Switching of Surface Composition and Morphology of Binary Polymer Brushes

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1. Introduction.

Materials with smart response of their surface properties to external stimuli are demanded by nanotechnology and medicine for manufacturing devices like sensors, switches, and microactuators [Kin02, Lah03, Ros02, Rus02, Yos91]. Biocompatible surfaces for controlled cell and protein adsorption/release, cell growth [Rüh99] are often required to adopt a hydrophilic-hydrophobic pattern [Dep98, Rot98] and switch the surface chemistry and morphology [Den02, Hay01] in response to temperature [Cun02, Jon02], pH [Pin03], ionic strength [Par93], or other external influences. Polymeric materials are perfect candidates for such applications because their chemical structure, which determines their properties, can be tailored in a desired way.

In the last decade, mixed polymer brushes have become a subject of theoretical and experimental research because of their remarkable responsive properties [Mar91, Bro94, Lai94, Sog96, Sid99, Mühl02, Min02, Min02a, Min03, Ion03, Lem03a, Zhao03]. The term “brush” means in this context a layer of chain-like polymers with one end immobilized on a substrate and the grafting density high enough so, that the polymers are obliged to stretch away from the grafting surface [Mil91]. In contrast to brushes, which consist of one type of homopolymers, the mixed polymer brushes can amplify the response due to combination of conformational changes and microphase separation [Sid99, Sog96, Lai94]. Anchoring of the polymer chains to a substrate prevents macroscopic segregation of the incompatible species. The phase behavior of mixed polymer brushes is determined by a competition of the mixing entropy, which favors homogeneously mixed state, and the interaction energy, which is reduced by spatial separation of the incompatible polymers [Mar91].

At the beginning of our research, few theoretical studies [Mar91, Bro94, Lai94, Sog96] and synthesis via surface-initiated radical polymerization [Sid99] of mixed polymer brushes were published. Marco and Witten [Mar91] studied phase segregation in mixed polymer brushes at melt conditions within the strong stretching theory (SST, Section 2.2). They found for a sufficiently high incompatibility ($\chi$) a second order phase transition from a disordered state to a laterally segregated morphology composed of oriented parallel to a substrate alternating cylindrical domains of the two polymeric species (the “ripple” morphology). Various simulations demonstrated formation of a laterally segregated morphology in melt state [Bro94] and in good solvent [Lai94, Sog96]. Effects of varying the brush composition under good solvent conditions were explored in Monte Carlo simulations of the bond fluctuation model by Lai [Lai94]. He observed that in a symmetric brush the grafted chains of the same type segregated laterally together while the layered state was not
observed. Layered structure was observed for asymmetric mixed brushes with the minority chains staying further away from the grafting plane. Soga et al. [Sog96] found with the coarse-grained simulation method that competition of phase separation of the two polymer species from one another and from solvent in binary mixed polymer brushes under poor solvent conditions causes additional variations in the morphology. When our research was in progress, Marcus Müller calculated a diagram of phase segregation in mixed polymer brushes via self-consistent field (SCF) approach [Mül02]. Details of the theoretical studies of mixed polymer brushes are given in Section 2.2.

The synthetic two-step “grafting from” procedure was developed by Sidorenko et al. [Sid99]. They showed ability of binary mixed polymer brushes to reversibly switch the surface composition in response to changes of solvent selectivity, i.e. better thermodynamic quality for one of the two polymer species. If a mixed brush of hydrophilic A and hydrophobic B homopolymers is exposed to good non-selective solvent, both polymers swell in equal extent and occupy the top layer of the film [Sid99]. The polymers A and B are incompatible and therefore they segregate from one another in lateral directions [Sog96, Lai94] (Figure 1.1 a). If the mixed brush is exposed to a hydrophilic solvent, the hydrophilic component A preferentially segregates to the top of the brush, while the hydrophobic polymer collapses and occupies the bottom layer [Sid99] (Figure 1.1 b). Exposure of the brush to a hydrophobic solvent switches reversibly the surface from the hydrophilic to the hydrophobic state [Sid99] (Figure 1.1 c).

Figure 1.1. Switchable mixed A/B polymer brush in (a) non-selective solvent; (b-c) solvents selective for the A and B polymers, respectively.

The remarkable responsive ability of mixed polymer brushes and lack of experimental studies in this field inspired us for their extensive experimental research. Many fundamental aspects of behavior of mixed polymer brushes were remaining unclear. In this work we found answers for the following questions: (1) how fast is the switching of the top layer composition in selective solvents? (2) Is it a gradual change or a sharp transition? (3) How does morphology of a mixed brush depend on solvent quality and chemical nature of the brush
polymers? (4) How does a real mixed brush behave in melt conditions? (5) Can mixed polymer brushes adopt a desired chemical pattern?

We synthesized mixed hydrophilic/hydrophobic brushes via two step surface-initiated radical polymerization according to [Sid99]. Details of the synthetic procedure and characterization of the samples are provided in Sections 4 and 5, respectively. The external stimuli used for switching of the mixed brushes were solvent selectivity (Section 7-8), heating to melt state (Section 9), and contact with a confining surface (Section 10). We studied switching of the top layer composition of mixed polymer brushes with water contact angle measurements (Section 7.1-3, 5), X-ray Photoemission Spectroscopy (XPS, Section 7.4), and Near Edge X-ray Absorption Fine Structure (NEXAFS) spectroscopy [Mor01, Stöhr92] (Section 8.2.3, 10). Kinetics of switching of the top brush layer upon exposure to selective solvents was measured with water contact angle measurements (Section 7.1). Morphology of the mixed polymer brushes was studied with Atomic Force Microscopy (AFM), X-ray Photoemission Electron Microscopy (XPEEM) [Mor01], and selective etching with oxygen plasma (Sections 8.1-3). Theoretical background of the physical techniques is provided in Section 3. Discussion of the experimental results and their comparison with the theoretical predictions (Section 2) are given in Sections 8.4 and 11.

Mixed polymer brushes are a broad field for research, therefore we were unable to explore everything ourselves. When our work was in progress, other experimentalists developed synthesis of di- [Sed00, Zhao00] and triblock [Boy02] copolymer brushes, synthesis of mixed homopolymer brushes via a controlled “grafting from” approach [Zhao03] and “grafting to” of end-functional homopolymers [Min02] and triblock copolymers with a short functional middle block [Wang00]. Schemes of synthesis of mixed polymer brushes are reviewed in Section 2.3. Some excellent results of other scientists on mixed polymer brushes are not discussed in this thesis because of their specific scopes and lack of space. In particular, those, whom it may concern, can read original publications about: AFM investigation of morphologies of diblock copolymer brushes by Zhao et al. [Zhao00a]; amplification of switching range of wettability of mixed polymer brushes grafted to rough substrates by Minko et al. [Min03]; fabrication of switchable chemical nano-pattern on surface of photocrosslinkable mixed polymer brushes by Ionov et al. [Ion03].
2. Theory of polymer brushes.

2.1. Theory of monocomponent brushes.

The mean field approximation is valid if [Mil88]: (1) a single chain in a brush emerging from the grafting surface encounters many other chains before it noticeably avoids itself and (2) each chain interacts with itself and the other chains only through the average concentration of the polymer segments.

State of a polymer brush is determined by a minimum of the free energy of a polymer chain [A1.16]. The minimization is done with respect to the brush height L and the concentration profile $\varphi^*(z)$. However, the representations of the two terms from the latter equation are different in various theories [Mil88, Zhu91]. Therefore, we skip the details and come directly to the conclusions derived from these theories.

The concentration profile of a polymer brush has a parabolic shape which can be described as:

$$
\begin{align*}
\varphi^*(z) &= \varphi_s^* \left(1 - \left(z/L\right)^2\right)^\alpha, \quad z \leq L, \\
\varphi^*(z) &= 0, \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad z > L.
\end{align*}
$$

[2.1.1]

where $\alpha = 1$ for good solvent, $\alpha = \frac{1}{2}$ for theta-solvent, and $\alpha = 0$ for poor solvent, $\varphi_s^*$ is the polymer volume fraction near the grafting surface [Zhu91, Kar94]. The theories predict a step-like concentration profile for a polymer brush in poor solvent. The height of the brush layer is proportional to the polymerization degree regardless on conditions: $L \sim N$ [2.1.2], where the coefficient of proportionality is different depending on the theory.

The mean field theory by Zhulina et al. [Zhu91] provides the equations for $L$ and $\varphi_s^*$:

$$
L_\theta \approx \frac{4}{\pi} \left(\frac{wp^*/2}{\sigma}\right)^{1/4} \frac{1}{\sqrt{\pi}} N_a \quad [2.1.3] \quad \text{and} \quad \varphi_s^* \approx \frac{4}{\pi} \left(\frac{2}{wp^*}\right)^{1/4} \sigma^{1/2} \quad [2.1.4]
$$

for theta-conditions;

$$
L_F \approx \left(\frac{8}{\pi^2}\right)^{1/3} \left(\frac{wp^*}{\sigma}\right)^{1/3} \frac{1}{\sqrt{\pi}} N_a \quad [2.1.5] \quad \text{and} \quad \varphi_s^* \approx \frac{3}{4} \left(\frac{\pi^{2/3}}{(wp^*)^{1/3}}\right)^{2/3} \quad [2.1.6]
$$

for good solvent conditions,

$$
L_{p.s.} \approx \frac{2w_1}{|v|} N_a \quad [2.1.7] \quad \text{and} \quad \varphi_{p.s.}^* \approx \frac{|v|}{2w} \quad [2.1.8]
$$

for poor solvent conditions, see [A1.4-5, 10, 14, A2.2] for explanations of the symbols. The self-consistent mean-field theory by Milner et al. [Mil88] provides equations similar to [2.1.5-6] for a brush in a solvent. The equations [2.1.3-8] differ from the scaling formulas by Alexander and de Gennes just by the proportionality coefficients (see Appendix 2).
The comparison of the brush height (L) and free energy (F) for the parabolic [2.1.1] concentration profile and for the step concentration profile predicted by Alexander [Ale77] and de Gennes [Gen80] was done by Milner et al. [Mil88]. According to them:

\[
\frac{F_{\text{parabolic}}}{F_{\text{step}}} \approx 0.89 \quad \text{[2.1.9],} \quad \frac{L_{\text{parabolic}}}{L_{\text{step}}} \approx 1.3 \quad \text{[2.1.10]},
\]

The equation [2.1.9] illustrates the thermodynamic reason for the stability of the parabolic profile. Scheme of the concentration profiles predicted by the mean-field and the self-consistent mean-field theories for polymer brushes at good, theta-, and poor solvent conditions is depicted in Figure 2.1.

The parabolic profile of monomer units concentration was found experimentally with neutron reflectometry [Kar94, Mar01] for swollen polymer brushes with low polydispersity (Mw/Mn ≤ 1.1). Transformation of the profile shape was studied as a function of solvent thermodynamic quality [Hab99, Kar94]. The step-like shape was found only at non-solvent conditions [Kar94]. The concentration profiles measured with ellipsometry on polystyrene brushes with broader polydispersity (Mw/Mn 2) showed an exponential “tail” at the outer region [Hab99]. Presence of the exponential “tail” was in agreement with self-consistent field (SCF) simulations by Milner et al. [Mil89], who predicted a transformation of the profile from the parabolic to the exponential shape for brushes with broad polydispersity. The exponential profile was found with ellipsometry for poly(4-vinylpyridine) brushes with polydispersity Mw/Mn ~ 2 at good solvent conditions (ethanol) [Bie02].

The coil-globule transition of a polymer brush grafted to a flat surface was explored theoretically by Zhulina et al. [Zhu91]. They found that: (1) at sufficiently high grafting density the chains in a layer are stretched with respect to their Gaussian dimensions both above and below the theta-point. (2) The collapse of the layer always begins from the most
dilute periphery region. (3) The coil-globule transition in a brush is a monotonic decrease of the brush height which is smoother and occurs at poorer solvent quality than for a bulk polymer solution. (4) The analytical expression for the transition looks as follows:

\[
\alpha^4 - \beta \alpha - 1 = 0 \quad [2.1.11],
\]

where \( \alpha \) is the brush expansion factor \( \alpha = \frac{L(T)}{L(0)} \), \( \beta \approx \frac{r}{r^*} = (1/3)\left(p^*/2\right)^{1/4}vw^{-3/4}\left(\sigma/a^2\right)^{1/2}, \) (\( \beta \gg 1 \) for good solvent, \( \left|\beta\right| \leq 1 \) for theta-solvent, \( \beta \ll -1 \) for poor solvent), \( \frac{w^{3/4}a}{v_0\sigma^{1/2}p^{1/4}} \) corresponds to the crossover point of the theta-state and the collapsed state. The equation \([2.1.11]\) transforms into:

\[
\frac{\pi}{2\beta^2} = -\frac{\alpha}{\beta} + (1 + \frac{\alpha^2}{\beta^2})\arctg\left(\frac{\alpha}{\beta}\right) \quad \text{for} \quad \beta \geq 0 \quad [2.1.12],
\]

and

\[
\frac{\pi}{2\beta^2} = -\frac{5}{2} \frac{\alpha}{\beta} + \frac{1}{4} + \frac{\alpha^2}{\beta^2})\arctg\left(2\frac{\alpha}{\beta}\right) \quad \text{for} \quad \beta \leq 0 \quad [2.1.13].
\]

The equation \([2.1.13]\) provides a monotonic function \( \alpha(\beta) \) of a similar S-like shape as the curve I in Figure A1.1.

2.2. Theory of phase segregation in binary polymer brushes.

The phase behavior of mixed polymer brushes is determined by a competition of the mixing entropy, which favors homogeneously mixed state, and the interaction energy, which is reduced by spatial separation of the incompatible polymers [Mar91]. The first study of mixed polymer brushes by Marko and Witten [Mar91] employed the strong stretching approximation (SST). Its basic assumption is that fluctuations of the chain conformations around the conformation that minimizes the free energy can be neglected. The approximation becomes better if the chain extension perpendicular to the grafting surface (\( L \)) exceeds the unperturbed chain extension (\( h_0 \)) by far. This condition can be fulfilled at very high grafting density and/or high molecular weight. Employing the SST, Marko and Witten [Mar91] demonstrated that a binary mixed polymer brush undergoes a second order phase transition to a laterally segregated state, when incompatibility (\( \chi \)) between the different polymer species is sufficiently high. They predicted the species to segregate into cylindrical domains (“ripple” phase), which run parallel to the grafting surface, and calculated the onset of lateral ordering (spinodals) in a melt brush. Within SST, density and composition fluctuations decouple, i.e. microphase separation does not affect the parabolic (total) density profile. Microphase separation occurs due to a balance between the reduction of energetically unfavorable contacts between the unlike species and the loss of entropy of free chain ends as they are
confined into regions in which the appropriate species is enriched. The wavelength of the “ripples” is approximately twice as large as the unperturbed end-to-end distance $h_0 = aN^{1/2}$ [A1.1] and similar to the length scale observed in the morphologies of diblock copolymers. Marko and Witten denoted this morphology as “ripple” phase. Intriguingly, this laterally structured morphology is thermodynamically more stable than the “sandwich” morphology in which one species segregates to the grafting surface while the other is enriched at the top of the brush, but the system remains laterally homogeneous.

The structure of end-grafted AB diblock-copolymer brushes in solution was explored by Zhulina and co-workers [Zhu96] using scaling considerations and two-dimensional self-consistent field (SCF) calculations. The authors found that in poor solvent and for low grafting density the brush self-assembles into an ordered array of clusters, which have “onion” or “garlic-like” structures. The characteristics of the morphology can be controlled via chain length, composition and solvent selectivity.

Several numerical studies of binary brushes have been undertaken in addition to the SCF approach. Soga et al. [Sog96] used a coarse-grained simulation method involving direct calculation of Edward’s Hamiltonian to study the behavior of the brush in a wide range of solvent conditions. They presented evidence for more complex morphologies in bad solvents. Effects of varying the brush composition under good solvent conditions were explored in Monte Carlo simulations of the bond fluctuation model by Lai [Lai94]. He observed that in a symmetric brush the grafted chains of the same type segregated laterally together and formed a “ripple” state while the layered state was not observed. Layered structure was observed for asymmetric mixed brushes with the minority chains staying further away from the grafting plane.

Recently, M. Müller has calculated the phase diagram of mixed polymer brushes using three-dimensional SCF calculations [Mül02, Min02a]. The theory assumes that (1) the two polymers in the brush are monodisperse and their polymerization degree equals N; (2) there is no preferential adsorption of the polymers to the substrate; (3) the distribution of the grafting points is random. The SCF exploration by M. Müller started from a hypothetical unperturbed chain of Gaussian statistics and described energy of polymer interactions in the brush via a second order virial expansion:

$$\frac{E[\phi_A, \phi_B]}{kT} = \int \left\{ \frac{v_{AA}}{2} \phi_A^2 + \frac{v_{BB}}{2} \phi_B^2 + v_{AB} \phi_A \phi_B \right\} d\phi'$$  \[2.2.1\]

where $v_{AA}$, $v_{BB}$, $v_{AB}$ are second virial coefficients which describe binary interactions between monomer units of polymers A and B; $\phi_A$ and $\phi_B$ are the densities of the corresponding
monomer units; \( \ell' \) is a radius-vector which points out monomer units; \( k \) is the Boltzmann constant, \( T \) is thermodynamic temperature. \[ v^* = \frac{v_{AA} + v_{BB} + 2v_{AB}}{4} \] [2.2.2]

denotes the average excluded volume interaction. Repulsion of the two unlike monomers (\( \chi' \)) and the solvent selectivity (\( \xi \)) were introduced as:

\[ \chi' = \frac{(2v_{AB} - v_{AA} - v_{BB})}{2v^*} \] [2.2.3] \quad and \quad \[ \xi = \frac{(v_{AA} - v_{BB})}{(2v^*)} \] [2.2.4].

If \( \xi > 0 \), the solvent is selective for the polymer A (the A segments repel from each other stronger than the B segments), in the opposite case it is selective for the polymer B. The commonly used Flori-Huggins parameter \( \chi \) relates to \( \chi' \) via \( \chi = v^* \chi' \) [2.2.5].

The grafting density \( \sigma \), \( N \), and \( v^* \) enter the calculations only in the combination:

\[ 1/\delta^* = \frac{3}{2}(v^* N^2 / h_0^3)^{(3/2)}(\sigma h_0^3)^{\gamma} \] [2.2.6], where \( h_0 \) is the mean Gaussian chain end-to-end distance. The dimensionless parameter \( \delta^* \) is inverse stretching [Net97]. The free energy of interaction takes the form \( F = E - T(S_A + S_B) \) [2.2.6], where \( S_A \) and \( S_B \) are the conformational entropies of A polymers and B polymers, respectively.

The spatial dependence of the brush composition was expanded in a set of orthonormal functions [Mat94] with the symmetry of the periodic structures presented at Figure 2.2. The free energy of the different structures was calculated within mean field approximation (Section 2.1) and minimized (see details in [Mül02]) with respect to the length scale of the two-dimensional periodic structure. If the brush is not strongly stretched, density

**Figure 2.2.** Morphologies of a symmetric binary polymer brush: (a) symmetric lamellar (ripple) morphology and its perpendicular profile (e); symmetric checkerboard cluster (dimple-S) morphology (b) has a profile similar to (e). Hexagonal cluster morphologies dimple-A (c) and dimple-B (d) and their perpendicular profiles (g) and (h), respectively. (f) Perpendicular profile for a layered morphology. Enrichment with the A and B polymers is shown with dark and light tones, respectively. Adapted from [Mül02] and [Min02a].
and composition fluctuations are coupled, i.e. the density is higher in segregated regions and lower at the internal interfaces of the morphology.

Figure 2.2 a depicts the ripple phase, where the cylinders are enriched alternatively with A-polymers and B-polymers. The Figure 2.2 b shows the checkerboard morphology, where both components collapse into dense clusters (dimples) which arrange on a quadratic lattice. In both morphologies the symmetry between the two components A and B is retained, their perpendicular profile is depicted at the panel (e).

Although the brush is symmetric, the symmetry between the A and B components can be broken spontaneously. One possibility would be the perpendicularly segregated but laterally homogeneous sandwich (1D) morphology (Figure 2.2 f). In accord with Marko and Witten’s calculations [Mar91] it was found by M. Müller that this morphology is unstable for $\delta' > 0.25$ and is pre-empted by laterally segregated morphologies, but it may become stable at stronger stretching. A morphology, which spontaneously breaks the AB symmetry and is thermodynamically stable for certain parameters, is the hexagonal dimple morphology. One component forms clusters which arrange on a triangular lattice, while the other component fills the interstitials. In this morphology, lateral segregation goes along with laterally averaged perpendicular segregation: the cluster forming component is located closer to the grafting surface while the other component is enriched at the brush top. Two kinds of the dimple morphology: dimple-A and dimple-B, depending on the polymer forming clusters, are depicted on Figure 2.2 c-d and their perpendicular profiles on Figure 2.2 g-h, respectively. The period between the laterally repeated structures is $1.85\cdot h_0$ for the ripple and the checkerboard cluster morphologies and $2.2\cdot h_0$ for the hexagonal dimple morphologies in the investigated range of incompatibility $\chi'$ (Figure 2.3 b, inset).

The locations of phase transitions between the different morphologies are obtained as a function of incompatibility of polymers $\chi'$, inverse stretching $\delta'$ (grafting density $\sigma$), brush composition, and solvent selectivity $\xi$. At low incompatibility or small stretching (e.g. low grafting density $\sigma$ and high $\delta'$), the brush remains disordered (Figure 2.3 a-c). Upon increasing the incompatibility, a second-order transition between the disordered phase and the ripple phase is found. All other phase transitions are of the first order. For small $\delta'$ (strong stretching) and stronger incompatibility ($\chi' > 2$, poor solvent) a transition from the ripple phase to a hexagonal dimple-A or dimple-B phase (see the panels b-c in Figure 2.3) is found. For bigger $\delta'$ values (weaker stretching) a transition to the symmetrical checkerboard cluster (dimple-S) phase is first encountered (Figure 2.3 a), while for higher incompatibilities a transition to the hexagonal dimple phase is found.
The diagram at the panel (c) in Figure 2.3 which displays the phases for a symmetric binary brush as a function of incompatibility and solvent selectivity is of a special importance because its qualitative comparison with experiment is relatively easy. It shows that for brush polymers of intermediate incompatibility there is a stable ripple phase in a non-selective solvent which transits into dimple-A or dimple-B phases in the solvents of appropriate selectivity. The ripple phase is unstable for binary brushes with highly incompatible polymers, and only the two hexagonal dimple phases exist.

Figure 2.3. Phase diagrams: (a) for a symmetric binary polymer brush as function of incompatibility $\chi'$ and inverse stretching $\delta'$, the layered 1D morphology (see Figure 2.2 f) was found to be not stable at $\delta' > 0.25$ and is pre-empted by the laterally segregated morphologies, however the hypothetical transition from the disordered phase to the 1D phase is shown with the dashed line; (b) for inverse stretching $\delta' = 0.5$ as function of incompatibility $\chi'$ and the brush composition $\Phi'$, the inset displays the variation of the lateral period d for the lamellar and checkerboard clusters (solid) and the hexagonal cluster structures (dashed); (c) for a symmetric binary polymer brush as function of incompatibility $\chi'$ and solvent selectivity $\xi$, the inset presents the laterally averaged perpendicular composition profile at $\chi' = 2.4$ for various solvent selectivity. Adopted from [Mül02] and [Min02a].
2.3. Schemes of synthesis of binary mixed polymer brushes.

This work concerns only brushes covalently attached to a substrate. There are two general approaches to synthesis of chemically immobilized polymer brushes. The “grafting from” approach implies surface-initiated polymerization. It enables preparation of brushes up to 100-200 nm thick [Bie02, Hus99]. Thickness of binary polymer brushes prepared via this approach was reported within 100 nm (see the references below). A simple way to synthesize mixed homopolymer brushes, which was exclusively carried out within this work, is shown in Figure 2.4 a, in which a slow rate of decomposition of radical initiator immobilized on a substrate is used for control of the ratio between two grafted homopolymers. The residual amount of the initiator after polymerization of the first monomer is used for further polymerization of the second monomer [Sid99, Min01, Min02a]. This methods provides polydispersity of the grafted polymers Mw/Mn ~2. Synthesis of binary mixed polymer brushes via combination of Atom Transfer Radical Polymerization (ATRP) and Nitroxy-Mediated Radical Polymerization (NMRP) initiated by two surface-immobilized initiators of the respective types has been recently carried out by Bin Zhao [Zhao03] (Figure 2.4 b). This method provides narrower molecular weight distribution of the polymers in the brush (Mw/Mn 1.2-1.3). Synthesis of end-grafted di- and triblock copolymer brushes via controlled radical polymerization from subsequently added monomers also enables preparation of switchable surfaces as the previous two methods, allows good control of molecular weight of the blocks, and requires only one type of surface-immobilized initiator [Zhao00, Boy02] (Figure 2.4 c).

The “grafting to“ approach implies immobilization of pre-synthesized end-functional polymers or block-copolymers onto a solid substrate. Maximal thickness of the brushes prepared in this way is limited by ability of polymer molecules to diffuse through the already anchored polymer layer and is about 8-9 nm [Luz00a, Min02]. Mixed homopolymer brushes can be synthesized either via step-by-step binding of end-functional homopolymers to one type of surface functional groups (Figure 2.4 d) [Min02, Min03, Ion03] or they can be attached simultaneously each to its complementary surface functionality (Figure 2.4 e). The latter scheme has not been experimentally realized yet according to our best knowledge. Synthesis of ACB type triblock-copolymers for preparation of binary brushes via grafting of the short middle functional block to a substrate was reported in literature (Figure 2.4 f) [Wang00].
Figure 2.4. Schemes of synthesis of binary polymer brushes. “Grafting from”: (a) two-step polymerization with slow rate of surface-initiation, the same initiator is used for the both steps; (b) two-step polymerization with different surface-immobilized initiators used for the two grafting steps; (c) end-grafting of di- (or tri-) block-copolymer brushes via living (controlled) polymerization from one kind of surface-immobilized initiator. “Grafting to”: (d) two-step anchoring of two end-functionalized homopolymers to one kind of surface reactive groups; (e) simultaneous anchoring of two end-functional homopolymers via different mechanisms to complementary functionalities on the substrate; (f) immobilization on surface of triblock-copolymers via the middle anchoring block; (g) combination of the “grafting to” and the “grafting from” approaches. I – initiator, X and Y – functional groups, M- monomer.
A combination of the “grafting to” and the “grafting from” approaches for synthesis of mixed polymer brushes has been recently proposed by Luzinov et al. (private communication, Figure 2.4 g). He proposed partial conversion of pre-prepared surface-immobilized epoxy-groups into bromide groups via treatment of the surface with bromoacetic acid. The remnant epoxy-groups can be used for anchoring of an end-functional polymer at the first step, while the bromide groups can initiate ATRP at the second step.
3. Theoretical background of experimental techniques.

3.1. Ellipsometry.

Ellipsometry is a reflection method in which thickness of a thin film is derived from a relationship of phases and amplitudes of the reflected and the incident beams [Azz79]. The electric field vector of the variable electromagnetic field can be described as:

\[
\mathbf{E}_{el}(\ell, t) = A \cos(\omega t - k\ell + \phi)
\]

where \(A\) is the amplitude of the electric field, \(\omega = 2\pi v\) is the angular frequency, \(|k| = \frac{2\pi}{\lambda}\) is the wave-vector, \(\lambda\) is wavelength, \(\phi\) is the phase shift. Consider an electromagnetic wave incident onto an interface between two optically isotropic media (Figure 3.1.1). The incident, reflected, and refracted beams lie in the same plane which is called plane of incidence [Lek87, Azz79]. The angles of incidence and reflection are equal \(\alpha_1 = \alpha_2 = \alpha\), while the angle of refraction \(\beta\) depends on the angle of incidence and complex refractive indices of the first and the second media \(N'_1\) and \(N'_2\), respectively, according to the Snell law:

\[
N'_1 \cdot \sin \alpha = N'_2 \cdot \sin \beta
\]

Interaction of light with matter is described with complex refractive index

\[
N' = n - i \cdot B
\]

where \(n\) is a conventional refractive index which equals a ratio of the rate of light propagation in vacuum to the corresponding rate for the particular media:

\[
n = \frac{c}{c_m}
\]

\(B\) is the extinction coefficient: \(B = \frac{\lambda B'}{4\pi}\), where \(B'\) is the coefficient of light absorption by the media and \(\lambda\) is the light wavelength.
When the incident wave is linearly polarized and the electric field vector vibrates perpendicular (s) to the plane of incidence, the reflected and transmitted waves are also linearly polarized perpendicular to the same plane. When the incident wave is linearly polarized parallel (p) to the plane of incidence, the reflected and transmitted waves are also polarized parallel to the plane of incidence. Thus, the p and s polarized waves can be considered separately and their combinations can be used for description of all other possible polarization states [Azz79].

The amplitudes of reflected p and s polarized beams relate to the amplitudes of the incident beam with respective polarization according to the reflective coefficients of Fresnel [Lek87, Azz79]:

\[
R_{12}^{p} = \frac{A_{r}^{p}}{A_{i}^{p}} = \frac{N_{2}' \cdot \cos \alpha - N_{1}' \cdot \cos \beta}{N_{2}' \cdot \cos \alpha + N_{1}' \cdot \cos \beta} = |R^{p}| \cdot \exp(i \cdot (\phi_{r}^{p} - \phi_{i}^{p})) \tag{3.1.5},
\]

\[
R_{12}^{s} = \frac{A_{r}^{s}}{A_{i}^{s}} = \frac{N_{1}' \cdot \cos \alpha - N_{2}' \cdot \cos \beta}{N_{1}' \cdot \cos \alpha + N_{2}' \cdot \cos \beta} = |R^{s}| \cdot \exp(i \cdot (\phi_{r}^{s} - \phi_{i}^{s})) \tag{3.1.6}.
\]

Figure 3.1.2. (a) Reflection and transmission on multiple layers. (b) Set-up of a null-ellipsometer.

The Figure 3.1.2 a shows the reflection and transmission of an electromagnetic beam for a thin layer immobilized on a thick substrate. The reflected beam is composed of the part of the incident beam which was reflected from the top of the thin layer and from the beam which was reflected from the interface between the thin layer and the substrate. The ratio of the amplitudes of the resulting reflected and the incident waves can be expressed through the reflection coefficients for the two interfaces and the thickness of the thin layer [Azz79]:
\[ R^p = \frac{R^p_{12} + R^p_{23} \cdot \exp(-i \cdot 2d_{opt})}{1 + R^p_{12} \cdot R^p_{23} \cdot \exp(-i \cdot 2d_{opt})} = \frac{\frac{A^p_i}{A^p_r} \cdot \exp(i \cdot (\phi^p_r - \phi^p_i))}{\frac{A^r_i}{A^r_r}} \]  \hspace{1cm} [3.1.7],

\[ R^s = \frac{R^s_{12} + R^s_{23} \cdot \exp(-i \cdot 2d_{opt})}{1 + R^s_{12} \cdot R^s_{23} \cdot \exp(-i \cdot 2d_{opt})} = \frac{\frac{A^s_i}{A^s_r} \cdot \exp(i \cdot (\phi^s_r - \phi^s_i))}{\frac{A^r_i}{A^r_r}} \]  \hspace{1cm} [3.1.8],

where \( d_{opt} \) is the optical thickness of the thin layer: \( d_{opt} = 2\pi \frac{d}{\lambda} N'_2 \cos \beta_i \)  \hspace{1cm} [3.1.9].

Multilayer systems are described in a similar way utilizing matrix formalism [Azz77]. The ratio of \( R^p/R^s \) equals:

\[ \frac{R^p}{R^s} = \frac{\frac{A^p_i}{A^p_r} \cdot \exp(i((\phi^p_r - \phi^p_i) - (\phi^s_r - \phi^s_i)))}{\frac{A^s_i}{A^s_r} \cdot \exp(i(\Delta))} = \tan \Psi \cdot \exp(i\Delta) \]  \hspace{1cm} [3.1.10],

where \( \Delta = (\phi^p_r - \phi^p_i) - (\phi^s_r - \phi^s_i) \)  \hspace{1cm} [3.1.11],

\[ \tan \Psi = \frac{\frac{A^p_i}{A^p_r}}{\frac{A^s_i}{A^s_r}} = \frac{R^p}{R^s} \]  \hspace{1cm} [3.1.12].

The equation [3.1.10] is the basic equation of ellipsometry [Azz79]. The values \( \Psi \) and \( \Delta \) are the ellipsometric angles which are directly obtained from an ellipsometric experiment. The thickness and refractive index of a thin film are calculated from the \( \Psi \) and \( \Delta \) basing on a physical model of the film (Figure 3.1.2 a, eq. [3.1.7-9]).

There are different methods for determination of the \( \Psi \) and \( \Delta \) parameters [Azz79]. We used null-ellipsometry [Mots91] in this work. The principal setup is depicted on Figure 3.1.2 b. The light source was a He-Ne laser producing monochromatic red light (\( \lambda = 632.8 \) nm). The beam passing through the polarizer and the compensator adopts elliptical polarization. It was incident at 70° to the sample (optimal for Si substrates with natural SiO₂ layer). The polarization state of the incident beam is chosen so (rotating the polarizer, the compensator position is fixed) that the reflected beam is linearly polarized and can be fully cancelled by the analyzer. The intensity of the beam passed through the analyzer is measured with the 4-section photodiode. The \( \Psi \) and \( \Delta \) values are derived from positions of the polarizer (P) and analyzer (A) which lead to zero intensity of the beam at the detector [Azz79, Mots91]: \( \Psi = A, \quad \Delta = 2P + 90° \)  \hspace{1cm} [3.1.13].

Glan-Thompson prisms made of calcite CaCO₃ were used as the polarizer and the analyzer. A Glan-Thompson prism splits a propagating beam into two beams of mutual perpendicular polarization: the extraordinary and the ordinary beam [Mots91a]. The prism is designed in a way that the extraordinary beam is totally reflected whereas the ordinary beam
is transmitted. The compensator was made of a properly cut quartz plate with two distinct orthogonal directions: the slow and the fast axis [Mots91a]. For an arbitrary orientation of the electric field vector of the propagated beam, the electric field vector is decomposed in its two components parallel to the fast and the slow axis. Since the refractive indices do not match a phase shift occurs. The thickness of the quartz plate is chosen so that the produced phase shift equals $\pi/2$. The compensator converts linearly polarized light into elliptically polarized light.

For thin layers of few nanometers thick the change of the $\Psi$ and $\Delta$ relative to the bare substrate is small, what makes impossible parallel determination of refractive index and thickness of the film [Zhan96]. In such cases the refractive index is measured in an independent experiment on a thick film of the same material or is taken from literature.

3.2. Contact angle measurements.

3.2.1. Cohesion, adhesion, a contact angle, the Young equation.

Properties of a solid surface can be determined with wetting experiments. Let us consider a small portion of liquid introduced onto a solid surface which was initially in contact with a gas phase. From the thermodynamic point of view, the system adopts a state with minimal free energy $G$: $G = \gamma_{13}S_{13} + \gamma_{12}S_{12} + \gamma_{23}S_{23}$  

where $\gamma$ is the energy of a unit surface (interface), $S$ is the surface (interface) area, the subscripts 13, 12, and 23 mean the solid-gas, solid-liquid, and liquid-gas interfaces, respectively. Assuming that $\gamma_{13}$, $\gamma_{12}$, $\gamma_{23}$ are constant, the free energy is minimized due to change of the interface areas $S_{13}$, $S_{12}$, $S_{23}$. Hence, three possible scenarios of the liquid behavior are possible depending on minimization of which interface is preferred: (1) $S_{13} \rightarrow \text{min}$, $S_{12} \rightarrow \text{max}$ the liquid spreads over the solid surface (full wetting); (2) $S_{13} \rightarrow \text{max}$, $S_{12} \rightarrow 0$, the liquid dewets from the solid surface and rolls off; (3) the three interfaces coexist, the liquid forms a sessile droplet (partial wetting) as shown on Figure 3.2.1 a. The scenario

![Figure 3.2.1](image-url)
followed for a particular system depends on a difference of its adhesion and cohesion works.

Work of cohesion \(W_{22}\) [Pau02] must be executed for creation of new surfaces (interfaces) upon separation of a given phase (2) by vacuum or another phase (3) (Figure 3.2.2 a). Work of adhesion \(W_{12}\) [Pau02] must be executed for creation of new surfaces (interfaces) upon separation of two different phases (1 and 2) by vacuum or a third phase (3) (Figure 3.2.2 b). Amount of energy equal to the work of cohesion or adhesion is released upon the inverse processes.

If the phase 1 is solid and the phase 2 is liquid, then \(S_{sp} = W_{12} - W_{22}\) \[3.2.4\], where \(S_{sp}\) is a spreading coefficient [Schw96]. If \(S_{sp} \geq 0\) \((W_{12} \geq W_{22})\), the free energy \(G\) of the considered system is minimized when \(S_{12}\) is maximal, and full wetting (1) occurs. If \(S < 0\) \((W_{12} < W_{22})\), the system prefers to minimize \(S_{23}\), and partial wetting (3) or full dewetting (2) occurs [Bey02].

Let us consider partial wetting depicted on Figure 3.2.1 a. The equilibrium state is reached when a sum of the forces acting on the three phases contact line becomes zero:

\[
\gamma_{13} - \gamma_{12} - \gamma_{23}\cos\Theta = 0 \quad \text{or} \quad \gamma_{13} = \gamma_{12} + \gamma_{23}\cos\Theta \quad \text{[3.2.5]},
\]

where \(\Theta\) is a contact angle, which is the angle between the liquid-gas and solid-liquid interfaces. The equation [3.2.5] is the Young equation [Pau02]. Work of adhesion for the system depicted on Figure 3.2.1 a, taking the equations [3.2.3, 3.2.5] into account, is [Pau02]:
\[
W_{12} = \gamma_{12} + \gamma_{23}\cos \Theta + \gamma_{23} - \gamma_{12} = \gamma_{23}(1 + \cos \Theta) \quad [3.2.6].
\]
\[
S_{sp} = W_{12} - W_{22} = \gamma_{23}(1 + \cos \Theta) - 2\gamma_{23} = \gamma_{23}(\cos \Theta - 1) \quad [3.2.7].
\]

If \(\gamma_{13} \geq \gamma_{12} + \gamma_{23}\cos \Theta\), then \(\Theta = 0\) and \(S_{sp} \geq 0\) (full wetting). If \(\Theta = 180^\circ\), then \(S_{sp} = -2\gamma_{23}\) (full dewetting). The formulas \([3.2.5-7]\) are also correct for the wetting experiment depicted on Figure 3.2.2 b.

Determination of surface energy of a solid substrate from a contact angle experiment is possible because \(\gamma_{12}\) is a function of \(\gamma_{13}\) and \(\gamma_{23}\): \(\gamma_{12} = f(\gamma_{13}, \gamma_{23})\). A number of analytical expressions (combining rules) were proposed for the f-function [Kwok00]. The Berthelot rule [Ber1898] says that the free energy of adhesion is geometric mean of the free energies of cohesion: \(W_{12} = \sqrt{W_{11}W_{22}} = 2\sqrt{\gamma_{13}\gamma_{23}} \quad [3.2.8]\).

Kwok et al. [Kwok00] have recently improved the combining rule of Hudson and McCoubrey [Hud60]:

\[
\gamma_{12} = \gamma_{23} + \gamma_{13} - 2\sqrt{\gamma_{13}\gamma_{23}} \left(\frac{4(\gamma_{13}/\gamma_{23})^2}{1 + \left(\gamma_{13}/\gamma_{23}\right)^2}\right) \quad [3.2.9],
\]

where \(\alpha = 1.17 \text{ m}^2/\text{mJ}\). This rule works well for polar solids and polar liquids. It assumes that \(\gamma_{12}\) is constant for the same solid surface, what is in general not true. The energy of adhesion [3.2.8] can be divided into dispersive and polar (d and p superscripts, respectively) interaction terms [Ko81, Kae70, Kae70a]: \(W_{12} = \gamma_{23}(1 + \cos \Theta) = 2\sqrt{\gamma_{13}\gamma_{23}^d} + 2\sqrt{\gamma_{13}\gamma_{23}^p} \quad [3.2.10]\).

