotted versus the root-mean-square roughness.

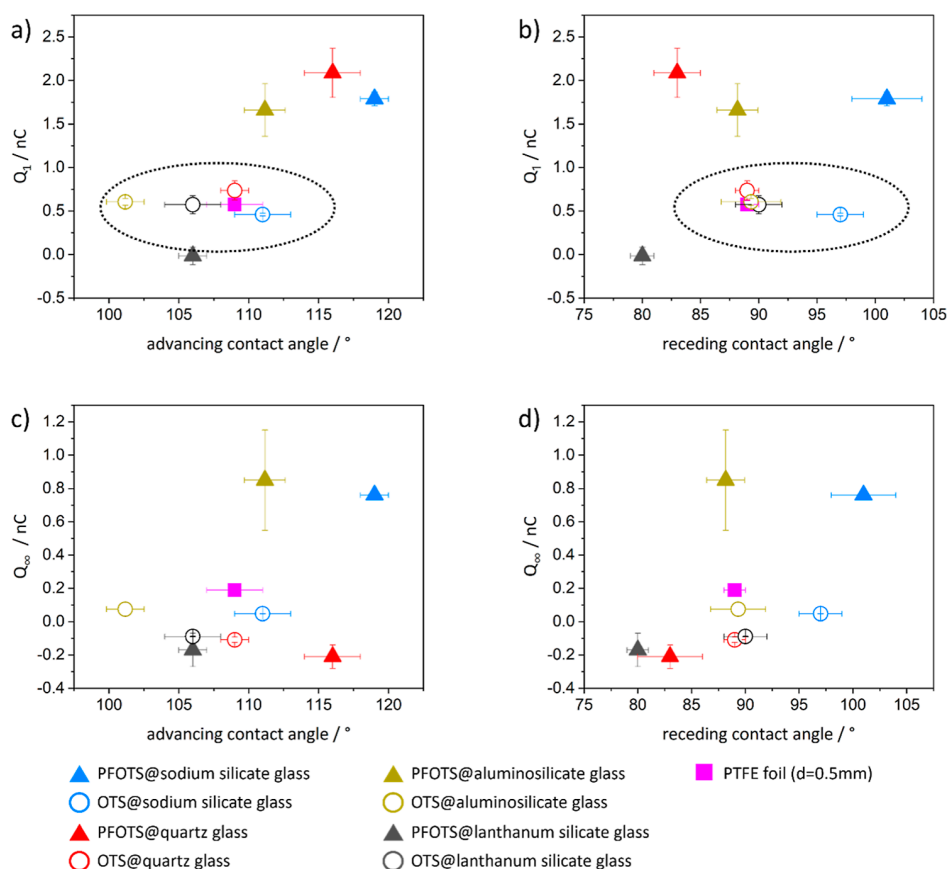


Figure 3. Drop charge is plotted against the static advancing and RCA of the OTS (hollow data points) and PFOTS (filled data points) surfaces. The drop charge of the first drop Q_1 is plotted against the (a) ACA and (b) RCA. The saturated drop charge Q_∞ is plotted against the (c) ACA and (d) RCA.

compared with the expected, i.e., theoretical values of chemical moieties that make up the OTS and PFOTS molecules. The unreacted OTS molecule has the overall chemical formula of $\text{CH}_3(\text{CH}_2)_7\text{SiCl}_3$. Based on the chemical formula of OTS, we can expect the following characteristic XPS contributions for the C 1s region: (a) $\text{C}-\text{Si}$ (from the carbon atom bonded to the trichlorosilane group) and $\text{C}-\text{C}$ (from the aliphatic CH_2 and CH_3 groups) contributions, with a characteristic (i.e., theoretical) quantitative ratio of 1:8 between the two contributions. Similarly, an unreacted PFOTS molecule has an overall chemical formula of $\text{CF}_3(\text{CF}_2)_5\text{CH}_2\text{CH}_2\text{SiCl}_3$. Considering the chemical formula of PFOTS, we can expect the following characteristic XPS signals for

the C 1s region: (a) $\text{C}-\text{Si}$ signal originating from the carbon atom bonded to the trichlorosilane group, a contribution of the CH_2 group adjacent to the perfluorooctyl chain (i.e., C^*-CF_2), a contribution from the $(\text{CF}_2)_5$ chain, and a CF_3 peak from the chain end. From the chemical formula PFOTS, we expect a characteristic quantitative ratio between the individual contributions constituting the C 1s spectrum of $\text{C}-\text{Si}/\text{C}^*-\text{CF}_2/\text{CF}_2/\text{CF}_3 = 1:1:5:1$. The close agreement between the theoretically expected and experimentally determined ratios can serve as a guideline for the chemical structure of the OTS and PFOTS layers. In the Cl 2p region, the presence of Cl-Si signals originating from the anchoring chlorosilane groups can be used to detect the presence of unreacted precursor molecules. The analyzer transmission

function, Scofield sensitivity factors, and effective attenuation lengths (EALs) for photoelectrons were applied for quantification. EALs were calculated using the standard TPP-2 M formalism. The BE scale was controlled by the well-known position of the photoelectron C–C and C–H, C–O and C(=O)–O C 1s peaks of poly(ethylene terephthalate), and Cu 2p, Ag 3d, and Au 4f peaks of metallic Cu, Ag, and Au, respectively. The BE uncertainty of the reported measurements and analysis is in the range of ± 0.1 eV.

Dielectric Spectroscopy. A Novocontrol Alpha frequency analyzer consisting of a broadband dielectric converter and an active sample head was used. Samples were measured with two stainless steel electrodes with a diameter of 20 mm. A broad frequency range from 10^{-2} to 10^7 Hz was employed. All measurements were conducted at an ambient temperature. The applied voltage had an amplitude of 1 V. More details about the measurement and the measurement uncertainty can be found in the [Supporting Information](#). We measured each sample in five different areas. We used the average of five measurements to determine the permittivity of each glass. The measurement uncertainty was calculated by the standard deviation of the five measurements.

ζ Potential of the Surface. ζ potential measurements, determined via the streaming potential, were carried out with a device from Anton Paar, SurPASS3 with a 10×10 clamping cell with a distance between the electrode and sample of $100 \mu\text{m}$. We measured the ζ potential in KCl solutions at constant conductivity of 10 mS/m and different pH values to obtain the ζ potential titration curve; it is known that the ζ potential depends on both of them.^{18,34} HCl and KOH were used to adjust the pH. To determine the measurement uncertainty, we measured a sample at pH 5.5 at 10 different points. We used the standard deviation of these values to determine the measurement uncertainty. The uncertainty in the calculated ζ potential was determined by propagating the uncertainty.

Sandblasting. Some sodium silicate glass slides were sandblasted in-house to enhance the surface roughness. The samples were placed in a box. Similar to work in a glovebox, the sandblasting gun was operated with gloves. The pressure was regulated with the sandblasting gun, while the distance between the sample and the sandblasting gun was approximately 20 cm. The gun was moved manually over the sample. The sand used (SiO_2) had a grain size of $100\text{--}200 \mu\text{m}$ (AUER, Germany). The slides were treated with a pressure of 1.5 or 2 bar.

RESULTS AND DISCUSSION

For the evaluation, we used the drop charge of the first droplet, Q_1 , and the averaged drop charge Q_∞ between droplets 200 and 500. We measured the drop charge and assumed that the counter charge to be on the surface. When measuring the drop charge for series of droplets sliding down at fixed interval time, the first droplet showed the maximum charge. Then the charge decreased to reach saturation ([Figure 2a](#)) in agreement with earlier reports.⁸ For PFOTS@silicate glass, Q_∞ was also positive. Quartz glass Q_∞ became negatively charged typically after 20 droplets ([Figure 2a](#)).

Furthermore, Q_1 decreased with increasing surface roughness ([Figure 2b](#)), which agrees with earlier observations.¹⁶

To check if the wetting properties affect the drop charge, we plotted Q_1 and Q_∞ against the static advancing contact angle (ACA) and the receding contact angle (RCA) ([Figure 3](#)). For both Q_1 and Q_∞ , we did not observe a significant correlation between the drop charge and the wetting properties, at least not in the range considered.

It was observed that Q_1 values on all OTS-coated substrates and on the PTFE foil were similar with $Q_1 \approx 0.5\text{--}0.8$ nC (dashed line, [Figure 3a,b](#)). In contrast, on the PFOTS-coated samples, Q_1 depended on the substrate. Q_1 values on PFOTS@quartz glass, PFOTS@silicate glass, and PFOTS@aluminosilicate glass were in the range around 2.0 nC, while no

drop charge was measured on PFOTS@lanthanum silicate glass.

When considering drop numbers 200–500 ([Figure 3d](#)), the drop charge on the PTFE foils decreased to roughly 30% of the first drop. For the OTS and PFOTS-coated samples, Q_∞ depended on the substrate: For OTS@silicate glass and OTS@aluminosilicate glass, Q_∞ was 20–30% of Q_1 . For the OTS on quartz or lanthanum silicate glass, however, the droplet became even negatively charged ($Q_\infty \approx -0.1$ nC). For PFOTS@silicate glass and PFOTS@aluminosilicate glass, Q_∞ was 40–45% of Q_1 . For PFOTS on quartz or lanthanum silicate glass, the droplet also became negatively charged ($Q_\infty \approx -0.2$ nC).

For the further discussion of [Figure 3](#), we analyzed the coating and substrate separately. [Figure 3a](#) (dashed circle) shows Q_1 to have a similar magnitude in the case of a fully hydrogenated (OTS) or fully fluorinated (PTFE) surface. For the PFOTS (mixed hydrogenated/fluorinated)-coated substrates, Q_1 was affected by the glass substrate. For glass, it is known that it is not as homogeneous as the network theory suggests.²⁷ The atomic force microscopy (AFM) characterization of the coated and pristine sodium silicate glass showed an inhomogeneous surface ([Figures S2 and S3](#)). Since the original sodium glass surface was inhomogeneous, we exclude that we leached the surface during the cleaning step or during the drop charge experiments. Only for the lanthanum glass, we observed leaching after the treatment with HCl and MeOH ([Figure S1](#)). Therefore, we did not use this cleaning step for the lanthanum glass. Therefore, we exclude that leaching influenced the drop charge experiment. Furthermore, we exclude that ion diffusion from the substrate to droplet affects the drop charge, because ion migration in alkali glass was observed experimentally only at temperatures above 100°C .³⁵ However, this raises the question to the extent to which the homogeneity of the coating is affected by the glass substrate.³¹ The chemical identification of the observed inhomogeneity remains a challenge. KPFM analysis was not done due to the low conductivity and the thickness (1 mm) of the glass slides. For Raman spectroscopy, the lateral resolution is around $1 \mu\text{m}$. We scanned the coated sodium silicate surface with AFM at a scan size of $1 \mu\text{m} \times 1 \mu\text{m}$ ([Figure S7](#)). Even at this scan size, we observed the inhomogeneity and we could not use Raman spectroscopy to investigate the homogeneity of the coating, because it is below the resolution limit of Raman spectroscopy. Due to the inhomogeneity properties of the glass, we prepared all samples at least three times and measured the drop charge on all samples three times. We used ellipsometry to characterize the thickness and to check how far the coatings differ from each other. The theoretical layer length of a OTS or PFOTS molecule oriented perpendicular to three oxygen atoms of the substrate was around 1 nm. These values were calculated with the open source software Avogadro (force field: universal force field, [Figure S8](#)).³⁶ For the OTS coatings, we indeed measured a layer thickness in the range of a calculated monolayer on all glass substrates (~ 1 nm, [Table 1](#)). In contrast, the thickness of the PFOTS layer differed from substrate to substrate. The thickness increased from the calculated values of a monolayer the PFOTS@quartz glass (1.1 ± 0.1 nm) and PFOTS@aluminosilicate glass (1.1 ± 0.4 nm) to values, indicating the formation of a multilayer siloxane network of 4.9 ± 1.8 and 5.6 ± 0.5 nm on PFOTS@silicate and PFOTS@lanthanum silicate glass substrates, respectively.

The ellipsometry results were corroborated by XPS (Figure 4). High-resolution C 1s XPS spectra of all OTS layers could

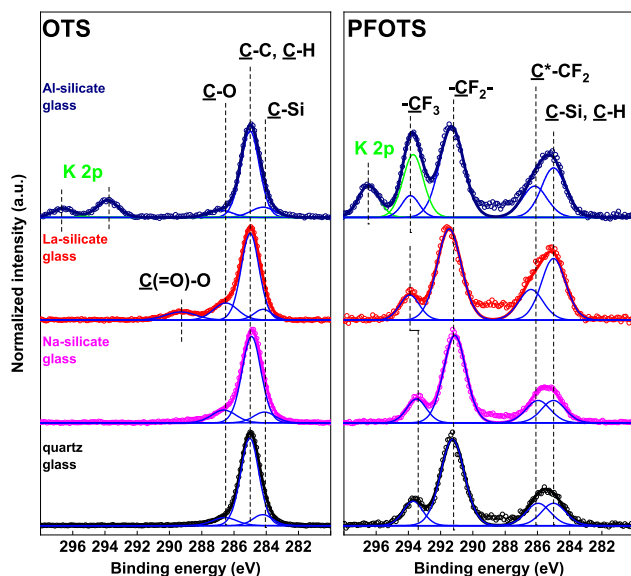


Figure 4. High-resolution XPS spectra in the C 1s region of PFOTS and OTS layers formed on quartz, sodium silicate, and lanthanum silicate glass. Measured spectra (open circles) were deconvoluted with individual contributions (blue lines). The resulting fitted envelopes of the PFOTS and OTS layers are presented with thick black, magenta, and red lines for the respective quartz, sodium silicate, and lanthanum silicate glass substrates.

be deconvoluted with a C-Si contribution at 284.2 ± 0.1 eV and a dominating C-C moiety at 285.0 eV arising from the aliphatic CH_2 and CH_3 groups. The chemical formula of OTS ($\text{CH}_3(\text{CH}_2)_7\text{SiCl}_3$) suggests a peak ratio of 1:8 between $\text{C-Si}/\text{C-C}$ moieties. The $\text{C-Si}/\text{C-C}$ amount ratios between the moieties on OTS layers formed on quartz, sodium silicate, lanthanum silicate, and aluminosilicate glass substrates were determined from the XPS surface data as 1.0:7.9, 1.0:6.9, 1.0:8.0, and 1.0:6.6, respectively, and thus agree with the expected values (Table S8). The observed minor contributions at 286.5 ± 0.2 and 289.3 ± 0.2 eV originate from various adversely physisorbed C-O hydroxyl or ether and C(=O)-O ester or organic acid species, respectively. In summary, ellipsometry and XPS show that OTS substrates have a coating with comparable chemical anchoring and a layer thickness of ≈ 1 nm, independent of the type of glass (Tables 1 and S8). Therefore, we assume that for the OTS coating, the surface coverages on all substrates are in the same range.

High-resolution C 1s XPS spectra of all PFOTS layers have been deconvoluted with a C-Si contribution at 285.0 eV

(strongly overlapped with C-C contributions of adventitious carbon contamination), a secondary shift C^*-CF_2 peak at 286.0 ± 0.1 eV, a dominating CF_2 peak at 291.1 ± 0.1 eV, and a CF_3 peak at 293.5 ± 0.1 eV. In comparison, for PFOTS surfaces the C-Si appeared at higher binding energy (285.0 eV, most probably due to the higher electronegativity of the (1H,1H,2H,2H-perfluorooctyl) chain in comparison to the n-octyl aliphatic chain. Based on the chemical formula of the PFOTS layer ($\text{CF}_3(\text{CF}_2)_5\text{CH}_2\text{CH}_2\text{SiCl}_3$), a chemically bound molecule on the substrates would lead to the expected peak ratios between the individual contributions of C-Si : $\text{C}^*-\text{CF}_2/\text{CF}_2/\text{CF}_3 = 1:1:5:1$. The quantitative ratios between the C-Si : $\text{C}^*-\text{CF}_2/\text{CF}_2/\text{CF}_3$ moieties on PFOTS layers formed on quartz, sodium silicate, lanthanum silicate, and aluminosilicate glasses were determined as 1.2:1.1:4.4:1.0, 1.3:1.0:4.4:1.0, 3.0:1.5:4.5:1.0, and 3.5:2.3:6.3:1.0, respectively (Table S8). Neglecting the adventitious carbon contamination contributions, the analysis of the C 1s spectra points to the attained PFOTS chemical structure. The decrease (in atom %) of the chemical species arising from the substrates and the concomitant increase of the carbon and organic fluorine content in the surface composition of PFOTS modified glasses indicate a different thickness of the siloxane layers (Table S8). Here, higher amounts of PFOTS were observed on sodium silicate and lanthanum silicate glass than on quartz glass and aluminosilicate glass. The different layer thicknesses are in agreement with the ellipsometry measurements (Table 1). Notably, all PFOTS and OTS layers lack Cl 2p contributions arising from Si-Cl (Table S8 and Figure S9), which further proves the complete conversion of the PFOTS and OTS molecules to single or multilayer siloxane structures.

In summary, the consistent results of ellipsometry and XPS show that all of the substrates coated with OTS and PFOTS have a coating with comparable chemical anchoring but different thickness.

To test how far the different surface coverage affects charge separation, we measured the ζ potentials of the coated ($\zeta_{\text{c\&s}}$ Table 1) and noncoated substrates (ζ_s Table 2). In all cases, the ζ potentials decreased with pH from -19 to $+17$ mV (pH 3.5) to ≈ -60 mV (pH 10) (Figure S10). Assuming that the individual ζ potentials are summable, we calculated the ζ potential of the OTS and PFOTS coating (ζ_c) by taking the difference between the $\zeta_{\text{c\&s}}$ potential of the substrate with each coating and the corresponding ζ_s potential of the substrates $\zeta_c = \zeta_{\text{c\&s}} - \zeta_s$. For the calculation, we used the ζ potential of a pH value of around 5.5 (corresponding to the pH value of the DI water used at the drop charge measurements). Contrary to expectations (same coating), the ζ_c potentials of the OTS and PFOTS coating differ from substrate to substrate (Figure 5). This agrees with the previous ellipsometry and XPS results and shows that the coatings differ from substrate to substrate.

Table 2. Density (ρ), $\zeta_{\text{substrate}}$ Potential, Mean Molecular Weight (M_{mean}), Permittivity (ϵ_r), and Polarizability (α) of the Glass Substrates. N_A is the Avogadro Constant. ϵ_0 is the Dielectric Permittivity of Vacuum. The ζ Potential Value Corresponds to the Measured ζ Potential at a pH of 5.5

substrate	$\rho/\text{g cm}^{-3}$	$\zeta_{\text{substrate}}/\text{mV}$	$M_{\text{mean}}/\text{g mol}^{-1}$	$\epsilon_r/\text{A s}^{-1} \text{V m}^{-1}$	$\alpha \times N_A \times \epsilon_0^{-1}/\text{cm}^3$
quartz glass	2 ± 0.5	-16 ± 2	60	3.65 ± 0.01	354 ± 1
sodium silicate glass	2 ± 0.5	-26 ± 2	60	6.53 ± 0.06	641 ± 1
lanthanum silicate glass	3 ± 0.3	-17 ± 2	133	10.95 ± 0.06	1106 ± 1
aluminosilicate glass	2.5^a	-26 ± 2	70.2	7.7^a	819 ± 1

^aData provided by Schott AG, Mainz.

