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Water-induced morphology evolution of block copolymer micellar thin films

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Abstract

Morphology evolution of diblock copolymer polystyrene-*block*-poly(4-vinylpyridine) (PS-*b*-P4VP) micellar thin film in the presence of water was investigated. Surface holes with nanoscale cavities in hexagonal order could be induced by water treatment for certain periods. The nanoscale surface cavities could be transformed into isolated nanospheres in a dry environment or back to protruding densely packed spheres by toluene (a selective solvent for PS coronae) treatment. The morphology evolution of micellar thin film strongly depended on the slow evaporation of toluene solvent, the swelling of P4VP cores in the humid environment, and the subsequent movement of PS chains induced by air and toluene. The incompatibility between solvent and block, and that between the unlike blocks also played an important role in the morphology evolution.

Keywords: Micellar thin films; Morphology evolution; Diblock copolymer

1. Introduction

Patterning of thin polymer films has been extensively studied in recently years because of its great significance in microelectronics [1], cell growth control [2], bio-mimetic materials fabrication [3], nanotechnology [4], and so on. Many strategies, for example, photolithography [1], soft lithography [5], templating [6], external field [7] and block copolymer microphase separation [8,9], have been employed to pattern thin polymer films.

As well known, diblock copolymer can self-assemble into structures on the length scale of tens of nanometer in bulk or in a solution [10]. For example, in a selective solvent for one of the blocks, nanometer-sized micelles consisting of a soluble corona and an insoluble core are formed above the critical micelle concentration [11]. These micelles can be arranged on the substrates to form ordered nanostructures with the rapid evaporation of solvent.

The nanopattern of micellar films can change under the influence of external factors. For example, the selective solvent for the core block can reorganize the core and corona of micelles to achieve core-corona inversion of micelles and form the inversed nanopattern of micellar film [12]. By alkaline solution treatment to PS–PAA micelles, hexagonal arrays of nanoscale surface cavities could be created due to hydration and swelling of the PAA cores [13]. Recently, evaporation-induced method has been reported to transform the aggregation of PS–PAA micelles to unusual polymeric microcubic particles [14]. The spindle-like aggregates and flower like arrays of PS–PAA micelles can be yielded after a given amount of freeze-thaw cycles [15]. These investigations present us efficient and facile ways to manipulate the morphologies of micellar films by tuning solvent selectivity, temperature, substrate, the rate of solvent evaporation or additive.

Polystyrene-*block*-poly(4-vinylpyridine) PS-*b*-P4VP is a non-ionic amphiphilic block copolymer. Its self-assembly behavior in a selective solvent for the PS block has been studied intensively [16]. Well-defined micelles with an insoluble P4VP core and a soluble PS corona are formed in toluene (a selective solvent for PS coronae). PS-*b*-P4VP

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micelles can arrange on the mica surface steadily due to the strong polar adhesive interaction of mica with the 4VP units [17,18]. Our strategy is to achieve the controlled patterned surfaces by tuning the environmental condition (hydrophilic/water and hydrophobic/toluene), and the rate of solvent evaporation. In this paper, we report the morphology evolution of diblock copolymer polystyrene-*block*-poly(4-vinylpyridine) PS-*b*-P4VP micellar thin film cast onto the mica substrate in the presence of water. Surface holes with nanoscale cavities of hexagonal arrays could be obtained by water treatment for certain periods. The nanoscale surface cavities could change into isolated small spheres with slow evaporation of water or back to protruding densely packed spheres by toluene treatment. The possible mechanism of the morphology evolution is discussed.

2. Experimental section

2.1. Sample preparation

Polystyrene-*block*-poly(4-vinylpyridine) (PS-*b*-P4VP, $M_n^{PS} = 21.4$ kg/mol, $M_n^{P4VP} = 20.7$ kg/mol, $M_w/M_n = 1.13$) from Polymer Source Inc. was dissolved in toluene to yield 0.5 wt% micelle solution. Equal-sized droplets of the micelle solution were cast onto the freshly cleaved mica by a 0.02 ml pipette. Then the samples were put into two different environments: one was in a sealed container (filled with drying agent) with relative humidity (RH) of 20–25%; the other was in a sealed container (pure water) with RH of 80–85%. The temperature inside the containers was 21–25 °C. After the samples were exposed to moisture (80–85% RH) for different times (4, 6 and 20 h), they were taken out of the chamber and imaged at 25–30% RH. The samples after water treatment were placed in two conditions: one was in a sealed container with RH of 20–25% for 1 week, the other was dipped into toluene for 20–30 s after the water in the micelles was removed rapidly and the morphology of the thin film was frozen.

