

Mixed Polymer Brushes with Locking Switching

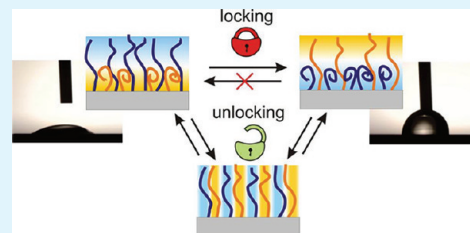
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S Supporting Information

ABSTRACT: Mixed polymer brushes, made of two different kinds of polymers randomly grafted to the same solid substrate, were introduced as switchable interfaces for a number of promising applications. The switching properties of the mixed polymer brushes are substantially dependent on grafting density, molecular weight, compatibility of two distinct grafted polymers, and their interaction with the solvent. This work reports the mixed polymer brushes with the property of locking switching. The wetting properties of such a mixed brush can be switched between the wetting properties of individual constituting polymers by appropriate selection of solvent. However, the mixed polymer brushes wetting behavior can be locked in the hydrophobic state. This kinetically frozen metastable state, however, can be unlocked via treatment by proper “unlocking” solvent. This locking and unlocking of the hydrophobic state of the mixed brush with specific solvents could find useful applications for the development of functional materials.

KEYWORDS: polymer brushes, grafting, switching, wetting



INTRODUCTION

Stimuli-responsive materials,¹ such as hydrogels, polymer brushes, shape-memory polymers, etc., were demonstrated to be highly promising for surface patterning with proteins,^{2,3} controlled encapsulation of drugs and cells,^{4–6} separation,⁷ control of adhesion, friction, adsorption and wetting,^{8–12} control biocatalytic activity,^{13,14} drug delivery,^{15,16} and design of actuators^{17–19} and sensors.^{20–22}

Mixed polymer brushes fall into the call of stimuli-responsive materials that are made of two different polymers randomly grafted to a solid substrate. Anchoring to the substrate prevents macrophase separation of unlike polymers while allows for a certain degree of segmental mobility. The polymer chains undergo dynamic vertical versus lateral nanoscale segregation, which can be reversibly switched by external signals.^{23–25} This behavior was used to tune/switch surface properties of the mixed brushes, such as wettability, adhesion, and adsorption. Because of their switching properties, mixed polymer brushes are particularly interesting for the switchable stabilization/destabilization of colloidal dispersions,²⁶ gating of mass transport,²⁷ sensors,^{28,29} elements of microfluidic devices,^{7,28} biointerfaces,^{30,31} surface transport,³² design of superhydrophobic surfaces and coatings,³³ surfaces with tuned adhesion,³⁴ and electrochemical devices.³⁵

The mixed brushes, which are made from hydrophobic and hydrophilic polymers, are capable of switching between hydrophobic and hydrophilic wetting behavior upon exposure to different selective solvents. The switching properties are, however, substantially determined by the composition, grafting density and molecular weight of the brushes. For example, at low grafting densities a thin brushes prepared by “grafting to” method often demonstrate a reduced switching range (the difference between hydrophobic and hydrophilic wetting properties).^{36,37} As a result, advancing water contact angles

on the brush after exposure to solvents selective to hydrophobic and hydrophilic polymers are smaller and larger, respectively, than those on the surface of the corresponding polymers. Moreover, values of water receding contact are often small indicating a high wetting hysteresis because of penetration of water droplet into a brush. For example, advancing water contact angle on a thin poly(acrylic acid)–polystyrene (PAA–PS) mixed brush consisting of highly hydrophilic PAA and hydrophobic PS, which were synthesized by “grafting to” approach, demonstrate a reduced switching range between 60° and 90° after exposure to water and toluene, respectively.³⁸ A surface initiated polymerization–“grafting from” allows synthesis of mixed brushes with high grafting densities. Mixed polymer brushes were prepared using different variations of the “grafting from” method including sequential polymerization of two monomers using thermo-^{39,40} or photoinduced⁴¹ free radical polymerizations. Bifunctional initiators or mixtures of two initiators of a controlled radical polymerization (ATRP, RAFT, and NMP) were proposed for a better control of the grafting density, molecular weight distribution, uniform grafting, and composition distribution of the mixed polymer brushes over the covered area.^{42–45} All these approaches require removal of oxygen from the reactor and, thus, special equipment. Recently, Matyjaszewski et al. reported the synthesis of monocomponent and block copolymer polymer brushes using activator generated by electron transfer (AGET) atom transfer radical polymerization (ATRP).⁴⁶ The main advantage of this method is in avoiding the preparation step that includes removal of oxygen from the reactor. The mixed polymer brushes prepared by grafting from approach are

