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pH-Sensitive Wettability Induced by Topological and Chemical Transition on the Self Assembled Surface of Block Copolymer*

Zhi Geng[a], Song Guan[a], He-ming Jiang[a], Long-cheng Gao[a**], Zhi-wen Liu[b] and Lei Jiang[a, c]

[a] *Key Laboratory of Bio-inspired Smart Interfacial Science and Technology of Ministry of Education, School of Chemistry and Environment, BeiHang University, Beijing 100191, China*

[b] *Agilent Technologies, Beijing 100102, China*

[c] *Beijing National Laboratory for Molecular Sciences (BNLMS), Key Laboratory of Organic Solids, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China*

Abstract pH-sensitive wettability of polystyrene-*b*-poly(4-vinylpyridine) (PS-*b*-P4VP) self assembled films, exhibiting superoleophobicity under water and hydrophilicity at low pH value, and oleophobicity under water and hydrophobicity at neutral condition, has been realized. The wettability properties resulted from the surface topological and chemical transition, which were confirmed by *in situ* AFM measurements under water at different pH. At low pH, P4VP chains, which were confined in the hexagonal-packed nanodomains, got protonated into a swollen state, while at high pH, P4VP chains were deprotonated into a collapsed state. The reversible protonation/deprotonation procedure on the molecular scale leads to surface topological and chemical transition, thereby pH-sensitive wettability.

Keywords: Block copolymer; Wettability; pH sensitive; Self assembly.

INTRODUCTION

Wettability of solid surfaces is a very important property. For example, the remarkable superoleophobicity of fish scales allows fish to survive in oil-polluted water[1]. The wettability can be tuned by both the surface geometry and the chemical composition. Recently, stimuli-responsive wettability surfaces have drawn considerable research attention, because of their potential applications in fields like water/oil separation systems, micro-fluidic devices, *etc*.[2, 3] These smart surfaces can reversibly switch their surface wettability by light irradiation, electric fields, temperature, pH, solvent treatment or combination of these stimuli[4–11].

The nano-ordered films self assembled by block copolymers (BCP), have attracted great interests[12, 13]. One advantage of nanostructures is that one block confers sufficient mechanical support for the materials, whereas the other block provides desired functions[14–16]. Various ordered structures, such as lamellar, cylindrical, bicontinuous gyroid nanodomains, *etc*. can be easily obtained, resulting in different surface patterns[17, 18].

Poly(vinylpyridine) (PVP) is a weak polybase, which undergoes a conformational transition owing to protonation at low pH and deprotonation at high pH of pyridyl groups. PVP based BCPs have been frequently chosen as the subject of pH sensitive wettability. Zhang *et al*.[19] made pH-sensitive wettability surfaces by grafting one layer of poly(2-vinylpyridine)-*b*-polydimethylsiloxane (P2VP-*b*-PDMS) BCP onto non-woven

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** Corresponding author: Long-cheng Gao (高龙成), E-mail: lcgao@buaa.edu.cn
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textiles and polyurethane sponges. The protonation/deprotonation of the P2VP blocks may response to the pH of the aqueous media and the high flexibility of the PDMS blocks result in the switchable surface oil wettability under water. Escalé *et al.*[16] investigated polystyrene-*b*-poly(4-vinylpyridine) (PS-*b*-P4VP) BCP films with hexagonally packed micro-pores by "Breath Figure" approach. Self-assembly of BCP is able to create a nanoscale phase separation. The hierarchical structure showed reversible pH-responsive wettability. A maximum switching contact angle (CA) gap of 75° between pH = 9 and pH = 3 was realized.

Herein, we researched on the PS-*b*-P4VP, to rediscovery the effect of surface topological and chemical transition on the surface wettability. *In situ* AFM measurements under water at different pH were carried out to monitor the morphology changes.

EXPERIMENTAL

Materials

PS-P4VP (48000–20300, PDI = 1.13) was purchased from Polymer Source, Inc. Hexane was obtained from Beijing Chemical Co. (Chemical purity). All the chemical reagents were used as received without any purification.

