Design of Smart Polymeric Materials with Responsive / Adaptive Adhesion Properties

DISSERTATION

zur Erlangung des akademischen Grades

Doktor rerum naturalium
(Dr. rer. nat.)

vorgelegt

der Fakultät Mathematik und Naturwissenschaften
der Technischen Universität Dresden

von

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geboren am 04.08.1984 in Moskau

Eingereicht am

Die Dissertation wurde in der Zeit von November 2008 bis November 2012 im Leibniz-
Institut für Polymerforschung Dresden e.V. angefertigt.
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<th>Description</th>
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<tbody>
<tr>
<td>$\Theta_{\text{Adv}}$</td>
<td>Advancing contact angle</td>
</tr>
<tr>
<td>$\Theta_{\text{Rec}}$</td>
<td>Receding contact angle</td>
</tr>
<tr>
<td>ADSA</td>
<td>Axisymmetric drop shape analysis</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic force microscopy</td>
</tr>
<tr>
<td>AGET ATRP</td>
<td>Activator generated by electron transfer atom transfer radical polymerization</td>
</tr>
<tr>
<td>APS</td>
<td>3-aminopropyltriethoxysilane</td>
</tr>
<tr>
<td>ARXPS</td>
<td>Angle resolved X-ray photoelectron spectroscopy</td>
</tr>
<tr>
<td>ATP</td>
<td>Adenosine triphosphate</td>
</tr>
<tr>
<td>ATRP</td>
<td>Atom transfer radical polymerization</td>
</tr>
<tr>
<td>BrInit</td>
<td>Bromide initiator</td>
</tr>
<tr>
<td>CA</td>
<td>Contact angle</td>
</tr>
<tr>
<td>CP</td>
<td>Colloidal probe</td>
</tr>
<tr>
<td>CSC</td>
<td>Core-shell-corona</td>
</tr>
<tr>
<td>DCA</td>
<td>Dynamic contact angle</td>
</tr>
<tr>
<td>DI</td>
<td>Deionized</td>
</tr>
<tr>
<td>DLS</td>
<td>Dynamic light scattering</td>
</tr>
<tr>
<td>DLVO</td>
<td>Derjaguin, Landau, Verwey, Overbeek</td>
</tr>
<tr>
<td>DMF</td>
<td>N,N-Dimethylformamide</td>
</tr>
<tr>
<td>DMT</td>
<td>Derjaguin-Muller-Toporov</td>
</tr>
<tr>
<td>DSA</td>
<td>Drop shape analysis</td>
</tr>
<tr>
<td>EbiB</td>
<td>Ethyl-2-bromoisobutyrate</td>
</tr>
<tr>
<td>IEP</td>
<td>Isoelectric point</td>
</tr>
<tr>
<td>GPC</td>
<td>Gel permeation chromatography</td>
</tr>
<tr>
<td>LCST</td>
<td>Lower critical solution temperature</td>
</tr>
<tr>
<td>LSA</td>
<td>Light switchable adhesives</td>
</tr>
<tr>
<td>MEO2MA</td>
<td>2-(2-methoxyethoxy) ethyl methacrylate</td>
</tr>
<tr>
<td>$M_n$</td>
<td>Number average molecular weight</td>
</tr>
<tr>
<td>$M_w$</td>
<td>Weight average molecular weight</td>
</tr>
<tr>
<td>OEGMA</td>
<td>Oligo(ethylene glycol) methyl ether methacrylate</td>
</tr>
<tr>
<td>OPGMA</td>
<td>Oligo(propylene glycol) methacrylate</td>
</tr>
<tr>
<td>NIPAM</td>
<td>N-isopropylacrylamide</td>
</tr>
<tr>
<td>nBA</td>
<td>$n$-butyl acrylate</td>
</tr>
<tr>
<td>PAA</td>
<td>Poly(acrylic acid)</td>
</tr>
<tr>
<td>PDI</td>
<td>Polydispersity index</td>
</tr>
<tr>
<td>PDMS</td>
<td>Poly(dimethylsiloxane)</td>
</tr>
<tr>
<td>PEG</td>
<td>Poly(ethylene glycol)</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Full Form</td>
</tr>
<tr>
<td>--------------</td>
<td>-----------</td>
</tr>
<tr>
<td>PEO</td>
<td>Poly(ethylene oxide)</td>
</tr>
<tr>
<td>PFDTDS</td>
<td>1H,1H,2H,2H-Perfluorodecyltrichlorosilane</td>
</tr>
<tr>
<td>PGMA</td>
<td>Poly(glycidyl methacrylate)</td>
</tr>
<tr>
<td>PMDTA</td>
<td>N,N,N',N'',N''-pentamethyldiethylenetriamine</td>
</tr>
<tr>
<td>PNIPAM</td>
<td>Poly(N-isopropylacrylamide)</td>
</tr>
<tr>
<td>PS</td>
<td>Polystyrene</td>
</tr>
<tr>
<td>P2VP</td>
<td>Poly(2-vinylpyridine)</td>
</tr>
<tr>
<td>rms</td>
<td>Root-mean-square</td>
</tr>
<tr>
<td>RNA</td>
<td>Ribonucleic acid</td>
</tr>
<tr>
<td>RNAse</td>
<td>Ribonuclease</td>
</tr>
<tr>
<td>SIS</td>
<td>Styrene-isoprene-styrene</td>
</tr>
<tr>
<td>SMP</td>
<td>Shape memory polymer</td>
</tr>
<tr>
<td>SPM</td>
<td>Scanning probe microscopy</td>
</tr>
<tr>
<td>STM</td>
<td>Scanning tunnelling microscope</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermo-gravimetrical analysis</td>
</tr>
<tr>
<td>vDW</td>
<td>van der Waals</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
</tr>
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1. Introduction

1. Preface

This work was carried out during the years 2008-2012 at Leibniz-Institut für Polymerforschung Dresden e.V. under the supervision of Professor Manfred Stamm and Doctor Alla Synytska. Collaboration with the group of Professor Costantino Creton made possible one part of this work carried out at ESPCI (École Supérieure de Physique et de Chimie Industrielles de la ville de Paris, laboratoire de Physico-Chimie des Polymeres et Milieux Disperses). The research was supported by funding from the Leibniz-Institut für Polymerforschung Dresden e.V. and Deutsche Forschungsgemeinschaft DFG (Grant SY 125/1-1).

2. Motivation and Goals

Adhesion between different objects is happening everywhere. Without it, simple procedures like walking or holding something in a hand or attaching a postage stamp would be impossible. The life itself depends on adhesion on all levels, starting from the interactions between the living cells.

The control of adhesion is very important in many fields ranging from industrial purposes to biomedical applications and everyday usage. There is a demand for “smart” materials with integrated functionalities that make them responsive, switchable, biocompatible, anti-bacterial, more energy efficient, or autonomous. In particular, materials for such cutting-edge applications like cell culture, drug delivery, tissue engineering, biosensors, anti/biofouling, microfluidics, climbing robots, sport equipment and many others should possess adjustable/tuneable adhesive properties.

Much effort has been directed toward the fabrication of materials with either weak or strong adhesion depending on the field of application. However, design of “smart” surfaces with reversibly controllable adhesion is still a very challenging task. There are numerous instances in nature where responsive surfaces have been observed [Yos08], [Xia08]. Borrowing this concept from nature and applying it for reversible switchability and adaptation of surface properties has created considerable excitement in the fields of material science and biotechnology [Nan10].
I. Introduction

Two main strategies are used to obtain materials with tuneable adhesion. The first one is exploited in locomotion behaviour of gecko lizards [Red07]. It is known that the gecko owes its extreme reversible adherence to a fine structure of hierarchically arranged fibrils, which enable to exploit van der Waals and capillary forces with great efficiency. This example aroused scientific interest especially over the last decade and has been mimicked in synthetic equivalents [Sit03], [Aks07], [Gre07].

Another strategy is to fabricate surfaces with switchable chemical functionality. In this case, switchable surfaces are generated from chemically heterogeneous thin polymer films covalently bonded to solid substrates, therefore modifying their surface chemistry in a well-controlled and reproducible way [Lev98], [Min02a], [Ion03]. As a matter of fact, it could be very perspective to combine in one material these two approaches, surface modification and surface patterning using material systems that are responsive to external stimuli [Syn12], [Kod12].

Functionalization with polymer brushes, which are formed by polymer chains attached by one end to a substrate [Stu10], [Min06], represents a particular method to obtain responsive surfaces. Anchoring to a substrate, on one hand, provides chemical stability to such films and, on the other hand, allows design switchable surfaces. Due to their unique switching properties, polymer brushes have demonstrated to be very promising for control of biomolecular transport [Ion08], [Ion06], design of sensors [Ion06a], [Tok04] microfluidic devices [Ion06b], logical devices [Mot08], functional coatings [Min03a], cell culturing [Yam90], patterning or proteins [Nat02], control wetting and adhesion [Min03a]. Switchable adhesion behaviour of materials based on such responsive polymer brushes can be achieved using external stimuli like temperature, solvent, pH, ionic strength, electric/magnetic field, light or small (bio-) molecules. Character of their response to external stimuli can be regulated by chain length, composition, architecture and topology, thus polymer films offer a great variety of opportunities to design such stimuli-responsive surfaces. Moreover, it was shown that grafting of two chemically different polymers on one substrate even implies responsive properties of the polymer film.

Therefore, the thesis aims on design of smart polymeric materials with responsive / adaptive adhesion properties. For this, fabrication and investigation of two types of switchable polymer layers based on stimuli-responsive polymer brushes will be performed. The first group is dealing with thermoresponsive polymer brushes: poly-(N-isopropylacrylamide) and two types of biocompatible polyethylene glycol-based systems. These polymer layers undergo phase transition below and above LCST between hydrophilic and hydrophobic states. The second part of the work is related to solvent-responsive comb-like and block copolymer brushes consisted of hydrophilic PEG and hydrophobic PDMS biocompatible and biodegradable polymers.
I. Introduction

Following steps will be performed in this work:

- **Synthesis** of the polymer brushes on flat and rough substrates using ATRP process;
- **Characterization and control** over their bulk and surface properties (grafting density, thickness, wetting and swelling properties, surface charges and surface topography);
- **Investigation and control of switchable adhesion behaviour** of designed materials under the influence of external stimuli by means of AFM force measurements. Monitoring of several important chemical and physical surface characteristics will be performed:
  - chemical functionality of brush layer;
  - polymer layers architecture;
  - polymer layers thickness;
  - surface topography/roughness.

Influence of AFM measuring process parameters will be investigated as well:
- parameters of scanning (applied force, scan rate, contact time);
- geometry/radius of the probing tip;
- surface functionality of the colloidal probe.

- **Investigation of effect of mechanical properties** of probing surfaces used in AFM and Tack test experiments;
- **Analysis** of all aspects and parameters influencing adhesion behaviour of stimuli-responsive polymer brushes.
3. Outline

The thesis is organized in six parts. The Introduction in the Chapter I gives the general information concerning the topic of this work. The field and directions of research, motivation and goals of the present work are defined here.

The theoretical background of adhesion phenomena and the possibilities of materials with tuneable adhesion properties are discussed first in Chapter II. Then, the progress of current research concerning stimuli-responsive polymers, materials made on their basis and the possible areas of their application are presented. Methods for preparation of polymer brushes as well as surface characterisation techniques are also the subjects of this chapter.

Chapter III presents the results of investigation of polymeric systems with switchable adhesion properties. This chapter is divided into three parts. The first one is dealing with temperature responsive polymer brushes, whereas the second part is about solution responsive brushes. In the third part, the results on comparative study of adhesion properties of solution responsive systems measured with soft and hard probes are presented.

The general conclusions are presented in Chapter IV Summary. The perspectives of the further work in the field of stimuli-responsive materials are presented in Chapter V Outlook. In the last part of the work, the literature sources, Curriculum vitae and List of publications are listed.
II. Theoretical Background. Adhesion and Tackiness. Fundamentals

1. Adhesion and tackiness. Fundamentals

1.1 General

The term adhesion is used when referring to the attraction between the substances. Two bodies are said to adhere when energy is needed to achieve separation [Gay02]. As a means of joining materials adhesives have been used by mankind for many centuries [Kin87]. The oldest known adhesive, dated to approximately 200,000 BC, is from spear stone flakes glued to a wood with birch-bark-tar, which was found in central Italy.

There are many samples of adhesives in nature. A lot of invertebrates secrete bioadhesives for different purposes: to secure themselves, their nests, or their eggs, to build and construct (attachment of pupae, spider’s webs), as well as for obstruction and predation (elastic "frog glue" of crucifix toad [Gra05], sticky saliva of velvet worms).

While bioadhesives from some marine molluscs are already being researched intensively [Mes02], [Bil10], [Sag06], many insects remain relatively unexplored field of potentially useful and promising adhesives. Study of bioadhesion may well uncover qualitatively new adhesion mechanisms [Gay02].

The science and technology of adhesion and adhesives have achieved a significant progress in the last decades [Kin87]. There is a plenty of various examples of adhesive or non-adhesive materials. These materials find wide applications in many industrial processes, health care applications (such as surgical adhesives and sealants), everyday usage, etc [Rus99], [Rus02]. The adhesives may be natural (starches or natural rubber cements, for example), organic (such as derivatives of collagen, proteins, or cellulose), or synthetic (usually polymer-based thermosets, thermoplastics, or elastomers) [Rus99], [Rus02]. Synthetic adhesives are usually soft sticky materials that do not flow, made of polymers of various molecular architecture (crosslinked polymers, block-copolymers) [Gay02], [Gay03], [Cre02].

Adhesion between two substrates is a complex phenomenon, which at present is still not well understood [Fou95]. There are several factors determining the strength of adhesion [Gay02], [Bur05], [Bhu06]: (i) molecular interactions at interface [Isr92], (ii) mechanical properties of adhesive [Car96], [Sha96] and (iii) area of contact between adhesive and probing surface [Gay02], [Bur05], [Bhu06], [Cre96], [Gre07]. Two surfaces are tacky when they possess the right balance between mechanical properties, molecular interactions at their interface and have large enough area of contact.
1.2 Molecular interactions at interface

When two individual atoms, macromolecules or surfaces are approaching each other, they can form chemical bonds or interact physically. There are several types of physical intermolecular interactions that could act and that should be taken into account while speaking about adhesion phenomena: van der Waals forces, electrostatic and hydrophobic interactions, hydrogen bonds, as well as steric effects.

**Van der Waals (vdW) forces**, have electrostatic nature and act between any molecules and macroscopic bodies [Isr92]. The vdW forces differ from chemical interactions that lead to molecular bonding and demonstrate saturation: two molecules attracted via vdW forces are able to attract other molecules [Dut00]. These interactions arise from the fluctuations in the electric dipole moments of molecules which become correlated as the molecules come closer together, giving rise to an attractive force. This force can be also repulsive, but is always attractive between similar molecules or materials [Isr01]. The vdW forces are long-range and depend on nature of interacting bodies and their surrounding medium. Significant values of vdW forces are present on smooth surfaces and in fluids, but decrease with growing of roughness [Jon02]. The forces are inversely proportional to distance between the surfaces [Hem11]. The energy of the vdW interactions received from quantum mechanical calculations is equal to:

\[
U_{\text{vdW}}(d) = -\frac{B}{d^6} \quad \text{(eq. 1)}
\]

where \(d\) – is the distance between molecules, \(B\) – characteristic constant; the negative value shows the attractive character of vdW forces.

The vdW forces depend on polarizability of molecules and include dipole-dipole, dipole-induced dipole, and instantaneous induced dipole - induced dipole forces.

**Dipole-dipole** or Keesom force arises between permanent dipoles because of asymmetric distribution of charges inside the molecules. They tend to align the molecules to increase the attraction reducing the potential energy.

**Dipole-induced dipole** interactions (Debye force) appear between a molecule that possesses a permanent dipole and other uncharged molecule. The dipole moment on the first molecule generates an electric field and induces a dipole moment on other molecule. These forces are weaker than dipole-dipole, but stronger than London dispersion forces.

Instantaneous induced dipole - induced dipole or **London dispersion forces** result from temporary charge imbalances and act between nonpolar molecules. The forces arise from electric field fluctuation results in shifting of electric clouds about the nucleus. In
such a way even on nonpolar molecules the formation of the fluctuated dipole moments is possible; they can even provoke shift of charges on neighbouring molecules. 

**Hydrogen bond** is a type of attractive (dipole-dipole) interaction of a hydrogen atom with an electronegative atom, such as nitrogen, oxygen or fluorine, which comes from another molecule or chemical group. Polar molecules, such as water molecules, have a weak, partial negative charge at one region of the molecule (the oxygen atom in water) and a partial positive charge elsewhere (the hydrogen atoms in water). Thus when water molecules are close together, their positive and negative regions are attracted to the oppositely-charged regions of nearby molecules. 

A hydrogen bond tends to be stronger than van der Waals forces, but weaker than covalent bonds or ionic bonds. However, if many hydrogen bonds are formed between two molecules (or parts of the same molecule), the resulting union can be sufficiently strong and be quite stable. This type of bond occurs in both inorganic molecules such as water and organic molecules like DNA.

Often the van der Waals attraction is balanced by electric double layer repulsion. In addition to the vdW force, this is the other major long-range force that usually exists between two macromolecules or surfaces in aqueous solutions. The electric double layer is created by mobile charges that interdiffuse through the contact due to the initial difference of electrochemical potential between adhesive and adherent [Pos05]. The long-range electrostatic interaction energy between two similarly charged macromolecules or surfaces is usually repulsive and roughly an exponentially decaying function of their separation [Isr01], [Ada97].

![Schematic DLVO plots showing how the attractive vdW and repulsive electrostatic double layer forces together determine the total interaction potential between two charged surfaces in aqueous electrolyte solutions](image.png)
II. Theoretical Background. Adhesion and Tackiness. Fundamentals

The van der Waals and electric double layer forces make up the two forces of the so-called DLVO theory of colloid stability, after Derjaguin&Landau (1941), and Verwey&Overbeek (1948) [Isr01] (Fig. 1). The DLVO theory has been found to adequately describe the long-range forces between similarly charged colloidal and some bio-colloidal surfaces in aqueous solutions [Isr01].

**Hydrophobic interactions** are long range attractive forces exhibited by hydrophobic molecules or surfaces in water and aqueous solutions [Fag02]. The first direct force measurement between two hydrophobic surfaces was reported by Israelachvili and Pashley in 1982 which showed that the magnitude of the force is greater than vdw force [Isr82]. Notably, it is not the interactions between the hydrophobic molecules that make them together, but generation of favourable entropy while decreasing of a surface area between the solvent and the hydrophobic solute component. This entropic gain is responsible for almost all associations in the medium water and hence of extreme importance for life (formation of membranes, micelles, protein folding etc.).

**Steric interactions.** Macromolecular interpenetrating [Rap92] or elongation [Lak67] may also influence the strength of the interface for specific substrate-adhesive pairs [Gay02]. Note, interdiffusion process is typical for polymer-based adhesives [Fou95]. It can arise between any two polymer-like molecules or surfaces that do not have a fixed structure. It involves the slow diffusive intermixing of molecular groups across an interface, which increases the number of vdw contacts (Fig. 2). The interpenetration layer is capable to bear mechanical load [Pos05]. Such processes can be slow – proceeding over hours or days, during which time both the effective adhesion energy and force continue to increase (often by a factor of 1000 or more), and the interacting species lose their original structure [Isr01]. The extent of adhesion is determined by the extent of diffusion and the interfacial thickness between the two polymers [Jab94].

Fig. 2. Stages of polymer-polymer interdiffusion for polymers A and B. a: wetting; b: interdiffusion. Adapted from [Jab94].
II. Theoretical Background. Adhesion and Tackiness. Fundamentals

On the molecular scale the adhesive forces of attachment also can be resulted from some specific interactions and generally involve a degree of mechanical interlock. Another factor determining the strength of adhesion is a formation of meniscus bridges built up around the contacting and near contacting bumps of two surfaces due to changing the presence of a thin liquid film such as an adsorbed water layer. Namely, molecular structure of surfaces (hydrophobicity/hydrophilicity) determines the formation of meniscus bridge at the contact interface [Bur05], [Bhu06]. If the film is flat, meniscus bridges are the dominant factor in the adhesion. For the hydrophilic surface, for instance, higher meniscus forces and a higher real area of contact are expected compare to the hydrophobic ones [SY125].

1.3 Mechanical properties (elasticity) of adhesives

The mechanical properties of the substrate must also be considered when describing surface wetting, adhesion and tack [Car96], [Sha95], [Gay99]. Since every solid substrate possesses some degree of surface roughness [Gre66], this feature can reduce significantly the apparent contact area to the adhesive. That is why the major requirement for mechanical properties of good adhesive is its softness and compliancy [Gay02], [Gay03].

![Fig. 3. Contact areas between a substrate and a rigid (A) and a soft (B) adhesive.](image)

There is a criterion introduced by Dahlquist which determines an upper limit of the stiffness of a material (E <100kPa) for it to appear sticky [Dah66]. If the material is highly deformable, a good contact may be achieved due to surface interactions on the molecular scale, with no need for applied pressure. On the other hand, the contact may remain poor even under reasonable pressure if the adhesive material is too rigid: the true area of contact is restricted to the summits of the rough surfaces (Fig. 3) [Gay99].
1.4 Contact area (surface roughness)

Surface roughness is another important factor having direct influence on the strength of adhesion between two surfaces [Gay02], [Cre02], [Cre96], [Gre07]. This influence is however ambiguously and governed by mechanical properties of materials [Sve12]. If the adhesive is rigid, its contact area with a rough sample will be diminished. Even if there are strong interactions on molecular scale, the tack will be reduced proportionally to the reduction of contact area between the two surfaces [Gay02].

Another situation can be observed in the case of soft adhesives that are able to adjust their form and fill the interstices of the rough surfaces. The contact area and therefore the adhesion in-between will increase [Sun05], [Gor05], [Rus99]. Furthermore, there is another phenomenon that contributes to the strength of adhesion at the interface with the soft adhesive. Tiny air bubbles can be trapped at the interface during the contact and generate suction effects upon traction. Usual suction effects on the macroscopic scale are achieved mechanically and the intimate contact is due interactions on the molecular scale [Gay02].

Thus, in man-made materials smoothening of the surface usually leads to improving of adhesion, whereas increase of the surface roughness decreases the adhesion (at least between rigid surfaces). On the other hand, natural systems use micro- and nano-structuring to achieve a just opposite effect, namely to provide extraordinary and yet switchable adhesion [Aut00], [Cre99]. This is possible due to easiness of alignment of such rough surfaces (containing high aspect ratio elastic micro-needles oriented perpendicularly to the surface) with various curved surfaces and also detach them from the surface, when necessary. Development of the synthetic analogies imitating such hierarchical structures is in full swing [Sit03], [Gre07], [Cam08], [Kam10], [Syn12].

The surface roughness can also be controlled through the melting phase transition in polymer material. The surface of a semi crystalline polymer is rough with crystalline lamellae protruding through the surface. Driving the polymer into the molten state causes a dramatic reduction in the surface roughness. This is particularly well illustrated by temperature switchable adhesives whose softness and consequently, roughness can be made to vary significantly over a narrow temperature range [Cre99]. In the molten state, the contact area between the two bodies will, in general, increase, thereby increasing the adhesion. Thus, by using a simple melting phase transition, de Crevoisier et al. [Cre99] achieved control over the surface and bulk mechanical properties of their polymer and could delicate balance the factors that enhance and reduce adhesion [Rus99].

Moreover, topographical patterns with different geometries can be formed using a combination of colloidal lithography, etching, moulding and “drawing” techniques. These surfaces could be used as substrates for binary brushes that facilitate switchable properties. Using “classical” lithography methods well-oriented periodic microstructures
II. Theoretical Background. Adhesion and Tackiness. Fundamentals

of different geometries and aspect ratio of asperities can be obtained [Syn07], [Cam08]. Colloidal lithography uses colloidal particles that can be easily assembled into highly ordered structures by numerous methods [Syn05], [Syn06], [SYN125] (Fig. 4a). Mixing of particles of different size can be used as well for the fabrication of more complex surface structures (Fig. 4b).

![Fig. 4. Representative topography images of regularly ordered particle layers: (a) AFM image of 1 μm particles assembly; (b) AFM image of mixed assembly from micro (2 μm) and sub micro (200 nm) colloidal particles [SYN125].](image)

2. Switchable and adaptable adhesion

Two strategies of altering the adhesion properties are possible: simple switch and continuous adaptation. **Switchable** adhesives are capable to switch their adhesion from one state to another without any transitional state, whereas, **adaptive** adhesives change its adhesion dynamically corresponding to influence of external stimuli or in compliance with the properties of the surface to what they applied [SY125].

Switchability and adaptation are very prominent properties of various biological molecular machines functioning in living organisms. Indeed, enzymes, RNA, ionic channels, molecular motors, etc. act not always and not everywhere, but only in a certain place and time. Being normally inactive, such machines transform (or reconform) in their active form when obtain the corresponding managing signal (e.g., upon interactions with ions, ATP, etc.). The switchability and adaptation of biological elementary sub-units are general principles of organization of matter, when it is necessary to achieve, for instance, a long-term co-existence and function of a great number otherwise incompatible species inside cells (e.g., RNA and RNase), or when it is necessary to initiate or terminate the desired process in certain time. One prominent example is the switching in multi-weak-interaction (hydrogen bonding) between the two cooperative bistable states of haemoglobin (T state and R state) and oxygen which is a
fully reversible process and that facilitates O\textsubscript{2} uptake in the lungs and release to organs and tissues [Xia08]. Obviously, the switchability and adaptation are important mechanisms for self-regulation of extremely complicated systems.

In sharp contrast to natural organisms, man-made materials are significantly less “smart”. Further advances in material science impose requirements for dual surface properties that frequently are in conflict: a given material, depending on the conditions under which it is utilized, has to be hydrophobic or hydrophilic, acidic or basic, conductive or insulating, adhesive or repellent, and be able to release or adsorb some species. Investigation of the systems, able to change the surface properties began few decades ago as response on rising interest to the “smart” or “intelligent” materials. While there are a plenty of various examples of adhesive or non-adhesive materials most of them have fixed properties - either tacky or non-tacky - that vary only slightly with the surrounding conditions such as humidity or temperature. There are only few examples of adhesives demonstrating change of adhesion in very broad range upon contact with another material or to an environmental change [Jul03], [Kho02], [Ret05], [Lah03], [Vis06].

Adhesion can be switched by two main factors: chemical functionality and topography. Combination of these factors may lead to novel hierarchical structures with curious properties [Syn12].

2.1 Switching of adhesion by chemical functionality

Control of intermolecular interactions such as formation of hydrogen bonds, electrostatic or hydrophobic interactions which depend on chemical functionality of materials, is used to manufacture smart materials with switchable and adaptive adhesion properties [Syn12]. Such materials possess an ability to adjust their properties to changing environmental conditions or external stimuli like: temperature, chemical and biochemical stimuli, visible and UV light, pH, solvent, electric and magnetic stimuli.

1) Switchability of adhesion by temperature

*Phase transitions in polymers*

The first class of systems with temperature-sensitive adhesion behaviour undergoes transitions that occur with polymers itself: melting, crystallisation and liquid crystalline phase transitions. There is a bulk transition between a highly ordered smectic and an isotropic phase in such systems. A sharp change from a rigid to a soft behaviour accompanying the transition affects the adhesion properties of the liquid crystalline polymer. This transition behaviour was used to develop switchable adhesives by the group of de Crevoisier [Cre99]. On each side of the phase transition, a different aspect of
the hybrid macromolecule becomes predominant and imprints its behaviour onto the system. Through the side-chain ordering, the smectic structure brings hardness and non-wettability. In contrast, in the isotropic phase, the presence of the backbone, which connects the side chains together, allows for a strong dissipation that leads to both a tacky behaviour and an ability to slow down the dynamics of wetting [Cre99], [Cho03]. This transition effect can be used to design versatile materials with highly flexible properties that vary with temperature [Cre99].

An advantage of an ordering transition in a polymer containing alkyl and perfluoroalkyl side chains to turn adhesion on and off has been shown. At low temperatures, the perfluoroalkyl side chains (which have low surface energy) segregate to the surface. The polymer is crystalline and has a fixed structure. At elevated temperatures, crystal melting imparts mobility to the polymer such that it can respond to external stimuli. If a hydrocarbon is brought in contact with the surface, a surface rearrangement occurs, moving the alkyl segments to and the perfluoroalkyl segments away from the interface. A delicate balance between factors that enhance and reduce tack gives rise to a maximum in the tack over a very narrow temperature range. It is, of course, no accident that the phase transition in the work of de Crevoisier et al. occurs at 35°C, slightly below body temperature. By altering the length of the pendant side chains on the polymer, the transition temperature can be fine-tuned further.

Second approach for design glues with fickle stickiness was suggested by Ferguson and Khongtong [Kho02], [Kho01]. They used oxidized cross-linked 1,4-polybutadiene (1,4-PBD-ox). It was suggested that the thermoresponsive adhesion of a polymer–metal interface (i.e. PBD-ox/Al) arises from rubber elasticity in the interfacial region of the polymer: at room temperature the functional groups of polymer strive to contact with the aluminium (oxide). It is facilitated by stretching of the polymer chains out of their random coil conformations, thus reducing the entropy in that region of the polymer. Due to this, there are strong adhesive joints at room temperature. When the material is heated, the polymer chains of the rubber contract, pulling aluminium-loving carboxylic acid groups away from the surface. As a result, the bond between the metal and the polymer loosens such that the adhesion between the two surfaces is 44% less at 80°C than it is at room temperature. After the rubbery glue returns to cooler temperatures, it regains its former sticking prowess, although slowly. It takes approximately forty hours to recover the initial level of adhesion, and this reversibility persists through multiple heating and cooling cycles.

