Switching Nanotemplates

Igor Tokarev[1], Alexander Sidorenko[1], Sergiy Minko[2] and Manfred Stamm[1]

*[1]Institut für Polymerforschung Dresden e.V., Hohe Str. 6,
01069 Dresden, Germany*

[2]Clarkson University, Department of Chemistry, Potsdam, NY 13699-5810

INTRODUCTION

Block copolymers (BC) in bulk or in thin films self assemble in ordered nanoscale structures. This property is explored for templating. In particular, BC were used as templates for synthesis of regular arrays of nanowires[1] and nanodots[2]. Fabrication of nanoporous templates from BC requires to remove selectively one of the blocks. Existing approaches involve the use of BC if rates of degradation upon UV radiation,[3] or plasma etching[4] very much different for the different blocks. An elegant approach to porous bulk materials has been reported by O. Ikkala et. al.[5] It is based on supramolecular assembles of a block copolymer and a low molar mass additive if the additive forms hydrogen bonds with one of the blocks. The additive can be extracted with a selective solvent producing empty channels.

For most of applications, the alignment of nanodomains in BC templates is of great importance. An array of standing on the substrate cylinders is one of the most asked alignments. Previously, the alignment of cylindrical domains perpendicularly to the substrate plane was achieved balancing the interfacial interactions of BC blocks[6] and using strong electric field.[7] Also, solvent induced orientation has been reported.[8]

We developed a simple method for the fabrication of nanoporous BC templates. The templates are based on thin films of supramolecular assemble of polystyrene-*block*-poly(4-vinylpyridine) (PS-P4VP) and 2-(4'-hydroxybenzeneazo)benzoic acid (HABA). We found conditions for switching between different alignments of cylindrical P4VP+HABA nanodomains from cylinders oriented perpendicular to the substrate to the cylinders in-plane. Finally, we use the templates for the fabrication of nanocomposite films.

EXPERIMENTAL

Materials. Diblock copolymer, PS-P4VP (PS 35500 g/mol, P4VP 3680 g/mol; M_w/M_n=1.06), was purchased from Polymer Source, Inc. HABA (≥99.5%) was purchased from Fluka. Chloroform, 1,4-dioxane, and methanol were obtained from Acros Organics. Chromium and gold target (≥99.98%) were purchased from MaTeck GmbH (Germany).

Sample Preparation. PS-P4VP were mixed with HABA in equimolar ratio. 1,4-dioxane solution of the mixture was stirred and filtered directly before use. Films of PS-P4VP+HABA were deposited by dip-coating on freshly cleaned silicon wafers from 1.5 % solution. The film thickness was about 30 nm. The films were swollen in saturated vapors of either 1,4-dioxane or chloroform to approach the swelling ratio of 2.75. Finally, HABA was extracted by rinsing in methanol. Chromium in the quantity of 0.7–1.8 μg/cm^2 was sputtered ($p = 2\cdot10^{-3}$ mbar and $I = 0.12$ A) on the top of the resulted nanotemplates.

Instrumentation. Chromium sputtering was performed in a sputter coater supplied by tectra GmbH Physikalishe Instrumente (Germany). The thickness of the films was measured by Rotating Analyzer Ellipsometer SE400 (SENTECH Instruments GmbH, Germany). Scanning Probe Microscopy (SPM) imaging of film morphology was performed with the Dimension 3100 (Digital Instruments, Inc., Santa Barbara) in tapping mode. Grazing Incidence Small Angle X-ray Scattering (GISAXS) measurements were performed at the beamline BW4 at Hamburg Synchrotron Radiation Laboratory (HASYLAB), Deutsches Elektronen-Synchrotron (DESY). The sample-detector distance was 2.21 m.

