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Mixed Polymer Brushes by Sequential Polymer Addition: Anchoring Layer Effect

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Smart surfaces can be described as surfaces that have the ability to respond in a controllable fashion to specific environmental stimuli. A heterogeneous (mixed) polymer brush (HPB) can provide a synthetic route to designing smart polymer surfaces. In this research we study HPB comprised of end-grafted polystyrene (PS) and poly(2-vinyl pyridine) (P2VP). The synthesis of the HPB involves the use of an "intermolecular glue" acting as a binding/anchoring interlayer between the polymer brush and the substrate, a silicon wafer. We compare anchoring layers of epoxysilane (GPS), which forms a self-assembled monolayer with epoxy functionality, to poly(glycidyl methacrylate) (PGMA), which forms a macromolecular monolayer with epoxy functionality. The PS and P2VP were deposited onto the wafers in a sequential fashion to chemically graft PS in a first step and subsequently graft P2VP. Rinsing the HPB in selective solvents and observing the change in water contact angle as a function of the HPB composition studied the switching nature of the HPB. Scanning probe microscopy was used to probe the topography and phase imagery of the HPB. The nature of the anchoring layer significantly affected the wettability and morphology of the mixed brushes.

Introduction

Polymer coatings that are responsive to environmental conditions are of great interest for various advanced applications. The advantage of these "smart" materials is the ability to switch and/or tune the surface properties of the coatings by applying external stimuli to vary, for example, adhesion, wettability, friction, roughness, reactivity, biocompatibility, and selectivity, etc. In recent years, various efforts have been reported on the development of such smart materials that can act in response to environmental stimuli, such as changes in electrical potential, temperature, and pH or the presence of a specific chemical substance.[1−9]

An important example of this type of smart material is a heterogeneous (mixed) polymer brush (HPB) composed of two immiscible polymers that are end-grafted to a solid substrate (Figure 1A).[5−13] The mixed brush forms as a result of high grafting densities causing the polymer chains to stretch to a height linearly related to the degree of polymerization. Under a range of solvent conditions two sufficiently immiscible polymers will laterally phase-segregate. The important experimental parameters that influence the lateral segregation are the differing solubility of the two polymers in a common solvent, substrate preference of the two polymers, grafting density, molecular weight, and composition. Due to the phase segregation the morphology of the mixed brushes is sensitive to the surrounding medium. Hence, mixed brushes can be switched between different surface energetic states upon exposure to different solvents.[5−9] It has been shown that the surface properties of the brush can be changed by treatment with a nonselective solvent or alternatively a selective solvent for one grafted polymer. For instance, a nonpolar solvent will act as a selective solvent swelling the hydrophobic polymer chains, while at the same time collapsing the hydrophilic chains (Figure 1B,C). The interaction of the HPB with selective solvent causes a change of the surface properties of the polymer film

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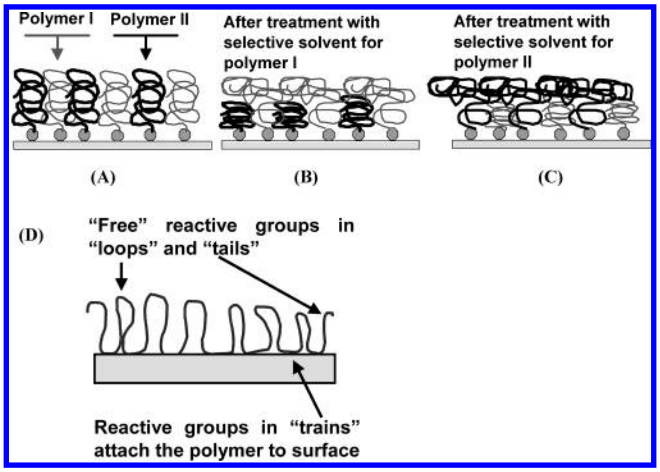

Figure 1. Schematic representation of morphology variation of HPB on exposure with nonselective (A) and selective solvents (B, C). Schematic representation of reactive polymer attached to substrate (D).

because one of the two polymers preferentially occupies the surface layer.[8,13]

Synthesis of the mixed polymer brushes can be readily accomplished by a "grafting to" method.[5] In the grafting to technique, end-functionalized polymer molecules react with complementary functional groups located on the surface to form tethered chains. The mixed brushes can be obtained by sequential or simultaneous grafting. When the simultaneous addition is used, both end-functionalized polymers to be grafted are deposited on the surface at the same time. According to the sequential approach, first one polymer is attached to substrate, and then after removing all ungrafted material the second component of the heterogeneous brush is anchored to the surface.

There are two common approaches for the attachment of polymeric chains by the grafting to method. The first one involves the formation of a monolayer consisting of functional groups active toward terminally functionalized (e.g. epoxide, amine, anhydride, or hydroxide) polymer.[14−17] A different approach relies on the reactions between end-functionalized chains and native functional groups originally present on the substrate surface.[18−20] Silane, thiol, and epoxy chemistries have proved to be suitable for the grafting in this case. A common feature of the two approaches is a restricted mobility of the functional groups located on the surface. As a result, at higher grafting densities the screened reactive groups cannot be reached by the end functionalities of the macromolecules being attached.

An alternative method for synthesis of the grafted polymer layers involves a primary polymer monolayer active toward both surface and end-functionalized macromolecules. The primary polymer monolayer can be prepared from linear[21−25] or hyperbranched[26,27] macromolecules. The polymer is used for the initial surface modification as well as generation of the highly reactive anchoring layer. When deposited on a substrate, the layer first reacts with the surface through formation of covalent bonds (Figure 1D). The reactive units located in the "loops" and "tails" sections of the attached macromolecules are not connected to the surface.[28] These free groups offer a synthetic potential for further chemical modification and serve as reactive sites for the subsequent attachment of the end-functionalized macromolecules. The major difference between this method of surface activation and the traditionally used self-assembled monolayer approach lies in the mobility of functional groups located in the loops and tails of the adsorbed macromolecule. In fact, throughout the grafting, not only are the end-functional groups of attaching macromolecules migrating toward the surface-located reactive sites but also the reactive sites may be moving in the direction of the end groups.

In this paper we report on preparation, surface morphologies, and wettability of mixed polymer brushes of varying composition of grafted chains of polystyrene (PS) and poly(2-vinyl pyridine) (P2VP) of similar molecular weights. The grafting to approach was used to attach the polymer chains to the substrate where each polymer type was sequentially grafted. Two different anchoring strategies were used to chemically attach the polymers to substrate. We study the effects of using a self-assembled monolayer of low-molecular weight epoxysilane (GPS) as an anchoring layer[14,16,17,29] versus employment of a primary polymer layer prepared from poly(glycidyl methacrylate) (PGMA) as an anchoring layer.[22−24] Changes in surface energy/composition and morphology were studied by exposing the polymer layers to selective solvents thereby switching these properties of the polymer layers.

Experimental Section

Materials. PS−COOH (M_n = 45 900 g/mol; M_w = 48 400 g/mol) and P2VP−COOH (M_n = 39 200 g/mol and M_w = 41 500 g/mol) were purchased from Polymer Source, Inc. Highly polished silicon wafers (obtained from Wacker-Chemitronics and Semiconductor Processing) were first cleaned in an ultrasonic bath for 30 min with dichloromethane or ultrapure water, placed in cleaning solution of either NH_4OH:H_2O_2 or piranha solution comprised of H_2SO_4:H_2O_2 at 60 °C for 1 h, and then rinsed several times with ultrapure water (18 MΩ·cm). (3-Glycidoxypropyl)trimethoxysilane (GPS) from Aldrich was used as received. Toluene, tetrahydrofuran (THF), methyl ethyl ketone (MEK), and ethanol were used as received (Mallinckrodt and VWR). Dichloromethane was dried on molecular sieves. PGMA (M_n = 84 000 g/mol; PDI = 3.4) was synthesized by solution radical polymerization and purified by multiple precipitations.