Another example of switchable adhesives uses a phase transition of admixed additives. This principle is applied in the technology known as “Warm-Off” [Chi01], [Cla93]. The additive in this case is a side chain crystallisable polymer which is intimately mixed in the crystalline state with a pressure-sensitive adhesive (PSA) [Cre02] prior to spreading on the backing. With growing ambient temperature, the additive will melt through a
Phase transition in polymer solutions (LCST polymers)

Polymers which demonstrate LCST (Low Critical Solution Temperature) behaviour in an aqueous environment are employed to design reversibly switchable adhesives. Well-known and the most widely studied system in this category is PNIPAM – poly(N-isopropylacrylamide). PNIPAM exhibits thermally responsive switching between hydrophilicity and hydrophobicity. This effect is explained by the competition between intermolecular and intramolecular hydrogen bonding below and above the LCST of about 32-33°C. At temperatures below the LCST, the predominantly intermolecular hydrogen bonding between the PNIPAM chains and water molecules contributes to the hydrophilicity of PNIPAM film, the polymer is in an extended, solvent-swelled conformation. At temperatures above the LCST, the polymer undergoes a phase transition, the solvent is excluded, intramolecular hydrogen bonding in the PNIPAM chains results in a compact and collapsed conformation of PNIPAM chains. It makes difficult for the hydrophilic C=O and N-H groups to interact with water molecules. Thus, the hydrophobic interactions become predominant [Sun04], [Gil04], [Lin99], [Lee10], [Ala05]. Moreover, above the LCST, PNIPAM coagulates also due to the hydrophobic interactions. When the temperature is below the LCST, the hydrophobic isopropyl groups in PNIPAM molecule should be embedded into the central part of molecule and the hydrophilic C=O and NH groups in molecule are dominantly exposed to the outer layer to contact with water to achieve higher composition of intermolecular hydrogen bonding. When the temperature goes beyond the LCST, the hydrophobic isopropyl groups are exposed to outer layer to form hydrophobic effect. So, the aggregation phenomenon of PNIPAM might be attributable to both the intramolecular interactions and the hydrophobic interactions [Lin99]. The thin films of PNIPAM are widely used for temperature regulation of adhesion of proteins and cells.

Another class of biologically inspired thermoresponsive molecules is based on elastin-like polypeptides (ELPs) [Hyu04]. The molecules are water-soluble at lower
temperatures but reversibly aggregate at elevated temperatures. The switching can be induced by changes in temperature, pH, or ionic strength. Elastin-like polypeptides have been micropatterned to capture and to release other proteins fused to ELPs via hydrophobic interactions upon transition [Nat03].

Fery et al. [Kes10] investigated the interaction forces between a native and a protein-coated probe and the thermoresponsive copolymer poly[2-(2-methoxyethoxy)ethyl methacrylate-co-oligo(ethylene glycol) methacrylate] [P(MEO2MA-co-OEGMA)]-coated surfaces using a colloidal probe technique. The sharp transition in adhesion properties was observed while passing though LCST and back. The system was switched many times without a loss of adhesive performance. Recently, Synytska et al. [Syn10], [Sve11] compared switchable adhesion behaviour of thermoresponsive polymer brushes with different architectures based on PNIPAM and polyethylene glycol polymers having LCSTs around 33°C. Temperature dependent adhesion measurements in water on flat and rough surfaces have been performed. As it was found, the synthesized via ATRP polymer brushes are completely non-adhesive below LCST and become adhesive at elevated temperatures. This behaviour was independent of substrate roughness, the geometry and hydrophobicity/hydrophilicity of the AFM probe. Moreover, the adhesion forces show full reversibility and repeatability. Amongst the other important polymers undergo phase transition in solutions are poly(N-vinylcaprolactam), poly(propylene oxide), polyacrylamide, and polypeptides [Ala05].

2) Switchability of adhesion by solvent

The successful control of wettability of a self-adapted polymer systems by exposing them to different solvents was reported [Min03a]. The heterogeneous binary polymer brushes were sensitive to toluene, ethanol, and water. The adaptive behaviour of the polymer chains was amplified by the microscale roughness of the material. As a result, the wettability of the mixed brushes could be switched from complete superhydrophilic to superhydrophobic states.

The group of Minko has recently fabricated adaptive systems made of biocompatible and biodegradable polymer brushes - polyethylene glycol (PEG) and polydimethylsiloxane (PDMS) [She08]. These brushes are widely used in medicine, food industry and cosmetics. At room temperature these polymers have very mobile chains because of low glass transition temperature (Tg) and they are able to immediately adapt their properties to changes in environmental conditions. It was demonstrated that PDMS-PEG brushes exhibit low adhesion in both wet and dry states.

Müller et al. synthesized core–shell cylindrical polymer brushes with poly(t-butyl acrylate)-b-poly(n-butyl acrylate), that were hydrolysed afterwards [Zha03]. Due to the responsive nature of the PAA blocks toward different kinds of solvent, conformational transitions were observed as a function of solvent quality.
Fischer and Schmidt made cylindrical brushes with PS side chains and studied solvent-induced length variation of the molecular brushes [Fis01]. They found that the lengths of the backbone and side chains become shorter in a poor solvent as compared to a good solvent. It is argued that the repulsion of the side chains represents the extension force, which acts against the entropic contraction force of the main chain. The adhesive properties of binary heterogeneous polymer brushes made from end-functionalised polystyrene (PS) and poly(2-vinylpyridine) (P2VP) chains have been investigated by Creton et al [Ret06], [Ret05]. The adhesion and wetting properties can be reversibly switched by exposure of the system to selective solvents for PS (toluene) and for P2VP (acidic water).

3) Switchability of adhesion by pH
Polyelectrolyte brushes tethered to surfaces are garnered increasing interest since they can reversibly alternate between different polymer brush conformations, from collapsed and extended states, and, as a consequence, gain control over surface properties such as wettability, hydration, and stiffness [Moy05]. The swelling behaviour of polyelectrolyte brushes is to a large extent governed by electrostatic interactions and the osmotic pressure of the counterions. Several reviews describing the possibilities in this field have been recently published [Luz04], [Min06], [Luz08], [Tok09].

One of the most common systems in polyelectrolyte polymer brushes utilizes acrylic acid [Ayr07]. The expansion of the poly(acrylic acid) brush upon addition of base was described as an example of the well-known polyelectrolyte effect. The swelling behaviour of a weak polyelectrolyte brush poly(methacrylic acid) in water as a function of pH and salt concentration has been also investigated [Bie02].

The pH-sensitive system was made by the group of M. Geoghegan [Spi07]. They demonstrated how two surfaces, one consisted of polyacid gel and another – a polybase grafted to a silicon substrate, stick together and separate in response to pH value. Possible applications of such surfaces pairs include microelectromagnetic components (actuators), components for microfluidic systems, or carries for pharmacological agents that could release their cargo under specific physiological conditions.

4) Photo-responsive surfaces
A photo switchable molecule can be converted from one form to another with light of one wavelength and can either revert thermally to the original state or can be reverted by irradiation with light of a different wavelength. The more commonly employed and most-studied classes of photo switchable molecular systems include: fulgides, azobenzenes, spiropyans, overcrowded alkenes, azulenes, alkylidenecycloalkanones, diarylethenes [Bro09]. Spiropyran is reversibly changed by UV irradiation from the more hydrophobic spiro conformation to the polar, hydrophilic zwitterionic merocyanine
conformation. The reverse isomerisation can be triggered by irradiation with visible light [Hig04].

The other approach by Edahiro et al. [Eda05] involved the use of a polymer material composed of PNIPAM having spiropyranchromophores as side chains to develop a reversible photo-responsive culture surface [Men08].

More recently, light-induced shape-memory polymers have been reported [Len05], [Jia06]. These materials can be deformed and temporarily fixed in a new shape. The polymers can change from its flat ribbon-like structure to a tight coil, then back to a ribbon, in response to light irradiation. Such polymers are composed of an elastic polymer network and a molecular switch, which determines their permanent shape and forms reversible crosslinks upon photostimulus, respectively [Len05], [Yos08].

Light switchable adhesives (LSA) are the special kind of switchable adhesives based on control of mechanical properties. These adhesives are composed of a functionalised methacrylate copolymer mixed with a photoinitiator activated by visible light. The photoinitiator induces a chain reticulation that decreases the peel strength of the adhesive and allows it to get away from the substrate when exposed to light [Boy01].

5) Chemically or biochemically-responsive surfaces

Enzyme-triggered activation of surfaces shows great promise as a method for altering surface properties in a controlled manner [Uli06]. Ulijn et al. [Tod07] reported a strategy which could enzymatically switch polymer surfaces from a state that prevented cell adhesion to another state in which cell adhesion and spreading were promoted.

Another example was shown by the group of Mrksich [Mrk03], gold surfaces carrying modified PEG-4-hydroxypheynyl valerate could be switched enzymatically from a redox inactive surface to a redox active surface by a deacylation reaction, either using the free enzyme or a engineered cell line that expressed this enzyme at the cell surface, thereby providing a way to interface cell behaviour with electrochemistry.

6) Electrically-responsive surfaces

An electrically conducting polymer is generally comprised of a conjugated polymer chain with π electrons delocalised along the backbone, yielding a semiconducting polymer that can be reversibly tuned through doping, an oxidation/reduction process where charge carriers are introduced to the polymeric backbone either chemically or electrochemically. Poly(N-methylpyrrolylium) poly(styrenesulfonate) (PMP+PSS-) [Mil87] and polypyrrole [Geo06] are particular interesting examples of electrically-switchable surfaces.

7) Magneto-responsive surfaces

Magnetic field sensitive polymer gels have been developed [Gil04], [Baw09], [Sza98], [Zri00]. This magneto-controlled elastic medium, called ferrogel, ferrofluid, or magnetic
II. Theoretical Background. Switchable and Adaptable Adhesion

fluid, is a diluted ensemble of noninteracting magnetic nanoparticles (with a typical size of ≈10 nm) homogeneously distributed in a polymer network. In ferrogels the magnetic and high elastic properties are coupled. As a result significant shape distortion occurs instantaneously and disappears abruptly when an external magnetic field is applied or removed.

For example, magnetic particles of colloidal size have been introduced into chemically cross-linked poly(N-isopropylacrylamide) and poly(vinyl alcohol) hydrogels [Zri00]. The influence of uniform and non-uniform fields has been studied. In uniform magnetic fields the gel beads form straight chainlike structures, whereas in nonhomogeneous fields the beads aggregates due to the magnetophoretic force directed to the highest field intensity. The ability of magnetic field sensitive gels to undergo a quick controllable change of shape can be used to create an artificially designed system possessing sensor and actuator functions internally in the gel itself. The peculiar magnetoelastic properties may be used to create a wide range of motion and to control the shape change and movement, which are smooth and gentle similar to those observed in a muscle. Thus, application of magnetic field sensitive gels as a soft actuator for robots and other devices has special interest. Unlike in metallic machine systems, devices made of gels work without noise, heat evolution, and exhaustion [Sza98].

8) Multi-responsive surfaces

Although many stimuli-responsive surfaces exhibiting reversible properties have been fabricated, they are only responsive to one kind of external stimuli. For some applications however dual/multiple-responsive materials are required. The most common are the dual-thermoresponsive polymers, showing LCST, UCST or both, combined with pH-responsiveness. In some cases, thermal response can be combined with magnetic or electric responsiveness, usually applied to hydrogels or nanoparticles [Lee10].

A copolymer that contains temperature-sensitive PNIPAM and pH-sensitive poly(acrylic acid) (PAA) was fabricated [Xia06]. Under external stimuli the copolymer demonstrates dual response. Reversible switching of the systems on rough surfaces between superhydrophilicity and superhydrophobicity occurs in both a narrow temperature range of about 10°C and a relatively broad pH range of 9. This behaviour can mainly be attributed to reversible changes in hydrogen bonding between the two polymer components, PNIPAM and PAA, and water.

Recently, superhydrophobic poly(3-hexylthiophene)-polyacrylonitrile (PANI-PAN) coaxial nanofibers were fabricated through combination of electrosprinning and polymerization. This nanofibers show a chemical dual-responsive surface in wettability, which can be controlled by adjusting the acid–base and redox properties of probe solution [Zhu07]. A reversible conversion between superhydrophobicity and superhydrophilicity was achieved.
Also, multi-stimuli-responsive surfaces, which reversibly switch between superhydrophilicity and superhydrophobicity in response to glucose, temperature, and pH, were fabricated [Xia07]. Temperature and pH sensitive PNIPAM was included in the surface as well as glucose-sensitive poly(acrylamidophenylboronic acid) (PPBA), which forms stable complexes with glucose via its borate groups [Xia08].

2.2 Switching of adhesion by surface topography

Many insects and animals, such as flies, spiders, and geckos have an amazing ability to firmly attach to and easily detach from almost any kind of surface and thus to move along vertical walls and even ceilings. This peculiar locomotion is possible due to hierarchically arranged structure of the animal pads: they are covered with long micro- to nano-sized hairs with characteristic geometries and mechanical properties [Aut00], [Aut02], [Arz03]. These structures facilitate conditions for appearance of van der Waals and capillary forces of great efficiency and thus play a crucial role in the phenomenon [Arz03].

Nowadays there is a plenty of publications that describe structuring methods applied to generate gecko-like fibrillar substrates with different geometries and dimensions. Particular attention is paid to effect of surface topography and roughness on wettability as well as to design of rough surfaces with switchable wetting properties [Que03], [Für05], [Boe10], [Xia08].

The design and fabrication involves patterning methods, which can be largely transferred from microelectronic and micromechanical processing [Cam08]. Microfibrillar surfaces are mainly produced by soft-lithography, photolithography using an SU-8 photoresist [Lam07], [Cro05], [Gre07], [Gla07] but also by indenting a wax surface with an atomic force microscope tip [Sit03] or by laser ablation of a metallic surface [Per04].

Micro- and nanosized fibrils with flat tips and also more complex geometries such as spatula-ended fibrils, tilted fibrils, or hierarchical fibrillar structures have been obtained as well [Lam07], [Gre07], [Cro05], [Sit03], [Aks07], [Jeo06]. Together with different patterning methods, micro- and nanoscaled rough surfaces can be also fabricated from assemblies with colloidal particles [Soe03], [Shi04], [Min05a], [Zha04], [Zha05a], [Ma06], [Sve11]. Recent reports deal with structured responsive materials in order to incorporate the reversible and adaptive character of gecko adhesion to artificial systems [Kus07], [Kam10].

The first article describing structured surfaces with switchable adhesion behaviour was published by Del Campo and co-workers [Red07]. The materials were made of the shape memory thermoplastics known for their ability to recover the original permanent shape from a temporary one via reheating the material about the glass transition temperature of the polymer.
Other system consisted of a shape memory polymer (SMP) layer and a smooth, non-structured, dry adhesive layer has been fabricated by Xie and Xiao [Xie08]. The material showed a slight curvature, which, in combination with the rigidity of the SMP layer, resulted in poor adhesion at room temperature. When the system is heated above the transition temperature, the adhesive deforms and comes into good contact with the test probe. After cooling to room temperature the deformed shape of the adhesive is maintained due to the SMP layer and the adhesion is retained. Upon heating the SMP returned to its original curved structure, and the contact area became small and the adhesive is thus released.

Since then, systems which respond to external stimuli, such as temperature, magnetic and electric fields, mechanical stretching, pneumatic pressure and preload, have been developed. In general, the expose to external field results in change in the topographical design of a surface that in turn influences the final adhesion performance. The adhesion switch is achieved in many cases by reversible maximization and minimization of the contact area upon influence of external stimuli.

*Magnetic and electric switching*

It was reported [Nor08] about the biomimetic systems with switchable adhesion behaviour able to undergo a reversible conformational change in magnetic field. They are composed of 10µm wide and 130µm long flexible nickel paddles coated by 200nm diameter aligned vertical polymeric nanorods (analogous to the hierarchical structure of gecko’s pads). When subjected to a magnetic field the paddles reorient themselves rotating away from the counter-surface, reducing the contact area of sticking surface, consequently, decreasing the adhesion force (by about a factor of 40 comparatively with an adhesive state without the magnetic field). The adhesion behaviour of presented systems is complete reversible allowing switching the adhesion countless times, that is advantageous over approaches based on shape memory polymers. The materials have perspectives to be used as everyday consumer products such as latching and fastening systems, as well as for high-tech applications, like microrobotics applied to extraterrestrial surfaces or harsh climates otherwise not accessible to man [Nor08].

An approach based on an electronically switchable capillary adhesion device was presented. Inspired by a leaf beetle able to generate adhesion forces exceeding 100 times its body weight, Vogel and Steen [Vog10] made their material with the surface tension force that arises from a large number of small liquid bridges that can be quickly made or broken with electronic control. Liquid was pumped through a hole into the device until contact is made and a liquid bridge is formed between the device and the substrate. In releasing, liquid was pumped back into the device until the bridge became unstable and broke.
Mechanical switching

Another group of materials with switchable adhesion using mechanics as stimulus was reported. Suh and co-workers [Jeo10] have utilised a wrinkled polydimethylsiloxane (PDMS) sheet with a thickness of 1 mm with built-in micropillars. The wrinkles were generated through to oxygen plasma treatment of the extended PDMS sheet and subsequent strain release. An active, dynamic control of normal and shear adhesion was achieved: relatively strong normal and shear forces were obtained for a fully extended (strained) PDMS sheet, whereas the forces could be rapidly reduced to nearly zero once the strain was released. Durability tests showed the ability of such systems to be switched in more than 100 attachment and detachment cycles.

Nadermann et al. showed structures with a fibrillar PDMS surface terminated by a continuous film that can be switched between two metastable states. In the first one, the film is stretched and held up by fibrils, it demonstrates strong adhesion compared to an unstructured flat PDMS. In the second state, the film collapses and adheres to the substrate between fibrils. To switch the system, the terminal film was then sucked in using air pressure or mechanical pressure. As a result, the surface gets rough surface composed of periodic arrays of bumps. The contact area and also the adhesion force will decrease. The surface can be switched again by removal of the pressure or through blowing up the film; the properties will be recovered [Nad10].

Fig. 5. (a) Switching from adhesive to non-adhesive states. The micropatterned surface is deformed mechanically above the transition temperature ($T_{\text{trans}}$). Cooling the system in the deformed position stabilizes the non-adhesive state. Recovery occurs by heating above $T_{\text{trans}}$. (b) SEM image of non-adhesive, tilted state. (c) Load–displacement curves measured on micropatterned surfaces [Red07].

Micropatterned PDMS surfaces in the work of Paretkar [Par11], [Par12] were fabricated using photolithography and moulding. The adhesion properties of the surface made of
30 μm length and 10 μm diameter fibrils can be switch reversibly with a compressive preload as an external stimulus (Fig. 5). Adhesion forces were measured with a flat probe as a function of preload. At low or moderate compression, there is a good contact between the surfaces, the adhesion force is big, whereas at high compressive preloads adhesion dropped to very low values. It can be explained by bending and buckling of the fibrils under high pressure and a subsequent loose of contact with the probe surface. The elasticity of PDMS contributes to the pillar recovery to regain the upright position upon removal of preload enabling repeatability of the switch. The switch can be controlled by fibril aspect ratio, tip shape and alignment to the test surface. The folding of end flaps at the tip of the fibrils facilitates larger difference in adhesion strength between the adhesive and non-adhesive states [Par12].

Pressure modulated adhesion between flat, stiff objects and elastomeric surfaces with sharp pyramidal features was presented [Kim10]. Rogers and co-workers fabricated elastomeric micropyramidal structures on a square surface, specifically designed for transfer printing applications. To peak up some object the pressure was applied to deform and collapse the region between the pyramids and make a big contact area with the object. After peak-up the sample relaxes and the picked-up object has a contact just with the pyramids. So the contact area is quite small that makes it possible to detach the object easily by gently pressing it on a receiver surface. In such a way, the adhesion strength could be switched by more than three orders of magnitude in a reversible fashion.

3. Stimuli-responsive materials and polymer brushes

A number of smart stimuli-responsive materials have been developed that are able to alter their properties upon exposure to internal or external stimuli [Boy01], [Ala05], [Min06], [Bun08], [Men08], [Yos08], [Bro09], [Nan10], [Lee10], [Stu10]. To minimize the free energy of the system such responsive systems undergo following transitions: from wetting to non-wetting, from adhesive to non-adhesive, from adsorbing to non-adsorbing, from attractive to repulsive, etc.

To provide surfaces with desired functions and properties, grafting of stimuli-responsive polymers on the surface is a widely used method. Surfaces modified with two or more thermodynamically incompatible polymers represent unique responsive properties [Sid99]. The attached chains are capable of molecular motions and micro-phase segregation in response to external environment [Sid99], [Min02b], [Min03b]. Upon exposure to stimuli which are selective for the components of the brush the reorganization of the structure occurs, for example, through migration of solvated polymer which migrates preferentially at the top of the brush and dictates the surface properties of the whole film [Ion03], [Hou03] (Fig. 6). Experimental and theoretical work
demonstrated that lateral versus vertical reorganization within the polymer layer is the origin of this switching behaviour.

![Diagram of polymer brushes changing conformation](image)

**Fig. 6. Schematic representation of the switching scenario from the hydrophilic to the hydrophobic state and vice versa, in the wet and dry state by using selective solvents [Syn07], [Ret06].**

### 3.1 Polymer brushes

Polymer chains grafted with one end to a surface have been first described by Alexander and de Gennes [Ale77], [Gen80]. The polymer layers could be attached to the surface through physical interaction forces or via covalent bonds which are preferable because of higher stability. Depending on the grafting density which is defined as the inverse distance between two neighbouring surface-attached polymers, three types of anchored polymer layers can be distinguished. If the distance between attached polymer chains is more than the size of the molecules and the chains do not overlap, two conformations can form. If there is a tendency to adsorb the polymer segments to the surface, flat “pancake” (Fig. 7, A) conformation is achieved. In the case of absence of adsorption, the polymer chains build “mushroom” conformation (Fig. 7, B). Here largely unperturbed polymer coils are grafted to the surface.

![Diagram of polymer conformations](image)

**Fig. 7. Schematic illustration of the conformation of polymers end-attached to surface: (A) “pancakes”; (B) “mushrooms”; (C) “brushes”.**
Interesting effects are observed when the grafting density increases. If the distance between grafted chains is smaller than an average end-to-end distance of the polymer chain, they start to overlap and interact with each other. The polymer chains stretch along the direction normal to the grafting surface because of the excluded volume effect and the necessity to minimize the interaction energy between polymer segments [Gen80], [Ale77], [Zha00]. The layer of the grafted chains assumes so called “brush” conformation (Fig. 7, C). The conformation is determined by the energy balance between the repulsion interactions between the polymer segments and elastic free energy of the stretched chain. This leads to a new equilibrium at a higher energetic state than that of isolated coils and this new behaviour of the stretched polymers differs considerably from that of flexible polymers in solution where chains adopt a random-walk configuration [Zha00]. The more is the grafting density of the polymer chains on the surface, the more stretching is observed and as a result, the thickness of the polymer brushes increases [Rüh04], [Hou05], [Min02a].

Linear polymer brushes tethered on solid substrate surfaces can be classified into homopolymer brushes, mixed homopolymer brushes, random copolymer brushes and block copolymer brushes [Zha00]. Polymer chains of homopolymer brushes consist of only one type of repeating units. Mixed brushes composed of two or more types of homopolymers. Random copolymer brushes are tethered polymer chains consisting of two different repeating units, which are randomly distributed along the chains. Block copolymer brushes are assembly of tethered polymer chains covalently connected to each other. Polymer brushes can be neutral or carry a charge (polyelectrolyte brushes), their chains can be rigid or flexible, semiflexible or liquid crystalline (Fig. 8).

*Fig. 8. Classification of linear polymer brushes* [Ion05].
solution. The phase behaviour of such polymer brushes is determined by a competition of the mixing entropy, which favours homogeneously mixed state, and the interaction energy, which is reduced by spatial separation of the incompatible polymers [Mar91]. Cylindrical polymer brushes are assembly of tethered polymer chains that consist of a backbone and side chains having different nature. These polymer brushes have the same number of side chains as degree of polymerization of the main chain. Intramolecular excluded-volume interactions between side chains densely grafted to the backbone contribute to the formation of the extremely extended conformation of the main chain. Depending on the type of side chains, the cylindrical polymer brushes can be divided into bottle-brushes if the side chains are homopolymers, and core-shell cylinders if the side chains are block copolymers.

Intramolecular phase separation between two chemically different side chains statistically or alternatingly attached to a backbone has been investigated theoretically and in practise. For this a number of parameters such as the incompatibility between the side chain molecules, the relative length of the side chains, flexibility/rigidity of the backbone and the solvent quality with respect to the two different side chains have been taken into account [Ste02], [Jon04], [Hsu07].

Influence of the solvent quality on statistical copolymacromonomers made from poly(2-vinyl pyridine) and poly(methyl methacrylate) macromonomers have been shown. The system has different shapes ranging from wormlike to horseshoe or meander structures when spin-cast onto mica [Ste02].

It was even reported about the possibility of formation of Janus-type phase-separated cylindrical brushes in solution, consisted of a rigid backbone and hetero side chains [Tsu01], [Zha03], [Hsu07], [Iru08].

3.2 Grafting approaches

There are two well-established routes for the fabrication of tethered polymer layers: “grafting to” and “grafting from” approaches.

In the “grafting to” method previously prepared polymer chains are used. They have end functional groups which are able to form covalent bonds with reactive sites on the surface of the substrate (Fig. 9). This method is very simple for generating polymer layers with narrow molecular weight distribution. However there are several disadvantages which limit the applicability of the “grafting to” procedure. Only relatively simple polymer molecules can be surface-attached by this method, because of the high reactivity of the end-functional groups which prevents the coexistence of most functional groups in the polymer [Rüh04]. In addition, once the surface is significantly covered with polymer chains the further attachment becomes more and more complicated, because of a strong kinetic hindrance (the diffusion of further polymers
II. Theoretical Background. Stimuli-Responsive Materials and Polymer Brushes

through already attached is considerably restricted) and for thermodynamic reasons (the already attached molecules should stretch to make the accommodation of the next chains possible, that is not energetically favourable) [Pru98]. The fabrication of tethered polymer layers in the brush-like regime by the “grafting to” process is thus limited and the systems got are usually in “mushroom” conformation or at the low graft density of the “brush” regime [Sid99]. Also the film thicknesses are limited to several nanometres [Rüh04].

“Grafting from” approach gives the possibility to overcome the limitations of the “grafting to” procedure. In the "grafting-from" process the polymer chains are polymerized directly at the surface from a surrounding monomer solution using a monolayer of surface-attached initiator molecules (usually using silane chemistry). Conventional radical polymerization or living polymerization methods are used to grow polymer brushes on planar and spherical surfaces (Fig. 10).

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**Fig. 9.** General scheme of a “grafting to” process for the end-attachment of polymer molecules to solid surfaces. The early build-up of the polymer monolayer is governed mainly by the diffusion of the molecules to the surface. However, at later stages adsorbed amount and thickness are limited due to kinetic and thermodynamic hindrances [Rüh04].

**Fig. 10.** Schematic description of a “grafting from” process for the in-situ generation of surface-attached functional polymer monolayers [Rüh04].
In the “grafting from” procedure only monomer has to diffuse to the growing chain end, thus eliminating the problem with the diffusion barrier, which strongly limits film growth in the “grafting to” approach [Rüh04]. High swellable polymer layers on very irregular surfaces can be thus made. Another advantage of the procedure: there is no need to synthesise a polymer with a functional group like in “grafting to” method. The thickness of polymer layers has direct correlation with quantity and conversion of the polymerization initiator and thus can be easily controlled. With “grafting-from” high thicknesses and grafting densities can be achieved, but it is rather difficult to control the grafting density. Other disadvantages of the procedure are high polydispersity index (PDI) of the chains (between 1.5 and 3 for conventional radical polymerization [Pru98]) and that the substrate must be immersed in a polymer solution. A type of the “grafting from” approach, called Atom Transfer Radical Polymerization (ATRP), has been used in this work for fabrication of polymer brushes on flat surfaces and spherical colloids.

Controlled radical polymerization (CRP), also called Living-radical polymerization is used for synthesis of polymers, in bulk, on particles and on the flat surfaces. Functionalization of surfaces by grafting of polymer chains using a “grafting from” approach with CRP provides an effective route to improve the physical and chemical properties of surfaces and enables preparation of polymer brushes of high grafting density, controlled structure and composition.

![Reaction scheme of conventional ATRP procedure](image)

*\(P_n^*\) *X initiator
*\(Mt^0/L\) transition metal catalyst with transition metal in lower oxidation state complexed by ligand L
*\(X-Mt^{n+1}/L\) oxidized transition metal halide complex
*\(P_n^*\) active radical that propagates by addition of monomer and deactivates by reaction with oxidized transition metal halide complex
*\(k_{\text{act}}\) reaction rate of activator species
*\(k_{\text{deact}}\) reaction rate of deactivator species
*\(k_p\) reaction rate of propagating species
*\(k_t\) reaction rate of termination (strongly suppressed)

*Scheme 1. Reaction scheme of conventional ATRP procedure [Ber10].*

There are several types of CRP, like as Nitroxide-Mediated Radical Polymerization (NMRP) [Bian05], Reversible Addition Fragmentation chain Transfer polymerization (RAFT) [Barn04] and Atom Transfer Radical Polymerization (ATRP). The last technique is
among the most effective and most widely used methods of CRP. ATRP was independently discovered by M. Sawamoto et al. [Kato95] and by K. Matyjaszewski et al. [Mat95] in 1995. ATRP differs significantly from conventional radical based polymerization methods. ATRP allows synthesis of fundamentally new materials with complex, well-defined nanoscale architectures and tailored functionalities, while employing a broad range of monomers. By varying temperature or other conditions of this living process, on can shut down and re-start the reaction making it possible to get multi-block-copolymers systems. The scheme of ATRP is schematically presented on Scheme 1.

The ATRP employs atom transfer from an organic halide \( (P_n-X) \) to a transition-metal complex \( (M^{n+1}/L) \) in the lower oxidation state to generate the propagating radicals \( (P_n^*) \). This radical then adds to an alkene followed by the back-transfer of the halogen from the transition metal in the higher oxidation state with a coordinated halide ligand \( (X-M^{n+1}/L) \) to the product radical, resulting in the final product. In this reaction a metal catalyst, usually a complex of a copper (I) halide undergoes a one-electron oxidation with simultaneous abstraction of a halogen atom from a substrate. This inner-sphere electron transfer process reversibly generates an organic radical and a copper (II) complex. After the back-transfer, the copper (I) complex is reformed along with alkyl halide, completing the catalytic cycle [Mat98], [Sing03]. Precise values for \( K_{\text{ATRP}} \) are difficult to measure during the polymerization reaction because copper(II) concentrations continuously change due to the persistent radical effect (PRE) [Fis01] and the equilibrium is strongly shifted towards deactivation \( (k_{\text{act}}<<k_{\text{deact}}) \).

