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Simple Fabrication of Honeycomb- and Pincushion-Structured Films Containing Thermoresponsive Polymers and Their Surface Wettability

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Achieving control over surface wettability has received much attention because of its importance in a wide variety of applications. As exemplified by the superhydrophobic lotus leaf,[1] both chemical and topological properties affect surface wettability. The contact angle of liquids on a rough surface, θ_w, is described by Wenzel's equation[2]

$$\cos\theta_w = r\cos\theta \qquad (1)$$

where r is the roughness factor and θ is the contact angle on a flat surface. The roughness factor, r, is the ratio of the actual surface area to the apparent surface area. The superficial contact angle at the interface between two components (e.g., air and polymer) is likewise given by a formula reported by Cassie based on the fraction of each component's surface area[3]

$$\cos\theta_c = \phi_1\cos\theta_1 + \phi_2\cos\theta_2 \qquad (2)$$

where θ_c is the superficial contact angle; θ_1 and θ_2 are contact angles on flat films of polymer and air, respectively; and φ_1 and φ_2 are surface area fractions of polymer and air, respectively. Using these two equations, artificial superhydrophobic surfaces have been designed by mimicking lotus leaves.[4] Tsujii et al. have reported that a fractal structure made from hydrophobic wax crystals strongly repelled water.[5] Hosono et al. have also shown that the water contact angle on inorganic nanopins coated with hydrophobic surfactants reached 178°.[6] According to the equations mentioned above, the wettability of a surface can change drastically depending on its chemical properties. Recently, Jiang et al. have generated photo- and thermoresponsive superhydrophobic surfaces from ZnO nanorod arrays[7] and poly(*N*-isopropyl acrylamide) (PNIPAm) grafted on rough surfaces,[8] respectively. In these reports, the properties of the superhydrophobic to superhydrophilic surfaces were reproducibly controlled by irradiation with UV light or by thermal stimuli.It has been reported that honeycomb-structured polymer films could be prepared by casting a polymer solution containing amphiphilic molecules under humid conditions.[9] The solution surface was cooled by evaporative cooling, which caused water droplets to condense onto the cooled surface. These water droplets stabilized the amphiphilic molecules in the polymer solution, and the amphiphilic molecules in turn prevented the fusion of the water droplets. Furthermore, pincushion-structured films could be prepared by peeling off the top layer of the honeycomb-structured films.[10] These patterned films showed high water repellency because of their high porosity (water contact angle ~170°). We have also reported that a transparent superhydrophobic surface was formed when the pore size of the honeycomb-structured films was smaller than the wavelengths of visible light.[11] A few efforts have been made to regulate the surface wettability of these honeycomb-structured polymer films. Stenzel et al. have reported that thermoresponsive PNIPAm was grafted onto a honeycomb-structured polymer film by reversible addition−fragmentation transfer (RAFT) polymerization.[12] Here, we report the simple fabrication of honeycomb- and pincushion-structured films with thermoresponsive functionalities. We have successfully synthesized amphiphilic copolymers with thermoresponsive functional groups. The water repellency of these thermoresponsive structured surfaces is discussed.

Three types of poly(*N*-dodecylacrylamide-co-*N*- isopropylacrylamide) (polymers **1**−**3**, see Scheme 1 and Table 1), which have different copolymerization ratio between DAm and NIPAm, were synthesized by free-radical polymerization according to the literature.[18] Azobisisobutyronitrile (AIBN) and *N*-isopropylacrylamide (NIPAm) were purchased. DAm, NIPAm, and AIBN were dissolved in benzene in a three-necked round-bottom flask equipped with a thermometer, a nitrogen cock, and a reflux funnel. The monomers and initiator solution was

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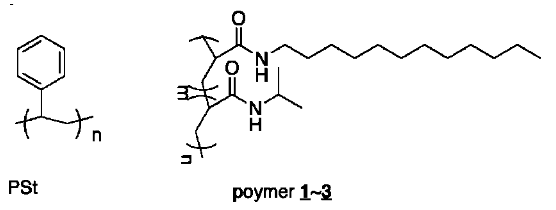
Scheme 1. Polymers Used and Synthesis in This Experiment



degassed three cycles of freeze−evacuate−thaw, and finally, the atmosphere was filled with dry nitrogen. The polymerization was conducted at 65−70 °C for 6 h. After reaction, the polymers **1**−**3** were purified by reprecipitation in acetonitril. The synthesized polymers were characterized by ^{1}H NMR (see the Supporting Information, S1, ECX-400, JEOL, Japan), Fourier transform infrared spectroscopy (FT-IR, FT-200, Jasco, Japan), and gel permiation chromatography (GPC, polystyrene standards, Shodex GPC K804 column, Showa Denko, Inc., Japan). FT-IR spectra of polymers **1**−**3** were measured to confirm their chemical structures (see the Supporting Information, S2). Table 1 shows copolymerization ratios, M_n, M_w, and polydispersities M_w/M_n for polymers **1**−**3**, and these results also indicated that the polymerization was successful.

