

# Fabrication of Highly Ordered Polymeric Nanodot and Nanowire Arrays Templated by Supramolecular Assembly Block Copolymer Nanoporous Thin Films

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**Abstract** Realizing the vast technological potential of patternable block copolymers requires both the precise controlling of the orientation and long-range ordering, which is still a challenging topic so far. Recently, we have demonstrated that ordered nanoporous thin film can be fabricated from a simple supramolecular assembly approach. Here we will extend this approach and provide a general route to fabricate large areas of highly ordered polymeric nanodot and nanowire arrays. We revealed that under a mixture solvent annealing atmosphere, a near-defect-free nanoporous thin film over large areas can be achieved. Under the direction of interpolymer hydrogen bonding and capillary action of nanopores, this ordered porous nanotemplate can be properly filled with phenolic resin precursor, followed by curation and pyrolysis at middle temperature to remove the nanotemplate, a perfect ordered polymer nanodot arrays replication was obtained. The orientation of the supramolecular assembly thin films can be readily re-aligned parallel to the substrate upon exposure to chloroform vapor, so this facile nanotemplate replica method can be further extend to generate large areas of polymeric nanowire arrays. Thus, we achieved a successful sub-30 nm patterns nanotemplates transfer

methodology for fabricating polymeric nanopattern arrays with highly ordered structure and tunable morphologies.

**Keywords** Supramolecular assembly · Nanoporous template · Hydrogen bonding · Polymeric nanodot arrays

## Introduction

Precise fabrication of large areas of ordered nanoscale structures is essential for microelectronic and information technology, the broad scope of top-down processes, including conventional immersion lithography, extreme ultraviolet lithography, and soft lithography have been proposed to meet the demands of devices miniaturization, these endeavors have enabled the lateral dimensions of devices to be readily shrunk below 100 nm [1–3]. However, as the lateral dimension goes smaller and smaller, these ‘top-down’ approaches become extremely difficult and expensive, hence, other methodologies of creating nanostructures are of great interesting if they can offer advantages in reduced production cost, smaller feature sizes, and more complex nanopatterns. Nanofabrication via block copolymer self assembly represents one of the most powerful candidates, and is now taking as the most promising methodology for next-generation lithography [4–6], mainly due to their intrinsic nanoscale dimensions, facile synthesis, and strict control of architecture. Ever since the self assembly of block copolymers was introduced as a powerful ‘bottom-up’ route to well-organized nanostructures decade ago, many efforts have been devoted: as through chemical modification of the block copolymer structure to achieve special functionalities, exploring electric fields, and interfacial interactions to

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control the orientation, and utilizing solvent induced ordering, salt complexes, and shear fields to achieve ordered arrays [7–10]. Among which solvent annealing is of particularly beneficial mainly due to their mild process condition and no need for additional complicated apparatus, and now it has turned out to be a very simple while robust approach to generate almost defect-free microphase separation structures in BCP thin films [11–13]. Even more, it appears to be the single possible way for thermal lible systems such as supramolecular block copolymers based on noncovalently bonding. Further research revealed the use of a co-solvent atmosphere, which enables one to enhance the ordering process even further [14, 15]. However, a critical drawback of solvent annealing is that BCP thin film often de-wets its substrate during solvent exposure as has been already pointed out by several researchers [16–19]. This makes it very difficult to obtain uniform and ordered BCP thin film over a macroscopic area without the direction of additional external fields. In many cases, realizing the vast technological potential of block copolymers requires both the precise controlling of the orientation and long-range ordering, however, weakness still remains, so far, only few works have reported to achieve highly ordered thin film nanotemplates, and the control of well-organized structures over large scale is still a challenging topic.

In recent decade, Ikkala and ten Brinke have thoroughly demonstrated that well-ordered nanostructures in the bulk may be fabricated through supramolecular assemblies (SMA) of low molecular amphiphiles and block copolymers [20, 21]. The amphiphiles can be physically bonded to homopolymers and block copolymers using noncovalent interactions, this complexation can lead to the formation of supramolecular block copolymer which can further assemble into hierarchy nanostructures with various responsive properties. More recently, we have demonstrated that ordered nanoporous thin film can be fabricated from a similar approach based on the supramolecular assemblies of block copolymers PS-PVP and small molecule (2,4-Hydroxybenzeneazo benzoic acid, HABA) [22–26], the SMA thin films demonstrated hexagonal cylindrical morphology with PS form the matrix. Solvent annealing in dioxane can enhance the ordering of thin films microphase separation, following extraction of HABA with selective solvent methanol results in a nanoporous thin film. The channels can be filled with metal, for example, nickel, by electrochemical deposition to fabricate an array of ordered metal nanodots or nanowires with some defects appear in the array due to the nonuniform electrodeposition kinetics of the metal clusters in nanochannels [23].

In this article, we further investigate the PS-PVP/HABA supramolecular assembly system in order to achieve a highly ordered morphology and to explore a high definition nanotemplate replication method for fabrication of highly

ordered polymeric nanodots and nanowire arrays. We will demonstrate that under a mixture solvent annealing atmosphere (with the dedicating choosing of an additional nitromethane as a selective solvent for the minor component), a near-defect-free nanoporous thin films with long-range ordering over a large areas can be achieved. Taking aim at high definition nanotemplate transfer technique which is another daunting obstacle to the application of the nanoporous template, we will further show that under the direction of the capillary action and hydrogen bonding, this ordered nanoporous template can be perfectly transferred, and thus achieved a methodology for the preparation of highly ordered sub-30 nm polymeric nanodot and nanowire arrays.

