Fabrication Gradient Surfaces by Changing Polystyrene Microsphere Topography

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A rather simple yet effective way to fabricate gradient surfaces by changing polystyrene (PS) microsphere topography in a temperature gradient field is proposed. The wettability of the film has an obvious gradient change from 88.7 to 148.1°. The changes of the PS microsphere topography are believed to be responsible for the changing of the wettability.

Introduction

Gradient surfaces with a gradually changing surface energy along their length are of great interest for numerous practical applications, such as biomolecular interaction investigations, cell-motility studies, diagnostics, nanotribology, and microfluidics. In the past years, a number of gradient preparation techniques for various substances have been described,¹⁻¹⁴ such as palladium deposition, gas diffusion technique, and corona and plasma discharge. Recently, Ganzer et al.³ demonstrated that one-dimensional planar molecular gradients with tunable wettabilities could be fabricated by combining the asymmetric vapor deposition method. Furthermore, they⁴ offered a novel strategy for generating substrates with positiondependent physical-chemical properties. They⁵ also reported on a simple methodology that facilitates the generation of surface-grafted assemblies comprising block copolymers with tunable composition and molecular weight gradients along flat solid substrates. They⁶ have shown that an orthogonal gradient in molecular weight and grafting density of surface-anchored polymers can be conveniently prepared by generating number density gradients of polymerization initiators on the surface followed by surface-initiated atom transfer radical polymerization. These orthogonal gradients were used as

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functional combinatorial templates to direct the assembly of nanoparticles. On the other hand, Ionov et al.^{10a} developed a novel approach for the synthesis of mixed polymer brushes with a unidirectional gradual change of composition, which allows for a fast screening of the switching behavior of mixed brushes. Furthermore, they^{10b} also developed a "grafting to" approach for translation of the temperature gradient into a gradient of polymer chain grafting density, which demonstrated gradual changes in wetting properties and morphology transition from pinned micelles to a brush regime along the substrate.

Most of these gradient surface preparation techniques reported so far are for fabricating a gradual density gradient in a unique geometry structure so as to form a surface energy gradient, which results in a position-bound variation in the physical properties. In this paper, we proposed a novel and simple method for fabricating a morphology gradient by changing polystyrene (PS) microsphere topography in a gradual temperature field on a millimeter to centimeter scale. Along the PS microsphere film length, one side was heated while the other was not under N₂ protection conditions. Thus, the temperature decreased gradually along the length. Therefore, the morphology of PS microspheres changed gradually, which resulted in the variation of the surface energy; that is, the wettability obviously changed along the length (water contact angles (CAs) changed from 148.1 to 88.7° continuously).

Experimental Section

PS microspheres were prepared by emulation polymerization according to a procedure described in the literature.^{15,16} The PS microspheres (with a diameter of ~240 nm) were dissolved in ethanol with a typical concentration of 0.1 wt %. Then, thin PS microsphere films were prepared by spin-coating the ethanol solution onto the silicon wafer at 3000 rpm and then heated at 40 °C in a vacuum to evaporate the residual solvent for 24 h. Prior to the spin-coating, the wafers were cleaned with a 70/30 v/v solution of 98% $H_2SO_4/30\%$ H_2O_2 at 80 °C for 30 min and then thoroughly rinsed with deionized water and dried.

Under N₂ protection conditions, heating one side of the abovementioned film at 130 °C for 48 h while keeping the other side at room temperature, a gradual decreasing temperature field was formed along the length of the film, which has been reported

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Figure 1. Analyzing the surface chemistry of PS microspheres by FT-IR.



Figure 2. (a) AFM of the relatively close-packed hexagonal microstructure. (b) Water contact angle of the relatively close-packed hexagonal microstructure film.

 $recently.^{10}$ The film was then used for water contact angle and atomic force microscope (AFM) measurements.

Contact angles were determined using a KRÜSS DSA10-MK2 contact angle measuring system at ambient temperature. The probe fluid was deionized water, and the droplet volumes were 2 μL .