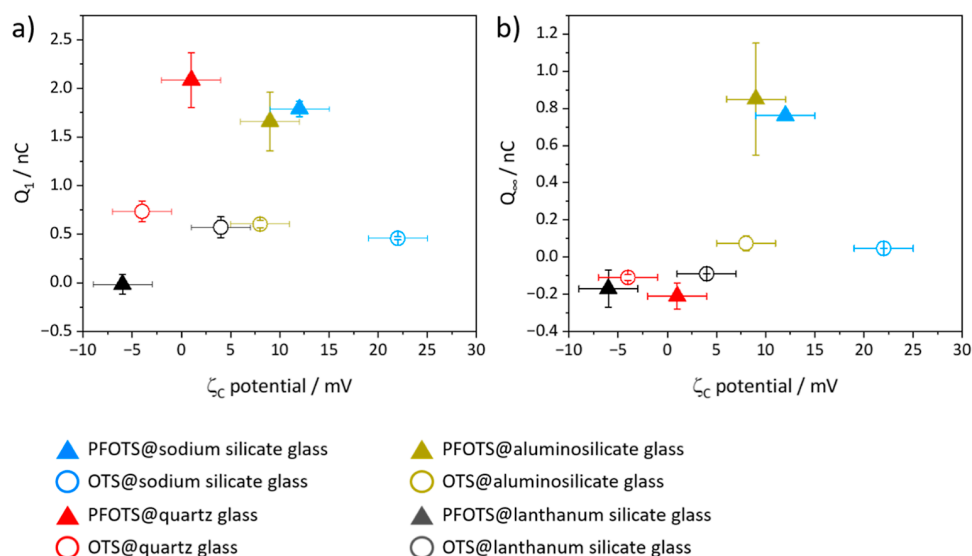


Figure 5. We calculated the ζ_c potential of the coating by the assumption that ζ potentials are addable. ($\zeta_{c\&s}$ potential = ζ_s potential + ζ_c potential). (a) Q_1 is plotted against ζ_c potential and (b) Q_∞ is plotted against ζ_c potential.

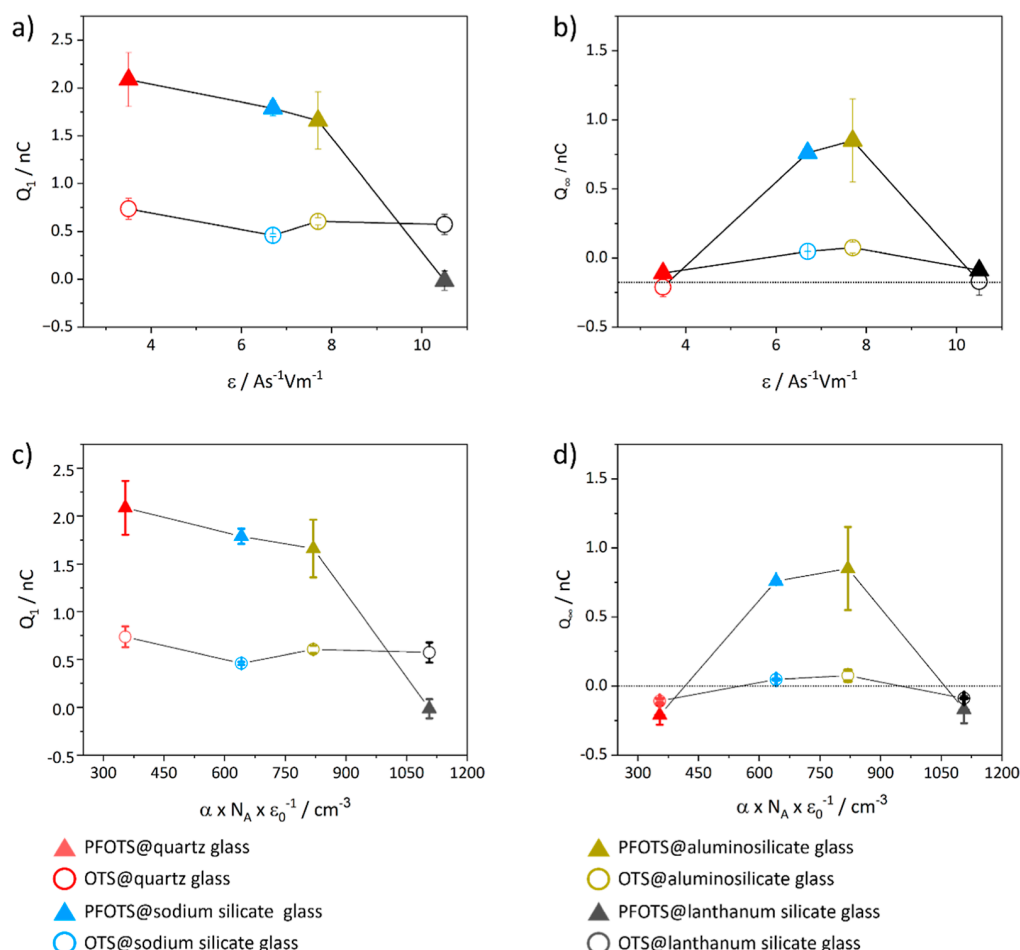


Figure 6. Drop charge plotted against polarizability α and permittivity ϵ . (a) Drop charge of the first drop Q_1 plotted against ϵ . (b) Saturated drop charge Q_∞ against ϵ . (c) Drop charge of the first drop Q_1 plotted against α . (d) Saturated drop charge Q_∞ against α .

Furthermore, there was no correlation between ζ_c potential and Q_1 or Q_∞ (Figure 5). We can state the following regarding the coating: For Q_1 , the degree of hydrogenation or fluorination is one parameter that influences slide electrifica-

tion. For a fully hydrogenated or fully fluorinated surface such as an OTS coated surface or a PTFE surface, Q_1 was in the same order of magnitude. With respect to the acid base model of slide electrification,¹¹ this agrees with a reported DFT

calculation that the absorption energy of a water molecule on a hydrophobic surface is related to the degree of fluorination/hydrogenation.²²

Furthermore, we confirmed that the thickness of the coating was substrate-dependent.³¹ Since neither the calculated ζ_c potentials of the coating nor the layer thickness correlate with Q_1 or Q_∞ , we assume that slide electrification is influenced by the substrate in addition to the coating. On the other hand, the results showed us that there could be an interaction between the surface coating and the substrate.

To analyze the influence of the substrate on slide electrification, we calculated the polarizability α (Table 2) with the Clausius–Mossotti equation.²⁸

$$\alpha \frac{N_A}{\epsilon_0} = 3 \frac{\epsilon_r - 1}{\epsilon_r + 2} \frac{M_{\text{mean}}}{\rho} \quad (1)$$

M_{mean} is the mean molecular weight of the glass substrate (Tables S1–S4). The density ρ was calculated using the measured weight and volume of each substrate (Table S9). N_A is the Avogadro constant, ϵ_0 is the vacuum dielectric permittivity, and ϵ_r is the relative dielectric permittivity of the substrate (Figure S9). The errors displayed in Table 2 of the density and polarizability were calculated with Gaussian error propagation. The measured weight and the length, width, and thickness of each glass substrate are listed in Table S9. In contrast to the other glasses, we had to cut the aluminosilicate glass ourselves. Due to its small thickness ($d = 0.330$ mm), we therefore used the density and permittivity provided by the supplier. For this reason, we do not report an uncertainty of this density or the permittivity.

When plotting Q_1 and Q_∞ against α or ϵ_r for the OTS coated substrates, we found no correlation (Figure 6). Q_1 was in all samples around 0.5 nC. For the PFOTS coated substrates, we observed that Q_1 decreases with increasing α or ϵ_r (Figure 6a,c). Q_∞ did not correlate with α or ϵ_r (Figure 6b,d). However, we observed that the Q_∞ values of the OTS- and PFOTS-coated sodium silicate glass and aluminosilicate glass had a positive drop charge. Q_∞ was negative in all other samples independent of the coating or substrate. The ζ_s potentials of the bare sodium silicate and aluminosilicate glasses are in a similar range, especially in the pH range of 3 to 6 (Figure S10). Assuming that the ζ potential is related to the hard soft acid–base (HSAB) principle, we analyzed the chemical composition of the substrates.³⁷ A comparison of the chemical composition of the surface (Table S8) and the bulk (Tables S2 and S4) of the two glasses revealed that both glasses contain magnesium, sodium, aluminum, and potassium. Furthermore, we saw that the distribution of the components on the surface and bulk are inhomogeneous.²⁷

As described in the previous paragraph, Q_∞ (Figure 2a,b) is smaller than Q_1 . We assumed that the adsorbed hydroxide ions on the surface can interact with the oxonium ions or protons of the following droplet (Brønsted acid–base reaction²⁶). It is known that the acidity or basicity of a substrate can be changed by the incorporation of special elements such as aluminum.³⁸ The acidity or basicity of a chemical species can be calculated by using the HSAB concept (involving the orbital energies). The Pearson concept is a system for classifying acids and bases in chemistry based on their specific properties. Hard acids and bases are characterized by small size, high charge, and low polarizability, while soft acids and bases are larger and have a lower charge and higher polarizability. This concept helps to

predict the stability of compounds, the outcome of chemical reactions, and the formation of compounds by associating hard acids with hard bases and soft acids with soft bases.³⁹ If we compare the calculated acidity (Pearson hardness) of sodium (21 eV), magnesium (33 eV), and aluminum (46 eV), we see that magnesium and aluminum have a high acidity.^{37,40} The quantities of these elements in the different substrates are summarized in Table 3. Thus, the positive Q_∞ value of the

Table 3. Species, Fraction of the Species, and the Pearson Hardness of Each Species of the Different

substrate	species	fraction/%	Pearson hardness η /eV	sum Pearson hardness η /eV
sodium silicate glass	Al ³⁺	1.25	46	493
	Na ⁺	13.99	21	
	Mg ²⁺	4.32	33	
aluminosilicate glass	Al ³⁺	16.24	46	1128
	Na ⁺	12.32	21	
	Mg ²⁺	3.73	33	
lanthanum silicate glass	Al ³⁺	0.38	46	17
quartz glass				0

aluminosilicate and sodium silicate glass could be attributed to the acidity of aluminum, sodium, and/or magnesium. The other components had a Pearson hardness below 20 eV; we just summarized species with a Pearson hardness above 20 eV, because we assumed that this is the hardness factor, which is important for the interaction with the hard hydroxide ion (Pearson hardness of 5.7 eV).^{37,40,41} We plotted Q_1 and Q_∞ against the Pearson hardness of the substrates (Figure 7). There is no obvious correlation for Q_1 between the drop charge and Pearson hardness, but Q_∞ increases with increasing Pearson hardness. Therefore, we assumed that the Pearson hardness in the saturated state affects the acid–base equilibrium between the droplet and the surface.

CONCLUSIONS

We were able to expand our understanding of slide electrification by analyzing the influence of the surface and substrate chemistry. We show that slide electrification is influenced by the surface and substrate chemistry. In a series of droplets sliding over a hydrophobic surface, the drop charge of the first drop Q_1 of a given series and the drop charge in the saturated state Q_∞ (drop charge after around 100 drops) cannot be described by one parameter. The charge of the first drop, Q_1 is influenced by the degree of hydrogenation or fluorination of the surface. For a fully hydrogenated or fluorinated glass surface, the influence of the substrate is negligible. For a mixed hydrogenated/fluorinated glass surface, Q_1 is influenced by the substrate. Here Q_1 decreased with increasing permittivity or polarizability of the substrate. In the saturated state, both the permittivity and the polarizability did not correlate with the saturated drop charge Q_∞ , regardless of the degree of hydrogenation or fluorination of the glass surface. Q_∞ correlates with the Pearson hardness of the substrate. With increasing Pearson hardness, Q_∞ is positive. The calculated ζ potential of the coating correlates analogously to the Pearson hardness only with the Q_∞ . In this way, we showed that the substrate chemistry plays an important role for the formation of the drop charge in the saturated state, Q_∞ . By varying the substrate (e.g., by incorporating Al³⁺), we demonstrate the

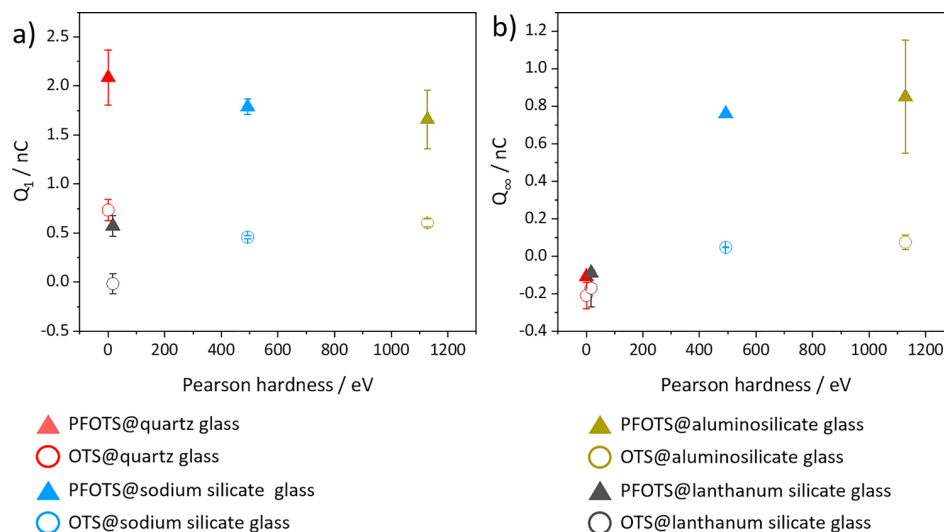


Figure 7. Drop charge plotted against the Pearson hardness. (a) Drop charge of the first drop Q_1 plotted against the Pearson hardness. (b) Saturated drop charge Q_∞ against the Pearson hardness.

impact of the substrate chemistry by exploiting the HSAB property (Pearson hardness) of Al^{3+} . We extended the model of the acid–base reaction between the droplet and surface by the HSAB model. As the Pearson hardness is a property of the substrate related to its acidity, the origin of the charge is the interaction of OH^- and H^+ with the substrate rather than the coating via acid–base reactions, i.e., the role of the substrate seems to be dominant. Therefore, future efforts to increase the drop charge in future applications should focus on manipulation of the substrate chemistry.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jacs.4c01015>.

Chemical composition of the different glass substrates, etching of the lanthanum silicate glass, analysis of the silanization, AFM analysis of all surfaces, description of the droplet charge measurement and all droplet charge measurements on all substrates, all measured parameters of the spectroscopic ellipsometry, XPS surface analysis, measured ζ -potential curve of all coated and noncoated substrates, parameters used to calculate the density of the glass substrates, and dielectric spectra of the glass substrates (PDF)

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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Notes

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Supporting Information for

How Surface and Substrate Chemistry Affect Slide Electrification

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Glass Substrates

Table S1. Chemical composition of the quartz glass slides taken from the manufacturer information Thermo Fisher Scientific, USA.

Chemical component	Molar mass / g·mol ⁻¹	Fraction / %	M _{mean} / g·mol ⁻¹
SiO ₂	60.08	99.99	60.08

The chemical composition of sodium silicate glass was analyzed by the IGR Institut für Glas- und Rohstofftechnologie, Göttingen, Germany.

Table S2. Chemical components of sodium silicate glass / Menzel microscope glass slides (Thermo Fisher scientific Gerhard Menzel B.V. & Co. KG, Germany).

Chemical component	Molar mass / g·mol ⁻¹	Fraction / %	M _{mean} / g·mol ⁻¹
SiO ₂	60.08	72.90	60.09
MgO	40.30	4.32	
Na ₂ O	61.98	13.99	
Al ₂ O ₃	101.96	1.25	
K ₂ O	94.20	0.93	
CaO	56.08	6.26	
SO ₃	80.06	0.28	

The chemical composition of lanthanum silicate glass was analyzed by IGR Institut für Glas- und Rohstofftechnologie, Göttingen, Germany.

Table S3. Chemical components of lanthanum silicate glass / N-LASF45 microscope slides (Schott AG, Mainz, Germany).

Chemical component	Molar mass / g·mol ⁻¹	Fraction / %	M _{mean} / g·mol ⁻¹
SiO ₂	60.08	24.9	107.02
ZnO	81.39	5.8	
La ₂ O ₃	325.81	14.2	
Al ₂ O ₃	101.96	0.38	
Nb ₂ O ₃	108.9	16.1	
TiO ₂	79.86	9.3	
CaO	56.08	24.6	
SrO	103.62	0.16	
ZrO ₂	123.22	4.5	

The chemical composition of the aluminosilicate glass was analyzed by IGR Institut für Glas- und Rohstofftechnologie, Göttingen, Germany.

Table S4. Chemical components of the aluminosilicatesilicate glass / AS 87® eco thin glass (Schott AG, Mainz, Germany).

Chemical component	Molar mass / g·mol ⁻¹	fraction / %	M _{mean} / g·mol ⁻¹
SiO ₂	60.08	60.00	70.21
MgO	40.30	3.73	
Na ₂ O	61.98	12.32	
Al ₂ O ₃	101.96	16.24	
K ₂ O	94.20	4.02	
CaO	56.08	0.13	
SO ₃	80.06	0.28	
ZrO ₂	123.22	0.87	
TiO ₂	79.86	0.02	
SnO ₂	150.71	0.07	
Fe ₂ O ₃	159.69	0.02	

Etching of Lanthanum Silicate Glass

After treatment with methanol and hydrochloric acid (37%) (ratio 1:1), the lanthanum silicate glass showed a blue reflection indicating a change of the surface composition. The AFM analysis revealed that the lanthanum silicate glass was etched (Figure S1). The XPS surface analysis showed that not only the roughness, but also the chemical surface composition of the lanthanum silicate glass had changed (Table S5 and table S6).

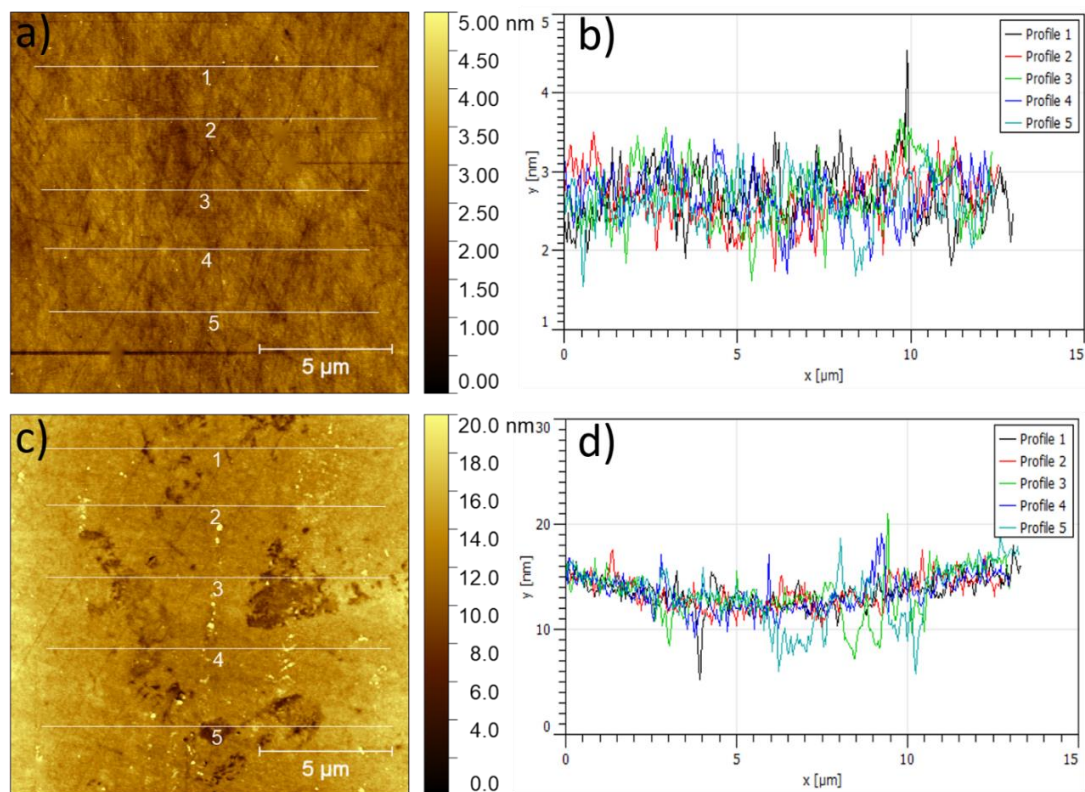


Figure S1. The AFM topography of lanthanum silicate glass was measured at a scan size of $15 \times 15 \mu\text{m}$ (tapping mode). a) AFM topography of lanthanum silicate glass before treatment with HCl/methanol (ratio 1:1, 30 min). b) Height profiles of the non HCl/methanol treated surface. c) AFM topography of lanthanum silicate glass after treatment with HCl/methanol. d) Height profiles of the HCl/methanol treated surface. Height profiles were drawn and measured through each AFM image at five different positions.

