NANO
LETTERS

2001
Vol. 1, No. 12
735−738

Nanoscale Polypyrrole Patterns Using Block Copolymer Surface Micelles as Templates

Michal Goren[†] **and R. Bruce Lennox***[,†]

Department of Chemistry, McGill University,
801 Sherbrooke Street West, Montreal, QC H3A-2K6

Received September 19, 2001

ABSTRACT

Arrays of polypyrrole (Ppy) dots (80–180 nm diameter) have been prepared in a highly parallel fashion. This process is achieved by templating Ppy growth on a 2D surface micelle array, initially formed by the Langmuir–Blodgett (LB) technique. Ppy growth on self-assembled (SA)-based surface micelles produces more complex structures, due to simultaneous reorganization of the SA micelles. These results demonstrate that template growth of conducting polymers can be used to fabricate configurations that are otherwise inaccessible.

The deposition and subsequent patterning of thin films of conjugated and conducting polymers is of great interest in micromechanical[1] and microelectronic applications.[2] A number of challenges have made the sequence of film formation and patterning difficult to realize, especially on the nanoscale. For example, the processability of conducting polymers is a major problem and has necessitated the use of novel monomer and dopant derivatization strategies.[3,4] Once a processable material is on hand using these strategies, the subsequent deposition methods such as spin coating and solution casting often compromise the performance of the resulting material. Films of conducting polymers have been transformed into patterned arrays by using photolithography techniques[5] or “soft” lithography techniques.[6] In the former, processing steps involving irradiation and solvent dissolution can be incompatible with the desired properties of conjugated polymers. In the latter, (micro)contact and (micro)injection molding tend to be compatible with the desired performance, but the feature sizes possible are usually modest (generally in the micrometer range). The soft lithography techniques have the advantage of being highly parallel in a preparative sense. Techniques that yield feature resolution in the desired nanometer range (such as inkjet[7] and SPM techniques[8]) tend, however, to be serial in nature. Access to a conducting polymer fabrication process that is parallel in nature, has nanoscale feature sizes, *and* yields a material with desired performance characteristics is therefore a real challenge.

Recognizing the difficulties in combining processibility and lithography compatibilities, we have combined two systems to produce nanoscale Ppy features in a parallel fashion. The two systems, each much studied in our laboratory, are block copolymer surface micelle arrays formed by both LB and SA techniques[9,10] and the selective templated growth of conducting polymers.[11,12]

Arrays of surface micelles can be formed via the LB deposition technique (AB diblock copolymers first deposited on a water surface[9]) or via SA (AB diblock copolymers deposited on mica and Si/SiOx surfaces[10]). The resulting array is then used as the reaction template. In regard to the aggregates formed on the water surface, a number of PS (A-block)-based diblocks (B-block = PEO, PVP, $RPVP^+$, PMMA, *n*-BuMA, etc.) have been shown to spontaneously form circular aggregates containing ca. 100 unimers when formed on a water surface and subsequently deposited as an LB film onto a solid surface. A symmetric diblock of MW ca. 1×10^5, for example, forms aggregates with a PS core (ca. 80 nm wide, ca. 5 nm high[13]) and a B-block corona (ca. 80 nm wide, ca. 1 nm high[14]). The dependence of surface micelle dimensions on A and B block sizes suggests that the differentiation between core and corona is sharp and probably occurs at most over a few nanometers. Aggregates formed directly on a mica or a Si/SiO_x surface are of a size similar to those formed on water. However, the aggregates in this case are believed to be chemically inverted (cf. those formed on water) and lie on an intermediary diblock brush rather than directly on the substrate surface.

Ppy growth has been shown to be kinetically preferred on hydrophobic vs hydrophilic surfaces[15,16] or the edges vs surfaces of complex lipid structures.[11,12] The highly defined chemical contrast of the cores and coronas of the A−B diblock surface micelles and the preferential growth of Ppy

---

* To whom correspondence can be addressed.
[†] E-mail: Bruce.Lennox@mcgill.ca and goren@chemistry.mcgill.ca.