RESULTS AND DISCUSSION

PS-P4VP+HABA assemble (Figure 1a) was studied as published in details elsewhere.[9] It was shown that hydrogen bonds between acidic groups of HABA and pyridine of P4VP block result in formation of a supramolecular P4VP+HABA assemble. Though the sample of PS-P4VP used in our study has a spherical morphology, the modification of P4VP with HABA increases the volume fraction of the minor block and brings changes of the symmetry. Thus thin films of the PS-P4VP+HABA assemble exhibit hexagonal cylindrical morphology with cylinders composed of the P4VP blocks and HABA.

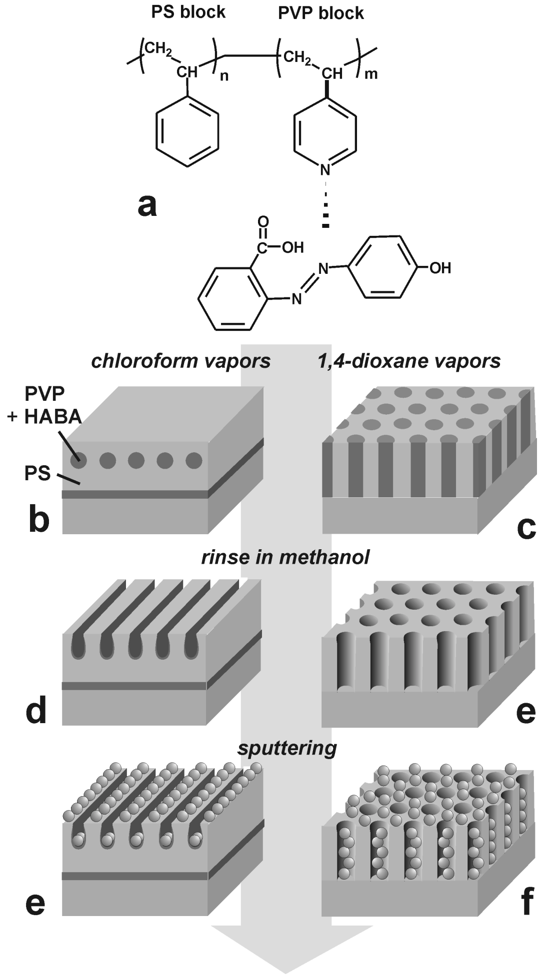

Figure 1. Scheme of the fabrication of well-ordered nanocomposite films.

We have shown that the alignment of the cylindrical domains depends on deposition conditions. If the deposition is performed from chloroform solution, in-plane oriented cylinders and terrace formation are observed. Whereas the films dip coated from 1,4-dioxane solution reveal cylinders aligned normal to the film plane (Figure 1c). Furthermore, we have found that the orientation of the cylindrical domains switches upon annealing in vapors of an appropriate solvent. Swelling PS-P4VP+HABA films deposited from chloroform solution in saturated vapors of 1,4-dioxane results in re-alignment of "in-plane" cylinders into the perpendicularly standing cylinders. Vice versa, swelling the films deposited from the 1,4-dioxane solution in saturated vapors of chloroform leads to the switching of the cylinder orientation from the perpendicular orientation to the in-plane alignment. Noteworthy, in both cases we observe considerable improvement of the order of the nanodomains.

Rinsing in a selective solvent, *i.e.* methanol, allows for the extraction of HABA from the film. That leads to formation either grooves (Figure 1d) or cylindrical channels (Figure 1e) which are formed in PS matrix. The walls of the channels are covered with P4VP brush.

We have used the switching effect described above for the fabrication of ordered arrays of nanowires either perpendicular or parallel alignment. Sputtering chromium or gold (0.7–1.8 μg/cm^2) on the top of templates results in loading of the grooves and the channels with nanometer-sized metal clusters (Figures 1e and 1f, respectively). The SPM images of the templates loaded with chromium clusters are shown in Figures 2a and 2b. The initial template order is preserved upon sputtering. The chromium clusters are clearly seen in the insets.

