

# Tuning Morphology And Surface Properties Of Smart Polymer Coatings From Mixed Polymer Brushes

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## INTRODUCTION

Smart polymer coatings are of great interest for microelectronic, textile industry, biomedical applications. A possibility to switch and/or precisely tune properties of the coatings by applying external stimuli is the desired advantage of the smart polymer materials to vary, for example, adhesion, wettability, friction, roughness, reactivity, biocompatibility, selectivity, etc. Binary (mixed) polymer brush composed of two incompatible polymers, grafted to a solid substrate, is an example of the smart polymer coating. These two grafted polymers form the brush-like layer of the polymer chains randomly attached by one end to the substrate and stretched in the direction perpendicular to the substrate surface because of the volume excluded effect. Due to the phase segregation the morphology of the mixed brushes is sensitive to surrounding medium.<sup>1-4</sup> Mixed brushes show the adopting behavior and can be switched between different surface energetic states upon exposure to different solvents.<sup>5-6</sup> The interaction of the binary polymer brush with selective solvent causes a change of the surface properties of the polymer film because one of the two polymers preferentially occupies a top layer. As well as the surface composition, external stimuli can switch morphology of the film.<sup>7</sup>

In this paper we focus on tuning of surface morphologies of polymer coatings prepared from mixed polymer brushes of different molecular weights of grafted chains. We use polystyrene (PS) and poly-2-vinyl pyridine (PVP), and PS and polyacrylic acid mixed brushes prepared by "grafting to" method. Additionally, we show that mixed brushes can be prepared from the combination of end-functionalized polymer chains and homopolymer chains grafted in the matrix of the grafted end-functionalized polymer.

## EXPERIMENTAL

**Materials.** Carboxyl-terminated polystyrene PS-COOH16;  $M_n=16900$  g/mol,  $M_w=21900$  g/mol was synthesized by atom free living polymerization using 4-(1-bromoethyl)benzoic acid as initiator, PS-COOH2  $M_n=2000$  g/mol,  $M_w=2980$  g/mol, PS-COOH9  $M_n=9700$  g/mol,  $M_w=10500$  g/mol, PS-COOH45  $M_n=45900$  g/mol,  $M_w=48400$  g/mol, PS-COOH72  $M_n=72300$  g/mol,  $M_w=75200$  g/mol and polyvinyl pyridine PVP-COOH;  $M_n = 39200$  g/mol and  $M_w = 41500$  g/mol were purchased from Polymer Source, Inc. Polyacrylic acids PA5,  $M_w=5000$  g/mol, PA8,  $M_w=8000$  g/mol, PA15,  $M_w=15000$  g/mol, PA30,  $M_w=30000$  g/mol were purchased from Aldrich. Toluene and tetrahydrofuran (THF) were distilled after drying over sodium. Dichloromethane was dried on molecular sieves. Highly polished silicon wafers (obtained from Wacker-Chemitronics) were first cleaned in an ultrasonic bath for 30 min with dichloromethane, placed in cleaning solution (prepared from  $NH_4OH$  and  $H_2O_2$ ) at 60 °C for 1 h and then rinsed several times with Millipore water (18 M $\Omega$ ×cm). 3-glycidoxypropyl trimethoxysilane (GPS) Aldrich was used as received.

**Grafting procedures.** The mixed brushes were prepared on Si-substrates by "grafting to" methods from carboxyl terminated PS and PVP.<sup>8,9</sup> The substrate after cleaning was dried under a stream of dry nitrogen, immediately taken into the nitrogen-filled glove box and immersed in an 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 ultrasonic bath to remove unattached silane. Thin layer of PS-COOH was spin coated from 1%

toluene solution onto the surface of GPS modified silica wafers. The thickness of these polystyrene films estimated by ellipsometry, was 50±5 nm. The silica wafers with the polystyrene grafted film was placed in 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.<sup>10</sup> The ungrafted polymer was removed by a soxhlet extraction with toluene for 5 h. The second polymer PVP-COOH was spin coated from 1 % THF solution, or in the case of PA, it was deposited from water solution, onto the same surface containing PS-COOH, placed in oven at 150 °C for different periods of time to graft it chemically to the epoxy surface and ungrafted polymer was removed by soxhlet extraction with THF (or water for PA) for 5 h. Every step of the modification of Si-wafers was controlled by ellipsometric measurements of the layer thickness.

## RESULTS AND DISCUSSION

In this investigation we vary the molecular weight of grafted PS-COOH and use the same PVP-COOH for preparation of the mixed brushes. The composition of the synthesized brushes are shown in Table 1.

Table 1. Composition Of Mixed PS/PVP Brushes

Sample	M <sub>n</sub> of PS-COOH	Grafted amount, mg/m <sup>2</sup>		Contact angle, deg	
		PS	PVP	After toluene	After water
PS2K/PVP	2000	1.2	3.4	-	45
PS9K/PVP	9700	1.8	2.9	81	54
PS16K/PVP	16900	3.7	3.7	84	55
PS45/PVP	45900	3.8	2.7	85	63
PS72K/PVP	72300	5.6	2.1	90	65