Preparation of BCP Films

Flat BCP films with arbitrary thickness were prepared by solution casting of 1.0 g/mL BCP solution in tetrahydrofuran (THF) on glass slide (2 cm × 2 cm) in a semi-closed box avoiding humidity. After the solvent slowly evaporated in 1 day, the glass slide was put into an oven at 50 °C for another day, then in vacuum to remove the residual solvent.

Characterization

Water and oil CAs were measured by the optical contact angle meter system (OCA40Micro, Dataphysics Instruments GmbH, Germany). 2.0 μL of deionized water or oil was dropped onto the samples and the static contact angle was determined by the average of at least five measurements taken at different positions on each sample. *In situ* atomic force microscopy (AFM) measurements were carried on in air and under water at pH = 2 and pH = 7. AFM experiments were performed using an Agilent AFM series 5500 (Agilent Technologies). Imaging was carried out in the AAC mode. The used cantilevers (Nanosensor) have frequencies within 204–497 kHz and force constant values of 10–130 N/m. Attenuated total reflection infrared (ATR-IR) spectra were recorded at room temperature using a NICOLET iN10 MX spectrometer (Thermo Scientific, America) in the range of 650–4000 cm^{-1}.

RESULTS AND DISCUSSION

PS-*b*-P4VP, with P4VP weight content of 29.7%, self assembles into hexagonal-packed-cylinder (HPC) nanostructure. Figures 1(a) and 1(b) show the AFM topography and phase images of a BCP film in air. An array of nanoscopic cylindrical domains is seen on the surface of the BCP film. Considering the weight fraction of the copolymer, the dark dots in the topography image are attributed to P4VP phase within bright PS matrix. The cylindrical nanodomains of P4VP are oriented normal to the substrate and organized into hexagonal packing regardless of some defects. The averaged center-to-center spacing of the dots is around 80 nm.

Measurements of water contact angle (CA) in air and oil contact angle (OCA) underwater at different pH values were conducted to probe the responsive wettability of the BCP surface. The water CAs increase from 31° to 95° and the OCAs (hexane) at the water/BCP interface decrease from 157° to 105° with the pH values increasing from 1 to 7 (Fig. 2). That is to say, the BCP film exhibits hydrophilicity and superoleophobicity at low pH value, while hydrophobicity and oleophobicity at neutral condition. The pH responsive wetting behaviors are reversible, which were conducted by measuring the OCAs under water between pH = 1 and pH = 7.

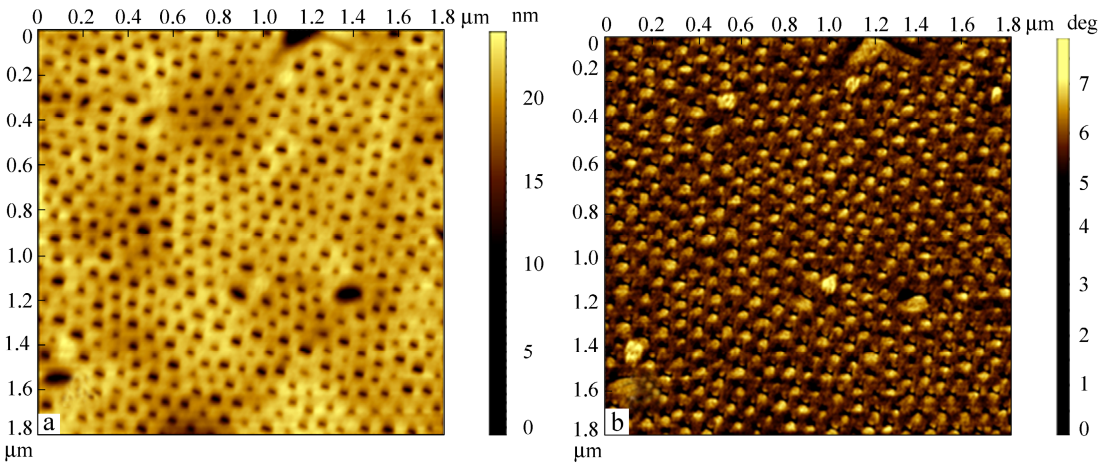

Fig. 1 AFM height (A) and phase (B) images of BCP film in air, indicating the HPC nanostructure