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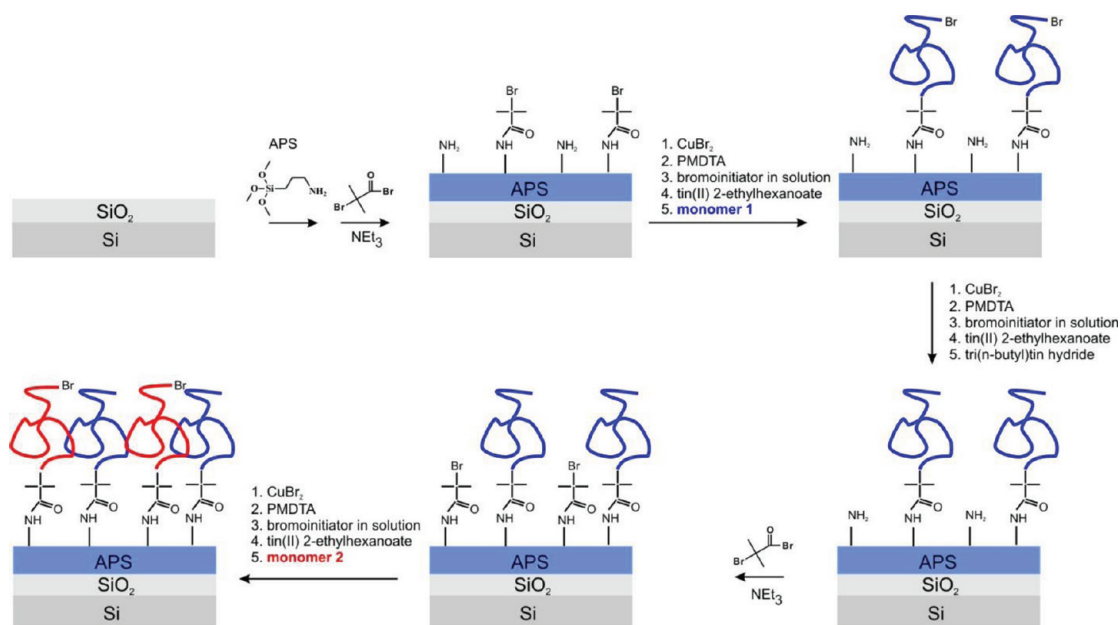


Figure 1. Scheme of the synthesis of mixed polymer brushes using AGET-ATRP. An initiator for ATRP is immobilized on the Si wafer substrate through a two-step procedure. The first polymer was grafted using AGET ATRP. The second polymer was grafted using AGET ATRP after removal of the terminal bromine groups.

expected to demonstrate more pronounced switching properties, which, however, is insufficiently explored because of complexity of “grafting from” synthesis.^{44,47,48}

In the present work, we report very simple “grafting from” synthesis, as well as switching properties, of mixed polymer brushes consisting of hydrophobic polystyrene and highly hydrophilic poly(acrylic acid). This combination of the polymers introduces very pronounced switching properties of the mixed brushes between values of advancing and receding water contact angle corresponding to those on the surface of individual constituting polymers. Moreover, the prepared mixed polymer brushes demonstrate unique locking of hydrophobic wetting behavior. The hydrophobic state is kinetically frozen in a metastable state, which can be unlocked after treatment by proper “unlocking” solvent.

EXPERIMENTAL SECTION

Materials. Highly polished single-crystal silicon wafers (Semiconductor Processing Co.) were used as a substrate for grafting of the mixed brushes. 3-Aminopropyltriethoxysilane (APS, Aldrich), N,N,N',N'',N''' -pentamethyldiethylenetriamine (PMDTA, Aldrich), ethyl-2-bromoisobutyrate (EBIB), anhydrous dichloromethane (Aldrich), 2-bromo-2-methylpropanoyl bromide (BMPB, Aldrich), triethylamine (NEt₃, Fluka), copper bromide (Aldrich), methanesulfonic acid (Merck), tin(II) 2-ethylhexanoate (TEH), and tributyltin hydride (TBH) have been used as received. *tert*-Butyl acrylate (tBA, Fluka) and styrene (St) were filtered through neutral aluminum oxide prior to the polymerization.

