Gradient Mixed Brushes: "Grafting To" Approach

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External stimuli, such as light, solvent, pH, or an electric field, allow for a fine-tuning of the surface properties of specially designed responsive polymer materials.[1−6] This behavior can be used for regulation and switching of wetting behavior, adhesion, adsorption, etc.[7−9] An important example of the stimuli responsive surfaces is represented by mixed polymer brushes consisting of two or more incompatible polymers grafted to the same substrate. Successful synthetic methods for mixed polymer brushes via "grafting to" and "grafting from" approaches were recently reported.[10−13] Theoretical and experimental studies gave evidence that the mixed brushes undergo phase transition upon external stimuli. The properties of the thin brushlike film depend on the balance between layered and lateral phase segregation mechanisms.[14−19] Selective solvents (good solvent for one of two grafted polymers) stabilize a dimplelike morphology: an unfavorable polymer forms clusters that are segregated to the grafting surface while the favorite polymer forms a discontinuous phase preferentially segregated to the brush surface (a top layer). In nonselective solvents, lateral segregation dominates and the mixed brushes form a ripplelike morphology: lamellar-like stripes are formed by alternating microphases of both polymers. In the latter case, both polymers are present on the surface in an equimolar ratio if the mixed brush is symmetrical (1:1 of both polymers). An increase in the compositional asymmetry of the mixed brushes, or an increase in incompatibility, results in dimple phases.[17] Thus, the morphology of the brush is a function of the composition and interactions with solvent.

In the present work, we describe an effective combinatorial approach for the investigation of phase segregation and the responsive behavior as a function of the brush composition and solvent selectivity. Specifically, for the first time we report here on the synthesis of mixed polymer brushes with a 1D gradient of composition. Recently, applications of thin polymer films with gradually changing properties and composition were successfully introduced as a combinatorial approach in polymer science.[20,21] Synthesis of homopolymer brushes with a 1D gradient of grafting density using "grafting from"[22−24] and "grafting to"[25] methods was recently reported.

Highly polished single-crystal silicon wafers (cleaned according to the procedure reported elsewhere[25]) were used as a substrate. Carboxyl terminated polystyrene (PS−COOH, M_n = 45 900 g/mol, M_w = 48 400 g/mol) and carboxyl terminated poly(2-vinylpyridine) (P2VP−COOH, M_n = 39 200 g/mol, M_w = 41 500 g/mol,) were purchased from Polymer Source, Inc. Poly(glycidyl methacrylate) (PGMA) (M_n = 84 000 g/mol) was synthesized by free radical polymerization of glycidyl methacrylate (Aldrich).[26]

Gradient brushes consisting of the two incompatible polymers PS and P2VP were prepared via a two-step procedure. A thin layer of PGMA (1.5 ± 0.1 nm) was deposited by spin-coating from a 0.01% solution in methylethyl ketone. The monolayer of PGMA attached to the silicon wafers served as a macromolecular anchoring layer.[27] Next, the 500 nm thick film of PS−COOH was spin-coated from 2% solution in toluene and annealed for 1 h on a specially designed stage with a temperature gradient. A 1D gradient of temperature was establish such that the temperature of the stage changed gradually from 90 °C on the left-hand side of the stage to 130 °C on the right-hand side of the stage. The distance between these two edges on the stage was 50 mm. Upon heating, the estherification reaction resulted in the formation of the grafted PS layer with a gradient of grafting density due to temperature dependence of the grafting kinetics. The temperature, measured by thermocouples, was stable during the annealing procedure. Afterward, the nongrafted PS was washed out using a Soxhlet extraction in toluene. This method for the fabrication of a PS brush with the 1D grafting density gradient was described elsewhere in more detail.[25]

In the second step a film (500 nm thick) of P2VP−COOH was spin-coated on the top of the gradient PS brush. The film was annealed at 150 °C for 8 h to graft P2VP. Subsequently the ungrafted polymer was removed by Soxhlet extraction in THF for 8 h. As a result we prepared the sample of the gradient mixed brush PS-*mix*-P2VP of the size $X \times Y = 50$ mm × 20 mm, where the 1D gradient of the brush composition (ratio PS/P2VP) was fabricated along the X-axis.