The polar term \(\gamma_{23}^p\) is negligible for non-polar compounds (e.g. methylene iodide). A harmonic mean approximation was suggested by Wu [Wu71]:

\[
W_{12} = \frac{4\gamma_{13}^d\gamma_{23}^d}{\gamma_{13}^d + \gamma_{23}^d} + \frac{4\gamma_{13}^p\gamma_{23}^p}{\gamma_{13}^p + \gamma_{23}^p} \quad [3.2.11].
\]

However, some contact liquids may interact with solids in an unpredictable manner what causes the operative \(\gamma_{23}, \gamma_{13}, \gamma_{12}\) to be different from the anticipated ones, and applicability of the Young equation becomes questionable [Kwok96, Kwok98]. A discussion of these matters is available [Kwok98a, Kwok99].

The surface tension (\(\gamma_{23}\)) of a liquid chosen for the wetting experiment can be found in a handbook or determined experimentally. For example, the ADSA technique (Axisymmetric
Drop Shape Analysis) calculates automatically $\gamma_{23}$ during the wetting experiment from the drop shape [Ada90, Wulf00]. This method utilizes the Laplace’s equation:

$$\Delta p = \gamma_{ij} \left( \frac{1}{R_1} + \frac{1}{R_2} \right)$$

[3.2.12],

where $\Delta p$ is pressure difference on a arched interface, $\gamma_{ij}$ is the interface tension, $R_1$ and $R_2$ are main radii of curvature for the arched interface.

A simple thermodynamic model for determination of the free wetting energy of a small sessile drop spreading on a solid surface was recently proposed by Extrand [Ext03].

3.2.2. Hysteresis of a contact angle.

An ideal surface, which is flat and homogeneous and does not rearrange itself upon contact with a liquid, reveals no hysteresis of a contact angle [Bey02, Pet03]. An ordinary surface has some roughness, irregularities in its structure, it can swell or rearrange [Cha00, Cha02] its chemical functionality when liquid is introduced onto it. The contact angle on such surfaces can adopt different values depending on conditions of its formation. For example, liquid advancing over a solid surface provides a higher contact angle than for the same pair liquid-solid when the liquid recedes (Figure 3.2.1 a-b, 3.2.3). It should be noted that in the

![Figure 3.2.3. General scheme of development of a liquid droplet with time in a wetting experiment. New portions of the liquid are continuously added to the drop in the time period from 0 to t₁ through a vertically inserted thin needle (Figure 3.2.1), the drop advances over the surface, its radius and volume increase. Starting from the time t₁, liquid is continuously withdrawn from the droplet, its volume decreases. The drop radius remains constant in the time period from t₁ till t₂, then it starts to decrease too. The contact angle remains constant $\Theta = \Theta_{adv}$ when the liquid advances, then it decreases to the value $\Theta_{rec}$ within the period from t₁ to t₂ and remains constant upon further receding of the droplet. Adapted from [Bey02].](image-url)
setup depicted on Figure 3.2.1 b, when the gas bubble (3) advances, the liquid phase (2) recedes. Note also that the correct contact angle is outside of the bubble (Figure 3.2.1 b).

The value of hysteresis is the difference between the advancing and receding contact angles [Sha02]: $\Delta \Theta = \Theta_{\text{adv}} - \Theta_{\text{rec}}$ [3.2.13]. In the setup depicted on Figure 3.2.1 a, some amount of the liquid may remain adsorbed by the solid substrate, what decreases the $\Theta_{\text{rec}}$. Therefore, for this setup $\Theta_{\text{adv}}$ is used as an approximation of the equilibrium contact angle $\Theta$ [Kwok00]. Theoretical approaches to the contact angle hysteresis and their practical application can be found elsewhere [Pet03, Sha02].

Sometimes a so-called stick-slip behavior of the contact line upon advancing and (or) receding is observed (see an example in Section 6.2). Explanation, what it is, will be given for the advancing contact angle. The $\Theta_{\text{adv}}$ and the volume of the droplet rise at a constant droplet radius (stick) and then the radius of the droplet suddenly increases while the contact angle value drops down (slip). Such cycles repeat again and again upon increasing the droplet volume. The reason for such behavior can be swelling of the solid substrate by the liquid from the droplet. The droplet upon increasing its volume prefers rather to stay in the contact with the swollen material than to create a new contact with the fresh area around. It is not clear for the case of the stick-slip behavior, which value of the measured contact angle is closer to the equilibrium contact angle. Sometimes it may be reasonable to use another test liquid.

### 3.2.3. Contact angles on heterogeneous and rough surfaces.

For a solid surface composed of small domains of two different materials, Cassie’s equation can be applied [Cas44]:

$$\cos \Theta = \varphi \cos \Theta_1 + (1 - \varphi) \cos \Theta_2$$

[3.2.14],

where $\Theta$, $\Theta_1$, and $\Theta_2$ are contact angles on the composite surface and surfaces of the two separated materials, respectively; $\varphi$ and $(1- \varphi)$ are the surface fractions of the first and the second material in the composite surface.

A rough surface can provide at least two possible equilibrium wetting states with different values of a contact angle. They are separated from one another with a potential barrier. The state when the liquid fills the grooves under the droplet is depicted on Figure 3.2.4 a. It is described with Wenzel’s formula [Wen49]:

$$\cos \Theta_r = \frac{\gamma_{13} - \gamma_{12}}{\gamma_{23}} = r_s \frac{\gamma_{13} - \gamma_{12}}{\gamma_{23}} = r_s \cos \Theta$$

[3.2.15],

where $\Theta_r$ and $\Theta$ are the contact angles on the rough and flat surfaces of the same material, respectively. The $\gamma_{13}$ and $\gamma_{12}$ are surface tensions of the solid-gas and solid-liquid interfaces for the rough substrate, they are proportional to the corresponding values for the flat substrate.
(γ₁₃ and γ₁₂) with the coefficient rₛ, where rₛ is a ratio of the actual area of rough surface to the projected area on the horizontal plane.

The second state when liquid does not penetrate into the grooves and the droplet is suspended on the crests of the rough pattern (Figure 3.2.4 b) is described by Cassie’s equation \[3.2.14\]. The contact area under the suspended droplet is composed of liquid-solid and liquid-gas interfaces. The contact angle of the liquid on a gas substrate is considered to be 180º. Hence, \( \cos \Theta_r = \varphi \cos \Theta - 1 + \varphi \) \[3.2.16\], where \( \Theta_r \) and \( \Theta \) are the same values as in Wenzel’s formula \[3.2.15\], \( \varphi \) is the area fraction of the liquid-solid contact [Cas48]. A transition from the Cassie regime to the Wenzel regime can occur when an external force is applied to press the droplet to the substrate [Bico99, Pat03].

The theories of Wenzel and Cassie are applicable for description of advancing contact angles on rough surfaces. But they are not applicable for the receding contact angles. It was proposed that the receding contact line leaves behind a thin liquid film on the peaks of the rough pattern instead of leaving behind dry surface [Rou02]. A correction which takes this effect to account was proposed [Pat03].

An approach, which combines Wenzel’s and Cassie’s equations \[3.2.15-16\] into one, was proposed [Feng02]: \( \cos \Theta_r = \varphi r_s \cos \Theta + \varphi - 1 \) \[3.2.17\].

![Figure 3.2.4](image)

**Figure 3.2.4.** Two different wetting regimes for a liquid drop on a rough solid surface. (a) Wenzel’s regime: the grooves underneath the droplet are filled-up with the liquid; (b) Cassie’s regime: the suspended droplet sits on the crests of the rough pattern; (c) the apparent contact angle on a rough surface as a function of the contact angle on a flat surface of the same material, predicted by Wenzel and Cassie. Adapted from [Pat03, Onda96].
The roughness coefficient $r_s$ for solid substrates with roughness on two or more levels (e.g. micro- and nanoscale elevations) as depicted on Figure 3.2.5 is calculated according to a formula from fractal geometry [Onda96, Feng02]:

$$r_s = \left( \frac{L}{\ell} \right)^{D-2} \quad [3.2.18],$$

where $L$ and $\ell$ are, respectively, the upper and lower limit scales of the fractal behavior of the surface (in the case depicted on Figure 3.2.5 they are diameters of the features of the first and the second order, respectively), $D$ is the fractal dimension. If a ratio of a number of features of a next order to a number of features of the previous order is constant for the fractal behavior:

$$\frac{N_{n+1}}{N_n} = N_f = \text{const},$$

then $D = \log_{\frac{\ell}{L}} N_f$, $2 \leq D < 3$ for fractal surfaces.

### 3.3. Atomic Force Microscopy (AFM).

#### 3.3.1. AFM. Contact, tapping, and non-contact modes.

*Atomic Force Microscopy* (AFM) is a subdivision of a more general group of methods Scanning Force Microscopy (SFM) in which a sample surface is scanned with a sharp probe and some probe-sample interactions are monitored. SFM was developed from Scanning Tunneling Microscopy (STM) invented by G. Binnig et al. [Binn86]. The information in STM is obtained from tunneling current between the probe tip and the sample surface.

AFM investigates properties of a top layer of materials through measuring interaction forces between the probe and the sample surface. Van der Waals, friction, electrostatic, and magnetic forces are the examples of interactions which can be sensed with AFM [DI99, DI99a]. AFM can investigate a broader range of materials than STM because there is no requirement for the samples to be conductive [Hans88]. AFM can be realized in three main modes: contact, tapping, and non-contact [DI99].
The set up of an AFM microscope (Figure 3.3.1) comprises a multi-sectional piezo element which extends or contracts in x, y, and z dimensions depending on bias applied to it. It determines motion of a cantilever (a plate-like spring) with a probing tip or (in some microscopes) the piezo moves the sample.

In the contact mode, when the tip interacts with the sample, the cantilever bends according to the Hooke law: $F = kz$, where $F$, $k$, and $z$ are the applied force, the cantilever spring constant, and the cantilever deflection, respectively. A laser beam reflects from the back side of the cantilever at a different angle depending on the cantilever bending (Figure 3.3.3) to a four-section photodiode. The difference in photo-current between the upper and the lower sections of the photodiode relates to the cantilever deflection in the vertical plane, while the photo-current difference between the left and right sections corresponds to cantilever twisting due to friction between the probing tip and the sample. The sample is scanned in lateral (x, y) directions at a constant deflection set-point (Figure 3.3.3 b) maintained by a feed-back loop of the microscope by means of extending and retracting the piezo. The constant tip-sample interaction force (cantilever deflection) means the constant tip-sample distance (Figure 3.3.2), what allows to record the vertical (z) piezo extension versus (x, y) location on a sample as the topography signal [DI99].

Figure 3.3.2. Force interactions between the sample surface and the probing tip. Adapted from [She00].

Figure 3.3.3. Contact Mode. (a) Force-distance diagram, solid line – approach, dot line – withdraw of the tip. (b) Maintaining the interaction force at the constant level. Adapted from [DI99a].
Typical force-distance curves (FDCs) for the contact mode are given on Figure 3.3.3a [Cap99]. When the tip enters the range of attractive van der Waals forces ($z_A$) which is usually about 10 nm from the sample surface [Ancz96], they bend the cantilever to the sample. The repulsive forces become dominant upon further approaching to the sample surface (Figure 3.3.2). They deflect the cantilever in the opposite manner. Hysteresis can be observed upon withdrawing the tip: the piezo should retract further than $z_A$ in order to detach the tip from the surface. This occurs due to increased area of adhesive interactions when the tip contacts the sample. Contact mode works well in liquid and at ambient conditions for hard surfaces. In the case of scanning soft polymeric materials in air the tip penetrates into the material and damages it upon movement in lateral directions [Mag97]. This happens on soft materials even at negative deflection set-points.

The **tapping mode**, in which an external periodic force is applied to the probe that causes the cantilever to oscillate perpendicular to the sample surface with a typical amplitude 20-100 nm, was developed [Zho93, Qui94] for investigation of soft materials. When the oscillating cantilever approaches the surface and the tip starts to interact with it, the amplitude of oscillation linearly reduces (Figure 3.3.4 c) and is maintained constant at a certain value (amplitude set-point) by the feed-back loop of the microscope. The lower is the set-point (or the amplitude set-point ratio $A/A_0$, where $A_0$ is the amplitude of free oscillations), the closer the tip can come to the sample. Changes in the vertical coordinate ($z$) of the sample (or the cantilever) upon scanning the surface needed to keep a constant amplitude of oscillation are monitored and displayed as a topography signal. The typical amplitude while imaging in air allows the tip to contact the sample surface through an adsorbed liquid layer without getting stuck. The time of contact of the tip with the surface and the friction energy are from one to two orders smaller in the tapping mode than in the contact mode [Tam96]. The contact time increases upon decreasing the amplitude set-point ratio.

It should be noted that imaging at constant amplitude leads to higher indentation depth on softer materials than on harder ones. Choice of the amplitude set-point affects the relative topography signal on a heterogeneous sample. At certain conditions, an inversion of topography contrast can occur as the set-point is changed [Bar00, Kopp00, Mag97a]. Deduction of the true sample surface is discussed in [Kno01].

The **non-contact mode** differs from the tapping mode by smaller amplitude of cantilever oscillations which is < 10 nm. The tip does not have enough energy to strike the sample but oscillates in the range of the attractive forces [DI99]. Application of the non-
contact mode is limited by materials where the adsorbed liquid layer is thin, otherwise the tip becomes trapped by it and scrapes the sample.

3.3.2. Theoretical background of phase imaging in AFM dynamic modes. Phase shift conventions.

The tapping and the non-contact modes are the dynamic modes of AFM. They are similar and can be considered together. They provide a possibility to record the phase difference between the oscillating tip end of the cantilever and the driving piezo element. Theory of vibrations provided here can be found in [Яво90] or [Fre71] and concise in [Pau02].

The equation of motion for an elastic harmonic oscillator of mass \( m \) and a spring constant \( k \) can be written considering the force acting on the center of mass (Figure 3.3.5): \( \vec{F} = -k\ell = ma \), where \( a = \frac{\partial^2 \ell}{\partial t^2} \) is acceleration. The equation can be rewritten: \( \frac{\partial^2 \ell}{\partial t^2} + \frac{k}{m} \ell = 0 \) \[3.3.1\].

The ratio \( k/m \) is always positive. Therefore it can be

![Figure 3.3.4. Amplitude-distance and phase-distance (the phase according to the DI convention) diagrams for the attractive (non-contact) (a, b) and the repulsive tapping (c, d) regimes. The data were obtained experimentally for a Si FM-W (Nanosensors) cantilever with a spring constant 1.3-3.6 N/m at the resonance frequency 57.56 kHz on a polystyrene/poly(2-vinylpyridine) brush.](image)

![Figure 3.3.5. Mechanic oscillations.](image)
substituted by \( \omega_0^2 = \frac{k}{m} \) \[3.3.2\].

Then the general solution of the equation (3.3.1) is:
\[
\ell = A_1 \sin \omega_0 t + A_2 \cos \omega_0 t
\]  \[3.3.3\].

where the \( A_1 \) and \( A_2 \) are some coefficients which can be found from initial conditions. The general solution can be rewritten as:
\[
\ell = A \sin(\omega_0 t + \varphi_0)
\]  \[3.3.4\].

where \( A = \sqrt{A_1^2 + A_2^2} \) and \( \varphi_0 = \arctg\left(\frac{A_2}{A_1}\right) \) (Figure 3.3.6).

**Figure 3.3.6.** General rule of addition of two harmonic oscillations \( A_1 \sin(\Phi_1) \) and \( A_2 \sin(\Phi_2) \), where \( \Phi_1 = \omega_1 t + \varphi_1 \), and \( \Phi_2 = \omega_2 t + \varphi_2 \). The result of the addition is \( A \sin(\Phi) \), where:
\[
A = \sqrt{A_1^2 + A_2^2 + 2A_1A_2 \cos(\Phi_2 - \Phi_1)}
\]
and
\[
\tan \Phi = \frac{A_1 \sin \Phi_1 + A_2 \sin \Phi_2}{A_1 \cos \Phi_1 + A_2 \cos \Phi_2}.
\]

Adopted from [Яво90].

The equation of motion for **free decaying oscillation** is:
\[
m \frac{d^2 \ell}{dt^2} + b \frac{d \ell}{dt} + k \ell = 0 \quad \text{or} \quad \frac{d^2 \ell}{dt^2} + 2\beta \frac{d \ell}{dt} + \omega_0^2 \ell = 0
\]  \[3.3.5\].

where \(-b \frac{d \ell}{dt}\) is the resistive force, \( b \) is the decay coefficient, \( \beta = b/(2m) > 0 \). For the case when the decay is not very big \( \beta < \omega_0 \), the solution of the equation [3.3.5] is:
\[
\ell = A_0 e^{-\beta t} \sin(\omega t + \psi_0)
\]  \[3.3.6\],

where \( \omega = \sqrt{\omega_0^2 - \beta^2} \), and the constants \( A_0 \) and \( \psi_0 \) depend on initial conditions. The value \( A_0 e^{-\beta t} \) is called amplitude of decaying oscillations.

**Quality factor** \( Q \) [QCnt, Яво90] of an oscillating system is a dimensionless physical value which equals \( 2\pi W(t)/(W(t)-W(t+T)) \), where \( W \) is the system energy at the time moment \( t \) and \( (W(t)-W(t+T)) \) is the energy loss upon one period of oscillations \( T \) which starts from the time moment \( t \). The energy of the system is proportional to the amplitude in the second power: \( W(t) \sim A_0^2 e^{-2\beta t} \), therefore: \( Q = 2\pi/(1- e^{-2\beta T}) \). When \( \beta T \) is small, \( T \approx T_0 \), and \( Q \approx \pi/(\beta T_0) = \omega_0/(2\beta) = \omega_0 m/b = k/(b \omega_0) \) \[3.3.7\].

Additionally, \( Q \approx \omega_0/B \), where \( B \) is the width of the resonance band at its half-power point [Bar00].
The equation of motion for \textbf{non-decaying oscillation driven} by variable external force $F(t)$ is:

$$\frac{\partial^2 \ell}{\partial t^2} + 2\beta \frac{d\ell}{dt} + \omega_0^2 \ell = \frac{F(t)}{m} \quad [3.3.8].$$

If the external force is a periodic function of time, for example $F(t) = F_0 \cos \omega t$, a transition regime of the driven oscillation appears. The oscillator simultaneously participate in two oscillations: 

$$\ell = A_0 e^{-\beta t} \sin(\omega t + \psi_0) + A \cos(\omega t + \phi_0) \quad [3.3.9],$$

where the first term corresponds to the free decaying oscillations [3.3.6] and $\omega = \sqrt{\omega_0^2 - \beta^2}$. The second term corresponds to the \textbf{non-decaying} oscillations at the frequency of the driving force. $A$ and $\phi_0$ in the second term can be found upon its insertion to [3.3.8] instead of $\ell$:

$$\ell = A \cos(\omega t + \phi_0), \quad \frac{d\ell}{dt} = -A \omega \sin(\omega t + \phi_0), \quad \frac{\partial^2 \ell}{\partial t^2} = -A \omega^2 \cos(\omega t + \phi_0).$$

We obtain an equation:

$$A(\omega_0^2 - \Omega^2) \cos(\omega t + \phi_0) - 2A\beta \Omega \sin(\omega t + \phi_0) = \frac{F_0}{m} \cos \omega t \quad [3.3.10].$$

Addition of the two terms on the left hand side can be done as described on Figure 3.3.6.

$$A(\omega_0^2 - \Omega^2) \cos(\omega t + \phi_0) - 2A\beta \Omega \sin(\omega t + \phi_0) = R \cos(\omega t + \delta - \frac{\pi}{2}) = \frac{F_0}{m} \cos \omega t \quad [3.3.11],$$

where $R = A \sqrt{(\omega_0^2 - \Omega^2)^2 + 4\beta^2 \Omega^2}$, $\tan \delta = \frac{(\omega_0^2 - \Omega^2) \cos \phi_0 - 2\beta \Omega \sin \phi_0}{(\omega_0^2 - \Omega^2) \sin \phi_0 + 2\beta \Omega \cos \phi_0}$. $\delta$ must be equal $\pi/2 + 2\pi n$ in order to make the equation [3.3.11] true. From this we derive

$$A = \frac{F_0}{m \sqrt{(\omega_0^2 - \Omega^2)^2 + 4\beta^2 \Omega^2}} \quad [3.3.12].$$

Now the equation [3.3.10] can be rewritten as

$$(\omega_0^2 - \Omega^2) \cos \phi_0 - 2\beta \Omega \sin \phi_0 = \sqrt{(\omega_0^2 - \Omega^2)^2 + 4\beta^2 \Omega^2} \quad \text{for } \Omega = 2\pi n,$$

or

$$\frac{\omega_0^2 - \Omega^2}{\sqrt{(\omega_0^2 - \Omega^2)^2 + 4\beta^2 \Omega^2}} \cos \phi_0 - \frac{2\beta \Omega}{\sqrt{(\omega_0^2 - \Omega^2)^2 + 4\beta^2 \Omega^2}} \sin \phi_0 = 1 \quad [3.3.13],$$

or $\sin(\delta - \phi_0) \cos \phi_0 + \cos(\delta - \phi_0) \sin \phi_0 = 1$ (according to the Figure 3.3.6). The left side can be simplified according to the known formula: $\sin(x+y) = \sin(x)\cos(y) + \cos(x)\sin(y)$ into

$$\sin \delta = 1, \ \delta = \pi/2 + 2\pi n.$$ From [3.3.13]:

$$\frac{-\cos(\pi/2 - \phi_0)}{\sin(\pi/2 - \phi_0)} = -\tan \phi_0, \ \tan \phi_0 = -\frac{2\beta \Omega}{\omega_0^2 - \Omega^2} \quad [3.3.14].$$

The amplitude $A$ [3.3.12] and the phase $\phi_0$ [3.3.14] are plotted on Figure 3.3.7 as functions of the driving frequency. At $\Omega = 0$ we obtain $\phi_0 = 0$ and

$$A = \frac{F_0}{m \omega_0^2} = \frac{F_0}{k} \quad [3.3.15],$$

$F_0/k$ is a static displacement which takes place under a constant force $F = F_0$. 28
while at $\Omega = \infty$ we get $A = 0$ and $\phi_0 = -\pi$ [3.3.16].

Maximal amplitude $A_{\text{max}} = \frac{F_0}{2m\beta\omega}$ [3.3.17] of the forced oscillation is reached at the frequency of the driving force $\Omega_r = \sqrt{\omega_0^2 - 2\beta^2} = \sqrt{\omega^2 - \beta^2}$ [3.3.18], where $\omega = \sqrt{\omega_0^2 - \beta^2}$. If $\beta$ is much smaller than $\omega_0$, then $\Omega_r \approx \omega_0$, $\phi_0 \approx -\pi/2$, and $A_{\text{max}} \approx QA_0$ [3.3.19].

![Figure 3.3.7](image-url) The amplitude $A$ (solid line) and the phase $\phi_0$ (dashed line) as functions of the driving frequency $\Omega$. The curves were simulated for $A_{\text{max}} = 40$ nm, $\omega_0 = 300$ kHz, $Q = 450$, $\beta = 30$ kHz.

The value of the phase shift $\phi_0 \leq 0$ what is not very convenient. A positive value $\psi = -\phi_0$ which changes from 0 at $\Omega = 0$ through $\pi/2$ at $\Omega = \omega_0$ to $\pi$ at $\Omega = \infty$ is used as a standard convention for the phase shift in literature [Mag97, Ancz96, Cle98, Tam96, Jam01]. The convention of Digital Instruments (DI) for the phase shift $\phi_\text{DI}$ realized in their AFM software is also often used: $\phi_\text{DI} = \frac{\pi}{2} - \psi$, $\phi_\text{DI}$ changes from $\pi/2$ through 0 to $-\pi/2$ as the driving frequency $\Omega$ rises from 0 through $\omega_0$ to $\infty$ [Jam01, Mag97]. Within this thesis, the AFM phase is dominantly expressed according to the DI convention ($\phi_\text{DI}$) because we made AFM imaging and further analysis with their software. The standard convention $\psi$ is sometimes more convenient for discussions of the theory of the AFM phase imaging. Due to this reason, some diagrams are plotted in the standard convention $\psi$ within this Section. AFM phase images are presented in a gray palette where the transition from the light to the dark tone corresponds to the change from bigger to smaller $\phi_\text{DI}$ values and at the same time from smaller to bigger $\psi$ values (Figure 3.3.8).
The work of the resistive force $F = -b \frac{d\ell}{dt}$ during the period of one cycle is:

$$A_1 = -b \int_{t(0)}^{T} \frac{d\ell}{dt} \, dt = -b A^2 \Omega^2 \int_{0}^{T} \sin^2(\Omega t + \phi_0) \, dt = -0.5b A^2 \Omega^2 T$$ \[3.3.20\].

The work of the driving force $F(t) = F_0 \cos \Omega t$ during the same period of time is:

$$A_2 = F_0 \int_{0}^{T} \cos \Omega t \, dt = -A\Omega F_0 \int_{0}^{T} \sin(\Omega t + \phi_0) \cos \Omega t \, dt = -0.5A\Omega F_0 T \sin \phi_0,$$

$$A_2 = 0.5A\Omega F_0 T \sin \psi$$ \[3.3.21\].

From $\psi \in [0; \pi]$, $\sin \psi \geq 0$. The work of the driving force $A_2$ is positive, while the work of the resistive force $A_1$ is negative. If a cantilever oscillates without interaction with a sample, the energy of the driving force is fully dissipated by the cantilever body oscillating in air:

$$A_2 = -A_1 \text{ and } \sin \psi = bA\Omega / F_0$$ \[3.3.22\].

If the tip starts to interact with the sample, an additional resistive force participates in the dissipation of the driving energy: $A_2 = -(A_1 + A_{\text{tip}})$, $A_{\text{tip}} = -0.5A\Omega F_0 T \sin \psi + 0.5bA^2 \Omega^2 T$, where $A_{\text{tip}} < 0$. Taking into account that $F_0 = kA_d$, where $A_d$ is the amplitude of the cantilever end fixed on the piezo, and $Q = k/(b\omega_0)$ \[3.3.7\], we obtain: $A_{\text{tip}} = \frac{1}{2} \Omega T (bA\Omega - F_0 \sin \psi)$,

$$A_{\text{tip}} = \frac{\Omega}{2} \left( \frac{kA\Omega}{Q\omega_0} - kA_d \sin \psi \right) = \frac{kA^2 \Omega}{2Q} \left( \frac{\Omega}{\omega_0} - \frac{Q A_d \sin \psi}{A} \right)$$ \[3.3.23\].

The last equation was published in [Cle98]. Other authors [Tam99, Jam01] expressed the phase shift $\psi$ as a function of energy $E_D \geq 0$, $E_D = -A_{\text{tip}}$, dissipated due to the tip-sample interaction. They utilized a simplification from [Cle98] for the tip amplitude $A_0$ on a free oscillating cantilever (when no interaction with the sample occurs): $A_0 = QA_d$ and finally obtained:

$$\frac{A_{\text{tip}}}{T} = -\frac{E_D}{T} = \frac{kA^2 \Omega}{2Q} \left( \frac{\Omega}{\omega_0} - \frac{A_0 \sin \psi}{A} \right) = \frac{kA_0 A\Omega}{2Q} \left( \frac{\Omega}{A_0 \omega_0} - \sin \psi \right),$$

$$\sin \psi = \frac{A\Omega}{A_0 \omega_0} + \frac{2QE_D}{kA_0 A\Omega T} = \frac{A\Omega}{kA_0 A} + \frac{2QE_D}{A_0 \omega_0} = \frac{A\Omega}{A_0 \omega_0} + \frac{QE_D}{\pi kA_0 A}$$ \[3.3.24\].

\[1\] The integration was done using the formula $\cos(2x) = 1 - \sin^2 x$.

\[2\] The integration was done using the formula $\sin(a+b) = 2\sin(0.5(a+b))\cos(0.5(a-b))$. 

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The last equation allows us to interpret experimental phase curves (see examples on Figure 3.3.4). When a cantilever is far enough from a sample and oscillates freely ($A = A_0$, $E_D = 0$), the phase shift $\psi$ is $90^\circ$ ($0^\circ$ in the DI software). When it comes closer to the sample, the oscillation is damped ($A < A_0$), and linear decrease of the damped amplitude is produced upon approaching the sample. If we assume that this interaction is conservative and no energy dissipates ($E_D = 0$), the equation [3.3.24] has two solutions which are shown on Figure 3.3.8.

**Figure 3.3.8.** Two solutions of the equation [3.3.24] for the case when the second term is zero upon the tip-sample interactions. The gray arrows show directions of displacement of the curves when the second term becomes $> 0$. Adapted from [Jam01].

Upon approaching the cantilever to the sample, the first branch (solid) goes down until the phase shift $\psi$ reaches $180^\circ$ ($-90^\circ$ in the DI software), while the second branch (dashed) goes up until the $\psi$ equals $0^\circ$ ($90^\circ$ in the DI software). The first solution corresponds to the non-contact regime (Figure 3.3.2), in which an attractive interaction is responsible for reduction of the cantilever oscillation. This interaction makes the effective spring constant of the cantilever smaller (Figure 3.3.9 a) and thus moves the cantilever resonance to lower frequencies producing the phase shift $\psi$ higher than $90^\circ$ (below $0^\circ$ in the DI software) (Figure 3.3.10 a). The second solution is associated with the intermittent repulsive regime (Figure 3.3.2), in which the repulsive interaction increases the effective spring constant of the cantilever (Figure 3.3.9 b) and displaces the cantilever resonance to higher frequencies producing the phase shift $\psi$ smaller than $90^\circ$ (Figure 3.3.10 a). The experimental amplitude-frequency and phase shift-frequency diagrams can be found elsewhere [Bar00].
Upon the tip-sample interaction, which includes energy dissipation, the second term of the equation [3.3.24] becomes $> 0$, and the both solutions of the equation are displaced closer to the middle of the phase-distance diagram (Figure 3.3.8). The energy dissipation leads to lower resonance amplitude and gentler slope of the phase-frequency diagram (Figure 3.3.10).

**Figure 3.3.9.** (a) The attractive interaction reduces the effective spring constant of the cantilever. (b) The repulsive interaction increases the effective spring constant of the cantilever. $k_1$, $k_2$, and $k_{eff}$ are spring constants of the free oscillating cantilever, the sample, and the oscillating cantilever which interacts with the sample, respectively. $\ell_1$ and $\ell_2$ are the cantilever deflection and deformation of the sample, respectively.

**Figure 3.3.10.** Two mechanisms of decrease of the oscillation amplitude. (a) The resonance moves to lower or to higher frequency depending on the effective spring constant (Figure 3.3.9) while the driving frequency remains constant. The amplitude decreases and the phase curve shifts to higher or to lower values, respectively. (b) The amplitude and the Q-factor are reduced due to energy dissipation, the slope of the phase curve becomes gentler. Adapted from [Jam01].

Upon the tip-sample interaction, which includes energy dissipation, the second term of the equation [3.3.24] becomes $> 0$, and the both solutions of the equation are displaced closer to the middle of the phase-distance diagram (Figure 3.3.8). The energy dissipation leads to lower resonance amplitude and gentler slope of the phase-frequency diagram (Figure 3.3.10).
b). The more dissipative features appear lighter in the non-contact regime, whereas they appear darker in the intermittent repulsive regime.

### 3.3.3. Qualitative rules for phase contrast.

Phase imaging is extensively used to qualitatively distinguish different materials on surfaces of heterogeneous samples. Quantitative information about materials constants, however, can hardly be extracted from phase images at present [Kno01].

Magonov et al. [Mag97] suggested that the difference \( \sigma = k_{\text{eff}} - k_1 \) between the effective spring constant \( k_{\text{eff}} \) of a vibrating cantilever interacting with a sample and a free-oscillating cantilever \( k_1 \) is proportional to the Young modulus of the sample (Figure 3.3.9) and to the tip-sample contact area. On the other hand, numerical simulations by Tamayo et al. [Tam96] of the AFM intermittent repulsive mode for pure elastic materials showed that the phase shift depends on the equilibrium tip-sample separation \( z_c \), which is introduced as the distance between the tip and the sample when the cantilever does not oscillate. This means that the suggestion of Magonov et al. does not fully describe the mechanism of the phase shift formation. Nevertheless their derivation of a formula \( \phi^{\text{DI}} \approx Q\sigma/k_1 \) [3.3.25], which describes the phase shift dependence on sample elasticity, from [3.3.14] is correct.

At high tip-sample separation \( z_c \) and the tapping frequency close to resonance, the phase shift \( \phi^{\text{DI}} \) is about 0º (\( \psi \) close to 90º originally in [Tam96]) because of weak interaction with the sample. The \( \phi^{\text{DI}} \) increases almost linearly to 90º (\( \psi \) decreases to 0º in [Tam96]) as \( z_c \) decreases in the case of pure elastic materials. The phase-distance curves have similar slopes for hard and soft materials and lie close to one another. The phase-distance curve for a harder material (higher Young modulus \( E_Y \)) lies at a slightly higher \( \phi^{\text{DI}} \) (lower \( \psi \)) values. The difference in phase shift for a soft and a hard material may be even smaller taking into account that the tapping mode is realized at constant amplitude set-point and that the amplitude starts to decrease earlier upon approaching the cantilever to a hard material than to a soft one. From the equation [3.3.24], the phase shift on pure elastic materials (in absence of energy dissipation) is determined by the amplitude set-point ratio \( (A/A_0) \) and the resonance frequency. The resonance displacement to lower or higher frequency due to the change of the cantilever effective spring constant is determined by the amplitude set-point and the shape of the resonance peak. The latter does not change significantly upon small resonance displacements. Therefore, according to this theory [Tam96], the phase shift must be similar on pure elastic materials with different Young modules. However, softer materials (lower \( E_Y \)) may dissipate energy stronger and therefore provide decreased \( \phi^{\text{DI}} \) (increased \( \psi \)) phase shifts.
in intermittent light (A/A₀ close to 100%) and hard (A/A₀ 70-40%) tapping mode relative to harder materials. On the other hand the softer materials form a bigger tip-sample contact area at very low amplitude set-points (A/A₀ < 0.4) and, consequently, reveal higher φ^{DI} (lower ψ) phase shifts than the harder materials. An example is the phase shifts φ^{DI} on mica, Si, and sapphire which gradually increase in a very similar way from -5º to 40º upon decreasing A/A₀ from 0.83-0.9 to 0.2 [Mag97]. The phase shifts φ^{DI} on mica are lower relative to the other two materials in this amplitude set-point ratio range. The φ^{DI} on mica becomes higher than on Si and sapphire at A/A₀ < 0.2.

Viscoelasticity is a property of polymeric materials which causes energy dissipation in the intermittent tapping mode. It is modeled as

\[ \sigma_v = E_v \varepsilon + \eta \frac{d \varepsilon}{dt} \]  

where σ_v, ε, and η are the stress, strain, and viscosity, respectively. The viscous deformation is time dependent, the relaxation frequency ω_v is \[ \frac{\eta}{E_v} \]. The phase shift is dominated by the pure elastic response for Ω > ω_v due to the resonant frequency displacement and changes in the tip-sample contact area as described above. For the cantilever driving frequencies Ω < ω_v, the phase shift is dominated by viscoelasticity of a sample. Viscosity force acting on the tip is proportional to the sample deformation velocity and the tip-sample contact area [Tam96]. There are two contributions from a viscoelastic material to the phase shift (Figure 3.3.10): (1) displacement of the cantilever resonance to higher frequencies in the intermittent tapping mode as in the case of the pure elastic response (ψ becomes lower than 90º, φ^{DI} rises up) and (2) amplitude damping and broadening of the resonance peak accompanied by displacement of the phase curve closer to the phase shift value of the free oscillating cantilever: ψ = 90º, φ^{DI} = 0º. Numerical simulations of the cantilever dynamics showed that for large tip-sample separations (relative to free amplitude), phase shifts φ^{DI} less than 0º are possible (ψ above 90º in the original paper [Tam96]). The proximity of the sample may increase the φ^{DI} (reduce the ψ) for low viscosity, but it never reaches 90º (0º for ψ). For a given tip-sample separation z_c, the higher is the viscosity, the lower is the phase shift φ^{DI} (the higher is the ψ). For a viscoelastic material the phase shift φ^{DI} decreases (ψ increases) as the sample viscosity η increases and the elastic modulus E decreases. High viscosity can decrease the total phase shift φ^{DI} below 0º (can increase ψ above 90º). These results of the cantilever dynamics simulations agree with some experimental data [Tam96] but still need more substantial confirmation.
The phase shift in the non-contact mode reflects adhesive properties of the sample [Jam01, Tam96]. The contrast of phase images recorded from the same location on a sample in the non-contact and intermittent tapping modes is reversal what is consistent with equation [3.3.24]. The pull-off forces cause energy dissipation and displace the phase shift towards the value for the free oscillating cantilever ($\phi_{DI}^0$). Water layer adsorbed on hydrophilic features on a sample amplifies the energy dissipation [Jam01]. The pull-off forces are the primary origin of energy dissipation also in the intermittent tapping mode at tapping frequencies higher than the relaxation frequency $\omega_r$ of a sample material [Jam01].

If (1) amplitude of cantilever oscillation is increased or (and) (2) the amplitude set-point is reduced while being in the non-contact mode, a bistable tapping regime can be observed, in which the cantilever oscillates in both the non-contact and the intermittent tapping regimes at the same microscope settings. The bistable regime is accompanied with artifacts in form of depressions on the topography image and jumps more than 90° in phase signal at points of transitions from the non-contact to the intermittent tapping [Jam01]. This illustrates importance of establishing of the stable non-contact or intermittent tapping avoiding the bistability [Jam01]. A trick, which is used by experimentalists, comprises a choice of the driving frequency $\Omega$ above or below the cantilever resonant frequency $\Omega_r$ in order to stabilize the non-contact or the intermittent tapping regime, respectively [Kopp00]. The phase shift $\phi_{DI}^0$ of the free oscillating cantilever will be different from 0° in this case [Kopp00, Ancz96].

Phase contrast may change upon increasing the indentation depth (can be several tens of nanometers [Bar00]) together with the topographic contrast in the case of a heterogeneous observed morphology:

![Figure 3.3.11](image_url)

**Figure 3.3.11.** Topography and phase contrast on heterogeneous surfaces in AFM tapping mode as a function of the indentation depth. Left: 1 – no indentation in the non-contact mode; 2a and 2b – shallower and deeper indentation on the glassy and viscoelastic materials in the intermittent tapping mode. Right: 1 – smooth topography and no phase contrast in the non-contact mode; 2a, 2b – patterned topography and phase images in the intermittent tapping mode due to different indentation depths and tip-sample interactions.
near-to-surface layer (Figure 3.3.11). There is a big number of publications on AFM imaging of deeper and deeper layers of heterogeneous polymer samples by means of subsequent measurements of a given sample area first in light tapping (A/A₀ ≈ 1.0) and then through gradually decreasing amplitude set-point ratio in the hard (A/A₀ 0.7-0.4) and, at last, in the very hard tapping (A/A₀ < 0.4) [Bar97, Kopp00, Mag97a, Rag00]. Experimental determination of the indentation depth δ as a function of amplitude set-point ratio from amplitude-distance diagrams is described in [Bar00, Kno01]. Calibration of phase shifts by δ was published in [Bar00].

