

# CONTROLLING DIBLOCK COPOLYMER NANOPATTERNING AND NANOPOROSITY ON SURFACES USING SMALL MOLECULES

A. Laforge, D. Gaspard, C. G. Bazuin and R. E. Prud'homme

Département de chimie, Université de Montréal, C.P. 6128 succ. Centre-ville, Montréal (QC), Canada H3C 3J7

## Introduction

The achievement of regular nanoscopic functional patterns on various surfaces is a key issue for numerous applications including nanolithography, catalysis, data storage, optics, and nanoelectronics.<sup>1,2,3,4,5</sup> Block copolymers,<sup>6</sup> which have been widely studied in the bulk,<sup>7</sup> in solution,<sup>8</sup> and as thin films,<sup>9,10</sup> are well known to self-assemble into meso- and nanoscale structures. A major challenge is obtaining and controlling long-range order and orientation of the nanostructured patterns. To achieve this in block copolymer thin films, various strategies have been developed. Among these, a strategy that combines supramolecular chemistry with block copolymer self-assembly provides a rather simple technique for controlling the formation of well-defined nanostructures in bulk<sup>11,12,13</sup> and in thin films.<sup>14,15,16,17</sup> This approach associates low molar mass substances with one of the blocks by non-covalent interactions.

We have applied the supramolecular approach to thin films of PS4VP block copolymers of high molar mass (about 100,000) and relatively high 4VP block weight fraction (about 30%). The 4VP block is "complexed" in THF solution with small molecules that hydrogen-bond to 4VP, notably, ditopic 1,5-dihydroxy-naphthalene (DHN), and, more recently, monotopic naphthol and naphthoic acid. The latter two differ only by the functional group, hydroxy versus carboxylic acid.

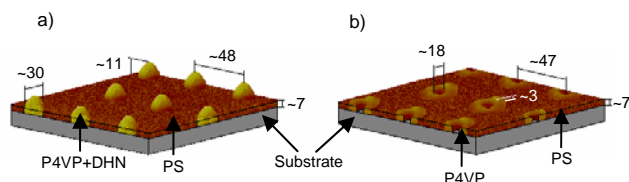
## Experimental Section

**Materials.** The block copolymer poly(styrene-*b*-4-vinylpyridine) (PS4VP), with  $M_n = 71900$  g/mol for PS and 30200 g/mol for P4VP and  $M_w/M_n = 1.08$  for PS and 1.13 for both blocks, was purchased from Polymer Source and used as received. 1,5-Dihydroxynaphthalene (DHN) (97%) was purchased from Aldrich, filtered in acetone using 0.45  $\mu\text{m}$  PTFE filters and recrystallized from acetone/hexane (50/50 v/v). Naphthol (>99%) and naphthoic acid (>97%) were obtained from Aldrich and Fluka, respectively, and used as received. Tetrahydrofuran (THF, 99.9%) and methanol (99.9%) were purchased from VWR and filtered twice with 0.2  $\mu\text{m}$  PTFE filters before use.

**Sample Preparation.** To obtain the supramolecular assembly, the copolymer and small molecule were dissolved together in THF at a constant copolymer concentration of 0.5 wt %. For DHN, solutions were prepared at various DHN to copolymer ratios (specified as moles of DHN molecules relative to the VP moieties); for the other two molecules, the solutions were equimolar with respect to VP. The solutions were stirred at ca. 70 °C overnight in closed vials to ensure homogeneous mixing of the components. They were filtered with 0.2  $\mu\text{m}$  PTFE filters just before use. The substrates were dip-coated by vertically immersing them into the solution at a rate of 10 mm/min, followed by a 20 s pause, and then withdrawal of the substrate from the solution at a rate of 5 mm/min (unless otherwise specified). To remove the small molecule, the coated substrates were immersed in methanol for 30 min, dried under nitrogen flow and then in a vacuum oven at 80 °C for 5 min to ensure complete methanol evaporation. The concentration of 0.5 wt % copolymer was found to give a film of uniform thickness over the entire surface of the substrate for equimolar DHN:4VP compositions.