Table S5. Chemical surface composition of lanthanum silicate glass before treatment with methanol and hydrochloric acid (37%) (ratio 1:1) (see Substrates and Surface treatment). The analysis was done using XPS.

Element specific peak	Amount / atomic %
Al 2p	0.3
Si 2p	13.1
B 1s	0.5
Nb 3d5	2.6
C 1s C-C	3.1
Zr 3p3	0.6
Ca 2p3	7.1
Ti 2p3	2.9
O 1s	63.2
F 1s	2.7
La 3d5	1.9
Zn 2p	2.0

Table S6. Chemical surface composition of lanthanum silicate glass before treatment with methanol and hydrochloric acid (37%) (ratio 1:1). The analysis was done using XPS (see Substrates and Surface Treatment).

Element specific peak	Amount / atomic %
Al 2p	0.3
Si 2p	32.6
Nb 3d5	0.2
C 1s C-C	1.7
Zr 3p3	0.2
Sb 3d5	0.3
Ti 2p3	0.1
O 1s	64.7

Silanization of Glass Substrates *via* CVD

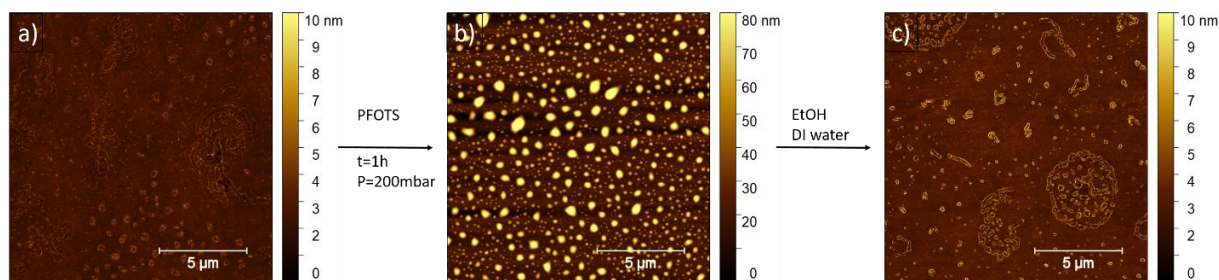


Figure S2. AFM analysis of sodium silicate glass after fluorination. AFM measurements were done in tapping mode at a scan size of 15x15 μm. a) Pristine sodium silicate glass. b) PFOTS@sodium silicate glass with side products. c) PFOTS@sodium silicate glass after rinsing with DI water and ethanol. The thickness of the PFOTS layer can not be detected by AFM. There is no distinction between clean and coated glass.

AFM Characterization of Coated Glass Substrates

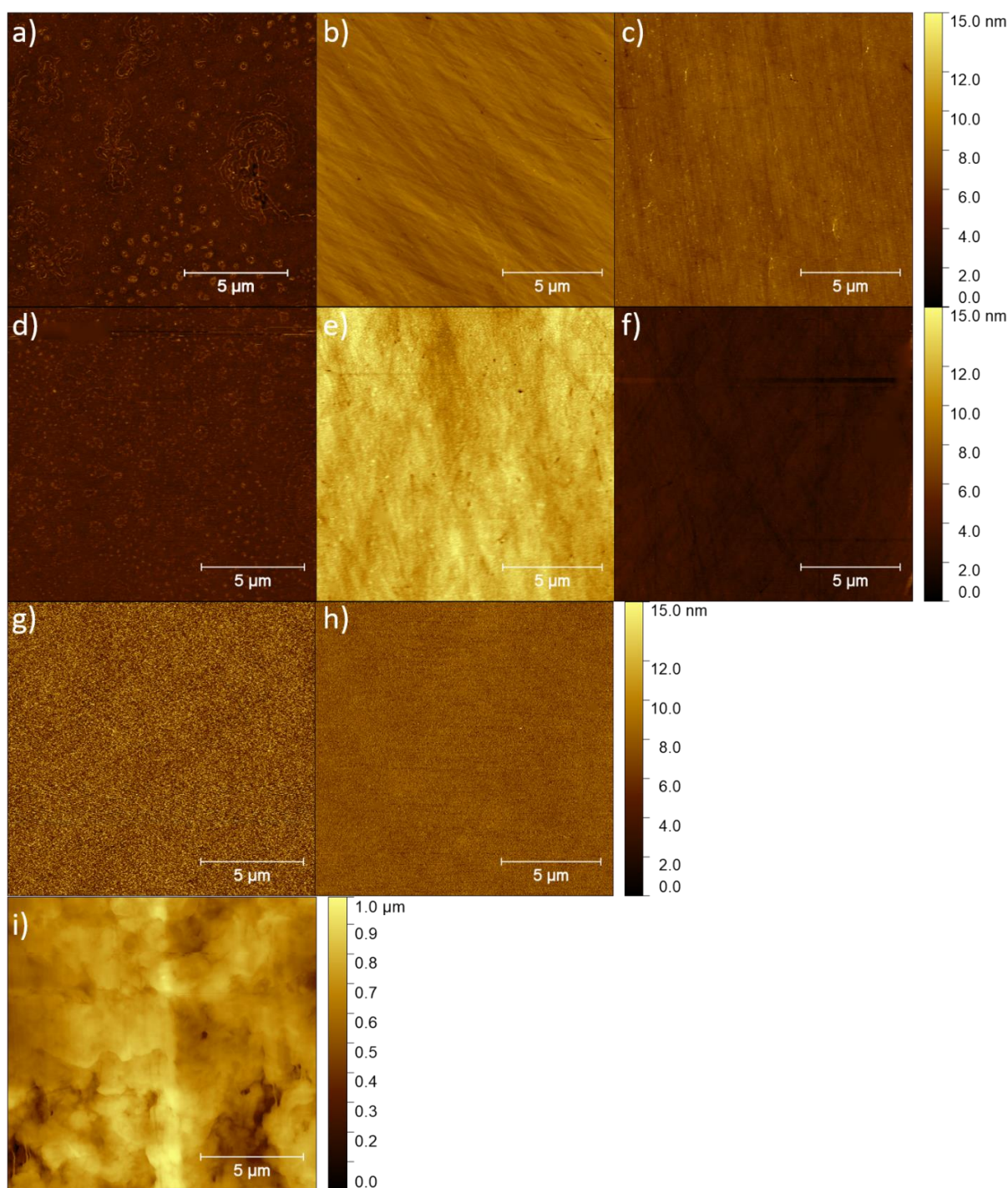


Figure S3. AFM measurements were done in tapping mode at a scan size of 15x15 μm. a) PFOTS@sodium silicate glass, b) PFOTS@quartz glass, c) PFOTS@lanthanum silicate glass, d) OTS@sodium silicate glass, e) OTS@quartz glass, f) OTS@lanthanum silicate glass, g) OTS@alumino silicate glass, h) PFOTS@aluminosilicate glass, i) PTFE foil.

Drop Charge

With our experimental setup the charge of the sliding droplets was obtained as follows. With the help of a current amplifier we measured the current of a sliding droplet. We obtained the discharge time (t^0 and t^1) of the droplet at the probe. By integrating the current over the discharge time ($\int_{t^0}^{t^1} I dt$) we calculated the charge of each droplet. For the analysis, we plotted the drop charge against the drop number.

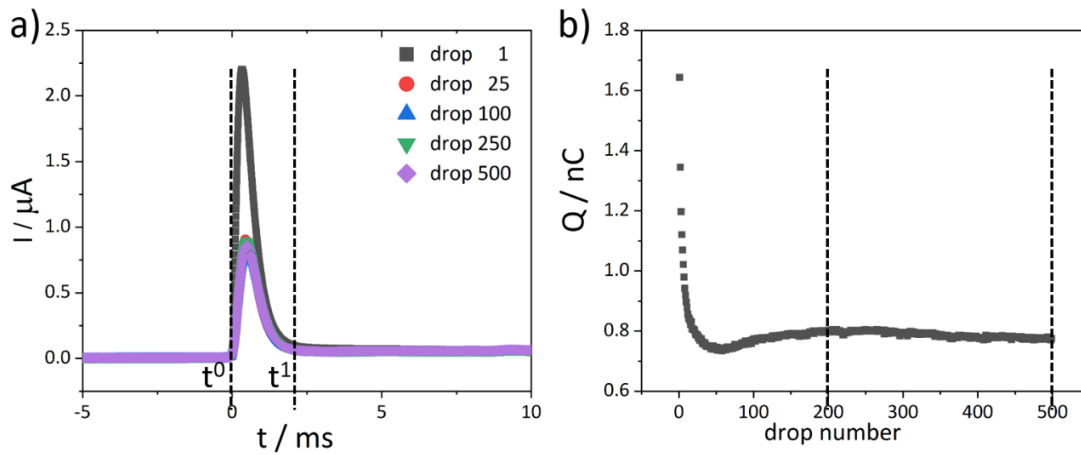


Figure S4. a) Current signal of a sliding droplet and discharge time of the droplet at the probe. By integration of the current over the discharge time (t^0 , t^1) we calculated the drop charge of each droplet. b) Calculated drop charge against the drop number. With increasing drop number the drop charge decreases. We used the average of the drop charge between droplet 200 and 500 as saturated drop charge Q_∞ .

Drop Charge evaluation

The drop charge experiments were evaluated as follows. We prepared each sample three times. We measured the drop charge at three different areas of each sample (Figure S5 a). Then we calculated the average value for each drop charge for with respect to the corresponding drop number (Figure S5 b). We used the standard deviation to determine the measurement uncertainty of each drop charge. For the measurement uncertainty in the saturated state, we used the standard deviation of the drop charge of drop number 250 (Figure S5 b). For the better overview we shifted this value from drop number 200 to 500 by an interval of 30 in Figure S6. Also for the better overview we did not plot the error bar of the first drop in Figure S6.

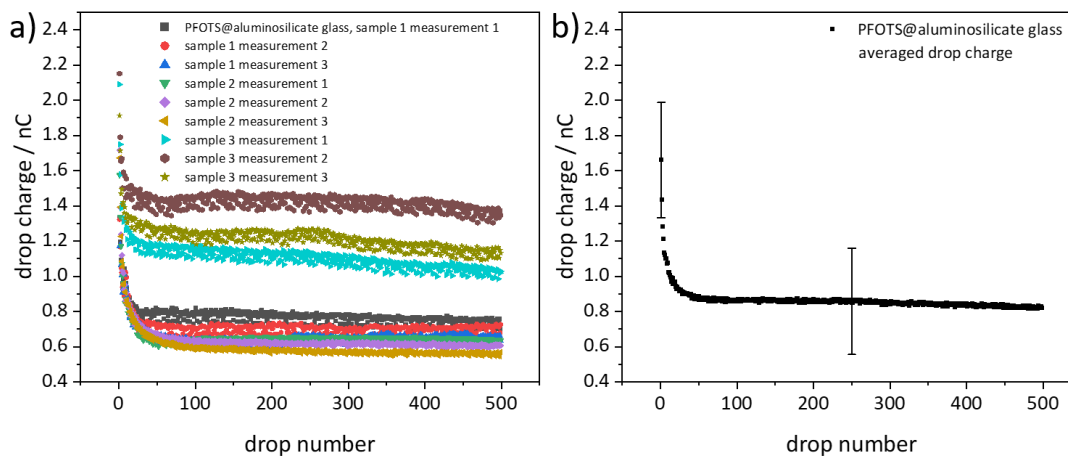


Figure S5. a) The measured drop charge of all three PFOTS@aluminosilicate glass samples. The drop charge is plotted against the corresponding drop number. b) We have calculated the mean value from the measured drop charges of the corresponding drop numbers and plotted the mean value against the respective drop numbers. The uncertainty of the drop charge was determined using standard deviation. For the saturated drop charge we used the uncertainty of the drop charge of drop number 250.

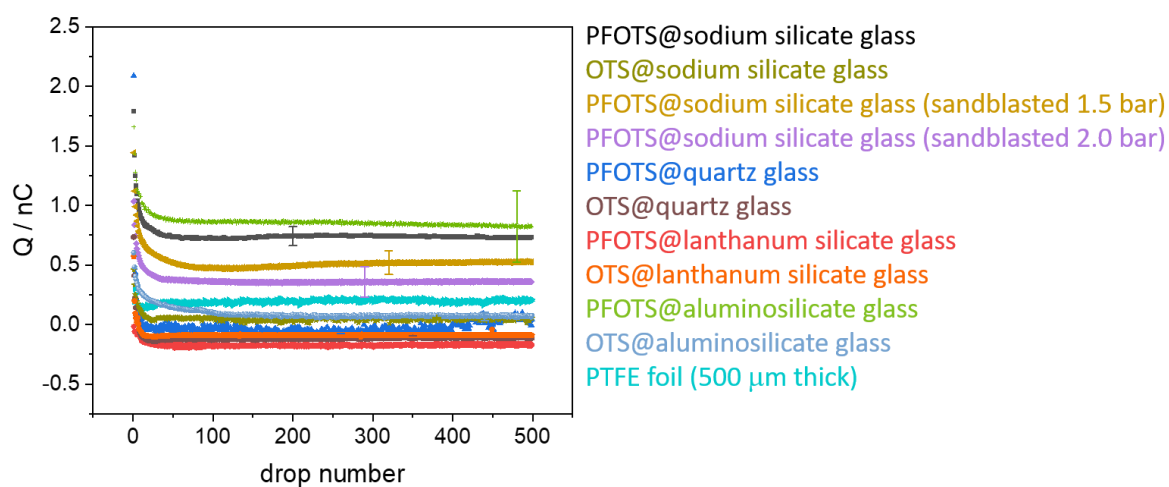


Figure S6. Averaged drop charge against the corresponding drop number of all measured samples. The calculation of the averaged drop charge is presented in Figure S5.

Table S7. Parameters of the Cauchy dispersion ($n(\lambda) = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4}$) and Urbach absorption tail ($k(\lambda) = k_1 \cdot e^{k_2(1240/\lambda - 1240/\lambda_b)}$) functions as determined from a fit of ellipsometry data.

Substrate or layer	A	B / nm ⁻²	C / nm ⁻⁴	k ₁	k ₂	λ_b / nm
quartz glass	1.443 ±4.357×10 ⁻⁵	3710 ±183	1.37×10 ⁷ ±1.28×10 ⁶	0.002 ±1.168×10 ⁻⁵	0.725 ±0.062	250
sodium silicate glass	1.500 ±3.991×10 ⁻⁵	5490 ±168	-1.36×10 ⁷ ±1.17×10 ⁶	0.075 ±8.392×10 ⁻⁵	0.608 ±0.001	250
lanthanum glass	1.769 ±3.022×10 ⁻⁴	7730 ±1297	7.75×10 ⁸ ±9.28×10 ⁶	0.132 ±9.581×10 ⁻⁵	1.338 ±0.011	250
alumino-silicate glass	1.485 ±1.331×10 ⁻⁴	6580 ±562	-2.59×10 ⁶ ±3.94×10 ⁶	0.015 ±4.24×10 ⁻⁴	1.786 ±0.069	250
OTS	1.419 ±3.592×10 ⁻⁴	17300 ±2180	-1.43×10 ⁸ ±3.2×10 ⁷			
PFTOS	1.300 ±6.784×10 ⁻⁴	10830 ±3976	-4.69×10 ⁸ ±2.52×10 ⁷			

AFM analysis of PFOTS@sodium silicate glass with a scan size 1μm x 1μm

The AFM measurements were done with the Bruker Dimension Icon with ScanAsyst device. The measurement were done with the Peak force mode in air. We used following cantilever: OLTESPA 70 kHz, 2 N/m; back side coating: reflective aluminum. The scan size was 1 μm x 1 μm.

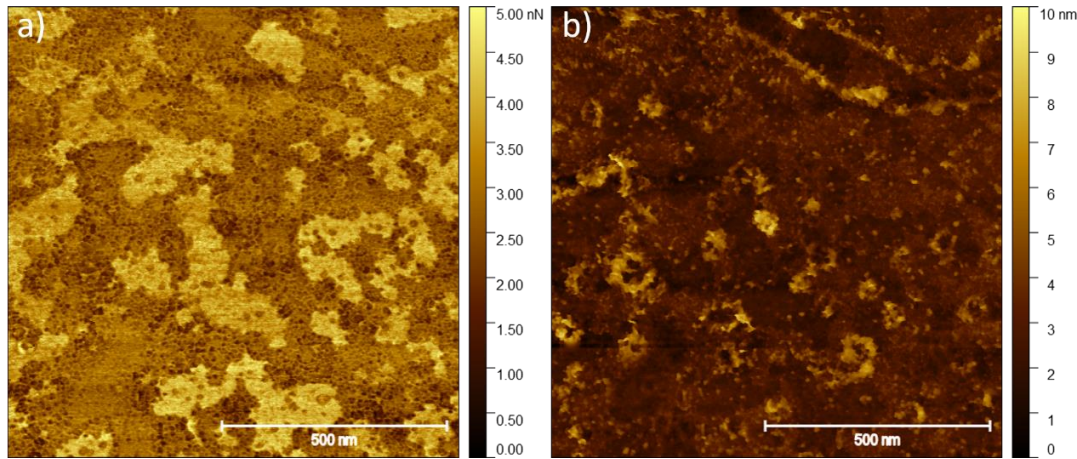


Figure S7. AFM images of the PFOTS coated sodium silicate surface. The AFM measurement were done in Peak force mode with a scan size of 1μm x 1 μm.

Model Structure and Length of an OTS and PFOTS Molecule on Glass

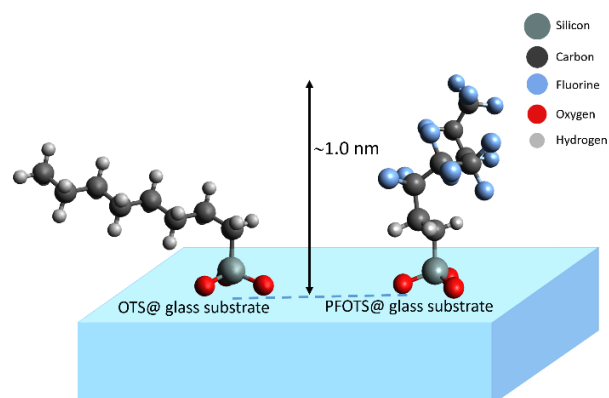


Figure S8. Model structure and length of OTS and PFOTS on glass. The molecule is bound to the three surface oxygen atoms. The calculation were done with the open source software Avogadro using UFF, a Universal Force Field. The calculation resulted in a length of 1 nm for an OTS molecule and a length of 1 nm for a PFOTS molecule bound to a glass surface.

