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1 **When a pH-triggered nanopatterned shape transition drives the**
2 **wettability of a hierarchically self-organized film: a bio-inspired**
3 **effect of “sea Anemone”**

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1 **Abstract**

2 **Hypothesis**

3 Hierarchically structured surfaces including sensitive materials presents the advantage to exalt
4 wettability variation due to the combination of micro structure effect directed by Cassie
5 Baxter and/or Wenzel behaviour which is tuned by the surface energy variation of sensitive
6 polymer films.

7 **Experiments**

8 Herein is reported the synthesis and the hierarchical structuration of a pH sensitive diblock
9 copolymer P(S-*stat*-MMA)-*b*-P4VP with a pH-sensitive Poly 4-vinylpyridine P4VP block.
10 Applying the Breath Figure method casting (minute time scale process), this diblock
11 copolymer allows to obtain a micro porous honeycomb film while a wall nano-structuration
12 due to self-assembly of diblock copolymer is observed.

13 **Findings**

14 The pH-triggered wettability is studied and correlated with the morphology evolution of
15 P4VP nano-domains investigated by AFM in a liquid cell. Indeed, a nano-dots to nano-
16 rings/donuts transition is highlighted when decreasing the pH below the pK_a of the P4VP.
17 This nano “sea Anemone” shape transition induces the macroscopic changes of the wettability
18 of a hierarchically self-organized honeycomb film, explained by the protonation of P4VP
19 chains inducing electrostatic repulsion and then hydrophilic surface.

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22

23 **Keywords:** Hierarchical structure, pH sensitive surface, wettability, micro and nano
24 structuration, Honeycomb film

1 Introduction

2 Sensitive materials able to switch properties according to different triggers as temperature,
3 pH, light [1,2] are widely developed for a large range of application as drug delivery,
4 antifogging, self-cleaning or tissue engineering [3,4]. Among them, the switch from
5 hydrophilic to hydrophobic form of polymeric surfaces is quite challenging and interesting
6 [5]. Different polymer families were identified as polyPEG or polyNIPAM sensitive to
7 temperature [6,7], polyazobenzene to light [8–11], polyamine to CO₂ [12–14] or polyacid and
8 polybase to pH [15–17]. However, in case of hydrophilic polymer, the problem of polymer
9 surface solubility in water appears, but can be overcome by using amphiphilic diblock
10 copolymers combining hydrophobic and switchable blocks, *i.e.* hydrophobic/hydrophilic,
11 respectively. Moreover, wettability effect can be enhanced using porous film by reducing the
12 contact surface and more particularly if the change from hydrophilic towards hydrophobic
13 forms is completed by a wettability transition from non-wetting Cassie Baxter to wetting
14 Wenzel states [18].

15 To combine these two effects, the present work consisted on the elaboration of a
16 hierarchically self-organized film presenting a double structure: the first one at the
17 macroscopic scale, as a porous honeycomb structure, and the second one at the nanoscale as
18 nano-segregation of a diblock copolymer. Herein, a fast bottom-up process based on solvent
19 evaporation in humid atmosphere, so-called “breath figure” process, was used to create the
20 first level of porosity. The directed self-assembly in “breath figure” templating of block
21 copolymers was then able to target the second one by using an amphiphilic diblock [15,19–
22 23]. A P4VP block was chosen as pH sensitive polymer for its ability to switch wettability
23 properties according to the media. Indeed, the protonation of pyridine moiety below its *pKa*
24 [24] introduces some intra/inter electrostatic repulsions in the polymers chains provoking
25 simultaneously a transition from a hydrophobic to hydrophilic surface and then a decrease of

1 the contact angle value. This macroscopic behaviour is attributed to the re-organization of the
2 P4VP nano-dots into nano-rings domains as a nano “sea Anemone” effect. Indeed, here the
3 mimicry between the nano to macroscopic scale is made by comparison of the
4 macromolecular chains and the sea anemone tentacles behaviors. The P4VP chains behaviour
5 can be compared to sea anemone tentacles which can be collapsed on its mouth, *i.e.* nano-dots
6 (Figure 1a & c), or stretched around the mouth, *i.e.* nano-rings (Figure 1b & d) just by a
7 modification of their close environment.