Scheme 2. The main principals of AGET ATRP procedure.

The ATRP, as in any radical process, has to be carried out in rigorously deoxygenated systems to prevent trapping of propagating radicals by oxygen. However the group of Matyjaszewski has developed and improved the ATRP giving the possibility to grow polymer chains even in the presence of limited amounts of air [Mat07]. This procedure called Activator Generated by Electron Transfer (AGET) ATRP. The air in the reactive vessel can be consumed by adding a sufficient amount of an appropriate reducing agent, such as metallic copper, tin(II) 2-ethylhexanoate or ascorbic acid. The activator (Cu(I) species) is first rapidly oxidized by oxygen to the Cu(II) species, but the latter is quickly
reduced to the Cu(I) state in the presence of a reducing agent (Scheme 2). This process has been successfully used to prepare well-defined products in organic media and also in miniemulsion [Min05], [Jak05].

4. Application of adhesives with responsive and adaptive properties

The increasing need for “smartness” in biomedical and engineering materials has generated a growing interest for synthetic polymers that exhibit environmentally responsive adhesion behaviour [Lee10].

4.1 Biomedical applications

Smart adhesives are very promising for a great variety of biomedical applications such as wound dressings and bandages, immobilization devices, transdermal delivery devices, biosensors, drug delivery, for bioseparation and tissue engineering [Nan10], [Ala05], [Stu10], [Wis08], [Syn12], as well as for fabrication of micro(nano)-electromechanical systems (MEMS/NEMS), microfluidic devices and biomedical equipment [Del05], [Gra04], [She08], [She09].

The light-switchable adhesives have attracted interest to be applied as plasters [Ium11]. Adhesives are very sticky in their normal state but lose their adhesion when exposed to visible light that is advantageous for delicate surfaces like skin. The disadvantage of LSA is that they can be switched only once. Pressure-sensitive adhesives have been also used to produce plasters [Chi01].

Thermoresponsive PNIPAM-containing systems are widely used for adhesion of proteins, cells and cell assemblies [Can05], [Aki04], [Men09]. In certain cases, cells and proteins will adhere to the thermoresponsive PNIPAM films at physiological temperature (37°C), and detach when the temperature is reduced to room temperature, i.e., below the LCST. Also polymer films comprising photo-responsive molecules such as spiropyran [Hig04] represent attractive candidates for controlling protein and cell adhesion on surfaces.

For the same purpose, coatings composed of thermoresponsive side chain oligo(ethylene glycol) have been fabricated by Laschewsky et al. [Wis08], [Kes10]. The advantage of the system comparatively to PNIPAM coating is a better inherent biocompatibility, reduction of nonspecific protein adsorption even above the LCST and more effective control of cell adhesion. Microfluidic devices are being developed to adsorb biological, organic, or inorganic materials from solution, hold them, and release on command, facilitating separation, purification, analysis, and delivery of substances [Hub03]. Wherever they are used, their functioning is restricted by fouling. For many purposes (preconcentration, separation, and sensing of analytes) the interfacial adsorption is however desired. Therefore, the
II. Theoretical Background. Application

Microfluidic devices have to be switchable, to adhere and release substances on demand. Thermally programmable protein capture and release has been achieved using both PNIPAM [Hub03] and elastin films [Hyu04]. The PNIPAM was integrated into microfluidic hot plate and could be switched between an antifouling hydrophilic state below LCST and a protein-adsorbing state that is more hydrophobic [Hub03]. Smart adhesives are also widely used in the field of drug-delivery. The ability of drugs to reach target tissues is limited by the body’s multiple barriers. To overcome them the materials with responsive adhesion properties are used [Mit08], [Ori03], [Lan04]. Peppas and co-workers have developed polymers that swell in response to pH change. At low pH values (like in stomach) they are collapsed but swell at higher pH’s, such as those encountered in the upper small intestine where they can release the required medicament [Tor02]. Multi-responsive poly(NIPAM-co-PBA) polymer brushes are used for novel non-invasive glucose sensors and insulin self-delivering systems for diabetic patients [Xia07], [Xia08]. Conducting [Geo06], [Ger02], [Zho89] and enzyme-responsive [Mrk03] polymers layers were also investigated for the purpose of drug delivery.

4.2 Engineering (non-biomedical) applications

There is a wide range of application of smart adhesives also for engineering purposes. For example, as anti-reflection, anti-corrosion and anti-icing coatings, for solar cells, textiles, for drag reduction and sensors [Liu12].

A novel antifogging strategy for simultaneous self-cleaning and antifogging materials was proposed by Howarter et al. [How07] via stimuli-responsive polymer brushes. Perfluorinated end-capped polyethylene glycol (f-PEG) surfaces exhibited stimuli-responsive and simultaneously PEG-like behaviour to water (hydrophilicity) and fluorinated behaviour to oil (oleophobicity), which is a promising solution for self-cleaning anti-fog coatings [How07].

Adhesives for industrial, consumer and military settings based on reversible adhesives inspired by mussels and geckos hat been developed [Lee07], [Mes07]. The results of this study are temporary adhesives – reusable tape that adhere equally well in wet and dry conditions.

A synthetic gecko foot-hair fabrication method was proposed by Sitti and Fearing [Sit03]. The dry adhesives made via nanomolding technique can be useful for future wall-climbing and surgical robots and also for other general dry adhesive applications. Fluorinated coatings with order-disorder structural transitions that tune the adhesive and wettability properties of a material in the range of human body temperature [Cre99] are suitable as responsive grips for sporting equipment such as baseball bats, tennis racquets, and golf clubs, or for garments with clinging.
II. Theoretical Background. Application

Gecko-inspired synthetic microfiber arrays were fabricated with a non-tacky stiff polymer [Lee08], [Sch08]. The materials with directional adhesion can easy attach (without requiring high pressure) and release. It could be also useful for sporting goods or climbing robots where a controllable and reusable adhesive is needed. Light-switchable adhesives are useful for electronics, paper and graphics industries. They are used as industrial tape, de-bond on demand adhesive foil, tamper-proof labels and residual-free labels [lum11].

The demand for such “smart” systems for engineering, biomedical, food and cosmetics industries grows continuously. This is a steadily expanding area of research and certain success has been already achieved. Nevertheless, there is still a chasm between the natural and the man-made materials, most of which still demonstrate static unchangeable properties. The progress is not very fast because of the complexity of the systems, but the potential for the design of the intelligent systems is very high. I believe the expansion of this complicated, but fascinating field of research will appear in the near future.

5. Surface characterisation techniques

5.1 Atomic force microscopy

Scanning probe microscopes (SPMs) are a family of instruments used for studying surface properties of materials. SPMs appeared in the early 1980s and were the first instruments making the three-dimensional real-space atomic-scale images of surfaces [Bin86]. The atomic force microscopy (AFM) belongs to a series of SPMs. This series started with the scanning tunnelling microscope (STM), which allowed the imaging of surfaces of conducting and semiconducting materials [But05]. It was developed by Gerd Binning and Heinrich Rohrer at IBM Research in Zürich and has brought the inventors the Nobel Prize for Physics in 1986. The atomic force microscope (AFM) grew out of the STM and today it is by far the more prevalent of the two [AFM05]. Unlike STM, the AFM allowed investigations of both, conducting and insulating surfaces [But05]. Its ability to study virtually any kind of solid – or even liquid interface in various media has made AFM one of the most important analytical tools in interface science. One can get not only high-resolution topography images, but in addition the information about adhesion, carrier concentration, conductivity, elasticity, electric fields, friction, hardness, magnetic fields, roughness, spreading resistance and temperature distribution of the investigated surfaces [Sch09], [Dem10]. Invention of SPM has lead to new discoveries in many fields including life science, material science, electrochemistry, polymer science, biophysics, nanotechnology and biotechnology.
II. Theoretical Background. Surface characterisation techniques

5.1.1 Topographical measurements

The microscope scans over the sample surface with a sharp tip, typically less than 5µm tall and often less than 10nm in diameter at the apex. The tip is located at the end of a cantilever that is usually 100-500µm long. The tip is brought into contact with or close to the sample and scans it over the surface [Lei05]. The scanning motion is provided by a piezoelectric scanner which scans the sample in a raster pattern with respect to the tip (or scans the tip with respect to the sample). Attractive or repulsive forces resulting from interactions between the tip and the surface will cause a positive or negative bending of the cantilever. The bending is detected by means of a laser beam, which is reflected from the back side of the cantilever [Vii08] into a position-sensitive photodiode detector (Fig. 11). By detecting the difference in the photodetector output voltages, changes in the cantilever deflection or oscillation amplitude are determined. A feedback loop maintains a constant tip-surface interaction force by vertically moving the piezoelectric scanner to maintain a constant photodetector difference signal [Gor05], [AFM05], [Lei05].

![Fig. 11. Schematic representation of working principle of AFM [www3].](image)

In general, the physical nature and character of the tip-sample interaction are quite complicated, since they are defined by the tip characteristics, surface properties and surrounding medium. The main forces which contribute to exert the tip are: the force coming from mechanical contact of the tip end atoms with the sample (Fig. 12), the van der Waals force and the capillary force arising from condensation of water vapour in the contact area [Dem10]. The forces acting on the tip vary, depending on the operating mode and the conditions used for imaging [Gor05]. A number of AFM modes of operation are available. The most commonly used are the contact mode, non-contact mode and the TappingMode™ (intermittent contact).
II. Theoretical Background. Surface characterisation techniques

Contact mode
In the Contact mode the tip is in intimate contact with a surface. The scanner gently traces the tip across a sample surface (or the sample under the tip), while the photodiode detector is monitoring the change in cantilever deflection because of its accommodation to changes in topography. The tip interacts with the sample, and the cantilever bends according to the Hooke’s law: $F = kz$, where $F$, $k$, and $z$ are the applied force, the cantilever spring constant, and cantilever deflection, respectively. The feedback loop maintains a constant force during imaging. At the right side of the curve in Fig. 12, the tip and the sample are gradually brought together, their atoms begin to weakly attract to each other. This attraction increases until the atoms are so close together that their electron clouds begin to repel each other. This electrostatic repulsion progressively weakens the attractive force as the separation continues to decrease. The total force goes through zero and finally becomes positive (repulsive) [AFM05]. Low spring constant ($k < 0.1$ N/m) probes are typically used to minimize the value of the applied force. Contact mode works well for hard surfaces in ambient conditions and in liquid [Gor05]. The contact mode can boast of scanning with high speeds, but the probability of damaging the surfaces, especially of soft samples, restricts the usage of this mode.

Non-contact mode
In the non-contact AFM the cantilever is vibrated near the surface of a sample. The spacing between the tip and the sample is of the order of tens of hundreds of Ångstroms and is indicated in Fig. 12 as the non-contact regime. The inter-atomic force between the cantilever and the sample in this regime is attractive (largely a result of van der Waals interactions) [AFM05].

Fig. 12. Intermolecular force curve [Gor05].
In non-contact mode, the system vibrates a stiff cantilever near its resonant frequency (typically 100-400 kHz) with amplitude of a few tens to hundreds of Ångstroms. The system detects changes in the cantilever’s resonance frequency or vibration amplitude and keeps it constant by moving the scanner up or down in response to changes. In this way, the average tip-sample distance is also kept constant and the Z feedback signal is used to generate the data set [AFM05]. Low forces are exerted in the non-contact mode, it is especially important while scanning of fragile and soft surfaces. Disadvantages of this mode are relative slower scan speed (to avoid contact with the fluid) and lower lateral resolution because of the tip-sample separation [Vil08].

TappingMode™
TappingMode™ AFM, the most commonly used of all AFM modes, is a patented technique (Veeco Instruments). During the scanning the cantilever oscillates slightly above its resonant frequency, and it contacts (taps) the surface for a short period during its oscillation cycle. By monitoring the changes in the cantilever’s oscillation amplitude caused by changing of the sample surface, the topography images can be obtained.

TappingMode has become an important AFM technique, because it overcomes some of the limitations of both contact and non-contact modes. Firstly, the tapping mode eliminates the lateral, shear forces. Since the contact time between the tip and the sample is two orders shorter as compared to contact mode, the TappingMode is less damaging. It is typically used for imaging topography of soft, fragile and adhesive materials without damaging them. Another major advantage of TappingMode is related to limitations that can arise due to the thin layer of liquid that forms on most sample surfaces in an ambient imaging environment. The amplitude of the cantilever in TappingMode is considerably higher than in non-contact mode and is usually in the range of 100 nm. It prevents the tip being stuck in this liquid layer that often happens by scanning in the non-contact mode.

In general, TappingMode is much more effective than non-contact AFM, but especially for imaging larger areas on the sample that may include greater variations in topography. TappingMode can be performed in gases and non-corrosive liquids [AFM05]. Because of the high amplitude of oscillation, the tip propagates through regions of attractive (van der Waals, electrostatic) and repulsive forces in a single oscillation cycle (Fig. 12). The amplitude and the frequency of the cantilever decrease while approaching the sample surface. Upon scanning, these parameters (and, hence, the force gradient) are maintained constant at a set-point level by the feedback loop [Dem10], [Gor05].
5.1.2 Force measurements

The atomic force microscope is not only a tool to image the topography of surfaces. AFM can also be used as a spectroscopy tool, probing the tip-sample interaction at a given point on the sample surface. This method produces force vs. distance curves, which characterize interactions between a tip and a surface as a function of the tip-sample separation. Such curves provide valuable information on local material properties such as elasticity, hardness, Hamaker constant, adhesion and surface charge densities. For this reason the measurement of force curves has become essential in different fields of research like as surface science, materials engineering, and biology. Force curves are used by many AFM researchers to characterize materials and single molecules, to calculate $M_n$, PDI as well as the adhesion of an individual polymer chains [Goo04], [But05], [She09].

When a force curve is acquired, the lateral movement of the scanner is stopped, and the scanner extends and retracts only the Z electrode. A force vs. distance curve is a plot of the deflection of the cantilever versus the extension of the piezoelectric scanner that changes the distance between the sample and the tip [AFM05]. A typical force-distance curve presented in Fig. 13 can be divided into several steps.

- **Approaching (A).** At this step the scanner extends gradually descending the cantilever to the surface. The cantilever is non-deflected since it is too far away from the surface and there is no interaction in between. The situation remains until the cantilever comes close enough to the sample surface for the tip to experience the attractive van der Waals force and they start to interact, the cantilever is not free anymore and the interaction has to be taken into account.

![Force Calibration Plot](image)

*Fig. 13. Typical force curve with schematic labelling corresponding tip-sample interaction points [AFM05].*
Jump to contact (B). At some point during this descent, the tip suddenly plunges toward the sample. This point is referred to as the “jump-to-contact” point and is usually due to electrostatic attraction or surface tension (capillary) forces.

Contact (C). As the scanner continues to extend, the tip is pressed into the surface and the cantilever deflects away from the surface approximately linearly.

Retraction. After full extension, at the extreme left of the plot, the scanner begins to retract. The cantilever relaxes downward until tip forces are in equilibrium with surface forces.

Adhesion (D). The piezoelectric scanner is retracting and the cantilever is pulling away from the sample. If attractive forces are strong enough, the tip clings to the sample surface as it pulls clear. The cantilever bends downward.

Pull off (E). As the scanner continues retracting, the sample eventually retracts and the tip rebounds sharply upward. By knowing the spring constant of the cantilever, it is possible to measure the attractive forces of tip-sample interactions with good precision.

Separation. The scanner goes on retracting, the tip continues its ascent. No further contact with surface during this cycle [Multimode04].

The direct result of a force measurement is a measure of the photodiode current $I_{PSD}$ that reflects the tip deflection, versus height position of the piezoelectric translator $Z_p$. To obtain a force-versus-distance curve, the raw data have to be converted. To make this, two parameters need to be known: the sensitivity of cantilever and the zero distance between the sample surface and a cantilever tip. Both of them can be inferred directly from a force curve: the linear part of the “contact regime” is assumed to be zero distance and its slope is the sensitivity. Some examples representing curve’s conversion for systems with different hardness and adhesion properties are presented in the Fig. 14 [But05].

To quantify adhesion force curves the spring constant of the cantilever must be known. There are numerous of methods allowing determination of the spring constant. One group is based on determination of geometry and dimensions of the cantilever. These methods are non-destructive, but they have several disadvantages that make them unreliable. Experiments showed that experimentally determined spring constants often differ significantly from calculated ones [Cli05], [Sad95], [But93]. Firstly, it is difficult to precisely determine the thickness of the cantilever that can in addition vary along the length. Secondly, Young’s modulus of a thin layer can deviate from that of the bulk material. After all, the unknown thicknesses of the native oxide layer (on silicon nitride cantilevers) and of the gold layer (evaporated onto the cantilever to increase its reflectivity) add significantly to the mass and thus resonance frequency [Haz99], [Sad95] and it might influence the spring constant as well [But05].
II. Theoretical Background. Surface characterisation techniques

*Fig. 14. Conversion of the photodiode current \( I_{PSD} \) versus height position of the piezoelectric translator \( Z_p \) to force vs. distance curves: where \( D \) is given by the sum of the cantilever deflection \( Z_c \) and the piezo position \( Z_p \) (a) Infinitely hard tip and sample without surface forces; (b) Infinitely hard materials but with a long-range repulsion; (c) Deformable materials without surface forces; (d) Deformable materials with attraction and adhesion force. The negative distance axis is interpreted as indentation \( \delta \) [But05].*

Another method implies the measurement of the static deflection of the cantilever. A reference cantilever is previously calibrated and then used to calibrate all other cantilevers by pressing them against the reference one [Gib96], [Li93], [Hut05]. The obtained force curve is a measure of the combined spring constants of the two-lever system. Since one of the spring constants is known, the other one can be easily deduced.

A special method which involves the placement of spheres of different masses at the tip of the cantilever was reported [Cle93]. The added mass is typically a spherical particle of gold or tungsten (used because of their high density). The spring constant of the cantilever can be determined from the inevitable change in its resonant frequency. The necessity for the determination of Young’s modulus is therefore eliminated. However, due to the step of attachment of spheres of differing mass to the cantilever, the method suffers from some practical difficulties which limit its accuracy [Sad05].

The measurement of intensity of thermal noise of the cantilever is a widely used method to determine a spring constant [Hut93]. The method doesn’t require the attachment of any mass and is implemented in many commercial AFMs. A force curve on a hard substrate is done to measure first the sensitivity of the cantilever. After that a noise spectrum of the deflection amplitude is taken. This spectrum has a peak at the resonance frequency, which corresponds to the first vibration mode. The first peak is fitted with a Lorentzian curve and the mean square deflection of the first peak is obtained by integration [But05], [Sed94], [Hut05].
II. Theoretical Background. Surface characterisation techniques

Force volume
With the force volume imaging of the atomic force microscope it is possible to collect a data set containing topographic data and force-distance curves simultaneously. During a single image scan a distribution of forces at various Z-positions and at thousands of XY positions are gathered (Fig. 15). In such a way one can reveal the lateral distribution of adhesion, elasticity, electrostatic and magnetic properties and directly correlate them with the topography of the given area of scanning [Multimode04], [AFM05].

![Force volume data set](image)

*Fig. 15. A force volume data set – an array of regularly spaced force curves yields three-dimensional force information. In a force volume data set, the force curves will vary with x-y position [AFM05].*

5.1.3 Colloidal probe technique

Colloidal probe technique, which consists of attaching a spherical particle to the atomic force microscope cantilever, was first introduced about 20 years ago. Ducker et. al. [Duc91], [Duc92] used silica spheres, while Butt – glass spheres [But91]. This technique had an aim to get more defined geometry of the tip and to know the real contact area of contact. This makes the analysis of the force curves easier and the information got is more reliable. By measuring with sharp tips, the surface roughness and high contact pressures may cause the tip to rotate and the surface to deform. That is why the method of replacing the tip by a colloidal particle in the size range 1-20µm and of well-defined spherical shape is widely used [Kap02], [Gol07], [Yan07]. Due to the higher contact area between the colloidal probe and the surface, the total forces are higher, so the measurements are more sensitive. The spherical shape of the tip provides controlled contact pressure, symmetry, and mostly elastic contacts. The contact geometry permits the use of elastic contact mechanics analysis such as Johnson-Kendall-Roberts (JKR) [Joh71] and Derjaguin-Muller-Toporov (DMT) [Der75] models for data reduction [Lei05], [Yan07]. Another opportunity that gives the colloidal probe technique is the attachment
II. Theoretical Background. Surface characterisation techniques

of the particles with different chemical composition. For example, the functionalised soft latex microspheres [Ass06], [Xu06] or polymer modified silica particle [Sve11] were used for force measurements.

In order to get geometry-independent values of adhesion measured with colloidal probes of different radii (R), the interaction energy (E) can be calculated by using the Derjaguin approximation [Der34]:

\[ E(D) = \frac{F(D)}{2\pi R} \quad \text{(eg. 2)} \]

Attachment of the colloidal particles is usually done by use of a micromanipulator under the control of optical microscope [Kap02]. First, a tiny amount of glue (often the two component epoxy) is placed onto the very end of the cantilever and then the colloidal probe is brought in contact with the spot [Nig04]. The Fig.16 shows the typical colloidal probe attached to a tipless cantilever (in this case NP-O tipless cantilever, Veeco). For some materials (e.g. polystyrene, borosilicate glass) sintering of the particles to the cantilever is feasible, avoiding possible surface contamination from the glue [But91], [But05], [Kap02].

![Fig. 16. SEM images of silica particles of 4.84 µm in diameter glued to a tipless cantilever.](image)

One of the limitations of the colloidal probe technique is the particle size of the glued sphere. It is experimentally very complex if possible at all to manipulate and attach particles that are smaller than 1µm in diameter [Gol07]. In the present work the colloidal probe technique will be used to probe the adhesion properties of prepared responsive materials.

5.2 Ellipsometry

Null-ellipsometry
Layer thicknesses were measured by null-ellipsometry, which is a non-destructive and contactless technique for the characterization of thin polymer layers on solid substrates.
II. Theoretical Background. Surface characterisation techniques

Ellipsometry is a very sensitive measurement technique and provides unequalled capabilities for thin film metrology. It has applications in many different fields, from semiconductor physics to microelectronics and biology, from basic research to industrial applications [Dem10]. Ellipsometry uses the fact that the reflection at a dielectric interface depends on the polarization of the light while the transmission of light through a transparent layer, changes the phase of the incoming wave depending on the refractive index of the material.

The polarization state of the light incident upon the sample may be decomposed into s and p components (the s component is oscillating perpendicular to the plane of incidence and parallel to the sample surface, and the p component is oscillating parallel to the plane of incidence). After reflection from the tested surface, the change of phase between p and s components of light depends on the sample thickness and its refractive index. They are normalized to their initial values, and are denoted by $r_s$ and $r_p$, respectively (Fig. 17). Ellipsometry measures the ratio of $r_s$ and $r_p$, which is described by the fundamental equation of ellipsometry:

$$\frac{r_p}{r_s} = \tan \Psi \ e^{i\Delta}$$  \hspace{1cm} (eq. 3)

where, $\tan \Psi$ is the amplitude ratio upon reflection, and $\Delta$ is the phase shift (difference). The measurement of $\Delta$ and $\Psi$ at one wavelength and one angle of incidence allows determining two real parameters such as the refractive index and thickness.

![Fig. 17. Principle of null-ellipsometry (simplified) (a), schematic of an ellipsometry experiment (b) [Ber10].](image)

The thickness of polymer layers on the wafer in the dry state was measured at $\lambda=632.8$ nm and an angle of incidence of 70° with a null-ellipsometer (Multiscope, Optrel Berlin, Germany) in a polarizer-compensator-sample–analyzer configuration as described elsewhere [Azz99], [Syn07]. From the obtained values, we calculated the grafting
density \( \Gamma = \mathcal{H} \cdot \rho \cdot \frac{N_A}{M_W} \) and distance between grafting points \( d = \Gamma^{-1/2} \), where \( \mathcal{H} \) is the ellipsometric thickness, \( \rho \) is the mass density, \( N_A \) is Avogadro’s number, and \( M_W \) is the molecular weight.

**In situ spectroscopic ellipsometry**

“\( \text{In situ} \)” ellipsometric measurements were performed to examine the swelling behaviour of the polymer brushes at different temperatures. A fast multi-wavelength M-44 ellipsometer (Woollam Co., Inc., USA) with a rotating analyzer and a detector array of 44 wavelengths between 428 and 763 nm was used. For modelling, a three-layer system (silicon/silicon oxide/APS-Br initiator/thermoreponsive hydrogel (+water as ambient) was assumed. The optical constants of Si and SiO\(_2\) were taken from the literature [Wer99]. The thickness and the optical constants of the polymer films were fitted assuming homogeneous layers. The measurements in the dry state were done at 22°C and 40–50% relative humidity with an angle of incidence 65°, 70°, and 75°. The swelling experiments were carried out by placing the sample into a home-built cell with an angle of incidence 74.8°. The sample was immersed in deionized (DI) water at room temperature and stored at 20°C overnight. The sample was then placed into the flow-cell containing DI water at 20°C, which was heated at a rate of 1°C/min and ellipsometry data were collected continuously. A rate of -1°C/min was applied for the cooling curve.

5.3 Gel permeation chromatography (GPC)

Average molecular weight and the molecular weight distribution of a polymer obtained after precipitation or removing of the solvent of ATRP products have been characterized by Gel Permission Chromatography (GPC) [Ber10]. The term gel permeation chromatography in known since 1964 and is now by far the most popular and convenient technology for polymer molecular weight characterization [Moo64].

GPC separates on the basis of molecular hydrodynamic volume or size. The polymer of interest is dissolved in an appropriate solvent and is injected into a column packed with porous particles of fairy defined pore size [Mor99]. The smaller molecules can enter the pores more easily and therefore spend more time in these pores, increasing their retention time. Conversely, larger molecules spend little if any time in the pores and are eluted quickly. Since GPC is a relative and not an absolute molecular weight technique, columns must be calibrated with polymer standards of known molecular weight or an online light scattering detector must be used [Mor99].
5.4 X-ray photoelectron spectroscopy (XPS)

X-ray Photoelectron Spectroscopy (XPS), also known as Electron Spectroscopy for Chemical Analysis (ESCA) is a widely used surface analysis technique. A sample is irradiated with monochromatic x-rays, resulting in the emission of photoelectrons whose energies are characteristic of the elements within the sampling volume. Energy analysis of the emitted photoelectrons is the primary data used for XPS. From the binding energy and intensity of a photoelectron peak, the elemental identity, chemical state, and quantity of an element are determined [Bri90].

All XPS spectra were recorded by means of an Axis Ultra photoelectron spectrometer (Kratos Analytical, Manchester, UK). The spectrometer was equipped with a monochromatic Al Kα (hν = 1486.6 eV) X-ray source of 300 W at 15 kV. The kinetic energy of the photoelectrons was determined with a hemispheric analyzer set to pass energy of 160 eV for wide-scan spectra and 20 eV for high-resolution spectra. During all measurements electrostatic charging of the sample was over-compensated by means of a low-energy electron source working in combination with a magnetic immersion lens. Later, all recorded peaks were shifted by the same amount which was necessary to set the C 1s peak to 285.00 eV for saturated hydrocarbons. Quantitative elemental compositions were determined from peak areas using experimentally determined sensitivity factors and the spectrometer transmission function. Spectrum background was subtracted according to Shirley. The high-resolution spectra were deconvoluted by means of a computer routine (Kratos Analytical, Manchester, UK). Free parameters of component peaks were their binding energy (BE), height, full width at half maximum and the Gaussian-Lorentzian ratio.

5.5 Wetting measurements

Contact angle (CA) measurements: static, apparent advancing and receding water contact angles were measured by the sessile drop method using a conventional drop shape analysis technique (Krüss DSA 10, Hamburg, Germany).

Static contact angle measurements
Liquid droplets of about 10 μL were dropped carefully onto the sample surface, at least 5 measurements at different positions of the same sample were made and the average values of the static contact angles were calculated (Fig. 18) [Ber10].
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During the measurement of the advancing and receding angles the syringe needle remains in the drop throughout the whole measurement. A liquid droplet is formed on the solid surface and is then slowly increased in volume at the constant velocity, the advancing contact angle is measured. When the pump was reversed, the drop volume started to decrease linearly and the receding contact angle is measured. Dynamic contact angles describe the processes at the liquid/solid boundary during the increase in volume (advancing angle) or decrease in volume (receding angle) of the drop (Fig. 19 A and B, respectively), i.e. during the wetting and dewetting processes [kruss]. By using the difference between the advancing and the receding angles it is possible to make statements about the roughness of the solid or chemical inhomogeneties [kruss].

All contact angle measurements were carried out at (24±0.5)°C and relative humidity of (40±3)%. The error of the mean contact angle values, calculated as the standard deviation, did not exceed 2° and 4° for advancing and receding angles, respectively [Ber10].
Axisymmetric drop shape analysis (ADSA), captive-bubble technique
An underwater captive-bubble contact angle technique in conjunction with Axisymmetric Drop Shape Analysis-Profile (ADSA-P) was used to study wettability of polymer materials. Dynamic temperature-dependant air-water contact angles of thermoresponsive polymer brushes were investigated below and above their phase transition temperatures. For this, polymers were synthesized on special silica wafers with a small hole in the middle. A wafer is placed with a sample looks down into rectangular glass cuvette on two stable supports. The cuvette is then filled with distilled water. A small air bubble is blown through the hole of about 1 mm in diameter with a motor-driven syringe. The syringe remains sticking in the wafer from above during all the experiment. The dynamic contact angle measurements were carried out by pumping air in and out of the bubble, advancing and receding contact angles were measured (Fig. 20). ADSA-P methods are based on the numerical fit between the shape of experimental drops (or bubbles) and the mathematical model given by the classical Laplace equation of capillarity [Rio97].