Grafting Procedures. The HPB were prepared on silicon substrates by grafting to methods from carboxyl-terminated PS and P2VP. Two separate procedures were used for synthesis of the HPB. The two procedures are differentiated by the use of GPS or PGMA to create the binding interlayer to which the HPB is built upon.

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In the procedure using GPS the substrate after cleaning was dried under a stream of dry nitrogen, immediately placed in a nitrogen-filled glovebox, and immersed in a GPS solution (1 vol %) in dry toluene for 16 h. After the deposition was completed, the modified surface was rinsed several times with dry toluene and ethanol in an ultrasonic bath to remove unattached silane. A thin film of PS−COOH was spin-coated from toluene solutions of different concentration onto the surface of GPS-modified silicon wafers. The silicon wafers with the polystyrene film were placed in a vacuum oven at 150 °C for different periods of time to covalently graft PS chains. At high temperature carboxylic groups are able to react with the epoxy and hydroxyl groups of the monolayer. The ungrafted polymer was removed by Soxhlet extraction with toluene for 5 h. The second polymer P2VP−COOH was spin-coated from 1% THF solution onto the same surface containing grafted PS−COOH and placed in an oven at 150 °C overnight. Ungrafted P2VP−COOH was removed by Soxhlet extraction with THF for 5 h. Every step of the modification of Si wafers was monitored by ellipsometric measurements of the layer thickness.

In the alternate procedure, PGMA was deposited via dip-coating onto the cleaned silicon wafer from a 0.2% solution in MEK. The PGMA was allowed to interact with the silicon wafer for a period of 1 h. at room temperature, and then rinsed in a clean solution of MEK to remove any unattached PGMA. PS−COOH was then deposited onto the PGMA primary layer via dip-coating from MEK solutions of differing concentrations. This layer was then melt-grafted at 150 °C in a vacuum oven overnight. Ungrafted polymer was then removed by multiple rinses and ultrasonication in MEK. This procedure was repeated for P2VP−COOH polymer. However, in each HPB synthesized, P2VP−COOH was deposited from a 1.0% solution in MEK. Every step of the modification of Si wafers was monitored by ellipsometric measurements of the layer thickness.

Each grafting procedure is effective when the nonpolar polymer is first grafted and the polar polymer grafted subsequently. In the reverse case very little PS was grafted through the P2VP layer.[5] This order of grafting is effective because of the higher affinity of P2VP for the GPS or PGMA deposited on the surface before the grafting.

The surface coverage (adsorbed amount), Γ (mg/m^2), was calculated from the ellipsometry thickness of the layer, h (nm), by the following equation:[30]

$$\Gamma = h\rho \qquad (1)$$

where ρ is the density of the attached (macro)molecules. The density of GPS is 1.020 g/cm^3,[31] the density of PS is 1.05 g/cm^3,[32] the density of P2VP is assumed to be the same as that for PS, and the density of PGMA (1.08 g/cm^3) is assumed to be the same as that for poly(propyl methacrylate).[32]

The grafting/attachment density, Σ (chains(molecules)/nm^2), i.e., the inverse of the average area per adsorbed chain or molecule, was determined by[30]

$$\Sigma = \Gamma N_{\mathrm{A}} \times 10^{-21}/M_{\mathrm{n}} = (6.023\Gamma \times 100)/M_{\mathrm{n}} \qquad (2)$$

where N_{A} is the Avogadro number and M_{n} (g/mol) is the (number-average) molar mass of the attached (macro)molecule.

Switching Procedure. The final mixed brushes were each rinsed consecutively in THF, ethanol, and toluene. The procedure for rinsing was to attach the wafer to the dip-coating apparatus at the edge of the wafer using an "alligator clip". The wafer was dipped three times to a point just prior to the edge of the clip. After each dip the wafer was immediately withdrawn from the solution to air-dry. A cover was placed over the sample during drying to prevent disruption of the sample by air currents. After rinsing in each solvent the samples were allowed to sit for a minimum of 2 h prior to any sample characterization.

Table 1. Surface Coverage Data for Synthesis of HPB and Composition of HPB

Γ (mg/m^2), HPB through GPS				Γ (mg/m^2), HPB through PGMA			
GPS	PS	PS + P2VP	% PS	PGMA	PS	PS + P2VP	% PS
1.6	2.3	5.8	40	1.6	1.9	6.2	31
1.6	2.6	6.1	43	1.5	3.6	9.1	39
1.6	3.0	6.3	48	1.6	3.2	5.7	56
1.7	4.0	6.3	63	1.5	5.6	8.6	65
1.7	4.3	6.0	72	1.6	5.5	7.9	70
1.6	5.9	7.5	79	1.6	10.5	11.2	93
1.8	5.7	6.5	87	1.3	11.4	12.2	94
1.8	6.6	7.1	93				
1.8	6.5	6.8	95				

Sample Characterization. Scanning probe microscopy (SPM) studies were performed on a Dimension 3100 (Digital Instruments, Inc.). We used the tapping and phase modes to study the surface morphology of the films in ambient air. Silicon tips with spring constants of 50 N/m were used. Imaging was done at a scan rate of 1 Hz. Tapping-mode SPM allows one the ability to adjust the force the tip applies to the sample surface. Adjusting the ratio between the free amplitude of the oscillation frequency A_0 and the set-point amplitude A_{sp} will affect the force applied by the tip. This is defined as the set-point amplitude ratio $r_{sp} = A_{sp}/A_0$.[33] Two regimes of set-point amplitude ratio were used. At an r_{sp} of 0.9 ± 0.05, the scanning is considered "light" and the forces between the tip and sample are attractive. Samples scanned under light tapping reveal the topmost surface characteristics of the sample. Due to the strong influence of attractive (adhesive) forces on the tip, areas of high adhesion on the surface will cause a more pronounced phase shift in the tip oscillation. At an $r_{sp} = 0.65 \pm 0.05$, the scanning is in "moderate" regime and the force between the tip and sample is repulsive. Moderate tapping provides sample detail just below the surface. In this mode the tip is able to penetrate softer polymers, while hard polymers show up as bright spots in the phase image due to the greater repulsion.[34] The root-mean-square (RMS) roughness of our samples was evaluated from the SPM images recorded. RMS roughness is the standard deviation of feature height (Z) values within a given area:[35]

$$\text{roughness} = \sqrt{\frac{\sum_{i=1}^{N}(Z_i - Z_{av})^2}{N}} \qquad (3)$$

where Z_{av} is the average Z value within the given area, Z_i is the current Z value, and N is the number of points within a given area.

Static contact-angle measurements were made using a contact-angle goniometer (Kruss, Model DSA10). Contact-angle measurements were made with water (pH 7.0) and a static time of 30 s before angle measurement. Ellipsometry measurements were made at an angle of incidence of 70° on a Compel (InOmTech, Inc.). Original silicon wafers from the same batch and silicon wafers with GPS and PGMA layers were tested independently and used as reference samples for the analysis of grafted polymer layers.