8

9 **Materials and methods**

10 To combine hierarchical structure and pH sensitive surface, the synthesis of an amphiphilic
11 diblock copolymer with hydrophilic P4VP and hydrophobic P(S-*stat*-MMA) blocks was
12 performed.

13 The Styrene S allowed a good control of the MMA polymerization [25]. Thus, a well-defined
14 high molar mass P(S-*stat*-MMA)-b-P4VP copolymer was synthesized by nitroxide-mediated
15 polymerization (NMP) [26] with a number average molecular weight M_n of 48,300 g.mol⁻¹
16 and a dispersity value \bar{D} of 1.29 with a symmetrical molar mass distribution (ESI Figure SI 1,
17 2 & 3). The final composition of the purified copolymer is of 78% of P(S-*stat*-MMA) and
18 22% P4VP in volume as measured by ¹H NMR in CDCl₃.

19 P(S-*stat*-MMA)-b-P4VP copolymer structure allowed manufacturing honeycomb films by the
20 “Breath Figure” method [27]. This method consisted on a fast evaporation of solvent under
21 humidity [28,29]. In case of amphiphilic diblock copolymer, polymer solution is casted on a
22 glass lamella and placed under humid air flow. While the solvent was evaporated
23 (endothermic phenomena), the temperature of the solution decreased and induced

1 condensation of surrounding humidity at the liquid/air interface. Thus, the hydrophilic part
2 allowed the stabilization of droplet while hydrophobic segment precipitated with water and
3 formed an anti-coalescence layer by a so-called “bag-effect”. Then, droplet self-organized in
4 hexagonal structure due to Bénard-Marangoni convection [30]. After total evaporation of the
5 solvent and water, a porous honeycomb structure was obtained by water droplet templating.

6 **Results and discussion**

7 **Hierarchical structure characterization**

8 *Micro structure: honeycomb porosity*

9 Micro structure of honeycomb films was checked by optical microscopy which revealed
10 porous surface (ESI Figure SI 5a). Thus, the different images allowed determining the surface
11 ratio of polymer using two methods. The first one, by manual measurement gave a pores
12 radius of 0.5 μm and a distance between two centres of pores of 1.6 μm . Then, using a basic
13 model considering a diamond joining four pores centre which represented an elementary mesh
14 of network, the surface fraction was done by the ratio between surface area (diamond - pore
15 area) and total area (diamond area). This model gave a value of surface fraction of 0.645
16 (Scheme 1). This value is comparable with the surface ratio of 0.65 ± 0.01 obtained with an
17 ImageJ threshold treatment describe in ESI.

18 *Nano structure: self-assembly of diblock copolymer*

19 The nano structure was investigated by AFM on continuous and honeycomb films (Figure 1 c
20 & e). Continuous films reveals a surface structuration characteristic of the nano-segregation
21 between P(S-*stat*-MMA) and P4VP blocks. On continuous films, characteristic length
22 between two nano-dots P4VP domains is 50 nm which is in accordance with molecular length
23 of two diblock copolymers containing around 500 units of monomers. Images obtained from
24 diblock copolymer honeycomb reveals a hierarchically structured organization. First of all,

1 micro porosity observed by optical microscopy is confirmed by AFM (Figure 1e).
2 Nevertheless, the principal aim of this characterization was to visualize the nano-segregation
3 of the block copolymer into the walls between pores (Figure 1e) which is similar with the
4 nano-structuration obtained on continuous films (Figure 1c).