2.2. Characterization

Samples were imaged at room temperature with a commercial scanning probe microscope (SPA300HV with a SPI3800N Probe Station, Seiko Instruments Inc., Japan) in tapping mode by using a silicon cantilever (nominal spring constant 2 N/m and resonant frequency ~70 kHz, Olympus, Japan). All analyses of the images were conducted in the integrated software.

3. Results and discussion

In general, for diblock copolymers in selective solvents, the solubility difference between different blocks makes one block expand and the other collapse. Block copolymers in such systems can self-assemble into spherical micelles with the insoluble blocks collapsing together to form the core and the soluble blocks forming the corona that extends into the solvent environment [13]. The micellization is driven by the repulsive interaction between the insoluble blocks and the solvents.

The relative affinity of solvent for each block can be estimated by polymer–solvent interaction parameter (χ_{ps}) [19],

$$\chi_{ps} = \frac{V_s(\delta_s - \delta_p)^2}{RT} + 0.34 \tag{1}$$

where V_s is the molar volume of the solvent, R is the gas constant, T is the temperature, and δ_s and δ_p are the solubility parameters of the solvent and polymer, respectively, which are also convenient to be used as a means of estimating the compatibility between polymer and solvent [19]. In this work, for PS, toluene and water, the solubility parameters reported are $\delta_{PS} = 18.6$ (J/cm^3)$^{1/2}$, $\delta_{toluene} = 18.2$ (J/cm^3)$^{1/2}$, $\delta_{water} = 47.9$ (J/cm^3)$^{1/2}$ [19]. Unfortunately, we did not find the solubility parameter of P4VP in the literature. Because P4VP is a lipophobic polymer that dissolves only in DMF ($\delta_{DMF} = 24.8$ (J/cm^3)$^{1/2}$), lower alcohols ($\delta_{methanol} = 29.7$ (J/cm^3)$^{1/2}$, $\delta_{ethanol} = 26.0$ (J/cm^3)$^{1/2}$, $\delta_{1\text{-}propanol} = 24.3$ (J/cm^3)$^{1/2}$, $\delta_{2\text{-}propanol} = 23.5$ (J/cm^3)$^{1/2}$), and aqueous mineralic acids [16], we assume the solubility parameter of P4VP to be about 25.0 (J/cm^3)$^{1/2}$ here. Thus, the calculated polymer–solvent interaction parameters (χ_{ps}) for different pairs of polymers and solvents at 23 °C are $\chi_{PS/toluene} = 0.347$, $\chi_{P4VP/toluene} \approx 2.001$, $\chi_{PS/water} = 6.641$, $\chi_{P4VP/water} \approx 3.848$. According to the Flory–Huggins theory criterion, polymer and solvent are completely miscible over the entire composition range when the obtained value $\chi_{ps} < 0.5$. Thus, the solvent toluene is a good solvent for PS but poor solvent for P4VP; water is non-solvent for both PS and P4VP. But water is a swelling solvent for hydrophilic P4VP due to the hydrogen bonding between 4VP and water.

PS-*b*-P4VP can self-assemble in toluene into spherical micelles with PS corona and P4VP cores above the critical micelle concentration (cmc). These micelles are rather stable so that the micellar films can be obtained by spin coating, dip coating or even directly casting on substrates. Here, mica is chosen as the substrate due to the strong polar adhesive interaction of mica with the 4VP units [17,18]. Fig. 1 displays the surface morphology of a cast micellar film stayed in a container with 20–25% RH. It can be seen that the micelles are not arranged in a good order due to the packed multilayers of micelles on the substrates. The structure of spherical micelles was frozen because of the rapid evaporation of toluene in the dry environment. So only sphere structure can be found on the mica surface. The lateral diameter of the micelles is about 40 nm. The similar structures have been discussed in detail in the earlier publications [20]. That is, the PS coronae of adjacent

