Superhydrophobic Surface from Vapor-Induced Phase Separation of Copolymer Micellar Solution

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The wetting behavior of solid surface is governed by both surface roughness and chemical composition. Increasing surface roughness and lowering surface tension can dramatically enhance surface water repellency.[1−3] In recent years, superhydrophobic surfaces have aroused much research interest experimentally and theoretically because of their potential important applications.[4−6] Conventionally, two strategies are adopted for the preparation of superhydrophobic surface. One is fabricating a rough surface by using low surface energy materials;[7] another is preparing a rough surface first and then modifying the rough surface with low surface energy compounds.[8] More recently, superhydrophobic surfaces with a hierarchical structure in nanoscale and micron scale mimicking that of a lotus leaf have also been reported.[9]

In this communication, we report a simple method for the preparation of the superhydrophobic copolymer poly(styrene)-*b*-poly(dimethylsiloxane) (PS-*b*-PDMS) surface by taking advantage of the features of the two blocks. It is well-known that micelle will be formed when dispersing a copolymer in a selective solvent as a result of the different solubility of the blocks.[10] And phase separation will always occur as solidifying a polymer solution in humid air, leaving a polymer surface with various morphologies.[11,12] Meanwhile, PDMS prefers to segregate on the surface of copolymer containing PDMS block due to its low surface energy and poor miscibility with other polymers.[13] We find that a rough surface with low surface tension, which exhibits superhydrophobicity, can be facilely fabricated in one step by casting the micellar solution of PS-*b*-PDMS in humid air based on the cooperation of vapor-induced phase separation and surface enrichment of PDMS block.

PS-*b*-PDMS (with $\bar{M}_n = 4.4 \times 10^4$, $\bar{M}_w/\bar{M}_n = 1.19$, and $\bar{M}_n$ of 1.7×10^4 for the PS block), a donation from DOW Corning Co., was dissolved or dispersed in various solvents of different solvent properties at a concentration of 5 mg/mL. The resulting solution was then cast on a clean glass slide to allow the solvent to evaporate in different circumstances. DMF is a selective solvent for PS, in which PS-*b*-PDMS micelle with soluble PS as the shell and insoluble PDMS as the core is formed. When the micellar solution of PS-*b*-PDMS in DMF was dried in a dry atmosphere in desiccator, the resultant coating exhibited no obviously visible microstructure by scanning electron microscopy (SEM) investigation (Figure 1a). Water CA of the surface was only 104.8 ± 1.5°. However, when the micellar solution was solidified in a humid air (with a relative humidity (RH) of 60 ± 5%), the morphology of the as-formed coating, as shown in Figure 1b, is much different. Small protrusions in micron size connected together and covered the surface, leading to an increase of surface roughness. As such rough surface formed on the hydrophobic copolymer, air would be trapped in the grooves at the interface between the water and solid surface, leaving the water droplets could only contact with the tips of these protrusions. As a result, the water repellency was dramatically enhanced.[3] Water drop stands on the coating spherically with a CA of 163.0 ± 1.0°. Moreover, water drop rolls off the coating easily, implying a low contact angle hysteresis, which is another crucial criterion for the superhydrophobicity.[14] The advancing and receding CA of the surface are 166° and 157°, respectively,[7c] and the sliding angle (SA) of 5 μL water on the superhydrophobic surface is only 7.0 ± 1.0° (see Supporting Information).