First Immobilization of Initiator. The silica wafers were rinsed in chloroform to remove dust and then washed in a water/H₂O₂/NH₄OH (1:1:1) mixture at 60 °C for 40 min. The washed wafers were dried and incubated in a 2% ethanol solution of APS for 2 h. After immobilization of APS, the wafers were washed multiple times in ethanol and incubated for 2 h in 100 mL of anhydrous CH₂Cl₂ with added 2 mL of NEt₃ and 1 mL of BMPB. The wafer with the BMPB immobilized initiator was washed multiple times in chloroform, ethanol, and water.

Grafting of Poly(*tert*-butyl acrylate). Fifteen milliliters of tBA, 100 μ L of 0.1 M CuBr₂ ethanol solution, 100 μ L of 0.5 M solution of

PMDTA in ethanol, and 2 μ L of EBIB were dispensed in glass vial with the initiator-modified wafer and sealed with a rubber septum; 0.5 mL of TEH was injected using a syringe. The reaction was allowed to proceed for 40 min at 70 °C. The polymerization was stopped by opening vial to air. The nongrafted polymer was removed by Soxhlet extraction and collected by precipitation in 1:1 water–methanol mixture.

Dehalogenation. Anisole (15 mL), 100 μ L of 0.1 M solution of CuBr₂ in ethanol, 100 μ L of 0.5 M solution of PMDTA in ethanol, and 2 μ L of EBIB were dispensed in a glass vial with the silicon wafer with grafted polymer and sealed with a rubber septum; 0.5 mL of TEH was injected using a syringe. The reaction vial was heated to 130 °C, and 2 mL of TBH was injected during 30 min. The reaction allowed to proceed for 3 h and was stopped by opening to air. The sample was rinsed several times in ethanol and 3% HCl. The reaction starts as ATRP by the generation of radicals that are deactivated in the reaction with TBH.

Second Immobilization of Initiator. The dehalogenated wafer was incubated in 10 mL of anhydrous CH₂Cl₂ with added 2 mL of NEt₃ and 1 mL of BMPB for 2 h. The wafer with the immobilized initiator was washed multiple times in chloroform, ethanol, and water.

Grafting of Polystyrene. Fifteen milliliters of St, 100 μ L of 0.1 M solution of CuBr₂ in ethanol, 100 μ L of 0.5 M solution of PMDTA in ethanol, and 2 μ L of EBIB were dispensed in a glass vial with the wafer and sealed with a rubber septum; 0.5 mL of TEH was injected using a syringe. The reaction was allowed to proceed for 40 min at 105 °C. The polymerization was stopped by opening vial to air. The nongrafted polymer was removed by Soxhlet extraction and collected by precipitation in methanol.

Synthesis of Mixed PAA-PS Brushes. The mixed PAA-PS brushes were obtained by hydrolysis of the mixed PtBA-PS brushes in methanesulfonic acid for 10 min. After hydrolysis, the samples were intensively rinsed in water. The thicknesses of PAA and PS layers were estimated based on decrease of the thickness after hydrolysis considering that the thickness of the PS layer remained constant during hydrolysis. Therefore, the thickness of the PAA layer was calculated as a difference between the thickness of the brush after hydrolysis and the thickness of the PS brush (the first grafting)

Gel Penetration Chromatography (GPC). Molecular weights of the polymers were measured with GPC using PMMA and PS as a

Table 1. Surface Density of Functional Molecules and Grafted Polymer Chains

sample	layer	molecular weight		thickness, nm	surface density, molecules/nm ²	distance between grafting sites, nm
		M_w , kg/mol	M_w , kg/mol			
APS	APS			0.8	4.7	0.5
IN	IN			0.3	0.9	1,05
PtBA20PS14	PtBA	44	68	20	0.17	2.4
	PS	93	136	14	0.06	4
PtBA20PS20	PtBA	44	68	20	0.17	2.4
	PS	109	154	20	0.08	3.5
PtBA20PS34	PtBA	44	68	20	0.17	2.4
	PS	258	322	34	0.06	4

standard, CHCl₃ as a mobile phase and PL MIXED-B-LS columns. RI and LS detectors were used.

