Novel Supramolecular Approach to Periodic Nanostrucutres in Thin Polymer Films

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INTRODUCTION

The ability of thin films of block copolymers (BC) for self organization in periodic structures makes them promising for patterning large areas with nanometer size arrays.[1] It can be further applied for nanolithography, nanotemplating, design of variety of microdevices etc. Fabrication of lithographic masks and templates for synthesis of regular arrays of nanowires/nanodots from BCs requires orientation of microdomains normal to a surface plane. Previously, the normal orientation was achieved balancing the interfacial interactions of BC blocks[2] and using strong electric fields.[3] Also, solvent induced orientation has been reported.[4]

O. Ikkala et. al. investigated microphase separation in block copolymer supramolecular assembles in bulk.[5,6] They used hydrogen bonding between nitrogen of pyridine and phenolic group of 3-pentadecyl phenol (PDP) to modify the morphology of poly(styrene-*block*-4-vinylpyridine) PS-PVP. Investigation of the bulk PS-PVP+PDP copolymer showed that supramolecular assembling of PVP and PDP may result in change of the BC morphology (from spherical to cylindrical). PDP can be easily removed simply by washing with selective solvent providing well ordered channels in majority component matrix.[5]

We investigate microphase separation in thin films of BC supramolecular assembles. As a low molar mass additive capable to form hydrogen bonds with pyridine groups of PS-PVP we used 2-(4'-hydroxybenzeneazo)benzoic acid (HABA) (Figure 1).

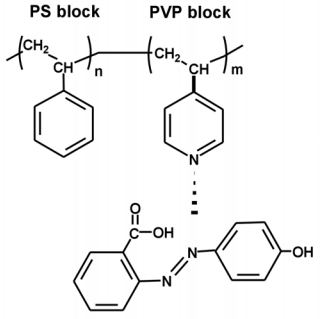

Figure 1. PS-b-P4VP + HABA assemble.

EXPERIMENTAL

Materilas. Diblock copolymers of polystyrene-*block*-poly(4-vynilpyridine) of different ratios between the blocks (SV1: PS 32900 g, P4VP 8080 g; SV2: PS 35500 g, P4VP 3680 g; polydispersity (M_w/M_n) of 1.06) were purchased from Polymer Source, Inc. 2-(4'-hydroxybenzeneazo) benzoic acid (HABA, ≥99.5% pure) was purchased from Fluka. Chloroform, 1,4-dioxane, and methanol were obtained from Acros Organics.

Sample preparation. SV1 and SV2 were mixed with HABA in equimolar ratios between P4VP-blocks and HABA. Chloroform and 1,4-dioxane solutions of the mixtures were stirred and filtered directly before use. Films of SV1+HABA and SV2+HABA were deposited by dip-coating on freshly cleaned silicon wafers from 1÷3 % solutions. The film thickness was varied in the range of 20÷90 nm. HABA was extracted by rinsing in methanol to complete nanotemplate.

Instrumentation. 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. UV-vis and FTIR spectra were taken with Cary 100 Scan UV-Vis spectrophotometer (Varian, Inc.) and Bruker IFS 66v FTIR spectrometer, respectively, in transmission mode.

RESULTS AND DISCUSSION

FTIR and UV-vis spectroscopy. Films of SV1+HABA and SV2+HABA assembles prepared by dip-coating are optically homogeneous with no signs of HABA macrophase separation. The study of FTIR spectra shows hydrogen bonding between HABA and the pyridine groups of the P4VP block. Thus, we observe shifts of the absorption peaks at 993 and 1415 cm^{-1}, which are characteristic to the pyridine ring,[8] on +8 and +5 cm^{-1}, respectively, upon formation of hydrogen bond.