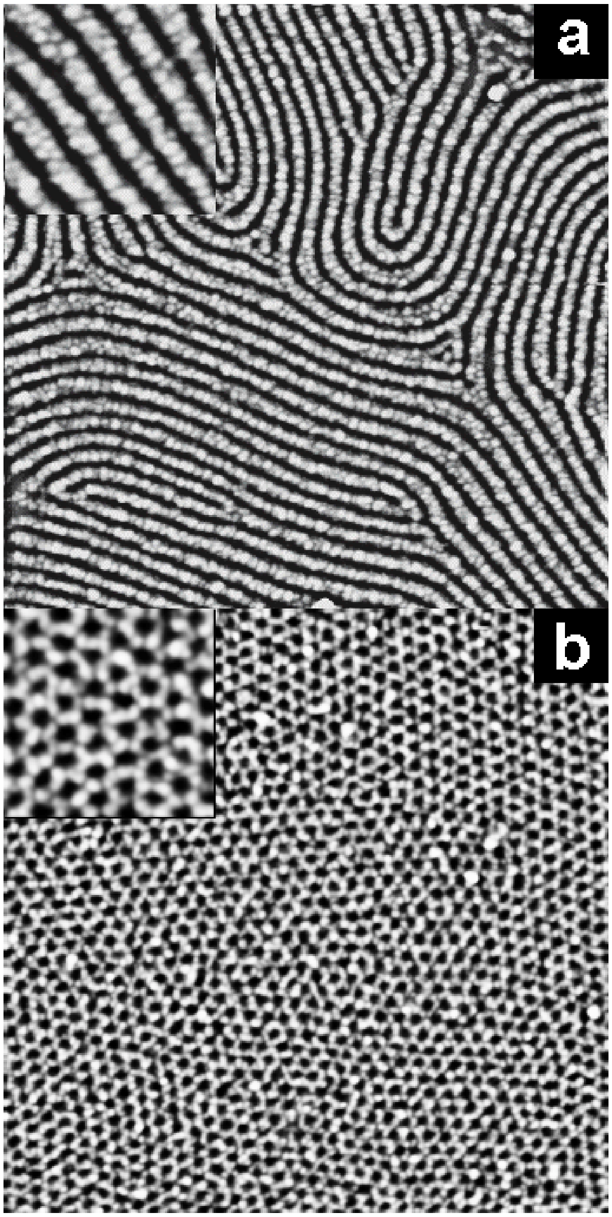

Figure 2. 1×1 μm^2 SPM images (0.2×0.2 μm^2 images in the insets) of 30 nm thick templates (a) with in-plane aligned cylindrical channels and (b) perpendicularly aligned cylindrical channels loaded with chromium clusters.

We performed GISAXS measurements of the loaded templates. The loading of the templates with the clusters considerably enhances X-rays scattering due to the large difference in the electron densities of the metal and polymers. The dominating length scale of in-plane features can be extracted from the horizontal slices (out-of-plane scans) of the 2D scattered intensity distribution. In the horizontal slice of the scattering from the template with the perpendicular aligned loaded channels, one can distinguish up to three out-of-plane peaks attributed to scattering from the channels. The peak positions relate as $1{:}\sqrt{3}{:}\ \sqrt{7}$ which gives evidence for hexagonal order. The mean periodicity of the channels determined from the position of the first peak is about 26 nm, which is in good agreement with the value obtained from SPM data. In contrast, the horizontal slice of the scattering from the metal loaded template with in-plane cylinders gives two peaks relating 1:2 in positions. We attribute them to a layer of the equally spaced loaded grooves.

CONCLUSIONS

We developed a simple method for the fabrication of well-ordered nanocomposite films via the deposition of chromium clusters into of the block copolymer templates. We explore the switching behavior of the block-copolymer-HABA thin film to change the alignment of nanocylinders from perpendicular to in-plane orientation for the fabrication of the ordered arrays of nanowires.

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