It is clearly shown that the humidity has a profound effect on the resultant surface morphology. In fact, casting polymer solution in the presence of moisture is a widely used technique for the polymer membrane fabrication.[11,12] The influence of moisture on the topology of the resulting membrane largely depends on the miscibility of the solvent with water. With a water-immiscible solvent, water microdroplets will condense on the solution surface due to evaporation cooling and then array in an ordered pattern. After solidification, a honeycomb-patterned porous film will be formed.[11] On the contrary, vapor-induced phase separation (VIPS) will occur when the solvent is water-soluble, as water is commonly a precipitant for many polymers.[12] Considering that DMF is a polar solvent miscible with water while water is a nonsolvent for PS-*b*-PDMS, we attribute the formation of the rough structure to a VIPS process. Since water from humid air will transport into the micellar solution during DMF evaporation, which is confirmed by monitoring the weight change of the solution during the solidification process (see Supporting Information), the solvent property becomes gradually poorer for the soluble PS block. As a result, the PS chains begin to shrink and micelles turn to aggregate, and then phase separation occurs. The polymer-rich phase will form the matrix (the connected protrusions shown in Figure 1b), while the polymer poor phase results in the cavities after solidification. Such a phase separation process closely relates with the behavior of the soluble PS block in the solvent, as similar phenomena will happen by casting the solution of homopolymer PS (a fractionated fraction of commercial products prepared in our laboratory, with a $\bar{M}_n = 5.2 \times 10^4$ and $\bar{M}_w/\bar{M}_n = 1.4$) in the same conditions. A transparent PS film was formed by solidifying the polymer solution of PS in DMF in the dry air, and no special microstructures appeared on the surface (Figure 1c). However, a white coating was obtained after the PS solution solidified in the humid air. The SEM image (Figure 1d) reveals that the homopolymer surface consists of numerous micron-sized particles. The particles stack together irregularly, thus increasing the surface roughness. As a result, the water repellency increases with a CA changed from 81.1 ± 2.8° to 139.5 ± 2.7°. The cross-section views of both copolymer and homopolymer

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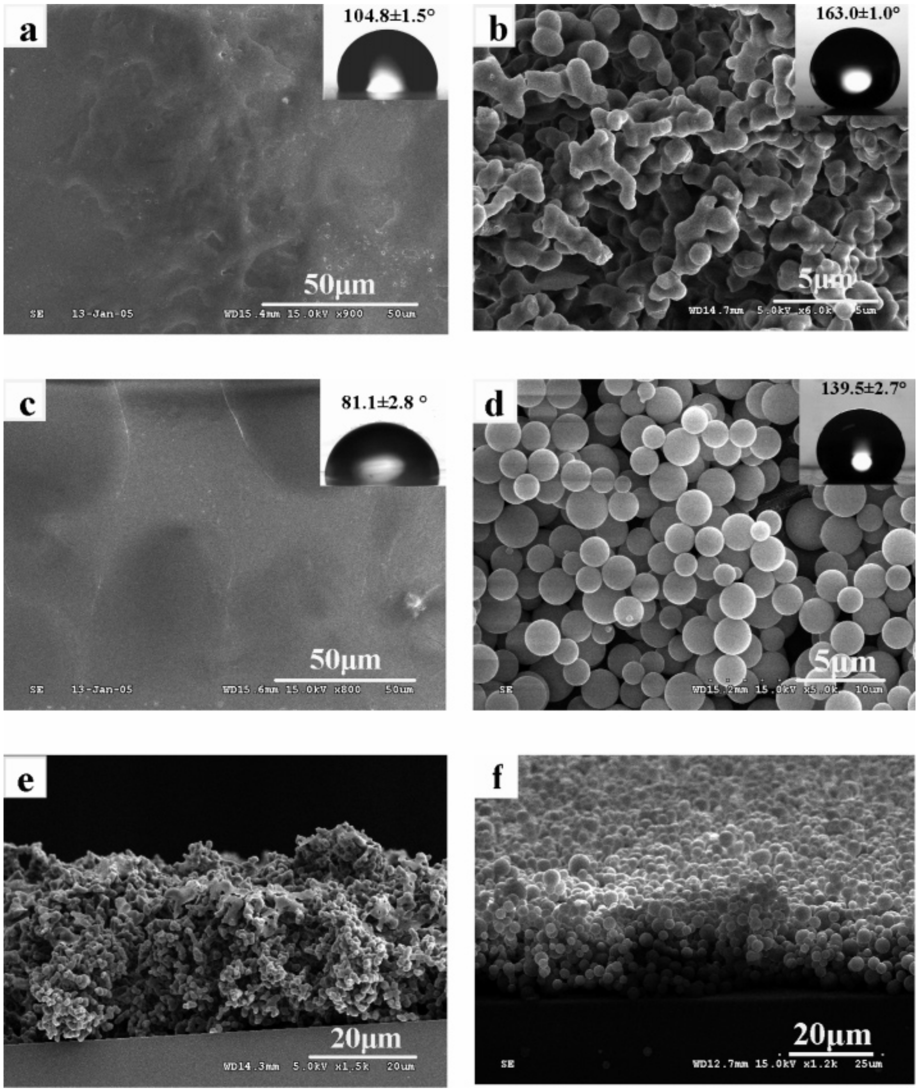

Figure 1. SEM images of the surfaces cast from a 5 mg/mL micellar solution of PS-*b*-PDMS in DMF in the (a) dry and (b) humid air and from 5 mg/mL homopolymer solution of PS in DMF in the (c) dry and (d) humid air at room temperature, respectively. The RH of the dry atmosphere is less than 10% and is 605% for the humid air. (e) and (f) are the side view of (b) and (d), respectively. Inset is water CA of each surface.