HABA is a chromophore exhibiting a broad absorption peak at 382 nm. UV-vis spectrum of PS-b-P4VP+HABA assemble shows the shift of the characteristic peak to 367 nm. According to the molecular exciton model, the red shift is an evidence of H (head-to-head) aggregation of azobenzene chromophores. We assume that the aggregation of HABA molecules linked to P4VP block by hydrogen bond plays a key role in formation of well developed morphologies directly after deposition of the assemble. Washing the films in methanol leads to disappearance of the characteristic absorption peak in UV-vis spectra that indicates an effective elimination of HABA from films.

SPM and ellipsometry characterization. We determined thickness of the films of PS-b-P4VP+HABA assembles before and after washing in methanol by AFM (scratch test) and ellipsometry. The AFM scratch test showed no appreciable change in thickness, while ellipsometry showed significant decrease. This discrepancy arises from porous nature of the studied films. The thickness values from the scratch analysis were used then as known parameter to determine the refractive index of the films from ellipsometric angles. The refractive indices of the films of SV1+HABA (deposited from chloroform) and SV2+HABA determined in this way are 1.410 and 1.497, respectively. We assumed that components of a heterogeneous film contribute to its refractive index in accordance with their volume fractions. Thus, accepting the refractive index of pores equal to 1 (air) and that of a matrix (composed from PS and P4VP) equal to 1.59, we obtained the volume pore fraction of 30.5% for SV1+HABA films and 15.8% for SV2+HABA films. These values are close to the volume fractions of HABA in the assembles, 31.2 and 17.8 %, respectively.

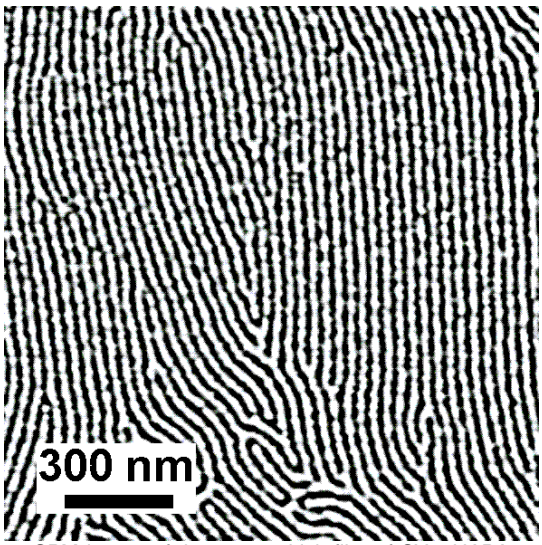

Figure 2. SPM image of the 74 nm thick film of SV1+HABA assemble dip-coated from chloroform.