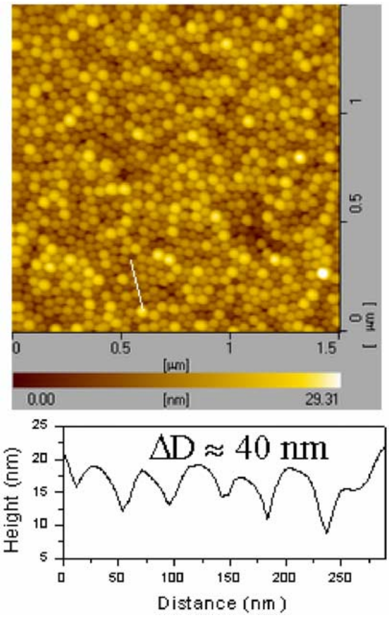

Fig. 1. AFM topographic image of PS-*b*-P4VP micelles film on a mica surface prepared by drop casting. The cross-section line scan profile gives out the micelle diameter.

micelles fuse together to form a continuous film matrix and P4VP cores are embedded into PS matrix.

Since PS-*b*-P4VP is a typical amphiphilic block copolymer of which the P4VP is hydrophilic and the PS is hydropobic, it's possible and may be interesting to investigate the effect of hydrophilicity or hydrophobicity of environment on the morphology of micellar films. The phenomena reported here is that when the PS-*b*-P4VP micelles solution are cast onto the mica surface and then treated in the high humidity environment for different periods, some new morphologies appear. After the sample was placed in the relative humidity (RH) of 80–85% environment for 4 h, the thin film became relatively flat without obvious protruding spherical features (Fig. 2(a)). With a longer treatment time (e.g. 6 h), holes appeared on the flat thin film (Fig. 2(b)). From the cross-section line scan profile of Fig. 2(b), it can be seen that the depth of the hole is about 8 nm. The holes would grow and fuse (Fig. 2(c)) when the treatment time extended for a longer period (e.g. 20 h). In the local amplified phase images (Fig. 2(b′) and (c′)), some nanostructures are found in the holes while the around area of the holes is still a flat film.

Interestingly, when we peered into the fine structure of the holes, nanoscale cavities of hexagonal arrays were found (Fig. 3). The hexagonal ordered structure can be confirmed by the two-dimensional fast Fourier transform (2D-FFT) pattern inserted in Fig. 3(b). But the cavity is very low (<1 nm in depth seen from the cross-section line scan profile of Fig. 3(a)) and the spacing between the cavities (~ 60 nm) is bigger than the micelle lateral size (~ 40 nm).

The surface cavities could also be transformed into spheres structure again by controlling the environmental condition. On the one hand, the sample of Fig. 2(c) after water treatment was placed immediately in a sealed container with RH of 20–25% (dry environment) for 1 week. The macroscopical morphology of the thin film (Fig. 4(a)) has no obvious change compared with that of the thin film treated by water (Fig. 2(c)), and the hole depth is still about 8 nm (cross sectional line scan profile of Fig. 4(a)). But isolated nanospheres with ~ 2 nm in height (determined from the height scale at the bottom of the Fig. 4(b)) were formed in the holes (Fig. 4(b)). On the other hand, when the sample after water treatment (Fig. 2(b)) was dipped into toluene (hydrophobic environment) for 20–30 s, the macroscopical morphology of the thin film changed a lot compared with that of Fig. 2(b). It can be seen that some island-like aggregates surrounded by low depressions (~ 5.5 nm in height) (Fig. 5(a) and (b)) are formed on the film surface. Furthermore, these island-like aggregates consist of densely packed protruding spheres (~ 31 nm in height) of hexagonal order in many local domains (Fig. 5(c) and (c′)). And the protruding spheres are very similar to micelles shown in Fig. 1.