AFM studies were performed in the SPA300HV with a SPI3800N probe station (Seiko Instruments Inc., Japan) in the tapping mode (set point ratio ≈ 0.90). Silicon tips on cantilevers (resonance frequency 70 kHz) with a spring constant of 2 N/m were used. The scan rate was in the range 1.0–2.0 Hz.

Results and Discussion

Since the surface chemistry of PS microspheres plays an important role in surface wettability, the surface chemistry of PS microspheres is analyzed first. The Fourier transform infrared (FT-IR) spectrum (Figure 1) shows that the absorbance peaks at 3060.44, 3026.27, 1601.13, 1493.59, 1452.77, 757.8, and 699.2 cm⁻¹ correspond to a phenyl group, the peaks at 2923.71 and 2850.17 cm⁻¹ to the methylene and methenyl groups, and the peaks at 1105.9 and 1028.8 cm⁻¹ to the C–C and C–Ph groups. There are no other absorbance peaks. It verifies that the product obtained only contains polystyrene and no other surface-active agent on the PS surface.

By spin-coating the colloid solution on the substrate, PS microspheres can self-assemble to form the relatively close-packed multilayer hexagonal microstructure (Figure 2a). The water contact angle (CA) of the surface is around 147.2° (Figure 2b), higher than that of the flat polystyrene film (CA = 91°).



Figure 3. (a) Calculation scheme for the curvature of the liquid-vapor interface. (b and c) Irregular structure influences on the curvature radius (R). When the film has irregular structure, R' will be always larger than R.



Figure 4. Water contact angle and the corresponding shapes of sessile water droplets $(1 \ \mu L)$, from the heated side $(130 \ ^{\circ}C)$ to the unheated (room temperature) side. The water contact angles of the different locations of the film are 88.7, 108.6, 121.2, 132.2, and 148.1°, respectively.

It is well-known that the wettability of the solid surfaces is governed by both the chemical composition and the geometrical microstructure of the surface.^{17,18} In our experiment, the FT-IR spectrum has proven that the material is pure polystyrene without any other active agents. Therefore, the wettability of the film is only governed by the surface geometry herein. The apparent contact angle of a droplet on a rough surface is often modeled by either Wenzel's¹⁹ or Cassie's formulas.²⁰ In Wenzel's approach,¹⁹ it is assumed that the liquid fills up the grooves on the rough surface, that is, the wetted contact with the rough surface. In Cassie's approach,²⁰ it is assumed that the liquid forms a composite surface on the rough substrate; that is, the liquid does not fill the grooves on the rough surface and this can be referred to as the

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Figure 5. AFM images at different locations of the film: (a) unheated side; (b) temperature $\sim T_g$; (c) temperature ~ 130 °C.

composite contact with the rough substrate. This case can be expressed by eq 1. Herein,

$$\cos \theta_{\rm r} = f(\cos \theta + 1) - 1 \tag{1}$$

 θ_r and θ are the contact angles on the rough PS surface and on the native PS film with a smooth surface, respectively. *f* is the solid fraction of the surface.

In recent research, Shui et al. have proven that Cassie's model is a better description than Wenzel's model for the water wetting behavior on the close-packed microstructure surfaces.²¹ In Cassie's model, it is necessary to know the area fraction of the solid-liquid contact line. As one step in this direction, we assume the model as shown in Figure $3a.^{22}$ In this model, *f* depends on the sphere radius (*h*) and the curvature radius of the liquid in trapped air pockets at the liquid-solid interface (*R*) (eqs 2 and 3).

$$f/(1-f) = h\psi/R\psi = h/R \tag{2}$$

$$f = h/(h+R) \tag{3}$$

In our experiment, the close-packed structure is not absolutely regular and there are some spheres packing irregularly in the film, which can be well found in Figure 2a. Although R cannot be calculated exactly currently, we can find that with some irregular structure being in the film, R will increase; that is, R' will be larger than R,

which has been shown in Figure 3b and c. Thus, when the film has some irregular structure, f(f = h/(h + R)) will decrease, which results in an increase in the CA. This is the reason our experimental result ($\theta e = 147.2^{\circ}$) is larger than the theoretical one ($\theta r = 133^{\circ}$), which has been calculated in refs 21 and 23 in detail.