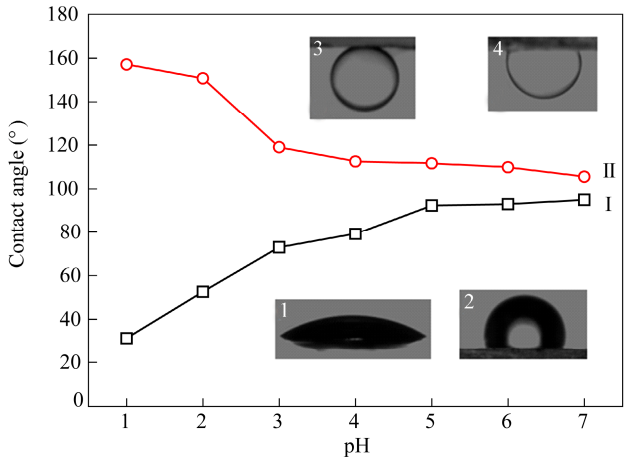

Fig. 2 pH dependences of water (I) and oil (II) CAs for BCP films
(Inset images (1–4) are the CA/OCA obtained at pH = 1 and 7, respectively.)

In order to determine the surface morphology and morphology change under different pH conditions, we applied *in situ* AFM measurements under water at different pH to monitor the morphology changes. Figure 3 shows AFM images of a BCP film under the buffer solution of pH = 2. Compared with Fig. 1, changes are obviously as a function of pH. A height inversion is observed. The former low-height P4VP dots become higher in the height image (see Fig. 3a), while the phase value of P4VP dots becomes lower in the phase image (see Fig. 3b). It means that both the topological and chemical structures undergo great changes. Nevertheless, the sixfold symmetry of P4VP dots and the average center-to-center spacing between dots are both invariant. It is crucial to point out that the PS matrix provides sufficient mechanical stability to the films. Otherwise, a continuous layer of P4VP may exhibit similar properties, but it would be dissolved in acidic solution. The P4VP was one-end connected to the PS wall. At low pH, the pyridyl groups are protonated and positively charged. The electrostatic repulsion between the pyridyl ionic groups leads the chain exclusively stretched. The P4VP dots get swollen. The protonated P4VP and resultant expanded P4VP domains are attributed to the hydrophilicity and superoleophobicity of the BCP surface, which will be discussed later.

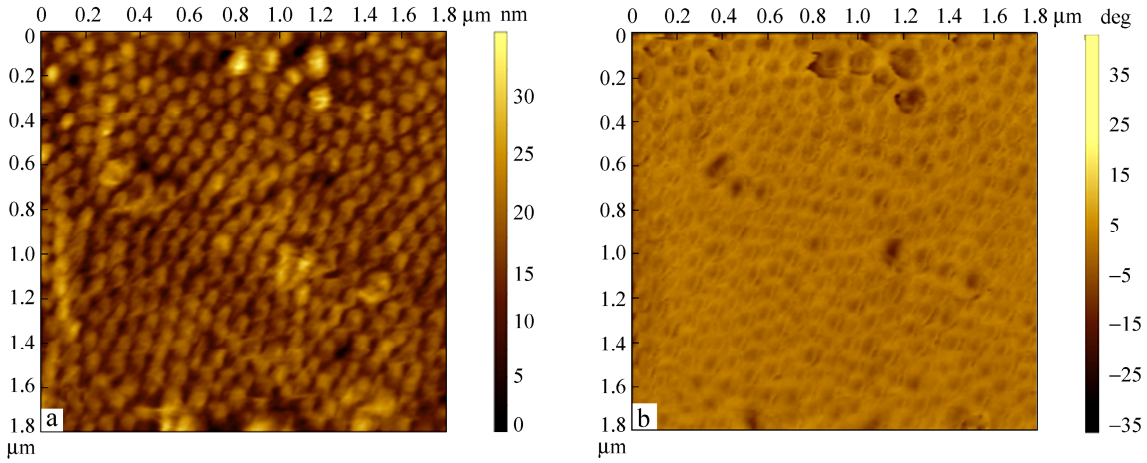

Fig. 3 AFM height (a) and phase (b) images of a BCP film under water at pH = 2, indicating the swelling of P4VP dots upon protonation of pyridyl groups in acid solution

When the BCP film contacted with water at pH = 7, the height and phase images were inverted again, as seen in Fig. 4. Compared with the images shown in Fig. 3, the P4VP dots in Fig. 4(a) become lower in the height image, while the phase (see Fig. 4b) becomes higher in the phase image, which are both similar with those shown in Fig. 1. The P4VP dots still possess hexagonal packed pattern, also the average center-to-center spacing between dots is unchanged. We can conclude that the P4VP dots collapse from the swollen state upon the deprotonation of the pyridyl group at high pH value.

