

Self-assembled monolayer-modified block copolymers for chemical surface nanopatterning

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ABSTRACT

Thin-film poly(styrene-*block*-methyl methacrylate) diblock copolymer (PS-*b*-PMMA) is used to create chemically patterned surfaces via metal deposition combined with self-assembled monolayers (SAMs) and UV exposure. We use this method to produce surfaces that are chemically striped on the scale of a few tens of nanometers. Atomic force and transmission electron microscopies are used to verify the spatially localized organization of materials, and contact angle measurements confirm the chemical tunability of these scaffolds. These surfaces may be used for arraying nanoscale objects, such as nanoparticles or biological species, or for electronic, magnetic memory or photovoltaic applications.

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1. Introduction

A variety of applications can benefit from surfaces that are chemically patterned on the nanoscale—from electronics and magnetic memory to sensing and photovoltaics. Currently, such surfaces are created via electron-beam lithography or by back-filling block copolymer scaffolds [1–7]. Unlike e-beam lithography, block copolymer lithography is a parallel processing method, covering large areas at once, which is a distinct advantage for industrial applications. However, it is a complex, multi-step process. Here we present a new, simple way of utilizing block copolymers coated with metals and self-assembled monolayers to create chemically nanopatterned surfaces.

Diblock copolymers provide a promising foundation for functional nanomaterials and devices [1–7]. A diblock copolymer consists of two chemically distinct polymer blocks, which are joined together by a covalent bond. The blocks' interaction is determined by their mutual repulsion as well as the entropic cost of stretching the chains. When the inter-block interaction is sufficiently repulsive, the diblock copolymer separates on the scale of tens of nanometers into spheres, cylinders, gyroids, or lamellae of one of the blocks in a matrix of the other. For a given molecular weight and composition of a diblock copolymer, the morphology depends on the volume fraction of each block. Thus,

by varying the molecular weight and relative composition of a diblock copolymer, it is possible to obtain a range of morphologies [7].

Films of diblock copolymers can potentially be used as platforms for photovoltaic devices, computer memory, and electronics, among other applications [7–13]. They provide a natural scaffold on length scales otherwise inaccessible by conventional top-down techniques, such as optical lithography. The addition of inorganic components, such as metals or nanoparticles, provides functionality, such as light absorption, electrical conductivity or magnetoresistance. The morphology of the resulting polymer–inorganic hybrid is especially important in determining its properties.

Out of panopoly of diblock copolymers, poly(styrene-*b*-methyl methacrylate) (PS-*b*-PMMA) is one of the most studied [14–24], as it presents both the PS and the PMMA blocks at the surface for thin films. There have been a number of studies concerning the deposition of nanoparticles onto and into PS-*b*-PMMA, which have been limited by the wetting of the two blocks by solvents compatible with the nanoparticles [20,23–25]. Here we report our findings with respect to a route to surface modification of PS-*b*-PMMA to overcome the wetting limitation.

We use silver deposition and self-assembled monolayers (SAMs) in conjunction with UV exposure, as described in the experimental section below. The resulting surfaces have a physical corrugation on the order of 5 nm, and either stripes of SAMs that are nanometers wide, or else a coating of SAMs everywhere. This approach provides a potential pathway to new functional nanomaterials.

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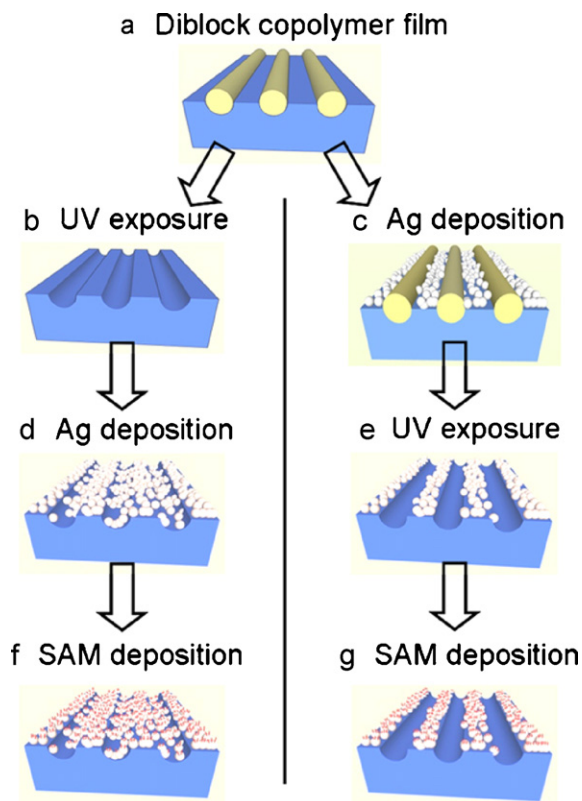


Fig. 1. Schematic of the surface modification procedure, which is described in the experimental procedure. Our procedure varied in the order in which steps were applied: either UV exposure was performed first, as in (b), (d), and (f) or metal deposition was, as in (c), (e), and (g).