The thickness of the polymer layers was measured at $\lambda = 633$ nm and an angle of incidence of 70° with a SENTECH SE−402 scanning microfocus ellipsometer (lateral resolution is defined by the beam spot of about 20 μm). The measurements were performed (with accuracy in thickness of the films ±0.2 nm) after each step of the modification using the measurements of the previous step as a reference for the simulation of ellipsometric data.[11] Advancing water contact angle was measured using "DSA-10" Krüss equipment (accuracy of measurements ±0.5°). Since the grafted layers obtained in this work exhibited low roughness (measured by AFM) ranging from 0.3 to 3 nm, the Cassie equation[28] was applied for the evaluation of the surface composition: $\cos\theta = \varphi\cos\theta_A + (1-\varphi)\cos\theta_B$, where θ = water contact angle on the mixed brush, θ_A and θ_B = the contact angles of water on the surface of reference homopolymer brushes PS and P2VP, respectively, and

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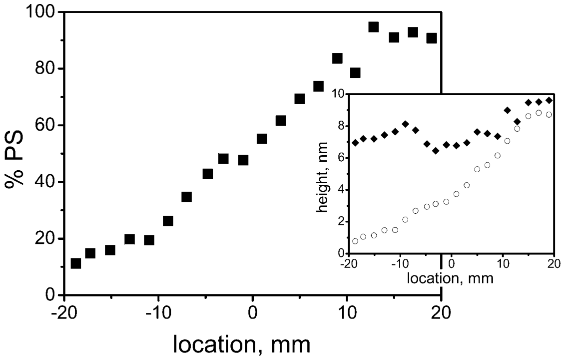

Figure 1. Fraction of grafted polystyrene vs location of the measured spot (on *X* axis) for the gradient PS-*mix*-P2VP brush. The inset demonstrates the ellipsometric thickness of the homopolymer PS and PS-*mix*-P2VP brushes (empty circles, PS; black circles, PS-*mix*-P2VP).

φ is the fraction of the surface covered by PS. The advancing contact angles on PS and P2VP homopolymer brushes were 90 and 65°, respectively. [10]

The results of the ellipsometric mapping of the 1D gradient PS brush following the first grafting step and the final PS-*mix*-P2VP brush are presented in Figure 1. The thicknesses of the gradient PS brush (synthesized in the first grafting step) and PS-*mix*-P2VP final brush are presented in the inset. These two plots in the inset were used to calculate the composition of the gradient PS-*mix*-P2VP brush. The thickness of the PS layer gradually increases along the *X*-axis from the left-hand side to the right-hand side reflecting the change of grafting density of PS. The inset demonstrates that the entire thickness of the mixed brush along the *X*-axis is almost constant value of about 7 nm, corresponding to the grafting density of approximately 0.1 chains/nm.[27] The distance between grafting sites of 3.5 nm is smaller than the gyration radius (R_g) of PS and P2VP polymer coils ($R_g \approx 5$ nm). Consequently, the polymer grafted film can be considered as a brushlike layer. Small variations in the brush height observed for the certain locations may be caused either by variations of the thickness of the PGMA anchoring layer or by variations in the local thermal contact between the Si-wafer and the thermal stage. Indeed, spin-coating results in a somewhat parabolic profile of the PGMA layer thickness where the thickness at the edges is slightly higher than in the middle of the sample resulting in the variation of anchoring group concentration on the substrate surface. Second, the contact between the wafer and the stage cannot be perfect as well, since the stage surface is not ideally flat.

The gradual change of the mixed brush composition was confirmed by the contact angle measurements performed on the brush surface after the brush was exposed to chloroform (nonselective solvent) for 10 min and dried afterward (see details of the experiment elsewhere[10,11]). The water contact angle increases almost linearly with the increase of the PS fraction (Figure 2a). The composition of the top of the brush calculated using the Cassie equation is very close to the composition obtained from the ellipsometric data (Figure 2b).