Note, that phase images are usually interfered by topography of a sample. The tip-sample contact area is bigger when the tip elevates across a slope than when it descends to a valley. The changes in the contact area produce respective changes in the tip-sample interaction force and thus in the phase signal. In the repulsive tapping regime, the phase shift φ°Dl changes upon crossing a bump as shown in Figure 3.3.12 b: the phase signal is lighter (Figure 3.3.8) upon climbing of the tip to the top of the bump, while it is darker upon descending of the tip to the valley. This behavior of the phase signal is described mathematically as the first derivative of topography. See an example on Figure 8.1.4 b. The phase signal in the attractive tapping regime shifts at the bump edges in the opposite manner (Figure 3.3.12 c, 8.1.5).

**Figure 3.3.12.** Influence of topography (a) on the AFM phase signal in the intermittent repulsive (b) and in the attractive (c) tapping regimes. The arrows show the direction of the tip motion.

3.4. Techniques relative to x-ray absorption.

3.4.1. X-ray Photoemission Spectroscopy (XPS).

X-ray Photoemission Spectroscopy (XPS) involves measurement of binding energies (E_b) of electrons ejected by interactions of a molecule with a monoenergetic beam of soft x-rays [Cla77]. The most commonly employed x-ray sources are Al_{Kα1,2} and Mg_{Kα1,2} with corresponding photon energies 1486.6 eV and 1253.7 eV respectively. In principle all electrons from core to valence levels can be studied. The probability for photoionization of
the core levels is generally considerably higher than for the valence levels. The core orbitals are essentially localized on atoms (do not participate in inter-atom bonds, Figure 3.4.3 a) and therefore have binding energies characteristic for a given element. These are two reasons for the emphasis in XPS on the study of the core levels. The electron binding energy is calculated from the photon energy \( h\nu \) of incident x-rays and the kinetic energy of the emitted electron according to the following equation:

\[
h\nu = E_b + E_{\text{kin}}\tag{3.4.1}
\]

The self-explanatory set up of an XPS spectrometer is depicted in Figure 3.4.1.

Removal of a core electron is accompanied by substantial reorganization of the valence electrons in response to the effective increase in nuclear charge. This perturbation gives rise to a finite probability for photoionization to be accompanied by simultaneous excitation of a valence electron from an occupied to an unoccupied level (shake up) or ionization of a valence electron (shake off). These processes give rise to satellites on the low kinetic energy side of the main photoionization peak (Figure 3.4.2). Sampling depth of this method at the take-off angles 0° and 75° (referring to the perpendicular to the sample) is ~8 nm and ~2 nm, respectively [Bri89, Sea79]. See Section 3.4.3 for more theory on x-ray absorption and electron photoemission.

### 3.4.2. Near Edge X-ray Absorption Fine Structure (NEXAFS) Spectroscopy.

*Near Edge X-ray Absorption Fine Structure* (NEXAFS) spectra are obtained by scanning the incident x-ray photon energy \( h\nu \) across a core absorption edge and measuring
photon absorption by a sample [Stöhr92]. The NEXAFS spectrum can be obtained directly by measuring x-ray transmission through a sample (thinner than 1 µm to avoid complete absorption). This method is named *X-ray Absorption Spectroscopy* (XAS). A related microscopic method exists which is named *Transmission X-ray Microscopy* (TXM) [Mor01]. The NEXAFS spectrum can be recorded indirectly by detection of emitted photoelectrons with *X-ray Photoemission Electron Spectroscopy and Microscopy*, XPEEM [Mor01]. Absorption of x-rays induces electron transitions in a sample when the photon energy of incident x-ray radiation (hv) matches the transition energy of an inner electron to a non-occupied antibonding π* or σ* molecular orbital (MO theory), Rydberg or continuum states (Figure 3.4.3 a). Our work was limited with NEXAFS spectra produced upon electron excitation from the K (1s) shell of low-Z elements (the second row of the periodic system). See Section 3.4.3 for further discussion of NEXAFS spectroscopy.

### 3.4.3. Intramolecular processes which occur upon x-ray absorption.

Formation of NEXAFS and XPS spectra is dominated by intramolecule electron structure [Stöhr92]. Comparing to the total lifetime of the electronic final state (10⁻¹⁵-10⁻¹⁴ s), the vibrational motions of the nuclei are slow because of their large mass (the ratio of proton and electron masses is 1836) and typically occur in ~10⁻¹³ s. This allows separation of the electronic and nuclear degrees of freedom (*Born-Oppenheimer approximation*). *Franck-Condon principle* states that the internuclear distances in a molecule can be assumed staying constant during the electronic excitation process.

*Ionization potential* (IP) or *binding energy* (Ec) is a minimum energy necessary to excite an electron to the continuum of states above the vacuum level. *Koopman’s theorem* states that the IP of an i-th electron is equal to the negative of its orbital energy Ei. Koopman’s theorem assumes that states of the other (non-excitated) electrons does not change (are frozen) upon the excitation. The latter assumption is inadequate for the electron excitations from the K (1s) shell of the second row atoms, and the predicted Ec can deviate from the experimental values by ΔEr = 10-20 eV, where ΔEr is the relaxation energy correction [Stöhr92].

If an electron from the K (1s) shell of an atom (molecule) is excited to a state with higher energy, a so-called *relaxation* occurs when the final energy levels of other electrons in this atom (molecule) shift to new equilibrium positions [Stöhr92]: the 1s level shifts to a smaller binding energy (Eb) (upwards in Figure 3.4.3 a) while the outer levels shift to bigger binding energies (downwards in Figure 3.4.3 a).
Figure 3.4.3. NEXAFS spectra. (a) Their origin – intramolecular electron structure. (b) An example of a NEXAFS spectrum. The resonances $\sigma^*$ (c) and $\pi^*$ (d) are maximal when the electric field vector $\vec{E}_{el}$ of incident x-rays is parallel to the characteristic $\Omega$ direction of $\sigma^*$ or $\pi^*$ orbitals. Adapted from [Stöhr92].

Figure 3.4.4. Decay of a hole at the K-shell proceeds via transition of a valence electron to the K-shell. It can be radiative with emission of a fluorescent photon or non-radiative with emission of an Auger electron. Adapted from [Stöhr92].
Sudden approximation is an assumption that the electron transition upon excitation possesses a one-electron character and that the primary excitation event is rapid or “sudden” with respect to the relaxation times of the other “passive” electrons [Stöhr92]. In this case a single photoemission peak is observed corresponding to the binding energy $E_b(i) = -E_i$, where $i$ is a subscript for the $i$-th electron. The sudden approximation is justified for excitation energies well above the IP of the core electrons of interest. The sudden approximation is applicable in X-ray Photoemission Spectroscopy (XPS).

For excitation energies lower or similar to the IP, an adiabatic approximation is applicable. It assumes that the “passive” electrons relax and multi-electron excitations may occur additionally to the main “one-electron” line. The main line is shifted to a binding energy with bigger absolute value ($E_b = -E_i - \Delta E_R$), while the multi-electron satellites appear at $E_b$ with smaller absolute values. The center of gravity of all photoemission features lies at the Koopman’s binding energy. The adiabatic approximation is valid in NEXAFS spectroscopy [Stöhr92].

Bound state transitions. Non-occupied $\pi^*$ and $\sigma^*$ MO in the ground state lie above the IP. Occupied $\pi^*$ orbitals in the ground state are located below the IP. Relaxation effect shifts $\pi^*$ orbitals below the IP upon excitation of an electron from the K (1s) shell. In all known K-shell spectra for low-Z molecules the $\pi^*$ resonance, if present, lies below IP [Stöhr92, Hov85]. Hence, the electron excitation to this state is a bound-state transition. The $\pi^*$ resonance can be observed only if the bond has a $\pi$ contribution (double and triple bonds). If present, the $\pi^*$ resonance is the lowest energy structure in a NEXAFS spectrum [Stöhr92]. In the $\pi^*$ resonance the final state lifetime and the resonance natural width (which is $\sim 0.1$ eV) are determined by the decay of the core hole, which dominantly proceeds via deexcitation of the excited electron in the $\pi^*$ state to the K-shell and simultaneous emission of a valence electron (Figure 3.4.4) [Stöhr92].

Between the $\pi^*$ resonance and the IP several sharp but weak resonances can be observed (Figure 3.4.3 b) which correspond to excitation to so-called Rydberg’s orbitals or, in the presence of bonds with hydrogen atoms, to a mixture of Rydberg’s and hydrogen-derived antibonding orbitals [Stöhr92]. The resonances merge into a continuos step-like feature about 2 eV below the IP.

Quasi-bound state transitions. The energy of $\sigma^*$ antibonding orbitals being occupied with excitated electrons lies above the IP. An electron excited to this level remains quasi-trapped by the intramolecular field [Hov85, Dehm76]. The intramolecular field often has centrifugal barriers extended above the vacuum level (Figure 3.4.3 a) [Stöhr92]. These
barriers are angle-dependent. Their maximums lie on the outer sides of the atoms forming the \(\sigma\) bond. Within the multiple scattering (MS) theory an electron on a \(\sigma^*\) antibonding orbital can be considered as scattering back and forth between the two atoms. The \(\sigma^*\) resonance is observed for all molecules with bonds formed by two low-Z atoms except H (too weak to be seen). The lifetime of an electron in the \(\sigma^*\) is shorter than its lifetime in a bound state (the \(\pi^*\) and Rydberg’s states). The higher the \(\sigma^*\) state lies in the continuum, the higher is the probability of its decay to continuum states. According to Heizenberg’s principle, this leads to a broader \(\sigma^*\) resonance peak relative to the peaks of the \(\pi^*\) and Rydberg’s resonances (Figure 3.4.3 b).

*The X-ray absorption cross section* \(\sigma_x\) of an atom or a molecule is defined as the number of electrons excited per unit time divided by the number of incident photons per unit time per unit area. Integral of \(\sigma_x\) by the photon energy is the optical oscillator strength \(f_{\text{osc}}\), which is a measure of intensity of a resonance: \(f_{\text{osc}} = \frac{mc}{\pi e^2 \hbar} \int \sigma_x(e) dE\), where \(m\) and \(e\) are the mass and the module of charge of an electron, \(c\) is the rate of light propagation, \(\hbar\) is Plank’s constant. For a given electron in an atom or a molecule, the sum of the oscillator strengths of all transitions to all other states, discrete and continuous, occupied and non-occupied, is unity. This rule is known as the *Thomas-Reiche-Kuhn sum rule* \([Stöhr92]\). Consequently, the total oscillator strength for the electronic excitation of an atom or a molecule is equal to the number of electrons in the atom or a molecule. This rule is approximately valid for a given subshell of an atom \([Stöhr92]\). The total oscillator strength of electron transitions (excitations) from the K-shell must be equal 2 according to this. Despite it is lower in reality, this rule has an important consequence: the overall absorption step in a NEXAFS spectrum (Figure 3.4.3 b) is proportional to the number of atoms, producing the absorption edge being scanned, in the sample. In a row of NEXAFS spectra recorded from three samples of different molecules (a number of the molecules is constant) which contain, respectively, one, two, and three atoms, producing the chosen absorption edge, the overall absorption steps will be in ratio 1:2:3, respectively \([Stöhr92]\).

The intensity of an electron transition from a state described with a wave-function \(|i\rangle\) to a state described with a wave-function \(|j\rangle\) driven by a harmonic time-dependent perturbation \(V_{\text{per}}\) is proportional to: \(f_{\text{osc}} \sim \left|\langle j | V_{\text{per}} | i \rangle\right|^2\). For the electron excitations from the 1s level, which has a spherical symmetry, the intensity is dependent on symmetry of the final state \(|j\rangle\) and its orientation relative to the vector \(V_{\text{per}}\) which is parallel to the electric field
vector $\mathbf{E}_{el}$ of the incident x-ray radiation. The intensity of electron transitions from 1s to $\sigma^*$ or $\pi^*$ orbitals is maximal when the vector $\mathbf{E}_{el}$ is parallel to a characteristic direction $\mathbf{O}$ for the $\sigma^*$ or $\pi^*$ orbitals, respectively (Figure 3.4.3 c-d) [Stöhr92]. Therefore, orientation of bonds in molecules can be sensed in NEXAFS spectroscopy with polarized incident x-ray radiation. The $\sigma^*$ resonances are maximal when the plane of polarization of the x-rays is parallel to the $\sigma$ bonds, while the $\pi^*$ resonances are maximal when the plane of polarization is perpendicular to the corresponding $\sigma$ bonds. There is no stereospecificity in XPS of the K-shell because of spherical symmetry of the final continuum states above the vacuum level.

The energy absorbed upon the excitation is specific for a particular kind of atoms (elemental contrast, Figure 3.4.5) and functional groups in which they participate (chemical shift, Figure 8.2.13 a). Selective absorption of x-ray radiation, which depends on chemical nature of atoms and their neighborhood in molecules and on orientation of the bonds in space in the case of polarized x-rays, is the base for applying the NEXAFS spectroscopy and microscopy for probing of chemical composition [Adewww, Dhez03, Hitch01, Hitch01a, Kop01, Mor01, Urq02] and spatial structure of polymer surfaces [Cos98, Fuji02, Sam96].

3.4.4. X-ray Photoemission Electron Microscopy (XPEEM).

_X-ray Photoemission Electron Microscopy (XPEEM)_ is a spectromicroscopic technique which uses the contrast in NEXAFS spectra for probing surface chemistry by detection of photoelectrons emitted from the surface. The emitted photoelectron flux is proportional to the intensity and photon energy of the incident x-rays, exposed area, and concentration of the emitting atoms in the sample [Stöhr92].

NEXAFS and XPEEM measurements were performed at the PEEM2 microscope at the bending magnet beamline 7.3.1.1 of the Advanced Light Source synchrotron at the Ernest Orlando Lawrence Berkeley National Laboratory, USA [PEEM2]. The microscope operates over the photon energy range from 175 to 1500 eV. The synchrotron radiation passed through a monochromator ($E/\Delta E=1800$ at 800 eV) is focused to a 30x30 µm spot at the sample. The flux in the image area is about $3 \cdot 10^{12}$ photons/s. The angle between the incident x-rays and the sample surface is fixed at 30º. The electrostatic optical system of the microscope images secondary electrons at a high magnification onto the phosphor screen and the CCD camera by means of a three-element high voltage objective lens, a transfer lens, an intermediate lens, and a projector lens. The maximal lateral resolution for elemental contrast is 20 nm, the typical resolution is 100 nm. The polymer samples must be ultrahigh vacuum compatible solids on a conductive or semiconductive substrate. Estimated sampling depth is about 10 - 15 nm.
depending on properties of the sample [Mor01]. In the present work, Si wafers were used as the substrates.

The PEEM2 microscope permits real-time studies of elemental (Figure 3.4.5) and chemical (Figure 8.2.13 a) properties of the top layer of materials. Linear polarization of incident synchrotron x-ray radiation allows investigation of orientation of chemical groups (Figure 3.4.3 c-d). Circularly polarized x-rays allow investigation of magnetic properties of materials. The latter kind of contrast is outside of the focus of this work. Its applications are described elsewhere [PEEM, Scho00].

The contrast in XPEEM is influenced by topography of a sample. From viewing trajectories of photoelectrons, convex features tend to have reduced collection efficiency, while concave features are enhanced (Figure 3.4.6). Sharp features tend to have increased electric potentials and therefore might have enhanced emission. In addition, the illumination of a sample at 30° leads to partial or complete shadowing.

Figure 3.4.5. Elemental contrast in XPEEM. Adapted from [PEEM2].

(b)

Figure 3.4.6. Topographical contrast in XPEEM. (a) PEEM image; (b) photoelectron trajectories. Adapted from [PEEM2].
4. Preparation of samples.

4.1. Materials.

Substrates. Polished Si wafers (100) with natural SiO₂ layer (~2 nm) were purchased from Silchem Handelsgesellschaft mbH (Freiberg, Germany) and Wacker-Chemicronics GmbH (Burghausen, Germany). A high value of refractive index of Si (n = 3.885) is suitable for ellipsometrical measurements of thickness of immobilized polymer layers. Therefore, Si substrates were dominantly used in this work. They were washed three times with dichloromethane in an ultrasonic bath for 5 min and afterwards in a mixture of water, ammonia solution (25%), and hydrogen peroxide (30%) in volume ratio 10:1:1 at 60°C for 1 hour. The substrates were rinsed 5-6 times with pure water and dried with nitrogen flux. The alkali bath transforms Si-O-Si bridges on the surface of the natural SiO₂ layer into Si-OH groups. One can easily observe the difference in contact angles of a water droplet put onto a Si substrate before (~60º) and after the alkali bath (~0º). This peculiarity was used for quality control of cleaning. If the washed substrates are not immediately used for further procedures, they can be stored under clear water for a period of time up to 1 month in order to keep the surface properties constant. Storage of cleaned Si wafers in water for 2 days is required to get a stable reproducible hydrophilic surface for very fine ellipsometric measurements. Root-mean-square (RMS) roughness of a cleaned substrate is less than 0.2 nm (from an AFM 2x2 µm scan).

Initiators. 4,4’-azobis(4-cyanopentanoic acid) (ABCPA) (Fluka) and 4,4’-azobis(isobutyronitrile) (AIBN) (Fluka) were used as received without additional purification.

Monomers. Styrene (S) (Aldrich), 2,3,4,5,6-pentafluorostyrene (FS) (Fluka), methylmethacrylate (MMA) (Aldrich), methylacrylate (MA), 2-vinylpyridine (2VP) (Merck) were purified on an aluminum oxide type 507C, neutral, 100-125 mesh (Fluka) chromatographic column.

Solvents. Toluene (Merck), tetrahydrofuran (THF) (Merck), hexane (Merck) were distilled after 1 hour boiling over sodium. Dichloromethane of 99.5% purity (Acros) was dried over molecular sieves overnight before the use. Water was cleaned with Milli-Q® ultrapure purification system, Ω’ >18.2 MΩ·cm. Ethanol of the analytical grade (Riedel-deHaën), ammonia solution (25%, for analysis, Merck), and hydrogen peroxide (30%, stabilized, Merck) were used as received.

Gases and other chemicals. Oxygen for plasma treatment with purity of 99.95% and Argon 99.998% were purchased from Messer Griesheim, Germany. (3-Glycidoxypropyl)trimethoxysilane (GPS) (from ABCR GmbH, Karlsruhe, Germany), ethylenediamine (ED,
ACROS Organics), and phosphorus pentachloride (Aldrich) were used as received. Triethylamine (Riedel-deHaën) was dried overnight over calcium hydride. Polydimethylsiloxane (PDMS) stamps produced from silicone elastomer SYLGARD 184 and exposed to oxygen plasma for 5 s at 0.5 mbar O₂ pressure in a Harrick plasma cleaner at the lowest power setting were kindly provided by V. Senkowsky, Universität Ulm.

4.2. Synthesis of mixed homopolymer brushes via the “grafting from” approach.

4.2.1. Silanization of Si substrates.

We used an improved procedure originally proposed by Boyen G. et al. [Boy90] which offered very reproducible results. Si wafers were treated with 1% GPS solution in toluene for 15 h under dry Ar atmosphere (<1 ppm H₂O). Then they were washed 3 times with dry toluene under the dry Ar atmosphere to avoid polymerization of the non-grafted GPS in volume and precipitation of particles. The Si wafers were washed afterwards 2 times with ethanol, cleaned 2 times in ethanol in ultrasonic bath for 5 min, and dried with nitrogen flux. The ellipsometric thickness of the GPS layer was 0.8 nm, what corresponds to the monolayer thickness [Luz00], in case of a freshly opened bottle with GPS, while the thickness increased up to 1.3 nm after 2 months of GPS aging. The time required for the silanization (15 h) was determined from a kinetic curve (Figure 4.1). It is consistent with the literature data [Luz00]. The concentration of the GPS solution in toluene (1%) was chosen so that the molar ratio of water traces in dry toluene to GPS was less than 1:1 in order to avoid polymerization of GPS in bulk [Luz00]. Role of water traces in formation of a 2D-network by trialkoxysilanes is also considered elsewhere [Kra02].

![Figure 4.1. Kinetics of silanization of Si-wafers with GPS.](image-url)
Topography of the immobilized GPS layers was studied with AFM (Figure 4.2). When the requirement of dry conditions is kept upon the synthetic procedures, a smooth layer without bumps is formed (bumps of various sizes are formed upon presence of moisture). An unsuccessful attempt was done to determine its thickness with an AFM scratch test according to Method 1 (Section 5.5.2). Although some material was removed from the scratched area, it was not possible to find any step on the topography profile.

(a) 5x5 µm, z scale 2 nm; (b) 1x1 µm, z scale 2 nm; (c) profile of b.

Figure 4.2. Topography of the GPS layer immobilized on Si wafer. Black horizontal line in (b) marks the origin of the profile (c). RMS roughness 0.25 nm.

Si (SiO₂) substrate

Figure 4.3. Introduction of GPS and ethylenediamine on Si substrates.

4.2.2. Introduction of ethylenediamine onto the immobilized GPS layer.

The Si wafers after modification with GPS were treated with 1.5 % ED in ethanol for 1.5 h (Figure 4.3), washed afterwards 3 times with ethanol and 4 times with a mixture of ethanol and water in ratio 1:2 in order to remove the rest of ED, and then they were dried with nitrogen flux.

This two-step technique of introduction of amino-groups onto Si wafers is reproducible unlike a one-step immobilization of (3-aminopropyl)-trimethoxysilane which
can be adsorbed upside-down with the amino-groups contacting the Si surface or occupying two adsorption sites with both amino- and alkoxy silane ends. However, there was a recent report that reproducibility and density of amino-functional silane layers can be improved via pre-adsorption of stronger amines like diethylamine onto Si or SiO₂ surface [Kan02].

4.2.3. Introduction of azo-initiator.

The chloroanhydride of ABCPA (Cl-ABCPA) was prepared by addition of a slurry of 40 g of PCl₅ (190 mmol) in 100 ml CH₂Cl₂ to a suspension of 5 g of ABCPA (18 mmol) in 50 ml CH₂Cl₂ at 0° C. The mixture was stirred overnight under the dry Ar atmosphere (<1 ppm H₂O) while it warmed up to room temperature. The yellow solid of PCl₅ was filtered off. The solution was concentrated via steaming CH₂Cl₂ out under reduced pressure in order to precipitate the major part of the dissolved PCl₅. The PCl₅ was filtered off. Cl-ABCPA was precipitated from the filtrate at 0° C as white powder in 300 ml dry cold hexane. It was filtered, washed with dry cold hexane, and dried under reduced pressure giving 84% yield.

The Si wafers modified with GPS and ethylenediamine were treated with a solution of 0.66 g Cl-ABCPA and 0.36 ml of triethylamine in 50 ml CH₂Cl₂ for 2 h. (Figure 4.4). Then the wafers were washed with CH₂Cl₂, twice with ethanol, twice with ethanol in an ultrasonic bath for 5 min, dried with nitrogen flux, and the thickness of the grafted layer was controlled with ellipsometry. The calculated total thickness of the GPS + ethylenediamine + attached ABCPA was in the range from 1.8 to 2.4 nm. We found out that the Si substrates with grafted azo-initiator can be stored at -25° C for one month without a significant loss of its reactivity.

The morphology of the immobilized initiator was studied with AFM (Figure 4.5). The grain size became bigger in comparison with the GPS layer (Figure 4.2), the RMS roughness increased from 0.25 nm to 0.92 nm. The scratching test via Method 1 (Section 5.5.2) revealed the thickness of the layer about 1 nm (Figure 4.6). That is rather the thickness of ED+ABCPA excluding the bottom GPS layer which was too strong to be removed upon scratching (Section 4.2.1.).

![Figure 4.4. Introduction of the azo-initiator.](image-url)
(a) 5x5 µm, z scale 7 nm; (b) 1x1 µm, z scale 7 nm; (c) profile of e.

**Figure 4.5.** AFM topography images of the immobilized GPS+ED+ABCPA layer on Si wafer. The black horizontal line at (b) marks the origin of the profile (c). RMS roughness 0.92 nm.

**Figure 4.6.** AFM scratching test of the GPS+ED+ABCPA layer according to the method 1 from Section 5.5.2. Left: contact mode scan of the scratched area, scale 5x5 µm, z range 10 nm. The black rectangle marks the origin of the averaged topography profile (right).

### 4.2.4. Radical polymerization on the surface.

The kinetic scheme of surface-initiated radical polymerization was discussed by Minko et al. [Min99]. The experimental procedure comprises the following steps. Monomer solution in THF (usually 50% wt.) was cleaned by four freeze-pump-thaw procedures (vacuum 1.2·10^{-5} mbar). For “grafting from” of PSF, the S and FS monomers were taken in weight ratio 3:1. The deoxygenated solution was condensed to a reactor with added AIBN (4.36·10^{-4} mol/l). The reactor was filled with Ar and afterwards four freeze-pump-thaw cycles were repeated. The Si wafers with the grafted azo-initiator were placed into the reactor under Ar atmosphere (O_{2} and H_{2}O <1 ppm). The reactor was immersed into water bath (60 ± 0.1° C) for different periods of time. After polymerization the Si wafers were rinsed several times with THF. The non-grafted polymer was removed by cold Soxhlet extraction in THF during 1 h. The thickness of the grafted layer was measured with ellipsometry. The second polymer was grafted using the residual after the first grafting azo-initiator (Figure 2.4 a) and the same procedure. The non-grafted polymer from the mixed brush was removed by Soxhlet extraction.
in THF during 12 h (Section 4.2.5). Optimal temperature and time of polymerization were estimated from the literature data about decomposition constants of AIBN and ABCPA (Table 4.1). The thickness of the binary brushes was measured with ellipsometry. We assumed that the molecular weight of the grafted polymers equals the molecular weight of the polymer in the bulk solution [Sid99]. The latter was determined with Size Excluded Chromatography (SEC, Section 5.2).

**Table 4.1.** Constants of decomposition ($k_d$) of azo-initiators and their half-life periods ($t_{1/2}$) at different temperatures.

<table>
<thead>
<tr>
<th>Azo-initiator</th>
<th>$T$, °C</th>
<th>$k_d$, c$^{-1}$</th>
<th>$t_{1/2}$, h</th>
</tr>
</thead>
<tbody>
<tr>
<td>AIBN in toluene and benzene*</td>
<td>50</td>
<td>$2.085 \times 10^{-6}$</td>
<td>92</td>
</tr>
<tr>
<td>AIBN in toluene and benzene*</td>
<td>60</td>
<td>$9.15 \times 10^{-6}$</td>
<td>21</td>
</tr>
<tr>
<td>AIBN in toluene and benzene*</td>
<td>70</td>
<td>$3.166 \times 10^{-5}$</td>
<td>6</td>
</tr>
<tr>
<td>ABCPA immobilized on SiO$_2$ surface**</td>
<td>60</td>
<td>$1.57 \times 10^{-5}$</td>
<td>12</td>
</tr>
<tr>
<td>ABCPA*</td>
<td>70</td>
<td>$4.58 \times 10^{-5}$</td>
<td>4</td>
</tr>
</tbody>
</table>

* From [Pol4]. ** Unpublished data of Minko, S. and Goreshnik, E. from polymerization kinetic experiments on SiO$_2$ particles.

### 4.2.5. Kinetics of extraction of non-grafted polymers.

Thickness of monocomponent and binary polymer brushes was measured with ellipsometry as function of time of Soxhlet extraction. The kinetic curves are plotted on Figure 4.7. The extraction was started immediately after the end of polymerization. The non-grafted polymers remaining after the polymerization in the brush layer are removed within 4-7

![Figure 4.7](image-url) **Figure 4.7.** Kinetics of (a) hot and (b) cold Soxhlet extraction on “grafted from” polymer brushes.
hours (the initial steep part of the kinetic curves). The slow decrease in thickness during the further continuous extraction is probably due to detachment of the grafted polymers from the substrate. The assumption about the fast extraction of the non-grafted polymer is supported by (1) a theoretical prediction of de Gennes [Gen80] that a polymer brush in contact with polymer melt expels the non-grafted chains. (2) The less dense brushes synthesized via the “grafting to” technique [Luz00a] prevent grafting of further polymer chains at the critical thickness ~8 nm, what is significantly less than the thickness of the “grafted from” brushes. The assumption about the slow detachment of the grafted polymer chains upon extraction is supported by our observations of decrease in thickness of the brushes, synthesized via the “grafting from” approach, upon storage. Selected samples of monocomponent and binary polymer brushes were stored for a certain period of time, than rinsed with chloroform, dried with nitrogen flux, and their thickness was determined with ellipsometry (Table 4.2).

**Table 4.2. Decrease of brushes thickness upon storage.**

<table>
<thead>
<tr>
<th>Brush and storage conditions</th>
<th>Period of storage, days</th>
<th>Initial thickness, nm</th>
<th>Final thickness, nm</th>
<th>Thickness decrease, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSF, 0º C</td>
<td>91</td>
<td>70.0</td>
<td>59.2</td>
<td>14.4</td>
</tr>
<tr>
<td>PS/P2VP, 0º C</td>
<td>145</td>
<td>21.5</td>
<td>16.1</td>
<td>24.1</td>
</tr>
<tr>
<td>P2VP, ambient conditions</td>
<td>109</td>
<td>19.0</td>
<td>14.3</td>
<td>19.5</td>
</tr>
<tr>
<td>PSF/PMMA, ambient conditions</td>
<td>31</td>
<td>121.7</td>
<td>84.7</td>
<td>29.6</td>
</tr>
</tbody>
</table>

4.3. Surface patterning of mixed polymer brushes via wet microcontact printing.

A PDMS stamp was cleaned via Soxhlet extraction in chloroform for 1 h and afterwards dried in vacuum overnight. A drop of a desired solvent was put onto the stamp surface. The drop volume was taken sufficient to cover the sample surface under the stamp. Immediately after that the stamp was introduced onto the surface being patterned, pressed down with tweezers for a second, and then left lying until complete evaporation of the solvent (~1 h).

4.4. Etching of polymer brushes with oxygen plasma.

The plasma treatment was done in a computer controlled customized MicroSys apparatus by Roth&Rau, Germany. The cylindrical vacuum chamber, made of stainless steel,
has a diameter of 350 mm and a height of 350 mm. The base pressure obtained with a turbomolecular pump was $<10^{-7}$ mbar. On the top of the chamber a 2.46 GHz ECR plasma source RR160 by Roth&Rau with a diameter of 160 mm and a maximum power of 800 W was mounted. The process gas was introduced into the active volume of the plasma source via a gas flow control system. When the plasma source was on, the pressure was measured by a capacitive vacuum gauge. The samples were introduced by a load-lock-system and placed on a grounded aluminum holder near the center of the chamber. The distance between the sample and the active volume of the plasma source was about 200 mm. For the plasma treatment the following parameters were applied: O$_2$ gas flow 25 standard cubic centimetres per minute, pressure $9 \cdot 10^{-3}$ mbar, effective microwave power 190 W. Exposure times are specified separately for each particular experiment (Section 8.2.2).

Two etching procedures were used. (1) A long rectangle sample (0.8x3 cm) was prepared and divided with marks (stripes made with a steel needle) into segments 0.5 cm in length. The thickness of the polymer film in each segment was determined with ellipsometry. The sample was covered with a clean mask (a Si plate of a size sufficient to cover the sample) so that one segment is not covered. After exposure to the plasma, the mask was shifted so that the second segment became also uncovered. The exposure to the plasma was repeated. The mask was shifted again to open one more segment with subsequent exposure to the plasma. This process was repeated until all segments were exposed to the plasma. The thickness removed by plasma is proportional to the time of exposure. Therefore, the segments, staying covered longer upon exposure to plasma, were thicker at the end than the segments opened earlier (Figure 4.8). Thickness of each segment was determined after the etching procedure with ellipsometry, the morphology was investigated, if needed, with AFM. The drawback of this method is that the change of morphology with etching depth is studied not at a constant location on the sample.

(2) In the second procedure, a suitable location on a sample was marked and investigated with AFM before plasma etching. The initial thickness of the polymer film was determined with ellipsometry (Section 5.1) and a scratch test (Section 5.5.2, Method 2). After
exposure of the sample to the plasma for a chosen period of time, the marked location was found (Section 5.5.3) and investigated with AFM. The steps comprising plasma etching with following AFM investigation of the marked location on the sample were repeated desired number of times.
5. Characterization of the synthesized samples.

5.1. Ellipsometry.

The amount of the chemisorbed initiator and the grafted amount of polymers was measured with *null ellipsometry* on Multiskop from the company Optrel, Germany. The light source was a He-Ne laser producing monochromatic red light (\( \lambda = 632.8 \) nm). The angle of incidence was fixed at 70°. For data interpretation, a multilayer model of the grafted films was used [Sid99]. For determination of the parameters \( n \) and \( B \) for a new layer, the parameters for the previous layers obtained from earlier measurements were inserted to the multilayer model. For calculations of thickness of layers thinner than 30 nm, we used values of refractive indices given at Table 5.1. For thicker films the refractive indices were obtained parallel with the layer thickness directly from the ellipsometric experiment.

Table 5.1. Refractive indices (n) and extinction coefficients (B).

<table>
<thead>
<tr>
<th>Material</th>
<th>n</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>air</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>PMA</td>
<td>1.48</td>
<td>0</td>
</tr>
<tr>
<td>PMMA</td>
<td>1.49</td>
<td>0</td>
</tr>
<tr>
<td>P2VP</td>
<td>1.59</td>
<td>0</td>
</tr>
<tr>
<td>PS</td>
<td>1.59</td>
<td>0</td>
</tr>
<tr>
<td>GPS + ABCPA</td>
<td>1.55</td>
<td>0</td>
</tr>
<tr>
<td>GPS</td>
<td>1.429</td>
<td>0</td>
</tr>
<tr>
<td>SiO(_2)</td>
<td>1.460</td>
<td>0</td>
</tr>
<tr>
<td>Si</td>
<td>3.885</td>
<td>0.018</td>
</tr>
</tbody>
</table>

5.2. Size Exclusion Chromatography.

The molecular weight of the grafted polymer was evaluated with size excluded chromatography (SEC) assuming that the polymer in the bulk has the same molecular weight as the polymer grafted to the substrate [Sid99]. There are contradictory reports in literature concerning this assumption. The kinetic scheme suggests almost the same molecular weight for grafted chains and chains in the bulk [Min99], but in some experiments an increased molecular weight and larger polydispersity index for the grafted polymer as compared to the bulk polymer was documented due to the Trommsdorff effect [Boy90, Luz96].

The SEC-experiments were carried out at room temperature. The application of the sample was 0.075 mg in 25 µL effluent. The flow rate of effluent was 1 mL/min.
PMA and PMMA. The SEC-measurements were performed using a modular built KNAUER-HPLC-system (KNAUER, Germany) equipped with refractive index (RI) detection and two columns PL MIXED-C (Polymer Laboratories Ltd, UK). Tetrahydrofurane (THF) was used as effluent. The molar mass averages were calculated using calibrations obtained by PMMA standards (Polymer Laboratories Ltd, UK).

P2VP. The SEC-measurements were performed using a modular built HPLC equipped with RI-detection (Hewlett Packard Series 1100, Germany) and a ZORBAX. A mixture containing dimethylacetamide (DMA) and water (98/2; v/v) was used as effluent. The effluent contained 3g LiCl/ L. The molar mass averages were calculated using calibrations obtained by P2VP standards (Polymer Laboratories Ltd, UK).

PS and PSF. The SEC-measurements were performed using a modular built HPLC equipped with RI-detection and two columns PL MIXED-C (Hewlett Packard Series 1100, Germany). THF was used as effluent. The molar mass averages were calculated using calibrations obtained by PS standards (Polymer Laboratories Ltd, UK).

As a sample-specific calibration for PMA and PSF was not available, the computed molar masses were relative values only allowing comparison between polymers of similar chemical structure.

5.3. Nuclear Magnetic Resonance (NMR).

$^1$H NMR measurements were carried out on a Bruker DRX 500 spectrometer operating at 500.13 MHz. CDCl$_3$ was used as solvent, lock, and internal standard ($\delta(^1$H) = 7.26 ppm).

The composition of the random copolymer poly(styrene-co-2,3,4,5,6-pentafluorostyrene) (PSF) was calculated from the $^1$H NMR spectra (Appendix 5) and for all samples the numeric fraction of the FS monomer units was found in the range 25-30 %.

The sharp signals in the spectrum were produced by contamination with monomers and water. The aromatic protons of the styrene units of PSF produced broad bands in the region 6.3 – 7.2 ppm with integral intensity 5.270. The aliphatic protons of PSF produced a broad band in the region 1.0-2.9 ppm with integral intensity 4.355. There are 5 aromatic protons in the S units and 3 aliphatic protons in each S and FS units. The numbers of the FS and S units in PSF were designated n and m, respectively. For the spectrum presented in Appendix 5, the ratio of integral intensities of an aromatic to an aliphatic proton was $I(\text{aromatic } ^1\text{H})/I(\text{aliphatic } ^1\text{H}) = 1.054/1.452$. The numeric fraction of the FS obtained from this spectrum was: $\frac{m(\text{FS})}{m(\text{FS}) + n(S)} = \frac{1.452 - 1.054}{1.452} = 0.27$.
5.4. Contact angle measurements.

The contact angle measurements via the sessile drop technique were conducted on DSA equipment produced by Krüss GmbH, Hamburg, Germany. A sample of a brush was exposed to a desired solvent, rapidly dried within few seconds with nitrogen flux, and the measurements were started immediately. The time period between the exposure to the solvent and the following contact angle measurement was minimized in order to avoid possible changes of the surface state upon storage at ambient conditions and to reduce time of the whole experiment, especially in the case of kinetic measurements (see below). Possible influence of remnant solvent traces on the contact angle value is considered in Section 6.2. Three water droplets were consecutively introduced onto a fresh area on a sample. Water was supplied to and withdrawn from the droplet through a syringe vertically inserted into its top (Figure 3.2.1 a). At least 20 contact angle measurements were done with time interval of 1 s at the lowest possible water flow for both advancing and receding of each droplet. Resulting values of $\Theta_{\text{adv}}$ and $\Theta_{\text{rec}}$ were averaged from the three droplets.

The kinetics of switching of mixed polymer brushes by selective solvents was measured as follows. A sample of a mixed polymer brush was exposed to a certain solvent for a desired period of time and dried as described above. The contact angle measurement were started immediately. Only one water droplet per one measurement was introduced onto the sample. A water droplet itself can cause switching of some kinds of mixed polymer brushes (e.g. PS/P2VP). A possible mistake due to this effect was minimized by introduction of the water droplet onto a fresh area on the sample where no previous droplets were introduced (or smaller number of the previous droplets, because the sample size is limited). Only advancing contact angles were measured because of the same reason. The remaining water droplet was blown off with nitrogen flux and the whole cycle was repeated until no more changes in the contact angle values were observed.

Surface composition of mixed brushes after exposure to various solvents (Section 7) was calculated via the Cassie equation (Section 3.2.3, [3.2.14]). The surface composition of PS/P2VP brushes exposed to organic solvents was calculated via substitution of the $\Theta_1$ and $\Theta_2$ in the Cassie equation by the advancing water contact angles averaged for each monocomponent PS and P2VP brush after exposure to toluene and ethanol (Table 6.2). The error of the calculated P2VP fractions due to the stick-slip behavior on the P2VP brush was estimated to be $3.6^\circ/20^\circ\cdot 100\% = 18\%$, where $20^\circ$ is the difference between the $\Theta_{\text{adv}}$ for PS and P2VP and the approximate switching range of the PS/P2VP brushes. The surface composition of the mixed PS/P2VP brushes after exposure to acidic water was calculated via the Cassie
equation using the water advancing contact angle on the monocomponent P2VP brush exposed to acidic water (Table 6.2). The estimated error of these calculations is 2.9°/50°·100% = 5.8%, where 50° the approximate switching range in this special case. The surface composition of PSF/PMMA brushes was calculated via substitution of the $\Theta_1$ and $\Theta_2$ in the Cassie equation by the water advancing contact angles of PSF exposed to toluene and PMMA exposed to chloroform. The error of the calculated PMMA fraction in the brush top layer due to the rearrangement of the different functional groups, which belong to the same polymer, on the surface (Section 6.2) is estimated as 3°/25°·100% = 12%, where 3° is the difference in the $\Theta_{adv}$ for PSF exposed to toluene and THF (Table 6.2), 25° is the approximate switching range.