Ellipsometry. Thickness of the polymer layers on the wafers in the dry state was measured at $\lambda = 632.8$ nm and an angle of incidence of 70° with a null-ellipsometer (Multiscopie, Optrel Berlin, Germany) in a polarizer–compensator–sample–analyzer configuration. Grafting density was calculated as

$$\Gamma \left(\frac{\text{molecule}}{\text{nm}^2} \right) = \frac{H\rho N_A}{M_w}$$

where H is the thickness of the brush in the dry state, M_w is molecular mass of the polymer, ρ is the density of the polymer, and N_A is the Avogadro's constant.

Atomic Force Microscopy. The (AFM) studies were performed with a Dimension 3100 (Digital Instruments, Inc., Santa Barbara, CA) microscope. The tapping mode was used to map the film morphology at ambient conditions.

RESULTS AND DISCUSSIONS

A two-step “grafting from” method was used for the synthesis of mixed polymer brushes (Figure 1). ATRP initiator groups were immobilized on the silica wafer. The first polymer was grafted using AGET-ATRP. Afterward, the terminal bromine atoms were removed by dehalogenation in order to avoid formation of block copolymer brushes and then, an initiator for the second polymerization was immobilized. Finally, the second polymer was grafted by AGET-ATRP mechanisms. Below, we discuss the synthesis in details.

An ATRP initiator was immobilized on the Si wafer using a previously developed two-step procedure.⁴⁹ First, amino-silane (APS) was immobilized by chemisorption from ethanol solution. The structure of APS layer is expected to be similar to layers formed by 3-glycidoxypropyltrimethoxysilane (GPS), which were investigated by XPS and FTIR earlier.⁵⁰ Second, BMPB was chemically immobilized on the APS-modified wafer. The thicknesses of the APS and BMPB layers, as measured by ellipsometry, were 0.8 and 0.3 nm, respectively. These values corresponded to a grafting density of APS $\Gamma_{\text{APS}} = 4.7$ molecules/nm² and initiator $\Gamma_{\text{BMPB}} = 0.9$ molecules/nm², respectively (Table 1). The obtained results show that 20% amino groups were used to graft the initiator and the residual 80% remained unreacted. The surface density of initiator groups can be controlled by concentration of components in solution and reaction time.

The first polymer, poly(*tert* butyl acrylate) (PtBA), was grafted using AGET-ATRP.⁴⁶ Polymerization time was adjusted to prepare 20 nm thick polymer layers. The grafting density of the obtained polymer layer was 0.17 chain/nm² that corresponded to the consumption of 18% immobilized initiator groups (Table 1). The considerably smaller density of the surface immobilized polymer chains comparing to the initiator

surface density is most probably either due to the inactivation of initiator groups in the initial stages of the reaction when a free oxygen is available in solution or due to screening initiator groups by the growing polymer chains. The grafted polymer layer was in the brush regime since the distance between grafting points was less than the thickness of the polymer layer.⁵¹

After termination of the polymerization, the terminal bromine groups in the polymer chains and nonreacted initiator groups on the substrate were removed by a dehalogenation procedure using TBH. This procedure is required to prevent formation of block copolymer brushes during grafting of the second polymer. Dehalogenation was performed using the same ingredients as those used for AGET-ATRP, but tributyltin hydride was used instead of monomer.⁴⁴ The dehalogenation starts as AGET-ATRP. After addition of THE, Cu (II) is reduced and yields Cu(I). Next, terminating Br atoms are transferred to copper(I) complex and free radicals are formed. These free radicals, however, are unable to grow in the absence of monomer and are deactivated by TBH. It was found that temperature of the reaction determines efficiency of dehalogenation, as tested by control polymerization of styrene on the dehalogenated PtBA brush. In particular, a 100 nm thick polystyrene layer was grafted to the PtBA brush that was dehalogenated at room temperature. An increase of dehalogenation temperature to 70 °C resulted in decreasing the grafted polystyrene layer thickness down to 5 nm. No polystyrene was grafted to the PtBA brush that was dehalogenated at 130 °C. Therefore, dehalogenation at 130 °C is required to remove the terminal bromine atoms completely.