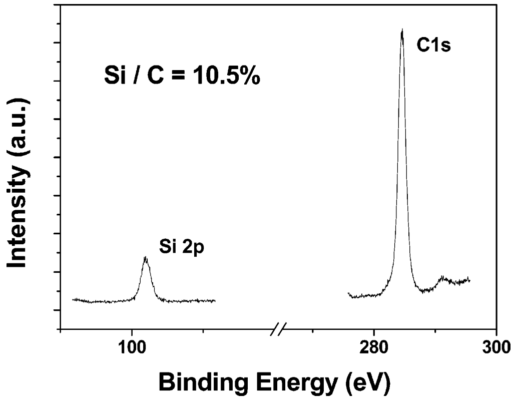

Figure 2. XPS spectrum of the superhydrophobic PS-*b*-PDMS surface at a takeoff angle of 10°.

coatings (Figure 1e,f) show that such coatings are totally built up by the protrusions and particles, respectively, demonstrating that VIPS occurs in the whole solution system.

The superhydrophobicity did not solely come from the increased surface roughness with respect to the surface activity of the PDMS block.[13] From the X-ray photoelectron spectroscopy (XPS) spectrum (Figure 2), the Si 2p peak is obviously observed at a takeoff angle of 10°, suggesting the appearance of PDMS on the topmost layer of the superhydrophobic surface.[13b] The DMS ratio at such depth determined by XPS is 52.6 mol %, whereas the molecule composition of the PDMS in the copolymer is 64.9 mol % (see Supporting Information for details). It means that part of the PDMS has migrated on the air side, which will efficiently lower the surface tension and contribute to the resultant superhydrophobicity. The appearance of PDMS on the copolymer surface and its contribution to decreasing surface tension were also confirmed by comparing water CA of the copolymer of a smooth surface with that of a smooth PS surface. As the surface wetting behavior is controlled by both the surface tension and roughness, CA is dominated only by the surface chemical composition if the surface is smooth.[1−3] Figure 3 shows the surface morphology of PS and PS-*b*-PDMS by drying the solution in a vacuum oven under reduced pressure at room temperature. The low pressure not only excluded the influence of moisture but also greatly accelerated the DMF evaporation, and thus restrained the phase separation to occur, resulting in the formation of a

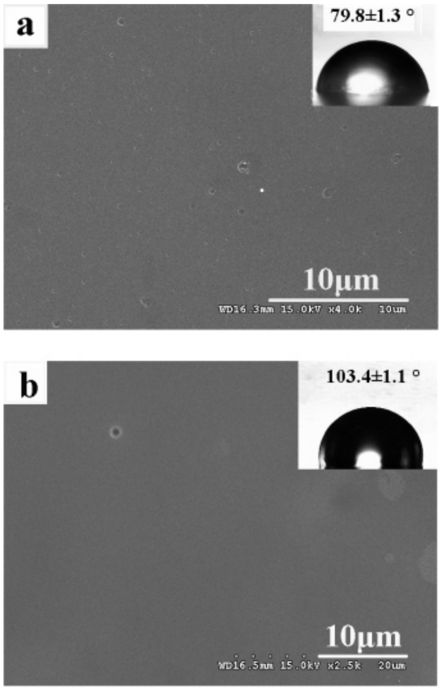

Figure 3. SEM images of the coatings cast from (a) PS and (b) PS-*b*-PDMS in DMF at a concentration of 5 mg/mL in a vacuum oven with a reduced pressure at room temperature, respectively. Inset is water CA of each coating.