2. Experimental methods

2.1. Diblock copolymer films

Ultra-thin films of $77,000 \text{ g mol}^{-1}$ PS-*b*-PMMA (70% PS) from Polymer Source, Inc. were spin-coated onto ultrasonically cleaned silicon nitride substrates, using 1.5% toluene solution at 3–6k rpm. This resulted in films that were 25–35 nm thick on average. The films were heated to 518 K in an inert atmosphere and kept at that temperature between 5 min and 6 h, then slowly cooled to room temperature [25].

2.2. UV irradiation

The films were either first UV-irradiated and then coated with metal, or first coated with metal and then irradiated. For UV exposure, the samples were placed 10 inches away from a deuterium Hamamatsu lamp L2793 in ~ 10 mTorr vacuum, with a measured flux of $600 \mu\text{W cm}^{-2}$, and exposed to the light for 15 min. Further irradiation did not show an increase in corrugation.

2.3. Metal and SAM deposition

Silver deposition was performed thermally to deposit either silver or chromium and gold. The nominal thicknesses of the metal layers were measured by a quartz crystal monitor and were between 3 and 12 nm for a series of samples, accurate to 0.1 nm. Since silver does not coat PS-*b*-PMMA uniformly, actual thicknesses varied locally. The samples were then coated with hydrophilic or hydrophobic SAMs, using mercaptoundecanoic acid (MUA) and decanethiol, by leaving the samples in 0.5% ethanol solution for at least 1 hour and subsequently rinsing with ethanol and methanol.

2.4. Imaging and contact angles

Imaging was done using tapping mode on a Veeco Multimode IV atomic force microscope (AFM) to observe topography. Samples were also imaged using a FEI 30 transmission electron microscope (TEM) at 100 and 300 keV. Contact angle measurements were performed using a custom-built apparatus. An image of a drop of deionized water was captured on a flat substrate immediately after the drop formed, and the contact angle measured.