An initiator for grafting the second polymer was immobilized using available amino-functional groups of the APS layer, which remained unreacted after the first immobilization of the initiator. The determination of surface density of initiator groups after second immobilization is impossible. In fact increase of the brush thickness after second immobilization of bromoisobutyl bromide is comparable to deviations of brush thickness across the sample. On the other hand because of low penetration depth (6–10 nm), XPS is unable to qualitatively determine Br atoms which are hidden under thick brush layer (10–30 nm). Grafting of polystyrene, the second polymer, was performed using AGET-ATRP at 110 °C. The grafting density of the polymer was 0.06–0.08 chains/nm² regardless of thickness of the PS layer (Table 1). Since the distance between the grafting sites was smaller than the thickness of the polymer layer, the PS layer was in the brush regime as well (Table 1).

The PAA–PS mixed brushes were obtained by hydrolysis of the PtBA–PS mixed brushes using methanesulfonic acid.⁴⁹ It was found that the thickness of the PtBA layer was reduced by 50% after hydrolysis that was in accord with the theoretical

estimations based on the decrease of molecular weight of the polymer. The characteristics of the synthesized PtBA-PS and PAA-PS mixed brushes are summarized in (Table 2).

Table 2. Characteristics of the PtBA-PS and PAA-PS Mixed Brushes

sample	thickness/fraction		sample	thickness/fraction	
	PtBA	PS		PAA	PS
PtBA20PS14	20 nm/ 58%	14 nm/ 42%	PAA10PS14	10 nm/ 41%	14 nm/ 59%
PtBA20PS20	20 nm/ 50%	20 nm/ 50%	PAA10PS20	10 nm/ 33%	20 nm/ 67%
PtBA20PS34	20 nm/ 37%	34 nm/ 63%	PAA10PS34	10 nm/ 22%	34 nm/ 78%

Switching properties of the synthesized mixed PS-PtBA and PS-PAA brushes were investigated using AFM and contact angle measurements. The brushes were exposed to different selective and nonselective solvents. Since both PtBA and PS are hydrophobic polymers with similar wetting behavior (water contact angle $\sim 90^\circ$), any switching of wetting properties of the mixed PtBA-PS brushes was not observed. The PS-PtBA brushes were investigated using AFM (Figure 2). Patterns of the phase-segregated domains of PS and PtBA were used to

track switching the thin film morphology in different solvents. As reported elsewhere,²³ two unlike polymers segregate in nonselective solvent by forming the ripple-like morphology of alternating domains of two different polymers. On the other hand, round clusters formed by one of the polymers in the matrix of another polymer are indicators of the dimple morphology in solvents that are selective for the matrix forming polymer. At a high incompatibility, the dimple morphology is the most stable structure of the mixed brushes. It was found that a more symmetric PtBA20PS14 brush morphology appears as dimple-like phases after exposure to ethanol (selective solvent) and chloroform (less-selective solvent). A mixed dimple- and ripple-like morphology was formed after exposure to less-selective toluene. The more asymmetric PtBA20PS34 brush formed an inverse dimple like morphology after exposure to all solvents in accord with the theoretical predictions.²³ It was found that the roughness in both cases decreased in the sequence ethanol-chloroform-toluene. The roughness is higher upon exposure to more selective solvents (Table 3).

Three samples of the PAA-PS mixed brushes with different PAA:PS ratios were synthesized by hydrolysis of the PtBA-PS brushes. PAA and PS are highly incompatible polymers with very different wetting properties. PS is a hydrophobic polymer (water advancing contact angle $\theta_{ADV} = 90^\circ$, receding contact