The interfacial tension was strongly related to the stability of condensed water droplets in the polymer solution.[13] When this tension was reduced, water droplets were embedded onto the solution surface. The amphiphilic copolymers formed a stable water-in-oil type emulsion, which floated on the surface of the solution, and they also prevented the fusion of the water droplets. This ultimately resulted in the formation of a honeycomb-structured polymer film. During solvent evaporation, the solution surface cooled to ca. 5 °C by evaporative cooling. It has been reported that the interfacial tension between a chloroform solution and water at 5 °C should be controlled in the 10 to 16 mN/m regime in order to form regular honeycomb-structured films.[14] The interfacial tensions between chloroform solutions of polymer **1**−**3** and water were measured by using a typical pendant drop type interfaical tension meter (DM-300, Kyowa Interface Science, Co. Ltd., Japan).[14] The values of the interfacial tension between chloroform solutions of polymers **1**−**3** and water were 16.0, 14.3, and 11.4 mN/m, respectively. These values showed that the synthesized polymers were suitable for preparing honeycomb-structured films.

Figure 1a shows a typical SEM image of the surface of a honeycomb-structured film of PSt with an amphiphilic polymer (the weight ratios of PSt and polymer **1**−**3** were 10/1). The honeycomb-structured films were pepared by casting 5 mL of 5 mg/mL solution of PSt and polymer 1−3 under applying humid air (relative humidity 60−90%) with its velosity of 4 L/min. In all cases, uniform and regular films were obtained. The pore sizes of honeycomb-structured films containing polymers **1**−**3** were 6.8 ± 0.6, 8.0 ± 0.2, and 6.5 ± 0.3 μm, respectively. The cross-section of the film is also shown in the inset of Figure 1a. The spherical shape of the pores reflected the shape of the template water droplets. Two porous polymer layers were stacked vertically, separated by pillars at the hexagon vertexes.Pincushion-structured films were also prepared, by simply peeling off the top layer of the honeycomb-structured films with adhesive tape. Figure 1b shows a typical SEM image of a pincushion-structured film of PSt with polymer **1**. Each pillar of the honeycomb-structured film was cleaved, leaving sharp spikes on the surface upon peeling.

It was reported that PNIPAm shows its LCST at 32 °C in water solution.[15] On the other hand, the chloroform solution of polymer **3** shows drastic transmittance decrease at 24 °C when the visible light (λ = 600 nm) transmittance change was observed. Panels a and b in Figure 2 show the water contact angles (CAs) on the PSt honeycomb- and pincushion-structured films, respectively. Both films contained thermoresponsive polymers, and measurements were made as a function of temperature. The water droplets were placed on the sample surfaces with every changing of sample temperature to avoid contact line movement because of evaporation or surface tention change. The CAs were higher on the honeycomb-structured films than on the flat film (~90°),[16] but there was no discernible change in this angle with changing temperature (Figure 2a). On the other hand, the water contact angles on the pincushion films decreased drastically with decreasing film temperature. This change is reversible and no hysterisis was observed. During the formation of the honeycomb-structured film, the water droplets were covered and stabilized by the amphiphilic polymers. After evaporation of the solvent and template water droplets, the amphiphilic polymers condensed locally on the inner surfaces of the pores (schematic model shown in inset of Figure 2a).[17] As a result, the top surface of the honeycomb-patterned polymer film consisted mainly of PSt, and thus, the CAs on the honeycomb-structured films did not depend much on substrate temperature. In the pincushion films, the amphiphilic polymer molecules condensed on top of the spikes (schematic model shown in inset of Figure 2b). We have observed and confirmed the detail structure in the pins by dye-labeled amphiphilic polymer.[16,17c] When the honeycomb-structured and pincushion-structured films were prepared from dye-labeled amphiphilic polymer and PS, the strong fluorescence was observed at the pillars and the top of the spikes. This result indicates that the amphiphilic copolymers condensed at the top of the spikes. The schematic illustration of Figure 2b shows the situation of the phase-separation of amphiphilic polymer and PS. As the result, the pincushion-structured film shows thermo-responsive behaviors. The composition of the two monomers of the polymer **1**−**3** did not affect the CAs and CA changes on honeycomb- and pincushion-structured films. Basically, the copolymerization ratio affects the three-dimensional structure of the honeycomb-structured films. As we reported in reference, the cross-sectional shape of template water

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Table 1. Characterization of Synthesized Polymers

sample	DAm ($\times 10^{-3}$mol)	NIPAm ($\times 10^{-3}$mol)	AIBN ($\times 10^{-5}$mol)	DAm/NIPAm (a)	yield (%)	Mn ($\times 10^3$kg/ mol)	M_w ($\times 10^3$kg /mol)	M_w/M_n
1	11.8	8.51	7.0	7.2/2.8	61	23	69	2.9
2	12.2	12.6	17	1.0/1.0	65	15	48	3.1
3	6.67	14.0	8.1	3.0/7.0	36	27	68	2.5