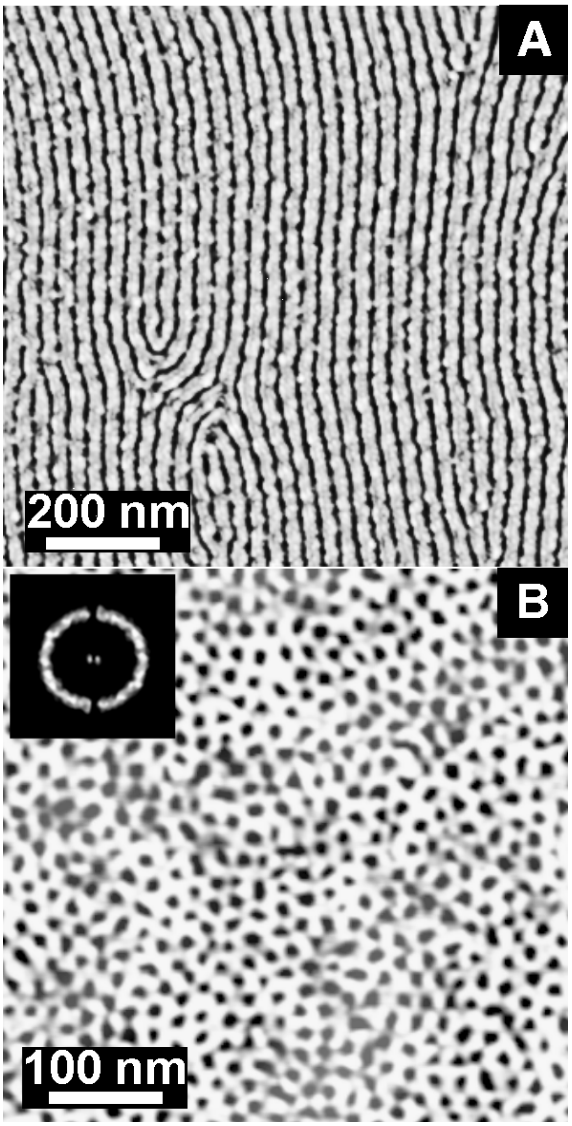

Figure 3. SPM images of SV1+HABA films a) 48 nm thick dip-coated from chloroform and b) 40 nm thick dip-coated from 1,4-dioxane (2D FFT in inset).

Further evidence of porous structure of the washed films comes from the SPM characterization of the film surface. Large scale SPM image (not shown here) of SV1+HABA film shows no terrace formation. Detail SPM investigation shows clearly seen lamellar morphology with lamellae normally oriented to substrate plane and periodicity of about 33 nm (Figure 2). The morphology of the films is independent on the used solvent.

Films of SV2+HABA assemble prepared from the chloroform solution demonstrates channels oriented parallel to substrate plane (Figure 3,a). If SV2+HABA assemble is deposited from the 1,4-dioxane solution, it shows hexagonally ordered cylinders oriented normally to substrate with a mean periodicity of about 21 nm (Figure 3b). However, there is no long-range lateral order as it follows from 2D FFT image.

Finally, we demonstrated re-orientation of cylindrical morphology SV2+HABA assemble in vapors of appropriate solvent. Swelling SV2+HABA films deposited from the chloroform solution in saturated vapors of 1,4-dioxane for 40 min results in transformation of the morphology into cylinders oriented normal to a film surface. Moreover, we observed considerable improvement of the hexagonal order. Relatively large domains (hundreds of nanometers ÷ a few micrometers in size) with a good orientational and translational order are seen on the SPM images (Figure 4). In contrast, SV2+HABA films deposited from 1,4-dioxane after exposition to saturated vapors of chloroform for 30 min demonstrate re-orientation to the in-plane cylindrical structure similar to that shown in Figure 3, a.

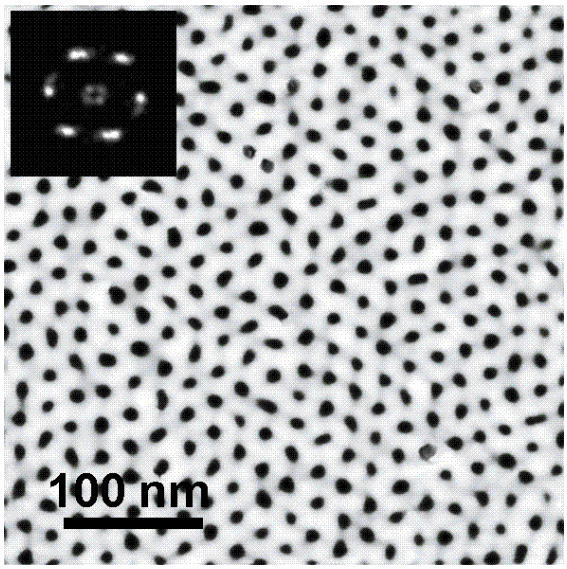

Figure 4. SPM image 0.5×0.5 μm^2 and corresponding 2D FFT (as inset) of the 53 nm thick film of SV2+HABA assemble swelled in vapors of 1,4-dioxane.

CONCLUSIONS

We developed a simple method of preparation of thin films exhibiting regular structures of nanometer-scale size which can be used as nanotemplates for fabrication of nanostructured materials. Depending on the ratio of block length, either lamellar or hexagonal cylindrical structures in thin films are obtained. One can achieve a desired orientation of cylindrical nanodomains by use of an appropriate solvent. The low molar mass additive can be easily extracted from films.

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