5 **Surface properties**

6 Surface properties of materials were investigated by contact angle measurement. This method
7 allows comparing different states of materials wettability according to the variation of
8 composition or the macro-structuration of polymers. Considering a polymer “A” presenting a
9 contact angle value θ_A , the introduction of a second polymer “B” with a contact angle value
10 θ_B , led to a resulting contact angle θ dependent of the surface ratio of each polymers
11 according to the equation 1.

$$12 \quad \cos\theta = \varphi_A \cos\theta_A + \varphi_B \cos\theta_B \quad (\text{Equation 1})$$

13 In case of rough surfaces, the contact angle can be differently affected in accordance with
14 Cassie-Baxter or Wenzel models. The difference between these two models is due to the
15 physical behavior of the surface. With Wenzel model, the droplet covered the entire surface
16 and the contact angle θ^* is led by the roughness r ($r = \text{Surface area}/\text{Surface area projected on a}$
17 plane) and the Young contact angle θ (due to the chemical nature of polymer which can be
18 determined from a continuous film), for a final equation equal to $\cos\theta^* = r \cos\theta$. When the
19 roughness is higher enough, the energy needed to cover the surface is more important than the
20 energy with air in pore. Therefore, the droplet rests on the top of ruggedness and the residual
21 contact angle θ^* is led by the surface ratio of polymer φ_s and Young contact angle θ ,
22 corresponding to the Cassie-Baxter model:

$$23 \quad \cos\theta^* = -1 + \varphi_s (\cos\theta + 1) \quad (\text{Equation 2})$$

1

2 where φ_s is the area in contact with liquid / Total area.

3

4 *Continuous film wettability*

5 By contact angle investigation, an experimental φ_s (P4VP) = 0.19 was determined using
6 equation 3 with a contact angle of the diblock copolymer equal to 78° while P(S-*stat*-MMA)
7 and P4VP respectively presented contact angle values of 85° and 48°.

$$8 \quad \varphi_s(\text{P4VP}) = \frac{\cos \theta_{\text{copolymer}} - \cos \theta_{\text{P(S-stat-MMA)}}}{\cos \theta_{\text{P4VP}} - \cos \theta_{\text{P(S-stat-MMA)}}} \quad (\text{Equation 3})$$

9 This value was close to the value of the volume fraction (0.22) that testified that block
10 copolymer was uniformly distributed between bulk and surface. The pH effect on film surface
11 can be tuned by the protonation/deprotonation of the pyridine moiety of P4VP. Diblock
12 copolymer presents an increase of contact angle between 45° to 78° when increasing pH from
13 1 to 10 (Figure 2). This variation follows a typical titration curve with two plateau on both
14 sides of a transition state around pH 5. This last one is attributed to the P4VP pK_a value of
15 5.2. Indeed, above this value, deprotonated amino group are pre-dominant while protonated
16 forms appear below the pK_a . This protonation leads to the formation of a pyridinium salt
17 which possessed more affinities with water, *i.e.* much hydrophilic form, than deprotonated
18 one, *i.e.* much hydrophobic. Such behavior can explain the pH-triggered modulation of
19 wetting on the continuous film.

20 *Honeycomb film wettability*

21 Whatever the pH is, honeycomb films present contact angle upper than continuous films
22 which are lower than 90° (Figure 2). For contact angle values below than 90°, Wenzel model
23 predicts lower contact angle for porous films than continuous film (Young angle). So, this

1 model can't be applied for the present system. Considering Cassie-Baxter approach and
2 assuming to keep the same chemical nature of the surface from continuous film and in
3 between pores for honeycomb film, a theoretical value of θ^* can be determined assuming the
4 experimental θ value of a continuous film, φ_s of the porous film (0.65 ± 0.01) and the equation
5 2.

6 Theoretical and experimental values are in accordance for pH above 6 where a nice fit is
7 observed with the Cassie-Baxter model (Figure 2). However, below this value, the model
8 diverges from the experimental values which are much lower than the predicted ones. This
9 divergence occurs for the pH values reaching the pK_a of the P4VP and thus enhancing its
10 hydrophilic polyelectrolyte character. So, for the protonated copolymer, the Cassie-Baxter
11 model cannot be applied. Indeed, considering Cassie-Baxter model, the contact angle
12 experimental values lead to a φ_s of 0.83 while SEM images of a honeycomb film after
13 treatment at pH1 reveals a $\varphi_{s,pH1}$ of 0.63 ± 0.01 close to initial value $\varphi_{s,initial}$ of 0.65 ± 0.01 . The
14 non-variation of the surface fraction can be explained by the glassy state of the PMMA block
15 with a glass transition temperature T_g close to 100 °C. Therefore, the increase of the surface
16 fraction cannot be assigned to the modification of micro-structure but to the water penetration
17 into the pores without total wetting due to the air confinement, avoiding then to be in Wenzel
18 model. This phenomenon was already observed in case of pillared surfaces in which one
19 water droplet entering to structure without contact with bottom part due to air confinement
20 [31,32].