XPS Surface Analysis

XPS was utilized to verify the formation of PFOTS and OTS layers on quartz glass, sodium silicate glass and lanthanum silicate glass samples Table S8. While the quartz glass samples show major contributions of silicon and oxygen, the surfaces of sodium silicate glass show additional contributions of sodium, potassium, calcium, and magnesium. The lanthanum silicate glass is characterized by additional amounts of lanthanum, boron, niobium, fluorine, and zinc. The formation of PFTOS and OTS silane layers is obvious from the decrease of the element content for the bare glass materials. In parallel, new signals appear from the formation of the PFTOS and OTS layers. The formation of PFOTS layer is accompanied by an increasing amount of fluorine. The appearance of distinct CF_2 and CF_3 signals in the C 1s (Figure 3) and the concomitant rise of different carbon species (Table S8) further demonstrates the formation of a PFOTS layer. The formation of an OTS layer can be demonstrated through the increasing carbon content above the level observed for the bare substrates. Notably, all PFTOS and OTS layers lack Cl 2p signals at about 199.0 eV (Figure S7), arising from Si-Cl units (Table S8) with amounts of chlorine below the detection limits of the XPS measurements. This shows the complete conversion of the silane precursors to single or multilayer siloxane structures.

Table S8. Binding energy and amount in atom% of chemical moieties present on the surfaces of quartz, sodium silicate and lanthanum silicate glasses before and after modification with PFTOS and OTS.

Region / Peak of found element	Binding energy (eV)	Bare quartz glass	Bare Na- silicate glass	Bare La- silicate glass	Bare Al- silicate glass	PFOTS@ Quartz glass	PFOTS@ Na-silicate glass	PFTOS@ La-silicate glass	PFTOS@ Al-silicate glass	OTS@ Quartz glass	OTS@ Na- silicate glass	OTS@ La-silicate glass	OTS@ Al-silicate glass
Al2p	75.1±0.2	-*	0.4	0.3	6.0	-	0.8	-	4.7	-	0.3	-	5.2
Si2p	103.4±0.1	35.2	31.2	13.1	22.6	25.9	17.1	11.1	21.8	31.1	30.2	12.2	23.6
B 1s	191.8±0.1	-	-	0.5	1.7	-	-	-	-	-	-	0.8	-
Nb 3d	207.2±0.1	-	-	2.6	-	-	-	1.7	-	-	-	2.8	-
C1s OTS $\underline{\text{C}}\text{-Si}$	284.2±0.1	-	-	-	-	-	-	-	-	0.8	0.6	0.6	1.1
C1s PFTOS $\underline{\text{C}}\text{-Si}$, $\underline{\text{C}}\text{-C}$	285	1.3	2.1	3.1	5.2	1.4	2.8	5.4	1.4	6.3	4.1	5	7.3
C1s $\underline{\text{C}}\text{-O}$, $\underline{\text{C}}\text{-O}$	286.0±0.2	-	-	-	-	1.2	2.2	2.7	0.9	0.8	0.8	1.3	0.8
C1s $\underline{\text{C}}\text{(=O)-O}$	289.3±0.2	-	-	-	-	-	-	-	-	-	-	0.8	-
C1s $\underline{\text{C}}\text{F}_2$	291.2±0.1	-	-	-	-	4.9	9.3	8.1	2.5	-	-	-	-
C1s $\underline{\text{C}}\text{F}_3$	293.6±0.2	-	-	-	-	1.1	2.1	1.8	0.4	-	-	-	-
K 2p	294.1±0.1	-	0.1	-	2.0	-	-	-	1.4	-	-	-	0.9
Zr3p	333.6±0.3	-	-	0.6	-	-	-	0.4	-	-	-	0.7	-
Ca 2p	347.2±0.5	-	1	7.1	0.3	-	0.6	3.7	-	-	-	6.5	-
Ti 2p	459.0±0.1	-	-	2.9	-	-	-	1.7	-	-	-	2.8	-
O 1s	532.3±0.8	63.6	64.1	63.2	56.9	46.7	33	36.9	54.5	61	63	61.4	58.2
F 1s $\underline{\text{F}}$	685.8±0.1	-	-	2.7	3.4	-	-	-	-	-	-	-	2.0
F 1s $\underline{\text{F-C}}$	688.5±0.1	-	-	-	-	18.9	31.8	25.2	11.4	-	-	2.1	-
La 3d	836.0±0.1	-	-	1.9	-	-	-	0.5	-	-	-	1.4	-
Zn 2p	1022.0±0.1	-	-	2.0	-	-	-	0.8	-	-	-	1.5	-
Na 1s	1072.5±0.1	-	0.8	-	1.4	-	-	-	0.7	-	0.9	-	0.6
Mg 1s	1304.7±0.2	-	0.4	-	0.5	-	0.4	-	0.3	-	0.2	-	0.3
Total amount:		100%	100%	100%	100%	100%	100%	100%	100%	100%	100%	100%	100%

*Values lower than detection limit of the XPS measurements, i.e. <0.1 atom %.

**The PFOTS and OTS layers formed on various glasses lack Si-Cl moieties from unreacted precursors.

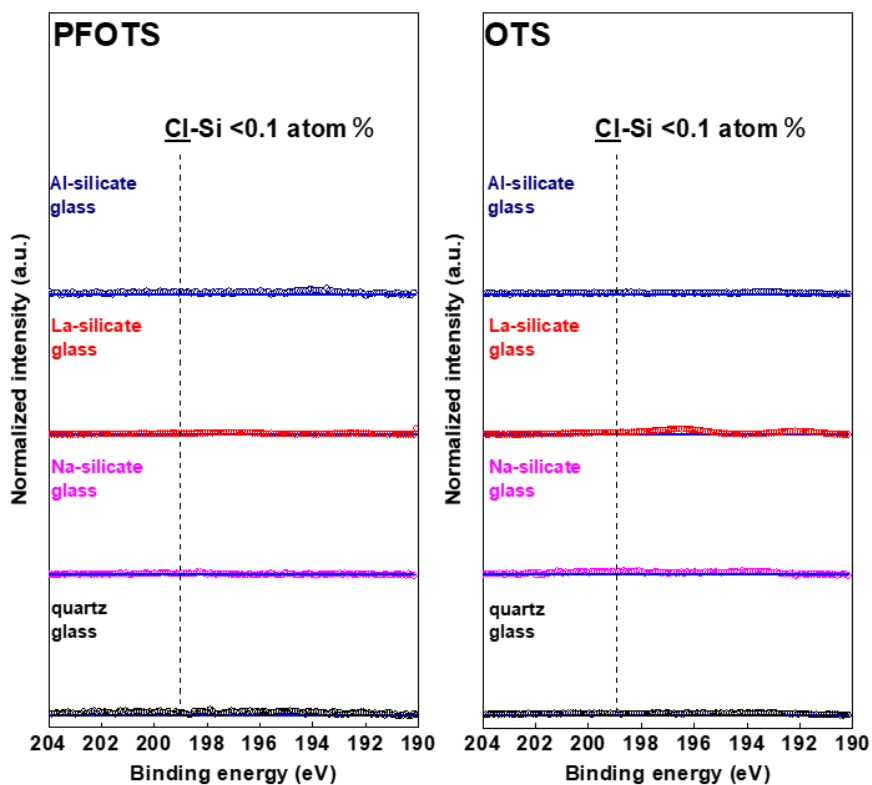


Figure S9. High-resolution XPS spectra in the Cl 2p region of PFOTS and OTS layers formed on quartz, sodium silicate and lanthanum silicate glass substrates. Measured spectra (open cycles) point to the absence of chlorine Cl-Si signals originating from precursor silane molecules thereby verifying the complete conversion of the silane precursors. The spectra are normalized to the maximum intensity observed in the C 1s spectra of the individual samples.

ζ Potential of Coated and Non-Coated Substrates

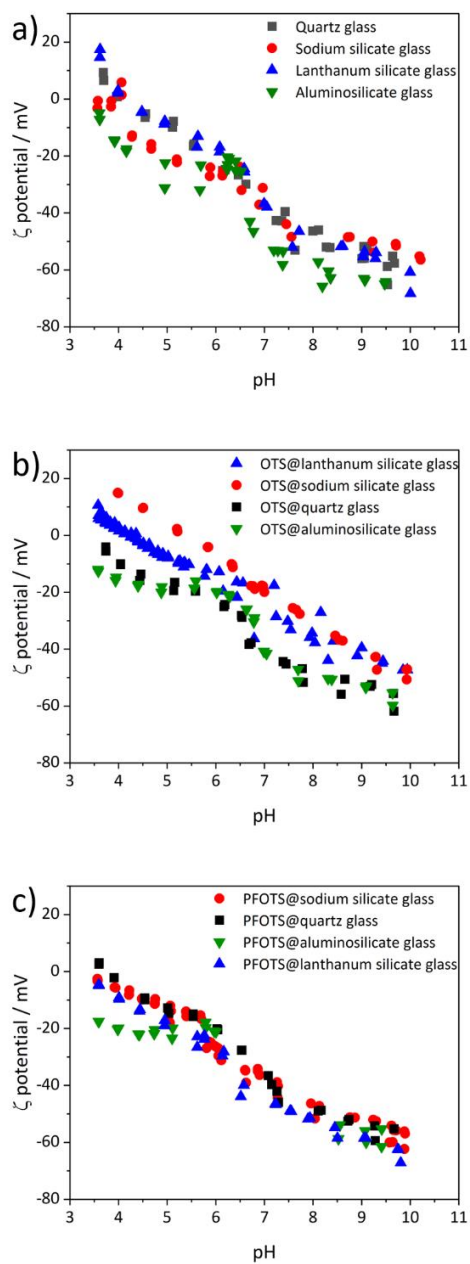


Figure S10. ζ potential of the coated and non-coated substrates in KCl solutions at constant conductivity of $10 \text{ mS} \cdot \text{m}^{-1}$ and different pH values to obtain the ζ potential titration curve. (a) ζ potential of the non-coated substrates. (b) ζ potential of the OTS coated substrates. (c) ζ potential of the PFOTS coated substrates. The measurement uncertainty was $\pm 2 \text{ mV}$. Because of the small dimension of the measurement uncertainty and a better overview we did not plot the error in this figure.

Table S9. Weight (m), length (l), width (w), thickness (d) and calculated volume (V) of the glass substrates. The error of the volume was calculated with a Gaussian error propagation. The error of the respective measuring device was used as the error of the measured quantities. The density of the aluminosilicate glass was given by supplier (Schott AG).

Glass substrate	m / g	d / mm	w / mm	l / mm	V / cm ³
Quartz glass	4.57143±0.00001	1.08±0.01	25.44±0.01	76.22±0.01	2.209±0.002
Sodium silicate glass	4.71285±0.00001	1.02±0.01	25.77±0.01	75.76±0.01	1.991±0.002
Lanthanum silicate glass	10.34304±0.00001	1.51±0.01	25.07±0.01	76.00±0.01	2.899±0.002

Dielectric permittivity

The dielectric function $\varepsilon^* = C_p^*/C_0$ results from the measured complex sample capacity, C_p^* , where C_0 is provided by the sample geometry. This is the case of an ideal (i.e., perfectly homogeneous capacitor). A stray field contributes an additional external capacity to the ideal one (C_{edge}) as $C_{meas}^* = C_p^* + C_{edge}$. The latter contribution for a round plate capacitor is given by:

$$\frac{C_{edge}}{C_0} = \frac{2d}{\pi D} \left[\ln \frac{8\pi D}{d} - 3 + (1+x) \ln(1+x) - x \ln x \right] \quad (1)$$

Here, D is the electrode diameter, $x = t/D$ with t being the electrode thickness, and d is the sample thickness. The maximum error without the edge correction is given as

$$\frac{\Delta \varepsilon'}{\varepsilon'} = \frac{C_{edge}}{C_p} = \frac{C_{edge}}{C_0 \varepsilon'} \quad (2)$$

Employing typical values ($t=1$ mm, $D=20$ mm, $d=1$ mm and $\varepsilon'=4$) and Eqs 1 & 2 results to an uncertainty of 3.7%.

There are two ways to reduce this uncertainty in the permittivity values. One is to use a sample with guard ring. The second, employed by the Novocontrol set-up and used here, is to take into account in the evaluation of the capacity the edge correction as described above. With this feature enabled in the software, the overall uncertainty in the dielectric permittivity values is estimated to be about 1%. We measured every sample five times. For the result and discussion part we used the average values of this five measurements. The measurement uncertainty was calculated via standard deviation.

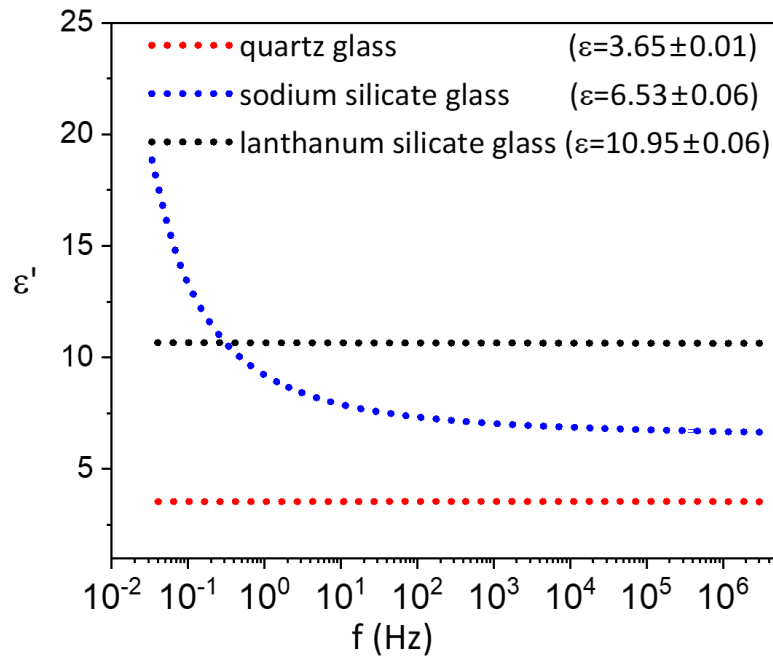


Figure S11. Dielectric spectra with corresponding permittivities ε of the quartz, sodium silicate and lanthanum silicate glass.

RESEARCH ARTICLE

Wetting of Surface Grafted Hydrophilic-*b*-Hydrophobic Block Copolymer Brushes

Benjamin Leibauer, Andres de los Santos Pereira, Diego Fernando Dorado Daza, Y. Wang, A.S. Hazrah, Ognen Pop-Georgievski, Hans-Jürgen Butt, and Rüdiger Berger*

The wetting of diblock copolymer brushes by water is studied. The goal of this work is to understand how the thickness of the bottom and top copolymer block affect the wetting behavior, respectively. For the synthesis of diblock copolymer brushes the bottom block, a hydrophilic poly(2-hydroxyethyl methacrylate) (PHEMA) brush is grafted from a undecyl-trichloro-self-assembled monolayer on silicon wafer. Then the top block, a hydrophobic polystyrene (PS) or poly(2-ethylhexyl methacrylate) (PEtHexMA) is grafted from the PHEMA block. Hereby, a hydrophilic-*b*-hydrophobic diblock copolymer is obtained. The top copolymer block determines the advancing contact angle of the copolymer brushes in their pristine state. The receding contact angle depends on the thickness of the top and bottom copolymer block. For a top copolymer thickness <30 nm the receding contact angle decreased. An increase in the thickness of the bottom block to 35 nm decreases the receding contact angle as well. By exposing the diblock copolymer brush with a thickness of the top block >30 nm to warm water the wetting properties switch from a hydrophobic to a hydrophilic. The surface switches back to the hydrophobic state by exposing it to toluene and subsequent temperature annealing.

contact angles. Thomas Young described the relation between the contact angle θ and the interfacial free energies of the liquid-vapor γ_{LV} , solid-vapor γ_{SV} , and solid-liquid γ_{SL} interfaces by^[5]

$$\gamma_{LV}\cos\theta = \gamma_{SV} - \gamma_{SL} \quad (1)$$

This relation assumes constant values for γ_{LV} , γ_{SV} and γ_{SL} . However, for polymer surfaces, γ_{SL} can change upon contact with a liquid.^[6] Thus the sample surface adapts in the presence of liquid.^[7] The timescale and the extent of adaptation, i.e., morphological and chemical changes, are often unclear. Here, we investigate changes of the surface wetting of surface grafted hydrophilic-*b*-hydrophobic block copolymer brushes.

Surface grafted polymer brushes swell in solvents due to polymer-solvent interaction. Exposing those polymer brushes to a non-solvent, the polymer-polymer and solvent-solvent interactions are preferred and the polymer chains aggregate or collapse.^[8–10]

Swelling and collapse of the polymer brushes can lead to different morphologies of surfaces.^[9,11,12]

The change in the morphology leads to a change in the surface roughness^[9] and the surface energy.^[6] Both the change of the surface roughness and the surface energy result in a change in the contact angles^[5,13] Surface binary polymer brush films have been used for biomedical devices or biosensors.^[14] The synthesis of diblock copolymer brushes with a hydrophilic bottom block and hydrophobic top block is described very well.^[9,11,15–17] Here, we follow the idea of using diblock copolymer brushes, which form a layered architecture. The top polymer layer may be used to protect or shield the underneath polymer from contact with solvents. For those coatings, the two copolymer blocks differ in terms of their affinity toward solvents^[11,18,19] and have been used for anti-fouling surfaces.^[14] Here we focus on the influence of block thickness on the advancing and receding contacts. How thick must the top polymer layer be in order to shield the influence of the polymer underneath on the advancing and receding contact angles? Can surfaces be reversibly switched in solvents? Can a layered structure be regained after annealing? Are the advancing and receding contact angles influenced by the thickness of the top and bottom polymer layers?