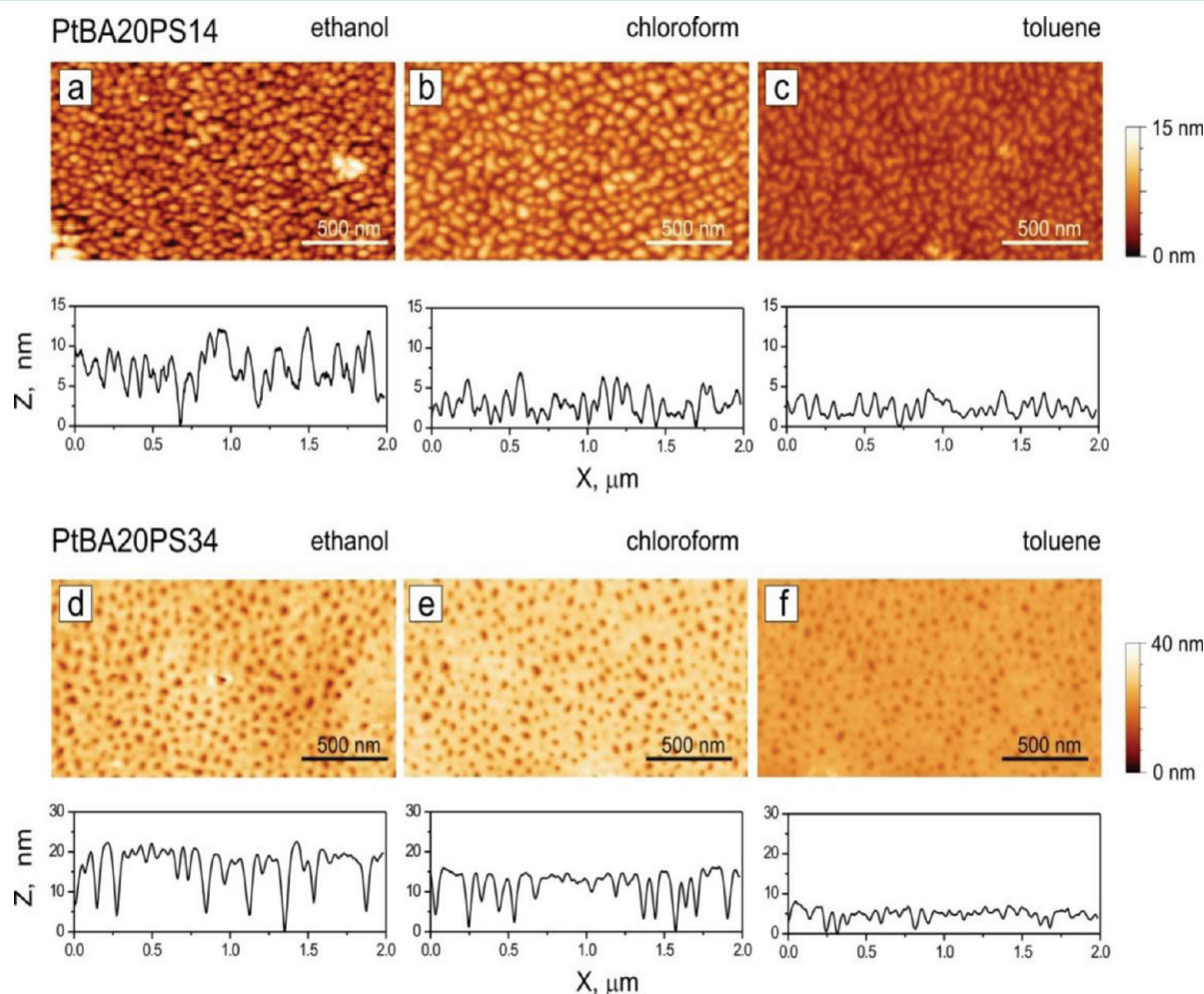


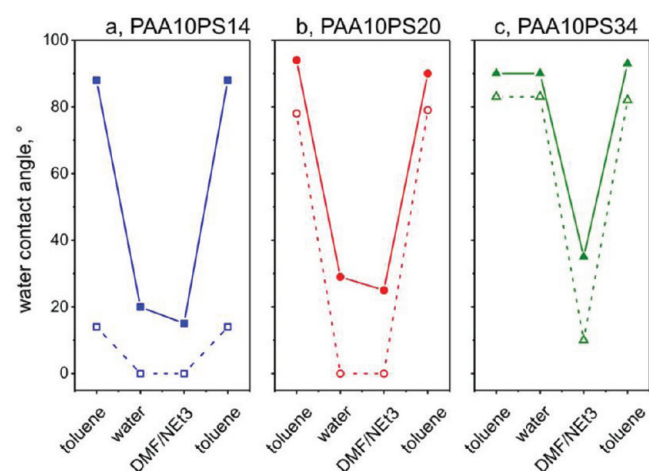
Figure 2. Morphology and topography cross sections of PtBA-PS mixed brushes after exposure to different solvents. AFM images of morphology of nearly symmetric PtBA20PS14 (a, b, c) and highly asymmetric PtBA20PS34 (d, e, f) brush after exposure to ethanol (a, d; selective solvent), chloroform (b, e; less-selective solvent), and toluene (c, f; less-selective solvent).

