

Mixed Polymer Brushes with Thermal Response Amplified by Roughness

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INTRODUCTION

Control of wettability is of great importance for numerous industrial and biomedical applications¹. Switching of wetting properties by small changes in temperature may find application for surface and tissue cleaning. Preparation of surfaces with thermally switching wettability from poly(N-isopropyl acrylamide) (PNiPAAm) has been recently reported.²⁻⁷ PNiPAAm undergoes a reversible transition between a water soluble state at ambient temperature and a water insoluble state at temperature higher than the lower critical solution temperature (LCST) which is near 32 °C. Surface immobilized PNiPAAm layers show reversible gradual change of water advancing contact angle from hydrophilic ($\Theta_{adv} \leq 50^\circ$) at ambient temperature to hydrophobic ($90^\circ \leq \Theta_{adv} \leq 120^\circ$) above 40 °C. The receding water contact angle remains unchanged ($\Theta_{rec} \sim 40^\circ$) upon the thermal transition.² In this report we describe an approach how to broaden the range of the thermal switching and simultaneously reduce the contact angle hysteresis, i. e. the difference between the Θ_{adv} and the Θ_{rec} . We use the concept of mixed polymer brushes covalently grafted to a rough substrate.⁸⁻⁹ The high roughness of the substrate amplifies the thermal switching of wettability^{8,9}, while presence of the second hydrophobic polymer in the brush elevates the Θ_{rec} and thus reduces the water contact angle hysteresis.

EXPERIMENTAL PART

Materials. 4,4'-azobis(4-cyanopentanoic acid) (ABCPA) (Fluka), (3-Glycidoxypropyl)-trimethoxysilane (GPS) (ABCR GmbH, Germany), ethylenediamine (ED) (ACROS Organics) were used as received. Polished Si wafers (100) with natural SiO₂ layer (~2 nm) were purchased from Silchem Handelsgesellschaft mbH (Freiberg, Germany). Polytetrafluoroethylene (PTFE) foils 0.5 mm thick were purchased from PTFE Nünchritz GmbH, Germany. Carboxy-terminated PNiPAAm, Mn 132000, Mw/Mn 1.29, was purchased from Polymer Source, Inc. Oxygen 99.95%, and ammonia 99.999% were purchased from Messer Griesheim, Germany.

Polymerization. α,ω -Dicarboxy-terminated poly(styrene-co-2,3,4,5,6-pentafluorostyrene) (PSF) Mn 445000, Mw/Mn 1.5 with 25-30 mol. % fluorinated units (from ¹H NMR) and α,ω -dicarboxy-terminated poly(methylacrylate-co-1,1,1,3,3,3-hexafluoroisopropyl methacrylate) (PHFA) Mn 61000, Mw/Mn 1.68, with 30 mol. % of fluorinated units (from ¹H NMR) were synthesized via conventional radical copolymerization at 60 °C in tetrahydrofuran (50 wt. %) in presence of $2.86 \cdot 10^{-4}$ mol/l ABCPA as initiator. Wetting properties of the synthesized polymers were characterized with water contact angle measurements on the spin-coated films (Table 1).

Modification of Substrates. μ m-Scale surface roughness was created on semicrystalline PTFE substrates via etching with oxygen plasma as described elsewhere.⁹ The original and the etched PTFE substrates were then activated with ammonia plasma.⁹ The activation quality was controlled with a water droplet: full wetting of both flat and rough PTFE substrates was observed. A scanning electron micrograph of the etched and activated PTFE substrate is given in Figure 1. Polished Si wafers with natural SiO₂ oxide layer were cleaned and treated with 1% GPS solution in anhydrous toluene at dry conditions for 15 h as described elsewhere.¹⁰ They were washed with anhydrous toluene 2 times at dry conditions and then 3 times for 5 min

in ethanol in an ultrasonic bath. Then the epoxy-groups of the immobilized GPS were converted to amino-groups via treatment with 1.5% ED in ethanol for 1.5 h.⁹ The modified Si-substrate showed less hydrophilic nature than the activated PTFE substrates: the Θ_{adv} , and the Θ_{rec} on the modified Si were 72° and 33°, respectively. Roughness of the Si and PTFE substrates was characterized with Atomic Force Microscopy (AFM) (Table 2).