5.5. Atomic Force Microscopy (AFM).

Morphology of polymer brushes was investigated with Atomic Force Microscopy (AFM) on Nanoscope IIIa (IV) Dimension™ 3100 and Nanoscope IIIa Multimode™ microscopes produced by Digital Instruments, Santa Barbara, USA.

The usual settings for tapping mode were as follows: scan rate 0.4-1.2 Hz, the proportional and internal gains 1.0-2.5 and 0.1-0.25, respectively, with ratio of the first to the second close to 10. The amplitude at the photodiode for the attractive (non-contact) and the repulsive tapping mode was 0.5-1.0 V and 1.5-3.0 V, respectively. The amplitude set-point ratio ($A/A_0$) was in the range 100-35% for the repulsive tapping mode, the value of 50% was most frequently used for phase imaging. The amplitude set-point ratio 100-90% was used for the attractive (non-contact) tapping mode. The fast scan direction was from left to right.

The following settings were used for imaging in contact mode: scan rate 3 Hz, the integral and proportional gains about 1, the deflection set-point was set to 0 before bringing the tip into contact with a sample, upon imaging from -1.3 to -1.5 V. The voltage difference (U-L) between the upper (U) and lower (L) parts of the photodiode was set to -2 V. See also scratch tests in Section 5.5.2.

5.5.1. Types of cantilevers and tips.

A. Si cantilevers for tapping (non-contact) mode AFM with ultrasharp tips from MikroMasch, Tallin, Estonia [MikroM, SPM]. Radius of curvature <10 nm, tip height (H) 15-20 µm, full tip cone angle <20°. Typical cantilever length (L) 230±5 µm, cantilever width (W) 40±3 µm, cantilever thickness (d) 7.0±0.5 µm. Resonant frequency 170±20 kHz, average spring constant (k) 40 (min 25, max 60) N/m. The reflective side coated with Al. These cantilevers were used for phase imaging in the repulsive tapping mode.
AFM on rough, adhesive (PSF/PMMA, PSF/PMA brushes) or electrostatic charged (annealed brushes) samples.

B. $n^+$-Si cantilevers for tapping mode AFM type A-NCH-W from Nanosensors [Nano].
Resistivity ($\Omega$') 0.01-0.025 Ohm·cm, $H = 10-15$ µm, $L = 117$ µm, $W = 28-30$ µm, $d = 3.7-4.5$ µm. Resonant frequency 348-424 kHz, spring constant (k) 39-72 N/m. These cantilevers were mainly used for recording topography images in tapping mode.

C. $n^+$-Si cantilevers for tapping mode AFM type FM-W from Nanosensors [Nano].
Resistivity ($\Omega$') 0.01-0.025 Ohm·cm, $L = 219$ µm, $W = 21-23$ µm, $d = 2.5-3.4$ µm. Resonant frequency 67-87 kHz, spring constant (k) 1.3-3.6 N/m. These cantilevers were used for phase imaging in tapping mode.

D. $n^+$-Si cantilevers for contact mode AFM type CONT-W from Nanosensors [Nano].
Resistivity ($\Omega$') 0.01-0.025 Ohm·cm, $H = 10-15$ µm, $L = 444$ µm, $W = 44-46$ µm, $d = 1.5-2.4$ µm. Resonant frequency 10-16 kHz, spring constant (k) 0.1-0.3 N/m. These cantilevers were used for contact mode AFM and scratching tests (Section 5.5.2).

5.5.2. Determination of thickness of polymer films with scratch tests.

Method 1 was utilized for thin films <10 nm. Area was preliminary imaged in contact mode (the settings are given in the beginning of Section 5.5) with big lateral scale (10x10 µm). Scratching was performed for 10 min at reduced lateral scale (1x1 µm) and hard settings: positive deflection set-point +2.0 V, the integral and proportional gains equal 15, scan rate 20 Hz. Then imaging of the scratched area was done at the initial settings and the initial lateral scale (10x10 µm). Then the lateral scale was reduced again to 1x1 µm and scratching was repeated for another 10 min at the same location with subsequent imaging of the scratched area at the bigger lateral scale in order to be sure that the depth of the made cavity does not increase any longer.

Method 2 was utilized for polymer films (brushes) 10-150 nm thick. A sample was manually scratched with a steel needle. The needle is harder then the polymer and softer than the Si substrate. It removes the polymer but does not scratch Si. The made stripe was imaged with tapping mode AFM and the average depth was obtained from its topography profiles in several places. This method was utilized for determination of the PSF/PMMA brush thickness after etching with oxygen plasma (see Section 5.5.3, 4.4).
5.5.3. Exact finding of a marked location on a sample.

We did these experiments with Nanoscope IIIa (IV) Dimension™ 3100 which has a built-in camera and illumination for optical observation of a sample. A line- or cross-like mark was manually made with a metal needle on a polymer film based on a hard Si substrate. The mark was investigated through the optical camera at maximal magnification. A suitable location on the polymer film (brush) close to the mark was chosen and moved underneath the AFM tip. An image of the tip location relative to the mark was recorded. A scan of the chosen location was done in tapping mode AFM at a big lateral scale (20x20 µm) so that a sufficient part of the mark was seen at the border of the recorded image. The visible part of the mark was used for determination of thickness of the polymer film (Section 5.5.2, Method 2). Polymer brushes have usually defects from silane particles underneath the brush layer (Section 4.2.1). Their positions relative to one another and to the mark were documented and used later as guides. Scans at smaller lateral scales (down to 2x2 µm) were made in order to document morphology of the polymer film (brush) itself. The chosen location was repeatedly found even after plasma etching (Section 4.4) utilizing the mark and the documented defects in the layer as the guides.

5.5.4. Micromechanical analysis.

Force-volume mode, which utilizes a collection of the AFM force-distance curves (FDCs) over selected surface areas, was used for micromechanical analysis of binary polymer brushes. A single FDC records the forces acting on the tip as it approaches to and retracts from a point on the sample surface (Section 3.3.1, [Cap99]). Force volume mode allows for the micromapping of the mechanical properties of polymer surfaces with nanometer scale resolution, while obtaining topographical information simultaneously [Rat98, Tsu99]. Typically, we used 64x64 or 32x32 pixels within 1x1 or 2x2 µm surface areas to do micromapping with a lateral resolution of 15 nm. The collected data were processed using software developed in the lab of V. V: Tsukruk at Materials Science & Engineering Department, Iowa State University, Ames, Iowa 50011, USA. The software provides means for calculation of localized elastic modulus, depth profile of elastic modulus, reduced adhesive forces, and surface histograms of elastic moduli and adhesive forces from experimental images as described elsewhere [Tsu02, Hua98, Tsu00]. Spring constants of cantilevers were determined from the resonant frequencies and the tip-on-tip method [Haz98, Haz99]. Tip radii were evaluated with scanning of reference gold nanoparticle specimens in combination with a deconvolution procedure [Rad93, Tsu01].
5.6. X-ray Photoelectron Spectroscopy (XPS).

XPS analysis was performed with AXIS ULTRA XPS spectrometer from Kratos Analytical, England. X-ray source was mono-Al Kα₁,₂ (1486.6 eV), power of the x-ray source was 300 W at 20 mA. Photoelectron analyzer pass energy was 160 eV or 20 eV for a survey or high-resolved spectra, respectively. The sample charging was overcompensated guaranteeing unadulterated peak shapes.

Normalized peak areas (Norm.Area) were calculated from peak areas (RawArea) of survey spectra according to the following equation:

\[
\text{Norm.Area} = \frac{\text{RawArea}}{\text{RSF} \cdot \text{Tx.Function}}
\]

where RSF is a sensitivity factor, experimentally determined for this spectrometer. The RFS factor accounts variations in proportionality coefficients between the electron yield and the concentrations of emitting atoms of different kinds. Tx.Function is the spectrometer’s transmission function.

5.7. NEXAFS/XPEEM.

The hardware description is given in Section 3.4.4. NEXAFS spectra were recorded without lateral resolution from spin-coated films of PSF and PMMA at the C edge: 280.0-284.5 eV, ΔE=1 eV; 284.5-291.0 eV, ΔE=0.15 eV; 291.0-305.0 eV, ΔE=0.3 eV; 305-320 eV, ΔE=1 eV), the O edge (525.0-534.0 eV, ΔE=1 eV; 534.0-545.0 eV, ΔE=0.15 eV; 545.0-570.0 eV, ΔE=0.15 eV), and the F edge (687.0-693.0 eV, ΔE=1.0 eV; 693.0-703.0 eV, ΔE=0.15 eV; 703-720 eV, ΔE=1.0 eV. The photon energy step was made smaller in the regions of the sharp 1s→π* peaks and bigger in the smooth pre-edge regions and at the broad 1s→σ* and continuum features. The regions of 30 eV above the edges were recorded for further proper off-line treatment of the spectra. The spectra from spin-coated PSF and PMMA polymers were recorded at various positions of a chopper (a slit between the monocromator and the microscope) in order to find the conditions when the damage of the samples is minimized. The polymers for spin-coating were taken from the bulk solutions after surface-initiated polymerizations in the synthesis of the PSF/PMMA brushes (Section 4.2.4). Clean Si wafer was used for recording the monocromator function (I₀) at the C and F edges. The natural SiO₂ layer on the wafer provided an oxygen peak, therefore, the PSF was used for determination of the monocromator function at the O edge. The exact photon energies for the bound state transition peaks at each edge were determined: 286.10 eV for C 1s→π* in PSF, 289.20 eV for C 1s→π* in PMMA, 535.95 eV for O 1s→π* in PMMA, and 696.00 eV for F 1s→π* in PSF.
The spectra recorded at the O and F edges were normalized by the monochromator function in order to neutralize the effect of contamination in the beamline and non-linearity in the intensity of the x-rays passed through the monochromator [Stöhr92]. This procedure was skipped for the carbon spectra because the monochromator function was close to a constant (Figure 8.2.13 a). Note that the synchrotron radiation flux exponentially decreased with time between the recharging procedures. Therefore each recorded spectrum had to be normalized by the synchrotron current. It was, however, not possible to record the synchrotron current parallel with the spectra (this option has only recently become available), therefore the presented XPEEM results are semi-quantitative.

The vertical scales of the C edge spectra were set by adjusting the difference in their intensities before (289 eV) and above the edge (308 eV) to a common arbitrary value of 10 [Mor01]. This procedure is a simplification (see Thomas-Reiche-Kuhn sum rule, Section 3.4.3) and causes deviations in the calculated polymer fractions in the top layer [Hitch03]. Proper alternative normalization procedures are in stage of development [Hitch03]. Our own efforts in this direction were realized in the B2 method, see below. The reference spectra at the oxygen and fluorine edges were not involved into the calculations.

High resolution XPEEM images were recorded from constant locations on each sample of the PSF/PMMA brushes for the 1s edges of C, O, and F at the photon energies corresponding to the pre-edge regions, the 1s→π* peaks, and far above (~30 eV) the edges. Lighter tone at the XPEEM images corresponds to higher photoelectron flux. Exposition time (t) was about 20 s per one high resolution image. Higher photoelectron flux linearly corresponds to lighter tone (12 bit tone depth) at an XPEEM image. In the case of the 1s O and F edges the images were scaled to equal arbitrary intensity and than the image recorded at the photon energy of the 1s→π* peak was normalized (divided) by the image recorded at the pre-edge photon energy. There were two 1s→π* peaks at the 1s C edge produced by PSF and PMMA in the case of PSF/PMMA brushes, and the pre-edge intensity was low. In this case the images were scaled to equal intensity and the image recorded at one of the two peaks was normalized by the image recorded at the other peak. The normalization procedure preserves the chemical contrast and removes the topographical effects described in Section 3.4.4 because they are constant at different photon energies.

Stacks (sequences) of XPEEM images (t ~ 1-2 s; 284.0-285.0 eV, ΔE=0.5 eV; 285.0-290.0 eV, ΔE=0.15 eV; 290.0-295.0 eV, ΔE=0.5 eV) were recorded at the 1s C edge from fresh areas on the samples of PSF/PMMA brushes. The time of recording the stacks was minimized in order to decrease the sample damage. NEXAFS spectra integrated over the
viewed areas were recorded simultaneously with the stacks and were scaled afterwards to the arbitrary vertical scale (the same as above) what was possible due to close intensities of the PSF and PMMA reference spectra near the upper end (294.5 eV) of the chosen photon energy range.

Calculation of the top layer composition was done via three methods. (A) *Semi-manual calculations* with Origin 5.0 software. Peaks and the overall intensity steps (Figure 3.4.3) in the reference spectra of PSF and PMMA were approximated with Gaussian curves:

\[
y = y_0 + \frac{A}{W \sqrt{\pi/2}} e^{-\frac{(x-x_c)^2}{w^2}}
\]

where \(y_0\), \(A\), \(W\), \(x_c\) are background, peak area, peak width at its half-height, and the peak position on the x axis. Each reference spectrum was presented as a sum of five Gaussian curves. Then the integral spectra recorded from the PSF/PMMA brushes were presented as a linear combination of the analytical approximations of the reference spectra. The average fraction of each polymer in the brush top layer was calculated as the ratio of the area of the PSF peak at 286.1 eV (or the PMMA peak at 289.3 eV) in the spectrum of the brush to the area of this peak in the corresponding reference spectrum. The correctness of the calculations was controlled with the sum of the fractions of both polymers which must be equal unity for each sample.

(B) *Automatic calculations* with free aXis00 2.1j (IDL 5.5 widget) software by Adam P. Hitchcock et al. [aXis00, IDL55] which applies a conjugate gradient optimization method to fit a spectrum to a set of reference spectra (see Figure 8.2.14 for an example). The methods A and B provided close results and therefore the automatic second method was preferred for the calculations. (B2) The difference from the method B is that the original NEXAFS spectra were set to equal arbitrary pre-edge intensity via multiplication by a certain number, while the difference in the intensities before and above the edge was not additionally adjusted (Appendix 12).

(C) *Semi-quantitative composition maps* [Mor01, Hitch01] were obtained from the recorded stacks of XPEEM images utilizing the aXis2000 2.1j software. The images in a stack were automatically aligned in order to remove their small shifts relative to one another. Composition maps for each polymer component were calculated through the least squares fit of the NEXAFS spectra at each pixel of a stack image to a sum of the reference spectra and a straight line representing the pre-edge background. The surface features of stamped brushes with a rough topographic profile provided different photoelectron intensities. This led to a
varying sum of the calculated PSF and PMMA fractions for different features. The obtained composition maps were additionally aligned in order to make the fractions sum equal to unity: the initial composition maps of PSF and PMMA were normalized by their sum with the IDL 5.5 software.
6. Properties of homopolymers constituting mixed brushes.


Reference measurements of advancing ($\Theta_{adv}$) and receding ($\Theta_{rec}$) water contact angles were carried out on spin-coated films of polymers, obtained from the bulk solutions upon synthesis of mixed polymer brushes. The measurements were performed with the *sessile drop* technique (Section 5.4), the results are summarized in Table 6.1.

PS is a hydrophobic polymer with $\Theta_{adv} \approx 93^\circ$. Substitution of 25% of hydrogen atoms in the aromatic rings with fluorine increases the advancing angle to $\sim 97^\circ$ and decreases the contact angle hysteresis ($\Theta_{adv} - \Theta_{rec}$) (PSF, Table 6.1). Other three polymers: PMMA, PMA, and P2VP contain polar hydrophilic groups and non-polar hydrophobic backbone. They show lower contact angles than the previous hydrophobic polymers. The heterogeneity increases in the row PMMA, PMA, P2VP and causes a rise of the contact angle hysteresis [Cha00, Cha02, Kob03, Rus02]. The values of contact angle hysteresis on the spin-coated polymer films are consistent with the corresponding values for the monocomponent polymer brushes (Table 6.2).

<table>
<thead>
<tr>
<th>Contact angle, °</th>
<th>PS</th>
<th>PSF</th>
<th>PMMA</th>
<th>PMA</th>
<th>P2VP</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Theta_{adv}$</td>
<td>92.8±0.9</td>
<td>96.7±1.6</td>
<td>76.9±2.1</td>
<td>82.0*± 2.6</td>
<td>71.8*± 1.7</td>
</tr>
<tr>
<td>$\Theta_{rec}$</td>
<td>76±2.2</td>
<td>84±3.7</td>
<td>64±6.2</td>
<td>41±1.1</td>
<td>25±1.1</td>
</tr>
<tr>
<td>$\Theta_{adv} - \Theta_{rec}$</td>
<td>17</td>
<td>13</td>
<td>13</td>
<td>41</td>
<td>46</td>
</tr>
</tbody>
</table>

* Stick-slip behavior observed, mean contact angle values are given.

6.2. Water contact angle measurements on surfaces of monocomponent polymer brushes.

Switching range of a surface energetic state of a binary mixed polymer brush is determined by properties of the constituent polymers. Influence of morphology and roughness will be discussed in Sections 7-8. Another factors may influence the surface state of the mixed brushes: (1) stretching of polymer chains in the grafted layer perpendicular to a substrate; (2) heterogeneity of constituent polymers may cause different functional groups of the same polymer to occupy the brush surface upon exposure to different solvents; (3) traces of a
solvent remaining inside of a mixed polymer brush after the fast drying procedure (Section 5.4) can influence the measured contact angle values.

Table 6.2. Water contact angles on “grafted from” monocomponent polymer brushes after: cold Soxhlet extraction in THF with following storage at ambient conditions for 24 h; exposure for 5 min to different solvents followed by the fast drying procedure (Section 5.4); annealing in vacuum at 150º C for 6 h.

<table>
<thead>
<tr>
<th>Contact angle, °</th>
<th>PS¹</th>
<th></th>
<th></th>
<th></th>
<th>P2VP¹</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>amb.</td>
<td>tolu-</td>
<td>ethanol</td>
<td>water</td>
<td>pH</td>
<td>annealed</td>
<td>amb.</td>
<td>tolu-</td>
</tr>
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* Stick-slip behavior observed, mean contact angle values are given.

¹ the monocomponent brush synthesized parallel with the brush SVP25 (Appendix 3).
² the monocomponent brush synthesized parallel with the brush FSMA9 (Appendix 3).
³ the monocomponent brush synthesized parallel with the brushes FSA1 and AFS1 (Appendix 3).

The monocomponent brushes were synthesized parallel with binary mixed polymer brushes in the same reactor, therefore, their parameters can be extracted from the data on the relevant mixed brushes in Appendices 3-4.
The difference between the contact angles on the spin-coated films (Table 6.1) and on the corresponding “grafted from” monocomponent polymer brushes after exposure to THF with following storage at ambient conditions for 24 h (Table 6.2) was mainly within 2º. The value of $\Theta_{\text{adv}}$ on spin-coated PMMA exceeded the corresponding value on the monocomponent PMMA brush, stored at ambient conditions for 24 h, by 3º probably due to some artifact in formation of the film upon spin-coating. The value of $\Theta_{\text{rec}}$ for spin-coated PSF was 4º lower than for the corresponding monocomponent brush stored for 24 h at ambient conditions. No notable difference in contact angles common for all respective pairs of the spin-coated and the “grafted from” films, stored for 24 h at ambient conditions, was found. This means that stretching of the polymer chains in the brushes does not affect the contact angles.

Let us consider the water contact angles on the monocomponent brushes after exposure to the organic solvents (Table 6.2). The $\Theta_{\text{rec}}$ stays in the most cases roughly at the same value as after the storage of the brushes at ambient conditions for 24 h. The exceptions are: the PSF brush exposed to THF and the PMMA brush exposed to any solvent. Treatment in the solvents does not significantly change the $\Theta_{\text{adv}}$ of the PS and P2VP brushes, while it decreases the $\Theta_{\text{adv}}$ of the PSF, PMA, and PMMA brushes by 3-7º. It is obvious that the change in the contact angles is small on the brushes of the homogeneous polymers PS and P2VP, while it is bigger for the brushes of the heterogeneous PSF, PMA, and PMMA. The heterogeneous polymers hide their hydrophobic groups below the film surfaces upon exposure to the solvents [Cha00]. We conclude from the small change of the contact angles on the brushes of the homogeneous PS and P2VP that the influence of the solvent traces remaining inside of the brush layers on the contact angles is negligible.

The P2VP brush dried after the exposure to acidic water showed much lower contact angles than after the treatment with the organic solvents (Table 6.2). This happens due to the acid remaining in the brush and forming salt with the basic nitrogen atoms in the P2VP monomer units. The acid can be fully removed from a brush through washing it with big amount of water, and the initial state of the brush can be restored. The contact angles on the reference PS brush decreased insignificantly after exposure to the acidic water (no chemical interaction). It should be noted that the error for the

![Figure 6.1](66)

**Figure 6.1.** Stick-slip behavior of an advancing water droplet on a P2VP brush.
$\Theta_{\text{adv}}$ on the P2VP brush (3-4°) is higher than for the other monocomponent brushes due to the *stick-slip* behavior of the water droplets (Figure 6.1, Section 3.2.2).

The monocomponent PS and P2VP brushes were annealed for 6 h in vacuum at 150° C together with the mixed PS/P2VP brushes (Section 9). The $\Theta_{\text{adv}}$ and $\Theta_{\text{rec}}$ on the annealed PS brush increased by ~7° and ~1°, respectively, relative to the same brush stored for 24 h at ambient conditions after exposure to THF (Table 6.2). We explain this effect by evaporation of absorbed liquids (water and organic solvents) upon the annealing. This suggestion is supported by strong charging of the annealed brushes observed upon approach of an AFM tip to the samples. The charging was never observed on non-annealed brushes (Section 6.3).

The annealed P2VP brush showed surprisingly pronounced stick-slip behavior of the $\Theta_{\text{adv}}$ in the range 85-113° lying notably higher than the ordinary $\Theta_{\text{adv}}$ angles on the non-annealed P2VP brush (Table 6.2). At the same time the $\Theta_{\text{rec}}$ was notably lower than on the non-annealed P2VP brush (Table 6.2) what suggests hydrophilic nature of this surface and contradicts an assumption about hydrophobic contamination of the surface. The unusually high advancing contact angle and the decrease of the receding contact angle could be explained by increased roughness but it is not the case (Section 6.3). We do not have a satisfactory explanation of this effect up to now.

### 6.3. Morphologies of “grafted from” monocomponent polymer brushes.

Morphologies of the PS and P2VP monocomponent brushes were studied in the intermittent tapping mode AFM after exposure to solvents of various thermodynamic quality (Appendix 8.1) and after annealing (Appendix 8.2). The brushes exposed to the solvents revealed smooth topography (RMS roughness < 1 nm) and uniform phase images. The roughness of the monocomponent PS and P2VP brushes increased insignificantly after exposure to poor solvents. Some of the topography images showed bumps produced by defects of the silane layer underneath the brushes (Section 4.2.1). The morphology of the annealed PS brush was smooth excluding the big scale defects from the consideration (Appendix 8.2 b). The annealed P2VP brush adopted a nano-pattern (Appendix 8.2 a) with a characteristic height of the features ~ 5 nm at the total thickness of the brush 10 nm (Section 6.2, Appendix 3). The nano-pattern was formed probably due to segregation of the P2VP from vacuum. The RMS roughness of the annealed P2VP brush was lower than for the annealed PS brush because the large-scale defects were absent. The AFM phase image of the annealed PS brush is uniform, while the phase image of the annealed P2VP brush is affected by the topographic nano-pattern.
The “grafted from” PSF and PMA monocomponent brushes were studied with AFM by Lemieux, M. et al. [Lem03]. These two brushes showed smooth morphologies (Appendix 8.3), what together with the data about the PS and P2VP brushes prompt a generalization that morphologies of monocomponent polymer brushes are smooth.
7. Switching of surface composition of binary mixed homopolymer brushes.

For investigation of switching of surface composition, we chose a model mixed polymer brush composed of PS and P2VP. These two polymers are well known, commercially available, accessible via radical polymerization, and have a sufficient difference in their wetting properties (see Section 6). The surface switching behavior of other systems like PSF/PMMA and PSF/PMA, synthesized for specific purposes, was also investigated and is reported here.

7.1. Kinetics of switching of binary mixed polymer brushes upon exposure to selective solvents.

A mechanism of switching of mixed polymer brushes in selective solvents can be considered as a combination of two main processes: (1) penetration of a solvent into the grafted glassy polymer film and (2) rearrangement of the lubricated (“unfrozen”) polymer segments. It was reasonable to investigate the switching kinetics on a thick brush which was expected to have a smaller switching rate due to the slower two processes determined above. Thus a PS/P2VP brush synthesized via the “grafted from” technique was chosen for the kinetic experiments because this synthetic technique provides mixed brushes of a significantly bigger thickness unlike the easier “grafting to” technique (Section 2.3). Surface of the brush SVP25 was switched upon a long (overnight) exposure to ethanol (the selective solvent for P2VP) or toluene (the selective solvent for PS) to the hydrophilic or the hydrophobic state, respectively. Afterwards switching to the opposite state upon short consecutive exposures to a solvent of the opposite selectivity (toluene, ethanol or acidic water of pH 2.5) was documented via measurements of the advancing contact angle of a water droplet on the mixed brush as described in Section 5.4. The results are presented in Figure 7.1 a-c.

The time of switching by each of the three solvents was shorter than the time (6 s) required to immerse the brush into the solvent, take it out, and dry in nitrogen flux. The rapid switching led to an idea to check: (1) whether a PS/P2VP brush can be switched by neutral water (pH 7) and (2) whether the switching time is longer than in the previous cases. We found that the switching of the brush by neutral water from hydrophobic to hydrophilic occurred within 500 s (8.5 min) (Figure 7.1 d). An obvious explanation for the increase of the switching time is the smaller rate of penetration of water (which is poor solvent for the brush polymers) into the brush in comparison with acidic water and the organic solvents.
Figure 7.1. Switching of a PS/P2VP brush SVP25 (Appendix 3) by selective solvents. Water advancing contact angle ($\Theta_{\text{adv}}$) and P2VP fraction on the brush surface are plotted vs. time of exposure to a particular solvent. The experimental data were fitted with exponential functions. Calculation of the surface composition is discussed in Section 5.4.

Time of switching of a surface state of a PSF/PMMA brush FSMA9 (36 nm thick, Appendix 3) from hydrophilic ($\Theta_{\text{adv}}$ 72.0º) to hydrophobic ($\Theta_{\text{adv}}$ 93.1º) by toluene and back to the initial state by chloroform (acetone) was shorter than 6 s (Figure 7.3 a). A shape of the obtained kinetic curves was similar to those in Figure 7.1 a-c. Although the switching kinetics of thick (60-130 nm) PSF/PMMA and PSF/PMA brushes was not measured with so high time resolution as in these experiments, their switching time was found less than 30 s.

7.2. Reversibility of switching of binary mixed polymer brushes upon exposure to solvents of various thermodynamic quality.

Knowing the switching time of a brush surface, it is possible to check reversibility of the switching. The PS/P2VP brush SVP25 (Appendix 3) was consecutively exposed to toluene, chloroform, ethanol, once again to toluene, HCl solution in water (pH 2.5), washed with big amount of water of pH 7, then exposed to ethanol, toluene, and neutral water again.
The exposure time was 5 min in all the cases. The advancing and receding contact angles ($\Theta_{\text{adv}}$ and $\Theta_{\text{rec}}$) were measured on the brush after each treatment followed by the fast drying procedure in $N_2$ flux according to Section 5.4. Unlike the P2VP monocomponent brush, the mixed PS/P2VP brushes showed no stick-slip behavior of advancing water droplets with the only exception after exposure of them to the acidic water. The results are plotted in Figure 7.2 a. The $\Theta_{\text{adv}}$ and $\Theta_{\text{rec}}$ are reproducible after the three exposures to toluene, the two exposure to ethanol, and the two exposure to neutral water and do not depend on previous history. Reproducibility and reversibility of the switching was additionally checked with five cycles of consecutive treatments of the brush with toluene and ethanol (Figure 7.2 b). The $\Theta_{\text{adv}}$ values are reproducible, while the $\Theta_{\text{rec}}$ jumps a little bit up and down after exposure to toluene due to not very proper measurements. The values of the $\Theta_{\text{rec}}$ in Figure 7.2 b differ from the

**Figure 7.2.** Switching of a PS/P2VP brush SVP25 by various solvents.

![Figure 7.2](image1)

**Figure 7.3.** Switching of a PSF/PMMA brush FSM A9 (Appendix 3). (a) Kinetics of switching by chloroform and toluene. (b) Reproducibility of the surface state after switching by various solvents. Exposure time was 5 min to each solvent.
corresponding values on Figure 7.2 a because they were obtained from two different areas on
the brush.

Reversibility and reproducibility of the surface state upon switching with organic
solvents was found also for PSF/PMMA brushes (Figure 7.3 b). The switching time was less
than 6 s (Figure 7.3 a). The values of $\Theta_{\text{adv}}$ and $\Theta_{\text{rec}}$ were well reproducible independently on
history of previous treatment (Figure 7.3 b). Chloroform being less polar caused the lower
$\Theta_{\text{adv}}$ and the lower hysteresis ($\Theta_{\text{adv}} - \Theta_{\text{rec}}$) values for the PSF/PMMA brush than acetone.
Explanation for this effect is provided in Section 7.4.

Stability of the surface state of PSF/PMMA brushes upon contact with water was
checked. The brush FSMA9 was switched to the hydrophobic state by exposure to toluene and
dried in N$_2$ flux. The $\Theta_{\text{adv}}$ and the $\Theta_{\text{rec}}$ were measured. The brush was exposed afterwards to
water for sufficiently long periods of time. The brush was dried in N$_2$ flux, and the $\Theta_{\text{adv}}$ and
the $\Theta_{\text{rec}}$ were measured again. They decreased by 1º and 2º, respectively, after 1 h of exposure
to water and by 5º and 12º, respectively, after exposure to water for 2 days. Hence, the surface
of PSF/PMMA brushes remains stable within the time scale of a water contact angle
measurement. Upon longer exposure to water, which is a poor solvent for the brush polymers,
the top brush layer rearranges slowly its structure.

Various PS/P2VP brushes with mass fraction of P2VP ranging from 0 to 100% and a
total brush thickness from 2.5 to 33 nm were synthesized. Their advancing and receding
contact angles after exposure to the selective organic solvents (toluene, ethanol) are presented
at 3D diagrams in Appendix 6 and at the 2D projections given in Figure 7.4. The receding
contact angles (Appendix 6 b and Figure 7.4 c-d) measured on thin ($\leq$20 nm) PS/P2VP
brushes after toluene and ethanol, had similar values lying between 25º and 30º. This
observation can be explained by switching of the PS/P2VP brushes to the hydrophilic state
induced by the water droplet itself upon the contact angle measurements (Section 7.1).
However, the receding contact angle for the thicker (27 nm) PS/P2VP brush SVP25 exposed
to toluene was much higher (50º) than after exposure to ethanol (25º). We consider that the
thicker PS/P2VP brush forms a thicker top layer of the hydrophobic PS upon exposure to
toluene. The thicker is the top PS layer, the bigger is a barrier, which slows penetration of
water into the brush, and, consequently, the slower is the switching. Therefore, we assume,
that the receding contact angle on a PS/P2VP brush exposed to toluene increases rather not
with increasing the total brush thickness but with increasing the grafted amount of PS. It
should approach a certain limiting value at longer exposure to water and then stay unchanged.
More experiments are needed to verify the assumption.
**Figure 7.4.** Water advancing contact angles on the PS/P2VP brushes exposed to toluene, ethanol, and chloroform vs. (a) thickness of the brushes and vs. (b) P2VP mass fraction in the brushes. Water receding contact angles for the PS/P2VP brushes vs. (c) thickness of the brushes and vs. (d) P2VP mass fraction in the mixed brushes. The $\Theta_{\text{adv}}$ and $\Theta_{\text{rec}}$ angles on the monocomponent brushes are marked with dashed black and light gray horizontal lines, respectively. PS/P2VP brush surface composition vs. the brush thickness (e) and vs. P2VP mass fraction in the mixed brushes (f).
Figure 7.4 a shows that: (1) the water advancing contact angle ($\Theta_{\text{adv}}$) on the PS/P2VP brushes exposed to toluene increases from 84-90° for the thin (<10 nm) brushes to 92-95° for the thicker (>20 nm) brushes; (2) the $\Theta_{\text{adv}}$ after exposure to ethanol decreases from 70-72° for the thin (<10 nm) brushes to 68-70° for the thicker (>20 nm) brushes; (3) the switching range ($\Theta_{\text{adv}}$) of the thicker brushes upon exposure to toluene and ethanol is broader than the range limited by the $\Theta_{\text{adv}}$ values for the monocomponent PS and P2VP brushes. These effects result in the unusual P2VP surface fraction calculated via the Cassie equation (Section 5.4) for the PS/P2VP brushes, exposed to toluene and ethanol (Figure 7.4 e). The P2VP surface fraction becomes often lower than 0% or higher than 100%, respectively. The most probable reason for this behavior could be roughness of the mixed brushes which increases with their increasing thickness. On the other hand, the RMS roughness of the PS/P2VP brushes ~26 nm thick is less than 6 nm (Section 8.1.2, Figure 8.1.11). It is too low value to expect the effects described above. However, this question requires a special study.

The Figure 7.4 b guides to an assumption that if the just described effects had been eliminated, the $\Theta_{\text{adv}}$ values for the PS/P2VP brushes treated in the selective solvents, toluene and acetone, would have been constant in the broad range (0.19-0.84) of the P2VP mass fraction in the PS/P2VP brushes. Assuming that the surface of the PS/P2VP brushes exposed to toluene or ethanol is fully covered by PS or P2VP (see Figure 7.4 f), respectively, the switching ($\Theta_{\text{adv}}$) of the PS/P2VP brushes would have been between the average $\Theta_{\text{adv}}$ values for the monocomponent PS (91.7°) and P2VP (72.5°) brushes, respectively. We assume further for the PS/P2VP brushes with highly asymmetric composition, when mass fraction of one (A) of the two polymers approaches unity, that the other polymer (B) cannot fully cover the brush surface anymore. Although, no highly asymmetric PS/P2VP brushes have been experimentally studied, the experimental data were approximated with hyperbolas in Figure 7.4 b, f taking all our assumptions into account.

The PS/P2VP brushes exposed to chloroform showed intermediate values of the water advancing and receding angles. Unfortunately, these measurements were carried out on few samples (Figures 7.2 a, 7.4 a-d). The P2VP fraction after exposure to chloroform (Figure 7.4 e-f) was in the range from 20 to 60%. Three conclusions are derived from this: (1) both polymers PS and P2VP are present on the top surface after exposure of a PS/P2VP brush to chloroform, (2) chloroform is a non-selective solvent for PS/P2VP brushes, (3) the surface composition of a mixed brush after exposure to a non-selective solvent may depend on the ratio of the polymers in the brush.
7.3. Switching of surface state of binary polymer brushes by binary solvents.

It is clear from the Sections 7.1-2 that the surface of the binary mixed brushes adopts different states upon exposure to different solvents. We addressed a question whether the surface composition of such a brush changes continuously or discontinuously, if the brush is exposed to a binary solvent with gradually changing volume fraction of one of the components from 0 to 1. The brush state in such a solvent mixture reaches equilibrium at each composition of the mixture, therefore the transition of the brush state is reversible at each its point unlike switching of a binary brush just upon immersing it to a solvent.

We took a PS/P2VP brush for this experiment because the constituent polymers are quite homogeneous, and such brushes provide relatively smooth morphologies (Section 8.1). The first experiment was done with ethanol + toluene mixtures because of broad range (ΔΘ_{adv} 20º) of switching of PS/P2VP brushes by these separate solvents. A series of ethanol + toluene mixtures was prepared with the ethanol volume fraction ranging from 0.000 to 1.000 with the step ~0.167. The water advancing contact angles were quickly measured on the PS/P2VP brush after exposure to each of these mixtures and a discontinuity in the measured values was found at the ethanol volume fraction between 0.500 and 0.667 (Figure 7.5 a). A new series of ethanol + toluene mixtures was prepared within the range of the ethanol volume fraction from 0.500 to 0.667 with a smaller step ~0.0167. Water contact angle measurements on the PS/P2VP brush after exposure to these new mixtures showed that the brush surface composition changes discontinuously: the Θ_{adv} drops from 92º to 70º upon change in the

![Figure 7.5](image-url)  
**Figure 7.5.** Switching of surface composition of the PS/P2VP brush SVP25 (Appendix 3) upon exposure to binary mixtures of (a) ethanol + toluene and (b) ethanol + chloroform with gradually changing volume fraction of ethanol from 0 to 1. Each point at the diagram was averaged from three contact angle measurements at different locations on the sample.
ethanol volume fraction from 0.517 to 0.567 (Figure 7.5 a).

The same PS/P2VP brush was exposed to a series of ethanol + chloroform mixtures in the next experiment. The brush surface composition changed discontinuously at the ethanol volume fraction between 0.03 and 0.08 (Figure 7.5 b).

It is clear from these two experiments that the switching of the brush surface occurs in the very narrow regions of the binary solvent composition, while the brush surface composition remains almost not changed at the other compositions of the binary solvents. Although Müller’s SCF theoretical approach (Section 2.2) does not consider solvent mixtures but only monocomponent solvents, this experiment supports its prediction about first order phase transitions between different morphologies of binary mixed brushes.

7.4. Composition of the brush top layer determined with X-ray Photoelectron Spectroscopy (XPS).

Composition of a mixed brush top layer calculated via the Cassie equation from the advancing water contact angles has sometimes a negative value or exceeds 100% (Sections 7.2-3). Additionally, it will be shown in Section 7.5 that the contact angle may be strongly influenced by roughness of the brush surface. Therefore, the top layer composition for selected PS/P2VP and PSF/PMMA brushes was independently determined with XPS (Table 7.2-3).

Fractions of the hydrophilic polymers in the top layer were calculated for two sampling depths 8 and 2 nm at the take-off angles 0º and 75º (Section 5.6), respectively, as described below. Normalized XPS peak areas [5.6.1] for particular kinds of atoms are proportional to concentrations of these kinds of atoms in a sample. For a polymer sample, the normalized peak areas are proportional to the number of atoms of a particular kind in a monomer unit. Let us assign the normalized 1s peak areas for carbon, nitrogen, and oxygen per one corresponding atom in a monomer unit (Table 7.1) as $I_A$, where A means the atom kind and can be C, N, or O, respectively. For the P2VP monocomponent brush the following equation is true (Table 7.2): $\frac{I_N}{7I_C} = 0.1272 = \gamma_0$ \[7.1\].

The ratio $I_N/I_C$ must be equal to unity after the normalization [5.6.1] in the ideal case. It is, however, 0.89 in the reality due to impurities adsorbed from atmosphere [Bri90]. For a PS/P2VP brush after treatment in any solvent, the molar fraction of PS $(1 - \phi_1)$ in the brush top layer must be accounted:

$$\frac{\phi_1 I_N}{8 \cdot (1 - \phi_1) I_C + 7 \cdot \phi_1 I_C} = \gamma$$ \[7.2\].
where \( \varphi_i \) is the molar fraction of P2VP in the brush top layer, \( \gamma \) is the ratio N/C of the total nitrogen and carbon 1s peak areas. From these two equations, the P2VP fraction in the PS/P2VP brush top layer is:

\[
\varphi_1 = \frac{8I_C}{I_C + \frac{I_N}{\gamma}} \times 100\% = \frac{8\gamma}{\gamma + 7\gamma_0} \times 100\% = \frac{\gamma}{\gamma_0 + 7} \times 100\% \quad [7.3].
\]

The P2VP fraction in the top layer of PS/P2VP brushes (\( \varphi_1 \)) equals approximately to \( 8\gamma/(7\gamma_0) \), the approximation is better for the top layers enriched with PS.