How did the thin films of PS-*b*-P4VP micelles break into holes and the nanoscale surface cavities of hexagonal arrays form in the holes after water treatment (Fig. 2)? It is difficult to observe the morphology evolution of block copolymer micellar thin films in situ. So the possible mechanism of morphology evolution is discussed below according to the experiment results. When the sample was placed in a very humid environment (80–85% RH), water would diffuse into the hydrophilic P4VP cores through the hydrophobic PS-rich coronae because of the hydrogen bonding between P4VP and water (Fig. 6(a)), which led to P4VP cores swell. The water diffusion was possible because the top PS corona layer that covered the P4VP cores was very thin [13]. On the other hand, in the enclosed chamber with water (hydrophilic environment), toluene in the micelles solution evaporated slowly. The relatively slow evaporation of toluene could permit surface movement of the swollen micelles. This is because polymer micelles have the unique feature of a soft corona that can be compressed and expected to change its stiffness in response to solvent or other environmental features [21]. PS chains tend to be compressed in the surface of the thin film and adopt flat morphology instead of protruding spheres to decrease the surface area of the film and the surface energy in the hydrophilic environment (Fig. 6(b)). Furthermore, the incompatibility between the solvent and the block has an important contribution to the morphology evolution. In toluene, PS chains adopt an expanded configuration and form the micelle corona due to the good compatibility of PS in toluene ($\chi_{\mathrm{PS/toluene}}=0.347$). While in the humid environment, the stretching PS chains adopt collapsed configuration due to the strong incompatibility of PS in water ($\chi_{\mathrm{PS/water}}=6.641$). The spherical PS coronae shrink to form flat layer to minimize their surface energy in the presence of water.

With increasing the water treatment time, the toluene in

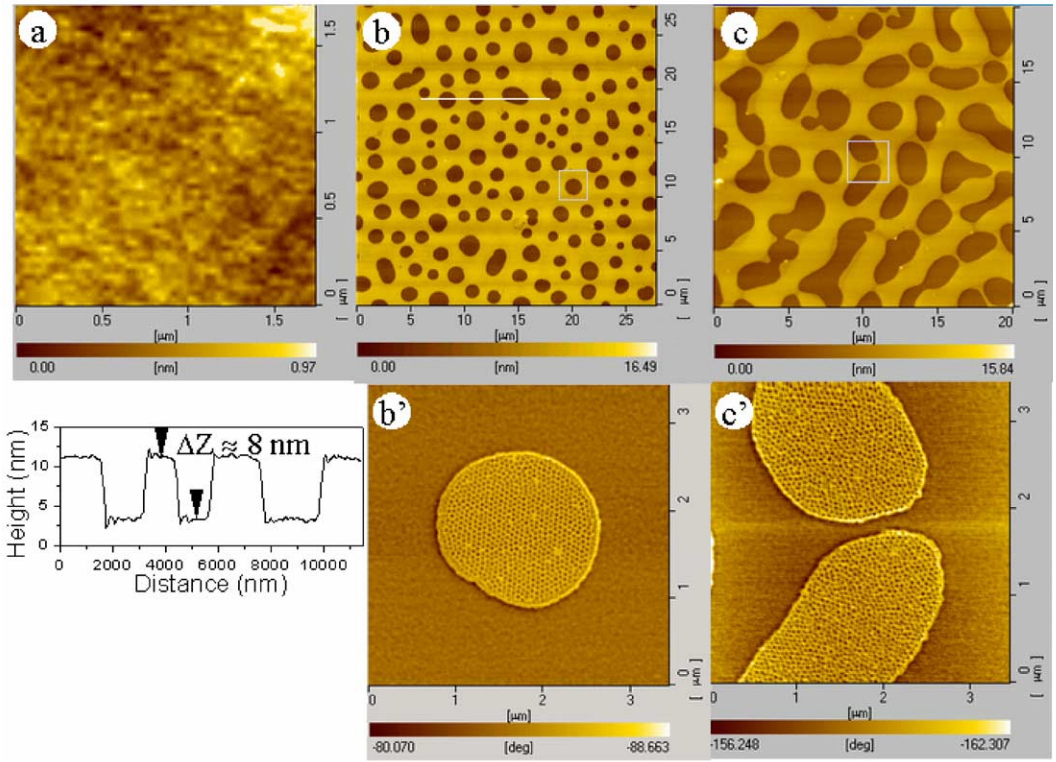

Fig. 2. AFM topographic (a, b and c) and local amplified phase (b′ and c′) images of PS-*b*-P4VP micelles film on mica surfaces after treated in an environment of 80–85% RH for different times, (a) 4 h, (b, b′) 6 h and (c, c′) 20 h. The cross sectional line scan profile of (b) gives out the hole depth.