10.1021/nl015630t CCC: $20.00

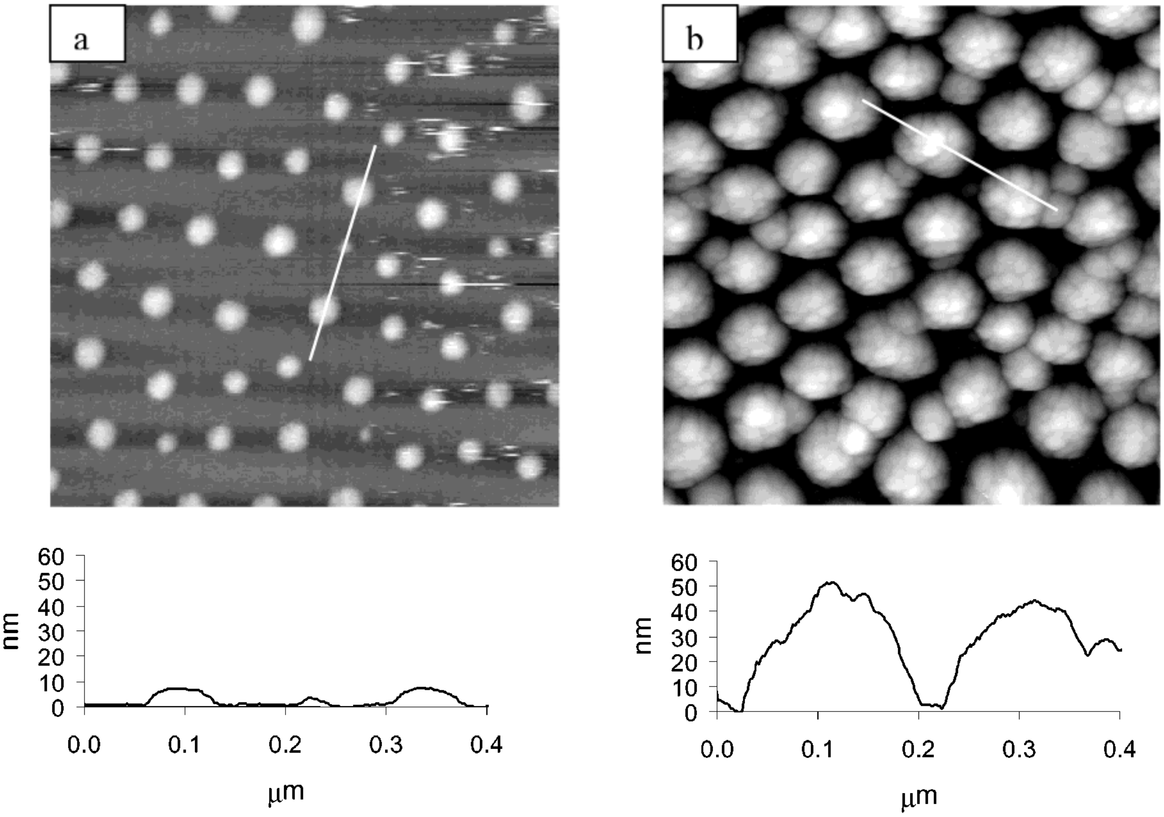

Figure 1. AFM (topology) images of the evolution of Ppy deposition on LB films as a function of polymerization reaction time: LB film (a) before Ppy deposition and (b) after 60 min of Ppy polymerization. Each LB film was formed on a freshly cleaved mica substrate. Image size: 1 μm × 1 μm.

on hydrophobic vs hydrophilic surfaces led us to explore their use as reaction templates.

To this end, block copolymers of polystyrene-*b*-poly(2-vinylpyridine) (PS_{580}-*b*-$P2VP_{450}$; Polymer Sources, Dorval, Canada) were deposited as Langmuir−Blodgett films onto freshly cleaved mica (Canemco Inc., Canada). In a typical experiment, 100 μL of a 0.5 mg/mL block copolymer solution (in $CHCl_3$) was spread on a pure water (MilliQ, 18 MΩ resistivity) surface. Twenty minutes elapsed before compression (KSV Langmuir film balance, Model 3000) was initiated. The LB film deposition was performed at 2 mN/m, a surface pressure at which these and related materials are well established to transfer as well-separated surface micelles.[9] Polypyrrole was synthesized in the presence of the LB-coated solid supports via chemical oxidation as per Huang et al.[15] The oxidative polymerization solution (0.5 mL of 0.2 M $(NH_4)_2S_2O_8$ in 100 mL of MilliQ water to which 30 μL of freshly purified pyrrole[17] was added) was mixed for 1 min. The solid substrates were placed vertically in the solution for 5, 10, 30, 60, or 150 min. After the designated reaction time, the substrates were removed, washed with MilliQ water, and air-dried overnight. The resulting samples were then imaged using noncontact AFM (Park Scientific Autoprobe CP) and tapping mode (Digital Instruments, multimode). Silicon cantilevers (Ultralevers, 0.6−1.0 μm thick, resonant frequency ca. 45 kHz; Park Scientific) were used in noncontact mode, and silicon cantilevers (3.5−5.0 μm thick, Digital Instruments, resonant frequency of ca. 280 kHz) were used in the intermittent contact mode.