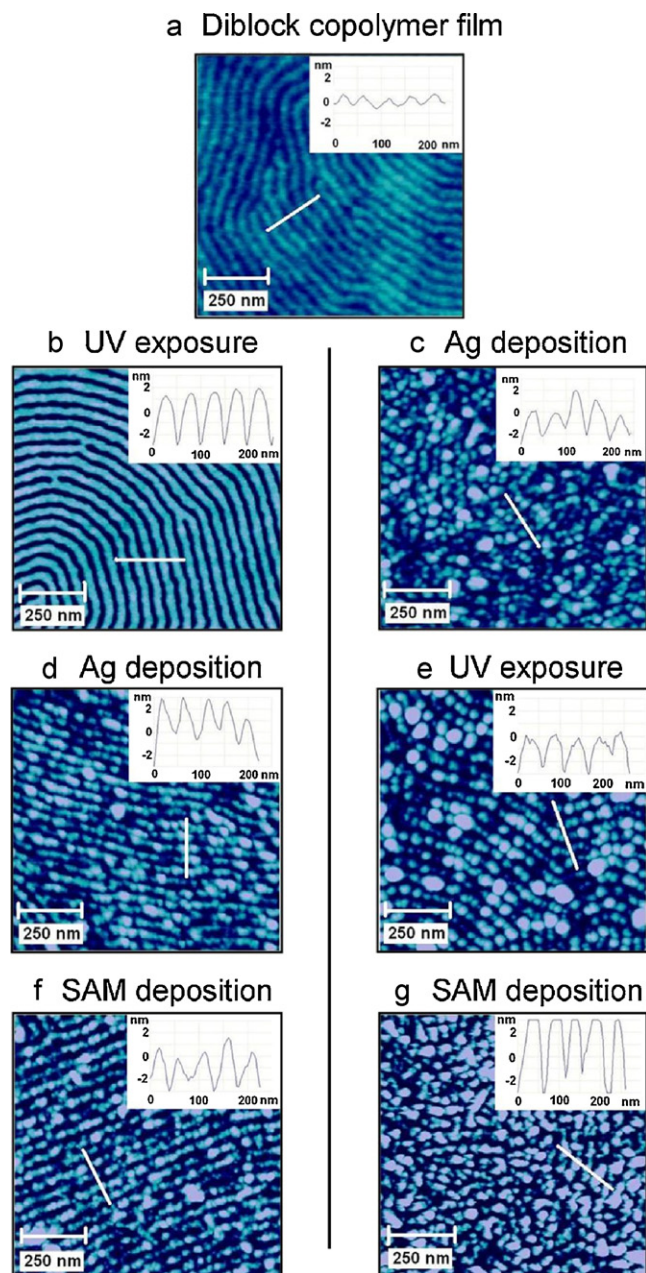


Fig. 2. AFM images of $1 \mu\text{m} \times 1 \mu\text{m}$ experimental results for Ag deposition. UV irradiation increases corrugation of plain PS-*b*-PMMA in (b), and narrows the silver stripes in (e). In (f) we have a SAM-coated surface with silver everywhere, whereas in (g) we have SAM-coated nanostripes of silver, as confirmed by TEM data.

3. Results and discussion

Starting with 30-nm thick films of PS-*b*-PMMA, which have a peak-to-peak vertical corrugation of 0.5 nm and are comprised of a single layer of self-assembled cylindrical domains oriented parallel to the substrate, as shown in Fig. 2a, we deposit metal and perform UV exposure. The resulting morphology depends on the sequential order of the last two steps. Subsequent SAM deposition changes the macroscopic wetting properties of the samples by altering their wettability on the nanoscale.

Silver was chosen as a metal for decorating PS-*b*-PMMA films because it forms a good scaffold for thiolate SAMs. Lopes and Jaeger have shown that silver forms nanowires on cylindrical thin-film PS-*b*-PMMA [19]. Each sample was coated with 3, 6 or 12 nm of silver, as measured by a quartz-crystal monitor.

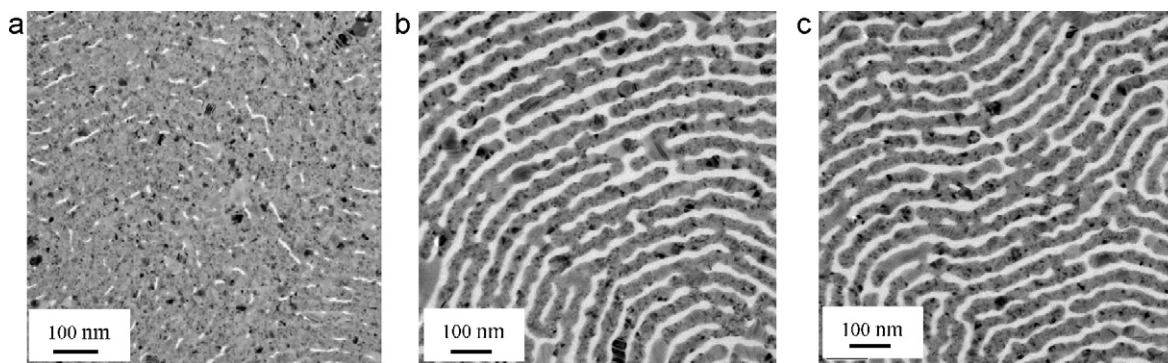


Fig. 3. (a) TEM image of 12 nm of silver deposited onto previously UV-irradiated PS-*b*-PMMA. The TEM image shows remnants of the diblock copolymer structure, covered almost everywhere with silver. (b and c) TEM of 12 nm of silver deposited on pristine PS-*b*-PMMA before (b) and after (c) UV exposure.

Metal deposition was either followed or preceded by *vacuum* UV exposure, which both scissions and removes the PMMA cylinders [25]. Since the PMMA is irradiated in vacuum, an acetic acid rinse is not needed as with atmospheric UV exposure. The increase in the physical corrugation of the sample shown in Fig. 2b demonstrates PMMA removal. The entire procedure is outlined in Fig. 1, while the AFM images of the resulting samples are shown in Fig. 2.

When UV exposure is performed on a pristine PS-*b*-PMMA film, it increases the corrugation of the film from 0.5 to 3–5 nm, as shown in Fig. 2b. Metal deposited onto this surface then coats the surface in a largely uniform way, while maintaining the topography of the underlying corrugated polymer film (Fig. 2d). The fact that silver, and thus also the SAM, is present on both crests and troughs of the fingerprint pattern in this case is confirmed by the TEM image in Fig. 3a.