the micellar thin film decreased and the water penetrating in the micellar thin film increased. Thus, the volume of the P4VP core increased because of the swollen P4VP segments. The holes appeared on the film surface when the volume of the swollen P4VP cores increased to fracture the coronae (Fig. 6(c)). The similar experiments have confirmed that the volume expansion of the micelle core lead to the rupture of micelle corona toward the film's surface [13]. It can be deduced that it may take several hours (presumable 4–6 h) for water to diffuse through PS to reach

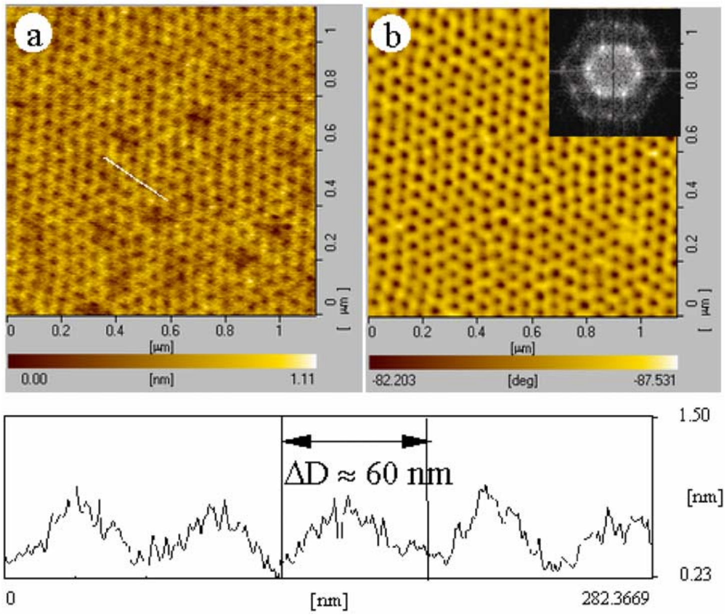

Fig. 3. AFM topographic (a) and phase (b) images of the surface cavity pattern in the hole area in Fig. 2(b). The insert to (b) is 2-dimensional fast Fourier transform (2D FFT) pattern. The cross sectional line scan profile of (a) gives out the cavity depth and diameter.