Table 1. Water Contact Angles of Spin-coated PSF and PHFA Films on Si Substrates.

Sample	Θ_{adv}	Θ_{rec}
PSF	96.7±1.6	84±3.7
PHFA	98.5±1.1	56.2±10.0

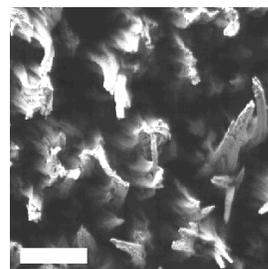


Figure 1. Scanning electron micrograph of the PTFE surface treated with O₂ plasma for 10 min and then activated with NH₃ plasma for 1 min. The white bar is 5 μ m.

Table 2. Roughness of the Substrates Obtained From AFM.

Sample	r_s^*	RMS** roughness, nm
Si wafer	1.09	1.35
original PTFE	1.2	200
etched PTFE	>4	>1200

* r_s is ratio of the surface area to the area of its projection on the substrate plane; ** root-mean-square.

Preparation of Mixed Polymer Brushes. Two polymers were covalently attached via their end carboxylic groups to the amino-groups on the PTFE and Si substrates. The polymer films were cast onto the substrates from 1% solution in THF. The first polymer (hydrophobic, i. e. PSF or PHFA) was grafted at 170 °C for 50 min in vacuum. The non-grafted polymer was removed via cold Soxhlet extraction in THF for 1 h. The second polymer (hydrophilic PNiPAAm) was grafted at the same conditions during 16 h. The non-grafted polymer was removed as described above. It was not possible to measure the ratio of the polymers grafted to the PTFE substrates, therefore, we used the model Si substrates for control of the grafted amount of the polymers via ellipsometry.⁹ Switching ability of the synthesized mixed polymer brushes upon exposure to selective solvents¹¹⁻¹⁴ (toluene is selective for PSF and PHFA, ethanol is selective for PNiPAAm) was controlled with water contact angle measurements after fast drying procedure with N₂ flux (Table 3).

Wetting Experiments. Water contact angle measurement were carried out with water sessile drop technique using a goniometer DSA 10 from Krüss GmbH, Germany. Temperature dependent water contact angle measurements were done in the similar way using a heating camera purchased from the same company.

Table 3. Water Contact Angles on Mixed Polymer Brushes Grafted to Rough PTFE Substrates after Exposure to Selective Solvents

Brush	toluene		ethanol	
	Θ_{adv} , °	Θ_{rec} , °	Θ_{adv} , °	Θ_{rec} , °
PSF/PNiPAAm	148±10*	148±10*	117±2	<20
PHFA/PNiPAAm	148±10*	148±10*	26±9	<5

* Water droplet rolls off from the surface.

RESULTS AND DISCUSSION

Thermal switching of wetting properties of a monocomponent PNIPAAm brush on substrates with different roughness (Table 2) was studied with water sessile drop technique. The $\mu\text{-scale}$ roughness of the PTFE substrate broadens the switching range of the Θ_{adv} from 50° on the flat PTFE to 130° on the rough PTFE (Figure 2). The Θ_{rec} remains low ($\leq 30^\circ$) for both flat and rough surfaces in the whole temperature interval in accord to the other report.² The thermally induced switching of the monocomponent PNIPAAm brush on the Si substrate occurs in the narrow range (10°) of the Θ_{adv} (Figure 2). The high value of the Θ_{adv} in the hydrophilic limit (75°) was attributed to smaller surface concentration of polar groups (see Experimental Part).