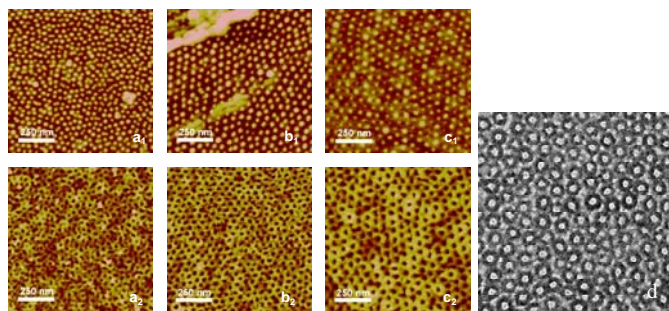
## Results and Discussion

Infrared spectroscopy showed that hydrogen-bonding of the small molecules to the 4VP block indeed occurred, and that rinsing of the dip-coated film by MeOH removed the small molecules completely. AFM, TEM of I<sub>2</sub>-stained films, water contact angle and cyclic voltammetry analyses of films dip-coated from a solution of PS4VP and DHN in 1:1 DHN:4VP ratio lead to the picture shown by the representations given in Figure 1 (see ref. 18 for details). The as-deposited films show a quasi-hexagonal array of nodules composed of P4VP and DHN that protrude above and penetrate a PS matrix. After rinsing in MeOH, a selective solvent for P4VP and DHN, the DHN is removed, leaving nanopores. Subsequently, a study was made of the effect of varying the DHN:4VP ratio in the solution from which the films were dip-coated.



**Figure 1.** Schematic representations of the nanostructured PS4VP+DHN (1:1) film (a) as deposited and (b) after immersion in MeOH to eliminate DHN. All data in nm. For clarity, the nanostructures have been laterally aerated. The PS covering the nodules in (a), the ultrathin layer of P4VP covering the PS matrix in (b), and an ultrathin P4VP wetting layer at the interface with the substrate are not shown.

Figure 2 (a-c) gives AFM height images of films deposited from solutions of different DHN:4VP ratios before and after DHN removal. At a DHN:4VP ratio of 1:2, the complex is stoichiometric with respect to the functional groups (OH:VP). The AFM images for this composition (Figure 2a<sub>1</sub>) show nodules that, compared to the 1:1 composition,<sup>18</sup> are closer together, are smaller on average, have greater size dispersity (with some fused into larger domains) and appear to have greater lateral disorder. After DHN removal (Figure 2a<sub>2</sub>), they are replaced by pores, still with significant lateral disorder and variability in sizes and shapes, including some lateral channels. These observations suggest that more DHN is necessary to obtain well-ordered patterns. Given the bifunctionality of DHN, it is possible that this is related, at least in part, to a physical crosslinking phenomenon that is, in principle, present for DHN:VP molar ratios below 1:1.



**Figure 2.** (a)-(c) AFM height images of PS4VP+DHN thin films dip-coated on silicon, as deposited (subscript<sub>1</sub>) and after rinsing by MeOH to remove DHN (subscript<sub>2</sub>). DHN:4VP molar ratios in solution: (a) 1:2, (b) 2:1, (c) 4:1. AFM height scale: 0-20 nm. (d) TEM image of the film dip-coated from the 4:1 solution, after removal of DHN and staining by I<sub>2</sub>.

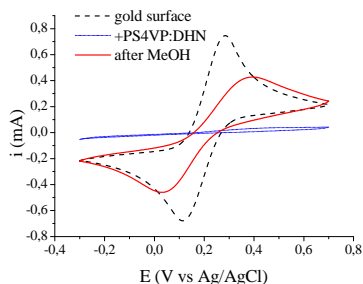
At a molar ratio of 2:1, the DHN molecules are present in excess relative to the pyridine moieties. The large white areas on parts of the film surface in Figure 2b<sub>1</sub> (also observed in TEM) are indicative of some phase separation. However, it did not interfere with the block copolymer deposition process, and, as shown in Figure 2b<sub>2</sub>, a regular pore pattern is obtained after DHN removal (the phase-separated areas also being removed by methanol rinsing). The geometric dimensions of the nanostructures are similar to those obtained with the 1:1 ratio, with a small increase in the average pore diameter and depth and in film thickness. In addition, no lips around the pores are visible. These results suggest that, despite phase separation of a fraction of the DHN, a somewhat greater than stoichiometric amount of DHN was incorporated into the P4VP phase, and had some influence on the structural parameters.