Results and Discussion

Grafting. In Table 1, the synthesis data from ellipsometry measurements are summarized for HPB made with GPS or PGMA. The surface coverage data for both sets of HPB show that the relative proportion of P2VP increases inversely to the thickness of the PS layer grafted in the initial step. The data also reveal that using PGMA results in a higher grafting density than with GPS, thereby

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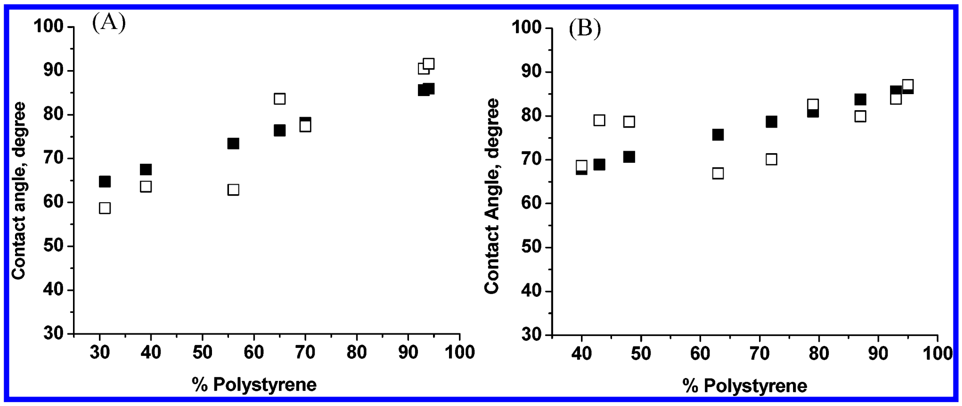

Figure 2. Plotted values of the contact angles for HPB rinsed in THF versus the brush composition: (■) values calculated using the Cassie equation (eq 4) with the composition of the brush taken from synthesis data (Table 1); (□) experimentally measured values of the contact angle. (A) HPB synthesized using PGMA. (B) HPB synthesized using GPS. Average measurement error is ±2°.

providing greater surface coverage of the polymer brush. As a first approximation the higher number of epoxy groups per unit area may describe the increase in the grafted amount for PGMA versus GPS.

The adsorbed amount, $\Gamma \approx 1.7$ mg/m^2, is estimated for GPS from the ellipsometry thickness by eq 1. Using Γ the number of molecules/nm^2 can be determined for GPS by eq 2. This value is calculated to be 4.7 molecules/nm^2, which corresponds to the same number of epoxy groups/nm^2 for GPS since there is one epoxy ring per molecule. A calculation of the attachment density Σ (chain/nm^2) needs also to be determined for PGMA in order to determine the number of epoxy rings per unit area. Using the molecular weight of PGMA as 84 000 g/mol and a thickness of 1.5 nm, Σ is calculated to be 1.16×10^{-2} chain/nm^2. The molecular weight of the glycidyl methacrylate repeat unit is 142 g/mol, which yields a degree of polymerization (DP) of 592. The number of epoxy rings/nm^2 is then $\Sigma \times \mathrm{DP} = 6.9$ epoxy groups/nm^2. This value is higher than the value determined for GPS. However, the value represents the upper bound for the surface concentration of the epoxy functionalities in the PGMA anchoring layer. The fraction of these groups responsible for the PGMA attachment to the surface is located in the train sections of the adsorbed chain (Figure 1D). According to Fleer et al.[28] the train fraction for relatively high molecular weight polymer adsorbed on the surface is about 0.15−0.25. Additionally, a maximum of 60% of the epoxy groups in the loops and tails may be lost due to PGMA self-cross-linking.[24] The surface-attached glycidyl methacrylate units, as well as the units involved in the PGMA self-cross-linking during the grafting at elevated temperatures, are not available for the attachment reactions. Therefore, we estimate that the PGMA layer used in this work had a surface concentration of active epoxy groups offered for the grafting at not less than 2.1 groups/nm^2. This (lower bound) value is lesser than the surface concentration previously reported for an epoxysilane monolayer (maximum 4.7 epoxy groups/nm^2). Thus, we can conclude that the effectiveness of the PGMA layer in grafting reactions cannot be explained solely by the high concentration of the epoxy groups. Definitely, the mobility of the groups adds to the grafting efficiency of the PGMA anchoring layer.[23]

Wettability. Once both polymers have been grafted creating the binary HPB, the surface properties of the HPB were examined by water contact angle. Initially the mixed brushes were exposed to THF, which is a good solvent for both PS and P2VP. At this point both polymer chains are swollen in the favorable solvent with the structure locked in place as THF evaporates. In the dry film under these conditions the polymers are in their glassy state providing a stable long-term structure.[5] The Cassie equation[36] provides a basis for comparing experimental results to those predicted for contact angle as a function of the fraction of each polymer present on the top layer of the HPB:

$$\cos\theta = f_1 \cos\theta_1 + f_2 \cos\theta_2 \tag{4}$$

where θ represents the contact angle for the mixed material, θ_1 and θ_2 are the contact angles of the pure components (PS and P2VP), and f_1 and f_2 are the fractions of each polymer. Experimentally measured values of 88−90° for PS and 45−55° for P2VP were obtained from pure films of each polymer. The values of θ_1 (89°) and θ_2 (50°) were used in our estimations. Using the Cassie equation with values for the brush composition taken from the grafting data (Table 1), a plot of the expected contact angle as a function of composition can be derived. This along with the experimental data shows that the intermediate contact angle values for THF-rinsed wafers provide evidence that both polymers contribute to the surface energy of the HPB (Figure 2).

The surface energy of the HPB was then reversibly switched by exposure to two selective solvents. Toluene is used as a selective solvent for PS and ethanol as the selective solvent for P2VP. The data supporting the switching of energetic states are presented in the contact-angle data (Figure 3). HPBs constructed using both PGMA and GPS, in fact, indicate changes in surface energy upon selective solvent exposure. In toluene the surface energy is lower, representing PS chains at the surface, and in ethanol the surface energy has a hydrophilic nature with P2VP chains at the surface. In Figure 3, we can observe that there are differences in the switching behavior of HPB made from GPS versus that with PGMA. At polymer ratios corresponding to >90% PS the PGMA HPBs show a decrease in the change in contact angle by solvent rinsing as compared to GPS. The overall degree of switching as measured by the difference in contact angle between ethanol and toluene remains relatively constant for the GPS HPB from a content of 40% PS to 90% PS. In contrast, PGMA exhibits a large degree of switching in the region where the polymers are approximately 1:1 in ratio.

There are two major differences in the structure of HPB attached to the GPS and PGMA. They are grafting density and mobility of the anchoring layer. Generally, the

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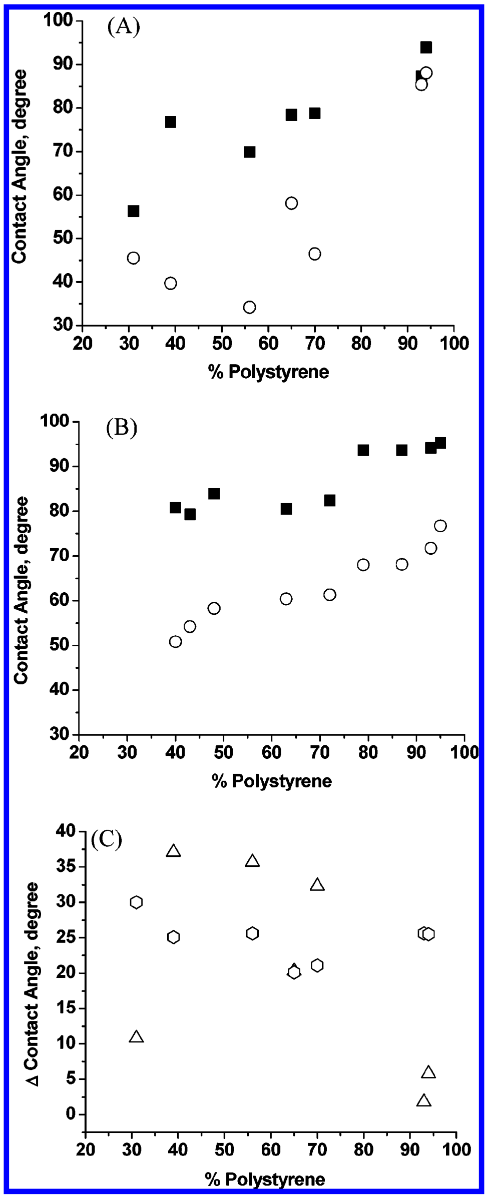

Figure 3. Water contact angles measured for HPB (A) with PGMA and (B) with GPS versus the brush composition: (■) toluene rinsing; (○) ethanol rinsing. (C) Difference in contact angle between toluene and ethanol: (△) PGMA; (⬡) GPS. Average measurement error is ±2°.

polymers constituting the brush attached to PGMA are grafted at higher densities. This may decrease their switching ability. On the other hand the switching may be aided by the mobility at points of grafting offered by the primary polymer layer. We believe that interplay between the two opposite trends contributes to the differences in the wetting behavior observed for HPB attached to GPS and PGMA.