Fig. 20. Above: Schematic representation of the experimental set-up for ADSA-P captive bubble contact angle measurements; below: In situ captive bubble contact angle measurement at the PNIPAM-water interface while the temperature was increased from 25°C up to 31°C [wwwi].
5.6 Electrokinetic measurements

Zeta-potential is the potential difference between the dispersion medium and the stationary layer of fluid attached to the dispersed particle. The charge at the particle surface influences the distribution of ions in the surrounding interfacial region. It results in an increased concentration of counter ions close to the surface. Thus an electrical double layer exists round each particle. The magnitude of the zeta-potential shows if the colloidal system stable or not. If all the particles in suspension have a large negative or positive zeta-potential then they will tend to repel each other and there is no tendency to flocculate. However, if the particles have low zeta-potential values then the system is unstable and will be tending to flocculate.

The streaming potential measurements were carried out using the Electrokinetic Analyzer (EKA) by Anton Paar GmbH, Graz, Austria in a special rectangular cell (developed and constructed at the Leibniz Institute of Polymer Research, Dresden, Germany) for small flat pieces. The measuring electrolyte \( (10^{-3} \text{ M KCl}) \) was circulated though this channel. Details of the measuring technique are reported elsewhere [Bel02], [Bel07], [Smo21]. In this work in addition to the common zeta-potential measurements, electrokinetic behaviour of thermoresponsive polymer brushes upon heating-cooling cycles was investigated. Such the switch between swelled and collapsed states of the brushes was confirmed.

5.7 Dynamic light scattering (DLS)

Dynamic light scattering (DLS) is one of the most popular technique used to determine the size distribution profile of small particles in suspension or polymers in solution. With this method particle sizes within a range from nm up to several \( \mu \text{m} \) can be determined [Gor05]. A monochromatic light beam, such as a laser, shines onto a solution with spherical particles. Due to the Brownian motion of the particles, a Doppler Shift occurs that changes the wavelength of the incoming light. This change is related to the size of the particle [sartor].

A Zetasizer Nano ZS by Malvern Instruments/UK was used for determination of particle size. The device is equipped with a 633 nm laser and with a non-invasive backscatter (NIBS) technology for increasing particle size sensitivity [Ber10].

5.8 Scanning electron microscope (SEM)

SEM is a type of electron microscope that is able to provide images of three-dimensional objects with resolution less than 1 nm. The principal of work is based on the collection of
II. Theoretical Background. Surface characterisation techniques

secondary electrons that are released from the sample by the electron beam impinging on it. All scanning electron microscopy micrographs were acquired on a scanning electron microscope (Zeiss Neon 40), operating at 0.5-30 kV in the secondary electron (SE2) and InLens detector modes.

5.9 Transmission electron microscope (Cryo-TEM)

The transmission electron microscope (TEM) operates on the same basic principles as the light microscope but uses electrons instead of light. This makes it possible to get a resolution a thousand times better than with a light microscope. As a beam of electrons is transmitted through an ultra-thin specimen, it is affected by the structures and objects on the slide. These effects result in only certain parts of the light beam being transmitted through certain parts of the slide. This transmitted beam is then projected onto the viewing screen, forming an enlarged image of the slide. Cryogenic transmission electron microscopy (Cryo-TEM) is a form of TEM where the sample is studied at cryogenic temperatures. The cryo-TEM is a popular technique in biology, it is uniquely suited for identifying the local microstructures in complex fluids at high water content such as micellar and vesicular dispersions. Cryo-TEM measurements were performed on a Libra 120 (Zeiss NTS GmbH, Oberkochen, Germany) at temperatures around 110 K. The TEM was operated at an acceleration voltage of 120 kV.

5.10 Tack test

Probe tack experiments were performed in the Soft Matter Science and Engineering Laboratory of the ESPCI ParisTech in the group of Professor Costantino Creton. The custom-designed probe tester allows macroscale measurements of adhesion forces and also gives the information about the mechanisms of debonding of the adhesive. The applied compressive force, contact time and debonding rate can be easily independently controlled during the experiments [Lak99]. The samples, glued to the cylindrical probe, have a diameter of 1 cm. During the experiments, they were brought into contact from below at a given velocity $V_{\text{app}}$ with an adhesive layer deposited on a glass slide. The parallelism between the sample and the glass slide is controlled through three micrometer screws which can finely adjust the position of the upper plate as described in Fig. 21 [Lak99].
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Fig. 21. (A) Overall schematics of the probe tack apparatus, and (B) detailed schematics of the upper plate showing the adjustment of the parallelism between the probe and the glass slide [Lak99].

The sample is maintained in contact with the film at a given pressure $P_c$ for a given contact time $t_c$ and is then subsequently removed from the adhesive at a constant debonding speed $V_{deb}$ [Lin04]. The whole process can be simultaneously observed and captured from above through the transparent glass slide with a microscope coupled to a CCD camera [Lin04]. The displacement resolution of the instrument is of the order of 1 pm while the force resolution is approximately 0.2 N [Lak99].

Fig. 22. Typical force and displacement curves as a function of time [Lak99]

The measurements allow a stress $\sigma$ versus strain $\varepsilon$ curve to be deduced (Fig. 22), where $\sigma$ is the nominal stress $\sigma = F/A$, with $A$ the area of contact between the probe and the
II. Theoretical Background. Surface characterisation techniques

adhesive during the compressive stage, and $\varepsilon = (h - h_0)/h_0$, where $h$ is defined as the time dependent thickness of the adhesive layer and $h_0$ as the initial thickness [Lin04]. The shape of the stress-strain curve obtained during the detachment of the sample from the adhesive film can be used to characterize the adhesive performance of the material tested and depends on the rheological properties of the adhesive layer and on the interfacial interactions between the adhesive and the sample. The general features of a stress-strain curve obtained in a test will be characterized typically with three parameters: a maximum stress, $\sigma_{\text{max}}$, a maximum extension, $\varepsilon_{\text{max}}$, and a work of separation, $W$, defined as the integral under the stress-strain curve [Cre02].

The debonding process can be divided into different stages. Images with the corresponding stages of force-displacement curve are shown in Fig. 23:

1. Homogeneous deformation of the film in tension. No cavities are optically visible;
2. Nucleation of the cavities at the interface, the cavities appear where surface defect was initially present. If the surface of the sample or of the films has some degree of roughness, pockets of air can remain trapped during the compression stage and act as germs for cavities during the traction stage [Ret05]. This mechanism occurs near the maximum in the measured nominal stress;
3. Further two different mechanisms can be observed: either more and more cavities progressively nucleate, eventually filling the space previously occupied by the adhesive film (the structure resembles foam), or the cavities continue growing laterally and form fibrillar structures [Lin04], [Cre03];
4. During the debonding on non-adhesive surfaces large interfacial cracks which propagate quickly from the border usually take place, whereas on more adherent surfaces multiple cavities in the bulk of the adhesive layer have been observed which grow slowly and lead to a fibrillar structure [Josse]. Video captures taken during the force relaxation process can reveal whether cavitation or fibrillation takes place;
5. Final stage of debonding: separation of the two surfaces either by failure of the fibrils (cohesive failure, i.e. some adhesive remains on both surfaces) or by detachment of the foot of the fibrils from the surface (adhesive failure, i.e. there is no adhesive left on the probe surface) [Ret05], [Lin04], [Cre02], [Cre01], [Ret08].

Cavitation takes place at the beginning of the debonding process, while the stress increases. Growth of the cavities leads to a decrease of the nominal stress until the fibrillation stage is reached, leading to a plateau value of the stress. Finally, the detachment of the fibrils occurs and complete debonding of the adhesive layer takes place [Lin04].

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Fig. 23. Schematic of the deformation mechanisms taking place during a probe tack test and corresponding images of the stages of debonding. The images are taken from [Lak98], [Cre02].
III. Results and Discussions

1. Thermoresponsive polymer brushes

1.1 Abstract

In this Chapter it is reported on design, investigation and comparison of the adhesive properties of poly-(N-isopropylacrylamide) and biocompatible polyethylene glycol-based thermoresponsive brushes. The brushes were synthesised on planar silicon wafers and silica particles via the surface-initiated atom transfer radical polymerisation. Switching of swelling, surface charge and surface morphology were investigated using spectroscopic ellipsometry, zeta-potential and atomic force microscope measurements, respectively. Adhesion properties were studied in situ in aqueous solutions at different temperatures using three kinds of AFM probes with well-defined tips geometries and radii.

1.2 Introduction

Stimuli-responsive systems found in nature evoke considerable interest of scientific community inspiring fabrication of artificial materials with similar properties [Aut00], [Lee07], [Xia08], [Yos08]. There are a lot of attempts for mimicking natural systems because of a great demand for “smartness” in adhesive materials for various fields of application, like as tissue engineering, wound dressings, sensors, climbing robots, adhesive foils etc. Polymers able to switch or adapt their adhesion properties as an answer to external stimuli or change of environmental conditions such as temperature, pH, light and others are already widely used as a basis for such responsive materials [Hub03], [Gra04], [Lee10], [Nan10], [Liu12]. Among the polymers demonstrating thermoresponsive behaviour in aqueous environment, there are polyacrylamides, polyvinylcaprolactone, polyethylene glycols, and polypeptides. Such thermoresponsive polymers possess low critical solution temperature (LCST) that is a certain temperature below which the polymers are water-soluble and hydrophilic, but water-insoluble and hydrophobic above this temperature. Adhesive properties of thermoresponsive surfaces play a keynote role for biotechnological applications. In fact, it was found that cells readily adhere to the thermoresponsive substrates at elevated temperatures when the polymer is hydrophobic and do not adhere or are released at lower temperatures when the polymer is swollen. Therefore, understanding and control of adhesion properties of thermoresponsive surfaces is very important for proper attachment/detachment of cells.
Three types of polymeric systems based on thermoresponsive polymers were studied in this work: poly-(N-isopropylacrylamide) PNIPAM, poly-(oligo(ethylene glycol) methyl ether methacrylate-co-2-(2-methoxyethoxy) ethyl methacrylate) P(OEGMA-MEO2MA) and poly-(oligo(ethylene glycol) methyl ether methacrylate-co-oligo(propylene glycol) methacrylate) P(OEGMA-OPGMA). The polymeric layers in brush regime conformation were synthesised via atom transfer radical polymerization (ATRP). The adhesion forces between these polymers grown on flat and rough microstructured surfaces and bare or polymer-modified probes were systematically investigated in aqueous environment as a function of temperature by means of AFM force–distance experiments. Several important factors influencing adhesion behaviour and the switching were studied: the chemical composition (functionality) and architecture of polymer chains, effect of tip geometry, as well as the effect of surface roughness. Moreover, the features associated phase transition and switch of adhesion performance of the polymers like their wetting behaviour, surface charges, surface morphology, and thickness of layers were thoroughly investigated.

1.3 Experimental Part

The experimental part relates all steps of sample preparation, which include modification of silica wafers and silica particles used for planar and rough substrates, as well as silica particles needed for colloidal probe technique. Several characterization methods objecting control of the quality of the modified surfaces were applied. Then the details concerning robustness of rough surfaces are considered. Polymerization procedure and characteristics of synthesized polymers are presented at the end of this part.

1.3.1 Materials

Ammonium hydroxide solution (Aldrich, 28-30% in H₂O), hydrogen peroxide solution (Aldrich, 30% in H₂O), 3-aminopropyltriethoxysilane (APS, ABCR, 97%), ethanol abs. (VWR, 99.9%), anhydrous dichloromethane (Aldrich), α-bromoisobutyril bromide (Aldrich, 98%), triethylamine (Sigma-Aldrich, 99.5%), chloroform (Aldrich, 99.9%), poly(glycidyl methacrylate) (PGMA, Polymer Source™, Mₙ = 65x10³ g/mol), N-isopropylacrylamide (NIPAM, Aldrich, 97%), L-ascorbic acid (Sigma, 99%), N,N,N',N",N"'-Pentamethyldiethylenetriamine (PMDTA, Aldrich, 99%), ethyla-bromoisobutyrate (EBiB, Aldrich, 98%), copper(II) bromide (Aldrich, 99.99%), N,N-Dimethylformamide (DMF, Aldrich, 99.8%), methanol (MeOH, Aldrich 99.9%) were used as received. Oligo(ethylene glycol) methyl ether methacrylate, (OEGMA, Aldrich, Mₙ = 475g/mol, contains 100 ppm MEHQ as inhibitor, 200 ppm BHT as inhibitor), oligo(propylene glycol) methacrylate (OPGMA, Aldrich, Mₙ = 375g/mol, di(ethylene glycol) methyl ether
methacrylate (or 2-(2-methoxyethoxy) ethyl methacrylate, MEO2MA, Aldrich) were distilled under nitrogen steam prior to the polymerization.

1.3.2 Modification of planar substrates

Highly polished single-crystal silicon wafers of \{100\} orientation (Semiconductor Processing Co.) were used as planar substrates. Several steps of wafers modification were carried out upon the polymerization procedure. First, wafers were cleaned in dichloromethane in ultrasonic bath during 30 minutes. Then after the removal of dichloromethane, the wafers were placed in a hot solution (70°C) of NH\textsubscript{4}OH (ammonium hydroxyde), H\textsubscript{2}O\textsubscript{2} (hydrogen peroxide) and MilliQ water with ratio 1:1:1. After an hour the wafers were rinsed several times with MilliQ water and dried with nitrogen flux. This treatment results in the formation of a thin silicon dioxide layer (about 1.3 nm). The thickness of this as well as all other layers after each step of modification was controlled via null-ellipsometry measurement.

The silicon surface was next modified with 3-aminopropyltriethoxysilane (APS). A thin layer of APS ($t_h = 0.6$ nm) was adsorbed at room temperature on top of the wafers from 2 wt\% ethanol solution.

Then the bromide initiator (BrInit) was immobilized on the surfaces by placing the wafers into solution of anhydrous dichloromethane (100 ml), triethylamine (1ml) and $\alpha$-bromoisobutyryl bromide (0.5 ml) for 2 hours at room temperature. Afterwards, the wafers were rinsed several times with dichloromethane, ethanol and MilliQ water and dried with nitrogen flux. The thickness of the APS+BrInit layer was measured to be 0.9 nm.

![Zeta potential measurements](image)

*Fig. 24. Zeta potential measurements after steps of SiO\textsubscript{2} native layer activization, silanization and immobilization of bromide initiator.*
III. Results and Discussions. Thermoresponsive polymer brushes

In order to control the evolution of surface properties after each step of modification, elektrokinetic measurements (Fig. 24) as well as the AFM topography images (Fig. 25) were performed. Zeta-potential shows gradually changing surface charges with transformation of the surface functionality: from silicon oxide layer over hydrophilic surface with amino groups to the moderate hydrophobic surface with bromide initiator. The surfaces of both, SiO$_2$ native and SiO$_2$/APS/Br-modified layers, are very smooth (root mean square (rms) roughness is below 0.5 nm) that appears also from the cross sections of their topography images (Fig. 25).

![AFM topography images and height profiles of SiO$_2$ native and SiO$_2$/APS/Br modified wafers.](image)

The rms roughness was calculated with the help of the AFM evaluation program WSxM 5.0 [WSxM]. The rms roughness is the standard deviation of the height values $Z_i$ of data point $i$ from the average height value $Z_{ave}$ of the image. $N$ represents the number of measured data points within the image (Eq. 4) [Manual03].

$$RMS = \sqrt{\frac{\sum_{i=1}^{N} (Z_i - Z_{ave})^2}{N}}$$  
(eq. 4)
1.3.3 Modification of curved substrates (colloidal particles)

The process of modification of colloidal particles is similar to that performed on planar substrates. First, silica particles were washed 3 times with dichloromethane followed by drying under reduced pressure at 110°C. The particle surfaces were hydrophilized by stirring in a mixture of \( \text{H}_2\text{O}_2/\text{NH}_4\text{OH}/\text{H}_2\text{O} \) like it was done on planar substrates. The particles were purified in 5 centrifugation-re-dispersion-process cycles in water and then dried at 100°C under reduced pressure [Syn08]. The 3-aminopropyltriethoxysilane (APS) was chemisorbed from 2 wt% ethanol solution at room temperature during 24 hours. The particles were purified in a 5 circles centrifugation-re-dispersion-process in ethanol to remove non-adsorbed APS. This procedure was applied to 1 µm large particles used for preparation of rough substrates and to particles of 4.84 µm in diameter that were further used for the symmetric adhesion experiments via colloidal probe technique (brush-brush interactions shown later). Then the ATRP-initiator was immobilized onto the surface of 4.84 µm large amino-modified particles. They were treated in a solution of \( \alpha\)-bromoisobutyryl bromide and triethylamine (2.9 mmol, 400 µL) in 7 mL dry methylene chloride. The reaction was carried out for 2 hours at room temperature. Light-brown dispersion was centrifuged and fully modified particles were washed three times with methylene chloride. Subsequently, the polymerization was performed via ATRP.

1.3.4 Preparation of rough substrates from core-shell particles

For the preparation of rough samples the following procedure was carried out. At the beginning the planar silicon wafers were exposed to steps of modification that were already described in the previous section dealing with flat surfaces: wafer cleaning, silicon dioxide layer formation and silanization. Then a thin and uniform poly(glycidyl methacrylate) (PGMA) layer was immobilized via spin coating. For this, the PGMA (\( \text{M}_\text{w}=65000, \text{PDI} = 1.5 \)) was first diluted in chloroform with concentration of 1wt. %. The solution was passed through a filter paper. Afterwards, the sample was accelerated with 1900 R/sec\(^2\) at 2000 rpm (revolutions per minute) and some PGMA solution was dropped onto the wafer surface. The sample was spinned at constant rate till the solvent has completely evaporated. Then the wafers were annealed at 150°C in vacuum for 20 minutes. The film thickness of obtained layer was measured to be about 80 nm.

Subsequently, the 1 µm large APS modified silica particles have been immobilized onto the preliminary coated substrate. It was performed via spin coating from 10wt. % solution in ethanol with the rate 600 rpm and acceleration 95 R/sec\(^2\). The wafers were then annealed in vacuum during 2 hours at 180°C. Finally, the samples immerged in ethanol were exposed for several seconds to US-bath to eliminate non-chemically
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grafted particles making up the second and the following layers. The SEM images of a typical rough surface prepared by this procedure are presented below (Fig. 26 A, C).

![SEM images](image)

Fig. 26. A, C - representative SEM images of rough microstructured substrates obtained by fusion of APS-modified silica particles in the 80 nm thick PGMA layer. SEM images of rough sample without APS layer before (A) and after (B) polymerization; rough samples with APS layer before (C) and after (D) polymerization; E – a photo of typical rough substrates of good quality demonstrating iridescence, made of 1µm particles on 1x2 cm silica wafers.

There are two important factors that contribute to the robustness of the rough layers. First of all, preliminary modification of SiO$_2$ native substrates with APS (silanization procedure) was found to be critical to get stable and robust rough layers. Without APS the PGMA layer swells during the following polymerization spoiling the particles (Fig. 26 B). Such surfaces are visible to the naked eye: they are whitish in appearance whereas the good samples are iridescent indicating the ordered rough structure (Fig. 26 E). The robustness of such samples results surely from the chemical bonds between epoxy and amino groups that provide chemical and mechanical stability of the particle layers. Moreover, the thickness of the PGMA layers influence quality of the samples as well. To find optimum conditions, the samples with different thicknesses of PGMA layer were prepared. The AFM topography images scanned in contact mode revealed the thickness should be at least 40 nm. The thinner layers can’t hold particles firmly enough and the cantilever tip tears them from the surface (see white lines and spots in the Fig. 27 A, B, C), thus the samples are not robust enough. On the other hand, the PGMA layers of about 200 nm swell during polymerization procedure even in the presence of the APS layer (see Fig. 27 F). Therefore, APS and PGMA layer with the thickness of about 80-100 nm were further used for the fabrication of rough surfaces. The layers were very stable and it was impossible to dislodge particle from the substrate during scanning in contact
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mode on AFM (Fig. 27 D). Swelling of the PGMA layers haven’t been detected either after ATRP procedure.

![AFM topography images of rough samples made in contact mode with different thicknesses of PGMA layers: A – 12nm, B – 25nm, C – 40nm, D – 80nm, E – 200nm, F - rough sample with 200nm PGMA (with APS layer underneath) after polymerization.](image)

Fig. 27. AFM topography images of rough samples made in contact mode with different thicknesses of PGMA layers: A – 12nm, B – 25nm, C – 40nm, D – 80nm, E – 200nm, F - rough sample with 200nm PGMA (with APS layer underneath) after polymerization.

Afterwards, ATRP initiator was immobilized on the rough layer made of APS modified silica particles, similar to the planar surfaces. The rough surfaces were thus ready for ATRP procedure.

In summary, two main factors contribute to the robustness of the rough substrates. Firstly, preliminary modification of the surfaces with the APS layer that facilitates formation of chemical bonds between the amino groups of APS and epoxy groups of PGMA deposited further above. This layer remains stable after polymerization. In addition, the thickness of the PGMA layer around 80 nm was found to be optimal – such layers can hold the particles securely enough. They don’t swell during the polymerization and the contamination of particles was not observed.

1.3.5 Polymerization on flat and rough surfaces

Polymer brushes were synthesised using AGET ATRP (the fundamentals about the technique were described in Chapter II.3). A ratio between comonomers
OEGMA:MEO2MA = 1:7 and OEGMA:OPGMA = 1:3 was yielding LCST close to that of PNiPAM homopolymer (LCST = 32°C) that is promising for materials for medical application. Polymer surface-grafted layers, thinner (about 12 nm) and thicker (40±5 nm) ones have been prepared. The information about the components of ATRP and their quantities used for preparation of thicker layers are summarized in the Tab. 1. The ATRP was carried out at 70°C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>MeOH, ml</th>
<th>Monomer, (g/µL)</th>
<th>CuBr₂, µL 0.1 in DMF</th>
<th>PMDTA, µL 0.5M in DMF</th>
<th>EbiB, µL</th>
<th>L-asc.acid,µL 1M in DMF</th>
<th>Time, min</th>
</tr>
</thead>
<tbody>
<tr>
<td>PNiPAM</td>
<td>2</td>
<td>2g NIPAM</td>
<td>8</td>
<td>8</td>
<td>1.1-3</td>
<td>60</td>
<td>40-60</td>
</tr>
<tr>
<td>P(OEGMA-MEO2MA)</td>
<td>2</td>
<td>234µL OEGMA 1764µL MEO2MA</td>
<td>16</td>
<td>16</td>
<td>1.1-5</td>
<td>120</td>
<td>30-40</td>
</tr>
<tr>
<td>P(OEGMA-OPGMA)</td>
<td>2</td>
<td>450µL OEGMA 1550µL OPGMA</td>
<td>32</td>
<td>132</td>
<td>1.0</td>
<td>240</td>
<td>60-70</td>
</tr>
</tbody>
</table>

Tab. 1. Quantities of AGET-ATRP components and time of polymerization used for preparation of 40±5 nm thick polymer layers.

The values of thickness and molecular mass were obtained using null-ellipsometry and gel permeation chromatography (GPC), respectively (Tab. 1). The estimation shows that grafting density is ca. 0.1–0.3 chain/nm², while the distance between grating points is D = 2–3 nm. Unfortunately, the gyration radius of the used polymers is unknown but expected to be more than 5 nm. For example the gyration radius of polystyrene with a similar molecular weight of about 30 000 g mol⁻¹ in a good solvent (toluene) is 10 nm [Siq95]. Since the distance between grafting points is smaller than the thickness of the polymer layers, the polymer-grafted layers can be considered as a brush-like in both dry and swollen states [Min06].

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>H, nm</th>
<th>Mn, g/mol</th>
<th>Mw, g/mol</th>
<th>Γ, chains/nm²</th>
<th>D, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>PNiPAM</td>
<td>12</td>
<td>28000</td>
<td>67200</td>
<td>0.11</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>30800</td>
<td>77000</td>
<td>0.31</td>
<td>1.8</td>
</tr>
<tr>
<td>P(OEGMA-MEO2MA)</td>
<td>12</td>
<td>29000</td>
<td>78300</td>
<td>0.1</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>38000</td>
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<tr>
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<tr>
<td></td>
<td>40</td>
<td>38000</td>
<td>11000</td>
<td>0.21</td>
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</tbody>
</table>

Tab. 2. Values of molecular weight, grafting density and distance of grafting points of PNiPAM, P(OEGMA-MEO2MA) and P(OEGMA-OPGMA) brushes.
III. Results and Discussions. Thermoresponsive polymer brushes

Although, all synthesized polymers have similar LCST, they possess both chemical and structural differences. In particular, PNIPAM is linear and has the smallest side groups – isopropylamide ones, P(OEGMA-MEO2MA) contains predominately larger diethylene glycol groups and small amount (12 mol %) of massive oligoethylene glycol chains, P(OEGMA-OPGMA) can be considered as a bottle brush (a brush-like macromolecule that is controlled by the steric repulsion of the densely grafted side chains [cmu]) with massive side oligoethylene glycol (25 mol %) and oligopropylene glycol (75 mol %) groups (Fig. 28).

![Polymer structures](image)

Fig. 28. Poly-(N-isopropylacrylamide) PNIPAM, poly-(oligo(ethylene glycol) methyl ether methacrylate-co-2-(2-methoxyethoxy) ethyl methacrylate) P(OEGMA-MEO2MA) and poly-(oligo(ethylene glycol) methyl ether methacrylate-co-oligo(propylene glycol) methacrylate) P(OEGMA-OPGMA).

In order to control the polymerization process and acquire knowledge about the thickness of a polymer layer on rough surfaces, the polymerization was carried out in the same reaction vessel simultaneously on flat and rough samples. The thickness of the synthesized polymers on the flat surface can be easily measured with null-ellipsometry. To prove if the grafting of polymer on rough surfaces was successful, the AFM topography images were obtained first in ambient and then in aqueous media at room temperature. The same images were performed on rough samples that have no polymer and that are modified solely with a bromide initiator.

The topography images of the samples without polymer look very similar in air and water, there is also no height difference on the AFM profile image (Fig. 29 A, B). Contrary to that, the topography image of a sample modified with polymer became fuzzy in water and the height profile appeared lower (Fig. 29 C, D). This identifies the swelled polymer molecules on the rough surfaces and thus detects their presence.
III. Results and Discussions. Thermoresponsive polymer brushes

![AFM images](image)

**Fig. 29.** Representative 5 x 2.5 µm AFM topography images and corresponding height profiles of rough substrates obtained by fusion of Br-modified 1 µm large silica particles (A – in air, B – in water), with subsequently grafted PNIPAM brush, in the dry state (C) and under water (D) (T=24°C).

In summary, all steps of samples preparation including modification of flat and rough surfaces with subsequent polymerization procedure have been shown. The quality of the samples after each step of modification was carefully controlled. Three types of polymer brushes based on thermoresponsive polymers have been successfully prepared.

1.4 Surface properties evaluation

Next, prepared samples were thoroughly characterized by advanced analytical tools such as ellipsometry, Zeta-potential and AFM topography measurements. The study of swelling and electrokinetic properties as well as the surface morphology in aqueous media at different temperature was carried out.

1.4.1 Swelling behaviour

Swelling behaviour of the thermoresponsive brushes was first investigated using spectroscopic ellipsometry. It was observed that all investigated samples reversibly swell (below LCST) and collapse (above LCST) upon cyclical change of temperature (Fig. 30). From the ellipsometric experiments it was also found that all polymer brushes swell with the high swelling ratio (defined as the ratio between the thickness in hydrated and the dry states) \( Q \) up to \( Q_{20^\circ C} = 6 \) at temperatures below LCST \( (T = 20^\circ C) \) (Fig. 30c). Although heating above the LCST \( (T = 40^\circ C) \) results in collapse of the polymer layer, the thickness of the collapsed polymer layers is larger than the dry layer measured in air, i.e. \( Q_{40^\circ C} = \)
III. Results and Discussions. Thermoresponsive polymer brushes

1.5 (Fig. 30). Experimental results show that the swelling ratio increases with the decrease of brush thickness (Fig. 30c) that is in good agreement with the previous theoretical and experimental results [Mal10]. Moreover, the degree of swelling decreases in the sequence PNIPAM, P(OEGMA-MEO2MA), P(OEGMA-OPGMA) which can be attributed to the increasing stiffness of polymer chains and advanced steric hindrances caused by the presence of 2–3 nm long side chains (oligomer units) in both P(OEGMA-MEO2MA) and P(OEGMA-OPGMA) systems (Fig. 30 a–b).

Fig. 30. Swelling properties of grafted thermoresponsive layers: brush height and swelling ratio of polymer brushes of 12nm (a) and 40 nm (b) measured in pure aqueous environment at 20°C and 40°C and; (c) comparison of swelling ratio of thermoresponsive layers depending on film thickness.

In addition, the swelling behaviour was proofed by scratch test performed on 40 nm brushes on AFM. The technique involves generating a scratch with a scalpel or a needle that is drawn across the coated surface under load. A substrate becomes bare inside the scratch, so it is possible to analyse the thickness of a polymer layer from the AFM
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topography height profiles. The topography profiles were performed at room temperature in aqueous media as well to get to know about the swelling behaviour of polymer brushes. The measurements were conducted in ambient and aqueous media with ultrasharp triangle cantilevers (CSC11/No Al, MikroMasch, tip diameter is less than 10 nm, resonant frequency 30 kHz, force constant 0.35 N/m). The results show swelling of the brushes in water and reveal the same sequence of swelling degree like it was measured on ellipsometer. Notably, the highest one was obtained on PNIPAM – about 4.25, P(OEGMA-MEO2MA) and P(OEGMA-OPGMA) had about 1.4 and 1.2, respectively (Fig. 31). Whereas the swelling degree on PNIPAN is almost the same according to both methods, the other two brushes swell less if measured on AFM.

Fig. 31. Scratch test. AFM topography images and height profiles of thermoresponsive brushes: PNIPAM, P(OEGMA-MEO2MA), P(OEGMA-OPGMA) measured in air (A, C, E); the corresponding samples in water – B, D, F, respectively.
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Generally, the difference in thicknesses measured on ellipsometer and on AFM is explained by the various mechanisms acting in these methods [Dre10]. The polymer brushes especially in solution may not have a defined surface and consist of a dense layer from which single molecules extend into the solution. While the ellipsometry measurements detect only the dense region of a polymer layer with a refractive index different from that of the solution, the cantilever tip is sensitive even to a single polymer chain stretched from the surface beyond the brush thickness measured by ellipsometer. However this argumentation would explain just an opposite situation, namely larger values of thickness measured on AFM. In our case the lower values measured on AFM could be explained via two factors. On the one part, the polymer inside the scratch was possibly not completely scraped off. Then the difference between the swollen and collapsed brush will be diminished via swollen polymer inside the scratch. On the other hand, the sharp tip used in the measurements on AFM could pierce deeper inside the swollen polymer layer that is less dense comparatively to collapsed brush.