Much greater effects were obtained with the 4:1 molar ratio (Figure 2c). In this case, we were able to obtain deposited films showing no DHN phase separation on the surface. This implies that it is possible to incorporate a large excess of DHN in the P4VP phase (although it cannot be affirmed that the molar ratio in the deposited film is actually 4:1). Despite the large increase in weight fraction of the P4VP+DHN phase (75% if all the DHN is incorporated), TEM imaging shows that the morphology of the deposited film remains in the form of P4VP+DHN nodules (stained by I<sub>2</sub>) in a PS matrix (unstained). The periodicity of the nodules is significantly greater than for the other compositions, at about 70-80 nm. The film thickness at the matrix level is approximately doubled compared to the 1:1 and 2:1 ratios; however, the

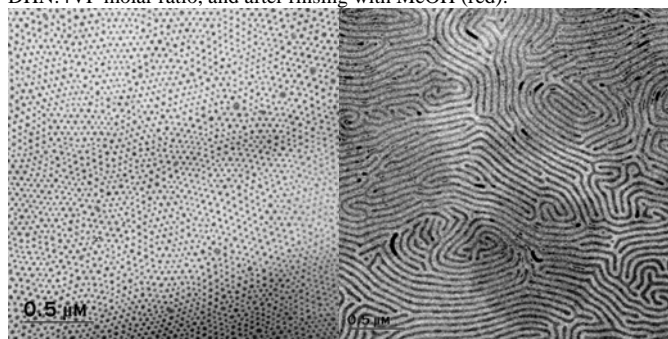
protrusion of the nodules is less, such that the total film thickness (at the nodule tops) is only moderately increased. The notable increase in the film thickness at the PS level with increase in DHN:4VP molar ratio above 1:1 suggests that the preference of THF for the PS phase is reduced by DHN in excess. Combining this with what was noted for the 1:1 ratio and the copolymer with no DHN added,<sup>18</sup> it appears that, whereas complexation of the P4VP block by DHN reduces the relative solubility of this block in THF, an excess of DHN beyond equimolar reverses this trend. An analogous effect is observed in aqueous solutions of polyelectrolytes with oppositely charged surfactants, where there is precipitation in the vicinity of stoichiometric compositions and resolubilization occurs as excess surfactant is added.<sup>19</sup>

After DHN removal, AFM images (Figure 2c<sub>2</sub>) show the pore-like surface morphology, which, by the absence of distinct lips around the pores, is similar to that for the 2:1 ratio. The corresponding TEM images (Figure 2d) of the I<sub>2</sub>-stained film are particularly revealing. The white-colored pores are very well defined, and are clearly delimited by a dark ring (indicating the location of stained P4VP). Thus, the P4VP phase appears to be strongly concentrated around the pores. The pore diameter is much greater than for the 1:1 molar ratio, as would be expected from the elimination of a much greater amount of DHN, and the pore depth appears to match the film thickness, suggesting complete or almost complete penetration of the film (despite its much greater thickness compared to the lower molar ratios).

Cyclic voltammetry (CV) measurements of the MeOH-rinsed 4:1 film deposited on a gold substrate indicate that the pores penetrate sufficiently deeply to permit electrochemistry (Figure 3), which was not observed for the 1:1 and 2:1 films.<sup>18</sup> The increased potential difference in the redox peaks for the rinsed film compared to bare gold is attributed to an electron tunneling mechanism through an ultrathin layer of copolymer remaining at the bottom of the pores. Calculation based on the CV results indicates a thickness of 1.3–2.5 nm for this residual surface layer.<sup>18</sup>



**Figure 3.** Cyclic voltammograms of  $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$  on gold substrates before (black) and after (blue) coating from a PS4VP solution of 4:1 DHN:4VP molar ratio, and after rinsing with MeOH (red).



**Figure 4.** TEM images of dip-coated films obtained from THF solutions of PS4VP and naphthol (left) and of PS4VP and naphthoic acid (right), for equimolar ratios of small molecule to 4VP.

This study using DHN was followed up by investigations with other hydrogen-bonding small molecules. In particular, two monotopic molecules,

naphthol and naphthoic acid, which differ only by the hydrogen-bonding group – OH versus COOH – were used in the place of DHN. As shown in Figure 4, dip-coated films from equimolar small-molecule:4VP solutions of identical concentration and using identical dip-coating conditions (substrate withdrawal speed of 2 and 3 mm/min) lead to drastically different film morphologies. The use of naphthol leads to the quasi-hexagonally ordered nodular film as above for DHN, whereas the use of naphthoic acid (NA) leads to the fingerprint morphology of alternating PS and P4VP+NA. Furthermore, a change of solvent to chloroform when using naphthol gives the fingerprint morphology, whereas a change of solvent to dioxane when using NA leads to the nodular morphology. On the other hand, when the substrate withdrawal speed is reduced to 0.5 mm/min, NA-containing solutions do lead to films with the nodular morphology. We are currently investigating these phenomena in detail, and will report our findings at the meeting.