The mixed brushes with PSF as the second brush polymer showed hydrophobic advancing water contact angle with no thermal switching (Figure 3). The mixed PSF/PNiPAAm brush preserved the switching ability upon exposure to selective solvents (ethanol and toluene, Table 3) similar to mixed brushes of other composition as it was reported earlier¹⁰⁻¹⁴. The absence of thermal switching of the wetting properties was attributed to the glassy state and segmental immobility of PSF.

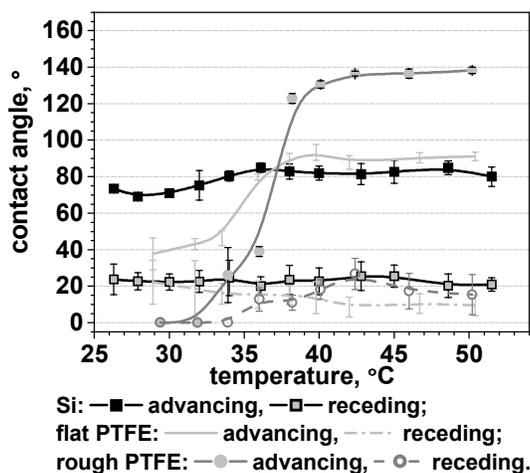


Figure 2. Thermally induced switching of wetting properties of surfaces covered with monocomponent PNIPAAm brushes.

We have been searching for a proper hydrophobic polymer which adopts a viscoelastic state at ambient conditions. Poly(methyl acrylate) has a low glass transition temperature (T_g 283K).¹⁵ Its hydrophobic properties were improved via copolymerization of methyl acrylate with 1,1,1,3,3,3-hexafluoroisopropyl methacrylate (see Experimental Part). The T_g of the yielding PHFA obtained from Dynamic Scanning Calorimetry (DSC) was 40°C (313K). The mixed PHFA/PNiPAAm brush grafted to the rough PTFE showed reversible thermal switching of the Θ_{adv} from 0° at ambient temperature to 140° at 50°C (Figure 3), i.e. in the same range as for the monocomponent PNIPAAm brush (Figure 2). The receding water contact angle (Θ_{rec}) on the PHFA/PNiPAAm brush grafted to the rough PTFE remained lower than 20° at the temperature below 50°C , while it jumped to 140° upon heating above 50°C (Figure 3).

Summarizing our results, the range of thermal wettability switching of thermoresponsive PNIPAAm brush was broadened by the high roughness of the substrate. Introduction of the viscoelastic hydrophobic PHFA into the brush as the second constituent polymer increases the water receding contact angle of the hydrophobic state of the brush at elevated temperature close to the value of the advancing contact angle. Thus the contact angle hysteresis of the mixed PHFA/PNiPAAm brush is low in both hydrophilic and hydrophobic limiting states what improves the effect of the thermal switching of wettability with respect to the monocomponent PNIPAAm surfaces.

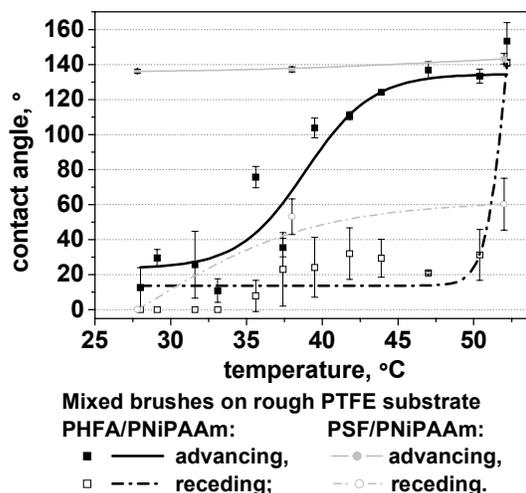


Figure 3. Thermally induced switching of wetting properties of surfaces covered with mixed brushes.

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