Surface Morphology. SPM was used to visualize the sample surface morphology and observe microphase segregation within the brushes and sample roughness. Figures 4 and 5 show how surface morphologies of the mixed brushes change with the content of PS and treatment with nonselective (THF) and selective (ethanol and toluene) solvents. The images were recorded using the tapping mode at the highest set-point value that permitted reproducible imaging (the lowest forces, light tapping). In this case the image reflects the morphology of the topmost layer.[34] The SPM images presented are dimensionally 1 μm × 1 μm. Images were also obtained at larger scanning dimensions of 10 μm × 10 μm at various locations on each HPB to determine the uniformity of the morphology. With this knowledge the images are representative of the overall morphology of the HPB.

The surface topography of the HPB made with GPS and PGMA show a general trend toward smoother surfaces as the ratio of PS increases to the 95% composition. For samples with lower PS content formation of clusters on the brush surface was observed. It reveals pronounced phase segregation in the grafted film where grafted PS and P2VP chains try to minimize their mutual contact. The surface morphology of the brushes is to a great extent affected by the solvent treatment and anchoring layer used for the grafting. Larger surface structures are observed for the brushes attached to the PGMA primary polymer layer. For these layers not only end-grafted chains are affected by the solvent treatment but the adsorbed PGMA macromolecules are also capable of conformational reconstructions at the experimental conditions. Thereby increased mobility of the attached chains at the grafting points may lead to phase segregation on the greater level in the case of the macromolecular anchoring layer.

RMS roughness data from the SPM topography images, presented in Figure 6, corroborate our conclusions about different cooperative responses to the solvent treatment of the chains attached to GPS and PGMA. In fact, the layers anchored to the self-assembled monolayer and primary polymer layer demonstrated different trends. The brushes grafted to GPS had notably higher roughness after the THF treatment. Thus, lateral segregation prevailed over the layered segregation. The observation is in good agreement with the contact angle data, suggesting that both PS and P2VP segments are exposed to the brush surface at low and medium PS contents. Naturally, the roughness for the THF treated grafted layers (and level of phase segregation) decreases, as PS becomes a dominating component in the brush. The roughness of the coating is significantly lowered by treatment with a selective solvent, suggesting that the layered segregation prevailed over the lateral segregation. An entirely different and somewhat incomprehensible trend is observed for the brushes attached through PGMA. At medium PS contents, the highest roughness is found for the samples exposed to ethanol (selective solvent for P2VP). The lowest roughness was observed for the THF-treated samples. Toluene demonstrated intermediate values for the roughness. We attribute the distinctions in the surface roughness parameter to different mobility of the PGMA chains in different solvents. THF is a good solvent for PGMA, but toluene and ethanol are nonsolvents. Of course, the solubility of the PGMA may be greatly affected by the grafted PS and P2VP macromolecules. However, as a first approximation we presume that higher mobility of the PGMA chains in THF may lead to the reduced roughness.

The next focus for these sets of HPB was to examine the SPM phase images. The phase image results from the change in the phase angle of the oscillating probe tip when in tapping mode. Numerous investigations have been made into the relationship between the properties of the sample and changes in the phase oscillation.[37-43] Some of

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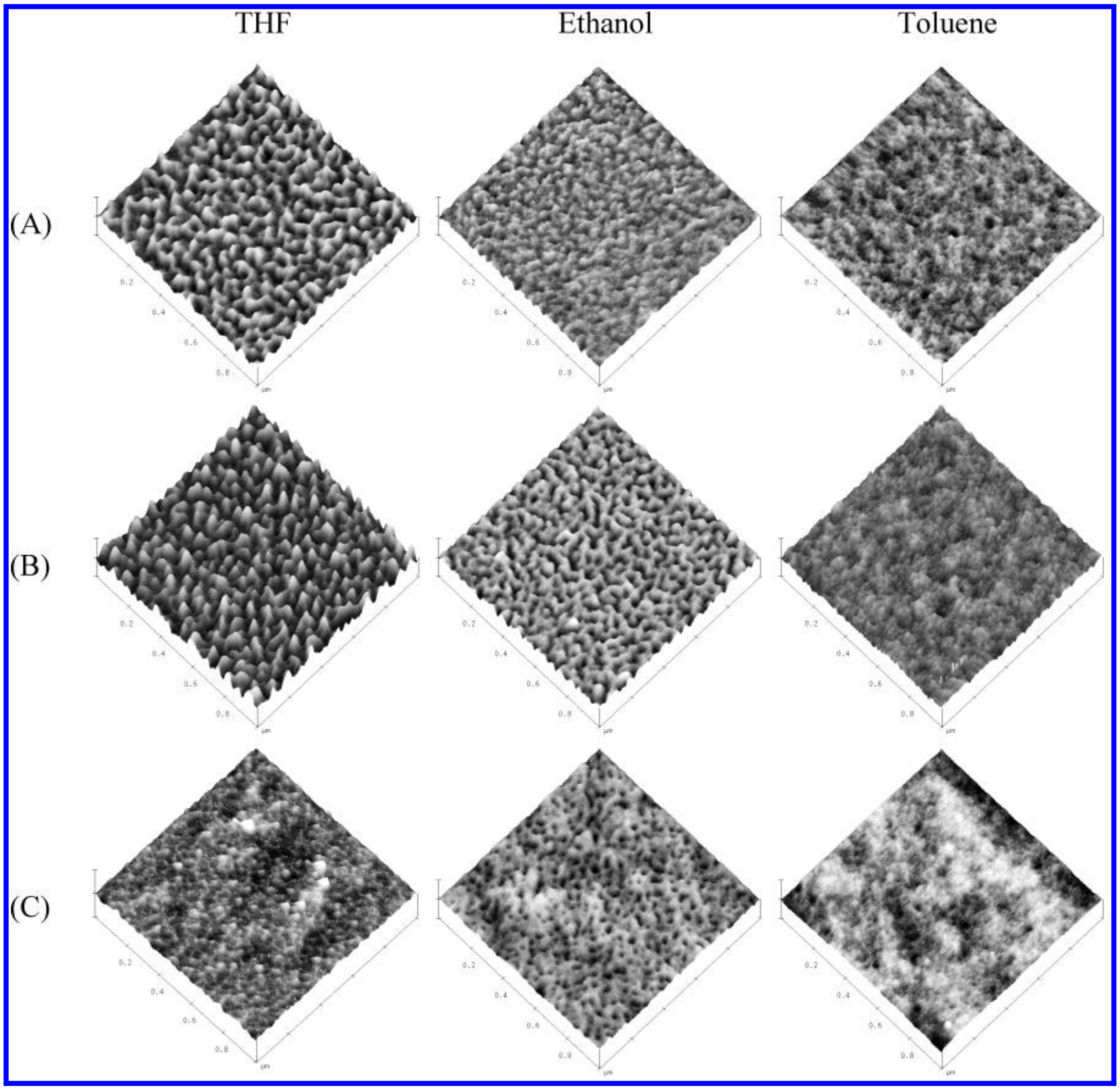

Figure 4. SPM topographical images of HPB (GPS anchoring layer) rinsed with different solvents: (A) 40, (B) 72, and (C) 95% PS. Dimensions are 1 μm × 1 μm with a 5 nm vertical scale.

the sources of phase shift can include stiffness, damping, and adhesive interactions. However, direct assignment of the phase shift to a specific property is by no means implied and is subject to numerous conditions under which the sample is probed. One such condition is the tapping force applied to the sample surface. Higher tapping force is related to the ratio of the set-point amplitude to the oscillation frequency of the SPM tip.