Figure 1 provides two AFM images obtained as a function of polymerization time. The surface micelle array is little-changed by exposure to the aqueous solution. Short time (5, 15 min) exposure to Ppy growth conditions leads to the formation of small (20−30 nm) spheres adhering to the PS cores. A definitive assignment of Ppy formation is not warranted, however, given the scale of the surface micelle array itself and because a control experiment involving samples exposed to water yields similar features appearing on the PS cores. However, longer reaction times (≥30 min) lead to notable changes not observed in control experiments. Ppy domains formed on the PS cores are readily apparent in the AFM images (Figure 1). This is as per expectations of preferential growth on PS cf. P2VP.[15,16] Well-spaced Ppy domains, clearly conformally grown on the PS cores, are apparent after 30 min reaction time. The Ppy growth is occurring in both vertical and horizontal directions with respect to the substrate, as the feature dimensions clearly change: height ca. 7 nm, edge-to-edge distance ca. 80 nm changes to ca. 20 and 50 nm, respectively. Further reaction time (60 min) leads to additional growth (ca. 50 nm high, edge-to-edge distance ca. 15 nm), and the Ppy domains remain clearly differentiated. Arrays of Ppy dots can thus be prepared by a relatively simple sequence of LB deposition followed by the chemical polymerization of pyrrole.

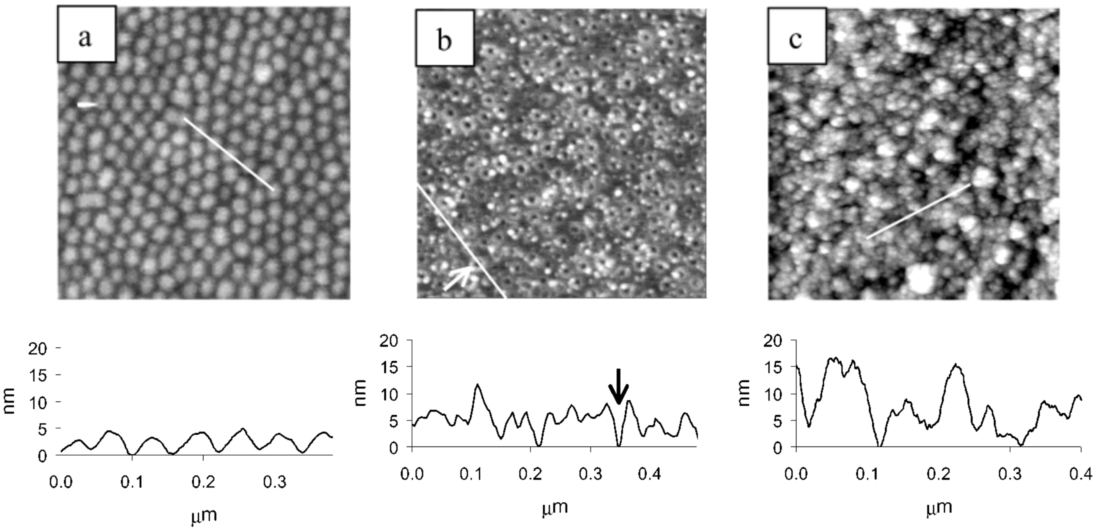

Figure 2. AFM (topology) images of the evolution of Ppy deposition on SA films as a function of polymerization reaction time: SA film (a) before Ppy deposition, (b) after 30 min of Ppy polymerization, and (c) after 150 min of Ppy polymerization. Each SA film was formed on a freshly cleaved mica substrate. The apparent lack of periodicity in the 1D line scan in (b) is caused by the fact that the topology of the Ppy is superimposed on the topology of the underlying SA film. Image size: 1 μm × 1 μm.