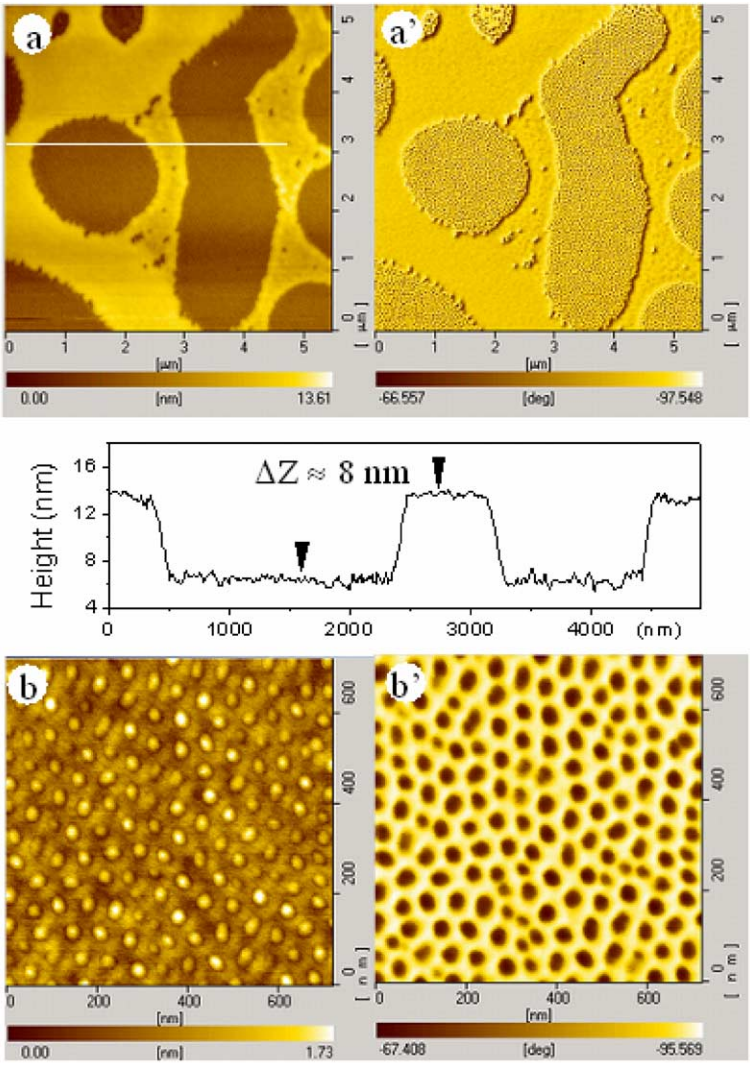

Fig. 4. AFM topographic (a and b) and phase (a′ and b′) images of PS-*b*-P4VP micelles film on mica surface stayed in 20–25% RH environment for 1 week after water treatment for 20 h. The cross sectional line scan profile of (a) gives out the hole depth.

P4VP when the micelles solution on the mica surface evaporates to form thin film in the humid environment. The swelling of the polymer causes the build-up of osmotic stresses in the film, and further swelling is prevented until these stresses have been dissipated by viscous flow of the stressed polymer chains [22]. So the holes on the thin film surface grew and fuse in lateral dimension (Figs. 2(b) and (c) and 6(d)). The rupture of micelle coronae leads to the formation of surface cavities in the holes (Figs. 3 and 6(e)). The inter-cavity spacing was bigger than the lateral micelle size mainly due to the swelling of P4VP blocks and thus induced the swelling of micelles. Furthermore, the height from the hole to the surface of the thin film is about 8 nm (Fig. 2(b)), a quarter of micellar monolayer film thickness (∼30 nm) [12]. Presumably, the top layer is a monolayer of PS coronae, which is in consistent with the above speculation.

When the sample after water treatment was placed immediately in a closed chamber with relatively low humidity (20–25% RH, dry environment) the water in the ruptured micelles evaporated slowly. With the slow evaporating of water, the polymer chains would collapse little by little, which resulted the cavities shrink slowly. While on the surface of the film, the PS chains adjacent to the cavities moved together slowly to the P4VP cores upside due to the lower surface energy as schematically shown in Fig. 6(f). The ruptured micelles were healed slowly due to the spontaneous movement of PS chains; this phenomenon can be called ‘PS heal’. But the trend of PS chains moving is very slow and weak. As seen from Fig. 4, after staying in dry environment for 1 week, the cavities were transformed into the isolated nanospheres of very low height. It can be deduced that the transformation from cavities to isolated nanospheres is related to the time. If the sample was treated in dry environment for a relatively short time (less than 1 week), the medium morphology of flat film should be