Figure 7 displays SPM phase images for the mixed brushes grafted to GPS and treated with ethanol and toluene. The images were recorded in the light tapping mode. At such tapping, the tip–sample interaction is strongly influenced by adhesion attractive forces.[29] The shift is greater on the surface areas with higher adhesion, because the duration of tip–sample contact is longer for these parts of the surface. For the HPB exposed to ethanol the contact-angle data revealed that mostly P2VP segments were present on the surface of the samples with high P2VP content. Accordingly, for the brushes treated with toluene the wettability measurements suggested that samples with high PS content covered entirely with PS material. For intermediate PS/P2VP ratios both polymers contribute to the surface energy of the HPB. However, regions on the surface demonstrating different adhesive interaction with the SPM tip were detected for all HPBs prepared. The variation in the adhesion can be mostly connected with the presence of both PS and P2VP segments on the HPB surface as well as with variation in the density of the topmost layer that can be caused by the chains located underneath the uppermost layer and affecting the local layer compactness.

In our next experiment the phase images were recorded using a moderate tapping mode. The SPM tip penetrates through the soft topmost layer during the moderate regime of scanning and interacts with the polymer segments situated somewhat deeper inside the brush.[44] Then, the phase image reflecting tip/sample interactions permits observation of the film structure that forms underneath the surface-located segments of the grafted polymer chains. For the scanning with lower set point, the elastic forces due to the deformation of the sample can be described by an additive term to the spring constant of

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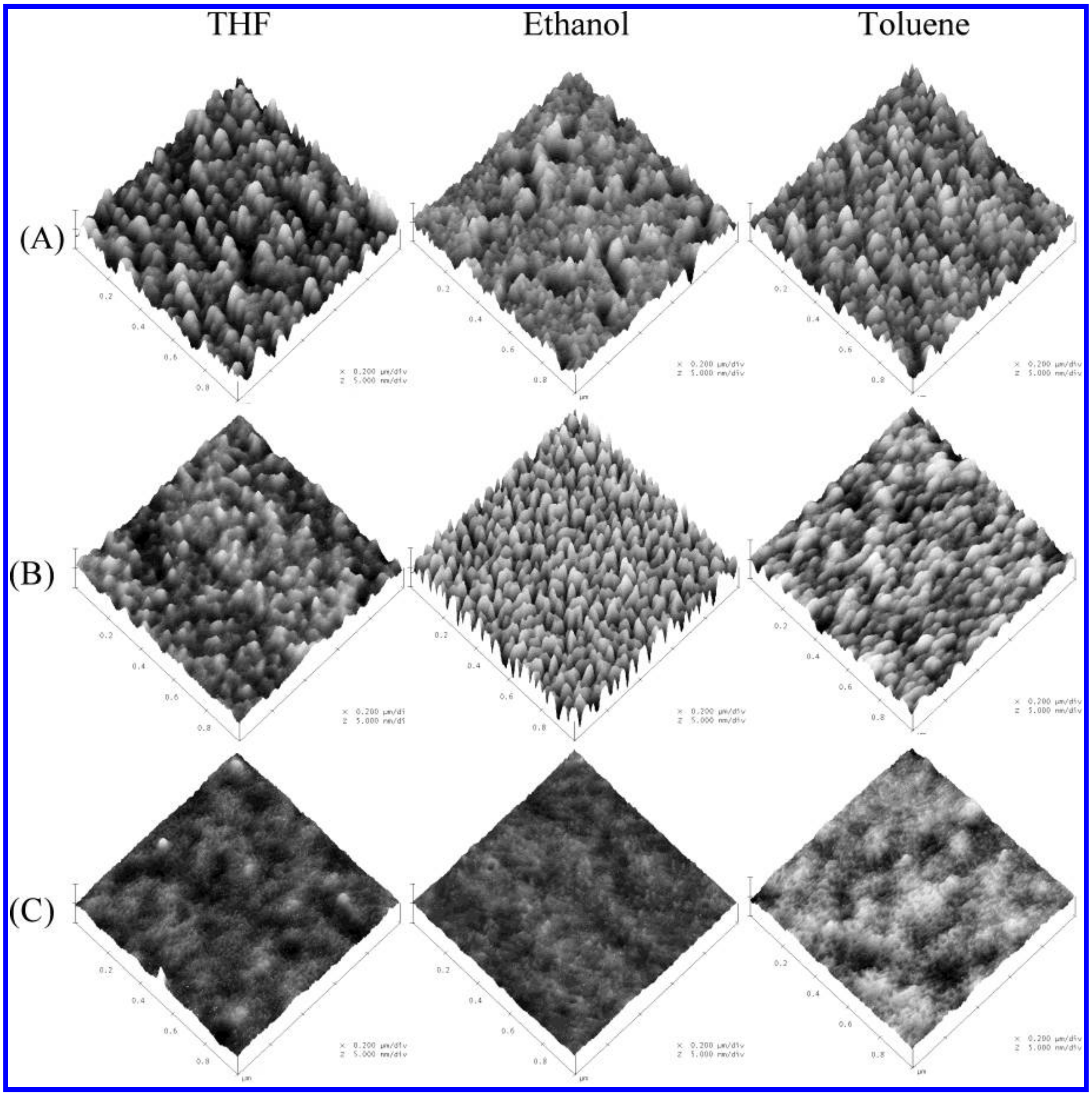

Figure 5. SPM topographical images of HPB (PGMA anchoring layer) rinsed with different solvents: (A) 31, (B) 65, and (C) 94% PS. Dimensions are 1 μm × 1 μm with a 5 nm vertical scale.

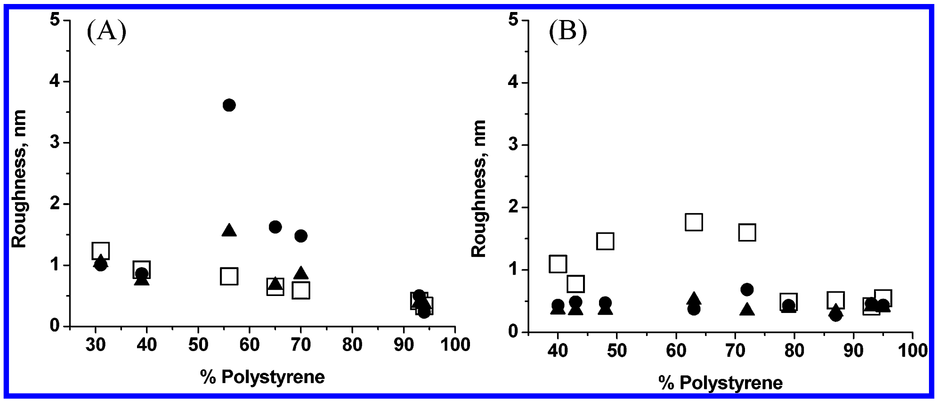

Figure 6. RMS roughness data taken from SPM topographical images of HPB rinsed with different solvents: (A) PGMA anchoring layer and (B) GPS anchoring layer. (□) THF, (●) ethanol, and (▲) toluene.

the cantilever−sample system.[43,45] As a consequence of the higher effective spring constant the resonance frequency increases, which keeps the drive frequency constant, and the phase shift increases. For softer material the phase shift is lower than for stiffer material. Accordingly, the fraction of the grafted polymer film possessing higher density will appear brighter in the phase images recorded in the moderate scanning regime.