21 For fitting the experimental curve, to consider another model taking into account this
22 parameter and determining the depth of penetration of water into pores is necessary. A model
23 is proposed and used considering the hypothesis that pores were in contact as describe in
24 Scheme 1. So, the pore radius (R) is determined as the half of the distance between to center
25 of pores (d). Thus, it is possible to calculate the pore depth ($2R-h$) where h is the height of

1 virtual dome covering the pore and dictated by $h = R - \sqrt{R^2 - r^2}$ where r corresponds to the
2 radius of virtual dome. The surface fraction φ_s is then calculated by equation 4.

$$3 \quad \varphi_s = \frac{S_{SA} + S_{WSIP}}{S_{SA} + S_{WSIP} + S_{AC}} \quad (\text{Equation 4})$$

4 where S_{SA} is the polymer surface area (top of the film), S_{WSIP} the wetting surface into pore and
5 S_{AC} the air contact area.

6 In this equation, the polymer surface area is constant, but wetting surface into pore and air
7 contact area depends of the penetration depth (p). Expression of wetting surface into pore and
8 air contact area are different if the penetration is higher ($p < R-h$) or lower ($p > R-h$) than the
9 pore diameter. These two behaviours are given by equations 5; 6 and 7; 8 (Scheme 1),
10 respectively. Using equation 4, 5, 6, 7 and 8, the φ_s versus the penetration depth can be drawn
11 (ESI Figure SI 4). Experimental values of contact angle give an experimental $\varphi_s = 0.83$,
12 corresponding to a penetration depth of 1.04 μm . Consequently, the height of air in bottom of
13 pore is estimated to be around 400 nm.

14 The pH-triggered effect on the surface wettability of the microscopic structure is well
15 understood, but we also wanted to focus on the nanostructure impact by AFM with liquid cell
16 at different pH.

17 *pH effect on P4VP nano domains*

18 In case of continuous films, the contact angle values are close to the non-treated films for high
19 pH, as explained by equation 2. Indeed, a media at pH 10 does not modify the structure of the
20 diblock copolymer self-assembly. Image of the immersed surface reveals a *hexagonal-close-*
21 *packed hcp* pattern with a characteristic distance of 50 nm between P4VP nano-domains
22 (Figure 1c). However, at pH 1 the domains of P4VP are protonated, showing up a shape

1 transition to nano-rings or nano-donuts, as a nano "sea anemone" effect (Figure 1d). Even if
2 the surface structure seems to be totally different from pH10 to pH1, a similar hexagonal
3 nano-pattern is observed in both cases with a characteristic distance between nano-donuts
4 center of 50 nm (Figure 1i). This shape transition of the P4VP nano-domains is attributed to
5 the protonation of P4VP inducing a quaternization and the appearance of positive charges
6 along macromolecular chain [33]. Thus, inter and intra macromolecular chain repulsions are
7 created and provoke the nano-holes at the center of P4VP domains (Figure 1g & h). The chain
8 stretching in the 3D directions induces a decrease of the external distance between P4VP
9 nano-donuts which seem to be almost in contact (Figure 1f & i). A concomitant effect is the
10 strong increase of the height of the P4VP nano-domains to deep holes inside the nano-donuts,
11 from 3 nm at pH=10 to 8 nm at pH=1, respectively (Figure 1i). The P4VP chains stretching
12 by a 2.5 times can be associated to a transition from a collapsed polymer brush in a non-
13 solvent to an extended polymer brush in a good solvent [34]. This pH-triggered shape
14 transition lead to an increase of P4VP surface ratio which can be determined by using the
15 experimental contact angle values in equation 3. The calculated surface ratio of P4VP is then
16 equal to 0.65 (0.19 at pH 10), considering P4VP totally protonated at pH = 1 and its
17 homopolymer contact angle close to 0 ($\cos(\theta_{\text{protonated P4VP}})$ close to 1).

