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.2,3 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 ºC. Surface immobilized PNiPAAm layers show reversible gradual change of water advancing contact angle from hydrophilic (Θadv≈50º) at ambient temperature to hydrophobic (90º≤Θadv≤120º) above 40 ºC. The receding water contact angle remains unchanged (Θrec≈40º) 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 Θadv and the Θrec. We use the concept of mixed polymer brushes covalently grafted to a rough substrate.8,9 The high roughness of the substrate amplifies the water contact angle hysteresis.

EXPERIMENTAL PART

Materials. 4,4’-azobis(4-cyanopentanoic acid) (ABCPA) (Fluka), (3-Glycidoxypropyl)-trime-thoxysilane (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 Silcham Handelsgesellschaft mbH (Freiberg, Germany). Polytetrafluoroethylene (PTFE) foils 0.5 mm thick were purchased from PTFE Nünchritz GmbH, Germany. Carboxy-terminated PNiPAAm, Mn 132000, Mn/Mn 1.29, was purchased from Polymer Source, Inc. Oxygen 99.99%, and ammonia 99.999% were purchased from Messer Griesheim, Germany.

Polymerization. a,ω-Dicarboxy-terminated poly(styrene-co-2,3,4,5,6-pentfluorostyrene) (PSF) Mn 445000, Mn/Mn 1.5 with 25-30 mol. % fluorinated units (from 1H NMR) and α,ω-dicarboxy-terminated poly(methylacrylate-co-1,1,3,3,3-hexafluorisopropyl methacrylate) (PHFA) Mn 61000, Mn/Mn 1.68, with 30 mol.% of fluorinated units (from 1H NMR) were synthesized via conventional radical copolymerization at 60 ºC in tetrahydrofuran (50 wt. %) in presence of 2.86·10-4 mol/l ABCPA as an initiator. Water contact angle measurements were done in the similar way using a contact angle goniometer (Krüss GmbH, Germany). Temperature dependent water contact angle measurements 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.

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 ºC 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).

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

<table>
<thead>
<tr>
<th>Sample</th>
<th>Θadv, º</th>
<th>Θrec, º</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSF</td>
<td>96.7±1.6</td>
<td>84±3.7</td>
</tr>
<tr>
<td>PHFA</td>
<td>98.5±1.1</td>
<td>56.2±10.0</td>
</tr>
</tbody>
</table>

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 µm.

Table 2. Roughness of the Substrates Obtained From AFM.

<table>
<thead>
<tr>
<th>Sample</th>
<th>r*</th>
<th>RMS** roughness, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si wafer</td>
<td>1.09</td>
<td>1.35</td>
</tr>
<tr>
<td>original PTFE</td>
<td>1.2</td>
<td>200</td>
</tr>
<tr>
<td>etched PTFE</td>
<td>&gt;4</td>
<td>&gt;1200</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Brush</th>
<th>Solvents</th>
<th>Θadv, º</th>
<th>Θrec, º</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTFE/PSF/PHFA</td>
<td>water</td>
<td>148±10*</td>
<td>148±10*</td>
</tr>
<tr>
<td>water</td>
<td>152±10*</td>
<td>26±9</td>
<td></td>
</tr>
</tbody>
</table>

* Water droplet rolls off from the surface.

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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 μm-scale roughness of the PTFE substrate broadens the switching range of the Θadv from 50° on the flat PTFE to 130° on the rough PTFE (Figure 2). The Θadv remains low (≤30°) for both flat and rough surfaces in the whole temperature interval in accord to the other report. The thermally induced switching of the monocomponent PNiPAAm brush on the Si substrate occurs in the narrow range (10°) of the Θadv (Figure 2). The high value of the Θadv 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 earlier. 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 (Tg 283K). Its hydrophilic properties were improved via copolymerization of methyl acrylate with 1,1,1,3,3,3-hexafluoroisopropyl methacrylate (see Experimental Part). The Tg 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 Θadv 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 (Θrec) 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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REFERENCES