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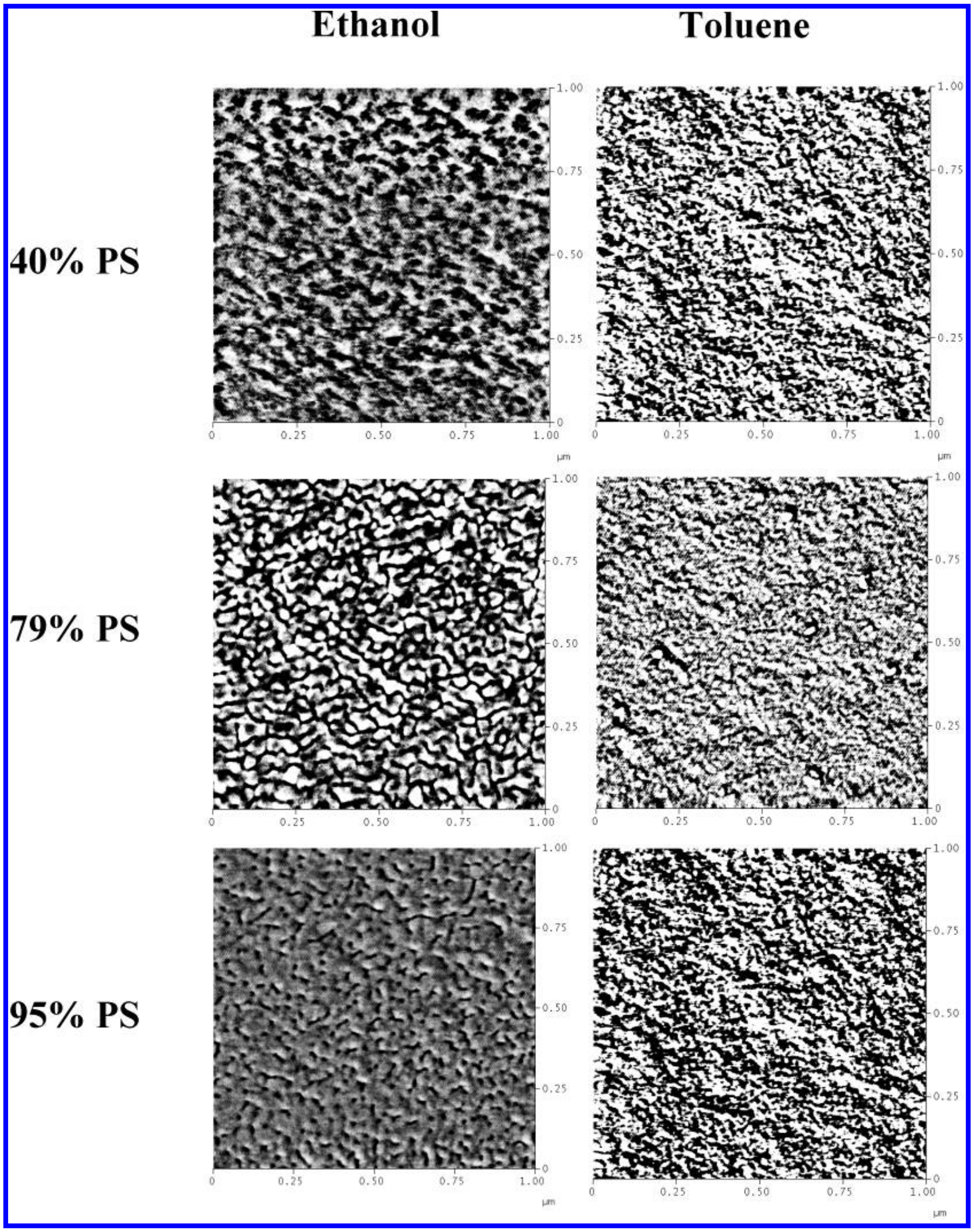

Figure 7. SPM phase images (light tapping) of 40, 79, and 95% PS HPB (GPS anchoring layer). Image dimension 1 μm × 1 μm. Vertical scale, 3°.

The scanning employing the moderate tapping lead to pronounced two-phase distribution for HPB anchored through GPS (Figure 8). It is obvious that the binary distribution results from segregation of the two (PS and P2VP) polymers into the PS-rich and P2VP-rich phases.[44] This binary-phase data were then used to determine the percent of each component from the SPM image. The light areas (higher phase angle) were supposed to represent a PS-rich phase for the ethanol-rinsed wafers, while the dark areas represent the P2VP-rich phase. The hypothesis was that exposing the brush to ethanol would swell the P2VP, making these polymer chains less dense, and cause the PS chains to contract to a higher density. Then, we presumed that collapsed thin polymer layers after solvent evaporation demonstrate some memory effect. Their density depends on solvent for treatment. Namely, in the ultrathin film of relatively low grafting density the difference in compactness may be introduced because of an extremely fast evaporation of the solvent and interface effect where monomer units may pack somewhat different then in the bulk. The opposite case should be true for toluene-rinsed wafers. Now the PS chains should expand while the P2VP chains will contract. In this scenario the high-phase region of the brush could be assigned to the P2VP-rich phase.

We analyzed the distribution of the areas possessing higher and lower density on the SPM phase images using standard bearing analysis and estimated fractions occupied by the phases with different compactness. The area of each polymer phase was obtained by selecting one side of an assumed Gaussian peak to represent the one phase area. Figure 9 is an example of the two-phase distribution