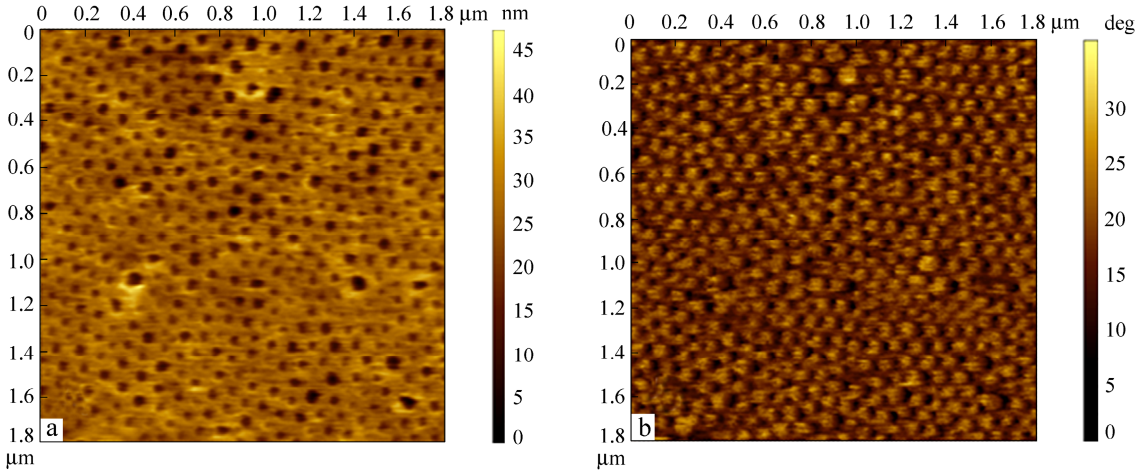

Fig. 4 AFM height (a) and phase (b) images of a BCP film under water at pH = 7, indicating shrinkage of P4VP dots upon deprotonation of pyridyl groups in the neutral solution

We used attenuated total reflection infrared (ATR-IR) spectroscopy for analysis of the interaction between pyridyl groups on the BCP film surface and the solution. Figure 5 shows the ATR-IR spectra of PS-*b*-P4VP in air, contact with deionized water and HCl solution with pH = 1. The strong absorption at 1597 cm^{-1}, corresponding to the pyridine ring, shift to 1599 cm^{-1} under water. Pyridyl groups are good hydrogen bonding acceptor, at the interface between P4VP domains and water, the lone electron pair of the pyridine nitrogen of P4VP allows coordination with water[20]. Weak hydrogen bonding with water is formed. When dipping into acidic solution with pH = 1, the characteristic peak further shifts to 1602 cm^{-1}. P4VP homopolymer is a weak polybase with a pK_a of around 4.5[21]. At pH below pK_a, protonated pyridyl groups are formed.

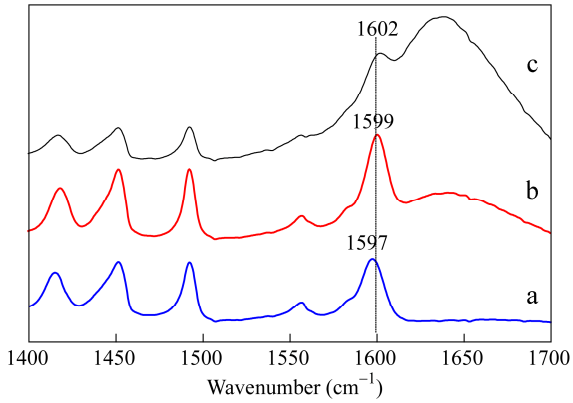

Fig. 5 ATR-IR spectra of (a) PS-P4VP in air, (b) in deionized water and (c) HCl solution (pH = 1)