1. Introduction

Polymers with engineered wetting properties are used as water-repellent surfaces in outdoor clothing,^[1] as protective coatings to prevent corrosion^[2] or to prevent the formation of ice.^[3,4] Typically, the wetting properties of water on surfaces are quantified by placing a drop of a surface and measuring

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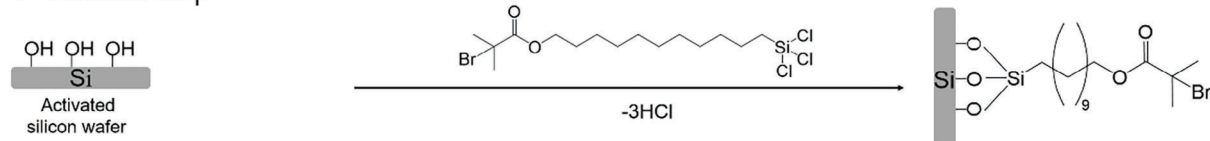
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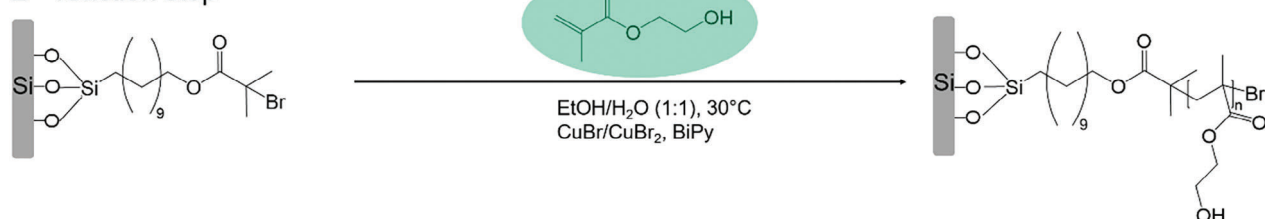
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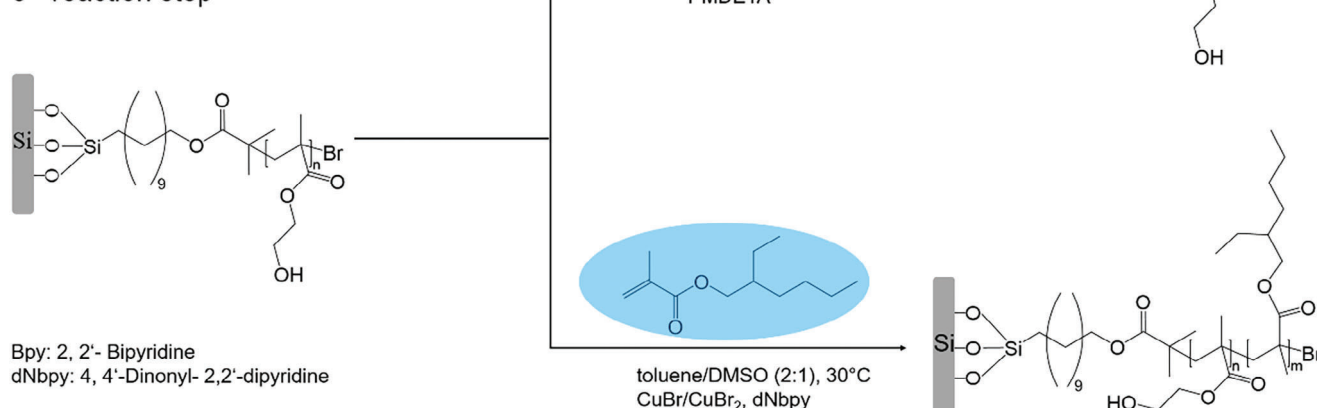
1st reaction step



2nd reaction step



3rd reaction step



Bpy: 2, 2'- Bipyridine
dNbpy: 4, 4'-Dinonyl- 2,2'-dipyridine

Figure 1. 3 Step reaction path of the diblock copolymer surfaces. first reaction step: Self assembled monolayer of the initiator (Br-SAM) on the activated silicon substrate. second reaction step: Grafting polymerization of PHEMA polymer brushes from the Br-SAM. third reaction step: Grafting of PS or PETHexMA polymer brushes from the PHEMA polymer brushes.

Diblock copolymers were synthesized in two steps. In the first step, we grafted poly(2-hydroxyethyl methacrylate) (PHEMA) brushes from a silanized silicon wafer. In the second step, we grafted polystyrene (PS) or poly(2-ethylhexyl methacrylate) (PETHexMA) from the PHEMA block (**Figure 1**). Due to different wetting properties with water (PHEMA: $\theta_{\text{PHEMA}} \approx 70^\circ$; $\theta_{\text{PS}} \approx 95^\circ$; $\theta_{\text{PETHexMA}} \approx 95^\circ$), we consider the PHEMA-*b*-PS and PHEMA-*b*-PETHexMA as hydrophilic-*b*-hydrophobic diblock copolymers. Here, we use the abbreviations of the polymers (PHEMA, PETHexMA, PS). The more hydrophilic PHEMA forms the bottom-block which is closer to the solid surface. Accordingly, the PS or PETHexMA copolymer blocks form the top block.

2. Results and Discussion

2.1. Structure of Hydrophilic-*b*-Hydrophobic Diblock Copolymer Brushes

The synthesis of diblock copolymer brushes is described in detail in the literature.^[11,15–17,20] We followed a three step synthesis procedure via *surface initiated atom transfer radical polymerization* (SI-ATRP) to synthesize ordered and stacked layered films on a solid substrate.^[21–23] First, we grafted the self-assembled monolayer as an initiator to the silicon substrates. Then, we grafted the bottom polymer from the initiator-surface. Finally, we grafted the

top copolymer from the bottom polymer, which acted as a macro-initiator (Figure 1). We followed a standard synthesis approach and therefore we described details about the synthesis in the (Supporting Information section, synthesis).

The thickness of the bottom block and the thickness of the diblock copolymer brushes were obtained by spectroscopic ellipsometry measurements. The polymerization kinetics of the bottom block (monitored from the polymer thickness changes with polymerization time) was reproducible, which indicated that the grafting density of the initiator layer remained constant between different synthetic runs (Supporting Information section, synthesis). We calculated the layer thickness of the top block by subtracting the thickness of the bottom block from the total diblock copolymer thickness (Supporting Information section, synthesis). All those measurements revealed that a top-block polymer grew, although its growth kinetics decreased significantly compared to the bottom block (Supporting Information section, synthesis). Variations of the reaction times led to bottom polymer thicknesses ranging from 16 to 35 nm while we obtained a thicknesses of 7–101 nm for the top polymer (Supporting Information section, synthesis). Since we observed variations in the kinetic of the top block polymer growth, we attribute this to variation in the grafting density of the top block.

We confirm a stacked layered film by XPS-depth profiling of diblock copolymer made of the PHEMA(15 nm)-*b*-PS(40 nm) and PHEMA(15 nm)-*b*-PEtHexMA(54 nm) (Figure 2a,b). We acquired spectra after increasing times of etching the samples with Ar⁺ gas clusters. In our analysis, we focus on changes in the high-resolution XPS spectra taken in the C 1s region and we compare the spectra with spectra taken from the homopolymer surfaces of PS, PHEMA, and PEtHexMA.

Before sputtering, the PHEMA-*b*-PS copolymer surface showed one dominating peak at 285.0 eV. We attribute it to the PS block (Figure 2a), because the spectra before sputtering match the spectra taken from a homopolymer surfaces of PS (Figure 2, top row). The depth profiling of the block copolymer surface gradually reveals contributions of the underlying PHEMA block. In the case of the PHEMA(15 nm)-*b*-PS(40 nm) this is evident from the appearance of new C—O and C(=O)—O contributions at 286.6 and 288.9 eV. Both peaks are not present in the PS homopolymer but in the spectra taken from the homopolymer PHEMA (Figure 2, bottom row). Close to the substrate interface, the intensity of the PHEMA peaks increased.

We measured a similar behavior for the PHEMA-*b*-PEtHexMA copolymer surface. The spectra showed a dominating peak at 285.0 eV, a peak at 286.6 eV, and a peak at 288.9 eV. These three peaks can be assigned to the PEtHexMA block (Figure 2b). The surface spectra before sputtering match the spectra taken from the homopolymer surfaces of PEtHexMA (Figure 2, top row). In the case of the PHEMA(15 nm)-*b*-PEtHexMA(54 nm) copolymer surface, the gradual removal of the PEtHexMA is evidenced by the concomitant increase of the C—O peak at 286.6 eV and C(=O)—O peak at 288.9 eV, which can be directly related to the higher concentration of HEMA monomer units (Figure 2, bottom row). Close to the substrate interface, the intensity of the PHEMA peaks increased.

The XPS-depth profiling of the PHEMA-*b*-PS and PHEMA-*b*-PEtHexMA copolymer surfaces confirmed that we have di-

block copolymer surfaces with stacked polymer layers. The PHEMA bottom block is situated closer to the substrate interface and the PS or PEtHexMA top block is at the air interface.

Topography measurements by scanning force microscopy (SFM) of the diblock copolymer exhibit an rms-roughness of 3–10 nm measured on an area of 4 μm² (Figure 3). This roughness is higher than the substrate surface (rms value of 1 nm). We found no correlation between the thickness of the top block and the rms roughness (Supporting Information section, SFM). In particular, protrusions were present on the polymer surfaces. However, these protrusions were not noticeable in phase contrast during SFM imaging (Figure 3). Thus we conclude that at the air interface only the PS or PEtHexMA blocks are present, respectively. The surface is rough but chemically homogenous. We attribute the elevations to local variations in the crosslinking of the multifunctional silane initiator, which then remains visible in the added polymer layers (Supporting Information section, SFM).

The wetting properties of the diblock copolymer surfaces were characterized by measuring the advancing (θ_{adv}) and receding water contact angles (θ_{rec}). For the PHEMA homopolymer surface, we measured $\theta_{adv} = 70 \pm 5^\circ$ and $\theta_{rec} = 15 \pm 5^\circ$ (dotted and dashed green line in Figure 4a, Supporting Information section, wetting). The θ_{adv} and θ_{rec} show the hydrophilic character of the PHEMA surface. Although PHEMA is not water-soluble, it swells in water. The contact angle hysteresis for the PHEMA brush surface is a result of swelling, chain reorientation, and exposure of hydrophilic groups during water contact.^[6] For the PS homopolymer surfaces, we measured an $\theta_{adv} = 95 \pm 2^\circ$ and $\theta_{rec} = 77 \pm 2^\circ$ (red dotted and dashed line in Figure 4a). For the PEtHexMA homopolymer surface we measured $\theta_{adv} = 103 \pm 1^\circ$ and $\theta_{rec} = 75 \pm 2^\circ$ (Supporting Information section, wetting). The PS and the PEtHexMA surfaces reflected more hydrophobic properties compared to PHEMA. The water contact angles of the homopolymer surfaces were independent of the thickness of the polymer surface. In addition, we measured the CH₂I₂ contact angles on a PHEMA homopolymer surface with different thicknesses to check how the brush length affects the wetting behavior. We did not observe a dependence on the thickness of the polymer brushes (Supporting Information section, wetting).

Such a stacked layered film could possibly switch upon exposure to a selective solvent.^[9] In particular, upon exposure to water, the hydrophilic PHEMA block could reach the surface and displace the PS or PEtHexMA block. The measurements of water contact angles are a sensitive method to study compositional changes of surfaces.^[6,24,25]

2.2. Switching of Diblock Copolymer Brushes

On a freshly synthesized PHEMA-*b*-PS diblock copolymer surface (thickness of 17 ± 1 nm for the bottom block and a thickness of 37 ± 1 nm for the top-block) we observed an θ_{adv} of $98 \pm 2^\circ$, which corresponds to the θ_{adv} of the top-block, i.e., PS (pristine, Figure 4a). The $\theta_{rec} = 77 \pm 1^\circ$. Then, we inserted the block copolymer samples into a DI-water bath at room temperature for 2 h. After removing the samples and drying them in an air stream, we

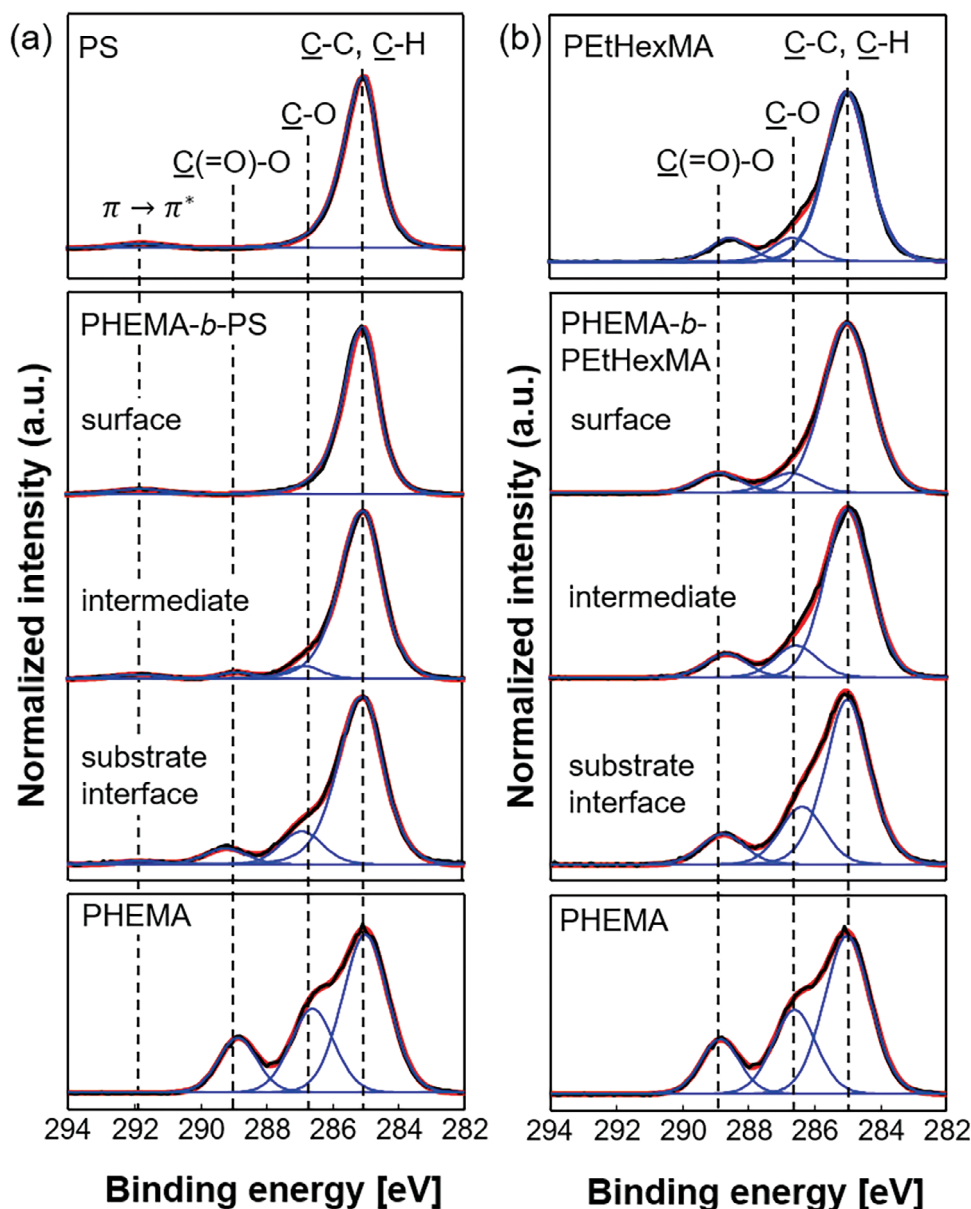


Figure 2. XPS depth profiling proved the block-copolymer structure of the polymer brushes. Comparison of normalized high-resolution XPS spectra of a) PHEMA (15 nm)-b-PS (40 nm), PS and PHEMA; b) PHEMA (15 nm)-b-PEtHexMA (54 nm), PEtHexMA and PHEMA brushes in the C 1s region. For the diblock copolymer surfaces three levels are presented: at the surface (0 nm depth), at intermediate level and at level approaching the PHEMA block/substrate interface (40–50 nm). Measured spectra (black thick lines) were deconvoluted with individual contributions (blue lines). The resulting fitted envelopes are presented with thick red lines. Depth profiling under selected conditions does not impose artefacts through the profile of thick polymer brush layers of PHEMA, PS and PEtHexMA. Comparison of normalized high-resolution XPS spectra of taken in the C 1s region for a) PS (125 nm), PHEMA (100 nm), and b) PEtHexMA (120 nm), PHEMA (100nm) brushes.

measured an θ_{adv} of $98 \pm 2^\circ$ and a θ_{rec} of $77 \pm 1^\circ$. These values are indistinguishable from the CAs of the pristine samples. Thus, samples with a top block layer thickness of more than 30 nm did not switch upon immersion in water at room temperature (Supporting Information section, wetting).

In order to promote switching, we increased the temperature of the DI-water bath to 40°C . Exposing the diblock copolymer sample to 40°C DI-water for 2 h, decreased the θ_{adv} from $98 \pm 2^\circ$ to $85 \pm 2^\circ$ and the θ_{rec} from $77 \pm 1^\circ$ to $26 \pm 3^\circ$ (Figure 4a). Thus

the θ_{adv} of the surface has a mixed character of the bottom- and top-block polymer. The θ_{rec} decreased to $25 \pm 3^\circ$ (Figure 4a). This θ_{rec} is close to the θ_{rec} of the PHEMA homopolymer, 15° (green dashed line in Figure 4a). After 40°C toluene treatment and annealing the sample at 120°C in a vacuum for at least 5 h we measured an θ_{adv} of $95 \pm 3^\circ$ and a θ_{rec} of $58 \pm 2^\circ$ (Figure 4a). The θ_{adv} was in the same order such the θ_{adv} of the pristine surface (red dashed line in Figure 4a). The changes in θ_{adv} after exposing the surface to 40°C DI-water and after toluene treatment were

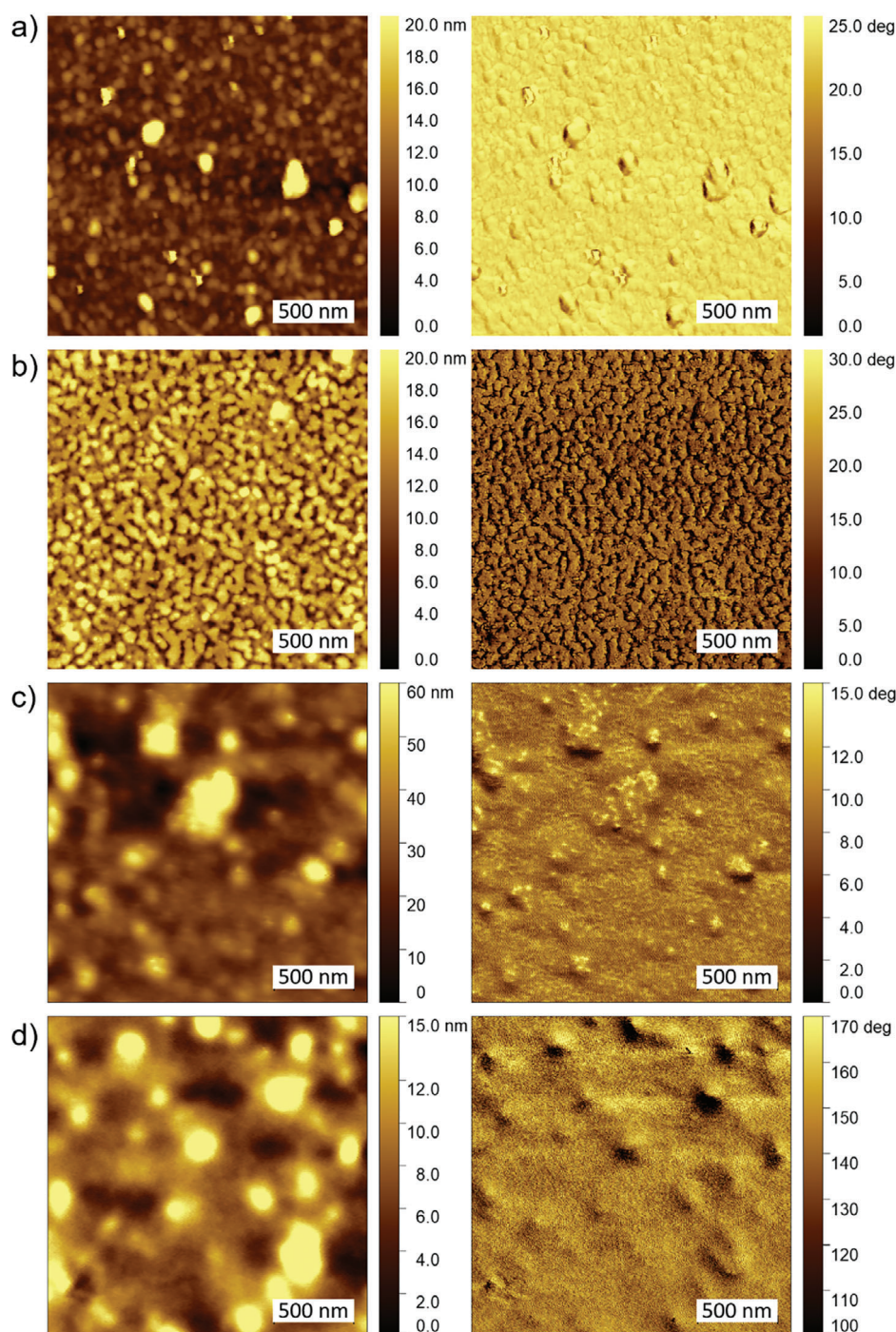


Figure 3. On the left side the topography and on the right side the phase images of the measured diblock copolymer surfaces by SFM in tapping mode in air at a scan size of $2 \times 2 \mu\text{m}^2$. a) PHEMA(17nm)-*b*-PS(19nm) diblock copolymer surface, rms = 2.9 nm. b) PHEMA(35nm)-*b*-PS(19nm) diblock copolymer surface, rms = 3.6 nm. c) PHEMA(17nm)-*b*-PETetHexMA(32nm) diblock copolymer surface, rms = 10.5 nm. d) PHEMA(34nm)-*b*-PETetHexMA(30nm) diblock copolymer surface, rms = 3.7 nm.

observed repeatedly in subsequent cycles as well. The θ_{rec} was 30° lower compared to the pristine sample surface. In subsequent cycle of exposure, the warm water and toluene treatment on the sample surface reproduced θ_{rec} of $30^\circ \pm 3$ and $56^\circ \pm 2^\circ$, respectively. The measurements of the θ_{adv} and θ_{rec} after exposure to

warm water indicate a mixed character of the bottom- and top-block polymer at the surface (Figure 4b).