The higher silver surface diffusion rate on PMMA compared to PS [26] leads to the formation of thick silver stripes preferentially decorating the PS on pristine PS-*b*-PMMA films (those without a previous UV exposure), as shown in Fig. 3b. Subsequent UV exposure leads to narrower silver stripes [21], as seen in Fig. 3c. This feature could be useful in making better separated structures in massively parallel wire arrays, which is beneficial for electrical applications, for example. When SAMs form on this surface, they selectively decorate the silver domains, leading to the creation of nanoscale chemical stripes.

In order to manipulate the samples' water wettability, we coated them with either a hydrophobic (decaneethiol) or hydrophilic (mercaptoundecanoic acid, denoted MUA) SAM using the procedure described above. The hydrophobic alkane tail of decaneethiol should inhibit water wetting, whereas the carboxylic acid tail of MUA should encourage it. On AFM images, a soft SAM layer on a hard metal surface does not show up (see, for example, Fig. 2g). Instead, the image only reveals the underlying polymer/metal topography. To establish that a SAM layer indeed formed on the surface, we performed water contact angle measurements.

We measured advancing water contact angles on silver-coated samples with decaneethiol and MUA. The decaneethiol-coated silver samples had an advancing water contact angle of 112° and 125° for narrower and wider silver stripes, respectively. For the MUA-coated striped silver sample, this angle was ~50°, which is well below the contact angle for the uncoated, UV-modified diblock of 90°.

Since a thiolate SAM does not form on the bare polymer substrate, as confirmed by the lack of change in contact angle for those samples, these data show that we have succeeded in creating tunable chemical stripes that are 10–15 nm wide. The difference between the advancing water contact angles for samples with UV before and after Ag and SAM deposition provides further evidence that the resulting morphologies in these two cases are distinct. Table 1 summarizes these results.

Table 1

Advancing water contact angles for various modified PS-*b*-PMMA thin film samples.

Sample type	Step 1	Step 2	Step 3	Water contact angle (°)
1	UV	N/A	N/A	90
2	Ag (12 nm)	UV	MUA	50
3	UV	Ag (12 nm)	Decaneethiol	125
4	Ag (12 nm)	UV	Decaneethiol	112
5	UV	Decaneethiol	N/A	90

Thin film block copolymers provide an inexpensive route to ordered nanoscale structures, especially when combined with channels to guide their alignment [27–30]. They can also be used as scaffolds for functional nanoarrays or sensors, but their usefulness is often limited by their wetting properties. In order for particles to attach to the polymer scaffold, especially from solution, the solvent has to wet the polymer surface. This is especially critical for biological species, since they prefer aqueous solutions, which do not readily wet many block copolymers. Here we have shown a pathway to creating a new class of polymer-based surfaces, which have a greater range of water contact angles than the original polymer: from about 90° for the original PS-*b*-PMMA to between 50° and 125°, depending on the SAM utilized and the order of the UV exposure and silver deposition steps. We have also successfully created chemically striped surfaces with alternating hydrophobic/hydrophilic domains by using silver and MUA on PS-*b*-PMMA.

Another possible application of this general method of functionalizing metal-coated PS-*b*-PMMA is for creating superhydrophobic surfaces [31]. In order to achieve this effect, it would be necessary to switch to a different block copolymer morphology that could yield greater corrugation upon UV exposure, such as vertically aligned cylinders or lamellae. For those cases, having 30-nm physical corrugation with chemically distinct crests and troughs, for example, through the preparation of a hydrophobic SAM on the crests and less hydrophobic polymer in the troughs, would lead to exciting new surface wetting properties.

4. Conclusions

Combining metals and nanoparticles with organic structures has been an area of active interest in recent years. One of the main challenges in this area is positioning the nano-objects in or on the scaffolding. Here we have reported a new way of preparing chemically striped as well as homogeneous, spatially corrugated surfaces based on diblock copolymer scaffolds.

The importance of our study is the demonstration that it is possible to create nanostructured surfaces with a variety of wetting properties. The surfaces may be used as they are, or as scaf-

folds for assembly of nanoscale objects—viruses, nanoparticles, etc. Currently, there exists a large number of methods of creating super-hydrophobic surfaces as well as scaffolds [31,32]. However, these methods either rely on lithography to create the necessary patterns, or else take tens of hours for the particles to decorate the surface. Here we utilize diblock copolymers to create patterns with a range of water contact angles. Resulting surfaces are compatible to a wide array of functional nano-objects and not just those compatible with organic solvents [22,25]. The general method of preparing these surfaces may prove to be useful for a variety of applications.

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