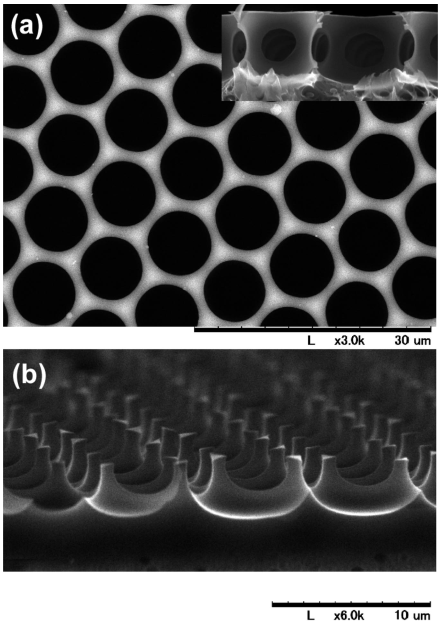

Figure 1. Typical SEM image of (a) honeycomb- and (b) pincushion-structured films of PSt and polymer **1**. The inset image of (a) shows a cross-section of the honeycomb-structured films.

droplet changes from spherical to ellipsoidal during the honeycomb-structured film formation with increasing the copolymerization ratio of PNIPAm moiety. This deformation change the depth of the holes. However, the hole depth is not theoretically related with CAs based on the Cassie equation, as the result, the difference of monomer ratio did not affect the difference of CAs. The hydrophilic PNIPAm moieties should be located on the surface of the holes due to stabilizing template water droplets. Thus, the composition ratio may affect the surface density of the PNIAPm moieties on the surface of the holes. However, the CAs and thermoresponsive properties were not changed with increasing the PNIPAm moieties. This result indicates that 30% containing of PNIPAm moieties is enough to represent thermoresponsive properties.

The wettability of these thermoresponsive amphiphilic polymers depended on temperature, and consequently, the resulting CAs depended on temperature as well. The reason why the gradual change of contact angles on the pincushion-structured film is the effect of hydrogen bonding. The thermo-responsive behavior of PNPAM is caused by changing the state of hydrogen bonding between amide group and water.[15] Because the NIPAM moieties are not solubilized by water in the solid state, not all the NIPAM moieties join the thermoresponsive properties.

Honeycomb- and pincushion-structured films containing thermo-responsive amphiphilic copolymers were prepared by simple casting of polymer solutions under humid conditions.

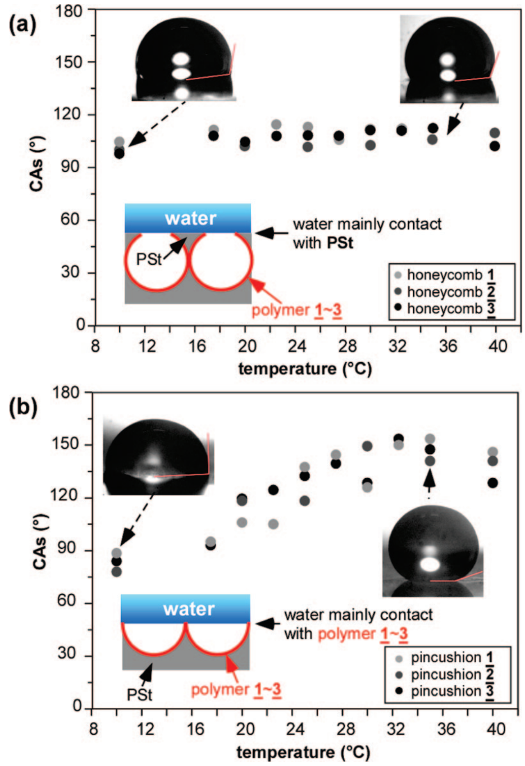

Figure 2. Temperature dependences of CAs on (a) honeycomb- and (b) pincushion-structured films. The gray, dark gray, and black dots show the CA values of honeycomb- and pincushion-structured films of polymers **1**−**3**, respectively.

Thermoresponsive superhydrophobic surfaces could be easily fabricated by casting solutions containing thermoresponsive amphiphilic copolymers. The honeycomb-structured films showed higher water repellency than flat films, though the CAs did not show noticeable temperature dependence. The pincushion-structured films showed a drastic decrease in CA with decreasing film temperature. These differences were thought to have originated from the localization of thermo-responsive polymers on the film surfaces. Such unique microstructured materials could find applications in stimuli-responsive separation membranes, water condensers, and other practical technologies. Moreover, the strategies shown in this paper gives a new insight to design stimuli-responsive superhydrophobic surfaces by using self-organization processes.

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Supporting Information Available: Additional figures (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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