18 Same phenomena were observed on honeycombs films with a switch of morphology into wall
19 (between pores) from self-assembled *hcp* nano-dots pattern to organized nano-donuts pattern
20 for pH above and below pK_a , respectively (Figure 1e & f respectively pH 10 & pH1 and ESI
21 Figure SI 5 b, c & d, respectively pH 8, pH 6 & pH 4)).

22 Correlation between the macroscopic and nanoscopic observations allow to well-understand
23 the water penetration into the pores covered by P4VP at low pH. Indeed, growing of P4VP
24 surface ratio lead to a total modification of surface properties and explained the large decrease

1 of the contact angle values for pH below pK_a leading to the gap with Cassie Baxter state
2 towards a Wenzel state³³.

3

4 **Conclusions**

5 In the large area of sensitive surface material already reported in literature [6-17], this work
6 describes the synergy of pH-triggered properties and hierarchal structure obtained using the
7 directed self-assembly in "breath figure" templating of a P(S-*stat*-MMA)-*b*-P4VP block
8 copolymers. This copolymer, with a high χ value close to 6.5 between the P(S-*stat*-MMA)
9 and the pH-sensitive P4VP blocks, drives the formation of the self-assembled P4VP nano-dots
10 into the walls between the micropores and leads to a nano-patterned honeycomb film, as a
11 hierarchically structured surface. Then, a pH sweep from 10 to 1 allows to trigger the
12 wettability of the honeycomb film and reveals a transition from a Cassie Baxter model
13 towards a model considering a partial water penetration into the pores below the P4VP pK_a .
14 The variation of the wettability properties of P4VP material based is enhanced by the
15 roughness effect induced by the hierarchical organization. This switch of model is explained
16 by AFM observations in liquid cell which revealed an increase of surface ratio of P4VP at low
17 pH. Indeed, due to the intra and inter electrostatic repulsion between P4VP chains, a shape
18 transition from nano-dots to nano-donuts is observed as a nano "sea anemone" effect without
19 affecting the surface ratio but provokes the increase of the hydrophilicity of the surface and a
20 better wettability. This pH effect on porous film was already observed for other pH sensitive
21 polymer like PAA [17] and a polypeptide [16], but going beyond the synthesis of a new
22 diblock copolymer presenting a pH-triggered hierarchical structure, this work established the
23 correlation of the variation of polymer nano domains from nano dots to nano "sea anemone"
24 shape leading to the macroscopic variation of the contact angle. This pH sensitive porous

1 material opens a large range of application as adsorption/desorption of species according to
2 pH, use P4VP as a precursor of gold salt reduction or for example use it as grafting function
3 [36] to fix some specific species. For the two last applications, according to pH applied, the
4 morphology of the grafted species can be dots or nano rings.

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8 **Conflicts of interest**

9 The authors declare no conflict/competing interest

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1 Figures and Scheme captions