Table 3. Root-Mean-Square (RMS)-Roughness of PtBA–PS Mixed Brushes upon Exposure to Different Solvents

sample	rms roughness, nm		
	ethanol	chloroform	toluene
PtBA20PS14	2.3	1.8	1.1
PtBA20PS34	3.5	3.0	1.4

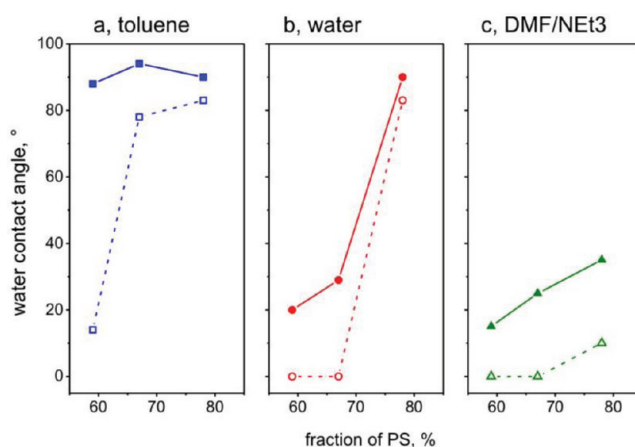
angle $\theta_{\text{REC}} = 80^\circ$). Because of a small hysteresis of contact angle, water droplets easily slide on PS surfaces. On the other hand, PAA is a strongly hydrophilic polymer (water advancing contact angle $\theta_{\text{ADV}} = 20^\circ$, receding contact angle $\theta_{\text{REC}} = 10^\circ$). Water droplets spread on the surface of PAA brushes.

In contrast to the PtBA–PS brushes, the PAA–PS brushes demonstrate considerable switching wetting properties after exposure to different solvents (Figure 3a–c). The PAA–PS

**Figure 3.** Switching of advancing (solid symbols and solid lines) and receding (open symbols and dashes lines) water contact angles after exposure to toluene (selective to PS), water (selective to PAA), a mixture of DMF, and triethylamine (NEt_3) (more selective to PAA).

brushes obtained directly after hydrolysis are hydrophilic. Exposure to toluene switches the brush to a hydrophobic state. The advancing water contact angle on the PAA–PS brushes exposed to toluene, which is a selective solvent for PS, corresponds to the contact angle of a homopolymer polystyrene brush regardless of the brush composition ($\theta_{\text{ADV}} = 90^\circ$, Figure 4a). On the other hand, the receding contact angle on the toluene-exposed brushes depends strongly on the composition. The brush with the lowest PS fraction (PS=59%) has a very low receding contact angle ($\theta_{\text{REC}} = 20^\circ$, Figure 4a), which is close to the receding angle for a homopolymer poly(acrylic acid) brush. Such a small value of receding contact angle indicates that water penetrates into the brush and swells PAA. An increase of the PS fraction leads to increase of the water receding contact angle to the value that corresponds to a homopolymer PS brush ($\theta_{\text{REC}} = 80^\circ$).

Afterward the samples of the mixed PAA–PS brushes were exposed to water for several minutes (pH = 6.5, a selective solvent for PAA). The brushes with a PS fraction less than 67% (PAA10PS14 and PAA10PS20) were switched to a hydrophilic state when both the advancing and receding water contact angles were small and corresponded to a homopolymer PAA brush ($\theta_{\text{ADV}} = 20^\circ$, $\theta_{\text{REC}} = 10^\circ$, Figure 4b). On the other hand, the brush with the larger fraction of PS (PAA10PS34) remained

**Figure 4.** Dependence of water advancing (solid symbols and solid lines) and receding angles (open symbols and dashes lines) on the fraction of PS in the mixed brush.