As mentioned above, wettability is governed by both chemical composition and surface structure. In the system, both the chemical properties and the surface topologies have corresponding changes as the pH values change. BCP self assembles into HPC structure in bulk, and shows sixfold symmetry of P4VP dots in PS matrix on the surface. PS has high glass transition temperature and is an inert component in aqueous media at various pH. At pH below pK_a, protonated pyridyl groups lead P4VP chains in solution to transform from a collapsed to stretched conformation. P4VP chains closed to the solid-liquid interface expanded to the solution (see Fig. 6a),

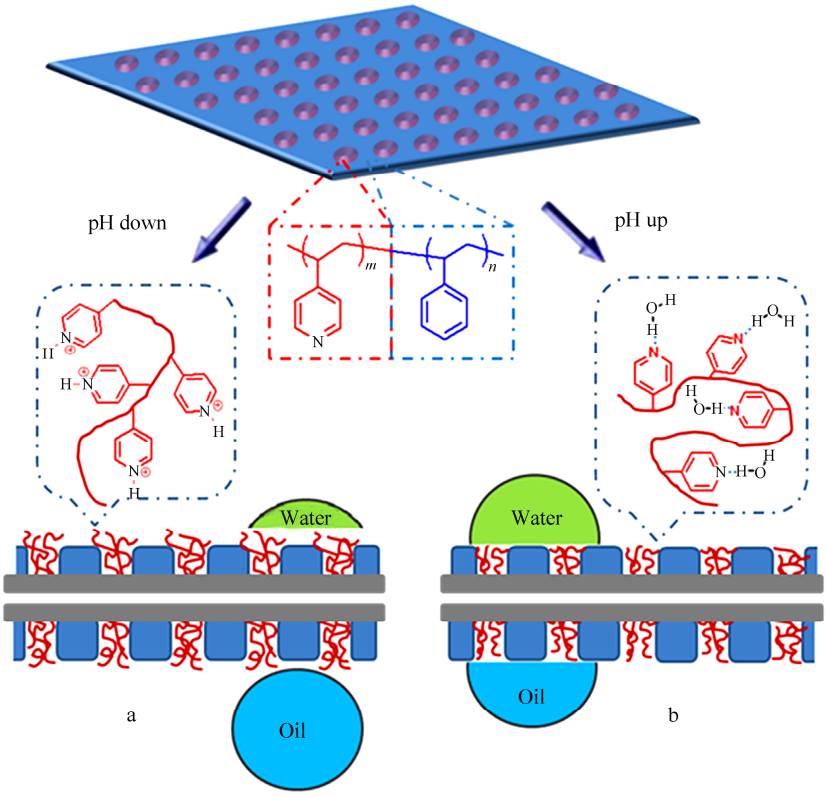

Fig. 6 Schematic description of pH-sensitive surface morphology transition of the BCP
At low pH, P4VP chains are protonated and expanded, exhibiting hydrophilicity and superoleophobicity (a); while at high pH, P4VP chains are deprotonated and collapsed, exhibiting hydrophobicity and oleophobicity (b).

which provides the surface with high ratio of water content. The surface is hydrophilic and wetted with water. A water-rich surface will effectively block the access of the oil. As the lower pH solution is applied, the more hydrophilic and oleophobic of the BCP film will be. At high pH, the P4VP block shrinks upon deprotonation of pyridyl groups (see Fig. 6b), and the hydration ability is reduced dramatically. Therefore, compared to the wettability at low pH, the wettability becomes more hydrophobic and less oleophobic.

CONCLUSIONS

pH-sensitive wettability of the PS-*b*-P4VP film, exhibiting hydrophilicity and superoleophobicity at low pH value, and hydrophobicity and oleophobicity at neutral condition, is realized. BCP forms hexagonally-packed P4VP nanodomains on the surface. *In situ* AFM measurements under water at different pH reveal the surface morphologies and morphology transition, as well as the chemical properties, owing to protonation at low pH and deprotonation at high pH of pyridyl groups. The local surface chemical and topological transition affects the wetting properties. These results benefit the understanding and fabrication of pH sensitive wettability surface.

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