In order to investigate changes in the composition of the surface, we analyzed samples before and after water treatment with XPS. However, we did not observe differences in the XPS

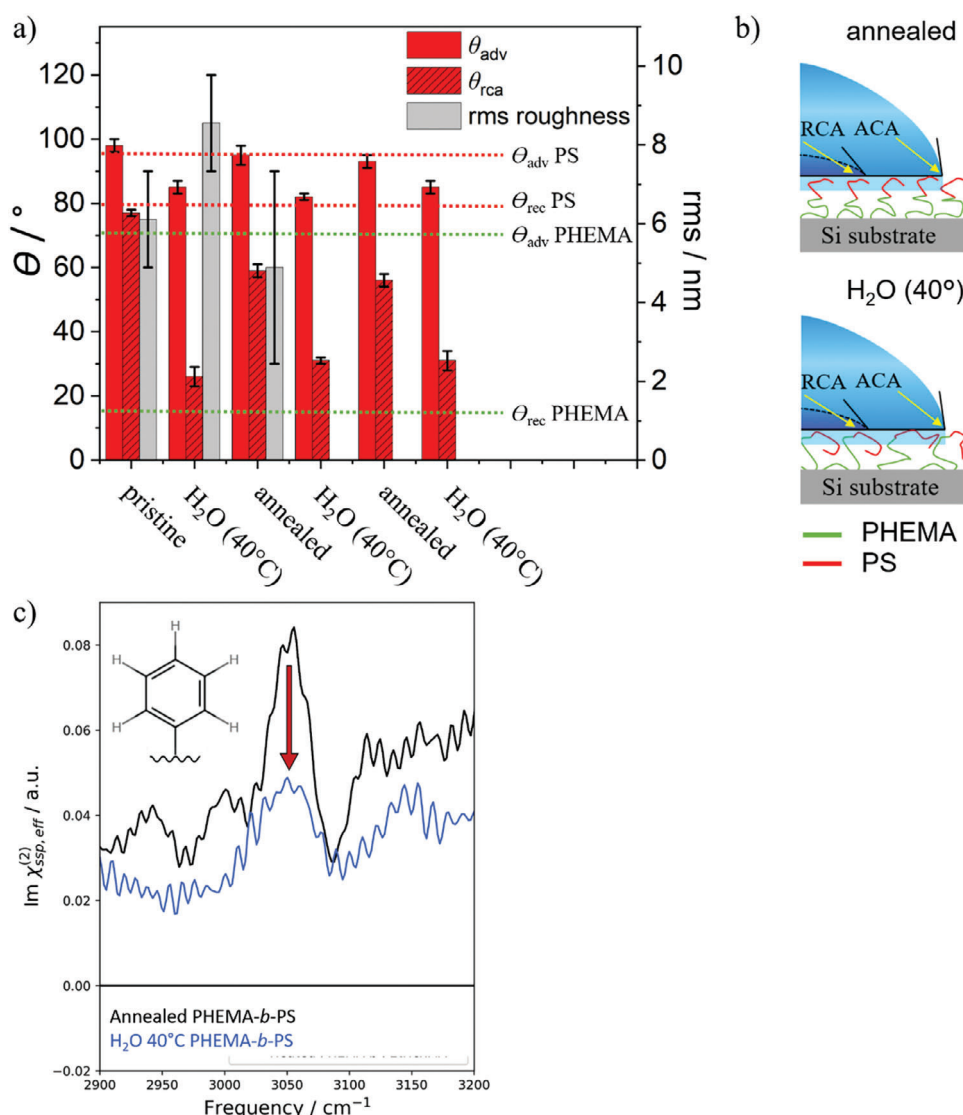


Figure 4. a) Advancing (θ_{adv} red columns) and receding (θ_{rec} red columns with pattern) contact angle, rms roughness (grey columns) of the PHEMA-*b*-PS surface. θ_{adv} and θ_{rec} after the synthesis (pristine). θ_{adv} and θ_{rec} after exposing the surface to DI-water (40 °C) for 2 h (H₂O(40 °C)). θ_{adv} and θ_{rec} after annealing (annealed). For the annealing we exposed the surface to toluene (40 °C) for 2 h, blew it dry and annealed the surface for at least 5 h at 120 °C in vacuum. b) Schematic illustration of the solvent effect on the PHEMA-*b*-PS diblock brushes. Top: Toluene is non-solvent for PHEMA but a good solvent for PS. Therefore the PS block is swollen, while the PHEMA block is collapsed. Bottom: After exposing to water (40 °C). Water is non-solvent for PS. Therefore the PS brushes are collapse while the PHEMA brushes are swollen in contact with water. c) HD-SFG spectra. The black line represents the recorded spectra after annealing. The blue line represents the recorded spectra after exposing the diblock copolymer surface to (40 °C) for 2 h.

spectra. For XPS measurements the sample stayed for a long time in a vacuum. Possibly the vacuum induces to a certain extent a hydrophobic recovery of the diblock copolymer surface. Therefore, we employed heterodyne-detected sum frequency generation (HD-SFG) spectroscopy to investigate the molecular orientation and structural changes at the solid/air interface of the PHEMA-*b*-PS copolymer brushes. HD-SFG spectroscopy was employed as it enables the selective probing of surface-specific vibrational modes without bulk contributions.^[26] This method also allows for the decomposition of the nonlinear susceptibility, $\chi^{(2)}$, into its real and imaginary components, where the imaginary part ($\text{Im } \chi^{(2)}$) can provide insights into the orientation and arrangement of molecular species at interfaces.^[27,28] As such, by

focusing on C—H stretching regions (2850–3050 cm^{-1}), we can assess changes in the molecular organization of PHEMA-*b*-PS induced by exposing the surface to warm water for 2h using HD-SFG spectroscopy. The measurements were conducted under two conditions: (1) after exposing the copolymer surface to water at 40 °C for 2 h and (2) annealing in a vacuum oven at 120 °C for 5 h after exposing the surface to toluene for 2h. In both the warm water treated and annealed surface, a prominent positive peak at 3050 cm^{-1} was observed, corresponding to the aromatic C—H stretching mode^[29] of the PHEMA-*b*-PS block (Figure 4c). While the quadrupole contributions make the interpretation of the aromatic C—H signals complex,^[30] the relative changes in amplitude between warm water treated and annealed spectra indicate a

decrease in out-of-plane molecular alignment after exposing the surface to warm water. The results of the HD-SFG experiments showed that there is a change in the orientation of the styrene group of the diblock copolymer brush surface. Thus, we conclude that there is a chemical variation of the diblock copolymer surfaces and that the change in the θ_{adv} and θ_{rec} after exposure to warm water results from the change in the surface chemistry.

After toluene treatment and annealing the θ_{adv} returned to the initial pristine sample value while the θ_{rec} did not. A decrease in receding contact angle indicates more heterogeneities, which could be on one hand due to chemical groups (Figure 4b) or on the other hand roughness on a molecular scale.^[31,32] In this case the toluene treatment may not be sufficient to achieve a similar ordering of the polymer chains in the brushes compared to the pristine samples. The pristine samples were never exposed to water. Thus during the first exposure to hot water, the PHEMA swells, reorients, and induces a different structure of the entire diblock copolymer system. Exposure to toluene does not fully recover the structure of both polymer blocks in the same way as obtained directly after synthesis.

Additionally, surface roughness affects the receding CA.^[9,33] To analyze the influence of surface roughness we imaged samples after synthesis in pristine state, after water and toluene treatment by SFM. We observed a variation in rms roughness from 4 ± 1 nm (pristine) to 8 ± 1 nm (after water) to 9 ± 3 nm (after annealing), respectively (Figure 4a). The θ_{adv} decreased from 99° to $\approx 83^\circ$ after exposing the surface to water (40°C). But at the same time the surface roughness increased from 6 to 8 nm. It was reported that an increase of the surface roughness from 0.2 to 13 nm of fluoroalkylsilane coatings leads to an increase of the θ_{adv} , while the receding contact angle remains in the error margin.^[34] Therefore the rms roughness is not dominating the wetting difference between differently oriented properties of our diblock copolymer systems. The surface chemistry changes probed by HD-SFG are possibly associated to a change in the molecular roughness. Therefore, the nanoscale chemistry variations and changes in the molecular roughness^[31,32] contribute to the decrease in advancing contact angle.

We measured the thickness of the diblock copolymer surface after the synthesis and when the surface wettability was switched from hydrophobic to hydrophilic two times. No change in the thickness of the diblock copolymer surface was observed. Therefore we excluded that degrafting^[35] occurs and influences the wetting behavior of the diblock copolymer surface by exposing it to DI-water at 40°C .

In conclusion, we can switch the wetting properties of PHEMA-*b*-PS diblock copolymer surface with a thickness of 17 ± 1 nm for the bottom block and a thickness of 37 ± 1 nm for the top-block diblock copolymer surfaces from hydrophobic to hydrophilic by exposure to warm DI-water (40°C) and warm toluene. However, we found no changes for an exposure for 2 h to room temperature water.

2.3. Switching of Diblock Copolymer Brushes: Varying the Thickness of the Top Copolymer Block

To find out how the top layer influences the adaptation of the layer to water-exposure, we reduced the thickness of top layer. In a first series of experiments, we kept the thickness of the bottom-

block between 15 and 25 nm and varied the thickness of the top-block (Figure 5). Directly after synthesis, we measured for all PHEMA-*b*-PS diblock copolymer surfaces that the θ_{adv} was in the range from 89° to 98° (Figure 5a). For the PHEMA-*b*-PEtHexMA diblock copolymer surfaces the θ_{a} ranged from 102° to 106° (Figure 5b). These contact angles fall in the same range as the θ_{adv} of the corresponding homopolymer of the top-block (Figure 5).

By immersion of samples, adaptation times in the range of minutes to hours can be studied. Shorter adaptation times require a moving contact line. Goniometer measurement allows contact angle measurements with an advancing contact line velocity of 3 to $30 \mu\text{m s}^{-1}$.^[36] Contact angles are determined by a thin region around the contact line. It is reasonable to assume a length scale of 10 – 100 nm at the three phase contact line which determines Θ_{adv} .^[7,24,25] Thus for all studied diblock copolymer surfaces the time scale of adaptation is >0.03 s.^[7] We conclude that on the time scale of few 10 ms, the surface does not adapt to the presence of water. Time scales of seconds are better accessible by measurements of the receding contact angle. When measuring the receding contact angles the dewetted surface had been in contact with the polymer surface for seconds.

In contrast to the measurement of the θ_{adv} , the θ_{rec} becomes thickness dependent of the top-block (Figure 5). For the PHEMA-*b*-PS copolymer surfaces with a top-block thickness between 7 ± 1 and 13 ± 1 nm we measured a θ_{rec} of $\approx 20^\circ$. This value corresponded to the θ_{rec} of the bottom-block polymer (Figure 5c). Increasing the thickness of the top-block to 40 ± 1 nm resulted in an increase in θ_{rec} to 70° . This θ_{rec} corresponded to the θ_{rec} of the top-block.

We observed similar wetting behavior for the PHEMA-*b*-PEtHexMA copolymer surfaces. With a top-block thickness between 6 ± 1 nm and 12 ± 1 nm we measured an θ_{rec} of $20 \pm 2^\circ$ which correlates to the θ_{rec} of the bottom-block. With a top-block thickness of 32 ± 2 nm we measured an θ_{rec} corresponded to the PEtHexMA surface an θ_{rec} of $\approx 70^\circ$ (Figure 5d).

We attribute the decrease of θ_{rec} for thin top-block thicknesses to restructuring of the surface at room temperature or a variation of molecular roughness, which can lead to water penetration.^[31,32] Parts of the bottom-block are exposed at the liquid interface. Only for thicknesses ≥ 20 nm for the PS top block and ≥ 30 nm of the PEtHexMA top-block, the bottom-block is shielded. We attribute the difference of the thickness where the transition occurs to two effects: (i) The different T_g of the PS ($T_g \approx 100^\circ\text{C}$) and PEtHexMA ($T_g \approx -5^\circ\text{C}$). (ii) The possibly different grafting densities of both types of top copolymer blocks. Styrene and EtHexMA monomers have different sizes and reactivity and the polymerizations were carried out in solvent media of different compositions, all of which can affect the grafting density. Thus, the grafting density between the PS and PEtHexMA systems could be systematically different. However, we exclude that the variation in grafting density of the PHEMA bottom block plays a major role. If the grafting density of PHEMA would be the dominating factor, then a change of the θ_{rec} would depend on the batch of the PHEMA grafted from. Thus θ_{rec} data would appear scattered in the diagrams (Figure 5), and a transition at a thickness of ≈ 20 and 30 nm for PS and PEtHexMA, respectively, would not be likely.

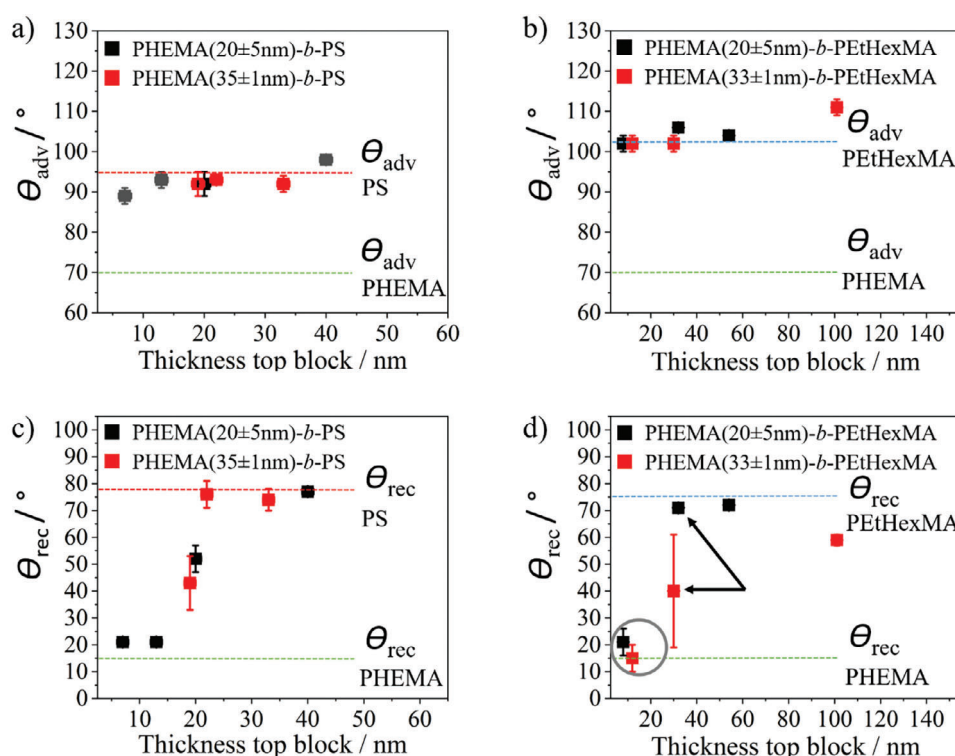


Figure 5. Contact angles are plotted against the thickness of the top block. a) θ_{adv} of the PHEMA-*b*-PS copolymer surfaces against the thickness of the PS block. b) θ_{adv} of the PHEMA-*b*-PEtHexMA copolymer surfaces against the thickness of the PEtHexMA block. c) θ_{rec} of the PHEMA-*b*-PS copolymer surfaces against the thickness of the PS block. d) θ_{rec} of the PHEMA-*b*-PEtHexMA copolymer surfaces against the thickness of the PEtHexMA block.

2.4. Switching of Diblock Copolymer Brushes: Varying the Thickness of the Bottom-Block of the Copolymer

The thickness of the bottom-block may influence the wetting properties of the diblock copolymer surfaces. Therefore, the thickness of the bottom-block was varied. A systematic variation of the bottom-block thickness while keeping a constant thickness of the top-block was not possible due to variations in growth rates of the top-block. We synthesized PHEMA with 20 ± 5 nm (black data points in Figure 5) and 35 ± 1 nm (red data points in Figure 5) while also the layer thickness of the top-block varied.

For all different bottom-block layer thicknesses of PHEMA-*b*-PS surfaces, we measured an θ_{adv} of $92 \pm 1^\circ$ (Figure 5a) and for all PHEMA-*b*-PEtHexMA surfaces we measured an θ_{adv} between 102° and 111° (Figure 5b). These θ_{adv} were in the range of the corresponding homopolymers of PS and PEtHexMA, respectively. The finding that θ_{adv} reflects the wetting properties of the top block indicates that the contact time during the advancing of the three phase contact line is too short to lead to swelling or reorientation of the diblock copolymer brushes.^[7]

For the PHEMA-*b*-PEtHexMA surface with a thickness of the top-block of 12 ± 1 nm, we measured an θ_{rec} of $15 \pm 5^\circ$ for both the 20 ± 5 nm and 33 ± 1 nm thick bottom block (grey circled data points in Figure 5d). This value corresponds to the θ_{rec} of the pure bottom-polymer surface. For an increased thickness of the top-block of $\approx 30 \pm 1$ nm, we measured a strongly scattered θ_{rec} with a mean value of $40 \pm 21^\circ$ for a 33 ± 1 nm thick bottom block. Decreasing the thickness of the bottom block to 20 ± 5 nm while

keeping a similar thickness of the top-block, the scatter in measured θ_{rec} reduced and corresponds to the θ_{rec} of the top-block (arrow in Figure 5d). Thus, increasing the thickness of the PHEMA bottom block results in more flexibility, porosity, or roughness of the top-block which enables switching of the surfaces upon exposure to water.