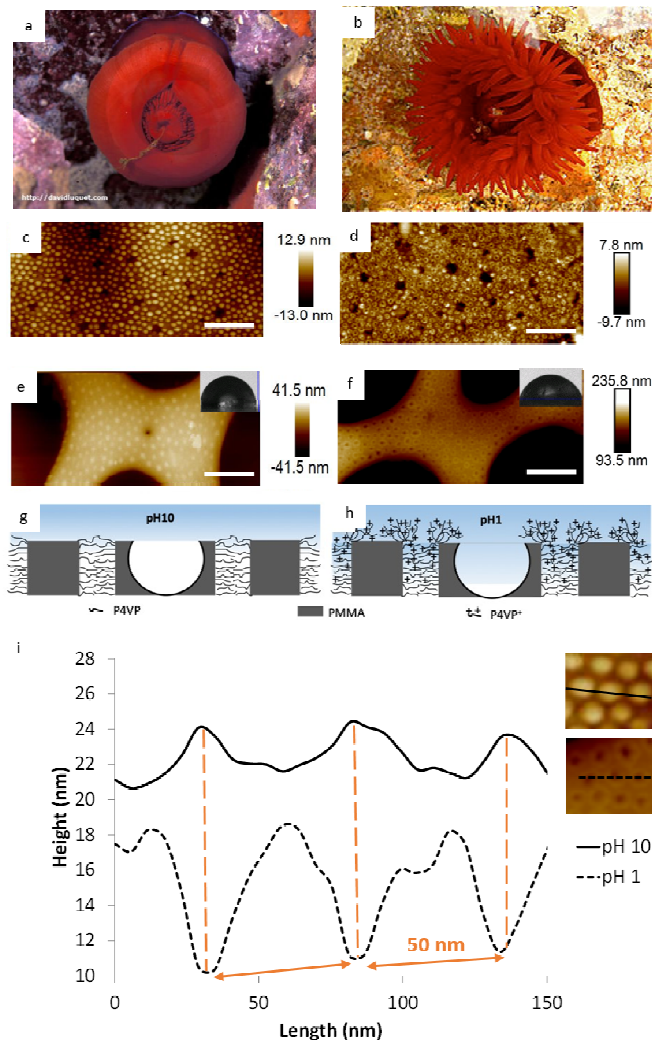


Figure 1 – Sea anemone pictures with collapsed (a) and stretched (b) tentacles. AFM height profile microscopy images (scale bar = 300nm) of continuous film at pH 10 (c) and pH 1 (d) and of honeycomb film at pH 10 (e) pH 1 (f). Schematic representation of neutral and protonated P4VP (g and h). Height & distance profile of P(MMA-stat-S)-b-P4VP nano self-assembly at pH 10 (full line) and pH 1 (dotted line) (i).

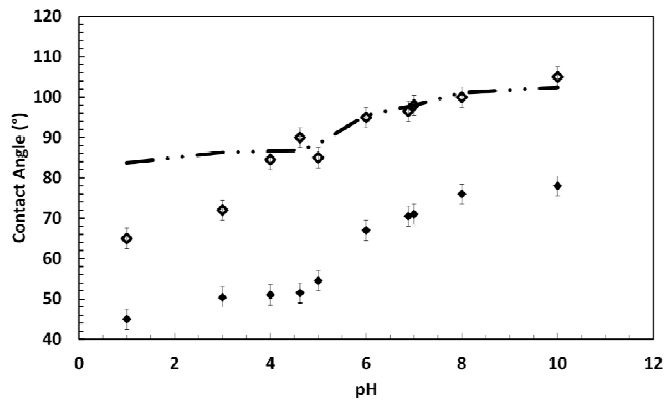
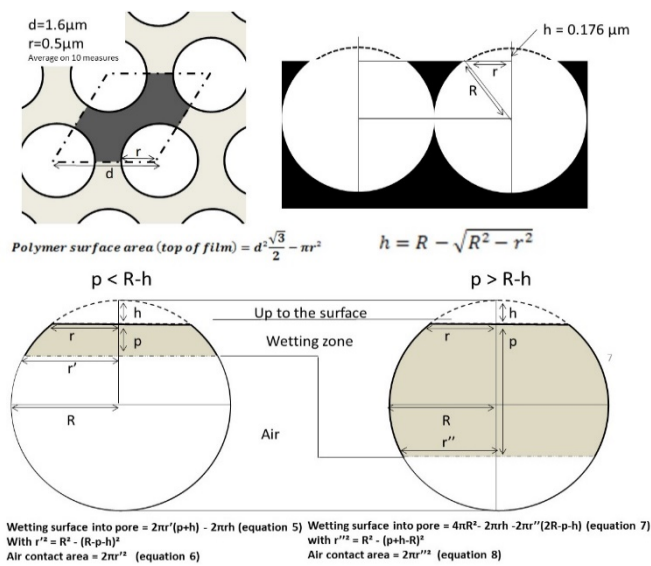


Figure 2 - Contact angle evolution with pH for continuous films (full diamonds) and honeycomb films (empty diamonds). Theoretical value of θ^* according to Cassie-Baxter model (dotted line).

1



Scheme 1 - Schematic representation of pores with characteristic distances and area used for model applicable in equation 4.

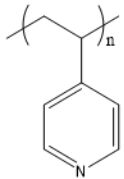
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P4VP



P4VP⁺