1.4.2 Wetting properties

Since the conventional methods for determination of water contact angle on hydrophilic surfaces are restricted to minimum about 20°, the wetting properties of the fabricated thermoresponsive polymer brushes have been investigated using underwater captive-bubble technique [wwwi]. The measurements were carried out on P(OEGMA-MEO2MA) brush in MilliQ water in temperature range 24-40°C. At each temperature point an air bubble was pumped in and out three times through a hole in wafer with a special syringe.

![Fig. 32. Dynamic contact angle of P(OEGMA-MEO2MA) thermoresponsive polymer brush depending on temperature measured using underwater captive-bubble technique.](image)
The Axisymmetric Drop Shape Analysis-Profile (ADSA-P) was used for data processing. In the Fig. 32 the most prominent dependence of inverse advancing CA of the P(OEGMA-MEO2MA) brush on temperature is presented. It is shown that the CA changes with growing temperature. In the temperature range between 24 to 28°C as well as at high temperatures (34-40°C) the values of CA demonstrate plateau behaviour at about 13.5° and 7°, respectively. These two equilibrium areas correspond to swollen (hydrophilic) and collapsed (hydrophobic) states of the polymer brush. In the middle the thermoresponsive brush undergoes switching between these two opposite states. A perpendicular, dropped on the X-axis from the point of inflection of the curve, shows an approximate value of the LCST inherent in this polymer brush.

1.4.3 Electrokinetic properties

Electrokinetic measurements further confirmed the switching behaviour of the grafted polymer layers (Fig. 33). It was found that the value of zeta-potential changes linearly with pH due to the charge building process of ion adsorption.

![Graphs showing apparent zeta potential as a function of pH for PNIPAM, P(OEGMA-MEO2MA), and P(OEGMA-OPGMA) at 25°C and 45°C.]

<table>
<thead>
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<th>IEP\textsuperscript{45°C}</th>
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<tr>
<td>P(OEGMA-MEO2MA)</td>
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</tr>
<tr>
<td>P(OEGMA-OPGMA)</td>
<td>4.9</td>
<td>4.1</td>
</tr>
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</table>

Fig. 33. Apparent zeta-potential of A: PNIPAM, B: P(OEGMA-MEO2MA) and C: P(OEGMA-OPGMA) thermoresponsive brushes in 10^{-3} M KCl as a function of pH. The values of isoelectric points (IEP) are also given. The thickness of all brushes in the dry state is 40 nm.
Since the investigated thermoresponsive brushes do not have dissociating groups, the change in the absolute value of zeta potential with pH is caused by the preferential adsorption of hydroxyl (OH\textsuperscript{–}) or Cl\textsuperscript{−} ions at pH > IEP and protons (H\textsuperscript{+}) pH < IEP from the electrolyte solution, respectively. Investigated films showed a flattish curve at 25°C (Fig. 33, blue curves). This behaviour can be attributed mainly to the strong swelling of polymer layers as was previously confirmed by ellipsometry measurements and scratch test and with it a high amount of adsorbed water or rather an open structure of the surface. On the other hand, apparent zeta potential changed strongly upon the heating cycle for all systems (Fig. 33), when phase transition from the swollen hydrophilic to collapsed hydrophobic state is observed. In this case the adsorption equilibrium state is more at the site of ion adsorption. Hence the absolute value of zeta-potential increases. It was observed that absolute values of zeta-potential of all thermoresponsive brushes reversibly increased upon the collapse of polymer layers at temperatures above the LCST (Fig. 33, red curves).

1.4.4 Surface morphology

Switching of surface topography was tested at room temperature (24°C) and at 40°C. The samples of two different values of brush thickness were investigated. For AFM imaging in water contact mode fluid cell was used. For topography measurements silicon tips with radius <10 nm, spring constant of 0.35 N/m and resonance frequency of 20–40 kHz (CSC11, Micromasch) were chosen. The morphology of all 40 nm thick layers remains smooth (rms = 1 nm), independent of the state of the polymer: either swollen or collapsed. Collapse of thinner (h\textsubscript{dry} = 12 nm) layers results however in a change of morphology from smooth and featureless below the LCST to rough one above LCST (Fig. 34, results presented for PNIPAM). The rough morphology may originate from the collapse of grafted polymer chains and formation of micelle-like morphology. For the two other systems P(OEGMA-MEO2MA) and P(OEGMA-OPGMA) the thermoresponsive films reveal smooth homogeneous surfaces both at elevated and ambient temperatures. This can be explained by steric hindrance arises from long and bulky side chains of P(OEGMA-MEO2MA) and P(OEGMA-OPGMA) systems that prevent them from such effective collapsed state observed for PNIPAM.
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Fig. 34. Representative topography images and corresponding height profiles measured with SiO$_2$ cantilever and PNIPAM brush grown from flat substrate (A, B) 12 nm and (C, D) 50 nm in DI water (pH = 5.8) at different temperatures: (A, C) 24°C (rms = 1 nm); (B, D) 40°C (rms = 2 nm).

1.5 Adhesion properties of thermoresponsive polymer brushes

There are several important aspects that influence strength of adhesion acting between any two surfaces (they were discussed in Chapter II.1). In order to examine their influence in respect to thermoresponsive polymers investigated in this work, a number of measurements on AFM have been performed. They included the study the influence of different chemistry and structure of polymer chains comprising thermoresponsive polymer brushes, the roughness of the surfaces to which the polymer chains are attached as well as geometry and chemistry of probing tips.

Interaction forces between the brush surface and colloidal probe were measured in a MultiMode AFM with a NanoScope III Controller (Veeco Instruments, Inc., USA) equipped with a closed fluid cell (contact mode fluid cell) in aqueous media in a temperature range from 24 to 40°C [MultiMode04]. Before each measurement series, the silicon wafer, the colloidal probe and the fluid cell were rinsed thoroughly with acetone, ethanol and water and exposed to UV radiation for 20 min to remove organic contaminations. After mounting the sample and the colloidal probe, the cell was flushed...
with the distilled water. The heating rate of the environmental cell was set to 2.0°C/min. After the required temperature was reached, the samples were equilibrated in cells over 30 min to achieve the thermal equilibrium, afterwards the measurement was started. The cantilever approached the brush with a speed of 300 nm/s until a defined maximum force was reached. Then the AFM cantilever was withdrawn from the contact with the same speed. The adhesion force, which is defined as the maximum force required to pull apart two surfaces after initial contact, was studied as a function of temperature.

1.5.1 Effect of scanning parameters of force measurements

Investigation of interaction forces is a complex task. To acquire the correct and reliable data on adhesion force measurements, it is critical to choose proper parameters for scanning and to control them during all the measurements. Among these parameters, the preload (force executed by the tip upon the sample surface), is known to have a considerable influence on adhesion performance. This force can be adjusted via the parameter “trigger threshold” that in turn determines the “maximal load” applied on the sample. There is a linear dependence between the trigger threshold and the maximal load (Fig. 35 A), as well as between the trigger threshold and the maximal pull-off or adhesion force (Fig. 35 B). The growth of adhesion is a response to increase of maximal load executed by the tip on the sample surface can be explained by the fact of growing contact area between the polymer brush and a probing tip if the last one is pressed strongly into the surface [Gre07], [Dre10], [Gor12].
Moreover, the influence of the scanning rate on adhesion forces between P(OEGMA-OPGMA) layers and a silica native probe was investigated. In the scan rate range between 0.1 and 1 µm/sec no dependence has been revealed (Fig. 35 C). That means that the system is in equilibrium, no disentanglements of the polymer chains happen while contact with an AFM probe [Dre10]. The tendencies presented in the Fig. 35 are qualitatively equal for all the measured systems independently on geometry and chemistry of the probing tip. Hereinafter the interaction between flat surfaces and AFM tip is given it terms of the measured force (Fig. 35 left vertical axis) and the geometry-independent interaction energy calculated using the Derjaguin approximation (Eq. 2), (Fig. 35 right vertical axis).

To unify adhesion measurements on different samples and to have an opportunity to compare the results, the experiments should be carried out under the same conditions. It was decided to set the trigger threshold to such a value (depending on the cantilever spring constant) that yields the maximal load of 20 nN. The scan rate of 1 µm/sec over the scan size of 10 µm has been used for the all following measurements. In the AFM laboratory the temperature was kept at 23±1.5°C and the humidity 45±3% the whole year round.

![Diagram](image)

*Fig. 36. Determination of cantilever sensitivity on a typical AFM force-distance curve.*

The primary curves obtained during the AFM force measurements yields the cantilever deflection and Z position of the tip relation (Fig. 36). To get the reliable information about the adhesion forces, the sensitivity of the cantilever and the distance between the tip and the surface have to be determined. Sensitivity is the relation between AFM output signal and cantilever deflection and is equal to the inverse of the slope of the force curve while the cantilever is in a hard contact with a sample surface (Fig. 36) [MultiMode04]. In the case of soft or swelled polymer brushes there is no defined brush surface, no hard contact occurs and the slope of the measured curve is not linear even if the probe and the brush are in contact [Elm09]. For such systems it is possible to determine the cantilever sensitivity from a force curve measured inside the scratch on
the brush surface or on a reference sample with a hard silicon oxide surface [Dre10]. From the curves obtained from measurements inside the scratch also the zero distance can be determined. The height difference on the scratch profile is the distance between a tip and substrate. The force-distance curves had to be shifted parallel to the distance axis until they crossed the force-distance point obtained in this way (Fig. 37 D) [Dre10], [Yam00].

Fig. 37. Determination of zero distance on swelled polymer brushes. A – Topography image of a scratch made on PNIPAM polymer brush; B – Normalised force-distance curve performed inside the scratch; C – Profile of the topography image of the scratch; D – Force-distance curve performed beyond the scratch.

Adhesion force measurements were performed with AFM in force volume mode. This mode optimizes investigations, yielding at ones a great number of force-distance curves collected from a defined area of a surface. In this work 256 curves were recorded on a 10 x 10 µm² area. Usually, a majority of the curves obtained in force-volume mode coincided very well. Some of the curves showed, however, deviations due to brush defects or to interference effects of the laser beam that could not be removed by readjusting the laser. Therefore, at least 20 representative single curves were chosen for
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each temperature and averaged to reduce the influence of inhomogeneities and statistical scattering.

Adhesion forces on reference silica wafers with bromide initiator (without polymer layers) were investigated firstly. The form of adhesion curves revealed hard contact between the surface and the silica native cantilever (Fig. 38). It was shown, that the moderately hydrophobic bromide initiator surfaces are slightly sticky in air and water. The values of adhesion were influenced neither by altering the media, nor by heating (Fig. 38).

![Graph showing adhesion forces on SiO2/APS/Br modified wafers in air and water](image)

*Fig. 38. Force and Interaction energy vs. distance of SiO2/APS/Br modified wafers in air and water measured with a colloid probe.*

The adhesion performance of the thermoresponsive polymer brushes grown from the substrates modified with BrInit was investigated next. In order to eliminate any rough morphologies and minor influences of surface roughness on adhesion forces, only thicker 40 nm polymeric grafted layers were used for the force–distance experiments. The typical pull-off force–distance curves, obtained for the interaction between the native colloid probe and the PNIPAM brush layer as a function of temperature, are shown in Fig. 39 A, B. It was found that all thermoresponsive brushes are completely non-adhesive below the LCST (as shown in Fig. 39 A, B). A purely repulsive character of force–distance curves indicates a complete shielding of substrate by the swollen polymer chains, as previously also proved by ellipsometric measurements. The adhesion tremendously increases above the LCST when the temperature was changed from 34°C to 40°C due to the phase transition of the brush to a collapsed hydrophobic state and development of hydrophobic interactions in aqueous media between the two hydrophobic surfaces [Isr01]. Moreover, the transition between the adhesive and non-adhesive states is found to be fully reversible and can be repeated in sequential heating–cooling cycles many times (Fig. 39 C, D). It was observed that values of the adhesion...
force obtained during the first cycle of heating are ca. 20% smaller than those obtained in second and third cycles. This may be related to the reduced time of the contact between the tip and the surface.

In summary, the settings of adhesion force measurements were discussed here. The scanning parameters, such as preload and scanning rate, influence in many cases the measured values of adhesion forces. Thus the importance of proper adjustment of these parameters was shown. Moreover, special details about evaluation of the force-distance curves performed on soft and compliance polymer layers were debated.
The force volume mode implemented on AFM allows very efficient investigation of samples. Due to this mode it is possible to achieve more reliable result of adhesion force values through collecting and averaging of a great number of experimental data. Afterwards, the typical force-distance curves measured on polymer-free (with bromide initiator) and polymer-modified surfaces were presented. The surfaces modified with BrInit have similar values of adhesion forces in air and water. The influence of temperature on adhesion behaviour hasn’t been detected. On contrary, the thermoresponsive polymer brushes demonstrate temperature responsive adhesion properties. They were shown to be completely non-adhesive in water below LCST and strong adhesive above this temperature. Moreover, the switching of adhesion could be repeated many times.

1.5.2 Effect of chain architecture

The thermoresponsive polymer brushes studied in this work reveal in their chain architecture structural differences. Whereas the chains of PNIPAM are linear with small side groups, the P(OEGMA-MEO2MA) possesses 12% of massive oligoethylene glycol chains, and the P(OEGMA-OPGMA) represents even bottle brush structure with large side chains. How these structural differences influence the adhesion performance of the polymer brushes were investigated via adhesion force measurements on AFM. The interaction forces were measured with AFM tip of three different geometries: a silicon oxide sharp tip (R = 5 nm), a thermal oxidized molten SiO2 tip (R = 40 nm) and spherical particle/colloid probe (CP) (R = 2420 nm). The force–distance measurements showed that the adhesion force (energy) decreases in the sequence PNIPAM, P(OEGMA-MEO2MA), P(OEGMA-OPGMA) independently of the tip radius (Fig. 40). Interestingly, the adhesion force in the case of P(OEGMA-OPGMA) is two times lower than that of PNIPAM. In order to elucidate the origin of difference in the adhesion properties of polymer layers, the aggregation behaviour of thermoresponsive polymers in solution at low and elevated temperatures (T = 20°C and 40°C) was investigated using dynamic light scattering (DLS) (Fig. 41), as well as performing cryo-TEM images of polymer brushes grafted onto 200 nm silica particles.
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Fig. 40. Adhesion force and adhesion energy of different thermoresponsive polymer brushes (thickness =40 nm) measured by three kinds of AFM probes: (a) sharp tip with radius 5 nm, (b) molten tip with radius 40 nm, (c) sphere with radius 2420 nm. T = 40°C.

It was found that polymer chains form aggregates with sizes of about 20–40 nm at 20°C that are comparable with the size of single polymer chains. An increase of the temperature above the LSCT resulted in the formation of larger aggregates with sizes 100–200 nm caused by the sticking of hydrophobic polymer chains together. Notably, the size of the aggregates formed at elevated temperatures decrease in the same sequence as adhesion decreases: PNIPAM, P(OEGMA-MEO2MA), P(OEGMA-OPGMA) (Fig. 41 a, b). On the other hand, it is well known that a higher amount of stabilizing groups leads to the formation of smaller aggregates. Therefore, the size reduction of aggregates effect in the sequence PNIPAM, P(OEGMA-MEO2MA), P(OEGMA-OPGMA) might be attributed to the increasing fraction of hydrophilic oligoethylene glycol (OEG) groups: PNIPAM does not contain OEG, P(OEGMA-MEO2MA) and P(OEGMA-OPGMA) contain 12 mol % and 25 mol % of OEG, respectively. These OEG groups stabilize the polymer aggregates by formation of a hydrated and non-adhesive OEG shell around the hydrophobic core.
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Fig. 41. CONTIN plots of thermoresponsive polymer solutions measured by DLS (1 mg/ml in DI water, \( T = 40^\circ C \)): (red) PNIPAM, (blue) P(OEGMA-MEO2MA), (green) P(OEGMA-OPGMA) (a); hydrodynamic radii of polymer micelles at 20°C (opened columns) and 40°C (filled columns) (b); Representative cryo-TEM images of thermoresponsive brushes grafted onto 200 nm large silica particles (c) PNIPAM, (d) P(OEGMA-MEO2MA), (e) P(OEGMA-OPGMA).

The cryo-TEM images revealed hells formed by swollen polymer brushes around silica particles (Fig. 41c–e). While the density of the shell gradually decreases with the distance from the particle surface in the case of PNIPAM and P(OEGMA-MEO2MA) brushes (Fig. 41c,d), there is a clear formation of two-layer shell morphology with the sharp border in the case of the P(OEGMA-OPGMA) brush (Fig. 41e). There is a first dense polymer layer which is in direct proximity to the particle surface and a second sparser one on the periphery (Fig. 41e). These denser and sparser shells have to be enriched by more hydrophobic OPGMA and more hydrophilic OEGMA, respectively. The assumption is based on a previous finding where it was demonstrated that while the P(OEGMA-OPGMA) copolymer is random, side OEG and OPG groups are fairly massive and flexible enough to undergo phase separation [Ish03]. Moreover, monomers have a different reactivity [Neu07] that causes formation of gradient copolymers and, as result, may lead to the formation of a core–shell structure. Independent of the origin of the formation of a core–shell structure, its observation gives an additional argument to consider that the adhesion properties of P(OEGMA-MEO2MA) and P(OEGMA-OPGMA) brushes are
affected by the presence of an oligoethylene glycol shell. Moreover, the clear formation of a two-layer shell morphology in the case of the P(OEGMA-OPGMA) brush leads to the stronger segregation of OEGMA chains in the outer shell and, therefore, significantly decreases the adhesion force comparatively to P(OEGMA-MEO2MA).

In summary, the effect of chain architecture on adhesion performance of thermoresponsive polymer brushes has been investigated. The adhesion decrease in the sequence PNIPAM, P(OEGMA-MEO2MA), P(OEGMA-OPGMA) was attributed to the increasing content of hydrophilic oligoethylene glycol (OEG)-groups in the same sequence. The OEG groups prevent aggregation of molecules in solution at temperatures above LCST as it was shown in DLS measurements thus drawing a parallel between the amount of OEG groups and decrease of adhesion forces of polymer brushes. The cryo-TEM images show even the formation of core shell structures attributed to OEG groups which are especially pronounce in the last, less adhesive system – P(OEGMA-OPGMA).

1.5.3 Effect of tip geometry/radius

Next, the effect of tip geometry and radius on adhesion forces was studied. The AFM force–distance experiments using, as mentioned above, three sorts of AFM probes were applied to elucidate the effect of tip geometry and radius on adhesion behaviour of investigated polymer brushes.

Commercial silicon oxide sharp tips of 5 nm in radius (Veeco Instruments, Inc., USA) were used as received without any chemical modification. The spring constant of (0.6 ± 0.07) N/m was measured via the method of thermal fluctuation on Dimension V AFM (Veeco Instruments, Inc., USA).

A thermal oxidized molten SiO₂-tip (R = 40 nm) was prepared as described by Hüttl et.al. [Hütt02]. Commercial silicon sharp tip was oxidized in a tube furnace MFT 12/38/400 (Carbolite, Hope Valley, UK) in air at 1150 °C. During the treatment an amorphous silica layer is formed on the tip surface. The layer has a low roughness and the tip gains a nearly ideal hemispherical shape of about 40 nm in radius after two hours of treatment [Hem11].

Colloidal probes were prepared by gluing dry silica spheres (Bang Labs, USA, mean diameter 4.84µm) onto tipless silicon nitride AFM cantilevers NP–O of resonant frequency 65-80kHz (Veeco Instruments, Inc., USA) by a micromanipulator using a two-component epoxy resin (UHU plus endfest 300, UHU GmbH, Germany). Spring constant was measured before gluing of colloidal probe also via the method of thermal fluctuation and it was in the order of 0.5 N/m to 0.6 N/m. The results of the method showed an error up to 20%. The effect of the glued sphere on the spring constant was within this error limit. The diameter of the spheres was determined after the
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measurement from the scanning electron microscope images (Phenom, FEI Co., USA) with accuracy of ±0.05 µm [Dre10], [Elm09].

To eliminate the influence of different radii (R) of the probing tips interacting with a flat surface, the force F was converted into a geometry-independent interaction energy (E) by using the Derjaguin approximation (Eq. 2). It was found that adhesion force nonlinearly increases while adhesion energy decreases with the tip radius (Fig. 42). However, according to models Derjaguin-Muller-Toporov (DMT) [Der75] and Johnson-Kendall-Roberts (JKR) [Joh71], the pull-off force should scale linearly with the probe tip radius. Adhesion energy, on the other hand, should be a constant. These deviations from the theoretical models arise most probably from the different depth of penetration of tips in the brush layer. In fact, the sharp tip penetrates deeper pushing grafted chains aside, the large sphere is unable to push polymer chains aside and only compresses the polymer layer as also suggested by Zhulina et al. [Hal10]. To estimate the relative degree of penetration of sharp, molten tip and sphere in the polymer layers, it was assumed that the force applied per contact area unit, which is required to detach the probe from the polymer surfaces, is independent of the tip shape and radius. Area of contact is $S = 2\pi Rh$, where R is probe radius and h is penetration depth. The ratios between degree of penetration of the molten tip ($h_{\text{molten} \text{ tip}}/h_{\text{sharp} \text{ tip}}$) and sphere ($h_{\text{sphere}}/h_{\text{sharp} \text{ tip}}$) to that of sharp tip in the polymer layer were found to be around $h_{\text{molten} \text{ tip}}/h_{\text{sharp} \text{ tip}} \approx 10^{-2}$ and $h_{\text{sphere}}/h_{\text{sharp} \text{ tip}} \approx 10^{-5}$, respectively meaning that the molten tip and sphere yield adhesive properties of the very topmost layer of the polymer brushes.

![Graphs](image_url)

**Fig. 42.** Adhesion force (left) and adhesion energy (right) of thermoresponsive brushes (thickness = 50 nm) tip vs. radius. (red) PNIPAM, (blue) P(OEGMA-MEO2MA), (green) P(OEGMA-OPGMA). $T = 40^\circ C$.

In summary, the comparison of adhesion forces of polymer brushes measured with three different types of AFM tip revealed non-linear character of pull-off forces with the probe tip radius unlike to theoretical predictions. This was explained by different depth
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of penetration of probing tips inside the polymer layer, which was confirmed by calculations.

1.5.4 Effect of surface roughness and chemical functionality of colloidal probe

To investigate the effect of roughness on surface adhesion properties, the thermoresponsive polymer brushes PNIPAM, P(OEGMA-MEO2MA) and P(OEGMA-OPGMA) were synthesized also on rough microstructure substrates made of spherical core–shell particles with 1 µm in diameter. The adhesion behaviour of the brushes on both, flat and rough surfaces, was investigated using either a hard bare silica colloidal probe (bare-CP) or a silica particle coated by the same thermoresponsive polymer as on the substrate (brush-CP, Fig. 43). The results obtained after all these measurements are summarized and analysed in this section.

![Fig. 43. Schematic representation of symmetric and asymmetric adhesion experiments: (a) bare SiO₂ colloid probe (bare-CP)—flat substrate modified with corresponding brush (brush/flat); (b) brush modified colloidal probe (brush-CP)—flat substrate modified with corresponding brush (brush/flat); (c) bare SiO₂ colloid probe (bare-CP)—rough substrate modified with corresponding brush (brush/rough); (d) brush modified colloidal probe (brush-CP)—rough substrate modified with corresponding brush (brush/rough). CP–SiO₂ sphere with diameter 4.84±0.05 µm.]

The representative pull-off force–distance curves, measured on PNIPAM and P(OEGMA-MEO2MA) brushes grafted onto rough substrates are shown in Fig. 44. They were measured in aqueous environment as a function of temperature with bare-CP and brush-CP, respectively. It was found that all thermoresponsive brushes also on rough substrates are completely non-adhesive below LCST independently of their structure and chemistry of the probing colloidal probe. A purely repulsive character of force—
distance curves at 24°C indicates a complete shielding of the substrate by the swollen polymer. On the other hand, the transition from the repulsive to attractive behaviour has been observed when the temperature was increased. Namely, both bare-CP and brush-CP adhere to the thermoresponsive layers at elevated temperatures (above LCST, \(T \geq 32^\circ C\), Fig. 44 A, B) and the adhesion force increases with temperature. As it was already mentioned while speaking about the polymer brushes on flat surfaces, this switching behaviour is caused by the switch from the hydrophilic to hydrophobic state of the brush due to the phase transition from a swollen to a collapsed state.

![AFM force–distance curves](image)

*Fig. 44. Typical AFM force–distance (pull-off) curves (normalized) measured between a bare-CP and PNIPAM (A) or brush-CP and P(OEGMA-MEO2MA) (B) both grafted onto rough substrate as a function of temperature.*

As the temperature is decreased (during the cooling experiment), the measured effective forces become repulsive again due to the transition of the brush to the hydrophilic state. Thus, the switching of adhesion in response to the temperature measured either between bare-CP or brush-CP and flat or rough brush-modified substrates is fully reversible and can be repeated many times (Fig. 45, results presented for the rough P(OEGMA-OPGMA) brush measured with a brush-CP).

While the adhesion behaviour on the rough surface is qualitatively very similar, the adhesion force is higher in the case of flat substrates than in the case of the corresponding rough microstructured ones. This effect is due to the reduced contact area between the hard spherical AFM probe and rough surface. Roughness is typically been held responsible for decreasing the pull-off forces magnitude on account of asperity contact rather than intimate contact of the spherical body with the flat substrate [Tor05]. In fact, the adhesion force on rough surfaces is ca. 4–5 times smaller.
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than that measured on flat ones. On the other hand, considering the radius of the AFM probe and particles on the surface, adhesion on a rough surface is expected to be 70% of that on flat one [Sku00]. The difference between experimental and predicted results may be due to the intrinsic roughness of the particles.

![Fig. 45. Example of reversible switching of adhesion force during heating–cooling cycle AFM measurement (24°C–28°C–30°C–32°C–34°C–36°C–40°C) between the brush-CP and P(OEGMA-OPGMA)-brush modified rough surface.](image)

In summary, the character of transition between adhesive and non-adhesive states depends on the chemical structure/architecture of the thermoresponsive polymer, surface properties of the probe and roughness of the substrate. It was found that PNIPAM has a sharp transition when probed by bare-CP as well as brush-CP (results summarized in Fig. 46 a and d). The P(OEGMA-OPGMA) has smooth and sharp transitions when probed by bare-CP and brush-CP, respectively (Fig. 46 b and e). The P(OEGMA-MEO2MA) has smooth transition in both cases (Fig. 46 c and f). It was also found that while the adhesion force between bare-CP and thermoresponsive brushes grafted onto the flat substrate decreases in the sequence PNIPAM, P(OEGMA-MEO2MA), P(OEGMA-OPGMA), the character of brush–brush adhesion is different (Fig. 46). In particular, PNIPAM and P(OEGMA-OPGMA) become more adhesive when probed by brush-CP (Fig. 46 d and f—empty squares). Surprisingly, adhesion in the case of P(OEGMA-MEO2MA) is almost independent of the surface properties of the probe (Fig. 46). This has resulted in decrease of the adhesion force between the AFM probe modified by grafted polymers and the same flat thermoresponsive brush in the different sequence comparing to the case of unmodified bare probe: PNIPAM, P(OEGMA-OPGMA) and P(OEGMA-MEO2MA) (Fig. 46).
In order to explain the observed difference in the adhesive properties and sharpness of transition and switching of polymer brushes probed by bare-CP and brush-CP modified particles (Fig. 43), the chemical structure/architecture of the thermoresponsive polymers have to be considered. The PNIPAM is a homopolymer and the collapsed PNIPAM brush is homogenous (no core-shell structure) and hydrophobic. On the other hand, both P(OEGMA-OPGMA) and P(OEGMA-MEO2MA) are random copolymers of hydrophilic OEGMA and hydrophobic (OPGMA and MEO2MA) monomers. Notably, MEO2MA is less hydrophobic than OPGMA because the LCST of MEO2MA homopolymer is LCST = 24 °C, while homopolymer of OPGMA is insoluble in water even at a very low temperature (LCST < 0 °C). Considering the hydrophobicity of the polymers, one can make the following conclusions. The PNIPAM is the most hydrophobic and has a sharp transition between adhesive and non-adhesive states. The P(OEGMA-MEO2MA) is the
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most hydrophilic system among three and has smooth transition between adhesive and non-adhesive states as well as weakest adhesive properties. The P(OEGMA-OPGMA) demonstrates an intermediate behaviour between PNIPAM and P(OEGMA-MEO2MA) and intermediate value of adhesion force obtained in the “symmetric” experiment with brush-CP.

1.6 Summary

The results of a comparative study on switchable adhesion of three kinds of thermoresponsive polymer brushes grown on flat and rough substrates and having low critical transition temperatures in biologically relevant region are presented and discussed.

In many studies the thermoresponsive polymer brushes were shown to exhibit a temperature-dependent solution and surface behaviour [Lin99], [Nat03], [Gil04], [Hyu04], [Sun04], [Ala05], [Kes10], [Lee10]. The results coinciding with the previous reports were demonstrated in this thesis. Firstly, all synthesized thermoresponsive brushes independently of their chemical structure and roughness of the supported substrate are found to be completely non-adhesive below LCST. On contrary, strong attractive interactions were observed on these systems at temperatures above LCST while probing with both hydrophobic (bare-CP) and hydrophilic (brush-CP) AFM tip. Moreover, the adhesion forces show fully reversible character and can be repeated many times.