in a hydrophobic state after exposure to water with pH = 7 and pH = 10 for several days. This quasi-stable hydrophobic behavior of PAA10PS34 brush is likely because of a hindered diffusion of water through a thick PS layer segregated to the brush surface. This brush was switched to a hydrophilic state by using DMF, the common solvent for PAA and PS with a small addition of NEt_3 (Figure 4c). The role of NEt_3 is to boost dissociation of PAA in DMF and to enhance its swelling. The DMF– NEt_3 solution was diluted by alkali water at pH = 9. This treatment forced PAA to occupy the topmost brush layer and the brush was switched in hydrophilic state. Exposure of all the PS–PAA brushes to toluene resulted in switching to the original hydrophobic state, when the water advancing contact angle was not composition dependent, while the receding angle increased with the fraction of PS in the brush. The switching cycle was repeated several times and the results of the contact angle measurements were reproducible.

The AFM experiments revealed dimple-like morphologies upon exposure to toluene, water, or DMF/ NEt_3 (Figure 5) because of a very high incompatibility of the polymers in accord with the simulations.²³ The obtained contact angle and AFM results clearly demonstrate reversible yet complex switching behavior of the PAA–PS brushes that strongly depends on the composition.

Solvent-induced switching mixed brush morphologies and wetting behavior was reported by many groups previously. Indeed, the selected example of the mixed PS–PAA brush revealed a new interesting aspect of wetting hysteresis of the amphiphilic mixed brush. This wetting hysteresis was approached for the mixed brush with a higher grafting density as compared to the previously reported similar mixed brushes prepared using “grafting to” method.^{36,37} The observed wetting hysteresis demonstrates that the hydrophobic state of the amphiphilic mixed brush can be “locked” and it remains unchanged in water for a very long period time until the brush is exposed to a common solvent for both the polymers. The common solvent acts as a “trigger” and switches the brush. This mechanism could provide a range of interesting applications when the surface properties do not adapt environment, but rather remain unchanged. However, they can be changed only by specific changes in the brush environment.

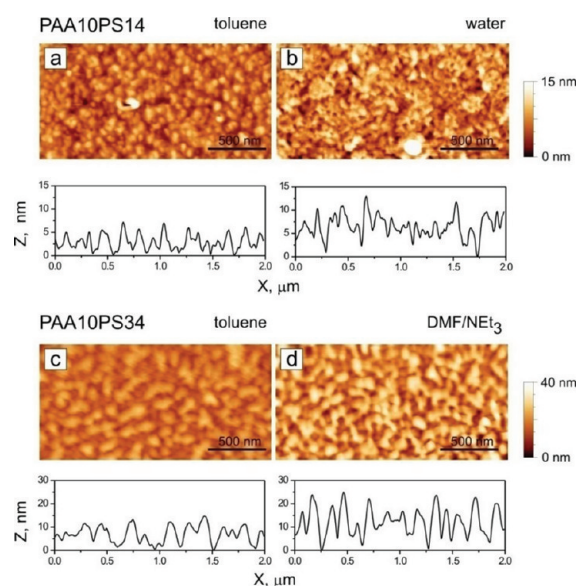


Figure 5. Morphology and topography cross sections of mixes PAA–PS brushes after exposure to different solvents. AFM images of morphology of nearly symmetric PAA10PS14 (the upper panel) and highly asymmetric PAA10PS34 (the lower panel) brush after exposure to toluene (selective solvent for PS), and water or mixture of DMF and NEt₃ (more selective solvent for PS).

CONCLUSIONS

We report the design of mixed polymer brushes with very pronounced switching behavior. The demonstrated in this work PS–PAA mixed brushes revealed interesting solvent-triggered switching with a wetting hysteresis. The wetting properties of amphiphilic brushes could be switched between values of advancing and receding water contact angles corresponding to those on the surface of individual constituting polymers. Moreover, the prepared mixed polymer brushes demonstrate unique locking of hydrophobic wetting behavior. Hydrophobic surface is kinetically frozen in a metastable state, which, however, can be unlocked after treatment by proper solvent. In particular, switching in a hydrophilic state is only possible in the organic solvent (DMF with traces of amines). This locking and unlocking of the hydrophobic state of the mixed brush with specific solvents could find useful applications for the development of functional materials, such as smart textiles, active elements of microfluidic devices, etc.

ASSOCIATED CONTENT

Supporting Information

Figure showing cyclical switching of advancing and receding water contact angles. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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