We measured a similar intermediate θ_{rec} for the PHEMA-*b*-PS surface at a thickness of the PS top-block of 20 ± 2 nm and a PHEMA bottom block of 35 ± 1 and 21 ± 1 nm, respectively (Figure 5c). With regard to the θ_{rec} of the PHEMA-*b*-PS and PHEMA-*b*-PEtHexMA diblock copolymer surfaces (Figure 5c and d), the scattering and an increase of error bars may also be attributed to the different T_g of the top blocks. The low T_g of PEtHexMA can result in a more mobile like surface affecting the wetting behavior.

2.5. Switching of Diblock Copolymer brushes: Variations of Roughness

The ratio between the thickness of the top and bottom blocks may influence the surface roughness or surface.^[16,37] All rms values of PHEMA-*b*-PS diblock copolymer surfaces were in the range of 3–4 nm (Figure 3a,b). We changed the ratio of the thickness between the bottom and top block from 1:1 to 1.8:1 by increasing the thickness of the bottom block. Although the roughness did not change significantly, the PHEMA(17nm)-*b*-PS(19nm) surface showed a dimple-like structure (Figure 3a).^[38] The

PHEMA(35nm)-*b*-PS(19nm) diblock copolymer surface showed a ripple-like structure (Figure 3b).^[38] The latter could be an indication of phase separation between the top and bottom blocks. Interestingly, both samples had a top block thickness of ≈ 20 nm where we also observed the wetting transition for the PS system for the θ_{rec} (Figure 5c).

In contrast to the PHEMA-*b*-PS copolymer surface, we observed no change in the surface morphology for the PHEMA-*b*-PEtHexMA copolymer surfaces (Figure 3 and d). However, a decrease in surface roughness from 10 to 4 nm was observed by increasing the thickness of the bottom block. To find out whether the roughness values are correlated, we plotted the surface roughness against the thickness of the top-block and we plotted the ratio between the thickness of the top block and bottom block versus the rms roughness values, respectively. Both plots do not indicate a systematic variation (SI, section SFM).

We note that the θ_{adv} of the PHEMA(32nm)-*b*-PEtHexMA(101nm) was higher than for the other PHEMA-*b*-PEtHexMA diblock copolymer surfaces (Figure 5b). In addition, θ_{rec} of these samples was lower than the θ_{rec} of the PEtHexMA homopolymer surface. A larger contact angle hysteresis indicates a higher surface roughness, which leads to stronger pinning of the θ_{rec} and the θ_{adv} increases.^[34]

3. Conclusion

We prepared PHEMA-*b*-PS and PHEMA-*b*-PEtHexMA grafted block copolymer brushes from a undecyl- trichlorosilane self-assembled monolayer. Both systems had a hydrophilic bottom and a hydrophobic top block. The main finding was that the wetting measurements with water revealed that both brush types are stable for top block thicknesses >30 nm at room temperature. When the top block thickness decreases below 30 nm, the surface switches upon contact with water. The receding contact angles decrease while the advancing contact angles remain constant. Thus at room temperature, switching takes place at a time scale of minutes.

4. Experimental Section

Materials: 2-Hydroxyethyl methacrylate (99%), 2-Ethylhexyl methacrylate (97%), dimethyl sulfoxide (DMSO, puriss. p.a. dried, $<0.02\%$), copper(II) bromide (99.999% trace metal basis) were purchased from Sigma-Aldrich, Germany. 2,2'-bipyridine ($>99\%$), copper (I) bromide ($>98\%$), 4,4'-dinonyl-2,2'-dipyridyl and *N,N,N',N',N''*-pentamethyldiethylenetriamine (PMDETA), were purchased from TCI Europe. Absolute ethanol was purchased from VWR, France. Styrene (99.5%, stabilized for synthesis) was purchased from Carl Roth, Germany. Anhydrous toluene (extra dry, 99.85%) was purchased from Fisher Scientific, UK. Toluene ($>99.8\%$) was purchased from Fisher, Netherlands. DI water (18 M Ω ·cm) was obtained from an Arium Pro system, Sartorius, Germany. The silicon substrate (P++/Boron <100 , thickness 525 ± 25 μm) was purchased from Si-Mat silicon Materials, Germany.

Silicon Substrate: After cutting ($1.3 \times 1.3 \text{ cm}^2 / 7.5 \times 2.5 \text{ cm}^2$) the silicon substrate was rinsed two times with ethanol, DI water and dried with a stream of nitrogen gas. Then the silicon substrates were activated by O_2 plasma (Diener electronic Femto, Plasma-Surface-Technology, Germany) adjusting an oxygen flow rate of $6 \text{ cm}^3 \text{ min}^{-1}$ and a power of 300 W for 20 min.

Self-Assembled Monolayer (SAM) on the Silicon Substrate: The silicon substrate was coated with a self-assembled monolayer of [11-[2-bromo-2-methyl] propionsyloxy] undecyltrichlorosilane] (Br-SAM). The Br-SAM

was synthesized according to previous work.^[21] The activated silicon substrates were placed in a petri dish and soaked in a solution of anhydrous toluene and the Br-SAM for 3 h. The Petri dish was covered with para film and placed in a desiccator.^[21] The volume ratio between the Br-SAM and the anhydrous toluene was 1:1000.^[23] After 3 h the Br-SAM coated silicon substrate was rinsed 2 times with toluene, ethanol, and DI water. Then the Br-SAM coated silicon substrate was dried with a stream of nitrogen gas and stored in an evacuated desiccator. The Br-SAM surfaces were used for the next reaction step within 7 days.

Poly(2-Hydroxyethyl Methacrylate) (PHEMA): 2-Hydroxyethyl methacrylate (14.42 g, 0.110 mol), 2,2'-bipyridine (365.9 mg, 93.7 mmol), copper(II) bromide (20.5 mg, 3.7 mmol), DI water/ethanol (25 mL, 1:1) were placed in a flask, provided with a septum and degassed with argon for 1 h. During this degassing process, the solution was stirred and cooled in an ice bath.^[22] Then the ice bath was removed and copper(I) bromide (136.1 mg, 38 mmol) was added under argon to the monomer solution. The copper(I) bromide was dissolved by ultrasound for 5 min. Then the monomer solution was transferred under argon to the glass reactors containing the Br-SAM coated silicon substrates with a syringe. Before adding the monomer solution the glass reactors containing the Br-SAM coated silicon substrates were degassed with argon for 30 min. The syringe was degassed with argon three times before using. The polymerization was done at 30°C . After the desired reaction time, the reaction was terminated by rinsing two times the PHEMA surfaces with ethanol, DI water and dried with a stream of nitrogen. The PHEMA surfaces were stored in an evacuated desiccator and used for the next reaction after 7 days at the latest.

Poly(2-Ethylhexyl methacrylate) (PEtHexMA): 2-Ethylhexyl methacrylate (35.52 g, 0.17 mol), 4,4'-dinonyl-2,2'-dipyridyl (293.2 mg, 0.717), copper(II) bromide (32.9 mg, 0.147 mmol) and toluene (26.6 mL)/DMSO (13.3 mL) were placed in a flask, provided with a septum and degassed with argon for 1 h. Then, copper(I) bromide (218 mg, 1.520 mmol) was added under argon to the monomer solution. After dissolving of the copper(I) bromide, the monomer solution was transferred under argon to the reactors containing the PHEMA copolymer surfaces or Br-SAM silicon substrates with a syringe. Before adding the monomer solution the glass reactors containing the Br-SAM coated silicon substrates were degassed with argon for 30 min. The syringe was degassed with argon three times before using. The reaction was done at 30°C . After the desired reaction time, the reaction was terminated by rinsing the PEtHexMA copolymer surfaces two times with toluene, ethanol, and water and dried with a stream of nitrogen.

Polystyrene (PS): Styrene was purified via distillation before the synthesis. According to the previous work, purified styrene (18.18 g, 0.174 mol), anhydrous toluene (10 mL), and PMDETA (346.6 mg, 2 mmol) were degassed in a Schlenk flask via three freeze-pump-thaw cycles at least.^[23] The monomer solution was transferred under argon to another Schlenk flask containing CuBr (248.2 mg, 1.73 mmol) and CuBr₂ (20 mg, 0.09 mmol). This Schlenk flask had been previously deoxygenated by three vacuum/argon-backfilling cycles. Also the syringe was degassed with argon three times before using. The flask containing the monomer solution was heated to 90°C for 1 h. Then the monomer solution was transferred to the degassed reactors containing the PHEMA copolymer surfaces or Br-SAM silicon substrates. The glass reactors containing PHEMA copolymer surfaces or the Br-SAM coated silicon substrates were degassed with argon for 30 min. The reaction was done at 90°C . After the reaction, the samples were rinsed two times with toluene, ethanol, DI water and dried with a stream of nitrogen gas.

Contact Angle Measurements: Advancing (θ_{adv}) and receding contact angles (θ_{rec}) were measured with a goniometer (OCA35, DataPhysics Instrument GmbH, Germany). A DI water drop with volume of 6 μL was placed with a needle of 51 mm length, 0.4 mm inner diameter, blunt end, and coated with PTFE connected to a Hamilton syringe onto the surface. After placing a drop on the surface, its volume was increased by 50 μL with a rate of $0.5 \mu\text{L s}^{-1}$. Then the volume was kept constant for 2 s and the drop volume was decreased by 50 μL with a rate of $0.5 \mu\text{L s}^{-1}$. After decreasing the droplet volume, the volume was kept constant for 2 s. The increase and decrease of the water volume describes one cycle. The time required

for one cycle was 3.4 min and three cycles for each measurement were made. Thus the sample surface was wetted by water for 10.2 min. Contact angles were determined by recording videos in side view, which were further analyzed with the help of the software SCA20 provided by Data-Physics Instrument GmbH. During the increase of the drop volume, the three-phase contact line advances and the contact angle reaches a constant value. This angle was taken as θ_{adv} . During decreasing the drop volume, the three phase contact line recedes. The contact angle at which the three phase contact line recede constantly was taken as the θ_{rec} .^[39] Every sample was measured three times in three different areas. The θ_{adv} and θ_{rec} of the three measurements and calculated the standard deviation were averaged.

Spectroscopic Ellipsometry: Measurements were performed on an ellipsometer (alpha 2.0 SE, Quantum Design, Germany). It was measured at an angle of incidence (AOI) in the range of 65–75°, with a step of 5°, and measured with a spectral range of $\lambda = 400$ –1000 nm. The data were analyzed with the software CompleteEASE 6.5. For the fit model, silicon was used as a substrate with a native oxide SiO₂ layer. The optical parameters of silicon were used from J.A.Woolam (Si.JAW). A thickness of 1.6 nm for the SiO₂ layer was measured and this value was kept for the SiO₂ layer for all measurements. For the polymer layer, the Cauchy dispersion relation was used to parametrize the refractive index (J.A.Woolam). By fitting the measured data the thickness of the polymer layer was obtained. After each polymerization step the thickness of the polymer brushes was measured. The difference between the total polymer brush thickness and the thickness of the bottom polymer brush layer was used to determine the thickness of the top polymer brush layer. Every sample was measured in three different areas. By forming the average value of the three measurements the thickness of the layer was calculated. The measurement uncertainty was obtained from the standard deviation of the three measurements.

Scanning Force Microscopy (SFM): Surfaces were imaged in tapping mode (JPK NanoWizard 4, Bruker Nano GmbH, USA) with cantilever (Olympus, OMCL-AC160TS, back side coating with aluminum) having a nominal resonance frequency of 300 kHz, a nominal spring constant of 26 Nm⁻¹ and a nominal tip radius <10 nm. The calculation of the root mean square roughness (RMS roughness) was done with the software Gwyddion for image areas of 2 × 2 μm² and 512 × 512 pixel. All images were leveled using a polynomial background of first degree (offset and plane). Each sample was measured at least in three different positions. The rms roughness was calculated using the average of three measurements, respectively. The measurements uncertainly was calculated with the standard deviation.

XPS Depth Profiling: XPS measurements were carried out with a K-Alpha+ spectrometer (ThermoFisher Scientific, East Grinstead, UK). Data acquisition and processing were performed using the Thermo Advantage software. The samples were analyzed using a micro-focused, monochromated Al K α X-ray source at an angle of incidence of 30° (measured from the surface) and an emission angle normal to the surface. The kinetic energy of the electrons was measured using a 180° hemispherical energy analyzer operated in the constant analyzer energy mode (CAE) at 200 eV and 50 eV pass energy for the survey and high-resolution spectra respectively. Spectral resolutions of 1.0 and 0.1 eV were used for the survey and high-resolution spectra, respectively. The measurements proceeded without the employment of surface charge compensation. XPS depth profiling was performed utilizing MAGCIS source operated in Ar+ cluster ion mode (2000 argon atoms per cluster) at 8000 eV. Each sputtering cycle lasted 10 s and an area of 4 mm × 2 mm was rastered. XPS spectra acquired in between etch cycles allowed qualitative and quantitative determination of the moieties present in the polymer and block-copolymer layers. Within this work spectra taken from three characteristic levels along the layer stacks of the block-copolymer brushes are reported: a) the surface of the polymer brushes (depth of 0 nm), b) the intermediate level (depth of 20–30 nm) and c) the level at which Si 2p substrate signals were detectable (depth of 40–50 nm). All reported XPS spectra were referenced to the C1s peak of hydrocarbons at 285.0 eV. The analyzer transmission function, Scofield sensitivity factors, and effective attenuation lengths (EALs) for photoelectrons were applied for quantification. EALs were calculated using the stan-

dard TPP-2M formalism. The BE scale was controlled by the well-known position of the photoelectron C–C and C–H, C–O and C(=O)–O C 1s peaks of polyethylene terephthalate and Cu 2p, Ag 3d, and Au 4f peaks of metallic Cu, Ag and Au, respectively. The BE uncertainty of the reported measurements and analysis was in the range of ± 0.1 eV.

The obtained XPS spectra were fitted with Voigt profiles obtained by convolving Lorentzian and Gaussian functions to determine the amounts in atomic % of individual chemical species present on the analyzed surfaces. Layers of ≈ 100 nm thickness of PHEMA, PS, and PETHexMA were depth-profiled and analyzed to prove that the cluster sputtering of the films does not incorporate artefacts and does not damage the chemical structure of the polymers. Understandably, such adverse effects would impede the reliable observation of the block-copolymer structure of synthesized PHEMA-*b*-PS and PHEMA-*b*-PETHexMA brushes. For the PHEMA, PS and PETHexMA layers, the ratios of identified chemical species in the high-resolution spectra taken in the C 1s region were compared to the expected, i.e., theoretical values of chemical moieties constituting the repeating units of these polymers. Namely, PHEMA has an overall chemical formula of $[-C(-CH_3)(-C(=O)-O-C_2H_4-OH)-CH_2-]_n$. Thus, it was expected that the following characteristic XPS contributions can be identified in the high resolution spectra taken in C 1s region for PHEMA brushes: a) C–C and C–H (from the aliphatic groups) at 285.0 eV, b) C–O contributions originating from alkoxy group and C–O–C moiety at 286.6 eV and c) C(=O)–O ester contribution at 288.9 eV, with a characteristic (i.e., theoretical) amount ratio between the three peaks of (C–C, C–H): (C–O): (C(=O)–O) = 3:2:1. PS has an overall chemical formula of $[-CH(-Ph)-CH_2-]_n$. This infers for only carbon species to be identified with the following characteristic signals to be present in the spectra of PS taken in the C 1s region: a) dominating C–C and C–H peak (from the aliphatic groups and the phenyl ring) at 285.0 eV and b) diagnostic shake-up satellite peak arising from $\pi \rightarrow \pi^*$ transition in the phenyl ring at 291.6 eV. The quantification of PS solely relies on the contribution of the dominating peak, whereas the satellite peak can be used as a diagnostic peak for the presence of the phenyl rings. PETHexMA has an overall chemical formula of $[-C(-CH_3)(-C(=O)-O-CH_2-CH(-C_2H_5)(-C_4H_9))-CH_2-]_n$, implying similar spectral contributions as in the case of PHEMA but with different ratios between the three peaks of (C–C, C–H): (C–O): (C(=O)–O) = 10:1:1.

Heterodyn-eDetected Vibrational Sum Frequency Generation (HD-SFG) Spectroscopy: The respective samples were measured using an HD-SFG spectrometer with a non-collinear beam geometry. The specifications of the spectrometer have been described in detail in previous studies.^[40,41] Briefly, a 1 kHz Spitfire Ace Ti:Sapphire regenerative amplifier system from Spectra Physics, centered at 800 nm, was used as the primary light source (5 mJ pulse energy, ~ 40 fs pulse duration, 1 kHz repetition rate). The subsequent output radiation was then split: one portion was directed to a pulse shaper utilizing a grating-cylindrical mirror system to create a narrowband visible pulse (~ 10 cm⁻¹), while another portion was converted into a broadband mid-IR pulse using a combination of an optical parametric amplifier (Light Conversion TOPAS-C, Spectra Physics) and an AgGaS₂ crystal. The IR and visible beams were directed onto a 100 nm-thick ZnO layer deposited on a 1 mm-thick CaF₂ window, facilitating the generation of a local oscillator (LO) signal. Subsequently, these beams were then re-focused using two off-axis parabolic mirrors, spatially and temporally overlapping at the sample surface. A fused silica glass plate, 1.5 mm in thickness, was positioned within the optical path of the LO signal to create a delay of ≈ 2 ps. The sample SFG signal interfered with the LO signal, creating an SFG interferogram, which was then directed into a spectrometer (Shamrock 303i, Andor Technology) and afterward captured by an Electron-Multiplying Charge-Coupled Device camera (Newton, Andor Technology). The complex- $\chi^{(2)}$ spectrum was extracted by Fourier analysis of the SFG interferogram and then normalized using a signal from a z-cut quartz reference.^[42] Each HD-SFG measurement was performed under a dry air atmosphere using the *ssp* polarization combination, where *ssp* denotes s-polarized SFG light, s-polarized visible light, and p-polarized mid-IR light. The spectrum presented in Figure 4c, was obtained by averaging 15 spectra, with an exposure time of 2 min for each spectrum.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

advancing and receding contact angle, diblock copolymer brushes, switchable hydrophilic-hydrophobic polymer surfaces

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ADVANCED FUNCTIONAL MATERIALS

Supporting Information

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Wetting of Surface Grafted Hydrophilic-*b*-Hydrophobic Block Copolymer Brushes

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Supporting Information

Wetting of Surface Grafted Hydrophilic-b-Hydrophobic Block Copolymer Brushes

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SI-Section 1: Synthesis of the PHEMA-*b*-PS / PHEMA-*b*-PEtHexMA surfaces

In general, every synthesis was done at least three times to check the reproducibility of our synthesis technique. We measured the thickness of the PHEMA block by spectroscopic ellipsometry for polymerization times, ranging from 5 to 45 minutes (Figure S1 a). We observed a linear increase in thickness for the polymerization of the PHEMA polymer corresponding to $1.24 \pm 0.06 \text{ nm min}^{-1}$. To check the reinitiation of the PHEMA surface, we used the PHEMA surface (*a*-PHEMA) as macro initiator for a further polymerization. We grafted a second PHEMA block (*b*-PHEMA) from the *a*-PHEMA surface. Here, the starting thickness of the *a*-PHEMA surface surfaces was $(35 \pm 1) \text{ nm}$ (Figure S1 a). We measured the total polymer surface (PHEMA-*b*-PHEMA) thickness after an additional polymerization time of 5, 15, 30, 45 minutes (Figure S1 a). For the *b*-PHEMA we determine a growing rate of $(0.95 \pm 0.06) \text{ nm min}^{-1}$ using a linear fit ($y=mx+b$). Both growing rates, of *a*-PHEMA and *b*-PHEMA blocks, agree with the reported rates of multiblock methacrylate copolymer surfaces.¹ The ratio between the growing rates of the *b*-PHEMA block and the *a*-PHEMA block corresponds to about 0.76.