The effect of tip radius and geometry on adhesion behaviour was investigated after that. Three types of AFM probe (sharp tip (R = 5 nm), molten tip (R = 40 nm) and colloid probe (R = 2420 nm)) were used for adhesion measurements. It was shown that the adhesive force scales nonlinearly with probe radius and that the adhesion energy obtained using Derjaguin-Muller-Toporov approaches decreases with the increase of tip radius. This is in fact a contradiction to the theory but can be attributed to different depths of penetration of probes in the polymer layers. The common is however the decrease of adhesion in the sequence PNIPAM – P(OEGMA-MEO2MA) – P(OEGMA-OPGMA) independently of the tip type. Based on the dynamic light scattering and cryo-TEM experiments, the latter effect is explained by the formation of a thin oligoethylene glycol shell around the hydrophobic polymer core in P(OEGMA-MEO2MA) system as well as in P(OEGMA-OPGMA) where the OEG layer is even more pronounced.

The adhesion force between the brush-modified tip and the same flat thermoresponsive brush decreases in the different sequence comparatively with the measurements with a bar colloidal probe: PNIPAM, P(OEGMA-OPGMA) and P(OEGMA-MEO2MA). This
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difference in adhesion properties is explained by the specific chemical architecture of polymers.
The samples are more adhesive on flat modified brush substrates than in the case of corresponding microstructured ones. This effect is due to a reduced contact area between the spherical probe and the rough surface.

The obtained findings could be useful for design of scaffolds for tissue engineering using thermoresponsive particles which undergo sol–gel transition as well as for the engineering of synthetic materials in interaction with biological objects.
As it was reported [Cun03], adhesion of cells to thermoresponsive surfaces is often irreversible – cells do not adhere to swollen polymer film at low temperature while becoming irreversibly adsorbed when the polymer layer collapses at an elevated temperature. One of the possible origins of this effect could be too strong adhesion. Therefore based on results presented in this work, it is expect that P(OEGMA-OPGMA) and P(OEGMA-MEO2MA) systems, which demonstrates moderate sticky properties, could be particularly promising to control adhesion of cells.

Although the PNIPAM is surely the most popular thermoresponsive polymer and can therefore be considered as the gold standard [Lut08] in this research area, it has several disadvantages which restrict its application for some biotechnology purposes. The PNIPAM isn’t a bioinert polymer because of the presence of multiple amide functions in its molecular structure which may lead to the formation of H-bonding interactions with amide groups of proteins [Bia04], [Wu05]. Thus, the thermoresponsive polymers based on biocompatible oligo(ethylene glycol) side-chains appear as promising alternative to conventional PNIPAM for bioapplications and for design of thermoresponsive materials [Lut08].
2. Solvent responsive and adaptive polymer brushes

2.1 Abstract

This chapter is dealing with investigation of switchable and adaptable adhesion properties of comb-like random and block copolymer brushes made of PEG-PDMS biocompatible polymers grown from flat and rough substrates. Influence of chemical composition, architecture of polymer chains, ratio of components, roughness of substrate and state of surrounding media on adhesion forces was thoroughly investigated. Surface segregation within the brush layer was investigated using XPS as well as contact angle, zeta potential, null-ellipsometry and adhesion measurements.

2.2 Introduction

Recent efforts were focused on design of responsive polymer brushes, which are either biocompatible or both biocompatible and biodegradable [Wis08]. Poly(ethylene glycol) (PEG) and poly(dimethylsiloxane) (PDMS) are synthetic biocompatible polymers. Both polymers have low glass transition temperatures ($T_g$) and polymer chain segments are mobile at room and at human body temperature. This mobility makes the systems as though “alive”: they are able not just switch their properties from one state to another, as it happens with polymers with high LCST (PNIPAM), adaptable systems are always on the move and respond very sensitive to every small change in the surrounding media. These peculiarities have opened great perspectives for the polymers to be used in biomedical applications, for food and cosmetic industries [Wis08], [Kes10].

Polymer brushes consisted of two or more types of polymers can amplify their response to external media due to combination of conformational changes and microphase separation [Sid99], [Sog96].

Minko et al. have made non-sticky surfaces in both, ambient and aqueous environment, based on mixed PDMS-PEO polymer brushes. The brushes are able quickly switch their adhesion properties via reorganizing of its structure: in air PDMS chains occupy the top of the layer, whereas in water it will be PEG. Such structures can be very useful as non-fouling coatings [She08].

The switching behaviour of hybrid polymer brushes made of PDMS and EPEI (polyethylenimine) is based on the same principals [Mot07]. The system immediately gain hydrophilic state in water and switch back to a hydrophobic state upon drying [Mot07].

In this work more complex responsive/adaptive brushes formed by comb-like PEG-PDMS random and block copolymers synthesised via ATRP have been studied.
2.3 Experimental Part

2.3.1 Materials

Additionally to the chemicals used for the preparation of thermo-responsive polymers, following chemicals were utilized for the fabrication of PEG-PDMS systems: anisole solution (purum, ≥99.0%, Fluka) and Tin(II) 2-ethylhexanoate (~95%, Aldrich), 1H,1H,2H,2H-Perfluorodecytrichlorosilane (PFDTS, 97%, ABCR) were used as received. Monomethacryloxypropyl terminated poly(dimethylsiloxane) (asymmetric, 6-9 cSt, Gelest) and oligo(ethylene glycol) methyl ether methacrylate ($M_n = 475$ g/mol, Aldrich) were purified by passing through an Al$_2$O$_3$ column.

2.3.2 Modification of planar substrates

Highly polished single-crystal silicon wafers (Semiconductor Processing Co.) were used as a substrate also for PEG-PDMS brushes. The wafers were modified through step activation of hydroxyl-groups, silanization and bromide initiator immobilization steps (all details in Chapter III.1).

2.3.3 Growing of polymer brushes from flat and rough surfaces

Three kinds of comb-like PEG-PDMS layers were synthesized: two block copolymer ones where either PEG or PDMS are grafted first and one random copolymer where both macromonomers are grafted simultaneously and randomly. Different ratios of components for each of the three types of brushes were used: 20%vol PEG + 80%vol PDMS, 50%vol PEG + 50%vol PDMS, 80%vol PEG + 20%vol PDMS. Homopolymer brushes PEG and PDMS were prepared as well. The chemical structures of PEG and PDMS and schematic structures of PEG-PDMS-based copolymers are presented in Fig. 47.

Two sets of brushes with different thicknesses – around 15 and 40 nm – were prepared. The thickness of polymer layers on the wafers in the dry state was measured using a null-ellipsometer.

The grafting density calculated based on the results of GPC (typical molecular weight of brushes with thickness $H = 15$ nm and $H = 40$ nm is $M_n = 20$ kg/mol and $M_n = 60$ kg/mol, respectively; PDI = 1.7 – 2.5) and ellipsometry was ca $\Gamma = 0.4$ chain/nm$^2$, while the distance between grating points was around $D = 2$ nm. The radius of gyration ($R_g$) of the used polymers is unknown but expected to be more than 5 nm. For example $R_g$ of polystyrene with a molecular weight of about 30000 g/mol in a good solvent (toluene) is 10 nm [Siq95]. Since the distance between grafting points is smaller than the thickness of the polymer layers, the polymer-grafted layers can be considered as a brush-like in both the dry and swollen states [Min06].
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Polymer brushes were synthesized using AGEP ATRP as described earlier (Chapter III.1), but in anisole solution and with Tin(II) 2-ethylhexanoate as a reducing agent. The polymerization of polymer brushes were done by mixing of 2 ml of monomer(s) and 356µL solution consisted of CuBr₂ (0,1g), PMDTA (0,78µm) in ethanol (20ml) in anisole solution (3ml). To start the polymerization 100 µL of Tin(II) was added into a reaction vessel. The procedure was carried out at 90°C. In general, the required thickness of PEG, PDMS polymer brushes can be achieved by varying two parameters: the duration of synthesis and quantity of catalyst of polymerization in solution (EbiB). As an example, the influence of these two parameters on the thickness of PEG homopolymer brush is presented in Fig. 48. The growth of PDMS brushes shows similar character.

Fig. 47. Chemical structures of poly(ethylene glycol) methyl ether methacrylate (PEG) – red, and poly(dimethylsiloxane) methyl ether methacrylate (PDMS) – the blue one. Schematic chemical structures of block copolymer and random copolymer based on PEG-PDMS polymer brushes.
III. Results and Discussions. Solvent responsive and adaptive polymer brushes

**Fig. 48.** A – Influence of polymerization time on PEG brush thickness, with the constant amount of EbiB catalyst – 4 µL; B – Influence of the amount of EbiB catalyst at 60 minutes polymerization time on the thickness of PEG polymer brush.

The detailed information about the components and parameters of synthesis procedure used for fabrication of 40 nm thick polymeric layers is presented in Table 3.

Two steps of ATRP procedure were done to get the block copolymer brushes. To match the appropriate ratio of the components the thickness of the layers was controlled after each step of polymerization with null-ellipsometry measurements. Thickness of second grafted layer was quantified as a difference between the total brush thickness after two steps of grafting and thickness of first grafted layer.

The desired composition of the random copolymer brushes was achieved by adding the monomers in corresponding quantities into polymerization solution. The elemental analysis using XPS measurements were done afterwards to estimate the resulted ratio of the components on the wafer surface (see Fig. 49). First, chemical composition of the random copolymer layers was quantified by XPS measurements at zero incident angle, which corresponds to 10 nm penetration depth. A linear change of C:O and Si:C with the feed ratio of co-monomers indicates that the composition of the resulting random copolymer brushes corresponds to feed ratio of co-monomers (Fig. 49 a).
### III. Results and Discussions. Solvent responsive and adaptive polymer brushes

**Tab. 3.** ATRP procedure components, conditions and resulted thicknesses of polymer brushes grown from flat substrates.
Afterwards, the surface segregation in dry PEG-PDMS brushes and their chemical composition in the topmost surface region was quantitatively analyzed by angle resolved XPS (ARXPS). For this, the samples were probed at three different angles of incidence 0°, 60°, 75° that corresponds approximately to 10 nm, 5 nm and 2.5 nm probing depth. Notably, the amount of silicon in the Si:C atomic ratios results only from the contributions of the PDMS sequences of the brush and not contributions of the silicon oxide to the Si 2p spectra. The last were subtracted from the Si 2p spectra. It was found that Si:C ratio decreases with the increasing probing depth for all samples (Fig. 49 b) that indicates a preferential segregation of hydrophobic PDMS chains in the topmost surface layer of the brushes and its depletion in the bulk. According to Schmidt [Ste02] and de Jong [Jon04] this effect is due to intramolecular phase separation occurred in copolymer cylindrical brushes with two chemically different types of side chains statistically attached to a flexible backbone.

Fig. 49. Results on elemental analysis using XPS measurements; C:O (filled circles) and Si:C (empty squares) ratio in random copolymer PEG-PDMS brushes as a function of fraction of PEG in polymerization mixture at the deepest XPS information depth (10 nm) (a) Correlation between the Si:C atomic ratios at different incident angles (0°, 60° and 75°) corresponding to different information depths (10 nm, 5 nm and 2.5 nm) obtained using angle-resolved XPS of the samples (b) (thickness th = 40nm).

The PEG-PDMS polymer brushes were also grafted to the rough substrates made of 1 µm silica particles. All details on preparation of rough surfaces are given in Chapters III.1.2. The similar procedure to proof the presence of polymer layers on the surface of the particles as for thermoresponsive brushes has been used. Briefly, the topography images of wafers with and without polymers were created in ambient and aqueous conditions. The images of surfaces without polymer and their profiles are very much alike in air and water (Fig. 50 A, B). Whereas, the topography images of the surfaces previously exposed to ATRP procedure demonstrate clear-cut distinction. They become fuzzy in water such identifying swelled polymer chains (Fig. 50 C, D). Moreover, the presence of polymer
leads to blurred and lower height profile in water than that made in air environment (Fig. 50).

To sum up, the PEG-PDMS homo-, random and block copolymer brushes were successfully synthesised on flat and rough surfaces. The resulted ratio of components in block and random copolymers was investigated via ellipsometry and XPS measurements, respectively. The effect of intermolecular phase segregation in random copolymer brushes was shown via ARXPS. The presence of polymer layers on rough surfaces was proved by means of AFM topography images.

Fig. 50. Representative 2 x 1 μm AFM topography images and corresponding height profiles of rough substrates obtained by fusion of Br-modified 1 μm large silica particles, and with subsequently grafted random PEG-PDMS (80% PEG) brush, in the dry state (A, C) and under water (B, D) (T=24°C).

2.4 Surface properties evaluation

2.4.1 Wetting properties

The wetting properties of prepared homo- and heterogeneous PEG-PDMS brushes in contact with aqueous environment (MilliQ water) were investigated using contact angle measurements via drop shape analysis method – DSA (like in Chapter III.1.3). The results on advancing and receding contact angles are presented in Fig. 51 (A, C, E). The PEG-PDMS homo- and copolymer brushes with growing (from left to right) PEG volume content and that have the same chains architecture are summarized in Fig. 51. The plot (A) shows \( \text{PEG}_{\text{bottom}} \cdot \text{PDMS}_{\text{top}} \) block copolymers, (C) represents \( \text{PEG} \cdot \text{PDMS}_{\text{random}} \) brushes, whereas the \( \text{PDMS}_{\text{bottom}} \cdot \text{PEG}_{\text{top}} \) copolymers are shown at the plot (E). Every group of copolymers is presented together with homopolymer brushes, PDMS on the left, and PEG on the right of each plot.
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Fig. 51. Advancing (green) and receding (orange) contact angles (A, C, E) and PEG surface fraction estimated by using Cassie equation (B, D, F) for PEG, PDMS homopolymers and copolymer brushes of different chemical compositions. A, B: blocks with PEG on bottom and PDMS on the top, C, D: PEG-PDMS\textsubscript{random} brushes E, F: blocks with PDMS bottom and PEG on the top. There is an increase of PEG content from left to right on each plot.
The homopolymer brushes PEG and PDMS are hydrophobic and hydrophilic, respectively. The values of advancing and receding water contact angles are equal to $\Theta_{\text{Adv}} = 111^\circ$ and $\Theta_{\text{Rec}} = 92^\circ$ for PDMS, and $\Theta_{\text{Adv}} = 47^\circ$ and $\Theta_{\text{Rec}} = 28^\circ$ for PEG. The values of the contact angles of PEG-PDMS copolymer brushes lie between the values measured on the homopolymers PDMS and PEG. It is significant that for all the systems both advancing and receding contact angles decrease with the increase of fraction of hydrophilic PEG polymer, but the character of this decrease is different: the curves representing contact angles of block copolymer brushes demonstrate plateau-like areas in the regions there one of the component prevails. The plateaus in the advancing contact angles of the system $\text{PEG}_{\text{bottom}}$-$\text{PDMS}_{\text{top}}$ and in the receding contact angles for the system $\text{PDMS}_{\text{bottom}}$-$\text{PEG}_{\text{top}}$ are the most pronounced ones (Fig. 51 A, E). On the other hand, the random copolymer brushes don’t have plateau region of CA values (Fig. 51 C). In order to explain the observed non-linear dependence between the contact angle and the volume fraction of PEG one can quantitatively estimate the fraction of PEG component accommodating the top layer of the copolymer brushes. For this, the Cassie equation was applied for each system considering both, advancing and receding contact angles:

$$\cos\Theta = \alpha_{\text{PEG}} \cos\Theta_{\text{PEG}} + (1-\alpha_{\text{PEG}}) \cos\Theta_{\text{PDMS}}$$  \hspace{1cm} (eq. 5)

where $\alpha_{\text{PEG}}$ is the PEG surface fraction, $\Theta_{\text{PEG}}$ and $\Theta_{\text{PDMS}}$ are the advancing/receding water contact angles on the surfaces of the homopolymer brushes PEG and PDMS, respectively.

It was found that the fraction of PEG on the surface obtained from advancing angles is smaller than that obtained from receding one (Fig. 51 B, D, F). This difference can easily be explained considering the state of polymer film during measurements of advancing and receding angles. First, water droplet contact the surface which is not wetted – the surface is dry during the measurements of the advancing contact angle and hydrophobic component (PDMS) is expected to dominate in the topmost brush layer [Mot07]. On the other hand, the polymer surface is wet during measurements of receding angle and fraction of hydrophilic component in the topmost brush layer is increased [Mot07].

Interesting is that the PEG fraction on the surface of block $\text{PEG}_{\text{bottom}}$-$\text{PDMS}_{\text{top}}$ (calculated from advancing and receding CA) and $\text{PEG}$-$\text{PDMS}_{\text{random}}$ (calculated from advancing CA) brushes for each ratio of components is smaller than that in the brush volume (Fig. 51 B, D). This result indicates a preferential surface segregation of PDMS to the top layer of the brushes in air that correlates with previous finding of Minko group [Mot07], [She08] and with shown above results of angle resolved XPS. This behaviour corresponds to the fundamental thermodynamic principle that each material endeavours to minimize its free energy. Since the surface free energy always gives a positive contribution to the total free energy of the material, hydrophobic parts of flexible polymer chains will be
directed to the air. Hence, in the case of these PEG-PDMS copolymers the more hydrophobic PDMS sequences were preferably used to form the outmost surface layer of the brush.

On the other hand, the PEG-PDMS$_{\text{random}}$ with 80vol% PEG and block copolymer PDMS-PEG that has 50 and 80vol% PEG shows preferential surface segregation of PEG component on the surface of the layer calculated from advancing and receding CA (Fig. 51 D, F). In these systems the predominant PEG fraction in random copolymer and displacement of the PEG component above in the block copolymer is obviously of importance.

Indeed, the architecture of the brushes influences significantly the wettability of the surfaces. Since the advancing and receding contact angles reflect hydrophobic and hydrophilic components, respectively, the plateau-like regions on the CA vs. PEG volume content curves in block copolymer brushes can be attributed to the stronger influence of the components grafted above (PDMS in the PEG$_{\text{bottom}}$-PDMS$_{\text{top}}$ and PEG in PDMS$_{\text{bottom}}$-PEG$_{\text{top}}$ brushes) that can effective segregate to the top layer of copolymer. Nearly linear character of decrease of contact angles in random brushes indicates mutual influence of both components and absence of preferable segregation of one of them. It can be clearly seen in Fig. 52 where the PEG-PDMS copolymer brushes are separated into groups with the same ratios of components, but of different architecture. It turns out that the block systems with PDMS layer on the top have the largest contact angle values and with PEG on the top – the smallest ones. The random brushes show intermediate values. The reason for this behaviour should be the increase of spatial hindrance in the sequence PDMS$_{\text{bottom}}$-PEG$_{\text{top}}$ – PEG-PDMS$_{\text{random}}$ – PDMS$_{\text{bottom}}$-PEG$_{\text{top}}$ that restricts the ability of PEG chains effectively swell and occupy the top of the layer thus contributing to the surface properties of the whole system.

![Graphs showing contact angles for 20vol%, 50vol%, and 80vol% PEG](image)

*Fig. 52. Dependence of contact angles (advancing – green circles, receding – orange circles) on polymer chains architecture. On the left diagram the systems have 20vol%, in the middle – 50vol%, in the right – 80vol% PEG volume content.*
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2.4.2 Swelling properties

The swelling properties of PEG, PDMS homo-, block and random copolymer brushes were investigated using null-ellipsometry. All measurements were performed at room temperature. The maximal layer thickness achieved under water was compared with the thickness in a dry state. The correlation between these two values is called swelling degree of the corresponding polymer brush.

It was found that surface with grafted pure PDMS almost do not swell in water and the systems with 20vol% of PEG swell slightly (Fig. 53). Further, considerable increase of swelling degree with growing PEG content was detected. This tendency is observed on all PEG-PDMS copolymer brushes independently of their architecture and can be explained by increasing content of hydrophilic PEG that swells well in water. The homopolymer PEG achieves the maximal degree of swelling that is equal to 3.

![Swelling properties](Fig. 53. Swelling behaviour in water of PEG, PDMS homo- and copolymer brushes with different chemical compositions. A: blocks with PEG on bottom and PDMS on the top, C: blocks with inverse sequence of components, B: PEG-PDMS \textsubscript{random} brushes. There is an increase of PEG content from left to right on each plot.)

It is worth notice that like if was found for the measurements of CA the block copolymer brushes demonstrate plateau behaviour of their swelling performance (plots A and C in Fig. 53), whereas the random systems have nearly linear dependence on PEG volume content (plot B). This should be because of the already mentioned spatial hindrances that restrict swelling and rearrangement of the hydrophilic PEG.

In the Fig. 54 the results on swelling (blue curves) and wetting (black curves) behaviour of PEG-PDMS copolymer brushes dependent on their chain architecture are summarized. Interesting is the mirror tendencies of contact angles and swelling degrees measured on systems with 20vol% PEG. There is a clear plateau character for both parameters because of the prevalence of PDMS component and its preferable segregation on the top of the brush. Almost no influence of chains architecture was
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indicated for this case. Different situation is observed in the other two groups of systems.

Symmetric brushes (with 50vol% PEG) have more gradual increase of swelling degree and decrease of contact angle values in the sequence PEG<sub>bottom</sub>-PDMS <sup>top</sup> -PEG-PDMS<sub>random</sub> - PDMS<sub>bottom</sub>-PEG<sup>top</sup>. This is because of the more balanced character of the brush properties due to the symmetry of components content and thus ability of mutual contribution to the properties of the whole brush. At the same time, homogeneous distribution of PEG and PDMS components along the backbone doesn’t permit phase segregation and prevalence influence of one component expressed in plateau formation.

The systems containing 80vol% of PEG demonstrate nearly straight linear form of contact angle decrease. It indicates the growing influence of PDMS component on the surface properties of the copolymer brushes in the sequence PDMS<sub>bottom</sub>-PEG<sup>top</sup> – PEG-PDMS<sub>random</sub> – PEG<sub>bottom</sub>-PDMS<sup>top</sup> as already discussed above. On the other hand, their swelling properties have a plateau because of the majority of hydrophilic PEG fraction and non-susceptibility to architecture of chains.

![Dependence of polymer chains architecture on static contact angle (black) and swelling degree (blue) of PEG-PDMS copolymers vs. Architecture of PEG-PDMS copolymer chains. On the left diagram the systems have 20vol% of PEG content, in the middle – 50vol%, on the right – 80vol%](image)

Fig. 54. Dependence of polymer chains architecture on static contact angle (black) and swelling degree (blue) of PEG-PDMS copolymers vs. Architecture of PEG-PDMS copolymer chains. On the left diagram the systems have 20vol% of PEG content, in the middle – 50vol%, on the right – 80vol%.

The observations made can be explained as follows. Since the contact angle is a characteristic of the topmost layer of a polymer brush, the processes of phase segregation to the surface influenced by architecture of polymer chains, play an importance role. On contrary, degree of swelling is a property of the whole layer and is more influenced by ratio of components in general.

In summary, swelling and wetting properties of PEG, PDMS homo-, random and block copolymer brushes were investigated. It was found, that with an increase of PEG content
the swelling of the brushes increases. This behaviour was shown to be independent in most cases of polymer chains architecture. At the same time, increase of PEG content means decrease of contact angle measured in water. This tendency is valid also for all systems, but in different manner. Whereas some systems demonstrated plateau behaviour, the others had gradual change of properties with growing PEG content or with change of chains architecture. The calculation of the PEG surface fraction has revealed dissimilar values for different copolymer brushes thus explaining the differences of contact angles. In general, the wetting behaviour is mainly influenced by properties of the sample topmost layer, whereas the swelling ability is rather dependent on bulk properties of the polymer, like ratio of components. The results of angle resolved XPS and contact angle measurements are in reasonable correlation for PEGbottom-PDMS\textsuperscript{top} copolymer brush where the preferential surface segregation of the hydrophobic PDMS chains to the top layer of brushes in air is shown. The contact angles of the other two copolymer systems, PEG-PDMS\textsubscript{random} and PDMS\textsubscript{bottom}-PEG\textsuperscript{top}, are mostly influenced by their chain architecture and ratio of components.

2.4.3 Electrokinetic measurements

The formation of surface charges during the brushes are in contact with aqueous solutions and changes of the formed charges in dependence on the pH value of the solution were studied by streaming potential measurements (Fig. 55 B, C)

It was found that the value of the apparent zeta-potential changes linearly with pH due to the charge formation by selective ion adsorption (Fig. 55 B). Since the investigated PEG-PDMS brushes do not have dissociating groups, the change in the absolute value of the zeta-potential with increased pH is caused by the preferential adsorption of hydroxyl (OH\textsuperscript{-}) ions at pH > IEP and hydronium (H\textsubscript{3}O\textsuperscript{+}) at pH < IEP from electrolyte solutions, respectively. This is supported by the result, that independently of the kind of the grafted polymer brush the isoelectric point (IEP = pH|_{\zeta = 0}) was about pH = 4 that is typically observed for the charge formation processes driven by ion adsorption. Moreover, investigated films showed a flattish curve for the pure PEG brush (Fig. 55, red dots). This behaviour can be attributed mainly to the strong swelling of the polymer layer. Charge-determining ions embedded in the swollen layer contribute to the net charge in the volume of the outer polymer layer. Hence, the apparent difference of ion concentrations between the brush surface and the surrounding aqueous electrolyte solution and consequently, the electric potential between these two phases is lowered and a smaller zeta-potential value is observed. PDMS is a non-hydrated hydrophobic polymer, which do not swell and incorporate ions in aqueous solutions. Hence, brushes of PDMS showed higher apparent zeta potential values (Fig. 55 B, black dots). Moreover, it was found that the apparent zeta potential of random copolymer brushes with a different PEG fraction linearly depends on the ratio between co-monomers and show
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intermediate trends between mono component PEG and PDMS (Fig. 55 C). In fact, since PEG swells strongly in water, one can expect that values of apparent zeta potential of the brushes must be close to that of pure PEG layer. The observed linear change of zeta-potential (Fig. 55 C) with an increase volume fraction of PEG in brush could be explained by the resolution of streaming potential method. In fact, the deeper sink into the flexible brush layer “open” structure could be expected during the streaming of electrolyte solution and, therefore, not necessary very topmost layer is measured. For instance, Duval et al. [Duv11] discussed so-called open structures at soft multilayered polyelectrolyte films illustrated by streaming current measurements. Furthermore, the overall tendencies in the changes of contact angle, swelling ratio and zeta-potential values with the brush composition are in good agreement. The lower value of PDMS content in the system corresponds to the lower value of advancing/receding contact angles, lower swelling property as well as lower value of apparent zeta-potential (Fig. 51 C, 55 A, C).

Fig. 55. Apparent zeta-potential vs. pH (measured in 10⁻³M KCl) for PEG, PDMS mono and random copolymer brushes with different chemical compositions.

2.4.4 Surface morphology

Next, the surface morphology of homo- and copolymer brushes was investigated in water and in air. The measurements were performed on Dimension V AFM (Veeco Instruments, Inc., USA) in TappingMode both in dry and aqueous media (with a Fluid Tip Folder) with silicon TappingMode tip (resonant frequency 200-400kHz) and ultrasharp silicon tip CSC11 (resonant frequency 20-40 kHz) (MikroMasch, Estonia), respectively. The surface morphology of homopolymer brushes is, as expected, smooth and featureless independently of the solvent (Fig. 56).
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Fig. 56. Surface morphology and height profiles of homopolymers PDMS (upper row) and PEG (lower row) in air and in water.

The topography images of all random copolymer brushes also demonstrate smooth and almost featureless morphology in both media – in air and in water (Fig. 57). This fact can be explained by the homogeneously distributed incompatible PEG and PDMS components along the methacrylate backbones. This displacement prevents the brushes from aggregation and formation of big clusters, otherwise that would be seen on surface topography.

The morphology of block copolymer brushes strongly depends on their composition (ratio between PEG and PDMS), sequence of block (either PEG or PDMS are the bottom layer), as well as on environment (air or water) (Fig. 58, 59).

Block copolymer PEGbottom-PDMS\text{top} with 20\text{vol}\% PEG has smooth surface morphology in air clearly because of the excess of PDMS that occupies the whole top area of the brush surface (Fig. 58, A). Exposure of the brush to water environment results however in formation of blobs, which should be formed by swollen PEG. Then the dark areas are formed by collapsed PDMS (Fig. 58, D). The morphology of PEGbottom-PDMS\text{top} brush with the equal ratio of components seems to be less homogeneous in air. 50\text{vol}\% of PDMS component is obviously not enough to cover fully the surface of copolymer. That is why small dimples formed by collapsed PEG are present here. In water the brush is almost featureless – the PEG polymer swells effectively, segregates to the surface of the copolymer and covers it completely (Fig. 58, B – in air and E – in water). The morphology
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of the brush where PEG is a major component appears as ripple-like in air and featureless in water (Fig. 58 C, F). The ripples most probably are formed by top PDMS layer. Exposure to water results in swelling of bottom PEG layer which then covers PDMS that results in formation of smooth surface.

Random copolymer brushes PEG-PDMS

20vol% PEG

50vol% PEG

80vol% PEG

Fig. 57. Surface morphology and profiles of random copolymer PEG/PDMS brushes in air (upper row) and in water (middle row), corresponding profiles (lower row) with 20, 50 and 80vol% of PEG fraction (increase from left to right).
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Block copolymer brushes PEG$_{\text{bottom}}$ - PDMS$_{\text{top}}$

<table>
<thead>
<tr>
<th>Ratio</th>
<th>Air</th>
<th>Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>20vol%PEG</td>
<td>0.80 nm</td>
<td>13.1 nm</td>
</tr>
<tr>
<td>50vol%PEG</td>
<td>0.92 nm</td>
<td>0.78 nm</td>
</tr>
<tr>
<td>80vol%PEG</td>
<td>3.10 nm</td>
<td>3.10 nm</td>
</tr>
</tbody>
</table>

Fig. 58. Surface morphology and profiles of block copolymers PEG$_{\text{bottom}}$-PDMS$_{\text{top}}$ with different ratio of components in air and in water.