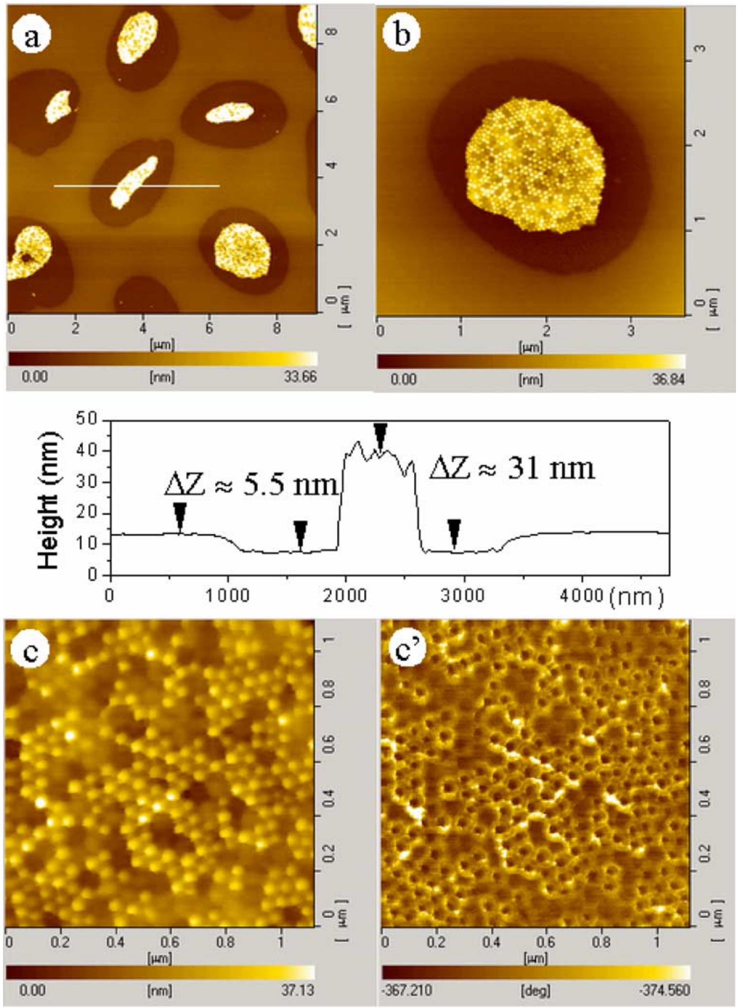

Fig. 5. AFM topographic (a, b and c) and phase (c′) images of PS-*b*-P4VP micelles film on mica surface treated in toluene for 20–30 s after water treatment for 6 h. The cross sectional line scan profile of (a) gives out the height of the island-like aggregate.

formed. Here, after treatment of 1 week, only isolated nanospheres of very low height were found in the holes (Fig. 6(h)).

During toluene treatment (selective solvent for PS), P4VP chains collapsed due to the incompatibility between P4VP and toluene ($\chi_{\mathrm{P4VP/toluene}} \approx 2.001$) and the cavities shrunk to form spheres. Whereas, PS chains extended in toluene due to the good compatibility between PS and toluene ($\chi_{\mathrm{PS/toluene}} = 0.347$) and moved to the film surface to decrease the toluene–P4VP interface energy (Fig. 6(g)). Furthermore, the incompatibility between the unlike PS and P4VP blocks [23] may have an important contribution to the morphology transformation. The incompatibility or the segregation strength in solutions largely normally depends on the solvent selectivity [24,25]. With treatment in toluene, the solvent selectivity is enhanced compared with the treatment in dry environment, and thus the intramolecular segregation is strengthened. Therefore, the strong incompatibility between the PS block and the P4VP block in toluene pushes the PS block away from the P4VP block [26]. As a result, the copolymer chains are highly stretched, leading to and increase in the sphere height (Fig. 5). It is clear that the height of the protruding spheres in Fig. 5(c) (∼31 nm) is much higher than that in Fig. 4(b) (∼2 nm). It indicates that the selectivity of solvent for PS corona has a major effect on the transformation of nanoscale cavities to densely packed spheres. The densely packed protruding spheres (Fig. 5) are similar to the initial micelle morphology (Fig. 1). But the reversibility was limited because the packing of micelles became poor and deteriorated. The formation of a very low depression (∼5.5 nm in height) around the densely packed protruding spheres (Fig. 5(a) and (b)) may be resulted by the protruding spherical PS coronae collecting some PS chains from their surroundings during the transformation of cavities to protruding spherical micelles.