Since the relatively close-packed multilayer hexagonal microstructure has a water contact angle (CA) of 147.2° (Figure 2b) and the flat polystyrene film has a CA of 91°, a gradient surface with a continuous change of CA can be made by gradually changing the surface topography. Under N₂ protection conditions, when heating one side of the relatively close-packed multilayer hexagonal microstructure film at 130 °C for 48 h while keeping the other side at room temperature, a gradual decreasing temperature field was formed along the length of the film.¹⁰ The gradual gradient wettability has formed from the heated side to the unheated side along the film length. On the unheated side, the wettability did not change and the CA was around 148.1°. With the length increasing from the unheated side to the heated side, the CAs changed from 148.1° to 132.2, 121.2, 108.6, and 88.7° continuously (Figure 4).

It is believed that the formation of the gradient surfaces is due to the variation of the microstructure of the film. To understand the mechanisms of this phenomenon, the microstructure of the film at different locations was investigated by AFM (Figure 5). On the unheated side, the temperature was much less than the glass transition temperature ($T_{\rm g}$) of the PS beads. At this time, the polymer

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Figure 6. (a) Relationship between root-mean-square (rms) roughness and temperature (T). With an increasing temperature, the rms roughness decreases. (b) The relationship between root-mean-square (rms) roughness and water contact angle (CA). With a decreasing surface roughness, the water contact angle decreases from 148.1 to 88.7°.

chains were frozen and could not move freely. Thus, the microstructure did not change at all (Figure 5a). Along the length from the unheated side to the heated side, the temperature increased obviously. At the location where the temperature was a little bit higher than T_g , the polymer chains in the PS microspheres could move at a low velocity, which resulted in the PS microspheres beginning to

collapse at their locations and adhere to the adjacent beads together little by little. Therefore, the relatively close-packed multilayer microstructure began to change to being flat gradually, but not completely (Figure 5b). On the heated side, the temperature was much higher than $T_{\rm g}$, so the PS chains could move in their PS beads at a high speed freely, which made the beads melt and adhere to the adjacent beads rapidly. After heating the film for 48 h, the relatively close-packed multilayer microstructure disappeared completely and a relatively flat surface formed (Figure 5c).

The surface roughness has a big effect on the surface wettability. Therefore, it is necessary to compare the surface roughness of the gradient film at different locations. Herein, we investigate the relationships between the root-mean-square (rms) roughness and temperature (Figure 6a) and between the rms roughness and CA (Figure 6b). From Figure 6a, we can find that, with the length from the unheated side to the heated side increasing, the surface morphology turns flat gradually with an increasing temperature; that is, the rms roughness of the film decreases with an increasing film temperature. With the surface morphology turning flat gradually, the surface rms roughness decreases from 46.3 to 14.6 nm, which results in the water contact angle changing from 148.1 to 88.7° continuously (Figure 6b). This is the main reason surface wettability changes gradually with increasing film length from the unheated side to the heated side.

Conclusion

In summary, we have succeeded in preparing the PS gradient surface (i.e., water contact angles varying between 148.1 to 88.7° gradually) by controlling the surface microstructure evolution along the film length in a temperature gradient. By heating one side of the relatively close-packed multilayer PS microspheres and keeping the other side at room temperature, the PS microspheres changed gradually to a flat PS surface, which resulted in the surface energy changing gradually. Through this simple and reproducible method, gradient surfaces with many properties, for example, hydrophilicity to hydrophobicity or hydrophobicity to superhydrophobicity, can be fabricated in many materials efficiently.

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