## Conclusions

In the present contribution, we have shown that a high molar mass, asymmetric PS4VP block copolymer (about 100,000 g/mol and 30 wt % VP) gives a dip-coated film with quasi-hexagonal nodular morphology of enriched P4VP in a PS matrix, using a ditopic molecule (DHN) in THF solution. Rinsing with methanol gives a nanoporous film, with the pores penetrating close to the surface only for sufficient excess of DHN (relative to 4VP), as shown by cyclic voltammetry. The use of naphthol similarly leads to a nodular morphology. However, naphthoic acid gives a fingerprint morphology from THF solution, unless the substrate withdrawal speed is reduced drastically. This indicates that the choice of small molecule, in addition to the solvent and substrate withdrawal speed, can be used to manipulate the morphology of the deposited film.

## References

- (1) Hamley, I. W. *Nanotechnology* **2003**, *14*, R39.
- (2) Park, C.; Yoon, J.; Thomas, E. L. *Polymer* **2003**, *44*, 6725.
- (3) Mendes, P. M.; Preece, J. A. *Curr. Opin. Coll. Interf. Sci.* **2004**, *9*, 236.
- (4) Glass, R.; Möller, M.; Spatz, J. P. *Nanotechnology* **2003**, *14*, 1153.
- (5) Krausch, G.; Magerle, R. *Adv. Mater.* **2002**, *14*, 1579.
- (6) Hamley, I. W. *The Physics of Block Copolymers*. Oxford: Oxford University Press, 1998.
- (7) Abetz, V.; Simon, P. F. W. *Adv. Polym. Sci.* **2005**, *189*, 125.
- (8) Gohy, J.-F. *Adv. Polym. Sci.* **2005**, *190*, 65.
- (9) Li, M.; Coenjarts, C.; Ober, C. K. *Adv. Polym. Sci.* **2005**, *190*, 183.
- (10) Green, P. F.; Limary, R. *Adv. Coll. Interf. Sci.* **2001**, *94*, 53.
- (11) (a) Ruokolainen, J.; Mäkinen, R.; Torkkeli, M.; Mäkelä, T.; Serimaa, R.; ten Brinke, G.; Ikkala, O. *Science* **1998**, *280*, 557. (b) Ruokolainen, J.; Saariaho, M.; Ikkala, O.; ten Brinke, G.; Thomas, E. L.; Torkkeli, M.; Serimaa, R. *Macromolecules* **1999**, *32*, 1152. (c) Bondzic, S.; de Wit, J.; Polushkin, E.; Schouten, A. J.; ten Brinke, G.; Ruokolainen, J.; Ikkala, O.; Dolbnya, I.; Bras, W. *Macromolecules* **2004**, *37*, 9517.
- (12) Hong, J.-Y.; Hong, J.-L. *J. Polym. Res.* **2004**, *11*, 89.
- (13) (a) Fahmi, A. W.; Braun, H.-G.; Stamm, M. *Adv. Mater.* **2003**, *15*, 1201. (b) Fahmi, A. W.; Brünig, H.; Weidisch, R.; Stamm, M. *Macromol. Mater. Eng.* **2005**, *290*, 136.
- (14) (a) Sidorenko, A.; Tokarev, I.; Minko, S.; Stamm, M. *J. Am. Chem. Soc.* **2003**, *125*, 12211. (b) Tokarev, I.; Krenek, R.; Burkov, Y.; Schmeisser, D.; Sidorenko, A.; Minko, S.; Stamm, M. *Macromolecules* **2005**, *38*, 507.
- (15) Liang, C.; Hong, K.; Guiochon, G. A.; Mays, J. W.; Dai, S. *Angew. Chem.* **2004**, *116*, 5909.
- (16) Lu, Q.; Bazuin, C. G. *Nano Lett.* **2005**, *5*, 1309.
- (17) Jeong, U.; Ryu, D. Y.; Kim, J. K.; Kim, D. H.; Wu, X.; Russell, T. P. *Macromolecules* **2003**, *36*, 10126.
- (18) Laforgue, A.; Bazuin, C. G.; Prud'homme, R. E. *Macromolecules* **2006**, *39*, 6473.
- (19) Goddard, E. D. In "Interactions of Surfactants with Polymers and Proteins"; Goddard, E. D. and Ananthapadmanabhan, K. P., eds. Boca Raton: CRC Press, 1993; Ch. 4, p. 177.