In the analogous way for the monocomponent PMMA and the PSF/PMMA brushes, respectively, taking into account the data from Tables 7.1, 7.3:

\[
\frac{2I_O}{5I_C} = 0.283 = \gamma_0 \quad [7.4]; \quad \frac{2\varphi_2 I_O}{8(1-\varphi_2)I_C + 5\varphi_2 I_C} = \gamma \quad [7.5],
\]

where \( \varphi_2 \) and \( (1-\varphi_2) \) are molar fractions of PMMA and PSF in the brush top layer, respectively. The ratio \( I_O/I_C \) is also less than unity due to impurities adsorbed from atmosphere and equals 0.7075. From the last two equations, the PMMA fraction in the PSF/PMMA brush top layer is:

\[
\varphi_2 = \frac{8I_C}{2I_O + 3I_C} \times 100\% = \frac{8\gamma}{5\gamma_0 + 3\gamma} \times 100\% = \frac{\gamma}{5 + 3\gamma_0} \times 100\% \quad [7.6].
\]

According to [7.6], the PMMA fraction in the top layer of PSF/PMMA brushes (\( \varphi_2 \)) significantly differs from the value of \( \gamma/\gamma_0 \).

**Table 7.1.** Molecular formulas of monomer units for PS, P2VP, PSF, and PMMA.

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<th>Polymer</th>
<th>Molecular formula of a monomer unit</th>
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<td>PS</td>
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<tr>
<td>P2VP</td>
<td>C₄H₇N</td>
</tr>
<tr>
<td>PSF</td>
<td>[C₈H₈]₀.70-0.75[C₈H₃F₅]₀.30-0.25 = C₈H₆.5₀⁻⁶.₇₅F₁₅₀⁻¹.₂₅</td>
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<tr>
<td>PMMA</td>
<td>C₅H₈O₂</td>
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Table 7.2. XPS data on the top layer composition of a PS/P2VP brush SVP25 (Appendix 3) after exposure to different solvents. P2VP fraction in the brush top layer ($\phi_1$) was calculated according to [7.3]. $\gamma$ and $\gamma_0$ are the ratios N/C of the normalized 1s peak areas [5.6.1] for the mixed PS/P2VP and for the monocomponent P2VP brush (10 nm thick), respectively.

<table>
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<th>PS brush</th>
<th>P2VP brush</th>
<th>PS/P2VP exposed to</th>
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<th>toluene</th>
<th>water</th>
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<td>27</td>
<td>66</td>
<td></td>
</tr>
<tr>
<td></td>
<td>P2VP fraction $\phi_1$, %</td>
<td>---</td>
<td>---</td>
<td>79</td>
<td>30</td>
<td>69</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$(\gamma/\gamma_0)_75^\circ/(\gamma/\gamma_0)_0^\circ$, %</td>
<td>---</td>
<td>---</td>
<td>121</td>
<td>91</td>
<td>119</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\phi_1(75^\circ)/\phi_1(0^\circ)$, %</td>
<td>---</td>
<td>---</td>
<td>119</td>
<td>92</td>
<td>118</td>
<td></td>
</tr>
<tr>
<td>RMS roughness (AFM data), nm</td>
<td>0.6</td>
<td>1</td>
<td>3</td>
<td>6</td>
<td>&lt;6</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Roughness was estimated on the base of AFM measurements on other brushes.

Analysis of the XPS data on composition of the top layers of the mixed brushes (Tables 7.2-3) leads to the following conclusions: (1a) toluene is selective for PS, ethanol is selective for P2VP upon treatment of the PS/P2VP brushes. (1b) Due to the poor thermodynamic quality, water provides the smaller perpendicular gradient of P2VP fraction than ethanol does. (1c) Toluene is selective for PSF, while acetone is selective for PMMA upon treatment of the PSF/PMMA brushes. The conclusions 1a, 1c agree with the results of the contact angle measurements (Section 7.2). (1d) Chloroform has intermediate polarity if compared with toluene and acetone and acts as a non-selective solvent for PSF/PMMA brushes. (2) The P2VP fraction in the top layer of the PS/P2VP brush measured at the XPS take-off angle 75° is higher than at the take-off angle 0° after exposure of the brush to ethanol and water. The opposite situation takes place after exposure to toluene. This means that the P2VP fraction rises up from the deeper layers to the brush top after exposure of the brush to the solvents selective for P2VP, while the P2VP fraction decreases in the same direction after exposure of the brush to the solvent of the opposite selectivity. (3) On the contrary, the PMMA fraction in the top layer of the PSF/PMMA brush is always lower at the take-off angle 75° than at 0°, regardless of the solvent selectivity. Segregation of the fluorinated units of PSF to the brush surface thus providing lower surface energy can be a reason for that [Cha00]. In
the case of the PSF/PMMA brush exposed to acetone, the rough cluster morphology (Section 8.2.1) may increase the effect (Figure 7.6). The typical height (H) and the typical lateral size of the clusters ($L_c^{AFM}$) for such brushes are 40-60 nm and 150-200 nm, respectively. The height of a cluster and the half of its base diameter form a right-angled triangle with the top angle: $\arctg(L_c^{AFM}/(2H)) = 59-62^\circ$ (Figure 7.6). This angle is sufficient to cause shadowing of the rich in PMMA valleys surrounding the PSF clusters at the XPS take-off angle 75°.

Table 7.3. XPS data on the top layer composition of PSF/PMMA brush FSMA9 (Appendix 3) after exposure to different solvents. PMMA fraction in the top brush layer ($\varphi_2$) was calculated according to [7.6]. $\gamma$ and $\gamma_0$ are the ratios O/C of the normalized 1s peak areas [5.6.1] for the PSF/PMMA and the monocomponent PMMA brushes.

<table>
<thead>
<tr>
<th>take-off angle, °</th>
<th>top layer composition</th>
<th>PSF</th>
<th>PMMA</th>
<th>PSF/PMMA brush exposed to acetone</th>
<th>chloroform</th>
<th>toluene</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1s peak area ratio O/C, $\gamma$</td>
<td>0*</td>
<td>0.283*</td>
<td>0.2602</td>
<td>0.208</td>
<td>0.0938</td>
</tr>
<tr>
<td></td>
<td>1s peak area ratio F/C</td>
<td>---</td>
<td>0</td>
<td>0.0114</td>
<td>0.0316</td>
<td>0.0856</td>
</tr>
<tr>
<td></td>
<td>$\gamma/\gamma_0$, %</td>
<td>0</td>
<td>100</td>
<td>92</td>
<td>74</td>
<td>33</td>
</tr>
<tr>
<td></td>
<td>PMMA fraction $\varphi_2$, %</td>
<td>0</td>
<td>100</td>
<td>95</td>
<td>82</td>
<td>44</td>
</tr>
<tr>
<td>75</td>
<td>1s peak area ratio O/C, $\gamma$</td>
<td>---</td>
<td>---</td>
<td>0.2386</td>
<td>0.1982</td>
<td>0.0785</td>
</tr>
<tr>
<td></td>
<td>1s peak area ratio F/C</td>
<td>---</td>
<td>---</td>
<td>0.0123</td>
<td>0.0252</td>
<td>0.0799</td>
</tr>
<tr>
<td></td>
<td>$\gamma/\gamma_0$, %</td>
<td>---</td>
<td>---</td>
<td>84</td>
<td>70</td>
<td>28</td>
</tr>
<tr>
<td></td>
<td>PMMA fraction $\varphi_2$, %</td>
<td>---</td>
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<td>90</td>
<td>79</td>
<td>38</td>
</tr>
<tr>
<td></td>
<td>($\gamma/\gamma_0$)$<em>{75^\circ}/(\gamma/\gamma_0)</em>{0^\circ}$, %</td>
<td>---</td>
<td>---</td>
<td>92</td>
<td>95</td>
<td>84</td>
</tr>
<tr>
<td></td>
<td>$\varphi_2(75^\circ)/ \varphi_2(0^\circ)$, %</td>
<td>---</td>
<td>---</td>
<td>94</td>
<td>97</td>
<td>86</td>
</tr>
<tr>
<td>RMS roughness (AFM data), nm</td>
<td>0.4**</td>
<td>0.55**</td>
<td>19.8</td>
<td>2.4</td>
<td>10.8</td>
<td></td>
</tr>
</tbody>
</table>

* The reference samples were spin-coated films 20-40 nm thick. ** Measured on the PSF and PMMA monocomponent brushes 30 and 38 nm thick, respectively.

(4) The fraction of PMMA in the top layer of the PSF/PMMA brush according to the XPS results is higher after exposure to acetone than after chloroform. This contradicts with the higher advancing water contact angle ($\Theta_{adv}$) on the PSF/PMMA brush after exposure to acetone than after exposure to chloroform (Figure 7.3 b). The most obvious explanation of this contradiction is influence of increased roughness of the cluster morphology of the PSF/PMMA brush exposed to acetone (Section 8.2.1) on the contact angle value. Validity of this idea is supported by the bigger contact angle hysteresis ($\Theta_{adv}-\Theta_{rec}$) on the PSF/PMMA
brush after exposure to acetone than after chloroform (Figure 7.3 b). It is known from Section 3.2.2 that the hysteresis may be caused by increased roughness. The morphology of this brush after exposure to chloroform is smooth, what assumes the smaller contact angle hysteresis and determination of the $\Theta_{\text{adv}}$ value rather by the surface composition than by roughness.

**Figure 7.6.** The valleys rich in PMMA, which lie between the PSF clusters on the PSF/PMMA brush exposed to acetone, may be not sensed by XPS at the take-off angle 75º. This may cause lower apparent PMMA fraction in the top layer (see further explanations in the text).

### 7.5. Effect of roughness of PSF/PMA brushes on water contact angles.

PSF/PMA brushes provided a very rough morphology after exposure to acetone (Section 8.3) what led to a significantly increased advancing water contact angle ($\Theta_{\text{adv}}$) and high water contact angle hysteresis ($\Theta_{\text{adv}} - \Theta_{\text{rec}}$) in comparison with smooth morphologies of these brushes after exposure to THF and toluene (Table 7.4).

According to Wenzel’s formula [3.2.15] the water advancing contact angle on the FSA1 and AFS1 brushes (Appendix 3) after exposure to acetone would be equal 103.3 and 101.7, respectively, if the surfaces were smooth. These values are high above the $\Theta_{\text{adv}}$ value (98.7º) on smooth PSF (Table 6.2) what leads to a conclusion that Wenzel’s regime of water droplet behavior does not take place in this case. It is reasonable to suggest that the Cassie regime takes place. The part of the water droplet bottom surface, which contacts the brush, was calculated according to the equation [3.2.14] assuming that the brush surface after exposure to acetone is fully covered with PMA ($\Theta_{\text{adv}}$ 80.4º). We obtained 66% and 72% for the brushes FSA1 and AFS1, respectively. The rest bottom surface of the water droplet contacts the air captured between the elevations on the brush surfaces. If these conditions are true, the contact line of water, brush, and air phases should locate on the vertical walls of topographical features of the brushes as it is shown for the brush FSA1 in Appendix 7 (see also the AFM study of this brush in Section 8.3).
Table 7.4. Effect of roughness of PSF/PMA brushes on water contact angles. $r$ is the ratio of the surface area to the area of its projection onto the substrate plane. The parameters of the brushes are given in Appendix 3.

<table>
<thead>
<tr>
<th>Brush code</th>
<th>exposed to toluene</th>
<th>exposed to THF</th>
<th>exposed to acetone</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>RMS roughness, nm</td>
<td>$\Theta_{\text{adv}}, ^\circ$</td>
<td>$\Theta_{\text{rec}}, ^\circ$</td>
</tr>
<tr>
<td>FSA1</td>
<td>1.8</td>
<td>95.7 ±1.24</td>
<td>63.5 ±7.28</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.01</td>
<td></td>
</tr>
<tr>
<td>AFS1</td>
<td>---</td>
<td>96.4 ±0.65</td>
<td>53.1 ±5.14</td>
</tr>
</tbody>
</table>
8. Switching of morphology of binary mixed polymer brushes.

Polymer components in mixed brushes are usually incompatible, therefore they segregate from one another. As it was theoretically discussed in Section 2.2, the nano-phase segregation takes place in the lateral and perpendicular directions and creates diversity of possible morphologies. Although the theory describes morphologies of mixed brushes in thermodynamically equilibrium states i.e. in melt and in solvents, it is easier experimentally to perform AFM investigations of the morphologies at ambient temperature and in dry state. We assume that the morphologies observed for the dried brushes are relevant to the morphologies in solvents to which the mixed brushes have been exposed [Min01, Min02a]. The ground for that: (1) the surface composition of mixed brushes is reproducible after their exposure to a certain solvent independently on history of previous treatments (Section 7, [Sid99]); (2) morphology after treatment in a particular solvent is reproducible and independent on previous history of treatments in other solvents (see AFM data in Section 8.1.1). The last two statements are true, if the solvent has sufficient thermodynamic quality to swell both brush polymers to certain extend; if the solvent is too poor for one of the polymers, traces of the previous brush state may remain.

8.1. PS/P2VP brushes.

8.1.1. Morphologies of PS/P2VP brushes after exposure to different solvents.

Let us compare morphologies of two PS/P2VP brushes after exposure to toluene (Figures 8.1.1 a and 8.1.2 b), ethanol (Figures 8.1.1 d and 8.1.2 a, c), and chloroform (Figures 8.1.1 c and 8.1.2 d).1 The morphologies of the two brushes are similar after exposure to the same solvents: (1) round clusters after exposure to toluene, (2) interconnected network of elevations with pits after exposure to ethanol, (3) worm-like morphology with the lowest RMS roughness after treatment in chloroform. The latter morphology provides a prominent phase contrast. Although the phase z range after treatment in chloroform is the smallest (low topographic contribution because of the smooth morphology, see Section 3.3.3), there are two distinct kinds of features providing different phase shifts. This is illustrated by an area-vs.-phase diagram (Figure 8.1.3) which reveals two dominant phase shifts for the brushes SVP6 and SVP12 after treatment in chloroform, while only one phase shift dominates after treatment of the brushes in ethanol and toluene. Such diagrams are representative, if the dominant phase shifts cover sufficiently big areas on an AFM phase image. This restriction

1 The morphology after treatment of the brush SVP6 in water will be discussed later within this Section.
allows us to ignore the topography interference which takes place on slopes of topographic features (Section 3.3.3) and broadens often the phase z range. It will be shown below (Section 8.1.2) that the morphologies obtained after exposure of the PS/P2VP brushes to toluene and ethanol have compact aggregation of one brush polymer underneath the top brush layer, what obscures the maximum of the respective phase shift in area-vs.phase diagrams. In the same manner, non-symmetric PS/P2VP brushes exposed to chloroform may produce one strong and one reduced peak in such a diagram as shown in Figure 8.1.3 a. Note that the dark and light features at the phase images of the PS/P2VP brushes, treated in chloroform, correlate with the elevations and valleys at the relevant topography images, respectively. Topography interference at the phase image would create a different correlation (Section 3.3.3, Figure 3.3.12).

Presence of the two distinct phase shifts in the AFM images recorded from the PS/P2VP brushes treated in chloroform agrees with the intermediate value of the advancing contact angle for these brushes exposed to chloroform (Figure 7.4). These two facts evidence simultaneous presence of PS and P2VP on the brush surface.

Reproducibility of morphology of the same PS/P2VP brush (after exposure to ethanol) in different locations is shown in Figure 8.1.2 a and c.

More than one kind of morphology was observed on PS/P2VP brushes after exposure to ethanol: Figure 8.1.4 c shows an example of a “coffee-grain” morphology, while Figure 8.1.4 a shows an intermediate (mixed) morphology of the interconnected network and the “coffee-grains”. Preferential formation of the interconnected network or the “coffee-grain” morphology may depend on the ratio between the polymers in the brush: the brushes presented in Figures 8.1.1-2 contain more PS, while the brushes presented in the Figure 8.1.4 contain more P2VP (see Appendix 3). Local ratio of the polymers in a brush may differ from the average one: a particular region (R2) of the brush SVP25 (the brush enriched with PS in average) revealed the “coffee-grain” morphology after treatment in ethanol, while the rest of the brush (R1) showed the interconnected network with pits (Figure 8.1.5). Additional experiments are required in order to understand the nature of transitions between the network and the “coffee-grain” morphologies.

The “coffee-grain” morphology was also observed after treatment of PS/P2VP brushes in water (Figure 8.1.1 b). Note, that water is not a solvent for PS, therefore, the brush might not reach an equilibrium state in it due to kinetic reasons. The last suggestion can be verified by exposure to water of two (or more) different samples of a PS/P2VP brush pre-treated in different solvents, for example in ethanol and toluene. It can be concluded that an equilibrium
(a) toluene, vertical scale 15 nm, 15°, RMS roughness 1.9 nm, PSD maximum at 75 nm;

(b) water, vertical scale 10 nm, 20°, RMS roughness 1.0 nm, PDS maximums at 44, 106 nm.

(c) chloroform, vertical scale 5 nm, 5°, RMS roughness 0.5 nm, PSD maximum at 72 nm;

(d) ethanol, vertical scale 10 nm, 10°, RMS roughness 1.2 nm, PSD maximum at 67 nm.

Figure 8.1.1. Tapping mode AFM of morphologies of the PS/P2VP brush SVP6 (Appendix 3) consecutively exposed to solvents of different selectivity. Repulsive regime, A/A₀ 50%. Left: topography (black horizontal lines mark origins of topography profiles), middle: phase contrast, 1x1 µm. Right: the topography profiles.
Figure 8.1.2. Tapping mode AFM of morphologies of the PS/P2VP brush SVP12 (Appendix 3) consecutively exposed to solvents of different selectivity. Repulsive regime, A/A₀ 50%. Left: topography (black horizontal lines mark origins of topography profiles), middle: phase contrast, 1x1 µm. Right: the topography profiles.
Figure 8.1.3. Analysis of the phase images of the PS/P2VP brushes (a) SVP6 (Figure 8.1.1), (b) SVP12 (Figure 8.1.2). The image area is plotted versus the relevant phase signal. The brush morphologies after treatment in chloroform have two kinds of features enriched with different polymers thus providing double peaks on these diagrams unlike the morphologies after the other solvents. Zero for the phase signal is set to the highest phase value (DI convention) for each phase image. Therefore, the relative peak positions for different morphologies are arbitrary. Higher phase value at these diagrams corresponds to the darker tone at the phase images.

state of the brush is reached in water, if an equal kind of morphology is observed after this treatment on both samples. However, this experiment has not been done yet.

The “coffee-grain” morphology should reveal two main characteristic lateral wavelengths after Fast Fourier Transformation (FFT) of the topography images. The bigger wavelength should correspond to the mean period between the “grains”, while the smaller wavelength should correspond to the mean “grain” diameter. The ordinary clusters and worm-like features provide one main characteristic wavelength which corresponds to the mean lateral period between the features. FFT was applied to all the topography images presented in this chapter till this point. The well formed “coffee-grain” morphologies provided two main characteristic wavelengths: 44 and 106 nm on the brush SVP6 after treatment in water (Figure 8.1.6 a), 62 and 128 nm on the brush SVP18 after treatment in ethanol (Figure 8.1.6 d), 51 and 133 nm on the brush SVP25 (R2) after treatment in ethanol (Figure 8.1.6 e). The morphologies obtained after treatment of the brushes in other solvents (toluene, THF, chloroform) provided one main characteristic wavelength. Some of the latter morphologies provided a second maximum of Power Spectrum Density (PSD) (Figure 8.1.6 a, b, c, e) located at the lateral wavelength region above 300 nm. These maxima correspond to non-
uniform distribution of features on bigger periods, what we explain by non-uniform grafting. The morphology presented in Figure 8.1.4 a, which is the mixture of the interconnected network and the “coffee-grains”, reveals only one PSD maximum in the region <300 nm. The maximum is shifted to lower wavelengths relative to the PSD maximum for this brush after treatment in toluene (74 versus 111 nm, Figure 8.1.6 c). This trend is valid for the other PS/P2VP brushes. The PSD maximum for their interconnected network morphology after treatment in ethanol lies at the lower wavelengths than for other their morphologies: see Figure 8.1.6 a (67 nm vs. 72 and 75 nm) and Figure 8.1.6 b (51 and 47 nm vs. 55 and 70 nm). This shift to the lower wavelength may be a consequence of the mixing of the interconnected network with the “coffee-grain” morphology.

Figure 8.1.4. “Coffee-grain” morphology after treatment in ethanol of the PS/P2VP brushes SVP17 (a) and SVP18 (c). Morphologies after treatment in toluene (b, d, respectively) are shown for comparison with other figures. Note: the panel b shows imperfect clusters (not round). Tapping mode AFM, repulsive regime, A/A₀ 50%. Left: topography, right: phase contrast. Scale 1x1 µm. Vertical scale: a-b 30 nm, 15º; c-d 14 nm, 10º. The fast scan direction is from left to right.

Taking into account the last consideration, the interconnected network observed on the brush SVP25 (R1) after exposure to ethanol (Figure 8.1.5 b) is pure because it produces the PSD maximum at 95 nm what is close to the PSD maxima for this brush after treatment in THF (95 nm) and chloroform (87 nm). The preferential formation of the interconnected
network or the “coffee-grain” morphology is determined probably only by the different local ratio of PS and P2VP (the region R2 is assumed to be richer in P2VP). It should be noted here that the polymers grafted at the regions R1 and R2 on the brush SVP25 have similar molecular weights and therefore the lateral size of the features in both regions must be equal according to Section 2.2. Therefore, the regions R1 and R2 may be considered together as one bistable sample. The identified problem of preferential formation of one or another morphology as a function of brush composition requires a more substantial study.

(a) ethanol, RMS roughness 3.0 nm; (b) ethanol, RMS roughness 2.8 nm; (c) chloroform, RMS roughness 1.2 nm; (d) THF, RMS roughness 2.1 nm.

**Figure 8.1.5.** The “coffee-grains” in the region R2 (a) and the interconnected network in the region R1 (b) of the PS/P2VP brush SVP25 (Appendix 3) after treatment in ethanol. Morphologies after chloroform (c) and THF (d) in the region R1 are shown for comparison with other figures. Tapping mode AFM, attractive regime, $A/A_0$ 90-97%, $A_0$ 11-13 nm. Left: topography, right: phase contrast. Scale 1x1 µm. Vertical scale 20 nm, 40º. The fast scan direction is from left to right.
Figure 8.1.6. Power Spectral Density (PSD) of the topographic AFM images: (a) from Figure 8.1.1, (b) from Figure 8.1.2, (c) from Figure 8.1.4 a-b, (d) from Figure 8.1.4 c-d, (e) from Figure 8.1.5. Two-dimensional isotropic PSD of roughness amplitude is plotted versus lateral wavelength.
8.1.2. Tapping mode AFM studies of PS/P2VP brushes at gradual decrease of amplitude set-point ratio.

Many nano-structured polymer films reveal topography and phase contrast inversion in tapping mode AFM upon imaging at different amplitude set-point ratios (Section 3.3.3). Aim of this experiment was to find out how topography and phase contrast of PS/P2VP brushes change at different amplitude set-point ratios and which polymer is relevant to which phase signal at various imaging conditions. This information is critical for understanding the nano-phase segregated structure of the mixed polymer brushes being investigated.

We recorded sequences of tapping mode AFM topography and phase images in the repulsive regime at amplitude set-point ratio \((A/A_0)\) gradually decreasing from \(~100\) to \(~50\%\)\(^1\) from a constant area on the brush SVP25 (R1) preliminary exposed to a certain solvent. The following solvents were used for the treatment: chloroform, toluene, ethanol, THF. The AFM tip indentation depth increases upon reducing the amplitude set-point ratio, what leads to visualization of deeper and deeper layers of the brush on both topography and phase images (Section 3.3.3). The recorded sequences of the AFM images are presented in Figures 8.1.7-10. The topography images remain almost unchanged at different \(A/A_0\), while the phase images change considerably. At high set-points the phase images are contaminated with the first derivative of the topography images (Figures 8.1.7 a-b; 8.1.8 a-c; 8.1.10 a-c): the tip-sample contact area increases, when the tip meets an elevating wall, and decreases, when it follows a slope (Section 3.3.3). The difference in the tip-sample contact area becomes smaller upon reducing the set-point ratio to 70-88 %, and the topography stops to contribute to the phase images. The Figures 8.1.7-10 make clear that the brush morphologies provide a notable phase contrast at a sufficiently low set-point \((A/A_0 \approx 50-80 \%)\) after treatment in any solvent from the listed above. Let us consider this phase contrast in more details. The interconnected network obtained after treatment of the brush in ethanol provides the lighter phase (higher \(\phi^{DI}\)), while the pits in between provide the darker phase (lower \(\phi^{DI}\)). The network covers the major area, and thus the phase image is also dominantly occupied with the lighter phase (Figure 8.1.9 a-g). The phase images recorded from the brush treated in chloroform, toluene, and THF comprise a major area occupied by the darker phase and islands of the lighter phase (Figures 8.1.7 c-f, 8.1.8 d-e, 8.1.10 d-f, respectively). The phase shift in the repulsive regime in the

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\(^1\) A similar experiment was made in the attractive regime at low free amplitudes \((A_0 \approx 12-17 \text{ nm})\). The obtained phase images at the amplitude set-points \(A/A_0\) from 100 to 60% were similar to those in Figure 8.1.5 and contained a significant topography interference (Section 3.3.3). The latter circumstance made their analysis complicated.
tapping mode is a function of viscoelastic properties of a sample (Section 3.3.2-3). We assume that the viscoelastic properties of the brush polymers are independent on the changes in the brush morphology. This assumption means that the brush polymer A provides always the lighter phase signal relative to the polymer B. From this we conclude that the top layer of the interconnected network obtained after treatment of the brush in ethanol (Figure 8.1.9 a-g) is mainly occupied by the polymer A, while the bottom of the included pits is occupied by the polymer B. From the selectivity of ethanol to P2VP we conclude that the polymer A is P2VP, while the polymer B is PS.

THF and toluene are selective for PS (Figure 7.2) which occupies the top layer upon treatment of the brush in these solvents, while P2VP collapses and forms compact clusters beneath PS. The P2VP clusters are sensed by the AFM tip, penetrating into the sample, as light islands in the phase images in Figures 8.1.10 d-f and 8.1.8 d-e, respectively. The light phase islands in these figures correspond to the elevations in the relevant topography images. It should be noted that the brush morphologies after treatment in THF and toluene are quite similar.

The light phase islands on the brush SVP25 (R1) exposed to chloroform (a non-selective solvent, Figure 8.1.7 c-e) do not strictly correspond to the topography depressions as in the case of the brushes SVP6 and SVP12 (Figure 8.1.1 c, 8.1.2 d) or to the topography elevations as in the case of the morphologies obtained on this brush after treatment in THF (Figure 8.1.10) and toluene (Figure 8.1.8). No interconnected network is formed by the light phase as in the phase images of the brushes SVP6 and SVP12 exposed to chloroform, probably, due to lower relative grafted amount of P2VP on the brush SVP25 (R1). It is essential that the morphology observed after exposure to chloroform is different from the morphologies observed after the selective solvents (ethanol, THF, toluene).

It is an important observation that there is no phase contrast inversion found for any of the brush SVP25 (R1) morphologies in the repulsive regime in the range of amplitude set-point ratios (A/A₀) from 100 to 60%. The phase images in the Figures 8.1.1-2, 8.1.4 were recorded in the repulsive regime at A/A₀ 50% and their contrast is similar to the phase contrast of the corresponding morphologies in the Figures 8.1.7-10: (1) after exposure to ethanol, the interconnected network produces the lighter phase signal, while the included pits produce the darker phase signal (Figures 8.1.1 d, 8.1.2 a, 8.1.9). (2) The cluster morphologies after exposure to toluene in Figures 8.1.1 a, 8.1.2 b, 8.1.4 b, 8.1.8 a-c, f-g contain topography interference, nevertheless it is seen that the clusters (elevations in the topography images) produce the lighter phase than the surrounding area in the corresponding phase images (see
also Figure 8.1.4 d, 8.1.8 d-e where no topography interfered). (3) The phase contrast after treatment in chloroform was already discussed. Thus, we can generally conclude that P2VP provides the lighter phase than PS in the repulsive tapping mode at \( A/A_0 \) from 100 to 50%.

Knowing qualitative difference in phase signals of P2VP and PS, we can speculate about the inner structure of the “coffee-grain” morphology. One can conclude from Figures 8.1.1 b and 8.1.4 a, c that it is similar to the inner structure of the interconnected network with pits found after exposure to ethanol: the “grain shells” occupy the major part of the top layer and produce the lighter phase similarly to the network structure, while the cavities inside the “grains” produce the darker phase similarly to the pits in the network. The top of the “grain shells” must be enriched with P2VP according to the speculations about the relative phase shifts of P2VP and PS. The top layer of the cavities in the middle of the “grains” must be enriched with PS. However, the latter features are shadowed in the phase images by the topography interference. Hence, the enrichment of their top layer with PS can be less pronounced than it seems to be. PS can be also covered in the cavities by a thin P2VP layer.

The data on RMS roughness of the morphologies of the brush SVP25 (R1), presented in Figures 8.1.7-10, are summarized in Figure 8.1.11 for clarity. The roughness continuously decreases by 16-19% upon decreasing the amplitude set-point ratio from 100 to 60% in the case of smooth morphologies (after treatment of the brush in chloroform and THF). If morphology contains deep cavities (the brush treated in ethanol), the tip has a poor contact with the bottom of the cavities at \( A/A_0 \) close to 100%. Upon decreasing \( A/A_0 \), the contact is improved, and the roughness rises quickly up (by 26% at \( A/A_0 \) 85.7%) and afterwards remains almost unchanged. If morphology contains tall features (the brush treated in toluene), the tip hits them down and the roughness gradually and significantly decreases (by 30%) upon decreasing \( A/A_0 \) from 100 to 50%. The latter kind of morphology is the most sensitive to modification by a tapping tip.

We made an important observation that roughness of the PS/P2VP brushes is higher after exposure to the selective solvents (ethanol and toluene), while it is smaller after exposure to less selective THF and non-selective chloroform. It will be shown later that this behavior is also relevant for other kinds of mixed polymer brushes. The mechanisms of formation of rough and smooth morphologies are discussed in Sections 8.2-4.
Figure 8.1.7. PS/P2VP brush SVP25 (R1) (Appendix 3) exposed to chloroform, AFM tapping mode, repulsive regime. Left: topography, right: phase contrast, z ranges 7.0 nm, 30°, respectively. Scale 0.5x2.0 µm. Free amplitude $A_0$ 45 nm. The fast scan direction was from left to right for both topography and phase images.
Figure 8.1.8. PS/P2VP brush SVP25 (R1) (Appendix 3) exposed to toluene, AFM tapping mode, repulsive regime. Left: topography, right: phase contrast, z ranges 40 nm, 15º, respectively. Scale 0.5x2.0 µm. Free amplitude $A_0$ 68 nm. The fast scan direction was from left to right for both topography and phase images.
Figure 8.1.9. PS/P2VP brush SVP25 (R1) (Appendix 3) exposed to ethanol, AFM tapping mode, repulsive regime. Left: topography, right: phase contrast, z ranges 15 nm, 20º, respectively. Scale 0.5x2.0 µm. Free amplitude A₀ 40 nm. The fast scan direction was from left to right for both topography and phase images.
Figure 8.1.10. PS/P2VP brush SVP25 (R1) (Appendix 3) exposed to THF, AFM tapping mode, repulsive regime. Left: topography, right: phase contrast, z ranges 10 nm, 5°, respectively. Scale 0.5x2.0 µm. Free amplitude \( A_0 \) 36 nm. The fast scan direction was from left to right for both topography and phase images.
8.2. PSF/PMMA and PS/PMMA brushes.

8.2.1. Morphologies of PSF/PMMA and PS/PMMA brushes after exposure to different solvents.

PSF/PMMA brushes were specially developed for experiments on direct sensing of chemical composition of the brush top layer with the XPEEM technique (Section 8.2.3). Morphology switching on these brushes was preliminary studied with AFM (Figure 8.2.1). A worm-like (distorted lamellae) morphology was found after treatment in toluene which is a good solvent for PSF and PMMA (Figure 8.2.1 a). There is a good phase contrast between the higher and the lower worm-like features, whose phase signals appear as the lighter and the darker regions at the phase image, respectively. A double peak at the area-vs.-phase diagram clarifies this (Figure 8.2.2 b).

We identified preliminary the worm-like morphology as the ripple phase and were searching for the dimple-PSF and the dimple-PMMA phases. According to the theory (Section 2.2), the dimple-PMMA phase should be stable in solvents with better selectivity for PSF, i.e. less polar than toluene. It is known from literature [Pol4, Zhao00a] that warm cyclohexane fits these requirements. However, the worm-like morphology remains after treatment of the PSF/PMMA brush in cyclohexane at increased temperature (Figure 8.2.1 b). The roughness increases dramatically (by 4 times) and interferes strongly the phase signal (Figure 8.2.1 b middle). The phase contrast becomes worse but the double peak is still clearly seen on the area-vs.-phase signal diagram (Figure 8.2.2 b). As it will be shown later, PMMA shows lighter phase signal at the repulsive regime of the tapping mode than PSF. However,
(a) toluene, vertical scale 30 nm, 30º, RMS roughness 5.5 nm, PSD max. at 167 nm;

(b) cyclohexane for 2 h at 74º C, vertical scale 100 nm, 30º, RMS roughness 23.9 nm, PSD max. at 175 nm;

(c) toluene (2nd turn), vertical scale 30 nm, 30º, RMS roughness 5.4 nm, PSD max. at 167 nm;

(d) acetone, vertical scale 100 nm, 30º, RMS roughness 20.9 nm, PSD max. at 178 nm.

**Figure 8.2.1.** AFM of morphologies of the PSF/PMMA brush FSMA1 (Appendix 3) consecutively exposed to solvents of different selectivity. Repulsive tapping mode, amplitude set-point ratio $A/A_0$ 50%, ultrasharp tip (Section 5.5.1 A). Left: topography (black horizontal lines mark origins of topography profiles), middle: phase contrast, 2x2 µm. Right: the topography profiles.
Figure 8.2.2. Analysis of the morphologies of the PFS/PMMA brush FSMA1 (Figure 8.2.1). (a) PSD of the AFM topography images; (b) phase contrast analysis.

Figure 8.2.3. Morphology of the PSF/PMMA brush FSMA9 (Appendix 3) after exposure to chloroform. AFM repulsive tapping mode, amplitude set-point ratio A/A₀ 50%, ultrasharp tip (Section 5.5.1 A). Left: topography (the black horizontal line marks the origin of the topography profile on the right). Middle: phase contrast. Scale 2x2 µm. Vertical scale 15 nm, 1.3°, RMS roughness 2.4 nm

the observed difference in phase can be caused be topography contribution. Therefore, it is not possible to make conclusions about phase segregation upon exposure of the PSF/PMMA brushes to cyclohexane without additional information. The poor thermodynamic quality of cyclohexane for PMMA hampers reaching the thermodynamic equilibrium, what is the most probable reason, why we did not find a cluster morphology even after much longer treatment (31.5 h) of another PSF/PMMA brush in cyclohexane at increased temperature (74° C).

The PSF/PMMA brush was exposed to toluene again. The initial worm-like morphology was reproduced with the roughness and the phase contrast as after the first treatment in toluene: compare Figure 8.2.1 a and c.

Acetone, which is a selective solvent for PMMA, switches the brush to a rough morphology composed of tall round clusters. The area-vs.-phase diagram (Figure 8.2.2 b) reveals a single maximum what suggests uniform composition of the top brush layer. As it is
known from the contact angle measurements and XPS (Sections 7.2, 7.4), the top brush layer after exposure to acetone is dominantly occupied by PMMA. We assume that this morphology represents the dimple-PSF phase (Section 2.2). Additional confirmations will be provided in Sections 8.2.2-3.

The morphology after exposure to chloroform was studied on the PSF/PMMA brush FSMA9 (morphologies of this brush after exposure to toluene and acetone are not shown because of their similarity to those in Figure 8.2.1 a (c) and d, respectively). A smooth worm-like structure with poor phase contrast of the features was found (Figure 8.2.3). We know from water contact angle measurements (Section 7.2) and XPS (Section 7.4) that the top layer of this morphology is enriched with PMMA. Therefore, this morphology possesses a different kind of perpendicular segregation of the brush polymers than in the worm-like morphology found after exposure to toluene. The worm-like morphology, found after exposure to chloroform, should be additionally studied in order to determine: (1) whether it comprises two kinds of the worm-like features, (2) whether there is or there is no phase transition between this morphology and the worm-like morphology found after exposure to toluene (see Section 8.4.5 for details).

We consider that smooth morphologies are formed, if the swelling coefficients of the two brush polymers are similar in a particular solvent: the two swollen polymers adopt equal volumes and cause equal pressure on one another, what suggests equal deformation of their domains perpendicular to the substrate. This must be true for good non-selective solvents. If the molecular weights of the two polymers are similar and the solvent evaporates with equal rates from their domains, the brush adopts upon drying a laterally segregated state with a smooth surface.

The lateral period between the features of the morphologies of the PSF/PMMA brushes is slightly higher for the cluster morphology after exposure to acetone than for the worm-like morphologies after exposure to toluene and chloroform (Figures 8.2.2 a, 8.2.4 a). This observation is valid for other PSF/PMMA brushes (Appendix 4) and agrees with the predictions of the SCF theory (Section 2.2). The period between the worm-like features after treatment of the brush FSMA1 in cyclohexane is similar to the period between the clusters after treatment in acetone. This may be an indirect illustration that cyclohexane changes the brush morphology in direction of a transition to the cluster morphology.

PS/PMMA brushes were briefly studied with AFM (Figure 8.2.5) and revealed worm-like and cluster morphologies after exposure to toluene and acetone, respectively, similar to the morphologies of their fluorine containing analogs, the PSF/PMMA brushes.
Figure 8.2.4. Analysis of the morphologies of the PFS/PMMA brush FSMA9. (a) PSD functions for the morphologies after exposure to acetone, toluene, chloroform. (b) analysis of the AFM phase image of the morphology after exposure to chloroform (see Figure 8.2.3 middle).

(a) acetone, vertical scale 100 nm, 60º, RMS roughness 19.5 nm, PSD maximum at 154 nm;

(b) toluene, vertical scale 20 nm, 10º, RMS roughness 3.3 nm, PSD maximum at 154 nm.

Figure 8.2.5. Morphologies of the PS/PMMA brush SMA1 (Appendix 3) exposed to solvents of opposite selectivity. AFM tapping mode, repulsive regime, amplitude set-point ratio 50%. Ultrasharp tip (Section 5.5.1 A). Left: topography (black horizontal lines mark origins of topography profiles), middle: phase contrast, 2x2 µm. Right: the topography profiles.
8.2.2. Plasma etching experiments on PSF/PMMA brushes.