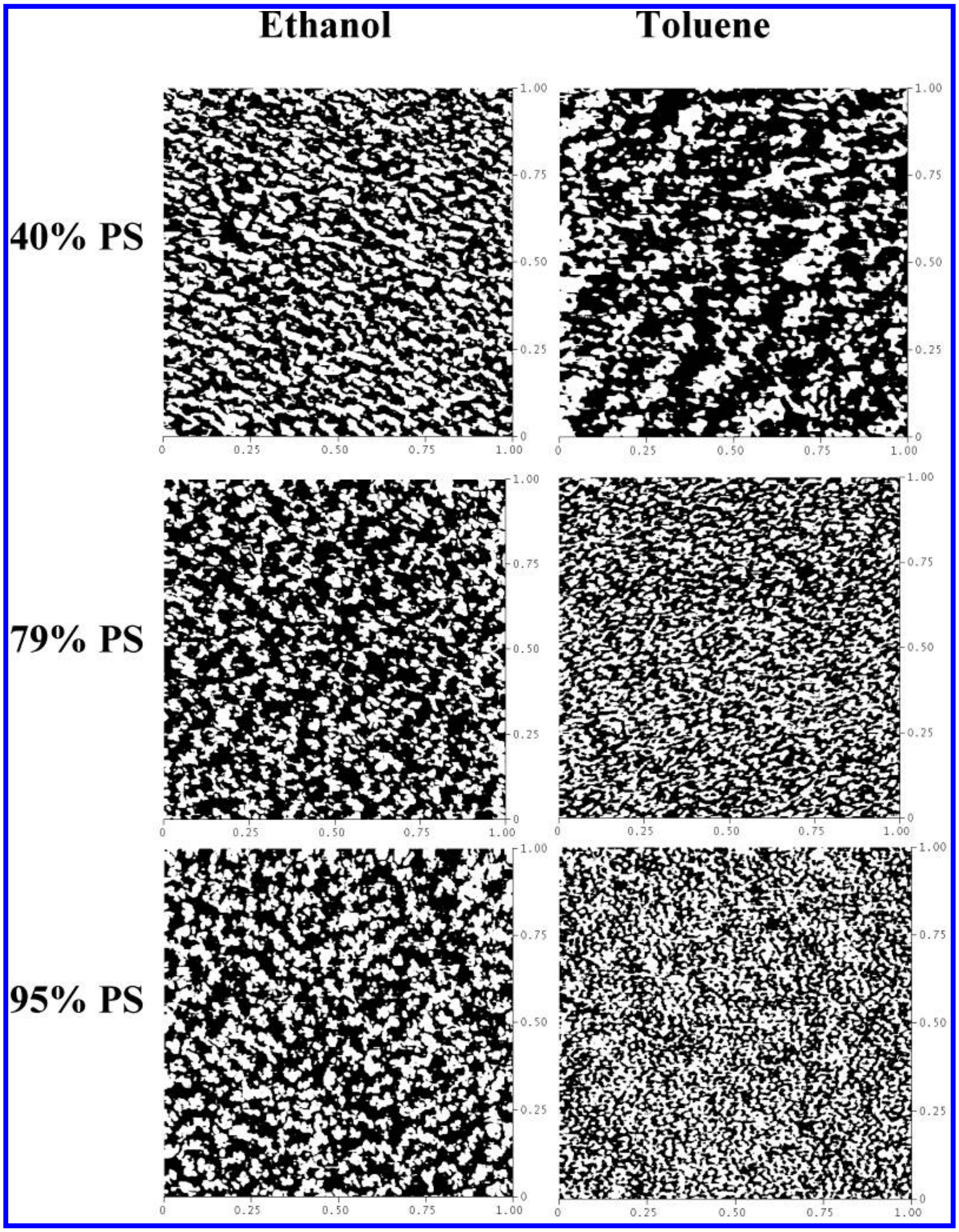

Figure 8. SPM phase images (moderate tapping) of 40, 79, and 95% PS HPB (GPS anchoring layer). Image dimension 1 μm × 1μm. Vertical scale, 3°.

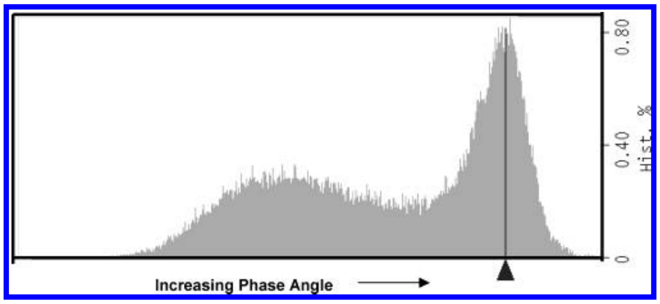

Figure 9. Bearing area data of the two-phase morphology of the 93% HPB (GPS anchoring layer) rinsed in ethanol and measured with moderate tapping. Marker at center of high-angle peak was used to determine peak areas.

Table 2. Fraction of the Areas with Higher Phase Shift Calculated from SPM Phase Images Obtained at Moderate Tapping Force

% PS as grafted	area %, HPB rinsed with ethanol	area %, HPB rinsed with toluene
40	12	45
43	26	77
48	33	52
63	32	97
72	31	59
79	47	52
87	75	56
93	64	90
95	58	86

of the phase data by bearing analysis of a 93% HPB rinsed in ethanol. The area represented by the high-phase-angle peak is representative of the PS-rich phase, while the low-angle peak represents the P2VP-rich phase. Table 2 shows area percentages calculated from the SPM phase images in the described manner. As can be expected from the synthesis data (Table 1), the calculated PS area

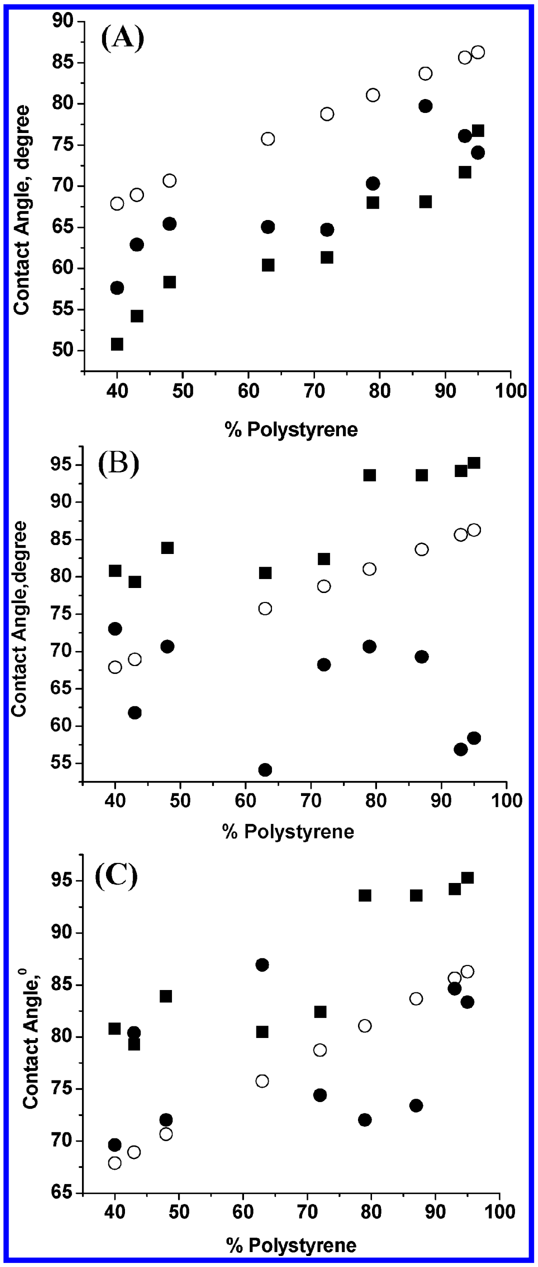

Figure 10. Contact-angle predictions for HPB (GPS anchoring layer): (A) ethanol-rinsed HPB assigning high-phase region to PS; (B) toluene-rinsed HPB assigning high-phase region to P2VP; (C) toluene-rinsed HPB assigning high-phase region to PS. (■) Experimental contact angles, (●) predicted from SPM data (Table 2), and (○) predicted from synthesis data (Table 1). Average measurement error is ±2°.

percentages from bearing data for the mixed brushes rinsed in ethanol increased from a value of 12% to 60−75%. The HPB rinsed in toluene did not exhibit such a trend in the increase in the area percentage as compared to the percentage obtained from the synthesis data (Table 1).

The Cassie equation (eq 4) was applied to predict contact angles for the surfaces covered with the mixed PS/P2VP brushes using the phase distribution data. The contact-angle predictions were based on area percentages for each phase region taken from the phase images. Figure 10 presents the correlation between the experimentally measured contact angles for the ethanol- and toluene-rinsed brushes (GPS anchoring layer) as compared to the predicted contact angle from the Cassie equation using bearing area percentages and contact angles for pure PS and P2VP. An observed correlation is present between the experimental values and those predicted by the Cassie equation for brushes rinsed in ethanol (Figure 10A). The predicted values tend to be slightly higher overall than the experimental values, with a crossover for the 95% PS brush at the extreme end. It may indicate that P2VP chains present in the PS-rich regions influence the wettability, decreasing the contact-angle values. In general, observed correlation supports our assumption that the high-phase-angle region of the ethanol-rinsed brushes is mainly comprised of the PS-grafted chains. Following the logic of assigning the high-phase region to P2VP for the toluene rinse shows a poor correlation between the predicted and experimental data (Figure 10B). Reversing the assignment of the high-phase region to P2VP marginally improves the correlation (Figure 10C).