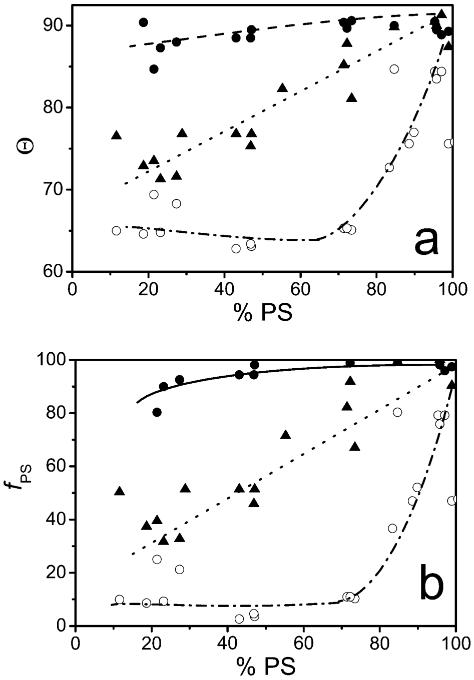

Figure 2. Switching of water contact angle (Θ) of the gradient PS-*mix*-P2VP brush after exposure to different solvents (a) and the fraction of PS (f_{PS}) on the top of the brush estimated with Cassie equation (black circles, toluene; black triangles, chloroform; empty circles, ethanol) and (b) in both cases vs the measurement location along *X* axis expressed in terms of PS fraction in percent (see Figure 1).

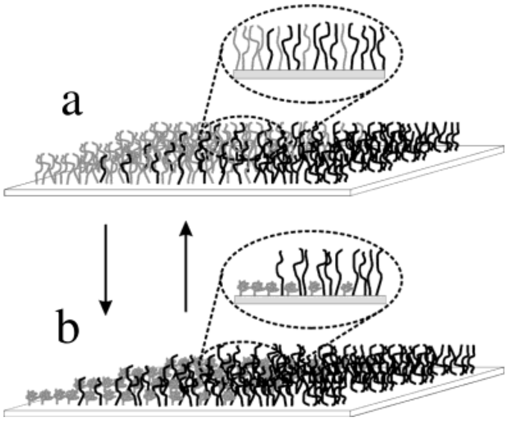

Figure 3. Scheme of the gradient mixed brush morphology upon treatment with nonselective (a) and selective (b) solvents. In nonselective solvents both polymers are on top: the gradient is "turned on." In selective solvent only a favorite polymer is on top: the gradient is "turned off".

However, the treatment of the brush with selective solvents (toluene and ethanol) reveals the unique switching behavior of the mixed brush. The gradient can be switched reversibly from the case when the wetting gradually increases from the left-hand side to the right-hand side to the case when the wetting is almost constant (at two different levels) along the *X*-axis (Figure 2). In other words, we can effectively "turn on" and "turn off" the wetting gradient upon treatment with the solvent (Figure 2b). This switching is limited by the brush composition and can be obtained within a reasonable compositional asymmetry of the mixed brush (from 30% to 70% of PS). The results show that in selective solvents one of the polymers preferentially occupies the top of the brush (PS in toluene and P2VP in ethanol) such that the wetting behavior gradient is switched into the state where the sample is entirely hydrophobic (after toluene) or entirely hydrophilic (after ethanol) (Figure 3). On the edges (PS < 30% and PS > 70%), the low surface concentration of one of the polymers decreases the switching effect. However, in these composition ranges, an extremely sharp surface energy gradient can be obtained by treatment with a selective solvent (Figure 2). The switching was performed many times (at least 10) with the same results, providing the reversible character of the phase segregation.

In summary, we developed the novel approach for synthesis of mixed polymer brushes with a unidirectional gradual change of composition. This approach allows for a fast screening of the switching behavior of mixed brushes. We believe that the reported combinatorial approach will contribute to further developments and investigations of responsive surfaces based on mixed polymer brushes.

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