We found experimentally that PSF is etched by oxygen plasma about two times slower than PMMA (Figure 8.2.8 a). The difference in the etching rates of these materials enables transformation of lateral variations in composition of morphologies of PSF/PMMA brushes into a topographic pattern. We decided to use etching in oxygen plasma for studies of nano-phase segregation in PSF/PMMA brushes. ¹

Two samples of the PSF/PMMA brush FSMA7 (Appendix 3) were exposed to toluene and acetone, respectively, for 5 min. Afterwards, the two samples were exposed for 5 min to a solvent of the opposite selectivity: the first sample was exposed to acetone while the second one was exposed to toluene. By means of this recursive double treatment, we obtained the worm-like morphology with prehistoric cluster morphology and vise versa. The samples were investigated with AFM. The observed morphologies were in agreement with the previous observations (Section 8.2.1): asymmetric worm-like structure² was observed after the last treatment in toluene (Figure 8.2.6 a), while cluster morphology was found after the last treatment in acetone (Figure 8.2.7 a). Different regions of the two samples were etched with oxygen plasma for stepwise increasing periods of time according to the procedure ¹ described in Section 4.4. The etched regions were investigated with AFM (Figure 8.2.6-7). We found that both morphologies were transformed into similar worm-like structures upon plasma etching. Several explanations for this effect are possible: (1) the time of exposure to a solvent was insufficient for formation of a perfect morphology in the whole thickness of the brush films; (2) the inner structure of the brush does not change at all upon exposure to different solvents. Our next experiments (below in this section) showed that the assumption (1) was true.

The brush thickness removed upon etching and the refractive indices of the remaining layers were obtained from ellipsometry (Figure 8.2.8 b and c, respectively). A model adopted for these calculations considered the brush film as a single layer. The etching rates for both brush samples were very similar and close to the etching rate for the spin-coated PSF film. The refractive indices of the remnant brush layers were also very similar to one another and decreasing with etching time. The explanation for the latter result is that PMMA is etched faster and leaves cavities between the remaining islands of PSF. The mean refractive index

¹ PS and P2VP have equal etching rates. Therefore, morphologies of the PS/P2VP brushes cannot be studied with this method.

² The more perfect worm-like morphology was identified in a different region on this sample (Figure 8.2.9 a).
decreases until all PMMA is eliminated. The RMS roughness (obtained from AFM) of both brush samples increases during the initial period (6 min) of etching due to the same reason. It starts to decrease (Figure 8.2.8 d) after 6 min etching when all PMMA is eliminated (clear from the thickness of the brush FSMA7 of 122 nm, Figure 8.2.8 a and Figures 8.2.6 e, 8.2.7 e). The decrease of the RMS roughness in the second etching period is caused by the reducing height of the remaining PSF islands. With respect to these considerations, the elevated features in Figures 8.2.6 b-e, 8.2.7 b-e are the PSF islands.

We made a new plasma etching experiment with another sample of the same brush consecutively exposed to acetone and then to toluene as described above. The sample was investigated with AFM after each etching step at a constant location (see the details in Section 4.4, procedure 2). Our scope was focused on the structure of the top brush layer, therefore, the time per an etching step was reduced from 2 min to 20 s. It is clear from the AFM topography images (Figure 8.2.9) that etching caused a topography inversion: the elevations transformed to depressions. The inversion is illustrated with topography profiles at the constant location (Figure 8.2.9 right). Two features are pointed out at the profiles with markers and their height is plotted vs. etching time in Figure 8.2.11 c. The height of the marked features became negative after etching for 40 s. We concluded that the tops of the elevations and the valleys before etching were enriched with PMMA and PSF, respectively, and the difference in their etching rates caused the topography inversion (Figure 8.2.12 a).

The elevations and the valleys before etching produced the lighter (higher $\phi^{DI}$) and the darker (lower $\phi^{DI}$) phase signals, respectively (Figure 8.2.1 a, c, 8.2.9 a). At the imaging conditions used (tapping mode, repulsive regime), the darker phase is relevant to a softer material providing stronger dissipative pull-off forces (Section 3.3.3). PS has a Young modulus of 3000 MPa vs. 3300 MPa for PMMA [Pol4], i.e. PS is softer. Consequently, the phase contrast agrees with the results of the etching experiment. The phase contrast extinguishes upon etching most probably due to modification of the top layer with oxygen plasma. The mechanism of the modification is out of scope of this work, but an evidence that oxygen plasma affects mechanical properties is available for another material (Appendix 10). Therefore, the phase in Figure 8.2.9 b-d is rather determined exclusively by the topography contribution (Section 3.3.3).

The thickness of the brush being etched was independently determined with AFM and ellipsometry (Figure 8.2.11 a). AFM provided the values about 17 nm higher than ellipsometry. The ellipsometric results are model-dependent, while AFM is a direct method. Therefore, the AFM data are more reliable.
Figure 8.2.6. Etching of the PSF/PMMA brush FSMA7 (d = 120 nm), after exposure to toluene, with oxygen plasma. Repulsive tapping mode AFM, an ultrasharp tip. Etching time: (a) 0 min, (b) 2 min; (c) 4 min; (d) 6 min; (e) 8 min. Left: topography, z range 105 nm. Middle: phase contrast, z range (a-b, e) 30º, (c) 50º, (d) 80º. Scale 2x2 µm. Right: topography profiles, their origins are marked on the topography images with black lines.
Figure 8.2.7. Etching of the PSF/PMMA brush FSMA7 (d = 120 nm), after exposure to acetone, with oxygen plasma. Repulsive tapping mode AFM, an ultrasharp tip. Etching time: (a) 0 min, (b) 2 min, (c) 4 min, (d) 6 min, (e) 8 min. Left: topography, z range 105 nm. Middle: phase contrast, z range (a) 15º, (b) 30º, (c) 50º, (d) 70º, (e) 40º. Scale 2x2 µm. Right: topography profiles; their origins are marked at the topography images with dark lines.
Figure 8.2.8. Etching of the PSF/PMMA brush FSMA7 (Figures 8.2.6-7), after exposure to toluene and acetone, with oxygen plasma. (a) etching rates for separated PSF and PMMA spin-coated films; etched thickness (b) and refractive indices of the remnant layers (c) of the brush obtained from ellipsometry; (d) RMS roughness of the etched brush layers.

We made an observation that the new elevations formed upon the etching contain depressions in the middle of their tops (Figure 8.2.9 b-d, the examples are pointed out with the inner markers; 8.2.6 b). The depth of these depressions decreases upon further etching, and they extinguish after etching period ranging between 2 and 4 min (Figure 8.2.6 b-c). This observation may probably mean that the boundaries of the PSF-rich features in the original non-etched worm-like morphology are elevated. We show this on a proposed etching scheme for the worm-like morphology (Figure 8.2.12 a).

We made a similar experiment with another sample of the PSF/PMMA brush FSMA7 which was exposed to toluene for 30 min and afterwards to acetone for 30 days. We expected that the long exposure period to acetone would eliminate the traces of the previous morphology in the deep brush layer. The brush adopted the cluster morphology (Figure 8.2.10 a). It was etched with oxygen plasma and the brush surface was scanned with AFM at a
Figure 8.2.9. Etching of the PSF/PMMA brush FSMA7 exposed to toluene with oxygen plasma. Repulsive tapping mode AFM on a constant region of the brush, ultrasharp tip. a – before etching; b – after 20 s etching; c – after 40 s etching; d – after 60 s etching. Left - topography, middle – phase contrast. Scale 2x2 µm, z range 30 nm, 15º. Right - topography profiles, their origins are marked in the topography images with dark lines. The coupled markers (red on the left, green on the right) point out the height (h_r and h_g, respectively) of example features upon etching.
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**Figure 8.2.10.** Etching of the PSF/PMMA brush FSMA7 exposed to acetone, with oxygen plasma. Repulsive tapping mode AFM on the same region of the brush, ultrasharp tip. a – before etching, b – after 20 s etching, c – after 40 s etching, d – after 60 s etching, e – after 90 s etching, f – after 120 s etching. Left - topography, middle – phase contrast. Scale 2x2 μm, z range 100 nm, 80°. Right - topography profiles, their origins are marked on the topography images with dark lines. The coupled markers (red on the left, green on the right) point out the height (h₁ and h₂, respectively) of example features upon etching.

constant area after each etching step (Figure 8.2.10 b-f). We found neither transformation of the cluster morphology into a worm-like structure, nor topography inversion like in the previous experiment (Figure 8.2.9). The shape of the clusters remained round at all the etching steps (Figure 8.2.10 a-f). The height of the features and the RMS roughness increased gradually upon etching (Figure 8.2.11 d, f). The brush thickness was measured parallel with ellipsometry and AFM (Figure 8.2.11 b) after each etching step. The layer thickness obtained from AFM is higher than from ellipsometry, in a similar manner as in the previous experiment. The contrast of the phase images in Figure 8.2.10 does not reveal any heterogeneity in the material properties of the brush top layer and is affected only by topography contribution. We conclude from the latter observation that the top brush layer has a uniform composition (constant fractions of PSF and PMMA). The cores of the clusters are enriched in PSF while the surrounding matrix is enriched in PMMA because the material around the clusters is etched faster (Figure 8.2.11 d, f). We conclude that the top of the clusters is rich in PMMA in the same extend as the matrix around the clusters from the top layer composition uniformity and the XPS data (Section 7.4). The lower initial refractive index (Figure 8.2.11 e) and the non-linear reduction of the ellipsometric thickness of the brush exposed to acetone for 30 days (Figure 8.2.11 b) unlike the same brush exposed to acetone for 5 min (Figure 8.2.8 b-c) take place rather due to higher degree of adaptation by the brush of the new structure upon the longer exposure period.
Figure 8.2.11. Etching of the PSF/PMMA brushes (from Figures 8.2.9-10). Etching kinetics of the samples exposed to: a – toluene, b – acetone. Change of the height of the example features upon etching of the samples exposed to: c – toluene, d – acetone. e – change upon etching of: e – refractive index (from ellipsometry), f - RMS roughness (from AFM).
The initial ellipsometric thickness of the brush FSMA7 of 86-89 nm in Figure 8.2.11 a-b is smaller than in the first two etching experiments (Figures 8.2.6-8), in which it was 122 nm, due to degradation of the brush upon storage (Section 4.2.5). We have summarized the results on etching of the cluster morphology in Figure 8.2.12 b-c. The panel b shows the scheme of etching for the morphology obtained after the short exposure to acetone. The deep brush layer still has the worm-like structure remaining from the previous treatment in toluene. (c) Etching of the cluster morphology obtained after the long (30 days) exposure to acetone. The clusters are perfect in the whole thickness of the brush film.

The initial ellipsometric thickness of the brush FSMA7 of 86-89 nm in Figure 8.2.11 a-b is smaller than in the first two etching experiments (Figures 8.2.6-8), in which it was 122 nm, due to degradation of the brush upon storage (Section 4.2.5). We have summarized the results on etching of the cluster morphology in Figure 8.2.12 b-c. The panel b shows the scheme of etching for the morphology obtained after the short exposure to acetone. The PSF/PMMA brush does not have sufficient time to adopt perfect cluster morphology and its deep layer still has the worm-like structure remaining after the previous treatment of the brush to toluene.

The etching scheme for the perfect cluster morphology obtained after the long exposure to acetone is given in the panel c.
8.2.3. XPEEM studies of the worm-like and cluster morphologies on PSF/PMMA mixed brushes.

The aim of this experiment was to directly observe chemical composition with nano-scale lateral resolution of a top layer of a mixed polymer brush adopted different morphologies. For this study we developed PSF/PMMA mixed brushes which satisfy the range of requirements formulated from the reasons: (1) to approach a desired level of contrast between two polymers for experimental investigations of the structure and composition, and (2) to compare the experimental results with the SCF calculations. The list of properties derived from the two reasons appears as follows:

(a) the contrast between the homopolymers for XPEEM which requires presence of different kinds of atoms or chemical groups in the two homopolymers;
(b) the contrast for contact angle method that requires \( \gamma_A^W <\ll \gamma_B^W \), where \( \gamma_A^W \) and \( \gamma_B^W \) are the interface tensions at the polymer A - water and polymer B - water interfaces, respectively;
(c) the contrast for AFM phase imaging;
(d) non-selective adsorption onto a substrate or in other words \( \gamma_A^S \approx \gamma_B^S \), where \( \gamma_A^S \) and \( \gamma_B^S \) are the interface tensions at the polymer A - substrate and polymer B - substrate interfaces, respectively;
(e) both homopolymers should be monodisperse and have the same molecular weight,
(f) grafting density should ensure the brush regime;
(g) distribution of grafting points should be random.

The properties of a mixed brush were optimized for the best fit to all the above listed requirements taking into account that it is hardly probable to simultaneously fulfill the requirements (b) and (d) in a real experiment.

We decided to use partially fluorinated polystyrene (PSF) and polymethylmethacrylate (PMMA) in order to satisfy the requirement (a). There is fluorine in PSF and oxygen in PMMA whose NEXAFS 1s edges lie at 696 eV and 536 eV, respectively. Additionally, there is a 3 eV shift between 1s→\( \pi^* \) carbon peaks of these two polymers in their NEXAFS spectra [Mor01] (Figure 8.2.13 a).

The water contact angles for spin-coated films of PSF and PMMA are 97° and 77°, respectively (Table 6.1). The contrast between the two polymers is well seen in AFM phase images (Figure 8.2.1 a, c). PMMA is more polar than PSF, nevertheless, it has rather not very high affinity to the substrate (Si) as compared to other polar polymers with carboxyl, hydroxyl, or amine functional groups.
We performed this experiment on the PSF/PMMA brushes FSMA2 and FSMA3 (Appendix 3) synthesized via the “grafting from” technique (Section 4). The polydispersity indices (Mw/Mn 1.6-1.8 for PSF and 2.2 for PMMA) are ordinary for polymers synthesized via conventional radical polymerization. A difference of ~2 times in the molecular weights of the two constituent polymers (Mw 4.5 - 4.7·10^5 for PSF and 8.1·10^5 for PMMA) is of the same value as the polydispersity and leads to only \( \sqrt{2} \approx 1.4 \) times difference in sizes of the unperturbed polymer coils [A1.1], which determine the lateral period of phase segregation in the mixed brushes (Section 2.2). We consider that this is a sufficiently good approximation of the restriction (e) introduced by the SCF approach of M. Müller (Section 2.2). In future, modern controlled radical polymerization techniques combined with initiation from surface (Section 2.3) can be utilized for better control of the molecular weights and reduction of polydispersity of polymers in mixed brushes. The root-mean-square end-to-end distances for both polymers in theta-conditions (\( h_{\text{PSF}}^{\Theta} = 48 \) nm, \( h_{\text{PMMA}}^{\Theta} = 58 \) nm) were of about 10 times larger than the average distance between the grafting points (4-6 nm, see Appendices 3-4) thus providing the brush regime.

In the beginning of the experiment, we separately recorded the NEXAFS spectra at the 1s C, 1s O, and 1s F edges of spin-coated PSF (d ~24 nm) and PMMA (d ~15 nm) films (Figure 8.2.13 a – c). Monocromator function (I_0) was mainly recorded from a bare Si substrate. The Si spectrum at the 1s C edge comprised a wavy curve close to a constant (Figure 8.2.13 a). The Si spectrum at 1s O edge contained a peak of a thin natural SiO2 layer (Figure 8.2.13 b). Therefore, the PSF spectrum should be used as I_0 in the 1s O region because it does not contain any oxygen signal and hides the signal of the natural SiO2 layer on the Si substrate (the PSF film was thicker than the XPEEM sampling depth). The intensity decrease at 535-540 eV in the PSF 1s O spectrum (Figure 8.2.13 b) evidenced presence of oxygen contamination in the beamline. The Si spectrum at the 1s F edge coincided with the spectrum of PMMA (both could be used as I_0).

One can use whether the 1s O and 1s F edges for extracting information about chemical composition top layer or the two different 1s→\( \pi^* \) C peaks of PSF and PMMA. The concentration of carbon atoms in the polymers is higher than of oxygen and fluorine, and, consequently, XPEEM micrographs of a better quality were extracted from the 1s C edge (Figure 8.2.15).

The positions of the PSF (286.1 eV) and PMMA (289.3 eV) carbon peaks found by ourselves slightly differ from the literature data ([Mor01], 285.1 and 288.4 eV, respectively) obtained on the same microscope. A probable reason for that can be drift in the
monochromator. The PMMA spectrum (Figure 8.2.13 a) has a very small peak at 286.1 eV indicating a damage of the polymer during the spectrum recording. Following Morin et al. [Mor01] we noticed that the 286.1 eV signal of both PSF (PS in the reference) and PMMA increases while the 289.3 eV signal of PMMA decreases at high radiation flux. The proposed explanation [Mor01] of this effect is that (1) the radiation leads to loss of the methyl ester of PMMA with associated reduction of the 289.3 eV $\pi^*_{C=O}$ signal; (2) photoelectrons transform the saturated backbone to C=C bonds producing the additional signal at 286.1 eV. We concluded from the small damage peak of PMMA (which is easier damaged than PSF or PS) at 286.1 eV (Figure 8.2.13 a) that the damage caused by photoelectrons is negligibly small at the chosen experimental conditions. Nevertheless the damage can be significant at higher radiation doses and shift intensity from the 289.3 eV peak to the 286.1 eV peak increasing the observed fraction of PSF.

Figure 8.2.13. As recorded NEXAFS spectra in arbitrary scale. Spectra of spin-coated PSF and PMMA at the 1s C edge (a), the 1s O edge (b), and the 1s F edge (c). (d) C spectra of the FFS/PMMA brushes FSMA2 and FSMA3 after exposure to toluene and acetone, respectively.
NEXAFS 1s C integral spectra (Figure 8.2.13 d) of the PSF/PMMA mixed brushes were recorded after treatment in toluene and acetone. The fractions of each polymer in the top layer were calculated from the spectra using aXis2000 software (see Section 5.7 method B and Figure 8.2.14 for the details) and are given in Table 8.2.1.

**Table 8.2.1.** PSF and PMMA fractions in the top layer (~15 nm) of the mixed PSF/PMMA brushes after exposure to toluene and acetone. The fractions were calculated from the NEXAFS/XPEEM spectra using aXis2000 software (Figure 8.2.14 d)

<table>
<thead>
<tr>
<th>Sample</th>
<th>PSF fraction, %</th>
<th>PMMA fraction, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>FSMA2 after exposure to toluene</td>
<td>92*</td>
<td>3*</td>
</tr>
<tr>
<td>FSMA3 after exposure to acetone</td>
<td>69*</td>
<td>40*</td>
</tr>
<tr>
<td>spin-coated PSF</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>spin-coated PMMA</td>
<td>0</td>
<td>100</td>
</tr>
</tbody>
</table>

*The sum of PSF and PMMA fractions deviates from 100% due to the calculation procedure.

**Figure 8.2.14.** Decomposition of NEXAFS 1s C spectra recorded from PSF/PMMA brushes after exposure to toluene (a) and acetone (b) into spectra of separated PSF and PMMA with aXis2000 software.

The results presented in Table 8.2.1 are semi-quantitative (Section 5.7) and do not represent the true top layer composition. The PSF fraction in the brush top layer calculated from XPEEM is too high both after exposure of the PSF/PMMA brush to toluene and acetone, if
**Figure 8.2.15.** XPEEM of the PSF/PMMA brush FSMA2 (Appendix 3) after exposure to toluene. Scale 5x5 µm. The contrast and brightness are optimized. The ellipses mark characteristic features. White lines point out origins of intensity profiles of the micrographs a-b, which have the best quality. The intensity profiles extracted from a and b are given in the original intensity scale in Figure 8.2.16.
compared with the XPS data. XPS is an approved analytical method [Bri90], while XPEEM has not reached the quantitative accuracy yet [Mor01]. Therefore, the XPS data on composition of the top layer of the PSF/PMMA brushes (Table 7.3) are more reliable.

A set of XPEEM micrographs was recorded at the 1s C, 1s O, and 1s F edges (Figure 8.2.15 a-b, d-e, g-h, respectively) from the same area on the PSF/PMMA brush exposed to toluene. Quality of the micrographs recorded at the 1s C edge is notably higher than of the micrographs recorded at the 1s O and 1s F edges, what agrees with smaller concentration of O and F atoms in the brush. The elongated features in the micrographs look similar to the worm-like structure observed with AFM on PSF/PMMA brushes after the same treatment (Figure 8.2.1 a). The most prominent peculiarity is the inverse contrast of the micrographs 8.2.15 (a) and (b) recorded at the energies of the carbon 1s→π* peaks of PSF and PMMA, respectively: the features, which appear light-gray in the micrograph (a), are black in the micrograph (b), while the features, which appear black in the micrograph (a), are light-gray in the micrograph (b). This means that there are two kinds of worm-like features whose top layer is enriched whether with PSF or PMMA. This agrees with conclusions made from the AFM phase images (Figure 8.2.1 a, c middle) and the plasma etching experiments (Section 8.2.2).

The contrast of features at the 1s O and 1s F edges correspond to the contrast at the 1s C edge. In order to decrease the effect of topography, the micrographs recorded at the 1s→π* peaks of the O and F edges (Figure 8.2.15 d, g) were normalized by the micrographs recorded at the corresponding pre-edge photon energies (Figure 8.2.15 e, h). The normalized images are shown in Figure 8.2.15 f and i, respectively. The light tone in the normalized images corresponds to regions with higher concentration of the relevant kind of atoms. The C pre-edge intensity is low, therefore, the micrograph (a) recorded at the 1s→π* C PSF peak

![Intensity profiles extracted from the XPEEM micrographs in Figure 8.2.15 a-b. The profiles correspond to the same location on the sample marked with white lines and have the original intensity scale.](image-url)
Figure 8.2.15 (a) was normalized by the micrograph (b) recorded at the 1s→π* C PMMA peak (Figure 8.2.15 b). The normalized image is shown in Figure 8.2.15 c. The lighter tone in this normalized image corresponds to higher concentration of PSF, while the darker tone corresponds to higher concentration of PMMA. Let us compare the contrast of features in the images (c), (f), and (i) in Figure 8.2.15. The following two rules must be true due to the fact that F is present only in PSF and O is present only in PMMA: (1) the features which are light-gray in the (c) image (more PSF, less PMMA) must be also light-gray in the (i) image and dark in the (f) image; (2) the dark features in the image (c) (less PSF, more PMMA) must obey the inverse rule. We pointed out several examples, how these two rules are obeyed, with round and elliptic markers in Figure 8.2.15. The rule (1) works for the features with forms of a ring with a loop-like companion on its right hand side (the dot-dashed elliptic marker) and a ring with a curved tail extended downwards (the bottom dashed elliptic marker). The inverse rule (2) works for the features which have forms of three rings (the upper dashed round marker), a ring with a double tail extended downwards (the right solid elliptic marker), and a single ring (the left solid round marker). There are also features which lose the right contrast in the oxygen (f) and fluorine (i) images due to worse quality of these images. An example of the wrong contrasted feature is the elongated downwards ring located at the upper-left corners of the XPEEM micrographs and the normalized images. It is light-gray at the energy of the PSF 1s→π* C peak (a) and in the normalized image (c), it inverses its contrast at the energy of the PMMA 1s→π* C peak (b) but not at the 1s O edge (d and f).

The original intensity scale of the micrographs in Figure 8.2.15 a-b is shown with their profiles depicted in Figure 8.2.16. The profile at 286.1 eV is of higher intensity than the profile at 289.3 eV. The two micrographs, from which the profiles were extracted, were recorded immediately one after another at the same hardware settings. Therefore, the relation of the profile intensities reflects the top layer composition of the sample. The intensity maxima at the 286.1 eV profile correlate with the intensity minima at the 289.3 eV profile and vise versa. The intensity of the profile at 286.1 eV varies in average between 64 and 72 a. u. (ΔI=8 a. u.), while the average range of the profile at 289.3 eV is between 58 and 67 a. u. (ΔI=9 a. u.). These values relate to the mean intensities and their standard deviations for the original micrographs, which are 67.9±4.53 (±6.62%) for 286.1 eV and 63.1±3.83 (±6.07%) for 289.3 eV. Assuming that the pre-edge background intensity is low, we estimate that the PSF- and PMMA-enriched features differ in average from each other in their top layer composition by 12%. Unfortunately, the micrographs in Figure 8.2.15 a-b alone provide insufficient information for calculation of absolute PSF and PMMA fractions in the brush top
layer (additional micrographs, recorded at the pre-edge photon energy range and ~30 eV above the edge, are required to determine the background level before and above the edge). A stack of XPEEM images in the required photon energy range was recorded from another location on this brush but its quality appeared too poor for the analysis.

The PSF/PMMA brush exposed to acetone does not show notable chemical contrast of features at the 1s C edge (Figure 8.2.17). Micrographs recorded at the 1s O and 1s F edges from several locations on the sample reveal the same result (not presented herein because they are not informative). The micrograph recorded at 289.3 eV (C 1s→π* electron transition of PMMA) has much higher mean intensity (I_{289.3}=126.6±7.94 a. u. (±6.27%)) than the micrograph recorded at 286.1 eV (C 1s→π* electron transition of PSF, I_{286.1}=58.3±4.19 a. u. (±7.19%)). The intensity profiles extracted from these micrographs (Figure 8.2.18) illustrate the observation. The micrographs (Figure 8.2.17 a-b) were recorded immediately one after another at constant hardware settings, therefore, the ratio of their intensities reflects the

![Micrographs](image)

(a) 286.1 eV; (b) 289.3 eV; (c) 289.3 eV/286.1 eV.

**Figure 8.2.17.** XPEEM at the 1s C edge of the PSF/PMMA brush FSMA3 (Appendix 3) exposed to acetone. Scale 5x5 µm. The contrast and brightness were optimized. The white lines mark the origins of extracted intensity profiles.

![Intensity profiles](image)

**Figure 8.2.18.** Intensity profiles extracted from XPEEM micrographs in Figure 8.2.17 a-b. The profiles correspond to the same location on the sample marked with white lines and have the original intensity scale.
composition of the brush top layer. The intensity ratio of the micrographs evidences strong enrichment of the brush top layer with PMMA. However, calculation of absolute PMMA fraction in the top layer from the micrographs in Figure 8.2.17 is not possible because of the same reason as for the previous sample. The two intensity profiles in Figure 8.2.18 reproduce the shape of one another. This effect is caused by domination of topographic contribution over the chemical contrast. The topographic contribution may dominate due to the high roughness of the PSF/PMMA brush after exposure to acetone (Figure 8.2.1 d). The second reason can be the weak chemical contrast, what agrees well with the uniform AFM phase images of this brush morphology (Figure 8.2.1 d, 8.2.7 a, 8.2.10 a).

Summarizing the most valuable experimental results of this section, we conclude that the worm-like morphology of the PSF/PMMA brushes consists of two kinds of the worm-like features, whose tops are enriched whether in PSF or PMMA. The chemical contrast in XPEEM of the features in the cluster morphology of these brushes is weak and totally masked by the topographic contribution. The top of the cluster morphology is enriched in PMMA more than of the worm-like morphology.

8.3. PSF/PMA brushes.

PSF/PMA brushes reveal morphologies of an interconnected network with pits with low roughness after treatment in THF and toluene (Figure 8.3.1 a-b) and with high roughness after exposure to acetone (Figure 8.3.1 c). The great difference in roughness of the PSF/PMA brush after exposure to toluene and acetone results in strongly different layer thickness (d) and refractive indices (n). This change is well seen by a naked eye on the brush immobilized on a silicon substrate (n = 3.885) (Figure 8.3.2). The dramatic change in roughness strongly affects water advancing and receding contact angles (Section 7.5).

Micromechanical analysis of the PSF/PMA brushes and their monocomponent precursors was carried out by M. Lemieux and V. V. Tsukruk at Iowa State University. They found that: (1) the top of the PSF/PMA brushes after exposure to toluene shows the Young modulus with main maximum about 900 MPa [Lem03a], what is close to the Young modulus of the monocomponent PSF brush [Lem03]. (2) The top of the PSF/PMA brushes after exposure to acetone shows the Young modulus within 50-100 MPa [Lem03a], what corresponds to the Young modulus of the monocomponent PMA brush [Lem03]. Herein, we refer to these two states of the PSF/PMA brushes as the glassy and the rubbery state, respectively (Figure 8.3.3).
(a) THF, vertical scale 10 nm, 3º, RMS roughness 2.2 nm, PSD maximum at 149 nm;

(b) toluene, vertical scale 10 nm, 5º, RMS roughness 1.8 nm, PSD maximum at 147 nm;

(c) acetone, vertical scale 150 nm, 90º, RMS roughness 37.1 nm, PSD maximum at 159 nm.

**Figure 8.3.1.** Morphologies of the PSF/PMA brush FSA1 (Appendix 3) consecutively exposed to solvents of different selectivity. AFM tapping mode, repulsive regime, amplitude set-point ratio 50%, ultrasharp tip. Left: topography (black horizontal lines mark origins of topography profiles), middle: phase contrast, 2x2 µm. Right: the topography profiles.

**Figure 8.3.2.** Optical photograph of a border between two regions with different morphologies on the PSF/PMA brush FSA1 (Appendix 3) grafted to a Si substrate. The upper part of the brush (light-blue) was treated in acetone, the lower part (dark-yellow) was treated in toluene. The contrast is optimized. The great difference in roughness resulted in strongly different layer thickness (d) and refractive indices (n) obtained from ellipsometry: $d_{\text{toluene}} = 60$ nm, $n_{\text{toluene}} = 1.51$; $d_{\text{acetone}} = 96$ nm, $n_{\text{acetone}} = 1.32$. 

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For the PSF/PMA brushes in the glassy state (after exposure to toluene), the brighter area in phase corresponds to the interconnected network, while the darker areas correspond to the pits (Figure 8.3.1 b). According to Sections 3.3.2-3, the darker phase signal in the repulsive tapping mode corresponds to a material which dissipates more energy. The PMA is more dissipative because of its viscoelastic properties. High resolution imaging of the glassy state morphology in the repulsive tapping mode \((A/A_0 \ 0.4-0.7)\) reveals two kinds of the pits: (1) covered with the PSF layer and (2) with complete holes in the PSF layers and open PMA domains (Figure 8.3.4). The pit of the second type shows two regions in phase: there is no change in phase at the edges of the pit relative to the surrounding area, and only at the deepest region a darker shift in the phase occurs. The difference in the phase is minor (several degrees) and can be due to a topographical contribution. Therefore, micromechanical analysis of this morphology is needed to make a final conclusion (see below). Interpretation of the rubbery morphology is more straightforward as the phase image in Figure 8.3.1 c shows a very homogeneous top layer except some topographical contribution from the edges. The conclusion can be made that the rubbery PMA dominates the top layer after exposure of the PSF/PMA brush to acetone.

The micromechanical analysis of the PSF/PMA brushes in the glassy state shows a mechanically heterogeneous surface in contrast to a homogeneous surface in the rubbery state [Lem03a]. For the glassy state, the pits correspond to areas of low elastic modulus and

![Figure 8.3.3. Surface histogram distributions from micromechanical mapping demonstrating the mechanical (adhesion, left; elastic modulus, right) difference of the layer of the PSF/PMA brush AFS1 (Appendix 3) in the glassy and rubbery states. Histograms are taken from 64x64 force volume scans for a total of 4096 data counts. The elastic modulus is the average value for each data point over the entire indentation range. Provided by M. Lemieux [Lem03a].](image-url)
increased adhesion, what indicates enrichment of these areas with more compliant and sticky rubbery PMA. Examination of individual force-distance curves (FDCs) in the glassy state reveals separate forms at different sampling locations indicated in Figure 8.3.4. Location 1 represents FDCs from the elevations of the layer, while location 2 corresponds to the hollows in the pits. The adhesion in the FDCs is larger for location 2, as is the pull-off force necessary to disjoint the tip/sample contact (Figure 8.3.5 upper row, left). The polar character of PMA compared with the fluorinated groups of PSF leads to higher adhesion. The energy required to pull off the surface increases with the area of mechanical contact, which is bigger for the compliant PMA. In addition, the slopes of the FDCs are very different for the locations 1 and 2, indicating differences in the actual cantilever deflection as it indents into the sample. A slope approaching unity describes the situation when the tip feels an infinitely hard surface, such as silicon. Slopes range from 0.6 to 0.8 for the location 1 and from 0.2 to 0.4 for the location 2. Conversion of the FDCs into load-penetration curves further confirms that a more compliant surface is associated with the location 2 as indentation is twice as deep under identical normal loads (Figure 8.3.5 middle row, left). Depth profiling of the elastic modulus shows a constant value of nearly 1 GPa at location 1. This behavior is in sharp contrast with location 2 as the initial modulus is close to 50 MPa until about 10 nm of penetration, at which point it climbs steeply (Figure 8.3.5 bottom row, left). The two latest results prove the heterogeneity of the surface of the PSF/PMA brushes in the glassy state.

Figure 8.3.4. High-resolution AFM tapping mode images of the glassy state morphology of the PSF/PMA brush AFS1 (Appendix 3) in the repulsive regime (A/A₀ 0.4-0.7). Tip radius was measured to be 10±1 nm. Top: 400 x 400 nm, bottom: 200 x 200 nm. Left panels: topography, z scale 10 nm, right panels: phase, z scale 20º. White solid rectangle indicates depression in the top PSF layer as phase is unchanged from the surrounding area, while the dashed rectangle indicates a complete hole in the PSF layer with the change in phase indicating the presence of the compliant PMA. The numbers at the bottom phase image correspond to different regions from which force-distance curves were recorded (Figure 8.3.5). Provided by M. Lemieux [Lem03a].
Results of micromechanical analysis of the rubbery state of the PSF/PMA brushes are given in the right column in Figure 8.3.5. The FDCs from the “tops” correspond to probing on the elevated network while the “holes” refer to the deep pits. For the rubbery state, nearly all FDCs indicated a highly compliant surface. Penetration into the PMA was routinely above 30 nm for a load of 50 nN, while for PSF in the glassy state the deepest penetration was 4 nm for the similar load (Figure 8.3.5 middle row). Depth profiling of the elastic modulus for the elevated network structure in the rubbery state showed a steady increase as the top layer was compressed but still did not exceed 70 MPa after 40 nm of indentation (Figure 8.3.5 bottom row, right). The effect of PSF was felt in the deepest pits as the elastic modulus quickly jumped to roughly 1 GPa after 6 nm of indentation, indicating a thin PMA layer within the pits. These results confirm the presence of the rubbery PMA layer all over the binary brush after exposure to acetone.

We consider that the mechanism of formation of smooth morphologies of mixed polymer brushes is similar to the already discussed mechanism for the smooth morphology of PSF/PMMA brushes after exposure to chloroform (Section 8.2.1).

We explain formation of the rough morphology of the PSF/PMA brushes after exposure to acetone and its difference from the cluster morphology of the PSF/PMMA brushes after exposure to this solvent as follows. PMA adopts viscoelastic state at ambient conditions, while PMMA is in glassy state: $T_g(\text{PMA}) = 282-290$ K, $T_g(\text{PMMA}) = 378-400$ K [Pol4]. The higher flexibility of the PMA chains causes their stronger swelling in comparison with the glassy PSF and PMMA. PMA is more polar than PMMA: a ratio of Flory-Huggins interaction parameters is: $\chi(\text{PS-PMA})/\chi(\text{PS-PMMA}) = 1.64$ [Zhao00a]. Although PS does not contain fluorine, the qualitative relationship of the interaction parameters remains valid for the brushes containing PSF. Consequently, PMA being more flexible and polar than PMMA swells in acetone much more and segregates from PSF much stronger. The morphologies of the PSF/PMA and PSF/PMMA brushes after exposure to acetone comprise round PSF clusters surrounded by the PMA or PMMA matrix. Therefore they both correspond to the dimple-PSF phase (Section 2.2). The strong swelling of PMA in acetone is a reason for the high roughness of the dimple-PSF morphology of the PSF/PMA brushes. The difference in the dimple-PSF morphologies of the PSF/PMMA and PSF/PMA brushes is that the PMMA matrix is depressed relative to the PSF clusters while the PMA matrix is elevated relative to the PSF clusters (Figure 8.3.6 a-b). This difference is rather a consequence of the higher incompatibility of PSF and PMA than of the higher swelling degree of PMA in acetone.
because the interconnected matrix (rich in PSF) in the glassy morphology of the PSF/PMA brushes is also elevated above the clusters (rich in PMA).

Figure 8.3.5. Typical force-distance curves (top, black symbols indicate approaching, gray symbols indicate retracting), load-penetration (middle), and elastic modulus-vs.-depth (bottom) profiles. Left: for the glassy state of the brush AFS1 (Appendix 3); locations 1 and 2 refer to the points depicted in Figure 8.3.4. Right: for the rubbery state of the same brush; “tops” and “holes” correspond to micromechanical probing on the PMA network structure and PSF dominated areas in the 100 nm deep holes, respectively. Provided by M. Lemieux [Lem03a].
The collapsed PMA in the glassy morphology after exposure of the PSF/PMA brushes to toluene forms the depressed clusters unlike PMMA in the PSF/PMMA brushes forming the worm-like structure upon exposure to this solvent. Basing on the results of AFM phase imaging and micromechanical analysis given above, we conclude that the glassy morphology of the PSF/PMA brushes corresponds to the dimple-PMA phase (Section 2.2). The glassy morphology of the PSF/PMA brushes is smoother than the rubbery morphology because of smaller swelling degree of PSF in toluene than of PMA in acetone.

The smooth morphology of the PSF/PMA brushes observed after exposure to THF provides similar phase images as the glassy morphology of these brushes after exposure to toluene. Probably, the morphology after exposure to THF also corresponds to the dimple-PMA phase, however, this assumption requires further confirmation. A scheme of formation of smooth morphologies is depicted in Figure 8.3.6 c.
The inverse grafting order in the case of the PSF/PMA brushes FSA1 and AFS1 does not cause any significant difference in the parameters of the grafted polymers, their grafting density and ratio in the mixed brushes (Appendix 3) as well as in the wetting properties (Section 7.5) and morphologies of these brushes (Figure 8.3.1 and Appendix 9).

8.4. Comparison of experimentally observed morphologies of mixed polymer brushes with predictions of the SCF theoretical approach.

The morphologies of the brushes were studied in metastable dry states obtained from the equilibrium states under particular solvents via the rapid drying procedure (Section 5.4). We found that the observed dry metastable states and composition of their top layers were relevant to the particular solvents and reproducible after new treatments with the same solvents independently on history of the previous treatments [Min01, Min02a] (Section 7.2, 7.4, 8.1.1, 8.2.1, 8.3). We concluded from these observations that the dry metastable states of mixed brushes possess “frozen” morphologies characteristic for the corresponding precursory equilibrium states in the solvents. This conclusion simplified the study of phase segregation in mixed polymer brushes and allowed us to apply a broader variety of physical techniques.

The polydispersity indices Mw/Mn of brush constituent polymers, estimated from SEC (Section 5.2) of the polymers from the bulk polymerization solutions (Section 4.2.4), were ~2 (Appendix 3), what was the ordinary value for polymers synthesized via conventional radical polymerization. Difference in the molecular weights (Mw) of brush constituent polymers ranging between 1:1 and 1:2 did not exceed the mean polydispersity index and led to only $\sqrt{2} \approx 1.4$ times difference in sizes of the unperturbed polymer coils (Appendix 1, 4), which determine the lateral period of phase segregation in the mixed brushes (Section 2.2). We consider that this is a sufficiently good approximation of the restrictions introduced by the SCF approach of M. Müller (Section 2.2). In future, modern controlled radical polymerization techniques combined with initiation from surface (Section 2.3) can be utilized for better control of the molecular weights and reduction of polydispersity of polymers in mixed brushes.