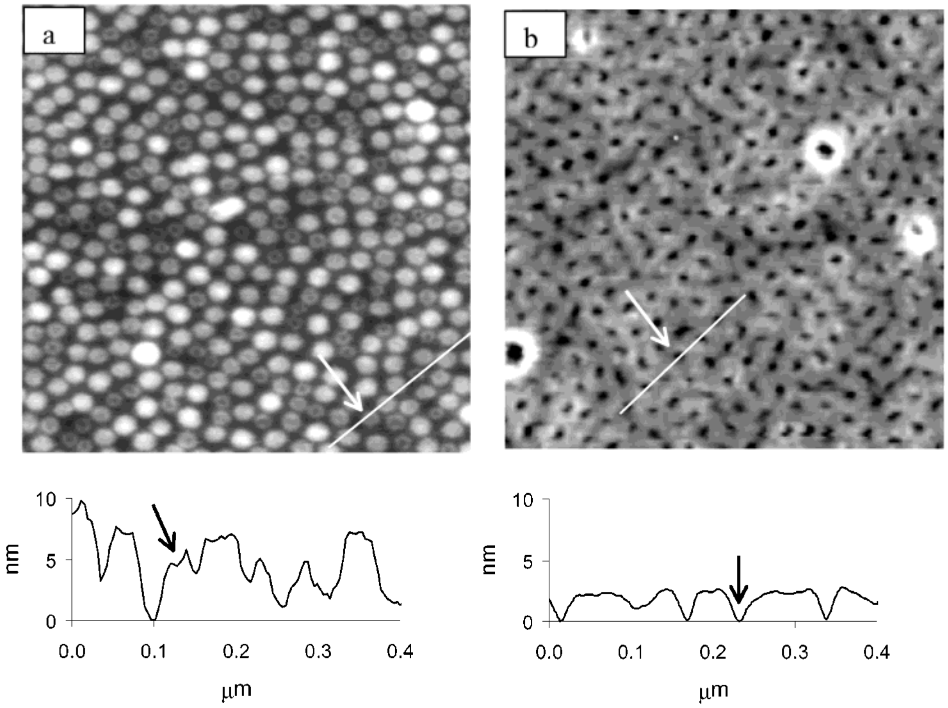

Figure 3. AFM (topology) images of the evolution of SA films as function of exposure time to water: SA film (a) after 5 s exposure to water and (b) after 24 h exposure to water. Each SA film was formed on a freshly cleaved mica substrate. Image size: 1 μm × 1 μm.

The successful preparation of this array of 50 nm high Ppy dots, covering square centimeters of surface, led us to ask if an inverted version (i.e., Ppy forming the "continuous" phase punctuated by nanometer length-scale holes) was possible to prepare. The requisite inverse template surface has been reported,[10,18] where the surface micelle cores are composed of P2VP and the coronas are composed of PS. These surface micelle arrays are formed via a solution-based self-assembly (SA) process rather than via the LB process. In this case, the surface micelle array lies on a PS/P2VP brush formed on mica or Si/SiO$_x$ surfaces, as mentioned above.

Incubation of a freshly cleaved mica surface in a toluene solution (1.5 mg/mL) for 10 min, followed by air-drying (10 min), yields the surface micelle array shown in Figure 2a. Ppy polymerization as per above (5, 10, 30 min) appears to yield a new material, evident as 30 nm thick rings formed around the P2VP cores. A definitive assignment of an "inverted" Ppy pattern is more difficult however. Neither noncontact nor intermittent contact AFM allows one to confidently distinguish Ppy from the PS and P2VP areas. This is important because control experiments involving short or long time incubation of the SA films in only water (seconds to 24 h) also reveal formation of rings surrounding depressions corresponding to the P2VP cores. These depressions gradually evolve from 1 nm deep, ca. 20 nm wide wells up to 4 nm deep, ca. 30 nm wide wells (Figure 3).

Even in the presence of only water, the wells that form in the center of the P2VP cores become more pronounced with time, and a corresponding lip forms. The surface micelle array and the underlying PS−P2VP brush are thus clearly prone to differential swelling and attendant reorganization.[19] Parallel experiments using transmission electron microscopy (TEM) and a surface micelle array formed on Si/SiO_x-coated TEM grids are unable to establish that the Ppy preferentially grows on what we believe to be PS regions. It is likely that the swelling of the P2VP causes so much reorganization of the surface micelles when they are immersed in the aqueous reaction environment that the PS regions are no longer accessible to the pyrrole solution. Any Ppy that forms likely does so in a simple conformal manner over the P2VP-rich surface.