The morphology of PDMS$_{\text{bottom}}$-PEG$_{\text{top}}$ block copolymer brushes in air gradually changes: from small dimples in the brush with 20% PEG to larger dimples when brush is symmetric to almost smooth with small number of cavities when PEG dominates (Fig. 59, A, B, C, respectively). Expose of these samples to water results in increase size of dimples for the systems with 20 and 50% PEG (Fig. 59, D). The formation of islands in the case of symmetric brush is observed (Fig. 59, E). The brush with the major PEG content turns into smooth and featureless one if to be exposed to water (Fig. 59, F). On the grounds of the last observation one can conclude that the dimples present in the first two samples are most probably formed by PEG component which is located on the PDMS surface and can easily swell in water.
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**Fig. 59. Surface morphology and profiles of block copolymers PDMS<sub>bottom</sub> - PEG<sup>top</sup> with different ratio of components in air and in water.**

Direct comparison of topography profiles of block copolymer brushes with the same volume content of the constituents reveals several interesting factors. Different architecture of polymer chains in excess of PDMS doesn’t influence strongly the topography of block copolymer brushes in air. Their profiles are similar smooth because of the effective segregation of PDMS component to the top layer of the copolymers (Fig. 60 A). However, after immersing in water the profiles look completely different (Fig. 60 B). The block copolymer with the hydrophilic PEG on the top demonstrates smooth profile because of the ability of the PEG to swell effectively in water and cover the whole polymer layer. In contrast, the block copolymer PEG<sub>bottom</sub> - PDMS<sup>top</sup> has high blobs-like profile and more than 10 times higher value of rms roughness. In this case the swelling
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ability of the PEG is obviously restricted due to its displacement on the bottom of the copolymer brush. Similar dependence on polymer chain architecture is observed in air at the blocks with 50vol% of PEG. In this case the hydrophobic PDMS grafted above contributes to the smooth surface in air, which is impossible if the PDMS is on the bottom of the brush (Fig. 60 C black and red curves, respectively). The values of rms roughness reflect the differences of topography profiles.

Comparison $\text{PEG}_{\text{bottom}}$-$\text{PDMS}_{\text{top}}$ and $\text{PDMS}_{\text{bottom}}$-$\text{PEG}_{\text{top}}$

![Graph showing topography profiles and values of rms roughness depending on architecture of polymer chains. Black curves correspond to $\text{PEG}_{\text{bottom}}$-$\text{PDMS}_{\text{top}}$ block copolymer brushes, red curves – to $\text{PDMS}_{\text{bottom}}$-$\text{PEG}_{\text{top}}$ block copolymer brushes.](image)

Fig. 60. Topography profiles and values of rms roughness depending on architecture of polymer chains. Black curves correspond to $\text{PEG}_{\text{bottom}}$-$\text{PDMS}_{\text{top}}$ block copolymer brushes, red curves – to $\text{PDMS}_{\text{bottom}}$-$\text{PEG}_{\text{top}}$ block copolymer brushes. Plots A, B show systems with 20vol% of PEG in air and water, respectively; C – system with 50vol% of PEG in air.

Since the topography and wetting properties characterize the topmost layer of the polymers brushes one can draw a parallel between the evolution of topography and the CA values of the corresponding systems. The surface topography of the random copolymer brushes is unsusceptible to surrounding media and ratio of components and remains smooth. This is explained by the homogeneously distributed PEG and PDMS components along the backbone and their inability to form clusters and aggregates. This architecture is responsible for the mutual contribution of the both components to the system properties, which was shown to be the reason for the linear change of CA values with the growing PEG content. On contrary, the non-gradual change of the wetting properties of the block copolymer brushes match well the uneven change of their surface topography and its roughness under external stimuli, change of the architecture of the polymer chains and ratio of the PEG and PDMS components.
2.5 Adhesion properties of solvent responsive and adaptive brushes

Next, adhesion forces of solution-responsive PEG, PDMS homo- and copolymer brushes with different architectures grafted onto flat and rough substrates were investigated. The interaction forces were measured on AFM with two types of colloidal probe: with hydrophilic SiO₂ native colloidal probe and with modified colloidal probe with hydrophobic surface chemistry. Interaction forces were investigated at room temperature in ambient and aqueous (MilliQ water) media. The colloidal probes were prepared via gluing of a spherical particle of 4.84 µm mean diameter (Bang Labs, USA) onto native oxide tipless AFM cantilevers NSC12 of resonant frequency 185-430kHz (MikroMasch, Estonia) by a micromanipulator using a two-component epoxy resin (UHU plus endfest 300, UHU GmbH, Germany). Spring constant was measured before gluing of colloidal probe via the method of thermal fluctuation and it was in the order of 7 N/m to 12.5 N/m. Firstly, several parameters of the AFM force measurements procedure were investigated to state their influence on adhesion forces and to choose the appropriate values.

2.5.1 Effect of Maximal Load

The cantilever with attached colloidal probe approaches and retracts a sample during the force measurement with the same speed of 300nm/s. When coming into contact with the surface the colloidal probe executes a certain force on it. The magnitude of this force, named “Maximal Load” can be adjusted by “Trigger Threshold” parameter in the AFM software. The load should be strong enough to ensure a good contact with the surface, but not spoils it. Experiments were done to find out the correlation between these two parameters and to investigate how they influence the adhesion of a colloidal probe to the sample surface in air and water. The results obtained on PEG-PDMS\textsubscript{random} copolymer brush (with 20vol% PEG content) are presented as an example in Fig. 61. The dependences are qualitatively relevant for all polymer systems investigated in this Chapter. The Trigger Threshold was varied between 5 and 45 nm causing a change of the Maximal Load from 75 to 500nN in air and from 210 to 440nN in water. As expected, there is a linear dependence between these two parameters in air as well as in water environment (black curves in Fig. 61, A, B, respectively). As regards the adhesion force in air, it doesn’t alter significantly upon increasing of Maximal Load (Fig. 61 A, green curve) –the system is suggests to be in equilibrium [Dre12]. In water, however, the adhesion force is first constant, then grows quickly till achieves a plateau region that corresponds to equilibrium state of force measurements (Fig. 61 B, green curve). Though the values of adhesion forces differ from sample to sample, the values of Maximal Load correspond to plateau regions are similar independently of the sample. Since the excessive load could damage scanned surfaces it was decided to perform the AFM force measurements at 350 nN – the minimum load needed for equilibrium state.
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2.5.2 Effect of Scan Rate

Moreover, the effect of Scan Rate has been investigated to indicate its influence on adhesion force measurements. Since the Scan Rate units are number of trace and retrace scan lines performed per second (Hz), the actual speed of a tip depends on two parameters: Scan Rate and Scan Size. These values should be set so that the feedback loop has time to respond to changes in the sample topography. Setting the scan rate too high could result in poor results [Manual03].

Adhesion force measurements were performed on the area of 10*10 µm (Scan Size = 10 µm) in the range of Scan Rate 0.25 to 2.0 Hz. The measurements with colloidal probe revealed no influence between Scan Size and adhesion forces neither in air nor in water (Fig. 62). Thus, for all further experiments Scan Rate was set to medium value of 1 Hz.

![Graph A: Maximal Load and Adhesion Force vs. Trigger Threshold in Air](image)

**Fig. 61.** Correlation between trigger threshold and maximal load and their influence on adhesion forces of PEG-PDMS\textsubscript{random} copolymer brush with 20vol% PEG fraction in air (A) and water (B).

![Graph B: Maximal Load and Adhesion Force vs. Trigger Threshold in Water](image)

**Fig. 62.** Influence of scanning rate on adhesion forces/energy of PEG-PDMS\textsubscript{random} copolymer brush with 20vol% PEG fraction measured with colloidal probe in air and water.
2.5.3 Effect of Ramp Delay

Force measurements with “Ramp Delay” were also performed. This parameter sets the amount of time to wait before the cantilever being in contact with a sample surface retracts [MultiMode04] (Fig. 63). Without a Ramp Delay, the tip is retracted immediately after the indentation has been made. For samples which exhibit “flow”, Ramp Delay may be appropriate to investigate. Since the PEG and PDMS polymer brushes have low glass transition temperature and their polymer segments are mobile at room temperature it was interesting to study how interactions between a sample surface and a probing tip progress over time.

Fig. 63. Artist’s impression of the processes involved in AFM of polymer brushes, showing approach of the surfaces (top), immediate complex formation upon first contact, interpenetration of chains and complex growth during a waiting step, stretching of the chains upon separation, and finally rupture of the complex before returning to the initial state. Adapted from [Spr10].

The adhesion force measurements with a colloidal probe were performed in air and water with Ramp Delay values varied from 0 to 200 seconds. In Fig. 64 the results of measurements performed on PEG-PDMSrandom copolymer brush with 20vol% PEG fraction are shown as an example. The logarithmic dependence between adhesion force and Ramp Delay has been established (Fig. 64). It was revealed that the copolymer brush needs about 2 seconds of contact with a colloidal probe to equilibrate and to achieve the plateau value of adhesion force (Fig. 64).
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Fig. 64. Influence of Ramp Delay on adhesion force/energy of PEG-PDMS<sub>random</sub> copolymer brush with 20vol% PEG fraction in air and water.

2.5.4 Effect of temperature

PEG and PDMS polymer brushes have low glass transition temperature ($T_{g}^{\text{PEG}}=-66^\circ\text{C}$, $T_{g}^{\text{PDMS}}=-125^\circ\text{C}$) [SY125], [Lot97] and are liquid at room temperature [Mit07]. Through softening of polymers at high temperatures an advanced contact area with a probing AFM tip and thus higher adhesion forces would be expected. To prove this the AFM force measurements were carried out in air at 50°C and 70°C. A heating stage HighTech Peltier-Element was used for the measurements.

Fig. 65. Adhesion forces/energy as a function of temperature in ambient environment measured with a native colloidal probe on symmetric PEG-PDMS<sub>random</sub> copolymer brush.

Interaction forces were measured between a native colloidal probe and PEG-PDMS<sub>random</sub> copolymer with 50vol% PEG. The results were compared with values got at room temperature ($22^\circ\text{C}$). Before each experiment about 15 minutes have been waited for equilibration of the sample with environment. The results shown in Fig. 65 didn’t reveal
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significant difference of adhesion forces. Thus the PEG-PDMS polymer systems don’t soften additionally at high temperatures.

In summary, several parameters of the AFM force measurements were proved to have an influence on adhesion performance of PEG-PDMS polymer brushes. It was found that adhesion behaviour is independent of Scan Rate and environmental temperature in air. On contrary, the values of Maximal Load in water influence strongly the adhesion. It was also shown that the adhesion behaviour of the brushes dynamically change over time if being in contact with a probing tip. The dependence of adhesion on the Maximal Load and Ramp Delay can reveal much about the contact mechanics and the mechanical properties of the materials involved in adhesion test. According to the DMT and JKR models no dependence of the adhesion force on the Maximal Load or the Ramp Delay is expected [Kap02]. In practice however this will hold only as long as the deformations remain purely elastic. If one of the materials shows viscoelastic deformation, the contact area and adhesion force increase with Ramp Delay. When plastic deformations occur, the adhesion depends on the Maximal Load as well [Kap02]. The reason for the observed dependencies in the case of PEG-PDMS copolymers is the mobility of polymer chains at room temperature because of their low glass transition temperature. The values of adhesion forces in equilibrium are more than two times higher than that measured without Ramp Delay.

To get comparable results on adhesion force measurements of different samples, it is important to perform the measurements under the same conditions and to use the same parameters. The Trigger Threshold which depends on cantilever spring constant was adjusted such that the Maximal Load executed on the surface was about 350 nN (the same in air and water). The scan rate was set to 1 Hz for scanning of 10*10 \( \mu \)m areas. The measurements were performed always at room (22°C) temperature.

2.5.5 Effect of chemical composition

Similarly to thermoresponsive systems, the adhesion properties of PEG-PDMS polymer brushes were measured using force volume mode. To perform measurements in aqueous medium, the samples were first equilibrated for 30 min after adding of water and then the measurements were started.

Representative force-distance curves on PEG-PDMS homo- and symmetric copolymer brushes on flat surfaces are presented in Fig. 66, 67. Different types of adhesion behaviour are shown on the sample of several systems: homopolymers PDMS and PEG(Fig. 66); symmetric copolymers PEG\text{bottom}+PDMS\text{top}, PEG-PDMS\text{random}, PDMS\text{bottom}+PEG\text{top} (Fig. 67). The black curves show force-distance curves in air, the blue curves – in water.
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**Fig. 66.** Typical force-distance curves represent homopolymers PDMS and PEG on flat surfaces. Black curves demonstrate adhesion forces in air, blue rows – in water.
Fig. 67. Typical force-distance curves represent PEG-PDMS random and block copolymers (50vol% PEG). Black curves demonstrate adhesion forces in air, blue rows – in water.

The results of adhesion force measurements of all homopolymers PEG and PDMS and their random and block copolymers in air and water are summarized in Fig. 68. The plot on the left side shows the adhesion behaviour of $\text{PEG}_\text{bottom}-\text{PDMS}_\text{top}$ block copolymer
brushes; the plot in the middle corresponds to PEG-PDMS\textsubscript{random} copolymer brushes; the plot on the right side represents block copolymers PDMS\textsubscript{bottom}-PEG\textsuperscript{top}. There is an increase of PEG volume content from left to right on each plot. The “PDMS” and “PEG” on the X axis correspond to PDMS and PEG homopolymer brushes.

The homopolymer brushes PEG and PDMS are both adhesive to colloidal probe in the dry state. However, their behaviour changes completely in water. While the PDMS is still tacky in water because of hydrophobic interactions (Fig. 68 A – in air, D – in water), the PEG becomes completely non-adhesive due to strong hydration of polymer chains.

In the case of block and random copolymers, exposure of the brushes to water results in changing of their adhesive interactions with the colloidal probe. Initially strongly adhesive to colloidal probe in air, the brushes become low- or even non-adhesive in water. Notably, with growing PEG volume content the adhesion forces increase in air and decrease in water. This behaviour is relevant for all systems independently of architecture of polymer chains (Fig. 68). The block copolymer polymer brushes with more than 50vol% PEG content are completely non-adhesive in water (Fig. 68, blue columns).

![Fig. 68. Results of adhesion force measurements on homopolymer brushes PEG and PDMS and their random and block copolymers versus PEG volume content in air (transparent columns) and water (blue columns).](image)

### 2.5.6 Effect of length of polymer chain

The effect of the polymer layer thickness on adhesion forces was investigated via AFM force measurements with a native colloidal probe in air and in water. “Thin” polymer brushes were about 15 nm, whereas the “thick” polymer chains had about 40 nm. Interestingly, the chain length of PEG-PDMS copolymer brushes influences their adhesion behaviour strongly. Note, the 40 nm thick brushes are more adhesive than 15 nm ones (Fig. 69, thick brushes are shown with filled columns, thin brushes – with empty columns). Homopolymer brushes demonstrated similar tendencies. The difference
achieves in some samples more than 100%. One can argue that the colloidal probe can sink deeper into a thicker brush and hence deform it more and dissipate more energy upon debonding than with a thinner one. This may however be also due to an increase of the contact area of the brush with the probe.

Fig. 69. Adhesion forces and adhesion energy vs. Composition of homo- and copolymer brushes on thin and thick polymer layers, in air (A, C, E) and in water (B, D, F).
Other important observations were made concerning the measurements performed in aqueous environment. The thin PEG\textsubscript{bottom}-PDMS\textsuperscript{top} block and random brushes with 50 and 80vol\% of PEG as well as the thin block copolymer PDMS\textsubscript{bottom}-PEG\textsuperscript{top} with 20vol\% of PEG still have adhesion in water, whereas the corresponding thick samples are completely non-adhesive (plots B, D, F in Fig. 69). This behaviour could be due to the effect of substrates, which are not completely covered with the brushes in the thin samples. That is why it was decided to use only thick polymer brushes for further investigations.

2.5.7 Effect of chain architecture

The influence of chain architecture on the adhesion behaviour of random and block copolymer PEG-PDMS brushes was investigated. In the Fig. 70 the copolymers of different structure of polymer chains but the same ratio of PEG and PDMS components are shown. The plot A demonstrates block and random copolymer brushes with 20vol\% of PEG, plot B shows symmetric systems, and the plot C – systems with 80vol\% of PEG content. There are homopolymer brushes PDMS and PEG also shown on each plot on the left and on the right side, respectively. The adhesion behaviour of the brushes was then compared with their swelling performance (the right column in the Fig. 70).

It is interesting to note that the homopolymer PDMS and the copolymer systems with 80vol\% of PDMS fraction (20vol\% PEG) have very similar values of adhesion forces measured in air. This behaviour can be explained most probably by the prevalence of hydrophobic PDMS polymer which occupies the top layer of the brush (that was already shown in ARXPS measurements mentioned above in 2.2.3) and has the main influence on the properties of the whole system. This influence is however suppressed in water where the decrease of adhesion forces is observed in the sequence block PEG\textsubscript{bottom}\textsuperscript{top}–PEG-PDMS\textsubscript{random}– block PDMS\textsubscript{bottom}\textsuperscript{top} (Fig. 70 A, blue columns). The last system becomes even completely non-adhesive in water in spite of merely 20vol\% of PEG. Thus the distribution of the components in the copolymer brush is important in this case.

The systems containing 50vol\% and more of PEG fraction are non-adhesive in water environment independently of architecture of polymer chains (Fig. 70 B, C). Apparently, this is because of the swelling and segregation of PEG to the topmost layer of the brush in favourable for hydrophilic polymer aqueous conditions. Notable is also the relatively weak adhesion in air of the symmetric block copolymers PEG-PDMS with the PDMS block above that surely strongly contributes to this effect.

The systems with 80vol\% PEG demonstrate architecture-dependent behaviour with gradual growth of adhesion in air detecting the increasing influence of PEG component with change of the brush architecture. The adhesion of the block copolymer PEG\textsubscript{bottom}\textsuperscript{top}
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PDMS$^{\text{top}}$ has the smallest values also among the brushes with 80vol% PEG content (Fig. 70 C).

![Graphs showing adhesion force and swelling behavior for 20vol%, 50vol%, and 80vol% PEG content.](image-url)

**Fig. 70.** Effect of chain architecture on adhesion force measurements and swelling behavior of the systems with (A) 20vol%, (B) 50vol% and (C) 80vol% PEG content.
Next, the adhesion properties of brushes were compared with their swelling behaviour in water environment. Since the PDMS is hydrophobic and doesn’t swell in water, the swelling ability of the copolymer brushes corresponds to the hydrophilic PEG component. Therefore, the swelling degree of the copolymers with 80vol% PDMS is close to that measured on homopolymer PDMS. The influence of chains’ architecture was not registered, neither on swelling behaviour of the brushes, nor on their adhesion force values (Fig. 70 A). The similar, nearly constant behaviour is observed on the brush with 80vol% PEG. The plateau character is related to both parameters, degree of swelling and adhesion performance in water (Fig. 70 C). The symmetric brushes demonstrate growth of adhesion forces and swelling degrees in the sequence PEG\textsubscript{bottom}–PDMS\textsuperscript{top} – PEG-PDMS\textsubscript{random}– block PDMS\textsubscript{bottom}–PEG\textsuperscript{top} (Fig. 70 B).

In general, the systems that contain at least 50vol% PEG and that have swelling degree ≥2, are non-adhesive in water independently on polymer chains architecture. The reason for this should be the overwhelming influence of the PEG major component that swells very well in water and makes the whole system non-adhesive. The disposition of PEG is thus of minor importance. The only non-adhesive system in water environment with low swelling degree is the block copolymer brush PDMS\textsubscript{bottom}–PEG\textsuperscript{top} with 20vol% PEG content. In this case the determinant factor – is the top layer position of PEG that even at low content can influence significantly the adhesion performance of the brush making it completely non-adhesive in water.

All mentioned observations confirm the ideas already expressed while speaking about the wetting and swelling properties of the copolymer brushes. In some cases there is a clear influence of the chain architecture on the adhesion behaviour of copolymers. For the most part this can be explained by different extent of spatial hindrance in the brushes having different distribution of side chains. This influences the ability of the brushes to rearrange their chains upon changing environmental conditions. The component placed on the top of block copolymer brush contributes stronger to the surface properties, in particular their adhesion behaviour on the whole system, as that placed on the bottom. For a component beneath, there is a spatial hindrance to segregate on the top of the polymeric layer and to contribute to the properties of the system in whole. For example, even upon conditions favourable for hydrophilic PEG the block copolymer brush PEG\textsubscript{bottom}–PDMS\textsuperscript{top} and the random brush of the same composition (20vol% of PEG) have relatively strong adhesion in water, whereas the block with the PEG on the top is non-adhesive. The random brushes have mostly intermediate values of adhesion between the both block copolymers. In general, a clear correlation between the adhesion properties of the PEG-PDMS copolymer brushes and their swelling behaviour was shown.
2.5.8 Effect of surface roughness

To study the effect of surface roughness on adhesion behaviour of PEG-PDMS homo- and copolymer brushes, the samples grown from rough substrates made of 1µm large spherical particles were investigated via colloidal probe technique on AFM. The measurements were performed in ambient and aqueous conditions at room temperature. In Fig. 71 the results are summarized: the plots in the left column show the values of adhesion forces and adhesion energy of each type of PEG-PDMS copolymer brushes measured in air dependently on the PEG volume fraction, whereas the plots on the right side represent the analogous measurements in water. The empty columns reflect the adhesion values of the flat surfaces, the filled columns – the rough ones.

The adhesion forces measured on rough surfaces in air show a sharp decrease comparatively to the flat ones. This behaviour is typical for all the PEG-PDMS homo- and copolymer brushes (Fig. 71 A, C, E). Similarly to the measurements on the thermoresponsive polymer brushes, the decrease of adhesion on rough surfaces is attributed to the reduction of contact area between the rough surface and a colloidal probe while scanning [Tor05], [Sku00]. On the other hand, the measurements in water have often an opposite character (Fig. 71 B, D, F). The values of adhesion forces are quite large on rough surfaces whereas the corresponding flat samples are completely non-adhesive. This could be explained by the effect of substrate that is possibly not completely screened by polymer layers. However, the tendency of the increasing adhesion forces in air and decreasing in water with growing PEG content is similar on flat and on rough substrates.
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Fig. 71. Effect of surface roughness on systems with the same architecture of polymer chains. Hollow columns – flat surfaces, filled columns – rough surfaces. A, B: $\text{PEG}_{\text{bottom}}$-$\text{PDMS}_{\text{top}}$ block copolymers; C, D: PEG-PDMS random copolymer brushes. E, D: $\text{PDMS}_{\text{bottom}}$-$\text{PEG}_{\text{top}}$; A, C, E – measurements in air; B, D, F – in water.
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2.5.9 Effect of surface functionality of colloidal probe

Until now all shown results on adhesion force measurements were about interactions between a sample surface and a hydrophilic colloidal probe (native silica particle). To study the effect of colloidal probe with another surface functionality on adhesion behaviour of PEG-PDMS homo- and copolymer brushes, the experiments with hydrophobic colloidal probe have been performed. To provide a colloidal probe with such functionality the tipless cantilevers (NSC12 MikroMasch, resonant frequency 185-430 kHz, spring constant 7-12.5 N/m) with previously attached native silica colloidal particles of 4.84 μm in diameter were placed for 4 hours in exsiccator with a 1H,1H,2H,2H-Perfluorodecyltrichlorosilane (PFDTS). PFDTS is often used to control the surface chemistry and to achieve ultrahydrophobic and super-repellent surfaces [Raz10]. The common adhesion force measurements were carried out afterwards. In the Fig. 72 the results of the measurements are summarized: the left column represents the adhesion force/energy of the samples in air (empty columns) and water (filled columns) with hydrophilic colloidal probe, the right column – with hydrophobic one. The investigations were performed on flat samples modified with homo-, random and block copolymer brushes.

First of all, the homopolymers PEG and PDMS demonstrate dissimilar adhesion behaviour if probed with the hydrophobic CP. Though the PDMS is similar adhesive in both media, the values are about 4 times higher than that measured with a native CP. The PEG is turned out to be less adhesive than the PDMS, but the value is similar to that measured with the native CP. The PEG is non-adhesive in water independently of the surface chemistry of the probing tip.

The overall tendencies of adhesion forces/energy on the random and block copolymer brushes have a clear difference. The copolymer brushes measured with hydrophobic CP become less adhesive with growing PEG content whereas the results achieved with the native CP have just an opposite trend: their adhesion increases. Moreover, the block copolymers PEGbottom-PDMS<sup>top</sup> have in general significantly stronger adhesion in air when measured with the hydrophobic CP (Fig. 72 A, B). The random systems with 50 and 80vol% of PEG are about 3 times less adhesive in air, but similar to native CP almost non-adhesive in water (Fig. 72 C, D). The block copolymer brushes PDMS<sub>bottom</sub>-PEG<sub>top</sub> are non-adhesive in water (Fig. 72 E, F).
Fig. 72. Effect of AFM tip surface chemical composition on adhesion force measurements of PEG-PDMS copolymer brushes. The plots A, C and E show the measurements with the hydrophilic colloidal probe, the plots B, D and F – with a hydrophobic one modified with 1H,1H,2H,2H-Perfluorodecyltrichlorosilane.
The described observations can be explained by preferential adhesion of hydrophilic colloidal probe to hydrophilic PEG and hydrophobic colloidal probe to hydrophobic PDMS. In water however the adhesion decreases with increase of PEG fraction independently of surface chemistry of colloidal probe.

2.6 Summary

Solvent responsive polymer brushes based on hydrophilic PEG and hydrophobic PDMS polymers were synthesised using AGET ATRP. Depending on distribution of PEG and PDMS side chains along the methacrylate backbone three types of architecture were possible: random copolymer brushes with homogeneously distributed PEG and PDMS components; block copolymer brushes ones where the PDMS is on the top and PEG on the bottom of the backbone, and block copolymer brushes with inverse sequence: PEG – on the top and PDMS – on the bottom. Moreover, the ratio of components has been varied: 20vol% PEG and 80vol% PDMS, 80vol% PEG and 20vol% PDMS, and symmetric 50vol% PEG and 50vol% PDMS brushes. Homopolymers PEG and PDMS have been also prepared and used for comparison with the copolymer systems. All polymer brushes were synthesised on flat surfaces and on rough ones made of 1 μm large spherical particles.

The resulted composition of the synthesised block and random copolymer brushes was examined by means of ellipsometric and XPS measurements, respectively, and was shown to correspond to the desired ratios.

The surface charges and morphology, wetting and swelling properties were systematically studied and discussed. Surface topography of the PEG-PDMS\textsubscript{random} copolymer brushes were shown to be smooth and featureless in both media that correlates well with their gradually changing swelling and wetting properties with growing PEG content. This is explained by the homogeneously distributed PEG and PDMS side chains along the backbone and their mutual contribution to the properties of the copolymer brush in whole. On the other hand, the block copolymer brushes have various and often rough topography depending on architecture of polymer chains and surrounding media. The non-linear evolution of the surface properties, swelling and wetting, of the block copolymers matches well their topography.

Using the colloidal probe technique for the AFM force measurements the adhesion properties of the homo- and copolymer brushes were thoroughly investigated. Influence of several parameters of scanning procedure was first studied in details. The force executed by a tip on the sample surface (Maximal Load) has often contradictory influence of adhesion performance of investigated surfaces depending on surface properties and geometry of probing tip [Cro05], [Gre07], [Kim06]. In the present work the preload was found to influence significantly the adhesion forces measured in water.
This was attributed to the non-equilibrium state and most probably viscoelastic deformation of the systems under probing with an AFM tip until a certain pressure is employed. In air however such influence of Maximal Load wasn’t observed.

The adhesion force measurements with different scan rates and at elevated temperatures didn’t reveal any influences on adhesion values. Experiments with different Ramp Delay that expresses the contact time between a tip and a sample surface during the adhesion force measurements were also performed. It was shown that the PEG-PDMS homo- and copolymer brushes become more adhesive with increasing time of contact with a CP and a certain time is needed to achieve equilibrium. Since the polymers have low glass transition temperature their chains are mobile at room temperature and are able to rearrange their structure in order to achieve the energy favourable state. For all further experiments identical parameters of scanning were used.

Next, the influence of several factors on adhesion behaviour of the brushes in changing environmental conditions (air and water) has been investigated in details: the effect of chemical composition of the polymer chains, the length of the polymer chains, chain architecture, surface roughness of substrates where the brushes are grafted and surface functionality of colloidal probes.

The general tendency found for the interaction forces between the PEG-PDMS copolymer brushes and hydrophilic CP is the increase of adhesion forces in air and decrease in water with growing PEG content. As it was shown by the ARXPS, the hydrophobic PDMS predominantly occupy the topmost layer of the random copolymer brushes in air but the fraction is decreasing with growing PEG volume fraction. The investigations of the wetting properties showed reduce of the CA values in water with growing PEG content. Obviously, the rearrangement of the brush structure takes place with the change of solvent. The reason for this behaviour (already observed by the group of Minko [Mot07], [She08]) is the ability of the PEG and PDMS polymer chains to move in response to the external stimuli. They are flexible at room temperature due to their low $T_g$. The component that occupies the top layer contributes stronger to the surface properties of the whole copolymer brush. Thus, the surface properties of the PEG-PDMS copolymer brushes are determined by the hydrophobic PDMS in air and hydrophilic PEG in water.

The same trends were revealed on thin (15 nm) as well as on thick (40 nm) polymer layers. The values of adhesion forces in air and water were however higher on thick samples as on the thin ones. This can be explained through the different depth of penetration of the CP into the polymer layer and formation of larger contact area between two surfaces in the case of thick brushes.

The architecture of the polymer chains influence strongly the adhesion behaviour of the copolymer brushes. Random, mixed or block copolymers, the molecular weight of the components and their ratio introduce unique mechanisms of the phase segregation thus
III. Results and Discussions. Solvent responsive and adaptive polymer brushes

affecting the properties of the layers including their adhesion behaviour [Min06]. It was shown that the adhesion forces increase in air and decrease in water in the sequence $\text{PEG}_{\text{bottom}}$-$\text{PDMS}_{\text{top}}$ –$\text{PEG}$-$\text{PDMS}_{\text{random}}$ – block $\text{PDMS}_{\text{bottom}}$-$\text{PEG}_{\text{top}}$ (applied for the same ratio of components). In the same sequence the values of the contact angle of the brushes in water decrease. As already told, the polymer chains undergo rearrangements, but this ability to transform was shown to be different depending on the architecture of the polymer chains. For example, swelling in water and segregation of PEG to the top layer is more restricted in the block copolymer $\text{PEG}_{\text{bottom}}$-$\text{PDMS}_{\text{top}}$ than in the block copolymer with the PEG on the top. The random brushes show intermediate values.