The tabulated data on polymer-polymer and polymer-solvent interactions available from handbooks [Pol4] are insufficient for determination of the average excluded volume interaction parameter $v^*$ which is necessary for the calculation of the other parameters $\chi', \xi$, and $\delta'$ introduced by M. Müller in his SCF theoretical approach [Mül02, Min02a] (Section 2.2). Therefore, only a qualitative comparison of the experiment and the theory is possible at present.
The Flori-Huggins interaction parameter $\chi$ can be evaluated from tabulated solubility parameters [Pol4] for dry polymer mixtures (blends) according to the eq. [A1.27] for $T = 298$ K and assuming that the $V_R$ equals 100 cm$^3$/mol: $\chi$(PS-PMMA) = 0.001; $\chi$(PS-PMA) = 0.164, what agrees with similar estimations of Zhao et al. [Zhao00a]. The solubility parameter for PSF was estimated using the group contribution method of Hoy [Pol4, Hoy70] and the resulting $\chi$ parameters were obtained via the formulas [A1.27, A1.25]: $\chi$(PSF-PMMA) = 0.006; $\chi$(PSF-PMA) = 0.266. The exact experimental values are available for the PS-P2VP and PS-P4VP mixtures: 0.09<$\chi_{PS-P2VP}$<0.11, 0.30<$\chi_{PS-P4VP}$<0.35 [Ikk00]. The presence of a solvent changes the $\chi$ parameter and the change cannot be estimated from the tabulated data [Pol4]. We speculate that for a mixed brush swollen in good non-selective solvent the second virial coefficients $v_{AB}$ remain approximately constant, while the coefficients $v_{AA}$ and $v_{BB}$ increase [2.2.1, 2.2.3], what leads to decrease of the $\chi$ ($\chi'$) parameter (a good non-selective solvent acts as a compatibilizer).

The solvent selectivity $\xi$ was qualitatively estimated from the wetting experiments and XPS (Section 7). The tabulated data on the second virial coefficients [Pol4] are insufficient for quantitative estimation of $(v_{AA} - v_{BB})$ in the upper part of the formula [2.2.4] for the solvent selectivity $\xi$.

8.4.1. PS/P2VP brushes.

We found that the PS/P2VP brushes (Section 8.1.1) may adopt whether the “coffee-grain” or the interconnected network morphologies after exposure to ethanol (water). Existence of the “coffee-grain” morphology is not considered by the SCF theory. The other morphologies adopted by these brushes are the cluster morphology after treatment in toluene and THF and the worm-like morphology after treatment in chloroform. The worm-like morphology exhibits two kinds of features enriched with one and another brush polymer, respectively (concluded from AFM phase imaging in tapping mode). The “coffee-grain”, interconnected network, and cluster morphologies show the top brush layer dominantly enriched with one polymer preferred by the solvent: P2VP after treatment in ethanol and water, PS after treatment in toluene (concluded from XPS, wetting experiments, AFM phase imaging) and THF (concluded from wetting experiments). AFM phase images recorded in intermittent tapping mode with high tip indentation depth suggest that the clusters, observed after exposure to toluene and THF, are composed of P2VP, which is the non-favorite polymer in these solvents.
These experimental data lead to a suggestion that the cluster morphologies, observed after the solvents selective to PS, are relevant to the dimple-P2VP phase predicted by Müller’s SCF theoretical approach [Mül02, Min02a] (Section 2.2). The worm-like morphology, found after exposure to the non-selective solvent chloroform, is rather the distorted lamellar morphology and is relevant to the ripple phase. The “coffee-grain” and the interconnected network morphologies found on PS/P2VP brushes after exposure to ethanol (water) possess the perpendicular phase segregation in agreement with Müller’s prediction for the dimple-PS phase (the top layer is enriched in P2VP). However, the lateral structures of these morphologies are not similar to the cluster structure predicted for the dimple morphologies. Therefore, an additional AFM study in the liquids is required in order to find out whether these metastable morphologies are relevant to equilibrium cluster morphologies of the PS/P2VP brush swollen in ethanol (water) or they correspond to a new phase not considered by the SCF theory.

8.4.2. PSF/PMMA and PS/PMMA brushes.

PSF/PMMA brushes (Section 8.2) reveal the worm-like morphologies after exposure to toluene and chloroform and the cluster morphology after exposure to acetone. The worm-like morphology found after exposure to toluene exhibits two kinds of the worm-like features enriched with PSF and PMMA, respectively (from AFM, XPEEM, and plasma etching experiments). The cluster morphology found after exposure to acetone shows the top brush layer dominantly enriched with PMMA (from wetting experiments, XPS, XPEEM). The plasma etching experiments show that the cores of the clusters are composed of PSF which is the non-favorite polymer in acetone. Basing on these experimental data, we conclude that the worm-like morphology of the PSF/PMMA brushes, found after exposure to toluene, is rather the distorted lamellar morphology and relates to the ripple phase predicted by M. Müller [Mül02, Min02a] (Section 2.2). In a similar way we conclude that the cluster morphology of the PSF/PMMA brushes, found after exposure to acetone, relates to the dimple-PSF phase.

The worm-like morphology of the PSF/PMMA brushes, found after exposure to chloroform, exhibits poor AFM phase contrast between the worm-like features. The top layer of this morphology is enriched with PMMA (according to XPS and wetting experiments). Therefore, this morphology possesses a different kind of perpendicular segregation of the brush polymers than in the worm-like morphology found after exposure to toluene. Therefore, the worm-like morphology, found after exposure to chloroform, should be additionally studied with plasma etching in order to find out: (1) whether the polymers are laterally
segregated into two kinds of worm-like features as in the case of the morphology found after exposure to toluene, (2) whether there is or there is no phase transition between this morphology and the worm-like morphology found after exposure to toluene (see Section 8.4.5 for details).

We have not found a morphology comprising PMMA clusters which could be relevant to the dimple-PMMA phase. Exposure to cyclohexane (this solvent improves its quality for PS with increasing temperature and becomes a theta-solvent for PS at 34º C [Pol4]) at ambient and increased temperature of the PSF/PMMA brushes pre-treated in toluene does not induce transformation of the initial worm-like morphology into clusters. The most probable explanation is that cyclohexane is a non-solvent for PMMA, and therefore the PSF/PMMA brushes cannot reach thermodynamic equilibrium under this solvent. The non-equilibrium state cannot be compared with the predictions of Müller’s SCF theoretical approach which considers exclusively stable equilibrium morphologies.

The dimple-PMMA phase can probably be found after exposure of the PSF/PMMA brushes to a mixture of cyclohexane and toluene. Toluene would increase mobility of the PMMA segments. But we have limited our morphological studies with pure solvents only in order to avoid preferential absorption of the solvents from their mixture by the brush polymers. The preferential absorption of solvents is a factor not considered by Müller’s approach.

We found that fluorination of polystyrene is not critical for adoption by the mixed brushes of the worm-like and the cluster morphologies upon exposure to toluene and acetone, respectively. Non-fluorinated PS/PMMA brushes adopt similar morphologies upon exposure to these solvents.

8.4.3. PSF/PMA brushes.

The PSF/PMA brushes adopt morphologies which have a similar topographic pattern after exposure to different solvents (THF, toluene, acetone). The topographic pattern consists of an interconnected network with pits (Section 8.3). The micromechanical analysis made by Lemieux et al. [Lem03a] quantitatively shows that the top layer of the PSF/PMA brushes is strongly enriched in the glassy PSF and the rubbery PMA after exposure to toluene and acetone, respectively. The uniform phase images recorded in hard (A/A₀ 0.4-0.7) repulsive tapping mode together with the micromechanical analysis of the rubbery morphology evidence uniform enrichment of the top layer in PMA. The hard PSF domains covered with the PMA layer were detected with the micromechanical analysis in the bottom of the 100 nm
deep holes of the rubbery morphology. This observation is the reason to assign the rubbery morphology to the dimple-PSF phase predicted by Müller’s SCF theoretical approach [Mül02, Min02a] (Section 2.2). The rubbery state of the PSF/PMA brushes exhibits the extremely high roughness and the reduced effective refractive index of the brush layer accompanied with the macroscopic optical effect seen with a naked eye (Section 7.5, 8.3). On the contrary to the hydrophilic properties of PMA, the high roughness of the rubbery state of the PSF/PMA brushes leads to the strong increase of the water advancing contact angle ($\Theta_{\text{adv}}$) which becomes higher than the respective value on the more hydrophobic surface of the brushes in the glassy state (Section 7.5). The high RMS roughness of the PSF/PMA brushes in the rubbery state (37 nm) is explained by the high swelling degree of PMA in acetone due to higher flexibility of its rubbery chains in comparison with glassy PSF and PMMA (PSF/PMMA brushes exhibit lower roughness after exposure to acetone).

The glassy morphology of the PSF/PMA brushes after exposure to toluene is smooth (RMS roughness 1.8 nm). The high-resolution AFM phase images recorded in hard repulsive tapping mode reveal heterogeneity of the top layer of the brush in the glassy state. A certain part of the depressions in the glassy morphology shows the darker phase signal than the surrounding areas. The darker phase may reflect open compliant PMA domains. The micromechanical analysis evidences the presence of the compliant PMA domains in the holes of the glassy morphology. It evidences also that their certain part is not covered by the glassy PSF. The pronounce perpendicular segregation resulting in enrichment of the top layer in PSF and presence of the PMA domains in the bottom of the depressions (pits) of the glassy morphology of the PSF/PMA brushes are the reasons to assign the glassy morphology to the dimple-PMA phase predicted by Müller’s SCF theoretical approach [Mül02, Min02a] (Section 2.2). The available information is insufficient to make such an assignment for the morphology of the PSF/PMA brushes found after treatment in THF.

We suppose that the high incompatibility of PSF and PMA (beginning of Section 8.4) makes the ripple phase unstable for the PSF/PMA brushes. Clarification of this point is important for verification of the theoretical predictions by M. Müller (Section 2.2) and requires additional studies (see Section 8.4.5 for details).

8.4.4. Lateral periods of the nano-phase segregated morphologies.

The lateral periods for the worm-like and cluster morphologies obtained experimentally have close values for the same mixed brushes. The values obtained from Fast Fourier Transformation (FFT) of AFM topographic images are 1.5-2 times bigger than the
values calculated from the estimated molecular weights (Mw) of the grafted polymers using the coefficients of Müller’s SCF theoretical approach (Section 2.2, Appendix 4). The most probable reasons for this are: (1) the theory considers mixed brushes built of monodisperse polymers of equal molecular weights; (2) the effective molecular weights of the polydisperse polymers in the experimentally obtained mixed brushes, which determine the period of the laterally segregated morphologies, exceed the weight-averaged molecular weights Mw which were utilized for the calculations presented in Appendix 4. AFM morphological studies of mixed polymer brushes with narrow polydispersity and equal molecular weights of the constituent polymers synthesized via controlled surface-initiated radical polymerization [Zhao03] (Section 2.3) may be helpful for understanding, why the theoretical and experimental lateral periods of the segregated morphologies are so different.

8.4.5. Other conclusions.

The SCF theoretical studies of phase segregation in binary mixed polymer brushes were done for the case of monodisperse brush polymers of equal molecular weight (Section 2.2). Polydispersity of the grafted polymers and, probably, local deviations from random distribution of the grafting points were the reasons why, on the contrary to the predictions of the SCF theoretical approach by M. Müller, no long-range order was experimentally found in the morphologies of the mixed polymer brushes (we made unsuccessful attempts to order the brush morphologies via long-term exposure to various solvents and their saturated vapors).

The surface composition adopted by the PS/P2VP brushes upon exposure to binary solvents (ethanol + toluene and ethanol + chloroform) changes step-like with gradually increasing volume fraction of one of the solvents: sharp switching of the surface composition through the whole switching range occurs within a definite narrow window in the composition of the binary solvents (Section 7.3). This observation supports the prediction of Müller’s SCF theoretical approach (Section 2.2) for the phase transitions between morphologies of binary mixed polymer brushes. This prediction requires further verification with AFM morphological studies and parallel contact angle measurements on mixed polymer brushes (PS/P2VP, PSF/PMMA, and PSF/PMA) after exposure to binary solvents. The PS/P2VP brushes can be studied further after exposure to the same solvent mixtures, while the mixed brushes of the other two kinds should be examined after exposure to chloroform-toluene, acetone-toluene, chloroform-acetone mixtures.
9. Switching of mixed polymer brushes upon heating above the glass transitions temperature.

We found experimentally that a binary polymer brush whose polymers have close glass transition temperatures (Tg) adopts a layered morphology upon heating above the higher Tg. The top layer of the new morphology is occupied by the polymer which provides a lower surface energy [Kob03, Cho00].

The experiment was performed on the PS/P2VP brush SVP25 (Appendix 3) whose polymers have Tg ~100º C [Pol4] and ~104º C [Wu02], respectively. Two samples of the brush were switched to the hydrophilic and hydrophobic states, respectively, via the routine procedure of exposure to the solvents of opposite selectivity: the first sample was exposed to ethanol while the second sample was exposed to toluene (Section 7.2). The samples were rapidly dried with nitrogen flux. The sample exposed to ethanol revealed the hydrophilic water contact angles corresponding to the brush surface occupied by P2VP, while the sample exposed to toluene revealed the hydrophobic contact angles corresponding to the brush surface occupied by PS (Table 9.1). This was in agreement with the previous results (Section 7.2). We examined the morphologies of the two samples with tapping mode AFM (Figure 9.1 a, c) and found them similar to the morphologies observed on other PS/P2VP brushes after exposure to the respective solvents (Section 8.1.1).

<table>
<thead>
<tr>
<th>Preliminary exposed to:</th>
<th>Before annealing</th>
<th>After annealing</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Θadv, °</td>
<td>Θrec, °</td>
</tr>
<tr>
<td>ethanol</td>
<td>71.2±2.5</td>
<td>22.2±4.8</td>
</tr>
<tr>
<td>toluene</td>
<td>93.6±2.1</td>
<td>36.6±6.6</td>
</tr>
</tbody>
</table>

The two samples of the PS/P2VP brush, whose surfaces were switched to the opposite (hydrophilic and hydrophobic) states, were annealed in vacuum at 150º C for 6 h. Monocomponent PS and P2VP brushes were annealed together with the mixed brushes for reference. Afterwards, the new surface states of the mixed and monocomponent brushes were studied with tapping mode AFM and water contact angle measurements, respectively.

Both samples of the mixed PS/P2VP brush revealed smooth morphologies with uniform AFM phase images (no contrasted features) after the annealing (Figure 9.1 b, d). The morphologies of the annealed monocomponent brushes were also smooth (see the discussion...
in Section 6.2-3, AFM images in Appendix 8.2). The annealed brushes exhibited a strong charging effect which was observed upon approach of an AFM tip to their surfaces. The charging caused decrease of the tip oscillation amplitude. The proper imaging in repulsive tapping mode of these samples was possible only with ultrasharp cantilevers (Section 5.5.1 A).

![AFM images](image)

(a) RMS roughness 4.2 nm;  
(b) RMS roughness 0.8 nm;  
(c) RMS roughness 8.0 nm;  
(d) RMS roughness 1.1 nm.

**Figure 9.1.** Morphologies of the PS/P2VP brush SVP25 (Appendix 3) before (a, c) and after annealing (b, d) at 150º C in vacuum for 6 h. (a) Topography of the brush after exposure to ethanol (z scale 15 nm); (b) the brush annealed after exposure to ethanol, left – topography (z scale 7 nm), right – phase contrast (z scale 10º), A/A₀ = 80%, A₀ = 84 nm. (c) Topography of the brush after exposure to toluene (z scale 40 nm); (d) the brush annealed after exposure to toluene, left – topography (z scale 10 nm), right – phase contrast (z scale 10º), A/A₀ = 63%, A₀ = 54 nm. Scale 2x2 µm. The b and d were recorded in the repulsive tapping mode AFM with ultrasharp cantilevers from MicroMasch (Section 5.5.1 A). The a and c were recorded in tapping mode AFM (A/A₀ 80%) with cantilevers FM-W from Nanosensors (Section 5.5.1 C).

The annealed samples of the mixed brush demonstrated very similar water contact angles (Table 9.1). The Θ_{adv} on both annealed samples of the PS/P2VP brush was similar to the respective value on (1) the sample of this brush exposed to toluene before the annealing
and on (2) the PS monocomponent brush after exposure to organic solvents or storage at ambient conditions for 24 h (Table 6.2). The $\Theta_{rec}$ on the annealed samples of the PS/P2VP brush was 20-25º higher than in the case (1) and similar to the respective value in the case (2) and to the respective value on the annealed PS brush (Table 6.2).

A reproducible effect of increase of the $\Theta_{adv}$ from ~92º to ~98º upon annealing was observed on the monocomponent PS brush (Table 6.2). A proposed explanation for that is that the adsorbed humidity and organic solvents were removed from the polymer upon annealing. On the contrary, the mixed PS/P2VP brush revealed after annealing the ordinary $\Theta_{adv}$ value of 92.1º (Table 9.1). The monocomponent PS and mixed PS/P2VP brushes were annealed simultaneously in the same oven what excludes presence of volatile hydrophobic compounds in the oven and leaves the question open.

The monocomponent P2VP brush revealed after annealing very unusual contact angle values. They are outside of the scope of this chapter and are discussed in Section 6.2.

The smooth morphologies observed with AFM and the hydrophobic contact angles for the annealed PS/P2VP brushes evidence a layered morphology with PS in the top and P2VP in the bottom adopted by the brushes upon annealing. Small hysteresis of water contact angle on the annealed mixed brushes suggests more pronounced perpendicular segregation of the two brush polymers than after treatment in toluene.
10. Microcontact printing on binary mixed polymer brushes.

This chapter illustrates how the ability of mixed polymer brushes to switch their top layer composition can be used for formation of chemically patterned surfaces. In these experiments a wet microcontact printing technique was used for the pattern formation. The local chemical composition of the top layer was sensed with XPEEM.

A PDMS stamp $5 \times 5 \text{ mm}^2$ was examined with AFM (Figure 10.1). Its surface had parallel trenches with dimensions as shown in Table 10.1. The cracks seen on the PDMS surface were formed upon oxidation due to losses of elasticity of PDMS (no cracks were observed with AFM on the original PDMS surface before oxidation, see Appendix 10). The water contact angles on the stamp surface right before usage were: $\Theta_{\text{adv}} 114^\circ$ and $\Theta_{\text{rec}} 84^\circ$. The respective values for original PDMS are $120^\circ$ and $79^\circ$. Hence, the main result of oxidation was introduction of a network of cracks on the stamp surface, while the difference in wetting properties achieved upon the oxidation was not significant.

![Figure 10.1. AFM topography image 10x10 µm (left) and a profile (right) of the PDMS stamp. The black line at the left image marks the profile origin.](image)

PSF/PMMA brushes were chosen for this experiment because their composition was optimized for sensing with XPEEM. The mixed brush FSMA2 was switched by toluene to the hydrophobic state, rapidly dried with nitrogen flux, and then patterned with the PDMS stamp in acetone as described in Section 4.3. A similar brush FSMA3 was switched by acetone to the hydrophilic state, rapidly dried with nitrogen flux, and patterned with the same PDMS stamp in toluene according to Section 4.3. Topography of the both patterned brushes was investigated with AFM (Figure 10.2). The both patterned areas contain parallel oriented imprinted ribs corresponding to the trenches on the stamp. The height of the ribs after patterning in acetone (Figure 10.2c) is about 3 times higher than after patterning in toluene (Figure 10.2f) probably due to better swelling of PMMA by acetone in the first case than of PSF and PMMA by toluene in the second case. The ribs in both cases have elevated boundaries due to capillary forces acting upon patterning on the liquid phase inside of the
The brush patterned in acetone adopted the network of cracks (Figure 10.2 b) from the oxidized PDMS surface (brushes patterned in acetone in the same way with original PDMS do not show such cracks, Appendix 11). We found that the worm-like structures of the brush stamped in toluene order upon the confinement into parallel lamellae (compare Figures 10.2 e and 8.2.1 a, c). The lamellae do not show pronounced phase contrast as in the case of no confining surface due to preferential attraction of PSF to the hydrophobic PDMS stamp.

**Figure 10.2.** AFM of the patterned PSF/PMMA brushes: a-c the brush FSMA2 (Appendix 3) after wet microcontact printing with acetone, d-f the brush FSMA3 after wet microcontact printing with toluene.

We recorded sequences of XPEEM micrographs at the 1s C edge (285.0-290.0 eV, DE=0.2 eV) from the two patterned PSF/PMMA brushes. A nice result was obtained from the
brush patterned in acetone. Two representative XPEEM micrographs recorded from it at the C 1s→π* peak energies corresponding to PSF and PMMA are shown in Figure 10.3 a and b, respectively. Three kinds of regions are seen in the first micrograph: (1) the three dark stripes corresponding to the imprinted ribs, (2) the gray area between the stripes, and (3) the light-gray narrow borders of the stripes. The second micrograph is mainly gray with the gray stripes corresponding to the ribs and having dark narrow borders. The light and dark borders in the two micrographs do not exactly correspond to each other because the distance \( l_1 \) (Figure 10.3 a) is bigger than \( l_2 \) (Figure 10.3 b). The lengths \( l_1 \) and \( l_2 \) lie between the lengths \( d_1 \) and \( d_2 \) obtained from the AFM scans of this pattern (Figure 10.2 c, Tables 10.1-2). This means that both the light and the dark borders in the XPEEM micrographs correspond to the outer walls of the imprinted ribs. The light (wider) borders correspond to the lower part on the walls while the darker (narrower) borders correspond to the upper part of the walls. Average NEXAFS spectra were extracted from the recorded sequence of the XPEEM micrographs for each of the four regions specified in Figure 10.3 a and b. The spectra are presented in Figure 10.4. The PSF peak at 286.2 eV increases upon transition from the region (1) through (2) and (4) to the region (3), while the PMMA peak at 289.3 eV decreases at the same time. This is the most obvious confirmation that the contrast in the micrographs a and b in Figure 10.3 reflects changes in chemical composition and not topographic effects. It is clear from Figure 10.4 that the richest in PFS region is (3), while the richest region in PMMA is (1).

We calculated a semi-quantitative composition map (Figure 10.3 c) from the recorded sequence of the XPEEM micrographs and from the NEXAFS spectra of separated PSF and PMMA as described in Section 5.7. For clarity, a smoothed profile of the map is provided in Figure 10.3 d. The profile shows a defect in the composition map caused by non-perpendicular incidence of x-rays (the angle of incidence was 30º). The defect comprises a significant difference (up to 35%) in observed composition between the left and right borders of the imprinted ribs. The data on composition of the top layer were averaged for each kind of the regions, the composition of the region (3) was averaged between the left and right rib borders (Table 10.3, method C). Independently, the top layer composition in each of the four regions was calculated from the NEXAFS spectra in Figure 10.4 (Table 10.3, methods A, B, B2). The details of the calculations are given in Section 5.7.

We concluded from the Table 10.3, that the whole brush top layer becomes enriched with PMMA upon stamping in acetone. This effect was expected because of selectivity of acetone to PMMA. In the region (1) the swollen by acetone PSF/PMMA brush can reach contact with the bottom of the PDMS stamp trenches: it is known from neutron reflectivity
experiments [Ivk01, Kar94, Mar01] that thickness of a monocomponent polymer brush swollen by a good solvent is 6–8 times bigger than of this brush in dry state. Upon evaporation of acetone its level decreases and the contact of the brush with the stamp in the region (1) is lost. As it is known from the kinetic measurements (Section 7.1), a brush top layer switches its composition in organic solvents very fast. Hence, we consider that the brush top layer in the region (1) has sufficient time to adopt a new state in contact with acetone vapor, and its composition is determined only by the difference of swelling of PMMA and PSF in acetone.

![Image](a) 286.2 eV;  
(b) 289.4 eV;

(c) composition map;

(d) smoothed (by 3 pixels) profiles of PSF and PMMA fractions in the top layer.

Figure 10.3. XPEEM of the PSF/PMMA brush FSMA2 (Appendix 3) patterned in acetone. (a) and (b) are the representative XPEEM micrographs scaled to equal arbitrary intensity. (c) Gray tones in the composition map from 0 to 255 linearly correspond to PMMA fraction in the top layer from 0 to 100%, respectively. The black line marks the origin of the profile (d).
**Figure 10.4.** NEXAFS 1s C spectra extracted from the four regions on the PSF/PMMA brush FSMA2 (Appendix 3) patterned in acetone. The regions are designated in Figure 10.3 with numbers coupled with thick white arrows. The spectra are set to arbitrary pre- and after the edge intensities according to Section 5.7.

**Table 10.1.** Dimensions of topographic patterns on the PDMS stamp and on the patterned surfaces of the PSF/PMMA brushes FSMA2 and FSMA3 (Appendix 3) stamped in acetone and toluene, respectively.

<table>
<thead>
<tr>
<th></th>
<th>D₁, µm</th>
<th>D₂, µm</th>
<th>d₁, µm</th>
<th>d₂, µm</th>
<th>H₁, nm</th>
<th>H₂, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>stamp</td>
<td>1.6</td>
<td>1.40</td>
<td></td>
<td></td>
<td>470</td>
<td></td>
</tr>
<tr>
<td>FSMA2</td>
<td>1.72</td>
<td>2.41</td>
<td>1.25</td>
<td>0.55</td>
<td>45-60</td>
<td>29-47</td>
</tr>
<tr>
<td>FSMA3</td>
<td>1.4</td>
<td>2.5</td>
<td>1.6</td>
<td>0.6</td>
<td>12-20</td>
<td>13-23</td>
</tr>
</tbody>
</table>

**Table 10.2.** Dimensions (µm) of the pattern observed with XPEEM on the PSF/PMMA brush FSMA2 (Appendix 3) stamped in acetone. The values were determined from the pattern period of 3 µm.

<table>
<thead>
<tr>
<th>L₁</th>
<th>l₁</th>
<th>L₂</th>
<th>l₂</th>
<th>L₃</th>
<th>l₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0</td>
<td>1.0</td>
<td>2.3</td>
<td>0.7</td>
<td>2.0</td>
<td>1.0</td>
</tr>
</tbody>
</table>
Table 10.3. PMMA fraction (normalized by the sum of PSF and PMMA fractions) in the top layer of the patterned PSF/PMMA brushes in the characteristic regions of the patterns. The results obtained from XPEEM.

<table>
<thead>
<tr>
<th>Code (Appendix 3) of the patterned brush, region in the pattern, description of treatment</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A</td>
</tr>
<tr>
<td>FSMA2 stamped with PDMS in acetone</td>
<td>73</td>
</tr>
<tr>
<td>stamped FSMA2, top of the ribs (1)</td>
<td>88</td>
</tr>
<tr>
<td>stamped FSMA2, between the ribs (2)</td>
<td>75</td>
</tr>
<tr>
<td>stamped FSMA2, light edges of the stripes (3)</td>
<td>39</td>
</tr>
<tr>
<td>stamped FSMA2, dark edges of the stripes (4)</td>
<td>69</td>
</tr>
<tr>
<td>FSMA2 exposed to toluene</td>
<td>2</td>
</tr>
<tr>
<td>FSMA3 stamped with PDMS in toluene</td>
<td>25</td>
</tr>
<tr>
<td>stamped FSMA3, dark stripes (5)</td>
<td>30</td>
</tr>
<tr>
<td>stamped FSMA3, light area (6)</td>
<td>22</td>
</tr>
<tr>
<td>FSMA3 exposed to acetone</td>
<td>35</td>
</tr>
</tbody>
</table>

* Difficult to identify this region at the map. See the map profiles in Figure 10.3 d.

** The same data as in Table 8.2.1.

Figure 10.5. The mechanism 1 of chemical patterning of a PSF/PMMA brush upon microcontact printing with a PDMS stamp in acetone. PSF and PMMA chains are drawn with black and gray lines, respectively. Light gray color means the solvent (acetone). Numbers point out the respective regions in Figure 10.3 a-b.

The top of the imprinted ribs (1) is the region richest in PMMA due to no contact with the hydrophobic PDMS surface and better swelling of PMMA than of PSF in acetone. The area between the ribs (2) was in tight contact with the stamp. We consider that the stamp repels polar PMMA to some extend what is the reason for the smaller PMMA fraction in the top layer of the region (2) (Table 10.3). The region (4) is connected to the region (1), they have similar top layer composition and can be considered together. The PMMA fraction in the region (3) is significantly smaller than in the other three regions. We explain this by layering of the PSF under the better swollen PMMA inside of the stamp channels upon the printing.
procedure (Figure 10.5). The layered composition profile is sensed by XPEEM on the vertical walls of the imprinted ribs.

Insignificantly small or no difference in surface composition of PSF/PMMA brushes patterned with a non-oxidized PDMS stamp was found with XPEEM between the regions type (1) and (2) (contacted and not contacted the stamp, respectively) for each of three solvents used for the patterning procedure: acetone, chloroform, and toluene. This observation excludes probability of the pattern formation due to selective interactions of the stamp surface with the brush constituents.

Results of the XPEEM investigation of the PSF/PMMA brush which was patterned in toluene are presented in Figures 10.6-10.7. The two representative XPEEM micrographs (Figure 10.6 a, b) recorded at energies of the $1s \rightarrow \pi^*$ C peaks of PSF and PMMA have similar contrast. The three stripes (region 5) which correspond to the imprinted ribs appear darker than the surrounding area (region 6) at the both micrographs. The calculated composition map (Figure 10.6 c) is quite uniform with weak traces of a chemical pattern. Its profile (Figure 10.6 d) smoothed (by 3 pixels) profiles of PSF and PMMA fractions in the brush top layer.

**Figure 10.6.** XPEEM of the PSF/PMMA brush FSMA3 patterned in toluene. (a) and (b) are the representative XPEEM micrographs scaled to equal arbitrary intensity. (c) Gray tones in the composition map from 0 to 255 linearly correspond to PMMA fraction in the top layer from 0 to 100%, respectively. The white line marks the origin of the profile (d).
10.6 d) reveals enrichment of the brush top layer with PSF. Unlike in the case of patterning in acetone, the profile of PSF lies always above the profile of PMMA. The profiles show that the region 5 is richer in PMMA than the region 6. Local NEXAFS spectra were extracted from the recorded sequence of XPEEM micrographs in order to be sure that this is not due a topography effect. The spectra scaled to equal arbitrary background intensity confirm the small difference in the top layer composition (Figure 10.7, Table 10.3). We consider that the weak chemical contrast of the pattern adopted by the PSF/PMMA brush upon microcontact printing in toluene is a consequence of preferential segregation of PSF to the hydrophobic PDMS stamp. No borders around the region 5 are observed like upon patterning with acetone due to similar swelling degree of both PSF and PMMA in toluene.

We note once again that the calculations of the top layer composition based on XPEEM data (Table 8.2.1, 10.3, Figure 10.3 d, 10.6 d) are semi-quantitative. They can be used for qualitative comparison of composition of the top brush layer after different kinds of treatment but the calculated values are significantly shifted from the true ones (compare the XPEEM data from Table 8.2.1 and accurate XPS data from Table 7.3) as discussed in Section 5.7.

![Graph](image)

**Figure 10.7.** NEXAFS 1s C spectra extracted from the two regions on the PSF/PMMA brush FSMA3 (Appendix 3) patterned in toluene. The regions are designated in Figure 10.6 with white arrows.
11. Conclusions.


The mixed brushes PS/P2VP, PSF/PMMA, PSF/PMA were synthesized via surface-initiated two-step radical polymerization. The molecular weight (Mw) of the grafted polymers was estimated assuming to be equal to the molecular weight of the respective polymers in the bulk solution after polymerization [Sid99]. The molecular weight of the bulk polymers was determined with size excluded chromatography (SEC, Section 5.2). The Mw ranged from $0.5 \cdot 10^5$ to $8 \cdot 10^5$, the polydispersity (Mw/Mn) was 1.8-2.2 (Appendix 3). Difference in the molecular weights (Mw) of brush constituent polymers ranging between 1:1 and 1:2 did not exceed the mean polydispersity index and led to only $\sqrt{2} \approx 1.4$ times difference in sizes of the unperturbed polymer coils (Appendix 1, 4), which determine the lateral period of phase segregation in the mixed brushes (Section 2.2). We consider that this is a sufficiently good approximation of the restrictions introduced by the SCF approach of M. Müller (Section 2.2). In future, modern controlled radical polymerization techniques combined with initiation from surface (Section 2.3) can be utilized for better control of the molecular weights and reduction of polydispersity of polymers in mixed brushes.

The brush regime of the grafted polymer layers was established due to the short average distance between the grafting points ranging between 10 and 4 nm, what was much less than the mean unperturbed chain end-to-end distance (30-60 nm) for polymers with Mw as given above (see also Appendix 4).

11.2. Switching of composition of the surfaces of mixed brushes by solvents.

The investigated mixed polymer brushes were composed of two polymer species with big difference in polarity. This property made possible to switch the surface composition of the brushes via exposure to selective solvents: the preferred polymer occupied the top layer while the second non-favorite polymer collapsed and occupied the bottom layer. Both polymer species occupied the brush top upon exposure to a good non-selective solvent. The surface composition of mixed polymer brushes in the wetting experiments was relevant to the particular solvents and reproducible (Sections 7.1-2). The switching of the mixed brushes was reversible.

11.2.1. Time of the switching.

We found with water contact angle measurements that the characteristic time of switching of surface composition of the PS/P2VP, PSF/PMMA, and PSF/PMA mixed brushes
(thickness up to 60 nm) from the hydrophilic to the hydrophobic state and backwards upon exposure to selective solvents, providing sufficient mobility of non-favorite brush polymers, was smaller than 6 s, what was the minimal time required to immerse the brush to a solvent, take it out, and dry in nitrogen flux (Section 7.1).

We observed that water, which is a selective solvent for P2VP with very poor quality for the non-favorite PS, switches a PS/P2VP brush surface significantly slower (within ~5 min) from the hydrophobic to the hydrophilic state likely due to smaller rate of diffusion of water into the brush layer.

11.2.2. Discontinuous change of surface composition of the mixed brushes in response to gradual change in solvent selectivity.

The surface composition adopted by the PS/P2VP brushes upon exposure to binary solvent mixtures (ethanol + toluene, ethanol + chloroform) was changing step-like upon gradually increased volume fraction of one of the solvents (ethanol): a sharp switching of the surface composition through the whole switching range occurred within a definite narrow window in the composition of the binary solvents (Section 7.3). This experimental observation supports the prediction of Müller’s SCF theoretical approach (Section 2.2) for the phase transitions between morphologies of binary mixed polymer brushes.

11.3. Studies of morphologies of mixed polymer brushes.

Morphologies of the mixed polymer brushes were studied in metastable dry states obtained from the equilibrium states under particular solvents via rapid drying in nitrogen flux. The observed dry metastable morphologies were relevant to the particular solvents and reproducible after new treatment with the same solvents independently on the history of previous treatments (Section 8, 8.1.1, 8.2.1, 8.3).

The mixed PS/P2VP (Section 8.1.1, 8.4.1) and PS(F)/PMMA (Section 8.2, 8.4.2) brushes showed worm-like morphologies with two kinds of the worm-like features enriched with one and another brush polymer, respectively, after exposure to good non-selective solvents (chloroform for PS/P2VP brushes, toluene for PS(F)/PMMA brushes). The worm-like morphology was found to be relevant to the ripple phase predicted by Müller’s SCF theoretical approach (Section 2.2) in which the two brush polymers segregate into two respective kinds of lamellae alternating across the surface. The worm-like structures in the case of the PS(F)/PMMA brushes were pronounced and notably longer probably due to smaller incompatibility $\chi$ (Section 8.4) than in the case of the PS/P2VP brushes. The
PS(F)/PMMA brushes showed a smooth worm-like morphology after exposure to chloroform. This morphology had the top layer richer in PMMA in comparison with the worm-like morphology after exposure to toluene (Section 7.2, 7.4, 8.2.1). Studies of surface (top layer) composition of the PS(F)/PMMA brushes after exposure to chloroform + toluene mixtures with gradually changing volume fraction of chloroform are required to find out whether there is a phase transition between these two states of the brushes.

Cluster morphologies for the mixed brushes were found after exposure to selective solvents. The PS(F)/PMMA brushes exhibited the cluster morphology after treatment in acetone: the round clusters were composed of non-favourite PS(F) and covered by PMMA. This morphology was found to be relevant to the dimple-PS(F) phase predicted by the SCF theory. No morphology relevant to the dimple-PMMA phase was found after treatment of the PS(F)/PMMA brushes in warm cyclohexane probably due to its poor quality for PMMA and low mobility of the PMMA segments. The PS/P2VP brushes exhibited the cluster morphology comprising the clusters of collapsed P2VP covered by favourite PS after exposure to toluene. This morphology was relevant to the dimple-P2VP phase predicted by Müller’s SCF approach (Section 2.2). No cluster morphology relevant to the dimple-PS phase was found after exposure to a solvent of opposite selectivity (ethanol): the PS/P2VP brushes exhibited whether the “coffee-grain” or the interconnected network morphology depending on the ratio between the polymers in the brush. These two morphologies were perpendicular segregated with the top layer rich in P2VP. The “coffee-grain” morphology is not considered by Müller’s SCF approach (Section 2.2) illustrating that phase behaviour of natural systems is more diverse. The question, whether the interconnected network morphology of PS/P2VP brushes found after exposure to ethanol corresponds to the dimple-PS phase or represents a different phase, remains open. Studies of morphological transitions of PS/P2VP brushes upon exposure to binary solvents parallel with AFM and contact angle measurements may be helpful for solution of this problem.

The PSF/PMA brushes (Sections 8.3, 7.5, 8.4.3) reveal interconnected network morphologies with pits (hollows) with the top layer enriched in the glassy PSF and the rubbery PMA after exposure to toluene and acetone, respectively [Lem03a]. The compliant PMA domains, located in the bottom of the pits in the glassy state of the PSF/PMA brushes, become visible in AFM phase images recorded in hard (A/A_0 0.4-0.7) repulsive tapping mode. Micromechanical analysis evidences that the PMA domains are covered by the glassy PSF layer, while their certain part remains open.
On the contrary to the smooth glassy morphology, the rubbery morphology found after exposure of the PSF/PMA brushes to acetone is very rough (depth of the hollows ~100 nm), what is accompanied with the visible change in colour and reduction of the effective refractive index of the brush layer down to 1.3 (λ 632.8 nm). Although the surface of the rubbery morphology is hydrophilic, the high roughness leads to the strong increase of water advancing contact angle (Θ_{adv} 113-117°) which is higher than on the same brush in the glassy state with more hydrophobic surface (Θ_{adv} 96°). The high roughness of the PSF/PMA brushes after exposure to acetone is explained by high swelling degree of PMA in acetone due to higher flexibility of its rubbery chains in comparison with glassy PSF and PMMA. The uniform AFM phase images suggest the uniform composition of the top layer of the rubbery morphology, what is confirmed by micromechanical analysis. The micromechanical analysis reveals hard PSF domains in the bottom of the 100 nm deep holes of the rubbery morphology. The PSF domains are covered by the PMA layer (Section 8.3).

The rubbery state of the PSF/PMA brushes after exposure to acetone is assigned to the dimple-PSF phase predicted by the SCF theory basing on the data of the micromechanical analysis (Section 8.3) and high incompatibility of the two polymers (Section 8.4, [Pol4, Zhao00a]). The smooth glassy morphology of the PSF/PMA brushes found after treatment in toluene is assigned to the dimple-PMA phase due to similar reasons. Note that the network with pits and the cluster morphologies may both represent dimple phases (Section 2.2) according to Section 8.3. The high incompatibility of PSF and PMA makes probably the ripple phase unstable for the PSF/PMA brushes. Clarification of this point is important for verification of the SCF theory and requires additional studies (see Section 8.4.5 for details).

Polydispersity of the grafted polymers and, probably, local deviations from random distribution of the grafting points are the probable reasons why, on the contrary to the predictions of the SCF theoretical approach by M. Müller (Section 2.2), no long-range order was experimentally found in the morphologies of the mixed polymer brushes (we made unsuccessful attempts to order the brush morphologies via long-term exposure to various solvents and their saturated vapors).