The poor correlation of toluene as compared to ethanol could be a result of the solvent effect on each polymer. Solubility value parameters were all found in the literature[46] for polystyrene ($\delta = 9.1$), toluene ($\delta = 8.9$), and ethanol ($\delta = 12.7$) in units of $(\mathrm{cal/cm^3})^{1/2}$. The solubility parameter for P2VP ($\delta = 9.9$) was calculated from a literature reported value of 0.1[47] for the PS−P2VP interaction parameter χ, using the following equation:

$$\chi_{PS-P2VP} = \frac{V_r(\delta_1 - \delta_2)^2}{RT} \tag{5}$$

where V_r is molar volume of monomer unit of the polymer, δ_1 and δ_2 are solubility parameters of PS and P2VP, R is the universal gas constant, and T is the temperature in kelvin. It was assumed that the molar volume of the two monomeric units would be nearly equal, and a value of 98 $\mathrm{cm^3/mol}$ was used. A general rule of thumb is that if $[(\delta_1 - \delta_2)^2]^{1/2} < 1$, the polymer will generally dissolve in the solvent.[48] It is apparent that this value is $\ll 1$ for PS−toluene and $\cong 1$ for P2VP−toluene, meaning that toluene should be considered a good solvent for PS and is a borderline solvent for P2VP. Values for PS−ethanol and P2VP−ethanol are both $\gg 1$, which indicates that ethanol is a nonsolvent for both polymers. However, ethanol is a strong hydrogen bonding solvent, and P2VP with the pyridine functionality will also form hydrogen bonds. It is known that hydrogen bonding is a strong secondary parameter to predicting solubility, and in this case can be used to explain the solubility of P2VP in ethanol in deference to the solubility parameter calculated in the first estimation.[48] Considering all of this, it can be predicted that the ethanol is a selective solvent for P2VP, while toluene is not as selective for PS compared to P2VP. Therefore, HPB rinsed in toluene may not experience as significant of a contraction of the P2VP chains at the brush surface. This could explain the better correlation of predicted contact angles for ethanol as compared to the prediction for toluene.

Figure 11 displays phase images for the mixed brushes synthesized with PGMA. The SPM images exhibit phase contrast, indicating a certain degree of phase separation within the brush. The areas possessing distinct density are larger if compared with the HPB attached to the self-assembled monolayer (Figure 8). However, bearing area data did not demonstrate the well-defined two-phase distribution seen in the GPS-synthesized mixed brushes

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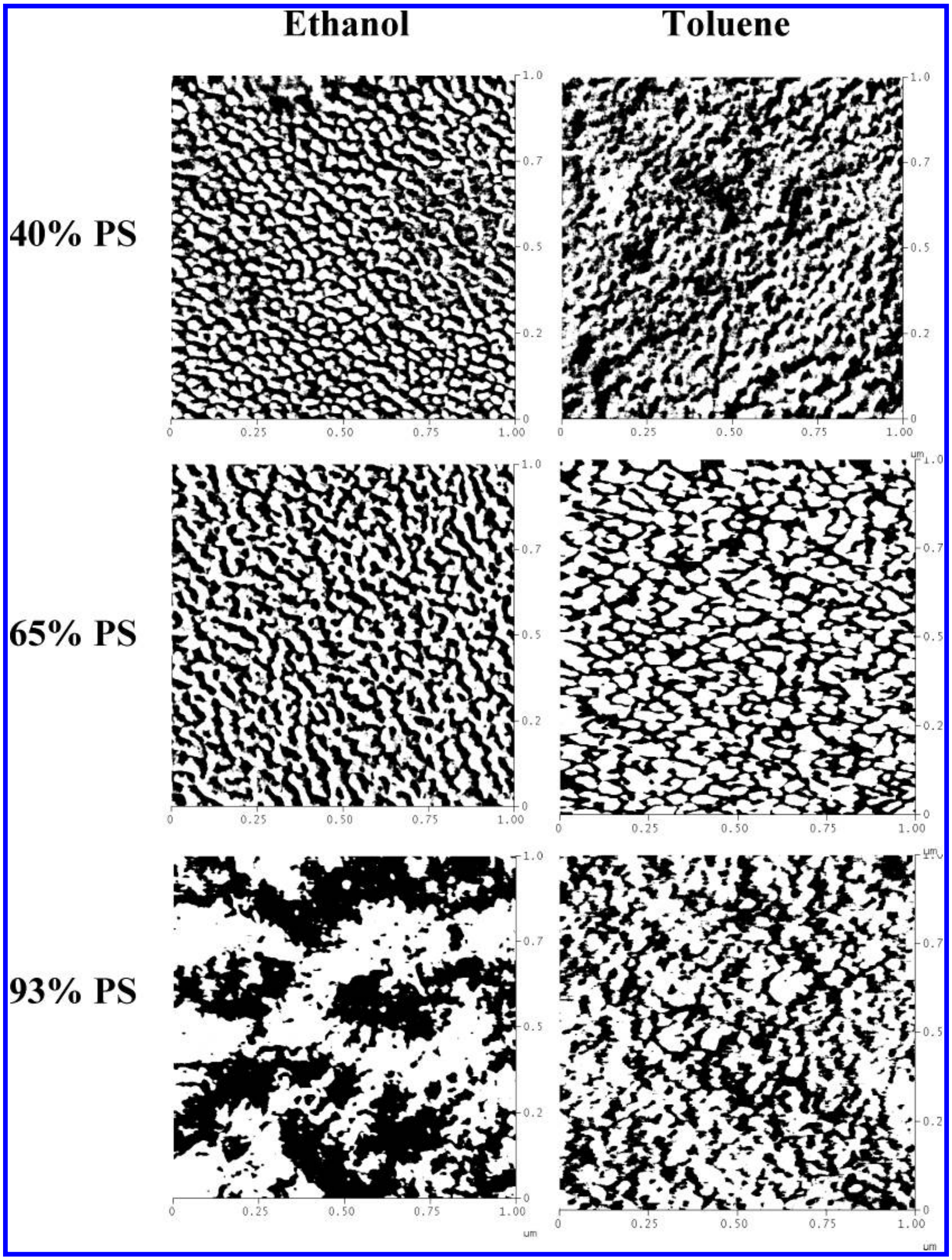

Figure 11. SPM phase imagery of HPB synthesized with PGMA. Image dimension, 1 μm × 1 μm. Vertical scale, 3°.

(Figure 9), nor did we observe a significant increase in phase contrast at elevated tapping forces. As a result, contact-angle predictions were not done for this set of HPB. Larger regions with dissimilar density and lack of sharp borders between them again indicate that the attachment of the mixed brush to the mobile anchoring layer significantly affect the morphology of the HPB.

Conclusions

In conclusion this investigation has demonstrated that it is possible to synthesize mixed polymer brushes of various composition by grafting to a silicon surface using GPS or PGMA as an anchoring interlayer between the polymer and the silicon wafer. The brushes were successfully grafted using a sequential approach whereby PS−COOH was grafted first followed by P2VP−COOH. The HPBs synthesized in this manner exhibit changes in surface energy as measured by contact angles. These contact-angle measurements follow well with the change in concentration of PS content and indicate switching between PS and P2VP with toluene and ethanol, respectively. The surface morphology of ethanol-rinsed brushes was used to adequately predict experimental contact angles for the mixed brushes using the Cassie equation. An explanation with regard to solubility differences is presented for the lack of correlation of experimental and predicted contact-angle values for HPB made with GPS and rinsed in toluene. The use of light and moderate tapping forces for GPS-prepared HPB indicated a level of perpendicular and lateral segregation of the two polymers.

This segregation led to utilization of bearing area analysis of the phase images to determine phase-area percentages and prediction of brush composition using the Cassie equation. This form of analysis was not successful for the HPB with PGMA as the interlayer. We propose that the brush segregation is not as pronounced due to the higher mobility of the PGMA layer and its penetrability to the PS and P2VP chains. Therefore, PGMA is an active participant in the composition of the HPB. This is in contrast to GPS that forms a molecular monolayer that behaves like a distinct interface without polymer penetration.

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