Surface roughness of substrates didn’t change the main tendencies, but the adhesion force values, as expected, are much lower than on flat samples if measured in air. The reason is the reduced contact area between the CP and a sample surface. In water however several copolymer brushes grown from 1 $\mu$m large particles are more adhesive than the corresponding flat samples. It was explained by the not completely covered particle surfaces comprising the rough samples.

At last, the surface functionality of the CP was changed from hydrophilic to hydrophobic one. Interesting, adhesion force obtained in air by using hydrophobic CP on homopolymer PDMS, block copolymer with the PDMS on the top and other systems with 80vol% of PDMS is higher than that obtained using hydrophilic CP. Moreover, with growing PEG content the adhesion forces measured in air decrease. This is related to preference of hydrophobic-hydrophobic contacts over hydrophobic-hydrophilic ones. The tendencies in water are mostly the same independently of the CP surface chemistry.
III. Results and Discussions. AFM vs. Tack Test

3. Comparative study of adhesion behaviour depending on elasticity of adhesion probe

3.1 Abstract

The adhesion behaviour of PEG-PDMS homo- and random copolymer brushes was studied using probe tack tester. This work was done in collaboration with the group of Professor Costantino Creton at ESPCI (École Supérieure de Physique et de Chimie Industrielles de la ville de Paris, laboratoire de Physico-Chimie des Polymeres et Milieux Disperses). The results were compared with the results achieved via colloidal probe technique on AFM. Thus, the adhesion performance of the fabricated materials on macro- and on microscale was derived. Moreover, it was shown how the mechanical properties of a hard CP used in AFM and a soft pressure-sensitive adhesive applied in tack tests contribute to the adhesion performance of the copolymer brushes on flat and rough surfaces. In addition, the dependence of adhesion properties on hydrophobic or hydrophilic chemical functionality of adhesives and colloidal probe was studied.

3.2 Introduction

The AFM force measurements used before for investigations of polymer brushes yielded information about the adhesion forces on nano- and microscopic scales. However, for the industry and real-life applications the same information on macroscale is rather of relevance. To implement such investigations the adhesion properties of PEG-PDMS homo- and random copolymer brushes were performed by means of probe tack apparatus [Lak99]. This method facilitates studying of the adhesion forces on the whole samples surfaces comprising 1 cm in diameter. Analysis of debonding process in tack test provides detailed information about the properties of the investigated samples rather than simply the maximum in tensile force [Zos89], [Cre02]. Afterwards, as it was described in Chapter II, among the factors influencing adhesion behaviour of materials, mechanical properties of surfaces play an important role. This factor that hasn’t been regarded up to now could be taken into account in tack test experiments. Whereas for the AFM force measurements always hard colloidal probes have been applied, in the tack test the soft (elastic) and compliance adhesives were used.

3.3 Sample preparation

Random comb-like PEG-PDMS brushes were synthesized on flat (silica wafer) and rough (made of 1 µm particles) substrates. All details on preparation of substrates for flat and rough samples as well as the polymerization procedure are given in Chapter III.2.
II. Results and Discussions. AFM vs. Tack Test

Two types of pressure-sensitive adhesives were used for the tack test experiments. The first one, hydrophobic adhesive, consists of a blend of a styrene-isoprene-styrene (SIS) block copolymer (Vector 4111 from ExxonMobil Chemical), a hydrogenated tackifier (Escorez 5380 from ExxonMobil Chemical) and paraffinic oil (Flexon 876) in the proportion 0.4 : 0.3 : 0.3, respectively. The second one, the more polar adhesive, contains a random copolymer of n-butyl acrylate (nBA, 98 wt %) and acrylic acid (AA, 2 wt %). In this way, the hydrophobic SIS and more hydrophilic PnBA-PAA (PAA) adhesives can be considered as macroscopic analogues of modified hydrophobic and unmodified hydrophilic (PAA adhesive contains 98% of hydrophobic polymer) AFM tip.

Since a fully hydrophilic soft adhesive is a hydrogel swollen with water, a hydrophobic polymer have been used which contains hydrophilic comonomer to maintain a low elastic modulus and maintain bulk properties insensitive to the environment. Nevertheless, the more polar nature of the PnBA and the hydrophilic character of the PAA comonomer should result in a different interaction with the random brushes than the SIS based adhesive. Both adhesive have shear moduli in the 30-80 kPa range at 1 Hz.

The model adhesives had a tunable elastic modulus and viscoelastic character for probe tack investigations. PSA films were prepared by water evaporation for the waterborne emulsion and by solvent evaporation (toluene) for the SIS based polymer on a clean glass slide. Their thickness was in the range 100-120 μm.

3.4 Tack test with elastic probe

A silicon wafer of 1cm in diameter functionalised with a polymer brush was glued to a cylindrical flat ended stainless steel probe. During the test, the probe comes in contact with a soft adhesive layer previously deposited on a glass slide. After a set contact time during which the desired compression force is kept constant, the probe is withdrawn at a constant velocity. Standard parameters were used for approach velocity ($V_{app} = 10$ μm/s), contact time ($t_c = 1$ s), and contact force ($F_c = 70$ N). The experiments were done at room temperature. The force was measured by a load cell (250 N, resolution 0.2 N).

The displacement of the probe was measured with an LVDT extensometer (range 5 mm, resolution 0.5 μm).

A mirror is installed behind the glass slide and allows the visualization of the debonding mechanism and the measurement of the real contact area for each test. Events occurring at the adhesive / brush interface are recorded with a CCD camera and synchronized with the stress-strain curve. Values of the maximum area of contact were determined by inspection of the images obtained during the compression stage.

The force and displacement for each curve were normalized by the contact area of the probe (as visualized with the camera) and by the initial thickness of the film to obtain a nominal stress vs. Nominal strain curve, which will be used to compare adhesive films. The adhesion energy $W_{adh}$ was defined as the integral under the stress vs. Strain curve.
multiplied by the initial thickness of the film. Below in the Fig. 73 the typical stress-strain curves obtained via tack test experiments with the PAA adhesive are shown.

\[\text{Stress, MPa} \times \text{Strain, } \mu\text{m} \]

\[\text{Stress, MPa} \times \text{Strain, } \mu\text{m} \]

Fig. 73. Typical stress vs. strain curves, representing A: homopolymer PDMS on flat surface, B: random PEG/PDMS with 20% PEG on rough surface; both measured with PAA adhesive. 1-4: images and corresponding areas on the stress-strain curve.

In general, three types of stress-strain curves are distinguished. The mechanisms of the debonding were discussed in details in several publications like [Zos89], [Josse], [Cre01], [Lin04], [Ret05]. Apart from the cohesive fracture happen within the polymer films and typical for the low-viscosity polymers, two other mechanisms are also possible. An example of the “brittle” separation is presented in Fig. 73 curve A. It was obtained on flat substrate modified with the homopolymer PDMS measured with the PAA adhesive. The “brittle” separation is characterised by a sharp maximum at rather low strains. The separation occurs quickly by prompt propagation of cracks from the border by purely adhesive debonding. According to the small area under the stress-strain curve the energy of separation is low [Zos89].

For the most interesting type of the tack test stress-strain curves (like is presented in Fig. 73 B) is typical fibrillar formation during the separation process. The orange curve B was measured on rough surface with grafted copolymer PEG-PDMS_{random} with 20vol% of PEG. The strain vs. stress plot has a pronounced “shoulder” which leads to a high strain. This
shoulder gives rise to a large area under the curve and thus a high energy of separation [Zos89]. The processes occur during the deformation of the polymer film are made visible by taking video during the separation (Fig. 73 images 1-4). The point and image number 1 of the orange curve (Fig. 73 B) corresponds to homogeneous deformation of the film in tension, the rapid increase of the force with displacement is observed, no macroscopic voids are visible. Then, the curve reaches a maximum (point 2) which corresponds to the set $F_c$. Next, the orange curve demonstrates first gentle decrease of stress which gradually passes into almost undistinguishable plateau (point 3) and then, there is a dip in stress at some value of the extension. After that a second plateau is present at lower values of stress (point 4) until a final fracture occurs. The form of the curve tells about the nucleation of macroscopic voids at the probe-film interface during the debonding process (corresponds to the photo and point number 2 in Fig. 73) [Josse]. They grow gradually until most of the initial contact area is occupied by the voids (numbers 2 and 3). After that the elongation of the void’s walls occurs (number 4) till the final debonding takes place. The maximum extension is typically very large in this case but the plateau stress is low. In terms of adhesion, the long fibrillation plateau of the adhesive when it is debonded is a signature of the good adhesion [Ret05].

![Stress-strain curves](image)

*Fig. 74. (Top) Stress-strain curves from probe tack tests between a more polar PAA (dark grey curve) and hydrophobic SIS (orange curve) elastomeric layers and flat (top arrow) and rough (below arrow) random copolymer PEG-PDMS brushes with different PEG content.*
III. Results and Discussions. AFM vs. Tack Test

To analyze tack test experiments it is possible to compare values of the maximum debonding stress (tack), but for the samples that intensive form voids during debonding, the calculation of adhesion energy (integral below the curve) is a more correct method. Several important parameters of tack test have been examined: the normal compression force (10-70 N), probe debonding velocity (1, 10, 100 µm/s) and contact time (1, 10, 100 sec). In Fig. 74 stress-strain curves obtained at 70 N preload, 10 µm/s debonding velocity and 1 sec contact time with PAA and SIS adhesives are presented. The value of the maximum tack and obviously the adhesion area under the curves is growing with the PEG volume content independently on the roughness of the samples and chemistry of adhesives.

The summary on adhesion energy, $W_{adh}$ for the PEG-PDMS$_{random}$ copolymer brushes with different PEG content and at different debonding velocity is presented in Fig. 75. The results show an increase of adhesion energy with growing debonding rate. This behaviour can be attributed to the viscoelastic losses occurring in the adhesive layer which increases with increasing of deformation rate of the adhesive layer [Lak99].

Unlike the results of adhesion force measurements performed using hydrophilic and hydrophobic AFM tips, the PDMS surface in tack test is almost non-adhesive as expected from its low $T_g$ and strong immiscibility with both adhesives. On the other hand, PEG is strongly adhesive and adhesion increases with PEG fraction in the brush when probed by both PAA and SIS adhesives. Most probably, strong adhesion between PEG and SIS as well as PAA adhesives are due to small molecular weight of side PEG groups ($M_w = 475$ g/mol), which are able to penetrate in the adhesive and act as plasticizer. Though the adhesion properties of PEG-PDMS$_{random}$ copolymer brushes probed by both kinds of adhesives are very close, there is a small difference in adhesion properties: an increase in PEG fraction results in a linear change of adhesion as probed by SIS and there is plateau behaviour when probed by PAA adhesives indicating some onset of interactions with the PnBA-PAA adhesive, for instance hydrogen bonds.
III. Results and Discussions. AFM vs. Tack Test

Fig. 75. Summary of tack experiments on random copolymer flat & rough PEG-PDMS brushes with hydrophilic PnBA-PAA and hydrophobic SIS adhesives.

3.5 Comparison of adhesion behaviour measured using hard and soft probes

It should be noted, that adhesion strongly depends not only on thermodynamic factors such as chemical functionality or surface roughness, but also on the mechanical properties or elastic modulus of the applied adhesives [Gor03]. If two rigid materials are placed in contact with each other, the effective contact area is actually much lower than the macroscopic geometrical one. This difference is due to the asperities, which increase the interplanar distance between the contacting surfaces over part of the nominal surface of contact. Surface energy and contact area considerations suggest that a non-adhesive surface should possess low-surface energy (hydrophobicity), a multiscale surface roughness, and a high elastic modulus [Rus99]. For soft materials, large contact areas result in strong adhesive forces, even though interfacial forces may be weak.
III. Results and Discussions. AFM vs. Tack Test

[Gay02]. PDMS networks are a good example of low-surface-energy materials that may be adhesive due to the low-elastic modulus.

As already mentioned, the colloidal probe in AFM and the adhesives used in tack tests have principally different elastic properties. Whereas the CP is hard, adhesive layer is elastic. During the AFM force measurements and the tack test experiments the probing object is pressed onto the sample surface to achieve the desired normal compressive force. Then the soft adhesive becomes deformed and assumes more or less the shape of the probing surface increasing the real contact area especially on rough surfaces (Fig. 76 D). On contrary, the pressing of a hard colloidal probe won’t be resulted in deformation of the particle and its contact area with a rough sample surface is significantly reduced (Fig. 76 C).

![Image](image)

Fig. 76. A sketch of contact areas (marked with red) between a flat sample surface and a hard colloidal probe (A) and soft adhesive layer (B); a rough surface with a hard colloidal probe (C) and an soft adhesive layer (D).

In the Fig. 77 the results of AFM force measurements and tack test experiments on PEG-PDMS homo- and random copolymer brushes attached to flat substrates are summarized. The measurements performed with hydrophilic CP and PAA adhesive (A, C) and with hydrophobic CP and SIS adhesive (B, D) are shown. It was found that with growing volume fraction of PEG, the adhesion increases when measured with hydrophilic CP and with both types of the tack test adhesives. The hydrophobic CP shows however an opposite tendency: the adhesion becomes smaller with growing PEG volume content (Fig. 77).
The interfacial adhesion between the hydrophilic PAA adhesive and brush showed a plateau in adhesion energy for the samples with 50, 80 and 100vol% of PEG (Fig. 77 C). In this case, the PEG chains cover the whole top surface and contribute to the overall adhesion performance. Note, similar behaviour in adhesion performance for PEG-PDMS \textit{random} brushes was observed in air during force measurements with native hydrophilic CP (Fig. 77 A).

![Figure 77](http://example.com/image)

\textbf{Fig. 77. Comparison of adhesion behaviour of PEG, PDMS brushes observed by AFM force experiments (the row on the top) and tack test (the row below), measured by hydrophilic colloidal probe and hydrophilic PAA adhesive (the left column) and hydrophilic colloidal probe and hydrophobic SIS adhesive layer (the right column).}

Roughness has a considerable effect on adhesion when surface probed by soft adhesives as well. To remind, the values of adhesion forces on rough surfaces measured on AFM decrease significantly as compared with the flat surfaces. On contrary, the adhesion of rough surfaces measured with PAA or SIS using tack testing is higher than that on the
corresponding flat one (Fig. 78). Note, the adhesion performance in air environment in both cases is discussed here.

This discrepancy can be qualitatively explained by considering the mechanical properties of the adhesive probes. An AFM CP is hard and cannot be deformed, as a result the contact area between particles and the AFM tip is very small (see Fig. 76). On the other hand, polymer adhesives are soft, able to deform and adjust their shape thus increasing the contact area between the rough surface and the adhesive. Moreover, roughness amplifies dependence of retraction speed (Fig. 75) that is due to increase of the dissipation and has no effect (at that size scale) on elasticity. Therefore at low speed where viscoelastic dissipation is low, smooth and rough become more similar. At high debonding rate, the viscoelastic dissipation becomes much more important and therefore the difference is pronounced. This is an interesting result since the roughness created by core-shell particles is very well characterized and regular.

3.6 Summary

In this Chapter investigation of adhesion properties of biocompatible PEG-PDMS homo- and random copolymer brushes grown from flat and rough (micrometer-sized particles) substrates has been performed in ambient conditions using elastic tack tester. The results were subsequently compared with the corresponding measurements using hard AFM-CPs. All details about the tack test measurement, parameters of the procedure and debonding mechanisms in particular were discussed. During the debonding on non- or low-adhesive surfaces large interfacial cracks which propagate quickly from the border were observed, whereas on more adherent surfaces multiple voids in the bulk of the
adhesive layer which grow slowly and lead to a fibrillar structure (Fig. 73) were detected [Josse].

It was shown, that the elasticity of a probing surface influences strongly the adhesion properties of investigated systems. Soft and compliant PAA and SIS adhesive layers used for tack tests facilitate larger contact area and thus tackiness on hard rough surfaces than that on the flat ones. The measurements on rough surfaces with a hard colloidal probe on AFM resulted in dramatically reduced contact area and thus much lower values of adhesion forces than it was measured on flat surfaces.

The increase of adhesion forces in air with growing PEG fraction in PEG-PDMS copolymer brushes measured with hydrophilic CP was confirmed also with the tack test. This tendency remains the same on flat and on rough surface if measured with both hydrophobic SIS and hydrophilic PAA adhesives. However the evolution of adhesion forces with growing PEG content measured with a hydrophobic CP had an opposite character.
IV. Summary

The aim of the thesis was preparation of smart functional materials with switchable and adaptive adhesion properties. The polymer brushes were successfully synthesised using ATRP procedure on flat and rough (made of 1 µm large spherical particles) substrates. Important parameters were varied and controlled to prepare desired samples of different chemical and architectural structure.

For control of quality and characterisation of the fabricated samples several advanced analytical tools were used. Ellipsometric measurements provided information about the thickness in dry state and degree of swelling of polymer layers in water. Investigation of wetting properties was done using ADSA on thermoresponsive polymer brushes and contact angle measurements on PEG-PDMS solvent responsive copolymers. Surface charges were studied using Zeta-potential measurements. Surface morphology and its rearrangements upon external stimuli were registered on topography images using AFM.

All-embracing investigation of switchable adhesion properties under the influence of external stimuli (temperature, dry/wet state) was performed by means of AFM force measurements. Theory about adhesion phenomenon points out three main factors that influence the strength of adhesion between any two surfaces: molecular interactions at interface, mechanical properties of adhesives, and contact area. Numerous parameters that influence these three factors were thoroughly investigated in this work.

1) Molecular interactions at interface of two objects are determined by their chemical functionality. The investigated polymers are stimuli-responsive wherefore the influence of surrounding media on these interactions has to be taken into account as well. Diversity of chemical functionality at interface was achieved through numerous ways:

- Three types of thermoresponsive polymer brushes have been investigated that differ in their chemical composition and structure of polymer chains (density of side chains);
- Chemical variety of the solvent-responsive systems was provided with different ratio of PEG and PDMS components comprising the copolymer brushes and through different architecture of polymer chains: random or block copolymers;
- Different thickness of polymer layers;
- Adhesion properties were influenced by temperature of the surrounding aqueous media (thermoresponsive polymer brushes), and by dry/wet conditions (solvent-responsive polymer brushes);
- Adhesion force measurements of thermoresponsive brushes were performed using colloidal probes of different surface functionality: native or brush-modified colloidal probes;
- Surface functionality of colloidal probes and adhesive layers used for AFM and tack test measurements, respectively, was varied between hydrophilic and hydrophobic ones.

2) Surface topography. The strength of adhesion is proportional to contact area between interacting surfaces. Contact area was altered using two approaches:
- The geometry of the AFM probing tip used for adhesion force measurements of thermoresponsive polymer brushes was changed between a sharp tip with 10 nm in diameter, molten tip of 40 nm, and, at least, spherical colloidal probe of 4.84 µm in diameter.
- The area of contact is strong dependent on roughness of the surfaces. The polymer brushes were synthesised on flat and rough made of 1 µm spherical particles surfaces.

3) Mechanical properties of interacting surfaces. It was shown, that the adhesion forces measured on flat and rough surfaces are quite different. However, it is remarkable that the interaction forces decrease strongly on rough surfaces if measured with AFM colloidal probe, but significantly increase if measured with adhesive in the tack test experiments. This fact is a consequence of the elasticity of the probing surfaces. The hard colloidal probe doesn't deform, whereas the soft adhesive layers are able to adopt the form of the probing rough surface such increasing contact area in between and adhesion forces as a result.

The schematic representation of factors influencing switchable adhesion of fabricated stimuli-responsive polymer brushes and investigated in thesis is presented below.

Control of switchable adhesion by:

- Chemical functionality at interface
  - Chemical composition of polymer brushes
  - Architecture of polymer chains
  - Thickness of polymer layers
  - External stimuli (t°C, solvent)
  - Surface functionality of colloidal probe / adhesive
- Surface topography
  - Flat / Rough surfaces
  - Geometry of AFM tips
- Mechanical properties
  - Hard colloidal probe
  - Soft adhesive
V. Outlook

The interest for “smart” stimuli-responsive materials has been growing during the last decades because of increasing demand for materials able to respond to external stimuli with dramatic and predictable structural changes. Such materials are broadening the horizons of applications in numerous areas from medicine and sportswear to food packaging and the aerospace and automotive sectors. Prepared from thermo-, light-, pH- and other responsive polymer systems, the commercial possibilities of these smart materials are literally endless.

The results achieved in this work show new possibilities for expanding field of stimuli-responsive materials. Since the investigated polymeric systems are biocompatible and biodegradable they are of a great interest for biomedical applications. Moreover, the temperature-responsive polymers presented in the work undergo their switching of adhesion in the body-temperature region. They could be used, for example, for biosensors, adhesion of proteins or tissue engineering. The solvent-responsive systems with low adhesion forces shown here could be promising as wound dressing materials to prevent the tissue from damages caused while detaching of a strong-adherent material.

On the other hand, the PEG-PDMS systems with high adhesion could be useful for surgery where highly biocompatible, strong and flexible surgical glue is of great need. Current surgical glues and sealants are either protein-based, in which case they exhibit low bond strength, and are in some cases derived from blood products, with associated risk of viral or prion contamination. Very strong synthetic glues are toxic to living tissues and form rigid, nonporous films that can hinder wound healing [Gra05].

There are several ideas concerning the next steps in continuation of the subject of this work. Firstly, it could be interesting to manufacture systems comprised of polymers responsive to another than temperature or solvent stimuli or even responsive to several stimuli. This could lead to smart systems where the responsiveness to a combination of stimuli allows for fine-tuning adhesion strengths.

Secondly, as it was shown in this work, the architecture of polymer chains play often crucial role in adhesion performance. That is why the synthesis of copolymers with varying chain architecture could yield materials with desired properties.

Moreover, the combination of stimuli-responsive surface coating with a patterned surface responsive as well to external stimuli would possibly lead to very interesting materials with fascinating switchable properties. Often used principal of maximization
V. Outlook

and minimization of the contact area would be combined with adhesion and non-adhesion properties of the polymer coating [Syn12].

Since the thin polymer brushes are quite vulnerable to scratches and other damages their switching behaviour undergoes gradual degradation with time and switching cycles. Therefore a promising idea was suggested to manufacture mechanically stable stimuli-responsive coatings made of thick (hundred nanometres to microns) block copolymer brushes [SY125]. The particular interest to the block copolymer brushes known from literature [Elb99], [Zha00a], [Goh01], [Boy02], [Lud03], [Boy04], [Lei04], [Fus05], [Tok05], [Nak06], [Sai08], is explained by their ability to reversibly change the surface properties via mobility of the block segments on the topmost polymer layer upon treatment with selective solvents. Utilization of such thick “nanostructured mixed polymer networks” as “smart” adhesives will significantly improve their lifetime because of a “self-repairing” effect. In general, in such multicomponent systems composed of heterogeneous polymers, the lower-surface-energy component is located on the surface. Being scratched the high-surface-energy component becomes bare that is energetically unfavourable. Therefore, the low-surface-energy component will remove to fill this scratch and recover the integrity of the low-energy surface layer [Rus02].

Besides the scratch-resistant surfaces, another possible fields of application of the multicomponent block copolymers include nanotechnology, in biomedicine for controlled release of bioactive molecules, for development of dispersants and stabilizers for pigments in aqueous and organic medium and many others [Rie03], [Sai08], [Lud03].

For the most part in this work the investigations of adhesion behaviour were performed via AFM in order to learn about fundamental processes occurring on nano- and micrometer scales. It would however make sense to carry out the tack test experiments to study also the processes on macrometer scale. It was shown here by way of example on PEG-PDMS random copolymer brushes and is believed to be useful to apply regularly on the systems developing for marketable products.

Biological solutions developed by nature over millions of years continue to inspire and give ideas for rational design and construction of multifunctional manmade “smart” materials. However there is still a long way before synthetic materials of comparable with natural complexity would be achieved. Therefore, further interdisciplinary cooperation of scientists and engineers is inevitably to reach the aim of such smart materials.
VI. References


[AFM05] “A practical guide to SPM Scanning Probe Microscopy”, Veeco, 2005


VI. References


VI. References


VI. References


[Der34] B. V. Derjaguin, “Theory of the adhesion of small particles”, Kolloid-Z., 1934, 69, 155


[Dut00] V. Dutschk „Oberflächenkräfte und ihr Beitrag zu Adhäsion und Haftung in glasfaserverstärkten Thermoplasten“, dissertation 2000


VI. References


VI. References


VI. References


VI. References


VI. References


VI. References


[Que03] D. Quere, A. Lafuma, J. Bico, J. “Slippy and sticky microtextured solids”, Nanotechnology 2003, 14, 1109-1112


VI. References


VI. References


[SY125] A. Synytska, DFG project

[Syn05] A. Synytska, "Einfluss chemischer und topographischer Inhomogenitäten auf die Eigenschaften von Polymeroberflächen", 2005


VI. References


VI. References


[Zha03] M. Zhang, A. Müller, „Amphiphilic cylindrical brushes with poly(acrylic acid) core and poly(n-butyl acrylate) shell and narrow length distribution“, Polymer 44 2003, 1449–1458


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09.1991-06.1997 Primary and Secondary school 947 in Moscow

PROFESSIONAL EXPERIENCE AND RESEARCH VISITS

2008-2012 Introduction into Atomic Force Microscope for master students in the course of lectures “Physical Chemistry of Surfaces” of Dresden University of Technology
VII. Appendix

11.2011
Guest researcher in the group of Prof. C. Creton in École supérieure de physique et de chimie industrielles de la ville de Paris (ESPCI), France

03.2007-05.2007
Guest researcher in Leibniz Institute of Polymer Research, Dresden, supervisor: Dr. A. Leuteritz, Department Processing

METHODS AND INSTRUMENTS

- Atomic force microscope (topography and force measurements)
- Scanning electron microscope
- Surface modification (ATRP, radical polymerisation)
- Null-ellipsometry
- Contact angle measurements
- Spin-coating
- Tack-test
- Nanoindentation
- Rheology investigations (ARES Rheometer)
- Twin-screw extruder

ADDITIONAL SKILLS AND COMPETENCES

Languages
Russian native speaker
German advanced level
English advanced level
French intermediate level

Software
MS-Office Software, Origin8, Photoshop, Lightroom
LIST OF PUBLICATIONS

JOURNAL ARTICLES


CONTRIBUTION TO CONFERENCES

1) **E. Svetushkina**, L. Ionov, M. Stamm and A. Synytska, “Nanostructured Intelligent Surfaces with Responsive Adhesion Properties” (Poster), European Polymer Congress (Graz, Austria), 12-17 July **2009**.

2) **E. Svetushkina**, C. Bellmann, L. Ionov, M. Stamm, A. Synytska, “Surfaces with Switchable Adhesion Response Based on Biocompatible Thermoresponsive Brushes” (Poster), 12th Dresden Polymer Discussions (Meissen, Germany), 18-21 April **2010**.

3) **E. Svetushkina**, C. Bellmann, L. Ionov, M. Stamm, A. Synytska, “Surfaces with Switchable Adhesion Response Based on Biocompatible Thermoresponsive Brushes” (Poster), Gecko-workshop (Saarbrücken, Germany), 06-10 July **2010**.

4) **E. Svetushkina**, C. Bellmann, L. Ionov, M. Stamm, A. Synytska, “Surfaces with Switchable Adhesion Response Based on Biocompatible Thermoresponsive Brushes” (Poster), 4th World Congress on Adhesion and Related Phenomena (Arcachon, France), 26-30 September **2010**.


6) **E. Svetushkina**, C. Hase, F. Simon, M. Stamm, C. Creton, A. Synytska, “Intelligent materials with adaptive adhesion properties from biocompatible comb-like polymer brushes” (Poster), 7th International Conference on Nanostructured Polymers and Nanocomposites (Prague, Czech Republic), 24-27 April **2012**.
ACKNOWLEDGEMENTS

I want to express my thanks to all the people who were with me during the last years helping and contributing to my work scientifically and spiritually.  
First of all, I would like to thank Professor Manfred Stamm for the opportunity to carry out my research in his group, for guidance, financial support and for nice and cheerful PhD workshops.  
My particular gratitude is addressed to Doctor Alla Synytska for her exacting and excellent scientific guidance and her steady and sincere willingness to help and support.  
I am truly indebted and thankful to Dr. Astrid Drechsler and Mr. Andreas Janke for opening me the world of the most exciting device – AFM. The AFM laboratory was my second home during the long time.  
I would like to express my deep thanks to Professor Costantino Creton for two excellent weeks in Paris which resulted in one chapter of my thesis. Especially I thank Doctor David Martina for his great help with my experiments on tack tester.  
Moreover, I am obliged to several people who facilitated my work: Dr. Bellmann and Mrs. Caspari I thank for Zeta potential and DLS measurements, Mrs. Hase for swelling and wetting experiments, Mr. Stoychev for cryo-TEM, Mr. Puretskiy for providing silica particles, and Dr. Simon for XPS investigations.  

I want to thank my dear colleagues Dr. Marta Horecha, Dr. Andriy Horechyy, Dr. Leonid Ionov, Nikolai Puretskiy, Dr. Ksenia Boyko and my best office mates Svetlana Zakharchenko, Ivan Raguzin and Georgi Stoychev for the great time together!  

Finally, I would like to deeply thank my parents, Violettta and Valeriy, and my sister Tatiana who always believed in me and stood by me through the good times and bad times. My darling husband Richard I thank for his continuous support, patience and for cheering me up. I could stand the most difficult moments and didn’t give up just due to my family.
VERSICHERUNG

Hiermit versichere ich, dass ich die vorliegende Arbeit ohne unzulässige Hilfe Dritter und ohne Benutzung anderer als der angegebenen Hilfsmittel angefertigt habe; die aus fremden Quellen direkt oder indirekt übernommenen Gedanken sind als solche kenntlich gemacht. Die Arbeit wurde bisher weder im Inland noch im Ausland in gleicher oder ähnlicher Form einer anderen Prüfungsbehörde vorgelegt.

Die vorliegende Arbeit wurde unter der wissenschaftlichen Betreuung von Prof. Dr. Manfred Stamm und Dr. Alla Synytska am Leibniz-Institut für Polymerforschung Dresden e.V. angefertigt.

Ich erkenne die Promotionsordnung der Fakultät Mathematik und Naturwissenschaften an der Technischen Universität Dresden an.

Dresden, 28.11.2012

Ekaterina Biehlig