The lateral periods of the worm-like and cluster morphologies obtained from Fast Fourier Transformation of AFM topographic images have close values for each particular mixed brush (Appendix 4). These values are 1.5-2 times bigger than the values calculated from the estimated molecular weights (Mw) of the grafted polymers using the coefficients provided by Müller’s SCF theoretical approach (Sections 2.2, 8.4.4, Appendix 4). The most probable reasons for this dissimilarity are: (1) the SCF theory considers mixed brushes built
of monodisperse polymers of equal molecular weight; (2) the effective molecular weights of the polydisperse polymers, which determine the periods of the laterally segregated morphologies in the synthesized mixed brushes, exceed the weight-averaged molecular weights \( M_w \) which were utilized for the calculations presented in Appendix 4. AFM morphological studies of mixed polymer brushes with narrow polydispersity and equal molecular weights of the constituent polymers synthesized via controlled surface-initiated radical polymerization [Zhao03] (Section 2.3) may be helpful for understanding, why the theoretical and experimental lateral periods of the segregated morphologies are so different.

11.4. Switching of mixed polymer brushes upon heating above \( T_g \).

The experiments on thermal switching were made on a PS/P2VP brush (Section 9), whose constituent polymers possess very close glass transition temperatures, 100° C and 104° C [Pol4], respectively. A sample of the PS/P2VP brush was exposed to toluene, while another sample of this brush was exposed to ethanol. They were dried in nitrogen flux and annealed at 150° C in vacuum for 6 h. The two annealed samples of the PS/P2VP brush exhibited smooth morphologies with the top layer enriched in PS. The explanation for the observed segregation of PS to the brush surface is its smaller surface energy than in the case of the more polar P2VP [Kob03, Cho00]. Similarity of the morphologies of the two annealed samples of the PS/P2VP brush with different initial states evidences that the equilibrium state was achieved upon annealing. The small water contact angle hysteresis on the annealed brushes resulted from (1) elimination of moisture from the brushes and (2) more pronounced perpendicular segregation of the two constituent polymers and, consequently, higher enrichment of the top layer in PS than after exposure of the PS/P2VP brushes to toluene.

11.5. Application of XPEEM for studies of chemical composition on sub-\( \mu \)m scale.

Information obtained with XPEEM on chemical composition of the top layers of the mixed polymer brushes was interfered by a number of factors like shadowing, topographic effect, and varying sampling depth for different polymers. Beside these factors, the quantitative results depend on accuracy of the data treatment, i.e. (1) normalization of the data by the intensity of the incident x-ray radiation and (2) accounting the overall intensity increase for a given x-ray absorption edge which differs for polymers with different concentration of atoms contributing to the x-ray absorption at the edge (Section 3.4.3, Thomas-Reiche-Kuhn sum rule).
The proper data normalization (1) was not possible at the time of the experiment due to incapability of the XPEEM setup to record the incident x-ray intensity simultaneously with a NEXAFS spectrum (this option has recently become available). Therefore, the XPEEM results presented herein about chemical composition of mixed polymer brushes are semi-quantitative (Tables 8.2.1, 10.3). Accounting the differences in the edge overall intensity increase in NEXAFS spectra of different polymers (2) makes sense, if the spectra are properly normalized. The XPEEM data on the top layer composition of the PSF/PMMA brushes seem to have a systematic error which causes an increased apparent PSF fraction (compare the XPEEM data in Tables 8.2.1 and 10.3 with the XPS results in Table 7.3). The XPS is at present a more accurate analytic technique [Bri90] than XPEEM [Mor01], therefore the XPS data are more reliable.

11.6. Patterning of mixed polymer brushes via microcontact printing.

A possibility to introduce a chemical pattern onto the surface of a mixed polymer brush via the microcontact printing technique was demonstrated in Section 10. The PSF/PMMA brush chosen for this experiment adopted topographical and chemical patterns upon stamping under acetone with a PDMS stamp. Although the topographic pattern adopted by the brush made a significant contribution to the XPEEM records, the presence of the well-contrasted chemical pattern was proven by the NEXAFS spectra extracted from the recorded XPEEM stack for several characteristic regions in the pattern. A semi-quantitative composition map was obtained.

The patterned brush surface comprised elevated parallel ribs ~ 1 µm in width and 400 nm in height separated from one another by valleys of ~2 µm in width. The imprinted valleys and the tops of the imprinted ribs were rich in the polar PMMA due to its better swelling in acetone, while the vertical walls of the ribs were enriched in the non-polar PSF, what results from the proposed mechanism: the PSF/PMMA brush adopts in acetone a morphology which is highly segregated in the perpendicular direction: PMMA enriches the top layer, while PSF enriches the bottom layer. The channels on the PDMS stamp isolate the respective regions of the PSF/PMMA brush swollen in acetone upon the wet microcontact printing procedure. The highly segregated perpendicular profile of the brush remains “frozen” on the walls of the topographic ribs imprinted on the brush in the isolated regions (Section 10, Figure 10.5).

A weak change in local brush top layer composition in response to contact with a confining wall is surprisingly unexpected. This suggests resistance of the perpendicular segment concentration profiles of the brush constituents at the applied solvent conditions.
against external perturbations. Therefore, identification of conditions of bistability near the theoretically predicted phase transitions may be very fruitful for development of new printing techniques. The obtained combination of the topographic and chemical patterns comprising channels with polar bottom and unpolar walls may find an application for manufacturing of microfluidic devices.
LIST OF ABBREVIATIONS AND SYMBOLS

*Important note:* the mixed polymer brushes synthesized in this work are listed in Appendix 3 together with their codes.

2VP – 2-vinylpyridine;
A – amplitude,
A₂, A₃ – the second and third virial coefficients;
ABCPA - 4,4’-azobis(4-cyanopentanoic acid);
ADSA – axisymmetric drop shape analysis;
AFM – Atomic Force Microscopy;
AIBN - 4,4’-azobis(isobutyronitrile);
ALS – Advanced Light Source;
ATRP – Atom Transfer Radical Polymerization;
a – linear size of a monomer unit;
adv. – advancing;
amb. cond. – ambient conditions;
a. u. – arbitrary units;
B – extinction coefficient;
B’ – light absorption coefficient;
BMPB(s) – binary mixed polymer brush(es);
b – decay coefficient for free decaying oscillations, b = 2mβ;
Cl-ABCPA – chloroanhydride of ABCPA;
c – (1) concentration, (2) rate of light propagation in vacuum;
D – fractal dimension;
deg. – degree;
DI – Digital Instruments, Inc., Santa-Barbara, CA;
DSA – drop shape analysis;
d – thickness;
d_opt – optical thickness;
E – energy [J] or [eV];
Eᵧ - Young modulus [Pa];
Ēₑₐ – electrical field vector;
ED – ethylenediamine;
e – absolute value of electron charge which is $1.60 \cdot 10^{-19}$ C (coulomb);
e.g. – for example;
eq – equation(s);
et al. – Latin abbreviation meaning and others;
eV – electron-volt, an energy unit which equals $1.60218 \cdot 10^{-19}$ J;
F – (1) force; (2) Helmholtz free energy;
f – force;
fosc – optical oscillator strength;
FDC – force-distance curve;
FS – 2,3,4,5,6-pentafluorostyrene;
FFT – Fast Fourier Transformation;
G – Gibbs free energy;
GPS - (3-glycidoxypropyl)-trimethoxysilane;
H – height,
h – (1) hour (time unit), (2) Planck constant $6.62608 \cdot 10^{-34}$ J s; (3) end-to-end distance between polymer chain ends:
I – intensity,
$I_0$ – background intensity or monochromator function in XPEEM;
i.e. – that is to say, Latin id est;
IP – ionization potential, a minimum energy necessary to excite an 1s electron to the continuum of states above the vacuum level;
$|i\rangle$ - wave-function;
J – joule, SI unit of energy, work, quantity of heat, $J = N \cdot m = m^2 \cdot kg/s^2$;
K – kelvin, SI unit of thermodynamic temperature;
k – (1) spring constant [N/m] from Hooke’s law: $F=kz$; (2) the Boltzmann constant $k = 1.38065 \cdot 10^{-23}$ J/K;
$k\bar{v}$ - wave-vector;
$k_d$ – decomposition constant;
kg – kilogram;
L – length;
$\ell$ – (1) length, (2) deformation;
$\ell'$ - radius-vector;
LCST – lower critical solution temperature;
M – molar mass;
MA – methylacrylate;
m – (1) mass; (2) meter, SI unit of length;
max. – maximum;
min – minute (time unit);
MMA – methylmethacrylate;
Mn – chain number averaged molecular mass;
mol. – molecular;
MO – molecular orbital;
MPa – megapascal, $1 \cdot 10^6 \text{ Pa}$;
MS – multiple scattering;
Mw – weight averaged molecular mass;
N – natural number; number of monomer units in a polymer chain;
N’- complex refractive index;
$N_A$ – the Avogadro constant which is the number of particles in one mole of matter, $N_A = 6.02214 \cdot 10^{23} \text{ mol}^{-1}$;
NMR – nuclear magnetic resonance;
NMRP – Nitroxy-Mediated Radical Polymerization;
Norm.Area – normalized peak area;
n – (1) refractive index, (2) natural number;
O - characteristic direction (vector) for a chemical bond;
P2VP – poly(2-vinylpyridine);
Pa – SI unit of pressure;
PDMS – polydimethylsiloxane;
PIPA – poly(N-isopropylacrylamide);
PMA – polymethylacrylate;
PMMA – polymethylmethacrylate;
PS – polystyrene;
PSD – power spectrum density;
PSF – poly(styrene-co-2,3,4,5,6-pentafluorostyrene);
PTFE – polytetrafluoroethylene;
p – (1) kind of an atom orbital for which the angular momentum quantum number equals 1; (2) number of monomer units per Kuhn’s segment; (3) polarization of light in (parallel to) the plane of incidence;
p. – page;
p* – number of monomer units in one Kuhn’s segment;

ppm – parts per million;

p.s. – poor solvent;

Q – quality factor of an oscillator;

QA, QB - single chain (type A or B) partition function;

R – (1) gas constant, \( R = N_A \cdot k = 8.31447 \text{ J/(mol·K)} \); (2) radius; (3) Fresnel reflective coefficient;

RawArea – as recorded peak area;

RI – refractive index;

RMS – root-mean-square;

RSF – sensitivity factor for an XPS spectrometer;

rs – ratio of area of a rough surface to the projected area (on a horizontal plane);

rec. – receding;

S – (1) styrene; (2) entropy;

Ssp – spreading coefficient (Section 3.2);

SCF – self-consistent field theory;

SEC – size excluded chromatography;

SST – strong stretching theory;

s – (1) second (time unit), (2) kind of an atom orbital for which the angular momentum quantum number equals 0; (3) polarization of light perpendicular (German senkrecht) to the plane of incidence;

surf. – surface;

T – (1) period of time, (2) temperature;

Tg – glass transition temperature;

Tx. Function – transmission function of an XPS spectrometer;

t – time;

t1/2 – half-life time;

THF – tetrahydrofuran;

V – volume;

VM – molar volume;

VR – volume of 1 mole of polymer segments which are considered as the smallest repeating units in the chains, \( V_R \) is often approximated by the value of 100 cm³/mol;

\( \overline{\nu}_{\text{per}} \) - harmonic time-dependent perturbation;

\( \nu \) – the second virial coefficient (dimensionless);
\( v^* \) - average excluded volume interaction for a binary polymer brush in a solvent;
\( v_0 \) - the excluded volume;
\( v_{AA}, v_{BB}, v_{AB} \) - second virial coefficients which describe corresponding binary interactions between monomer units of polymers A and B;
\( v_s \) - versus;
\( W \) - (1) width, (2) work;
\( w \) - the third virial coefficient (dimensionless);
\( w_A, w_B \) - external field acting on a polymer chain type A or B;
\( wt. \) - weight;
XPEEM- X-ray Photoemission Electron Microscopy;
\( Z \) - chemical element number;
x, y, z - (1) dimensions of space or (2) variables;
\( \alpha \) - (1) chain expansion factor in units of the mean unperturbed chain end-to-end distance, (2) angle;
\( \beta \) - (1) a coefficient in equation of motion for free decaying oscillations; (2) angle;
\( \gamma \) - ratio of normalized XPS (NEXAFS) peak areas;
\( \gamma_g \) - surface (interface) tension, where the subscripts mean two contacting phases;
\( \Delta \) - (1) difference (e.g. \( \Delta x = x_2 - x_1 \)); (2) ellipsometric angle;
\( \delta \) - (1) phase shift between two oscillations, (2) chemical shift of an NMR signal;
\( \delta' \) - inverse stretching parameter;
\( \delta_i^* \) - solubility parameter for i-th material;
\( \varepsilon \) - strain;
\( \eta \) - viscosity [Pa·s];
\( \Theta, \Theta_{adv}, \Theta_{rec} \) - water static, advancing, and receding contact angles, respectively;
\( \theta \) - theta-temperature;
\( \lambda \) - wavelength,
\( \nu \) - frequency, \( s^{-1} \);
\( \xi \) - solvent selectivity parameter;
\( \pi (\pi^*) \) - bonding (antibonding) molecular orbital which has a plane of symmetry containing the line connecting centers of the bond-forming atoms and maximal electron density outside of this line (Figure 3.3.1.1 bottom right);
\( \pi' \) - osmotic pressure;
\( \rho \) - density;
σ (1) (σ*) – bonding (untibonding) molecular orbital of cylindrical symmetry with the axis of symmetry and maximal electron density on the line connecting centers of the two bond-forming atoms (Figure 3.4.3 c); (2) term which should be added to a free oscillating cantilever spring constant k in order to obtain an effective cantilever spring constant k_{eff} for the cantilever oscillating in vicinity to a sample; (3) dimensionless grafting density (Section 2.1);

σV – stress;

τ - difference between actual thermodynamic temperature and theta-temperature normalized by the theta-temperature [A1.20];

Φ – phase of an oscillation;

Φ’ – brush composition (number fraction of grafted chains of one of the two polymers);

ϕ - phase shift;

ϕ_A, ϕ_B - densities of monomer units of polymers A and B;

ϕ (or ϕ_i) – (1) surface fraction of a specified (i-th) material on a composite surface, (2) molar fraction in the top layer of a film;

ϕ^* - volume fraction in a mixture;

ϕ^*_s - volume fraction of grafted polymer near the grafting surface;

ϕ^{DI}_d - phase shift between a tapping AFM tip and the driving force in the convention of DI;

χ - Flori-Huggins interaction parameter;

χ’ - repulsion (attraction) parameter for two unlike monomer units;

Ψ – ellipsometric angle;

ψ - phase shift between a tapping AFM tip and the driving force in the standard convention;

Ω - frequency of driven non-decaying oscillation;

Ω’ - resistivity [ohm·cm];

ω – angular frequency, ω = 2πν.
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Appendix 1. Selected theoretical background on polymers.

Several important formulas must be recalled in order to describe the theory in Section 2 and Appendix 2.

Mean square distance between ends of an ideal freely-joint chain is [Alg97 p.209, Pol4 p.VII/4]:
\[
\langle h^2 \rangle_0^{1/2} = N^{1/2} \cdot a
\]
[A1.1],
where \(N\) is the number of monomer units in the chain and \(a\) is the linear size of a monomer unit, respectively. The term ideal (or Gaussian) chain means that only interactions between neighbor chain units are considered while the interactions between the units, which are far from one another, are neglected. Polymer chains behave themselves as ideal in so-called theta-conditions (0-conditions).

Mean square distance between ends of a Flori freely-joint chain [Flo53, Sun94, Gen80] is:
\[
\langle h^2 \rangle_F^{1/2} = N^{3/5} \cdot a
\]
[A1.2].
The Flori freely-joint chain does not cross itself. This formula takes into account excluded volume interactions and describes a polymer coil at good solvent conditions.

At poor or non-solvent conditions [Zhu96]:
\[
\langle h^2 \rangle_{p.s.}^{1/2} \sim N^{1/3} \cdot a
\]
[A1.3].

Kuhn segment. A real chain is more rigid than the ideal one and can be approximated with a freely-jointed chain [Alg97 p.209] composed of longer Kuhn segments [Alg97 p.282] of length
\[
\ell = \frac{\langle h^2 \rangle_\theta^{1/2}}{N a}
\]
[A1.4].

If \(p^* = \ell / a\) is a number of monomer units per one Kuhn segment, the formulas [A1.1-3] can be rewritten for the Kuhn chain as:
\[
\langle h^2 \rangle_\theta^{1/2} \approx \sqrt{\frac{N}{p^*}} \ell = N^{1/2} p^{*1/2} \cdot a
\]
[A1.5],
\[
\langle h^2 \rangle_F^{1/2} \approx \left( \frac{N}{p^*} \right)^{3/5} \ell = N^{3/5} p^{*2/5} \cdot a
\]
[A1.6], \(\langle h^2 \rangle_{p.s.}^{1/2} \approx \left( \frac{N}{p^*} \right)^{1/3} \ell = N^{1/3} p^{*2/3} \cdot a
\]
[A1.7].

Radius of gyration [Alg97 p.484] of a system is defined as:
\[
R_G = \sqrt{\frac{\sum m_i \overline{r}_i^2}{\sum m_i}}
\]
[A1.8],
where \(m_i\) is a mass of an i-th part of the system, \(\overline{r}_i\) is a vector from the center of mass of the system to the i-th part of the system. The radius of gyration for a polymer coil relates to the mean square distance between the chain ends as:
\[
R_G^2 = \frac{\langle h^2 \rangle}{6}
\]
[A1.9].
Osmotic pressure (\(\pi^\prime\)) exhibited by a polymer solution \([\text{Alg97 p.512}]\) obeys the virial formula:

\[
\frac{\pi^\prime}{c} = \frac{RT}{M} (1 + A_2 c + A_3 c^2 + ...)
\]  \[\text{A1.10}\],

where \(c\) is concentration of polymer ([c] = [kg/m^3]), \(R\) is the gas constant (\(R = N_A \cdot k = 8.31447\) J/(mol·K)), \(T\) is thermodynamic temperature, \(M\) is the molar mass of the polymer ([M] = [kg/mol]), \(A_2\) and \(A_3\) are the second and the third virial coefficients. \(A_2 \sim \frac{T - 0}{T} v_0\),

where \(0\) is the theta-temperature, \(v_0 \sim a^3\) is the excluded volume \([\text{Sun94, Zhu91}]\); \(A_2 = 0\) at \(T = 0\), \(A_2 > 0\) in good solvent conditions, \(A_2 < 0\) in poor solvent conditions,

\[A_2 = [1/c] = [m^3/kg]\] \[\text{A1.11}\], \(A_3 \sim v_0^2 > 0\), \([A_3] = [1/c^2] = [m^6/kg^2]\] \[\text{A1.12}\].

The formula \[\text{A1.10}\] can be expressed in dimensionless virial coefficients \(v\) and \(w\) and volume fraction of monomer units \(\varphi^*\):

\[\frac{\pi^\prime}{\varphi^*} = \frac{kT}{N_a \cdot a^3} (1 + v \varphi^* + w \varphi^* + ...)
\]  \[\text{A1.13}\],

where \(N_A\) is the Avogadro constant, \(N\) is the degree of polymerization The modified equation \[\text{A1.10}\] looks as:

\[
\frac{\pi^\prime}{\varphi^*} = \frac{kT}{N \cdot a^3} (1 + v \varphi^* + w \varphi^* + ...)
\]  \[\text{A1.14}\],

where \(k = 1.38065 \cdot 10^{-23}\) J/K is the Boltzmann constant.

**Coil-globule transition of linear macromolecules** was theoretically studied by Birshtein et al. \([\text{Bir91, Bir91a}]\) on the basis of the Flori scheme \([\text{Flo53}]\). They determined an equilibrium value of a mean square chain expansion factor \(\alpha\),

\[
\alpha = \left( \frac{\langle h^2 \rangle}{\langle h^2 \rangle_0} \right)
\]  \[\text{A1.15}\],

from the condition of minimum of free energy of a polymer chain, which is composed of the elastic free energy and the free energy of volume interactions between units distant from each other along the chain: \(\Delta F_{\text{total}} = \Delta F_{\text{elastic}} + \Delta F_{\text{volume}}\) \[\text{A1.16}\].

The equilibrium condition means that \(\partial \Delta F_{\text{elastic}} / \partial \alpha = -\partial \Delta F_{\text{volume}} / \partial \alpha\) \[\text{A1.17}\],

where the left and right parts are the oppositely directed forces of the corresponding nature acting on the chain. The following equations are derived from \[\text{A1.17}\]:

\[
\alpha^5 - \alpha^3 = \frac{2}{\pi^2} BN^{1/2} \tau, \ \tau > 0 \ [\text{A1.18}]; \ \alpha^3 - \alpha = \frac{2}{9} (BN^{1/2} \tau + C(\alpha^{-3} - 1)), \ \tau < 0
\]  \[\text{A1.19}\],

where \(B \sim v \varphi^{-3}, C \sim w \varphi^{-6}, \tau = (T - 0)/0\) \[\text{A1.20}\].

The formula \[\text{A1.19}\] describes chain globularization (\(\alpha < 1\)). It provides two characteristic types of the function \(\alpha(\tau)\) depending on the parameter \(C\). The function \(\alpha(\tau)\) is monotonic when \(C\) exceeds a certain value \(C_0\); and it has a loop at \(C\) below \(C_0\) (Figure A1.1). The monotonic function is characteristic for common flexible linear polymers while the loop is
characteristic for stiff polymers. In the latter case, the phase transition takes place along the dashed line (Figure A1.1).

![Diagram showing average chain size α vs. τ for flexible (C > C₀, curve I) and stiff (C < C₀, curve II) linear polymers. The dashed line divides the loop into two parts of equal area. Adapted from [Bir91].](image)

**Flori-Huggins interaction parameter χ.** The free Gibbs energy of mixing of two polymers is [Kro98 p.629]:

\[
\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T \Delta S_{\text{mix}}
\]

where \(H_{\text{mix}}\) and \(S_{\text{mix}}\) are enthalpy and entropy of mixing, \(T\) is thermodynamic temperature. In the regular solvent approximation [Alg97 p. 201], the entropy of mixing equals the entropy of ideal mixture:

\[
\Delta S_{\text{mix}} = -R \left( \frac{V_M}{V_R} \right) \left( \frac{\phi_1}{N_1} \ln \phi_1 + \frac{\phi_2}{N_2} \ln \phi_2 \right)
\]

where \(R\) is the gas constant, \(V_M\) is the total molar volume of the two polymers 1 and 2; \(V_R\) is the reference volume of 1 mole of polymer segments, which are considered as the smallest repeating units. \(V_R\) is usually approximated by the value of 100 cm³/mol. \(\phi_i\) and \(N_i\) are the volume fraction and the number of segments in a chain (degree of polymerization) for \(i\)-th polymer, respectively. The enthalpy of mixing differs from the ideal value and can be expressed as [Kro98 p. 630]:

\[
\Delta H_{\text{mix}} = RT \left( \frac{V_M}{V_R} \right) \chi_{12} \phi_1^* \phi_2^*
\]

where \(\chi_{12}\) is the Flori-Huggins interaction parameter. The final equation for the Gibbs free energy of a binary polymer mixture is:

\[
\Delta G_{\text{mix}} = \frac{RTV_M}{V_R} \left( \frac{\phi_1^*}{N_1} \ln \phi_1 + \frac{\phi_2^*}{N_2} \ln \phi_2 + \chi_{12} \phi_1^* \phi_2^* \right)
\]
The overall Flori-Huggins parameter for a polymer blend composed of two statistical
copolymers \( P(A_x\text{-co-B}_{1-x}) \) and \( P(C_y\text{-co-D}_{1-y}) \) can be calculated as [Kro98 p.632, Ikk00]:

\[
\chi_{\text{blend}} = xy\chi_{AC} + y(1-x)\chi_{BC} + x(1-y)\chi_{AD} \\
+ (1-x)(1-y)\chi_{BD} - x(1-x)\chi_{AB} - y(1-y)\chi_{CD}
\]

[A1.25].

The Gibbs free energy for various cases of mixing and demixing in binary mixtures is
depicted in Figure A1.2 as a function of system composition. The criterion for the starting of
separation into two phases [Kro98 p.630] is \( \partial^2(\Delta G_{\text{mix}})/\partial \phi_2^2 = 0 \)

[A1.26].

![Figure A1.2. Mixing and demixing of binary mixtures. The thicker lines mark the regions of
stability of a mixture \( \partial^2(\Delta G_{\text{mix}})/\partial \phi_2^2 > 0 \), while the
thin lines mark the regions where the mixture separates into two phases \( \partial^2(\Delta G_{\text{mix}})/\partial \phi_2^2 < 0 \). 1-
demixing into two phases; 2- partial mixing (the
points A and D show the minima of \( \Delta G_{\text{mix}} \), B and C
show the borders of the demixing region where
\( \partial^2(\Delta G_{\text{mix}})/\partial \phi_2^2 = 0 \)); 3- mixing in the whole range of concentrations.]

The Flori-Huggins interaction parameter can be expressed via solubility parameters \( \delta_i^* \) for
each of the polymers [Kro98 p.631, Alg97 p.201, Zhao00a]:

\[
\chi_{12} = \frac{V_i^a}{RT}(\delta_i^* - \delta_j^*)^2
\]

[A1.27].

The solubility parameter is related to the cohesive energy \( E_{\text{coh}} \) which is required to separate
(vaporize) molecules in unit volume of a pure liquid i [Kro98 p.631]:

\[
\delta_i^* = \sqrt{\frac{E_{\text{coh}}}{V_i}}
\]

[A1.28].

Methods of determination of the Flori-Huggins parameter for binary polymer mixtures are
described in [Ikk00, Pol4 p.VII/680] and references therein.

In the lattice theory of Flori and Huggins for polymer solutions [Kro98 p.1670]:

\[
\Delta H_{\text{mix}} = z\Delta E n_1 \phi_2 = RT\chi_{12} n_1 \phi_2, \quad \chi_{12} = z\Delta E/(RT)
\]

[A1.29].

where \( n_1 \) is the number of moles of solvent, \( z \) is the average number of solvent molecules and
solvent-sized segments of the polymer in contact with one solvent molecule (coordination
number of the lattice), \( \Delta E \) is the difference between the intermolecular contact energy
between a segment of the polymer and a solvent molecule and the average interaction for a
pair of polymer segments and a pair of solvent molecules: \( \Delta E = E_{12} - \frac{E_{11} + E_{22}}{2} \)

[A1.30].
Appendix 2. Scaling approach to monocomponent brushes.

The scaling approach was developed by Alexander [Ale77] and de Gennes [Gen80].

In a monolayer of end-grafted polymer coils which do not overlap the coil shape is a semi-sphere (Figure A2.1). The volume fraction of monomer units (\( \phi^* \)) inside a single coil is

\[
\phi^* = \frac{N a^3}{R^3}
\]  \[\text{[A2.1]}\]

where \( R \sim \langle h^2 \rangle^{1/2} \) is the coil radius from [A1.1-3, A1.9]. Here we determine only order of the values and therefore omit all coefficients. We introduce dimensionless grafting density \( \sigma \) which is the ratio of the number of occupied grafting sites to the total amount of the grafted sites. Fraction of the grafting surface covered by the attached coils is:

\[
\sigma R^2 / a^2
\]  \[\text{[A2.2]}\]

Combining [A2.1] and [A2.2], the volume fraction of polymer chains on the distance \( z \approx R \) from the grafting surface equals:

\[
\phi^* (z \approx R_f) = (Na^3 / R_f^3) \cdot (\sigma R_f^2 / a^2) = N \sigma a / (N^{3/5} a) = N^{2/5} \sigma \text{ in good solvent}
\]  \[\text{[A2.3]}\]

\[
\phi^* (z \approx R_\theta) = (N a^3 / R_\theta^3) \cdot (\sigma R_\theta^2 / a^2) = N \sigma a / (N^{1/2} a) = N^{1/2} \sigma \text{ in theta-solvent}
\]  \[\text{[A2.3a]}\]

\[
\phi^* (z \approx R_{p.s.}) = (N a^3 / R_{p.s.}^3) \cdot (\sigma R_{p.s.}^2 / a^2) = N \sigma a / (N^{1/3} a) = N^{2/3} \sigma \text{ in poor solvent}
\]  \[\text{[A2.3b]}\]

At the lower limit \( z \approx a \) \( \phi^* = \sigma \) \[\text{[A2.4]}\]

The concentration profile between these two limits can be interpolated with a power law:

\[
\phi^* (z) = \sigma (z / a)^m
\]  \[\text{[A2.5]}\]

From the limit \( z \approx R \) we obtain:

\[
\sigma (R_f / a)^m = \sigma (N^{3/5} a / a)^m = \sigma N^{2/5} \text{ and } m_f = 2 / 3 \text{ in good solvent}
\]  \[\text{[A2.6]}\]

\[
\sigma (R_\theta / a)^m = \sigma (N^{1/2} a / a)^m = \sigma N^{1/2} \text{ and } m_\theta = 1 \text{ in theta-solvent}
\]  \[\text{[A2.6a]}\]

\[
\sigma (R_{p.s.} / a)^m = \sigma (N^{1/3} a / a)^m = \sigma N^{2/3} \text{ and } m_{p.s.} = 2 \text{ in poor solvent}
\]  \[\text{[A2.6b]}\]

Figure A2.1. Separated polymer coils end-grafted to a solid surface. Adapted from [Gen80].

For the end-grafted polymer coils in the brush regime the average distance between the grafted sites (D) equals:

\[
D = \sqrt{n a^2} / n = a / \sqrt{\langle n a^2 \rangle} / S = a / \sqrt{\sigma}
\]  \[\text{[A2.7]}\]
where $S$ is the surface to which $n$ polymer chains are grafted, $\sigma$ is the dimensionless grafting density. For a polymer monolayer in the brush state the coil size is bigger than the grafting distance: $R > D$. A grafted chain may be subdivided into “blobs” of linear size $D$, each of them containing a number $g$ monomers, $g < N$. From [A1.2, A1.1, A1.3]:

$$D = g_{F}^{3/5} \cdot a \quad \text{in good solvent} \quad [A2.8], \quad D = g_{0}^{1/2} \cdot a \quad \text{in theta-solvent} \quad [A2.8a],$$

$$D = g_{p.s.}^{1/3} \cdot a \quad \text{in poor solvent} \quad [A2.8b].$$

In the region occupied by the grafted chains, the blobs act as hard spheres and fill space densely (Figure A2.2 a). Volume fraction of polymer is:

$$\varphi_{F}^{*} \cong \frac{g_{F}a^{3}}{D^{3}} = \left(\frac{D}{a}\right)^{5/3} \left(\frac{a}{D}\right)^{3} = \left(\frac{a}{D}\right)^{4/3} = \frac{a^{4/3}}{(a/\sqrt{\sigma})^{4/3}} = \sigma^{2/3} \quad \text{in good solvent} \quad [A2.9],$$

$$\varphi_{0}^{*} \cong \frac{g_{0}a^{3}}{D^{3}} = \left(\frac{D}{a}\right)^{2} \left(\frac{a}{D}\right)^{3} = \frac{a}{D} = \frac{a}{(a/\sqrt{\sigma})} = \sigma^{1/2} \quad \text{in theta-solvent} \quad [A2.9a],$$

$$\varphi_{p.s.}^{*} \cong \frac{g_{p.s.}a^{3}}{D^{3}} = \left(\frac{D}{a}\right)^{3} \left(\frac{a}{D}\right)^{3} = 1 \quad \text{in poor solvent} \quad [A2.9b].$$

On the other hand: $\varphi^{*} = Na^{3}/(LD^{2})$ [A2.10],

where $L$ is the thickness of the grafted layer. From the equations [A2.9-10, and A2.7], the

**Figure A2.2.** Polymer brush (a) and its concentration profile (b) according to the scaling approach. Adapted from [Gen80].
layer thickness is derived for good, theta-, and poor solvents, respectively:

\[
L_F \approx \frac{Na^3}{D^2 \sigma^{2/3}} = \frac{Na^3}{(a/\sigma^{1/2})^2 \sigma^{2/3}} = Na^{1/3} \sigma^{1/3} \quad \text{[A2.11].}
\]

\[
L_\theta \approx \frac{Na^3}{D^2 \sigma^{1/2}} = \frac{Na^3}{(a/\sigma^{1/2})^2 \sigma^{1/2}} = Na^{1/2} \sigma^{1/2} \quad \text{[A2.11a].}
\]

\[
L_{p.s.} \approx \frac{Na^3}{D^2} = \frac{Na^3}{(a/\sigma^{1/2})^2} = Na \sigma \quad \text{[A2.11b].}
\]

The concentration profile of a polymer brush derived from the scaling approach is imaged at Figure A2.2 b. It is essentially flat according to \([A2.11-A2.11b]\) except the region near the wall \(a < \sigma < D\), where the profile is determined by \([A2.5]\) and \([A2.6-A2.6b]\).
Appendix 3. Parameters of mixed polymer brushes synthesized via the “grafting from” approach.

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<th>Polydispersity Mw/Mn</th>
<th>Ellipsom. thickness, nm</th>
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Appendix 4. Comparison of theoretically predicted ($L_{C}^{SCF}$, $L_{L}^{SCF}$) and obtained from AFM ($L_{C}^{AFM}$, $L_{L}^{AFM}$) lateral periods of cluster (C) and worm-like (L) structures, respectively, for selected binary mixed brushes. The chain end-to-end distances for theta-conditions ($h_0$) were calculated according to the formula $h_0/M^{0.5}\times10^4 = x$, where x equals 670 nm for PS, 640 nm for PMMA, 680 nm for PMA, 660 nm for P2VP [Pol4]. The periods $L_{C}^{SCF}$, $L_{L}^{SCF}$ were calculated according to the formula $h_0\cdot\kappa$, where $\kappa$ equals 2.15 and 1.85 for the cluster and lamellae morphologies, respectively [Min02a]. The periods $L_{C}^{SCF}$, $L_{L}^{SCF}$ were calculated for $h_0$ of each brush polymer separately (two first lines for each brush), while the mean values for the two brush polymers are provided in the third lines below.

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Appendix 5. H NMR spectrum of PSF.
Appendix 6. Switching of mixed PS/P2VP brushes by selective organic solvents, toluene and ethanol, as a function of the brush thickness and the mass ratio of the grafted polymers. Water advancing ($\Theta_{\text{adv}}$) and receding ($\Theta_{\text{rec}}$) contact angles are plotted at the diagrams (a) and (b), respectively. The $\Theta_{\text{adv}}$ and $\Theta_{\text{rec}}$ angles on the monocomponent brushes are marked with dashed black and light gray horizontal lines, respectively.
Appendix 7. Location of the contact line of water, air, and brush phases upon spreading of a water droplet on the surface of the PSF/PMA brush FSA1 (Appendix 3) according to our calculations via Cassie’s formula [3.2.14]. (a) AFM topography image 2x2 µm of the brush exposed to acetone, where the gray color means the elevations which contact the water droplet, the black color means the cavities with trapped air. The multiple contact line lies on the border of the gray and black regions. (b) Area projected from the brush surface to the substrate plane vs. depth (perpendicular coordinate) of the brush surface. The projected area is higher under the regions on the brush surface oriented parallel to the substrate plane. The left maximum corresponds to the top of the elevations (gray at the panel a), the right maximum corresponds to the bottom of the valleys (black at the panel a). The minimum in the middle corresponds to the walls surrounding the valleys. The vertical line marks the position of the contact line at 90.284 nm depth and 66% of the brush surface lying above this point (at the lower depth).
P2VP brush

(a) ethanol, RMS 1.0 nm;  
(b) toluene, RMS 0.9 nm;  
(c) HCl in water pH 2.5, RMS 0.6 nm;  
(d) water pH 7.0, RMS 1.1 nm;

PS brush

(e) ethanol, RMS 0.6 nm;  
(f) toluene, RMS 0.9 nm;  
(g) HCl in water pH 2.5, 1.0 nm.

Appendix 8.1. Tapping mode AFM of monocomponent P2VP (a-d) and PS (e-g) brushes (synthesized parallel with the PS/P2VP brush SVP25, see Appendix 3) after treatment in solvents of various thermodynamic quality. Scale 1x1 μm, left: topography, right: phase contrast, z ranges 10 nm, 20°. Thickness of the PS and P2VP brushes obtained from ellipsometry was 16 and 10 nm, respectively. Cantilever A-NCH-W, A₀ 40 nm, A/A₀ 85%. The bumps were formed by silane particles underneath the brushes. Phase images were obtained in the repulsive regime, except f which was recorded in the attractive regime at the same settings.
Appendix 8.2. Morphologies of P2VP (a) and PS (b) monocomponent brushes (synthesized parallel with the PS/P2VP brush SVP25, see Appendix 3) after 6h annealing at 150° C in vacuum. Thickness of the PS and P2VP brushes obtained from ellipsometry was 16 and 10 nm, respectively. Scale 1x1 µm. Left – topography, right – phase contrast. Z range 10 nm and 10°, respectively. Repulsive tapping mode AFM, amplitude set-point ratio $A/A_0$ 80 and 88%, $A_0$ 73 and 55 nm for (a) and (b), respectively. Ultrasharp tip (Section 5.5.1 A).

(a) PSF brush, 10x10 µm, topography (left) z scale 10 nm, phase z scale (right) 40°;  
(b) PSF brush, 1x1 µm, topography (left) z scale 10 nm, phase z scale (right) 40°;

(c) PMA brush, 10x10 µm, topography (left) z scale 20 nm, phase z scale (right) 40°;  
(d) PMA brush, 1x1 µm, topography (left) z scale 20 nm, phase z scale (right) 40°.

Appendix 8.3. Non-contact AFM images of PSF (a-b) and PMA (c-d) monocomponent brushes synthesized parallel with the brush AFS1 (Appendix 3). Surface RMS roughness of the PSF and PMA brushes ranged from 0.2 to 0.6 nm and from 0.1 to 0.4 nm, respectively. Thickness of the PSF and PMA brushes obtained from AFM scratch tests and ellipsometry was 87 and 50 nm, respectively.
Appendix 9. The glassy and the rubbery morphologies of the PMA/PSF brush AFS1 (Appendix 3) after treatment in toluene (left column) and acetone (right column), respectively. AFM images 5 x 5 µm in the attractive tapping regime (A/A₀ 0.9-1): (a) z scales of the topography (left) and the phase image (right) are 10 nm and 20º, respectively; (d) z scales of the topography (left) and the phase image (right) are 150 nm and 40º, respectively. AFM images 1 x 1 µm in the repulsive tapping regime (A/A₀ 0.4-0.7): (b) z scales of the topography (left) and the phase image (right) are 10 nm and 20º, respectively; (e) z scales of the topography (left) and the phase image (right) are 150 nm and 40º, respectively. The bottom row: topography profiles for the glassy (c) and the rubbery (f) states. Provided by M. Lemieux [Lem03a]. Compare with the morphologies of the PSF/PMA brush FSA1 (Appendix 1) with inverse grafting order of the polymers.
Appendix 10. AFM tapping mode scans of a PDMS stamp: (a) original surface, (b) exposed to oxygen plasma. The PDMS surface adopts web-like cracks upon the oxidation most probably due to a decrease in elasticity of the modified material. The etching was carried out at the conditions provided in Section 4.4 for a period of 60 s.

Appendix 11. PSF/PMMA brush patterned with a natural PDMS stamp in acetone. No cracks are imprinted on the surface unlike in the case of the oxidized PDMS (Figure 10.2 a-b). AFM tapping mode, attractive regime, A₀ 45 nm, A/A₀ 95%. The white quad in the top images shows the area magnified in the bottom images.
Appendix 12. NEXAFS 1s C spectra scaled to equal pre-edge intensity via multiplication by a certain number. The scale of the intensity step over the edge was not additionally modified. (a) Overview spectra of spin-coated PSF and PMMA films. (b) Spectra of the spin-coated PSF and PMMA films recorded at the same hardware settings as the spectra of the PSF/PMMA brushes in the next panel. The spectra shown in this panel were used for the calculations of the top layer composition of the PSF/PMMA brushes (Tables 8.2.1, 10.3). (c) Integral (averaged due to recording from big areas) spectra of PSF/PMMA brushes after exposure to acetone and toluene and after microcontact printing with the PDMS stamp in the same solvents.
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