We plotted the total thickness of the diblock copolymer brushes against the polymerization time in Figure S1 b. We observed that the growth rate of the top-copolymer block was dependent on the batch of the PHEMA surfaces. Possibly, the reactive end groups differ from batch to batch. It was described that there may be a decrease in activity of the macro- initiator by contact with oxygen due to washing or stored.¹ Therefore, we carried out the synthesis three times to calculate a growing rate for both different top-copolymers (run1, run2, run3,). The thickness at the time interval of zero hours represents the thickness of the used PHEMA surface respectively. We measured and plotted the total diblock copolymer surface thickness against the polymerization time, respectively. The growing rate was then calculated by averaging the growing rates of the three runs using a linear fit. The uncertainty of the growing rate was determined by the standard deviation. The growing rate of the PS of the PHEMA-*b*-PS diblock copolymer surface was $1.0 \pm 0.5 \text{ nm h}^{-1}$. The growing rate of the PEtHexMA of the PHEMA-*b*-PEtHexMA diblock copolymer surface was $5 \pm 2 \text{ nm h}^{-1}$.

All used samples with the corresponding thickness of the bottom and top block, contact angles are listed in table S1.

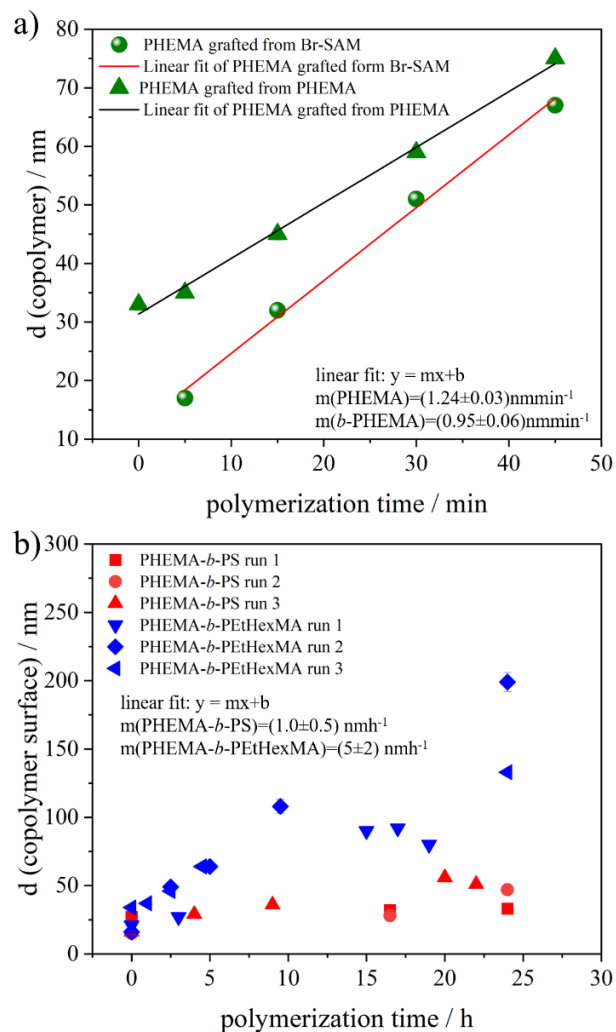


Figure S1. The thickness of the homo or diblock copolymer brushes is plotted against the polymerization time. a) a-PHEMA brushes (green circles) and the reinitiated PHEMA-*b*-PHEMA brushes (b-PHEMA, green triangle). The growth rate was calculated using a linear fit ($y=mx+b$). The linear fit was not set to zero because the b-PHEMA brushes has a layer thickness > 0 nm at the time of 0 min. b) PHEMA-*b*-PS (red data points) PHEMA-*b*-PEtHexMA (blue data points) diblock copolymer surface. The data point at the time point 0 indicates the initial layer thickness of the PHEMA block. As the reaction is dependent on the reactive a-PHEMA end groups, we performed each reaction three times (run 1, run2, run 3). The growth rate of each synthesis was calculated by the slope m of a linear fit ($y=mx+b$). Here the averaged growing rate expressed by $\bar{m}$ is given. The measurement uncertainty was determined using standard deviation.

Table S1. Measured parameters of the homopolymer and diblock copolymer surfaces.

Sample	Thickness of bottom-copolymer / nm	Thickness of top-copolymer / nm	ACA/°	RCA/°
PHEMA	16	-	65±5	15±5
PHEMA	41	-	74±2	15±5
PS	19	-	96±2	77±2
PS	107	-	93±1	76±1
PEtHexMA	15	-	103±1	73±1
PEtHexMA	47	-	103±1	76±2
PHEMA- <i>b</i> -PS	25±1	7±1	89±2	21±1
PHEMA- <i>b</i> -PS	16±1	13±1	93±2	21±1
PHEMA- <i>b</i> -PS	17±1	19±1	93±2	21±3
PHEMA- <i>b</i> -PS	17±1	40±1	98±1	77±1
PHEMA- <i>b</i> -PS	17±1	37±1	98±2	77±1
PHEMA- <i>b</i> -PS	35±1	19±1	92±3	43±10
PHEMA- <i>b</i> -PS	35±1	22±1	93±1	76±5
PHEMA- <i>b</i> -PS	35±1	33±1	92±2	74±4
PHEMA- <i>b</i> - PEtHexMA	21±1	8±1	102±2	21±5
PHEMA- <i>b</i> - PEtHexMA	17±1	32±1	106±1	71±1
PHEMA- <i>b</i> - PEtHexMA	26±1	54±1	104±1	72±1
PHEMA- <i>b</i> - PEtHexMA	34±1	12±1	102±2	15±5
PHEMA- <i>b</i> - PEtHexMA	34±1	30±1	102±2	40±21
PHEMA- <i>b</i> - PEtHexMA	32±1	101±2	111±2	59±2

SI-Section 2: XPS and XPS-depth profiling

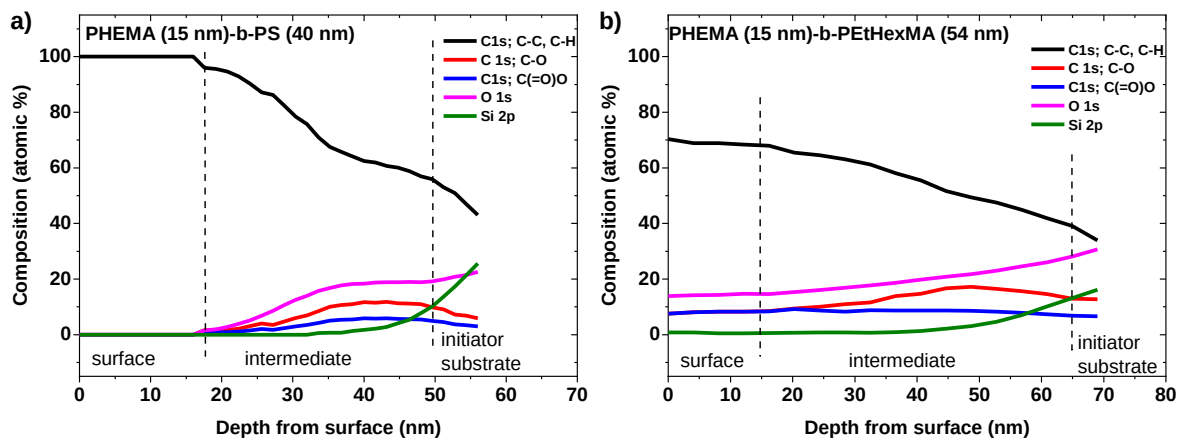


Figure S2. Composition of a) PHEMA (15 nm)-*b*-PS (40 nm) and b) PHEMA (15 nm)-*b*-PETHexMA (54 nm) brush surfaces in dependence of etch depth (depth from surface). The concentration profiles of the PHEMA (15 nm)-*b*-PS (40 nm) and b) PHEMA (15 nm)-*b*-PETHexMA (54 nm) brushes have three clear regions: surface region displaying strong predominance of PS and PETHexMA, respectively, intermediate region in which contributions of the PHEMA block are obvious, and a PHEMA block/initiator/substrate interface region.

SI-Section 3: Scanning force microscopy (SFM)

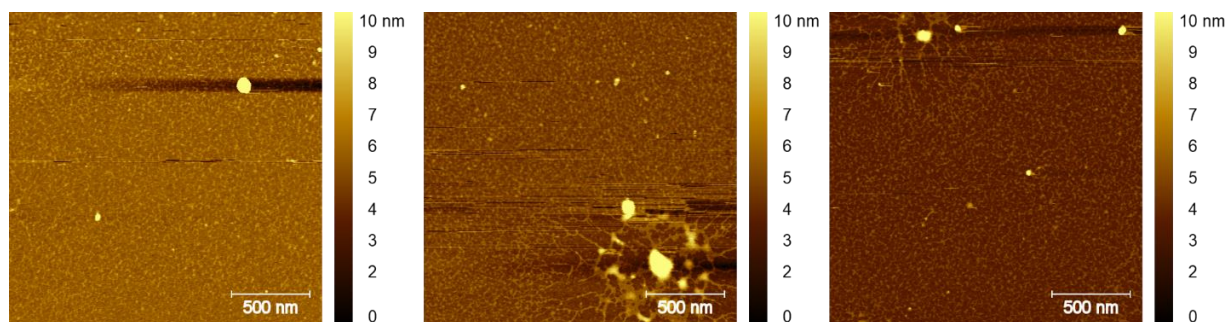


Figure S3. Surface topography measured by SFM in tapping mode in air at a scan size of $2 \times 2 \mu\text{m}$. Br-SAM on silicon wafer.

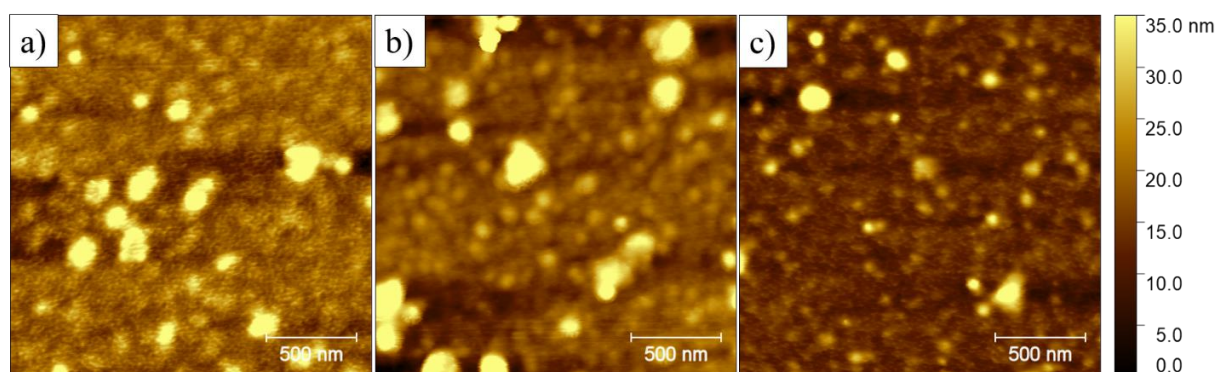


Figure S4. Surface topography of PHEMA(17nm)-b-PS(37nm) surface measured by SFM in tapping mode in air at a scan size of $2 \times 2 \mu\text{m}^2$. a) after synthesis, rms: 5 nm. b) after exposing to DI-water at 40°C for 2h, rms: 7 nm. c) after exposing to toluene at 40°C for 2h and annealing at 120°C for 5h, rms: 4 nm.

Table S2. The calculated rms-roughness of each measurement of the sample PHEMA(17nm)-b-PS(34nm) for scan sizes of $2 \times 2 \mu\text{m}^2$. Pristine corresponds to measurements after the synthesis.

Sample treatment	rms roughness / nm
pristine	3
Pristine	4
Pristine	5
After expose to H2O at 40°C for 2h	5
After expose to H2O at 40°C for 2h	7
After expose to H2O at 40°C for 2h	7
After expose to toluene for 2h and annealing	4
After expose to toluene for 2h and annealing	12
After expose to toluene for 2h and annealing	10

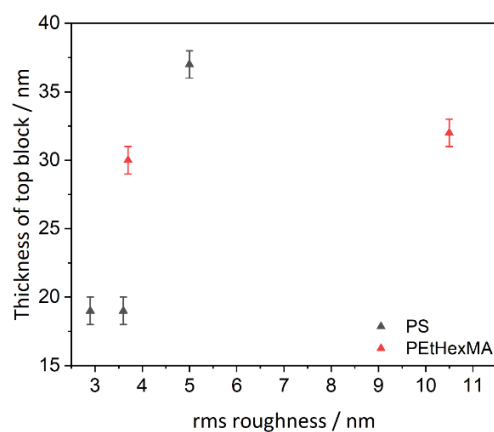


Figure S5. The thickness of the top block is plotted against the rms roughness of the diblock copolymer surfaces, respectively. The rms roughness was calculated from the SFM images in Figure 5 and Figure S4.

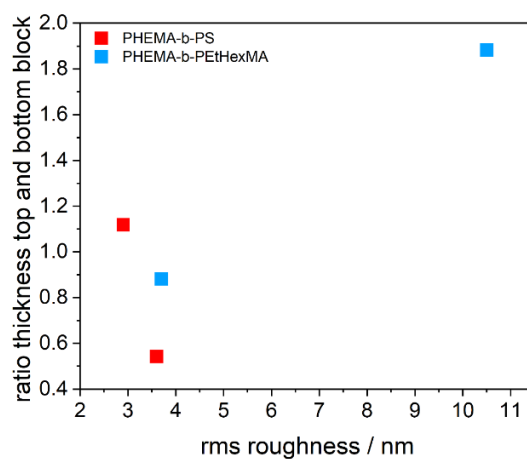


Figure S6. The ratio between the thickness of the bottom PHEMA block and PS or PEtHexMA top block is plotted against the rms roughness.

SI-Section 4: Wetting properties

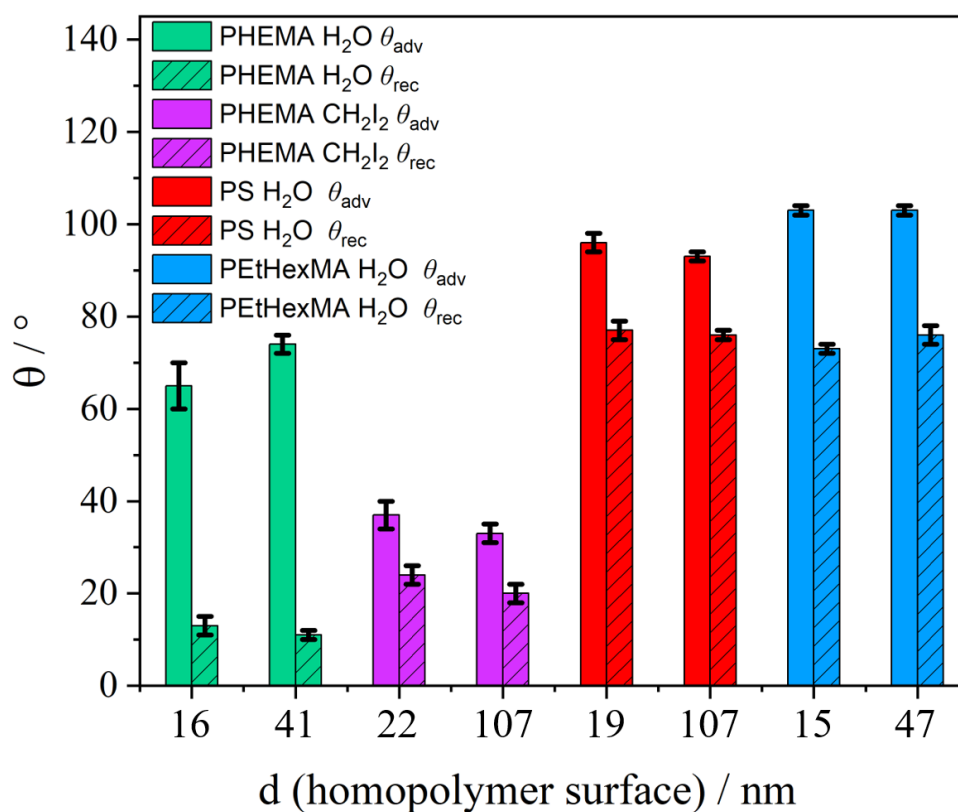


Figure S7. The H₂O contact angles of the homopolymer surface PHEMA (green), the CH₂I₂ contact angle of the homopolymer surface PHEMA (purple), the H₂O contact angles of the homopolymer surface PS (red) and the H₂O contact angles of the homopolymer surface PEtHexMA (blue) are plotted against the thickness of the homopolymer film, respectively. The advancing contact angle corresponds to the filled color of the homopolymer, respectively. The receding contact angle is plotted in diagonally dashed color of the homopolymer, respectively.

Table S3. Measured advancing (θ_{adv}) and receding (θ_{rec}) contact angles after synthesis. During the measurement were the surface exposed 10.2 min to water. To investigate the influence of the exposing time of water to the surface, we immersed the samples 2 hours to DI water and measured the ACA and RCA again.

Sample	Thickness bottom copolymer / nm	Thickness top copolymer / nm	θ_{adv} after synthesis / $^{\circ}$	θ_{rec} after synthesis / $^{\circ}$	θ_{adv} after 2h DI water / $^{\circ}$	θ_{rec} after 2h DI water / $^{\circ}$
PHEMA- <i>b</i> - PEtHexMA	17 $\pm$ 1	32 $\pm$ 1	106 $\pm$ 1	71 $\pm$ 1	103 $\pm$ 1	71 $\pm$ 3
PHEMA- <i>b</i> - PEtHexMA	34 $\pm$ 1	30 $\pm$ 1	102 $\pm$ 2	40 $\pm$ 21	100 $\pm$ 1	50 $\pm$ 7

SI-Section 5: Heterodyne-detected sum frequency generation (HD-SFG) spectroscopy

Interestingly, no distinct signature was observed in the O–H stretching region. This could be attributed to two factors: First, as evident from Figure 4d, the aromatic signal in the FTIR spectrum is significantly stronger than the O–H stretch (Figure 4d). In SFG, where the C–H signal is already weak, the O–H signal may be buried in noise. Second, the aromatic groups are likely more ordered compared to the aliphatic chains with terminal O–H groups. The latter may adopt a more random orientation, resulting in SFG signal cancellation.

References

- (1) Tomlinson, M. R.; Efimenko, K.; Genzer, J. Study of kinetics and macroinitiator efficiency in surface-initiated atom-transfer radical polymerization. *Macromolecules* **2006**, *39* (26), 9049-9056.

8.5 Curriculum Vitae

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