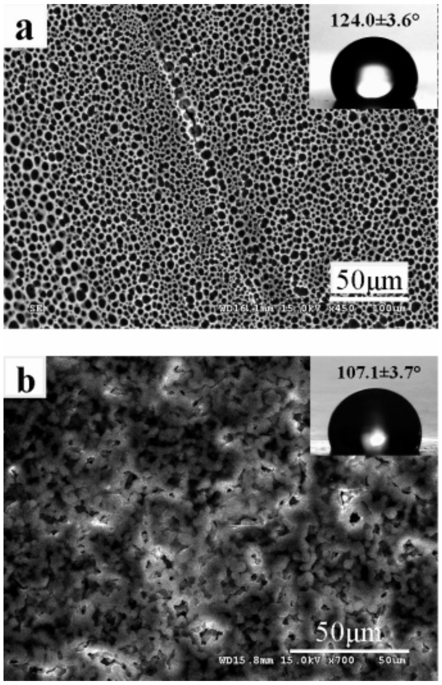

Figure 4. SEM images of the copolymer cast from 5 mg/mL (a) micellar solution in heptane and (b) solution in butanone in humid air. Inset is water CA of each surface.

transparent smooth coating. No microstructure appeared on both the PS and PS-*b*-PDMS surfaces, and atomic force microscopy (AFM, by tapping model) investigation has demonstrated that the root-mean-square (rms) roughnesses of the resultant smooth PS and PS-*b*-PDMS surface are 5.1 and 1.6 nm, respectively. Therefore, it is safe to neglect the roughness influence on the water CA. Water CA on smooth PS surface is just $79.8 \pm 1.3°$, whereas it is $103.4 \pm 1.1°$ on the smooth PS-*b*-PDMS surface, implying that the PS-*b*-PDMS coating has a lower surface tension than that of the PS surface, which is consistent with the XPS investigation. The enrichment of PDMS on the surface might be due to that when the system was getting very close to a solid state before the solvent evaporated completely; the PS block was still swollen by solvent molecules. Considering the plasticization effect of the solvent, the PS chain segment had certain movability at room temperature. The PDMS blocks, joining at the end of each PS blocks, are very movable at room temperature for its very low glass transition temperature T_g (−123 °C). Therefore, the chain conformation of the copolymer at the air surface was capable of rearranging before solidification as some solvent molecules still swelled the PS chains. To lower the surface energy, the PDMS block was rearranged to the surface. Such driving force was limited by the unfavorable circumstance of selective solvent molecules, resulting in the copolymer surface only partly covered by the low surface energy block. Moreover, a small amount of free homopolymer PDMS consisting in the copolymer we used may also contribute to the surface enrichment of PDMS. However, it should not be the primary source with respect to its small content and insolubility in the solvent used. Therefore, although the copolymer PS-*b*-PDMS was cast from DMF, in which PDMS was insoluble and surrounded by the soluble PS blocks, surface migrating of PDMS still occurred on the surface. The appearance of the PDMS block on the topmost layer will decrease the interaction between water and the solid, contributing to the easy rolling of the water drop off the surface. Different from other superhydrophobic surfaces, which have both high water CA and low SA based on the hierarchical structure in nanoscale and micron scale,[9] the superhydrophobic surface prepared here is rough only in micron scale.We believe it is just because the efficient decrease of surface tension by the migration of PDMS on the topmost layer that the low contact angle hysteresis is realized.

When the copolymer coating was cast from heptane, a PDMS-selective solvent, or from butanone, a common solvent for both blocks, under the same conditions, however, only general hydrophobic surfaces without rough microstructure were obtained, as shown in Figure 4. The formation of the arrays of holes (Figure 4a) on the copolymer surface cast from heptane, a water-insoluble solvent, can be attributed to the phenomenon of “breath figures”.[11] The lack of surface roughness on the copolymer surface prepared here may be due to the fact that the surface is covered mostly by PDMS block when it is soluble in the solvent.[13] For example, XPS investigation has demonstrated that the PDMS concentration at the topmost layer of the surface cast from heptane is as high as 93.1 mol % (see Supporting Information). As linear PDMS has a T_g of −123 °C, the long PDMS chains are very flexible at room temperature and prefer to flatten on the surface; therefore, rough microstructures are unlikely to be formed.

In conclusion, we have reported a simple approach for preparing a superhydrophobic copolymer surface with both rough surface morphology and low surface tension in one step by casting the micellar solution of PS-*b*-PDMS in humid air. The rough surface structure derives from vapor-induced phase separation, and the low surface tension results from the surface migration of the PDMS block. This method provides as a simple way to fabricate a superhydrophobic surface for other copolymers containing low surface energy block under mild conditions.

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Supporting Information Available: XPS pattern, details of calculation of surface chemical composition, sliding behavior of water drop on the superhydrophobic surface, and the weight change of the copolymer solution during solidifying. This material is available free of charge via the Internet at http://pubs.acs.org.

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