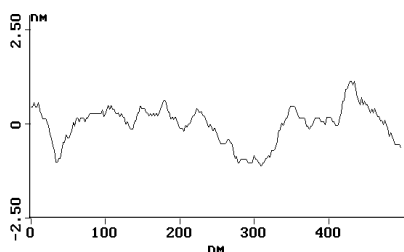
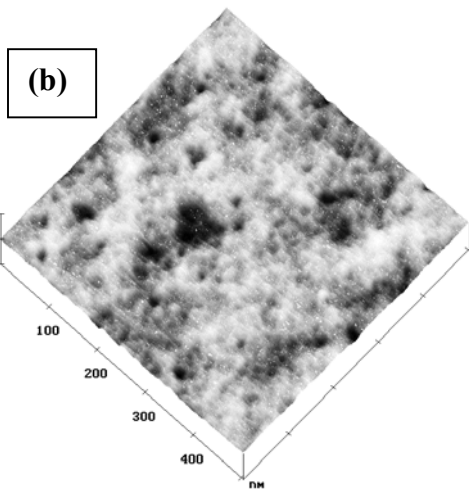
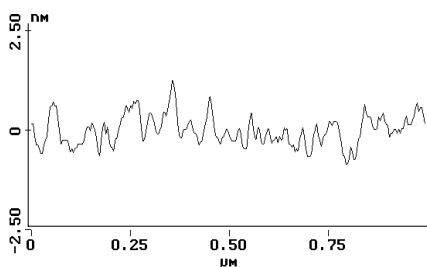
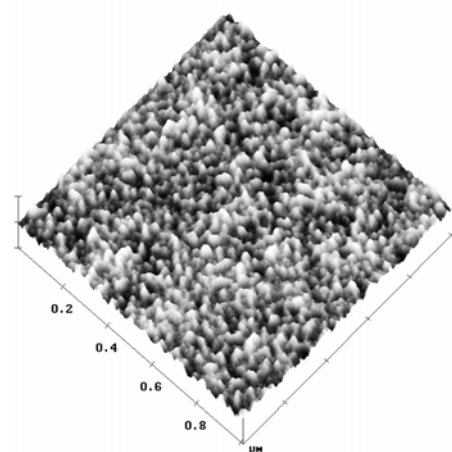
The same experiment was done for PS/PA brush, but in most cases we varied molecular weight of PA at constant molecular weight of grafted PS (Table. 2).

Table 2. Composition Of Mixed PS/PA Brushes

Sample	M <sub>n</sub> of PS-COOH	M <sub>w</sub> of PA	Grafted amount, mg/m <sup>2</sup>		Contact angle, deg	
			PS	PVP	After toluene	After water
PS16//PA5	16900	5000	7.8	1.7	88	68
PS16/PA8	16900	8000	4.2	2.9	91	76
PS16/PA15	16900	15000	4.0	3.4	85	76
PS16/PA30	16900	30000	4.1	3.4	88	68
PS45/PA30	45000	30000	5.6	2.1	84	68
PS45/PA15	45000	15000	16.2	3.7	89	74

Finally, we synthesized binary polymer brushes of 6-20 mg/m<sup>2</sup> grafting amount. The composition of grafted layers was calculated from the ellipsometric measurements performed after every step of grafting. The chemical composition of the coatings was proved with FTIR ATR spectroscopy. It is noteworthy that the binary brush can be synthesized if PVP-COOH or PA is grafted after PS-COOH. For the inverse case we did not detect grafting of PS-COOH after PVP-COOH or PA. It is evidence that high affinity of polar polymers is a driving force to overcome the repealing of PS brush and reach the Si-substrate surface.

Switching properties of these smart coatings are demonstrated using contact angle method and atomic force microscopy. The silica wafers with the two grafted polymers were dipped in different solvents for 10–15 min. So that the layer reorganization occurs within this time. The selective solvent swells the chains of one polymer while chains of other polymer adopt a collapsed confirmation. Such behavior can be detected with contact angle experiments using water as a probe liquid.



**Figure 1.** AFM images of binary brushes PSCO0H45/PVP (a) and PSCO0H2/PVP (b) grafted to the Si-wafers after treatment with THF.

After exposure to different solvents the silica wafers were taken out from the solvent and rapidly dried under nitrogen flux. Then the contact

angle of water was measured on the surface of the wafer immediately after the drop was set on the substrate. In such experiments we measure contact angle on the surface of the frozen layer structure before it is changed under the water drop. The same experiment was carried out two to three times to check the reproducibility of the results. The values of contact angle found to be reproducible, shown in Table 1 and Table 2. Then the wafer was exposed to the next solvent and the same measurements were carried out. The contact angle data clearly show that, a top layer of the binary brush switches from hydrophobic to a hydrophilic energetic state, upon exposure to selective solvents toluene and water, respectively. When we expose the sample to toluene, the top of the layer is preferentially occupied by PS, while in acidic water (pH=3.0) the surface is dominated by PVP or in water (pH=7.0) by PA for PS/PVP and PS/PA brushes respectively. The switching effect was also confirmed by AFM. The morphology of the surface differs upon exposure to different solvents in the same way as it was shown in our previous publications.<sup>6-8</sup>

The variation of molecular weight in mixed brushes changes the range of switching but the effect is not large. In a selective solvent the surface of the coating is preferentially occupied by one of the polymers independently on the ratio between molecular weights of both grafted polymers even if this ratio approaches the value of 10. In contrast to the change of the surface energetic state, the morphology of the film is much more sensitive to the ratio of molecular weights as it is seen from AFM images (Fig. 1). The latter effect is caused by a change of the incompatibility of the polymers with the change of molecular weight. Both incompatibility parameter and molecular weight effect the sizes of segregated phases.

## CONCLUSIONS

We synthesized mixed polymer brushes composed of two incompatible polymers of different polarity: PVP and PS; PA and PS using the polymers of different molecular weights. The brushes synthesized show very similar switching behavior with a slight effect of molecular weight on the wetting properties of the coatings. The variation of molecular weight has the pronounced effect on surface morphology of the coatings.

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