4. Conclusion

In conclusion, morphology evolution of diblock

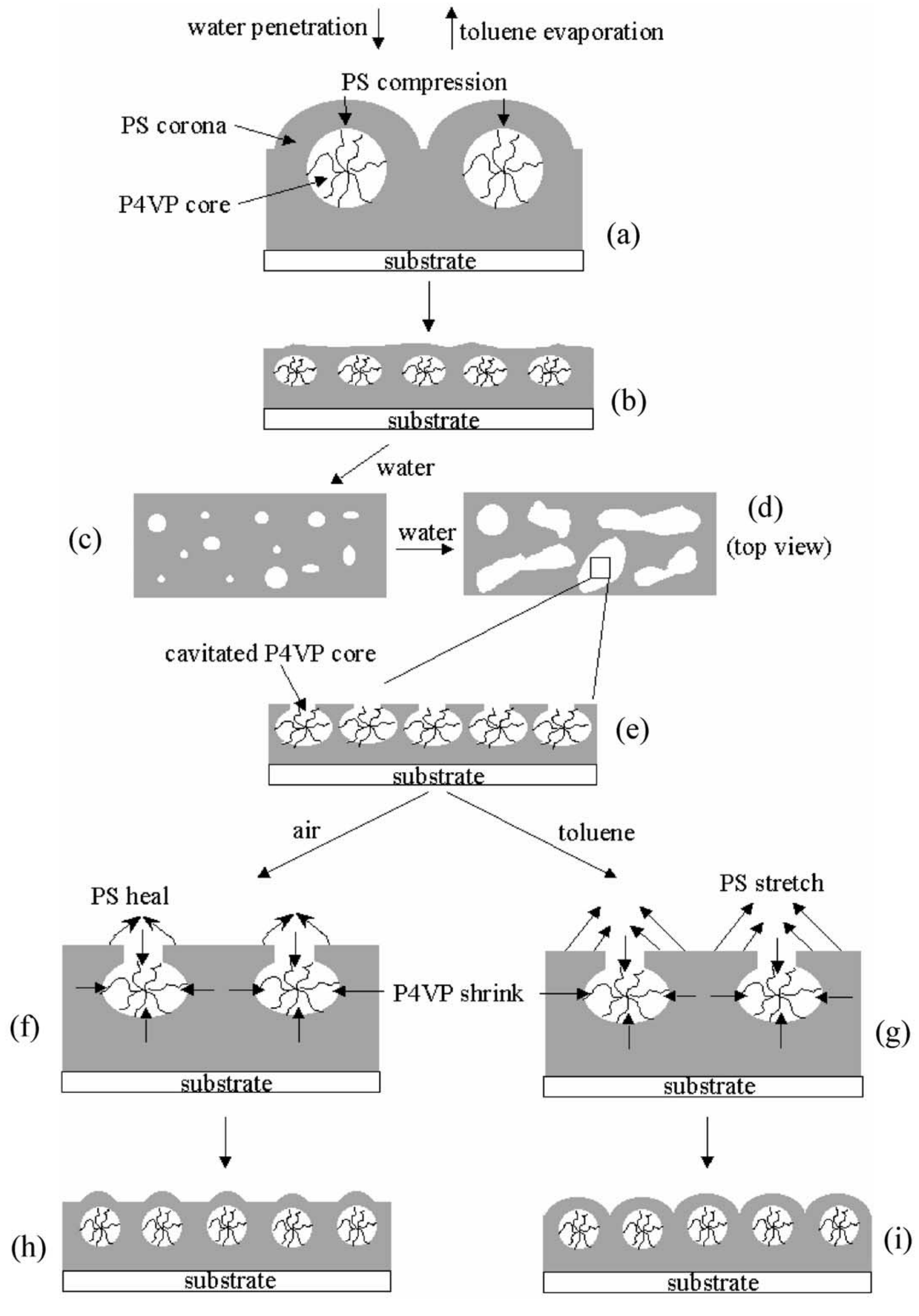

Fig. 6. Schematic illustration of water induced morphology evolution of PS-*b*-P4VP micelles film. The cast-films could be multilayers.

copolymer PS-*b*-P4VP micellar thin film drop-cast onto the mica surface in the presence of water was studied. The new morphology of surface holes with nanoscale cavities of hexagonal arrays was formed by water treatment for certain periods due to the swollen P4VP cores. The nanoscale surface cavities could be transformed into isolated nanospheres by PS healing in a dry environment or back to protruding densely packed spheres by toluene (selective solvent for PS coronae) treatment due to the incompatibility effect. The morphology evolution of micellar thin film strongly depends on the slow evaporation of toluene solvent and the swelling of P4VP cores in an atmosphere of high humidity, and the following movement of PS chains induced by air and toluene. The incompatibility between solvent and block, and that between the unlike blocks play an important role in the morphology evolution. The process presented here represents a simple method to create patterned surfaces by controlling the environmental condition (hydrophilic/water and hydrophobic/toluene), and the rate of solvent evaporation.

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