The preparation method described here uses diblock copolymer surface micelle arrays as the reaction template. The chemical differentiation present in the surface micelles (PS/hydrophobic, P2VP/hydrophilic) leads to spatially resolved Ppy growth. Applications related to the conductivity of individual nanostructures and their relationships are of particular interest in the future.

Acknowledgment. We thank Prof. Adi Eisenberg for useful discussions over the years regarding surface micelles and Prof. A. Badia for helpful discussion regarding AFM imaging. NSERC (Canada) and McGill Graduate Faculty, in the form of a scholarship to M.G., provided financial support of this project.

References

(1) Jager, E. W. H.; Smela, E.; Inganas. O. *Science* **2000**, *290*, 1540.

(2) Skotheim, T. A.; Elsenbaumer, R. L.; Reynolds, J. H. *Handbook of Conducting Polymers*, 2nd ed.; Dekker: New York, 1998; Chapter 32.

(3) Nguyen, M. T.; Leclerc, M.; Diaz, A. F. *Trends Polym. Sci. (Cambridge, U.K.)* **1995**, *3*, 186.

(4) Joo, J.; Lee, J. K.; Hong, J. K.; Baeck, J. S.; Epstein, A. J.; Jang, K. S.; Suh, J. S.; Oh, E. J. *Macromolecules* **1998**, *31*, 479.

(5) Bargon, J.; Behnck, W.; Weidenbrueck, T.; Ueno, T. *Synth. Met.* **1991**, *41*, 1111.

(6) Gorman, C. B.; Beibuyck, H. A.; Whitesides, G. M. *Chem. Mater.* **1995**, *7*, 526.

(7) Fan, H.; Lu, Y.; Stump, A.; Reed, S. T.; Baer, T.; Schunk, R.; Perez-Luna, V.; Lopez, G. P.; Brinker, C. J. *Nature* **2000**, *405*, 56.

(8) Xu, S.; Liu, G. H. *Langmuir* **1997**, *13*, 127.

(9) Zhu, J.; Eisenberg, A.; Lennox, R. B. *Macromolecules* **1992**, *25*, 6547 and references therein.

(10) Li, Y. Z., W.; Liu, Y.; Rafailovich, M. H.; Sokolov, J.; Khougaz, K.; Eisenberg, A.; Lennox, R. B.; Krausch, G. *J. Am. Chem. Soc.* **1996**, *118*, 10892.

(11) Goren, M.; Qi, Z.; Lennox, R. B. *Chem. Mater.* **2000**, *12*, 1222.

(12) Qi, Z.; Lennox, R. B. *Proc. Electrochem. Soc.* **1997**, *97−5*, 173.

(13) Cox, J. K.; Eisenberg, A.; Lennox, R. B. *Curr. Opin. Colloid Interface Sci.* **1999**, *4*, 52.

(14) Li, Z.; Quinn, Z. W.; Rafailovich, H.; Sokolov, J.; Lennox, R. B.; Eisenberg, A.; Wu, X. Z.; Kim, M. W.; Sinha, S. K.; Tolan, M. *Langmuir* **1995**, *11*, 4785.

(15) Huang, Z.; Wang, P. C.; MacDiarmid, A. G.; Xia, Y.; Whitesides, G. *Langmuir* **1997**, *13*, 6480.

(16) Fou, A. C.; Rubner, M. F. *Macromolecules* **1995**, *28*, 7115. These authors suggest that the preferential formation of Ppy on hydrophobic vs hydrophilic surfaces originates from the intrinsic differences in affinity of the solution-based nuclei for the two surfaces.

(17) Qiu, Y. J.; Reynolds, J. R. *J. Polym. Sci., Part A: Polym. Chem.* **1992**, *30*, 1315.

(18) Meiners, J. C.; Quintel-Ritzi, A.; Mlynek, J. E., H.; Krausch, G. *Macromolecules* **1997**, *30*, 4945.

(19) Elbs, H.; Fukunaga, K.; Stadler, R.; Sauer, G.; Magerle, R.; Krausch, G. *Macromolecules* **1999**, *32*, 1204.

NL015630T