## Experimental

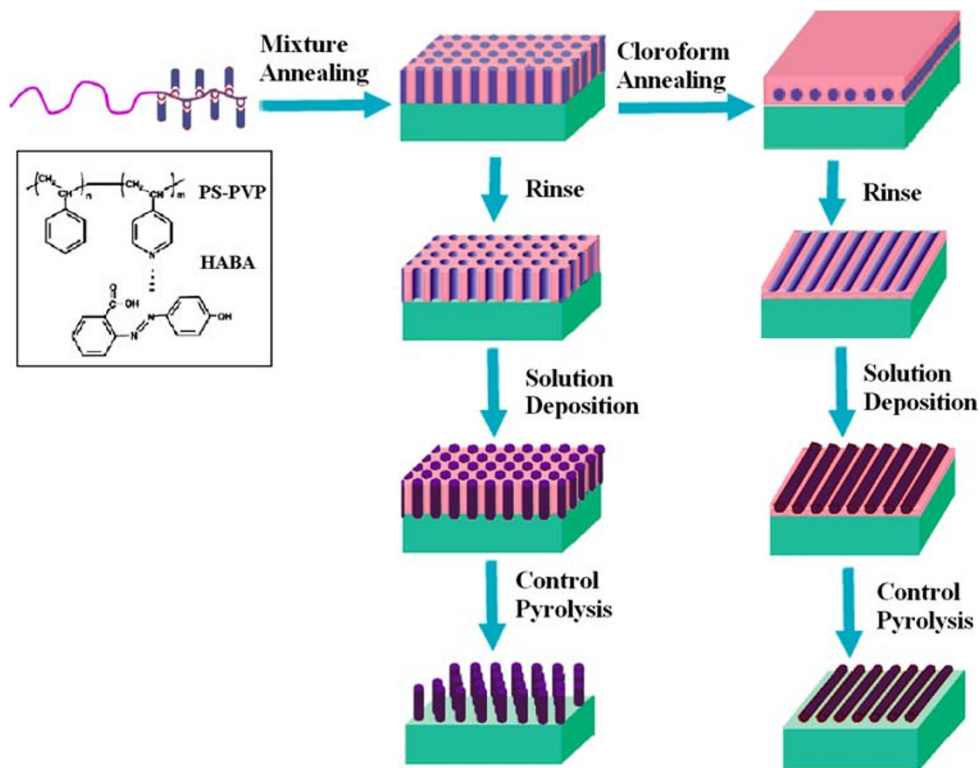
### Materials

Poly(styrene-block-4-vinylpyridine) (PS-PVP), with Mn PS 4000 g/mol, PVP 5600 g/mol, Mw/Mn 1.06) for both blocks, was purchased from Polymer Source Inc. A soluble low-molecular-weight phenolic resin precursor solution was prepared from phenol and formaldehyde using a basic polymerization method [20]. The final product was redissolved in Ethanol before use as dip coating solution. 2-(4-Hydroxybenzeneazo) benzoic acid (HABA) was purchased from Sigma-Aldrich. Solvents 1,4-dioxane, chloroform, methanol, and dichloromethanes were purchased from Acros Organics and used as supplied.

### Fabrication of Ordered Nanodots and Nanowire Arrays

PS-PVP and HABA (1 mol of HABA and 1 mol of 4-vinylpyridine monomer unit) were dissolved separately in 1,4-dioxane. PS-PVP solution was slowly added dropwise to HABA solution while heating to 95 °C in an ultrasonic bath. The resulting solution was kept at least overnight to complete hydrogen-bond formation. Thin films were prepared by dip coating from the filtered solutions. Additional 1,4-dioxane/nitromethane mixture solvent vapor annealing of a thin film was applied to improve the order of nanodomains. Alternatively, the samples were treated in vapors of chloroform to arrange parallel alignment of the nanodomains. Nanoporous thin film was fabricated by selective extraction of HABA with methanol. The nanoporous template was dip coating from the ethanol solution of phenolic resin precursor, the thin film was sequentially cured by exposure to formaldehyde gas at 100 °C for 4 h. The cured film was finally pyrolysis at middle temperature (heating to 450 °C in 2 h and keep 2 h), to remove the PS-PVP and resulted ordered nanodots arrays (Fig. 1).

**Fig. 1** Scheme of the fabrication of highly ordered polymeric nanodot and nanowire arrays templated by nanoporous thin films



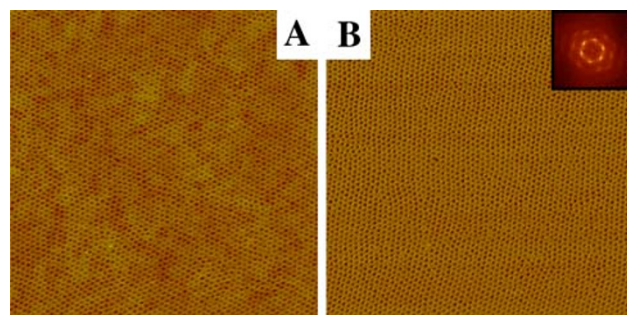
### Characterization of the Ordered Thin Films

The thickness of the polymer films was measured by a SE400 ellipsometer (SENTECH Instruments GmbH, Germany) with a 632.8 nm laser at a 70° incident angle. Atomic force microscopy (AFM) imaging was performed using a Dimension 3100 scanning force microscope (Digital Instruments, Inc.) in the tapping mode. Analysis of the AFM images (fast Fourier transform) was performed with WSxM software (Nanotec Electronica).

### Result and Discussions

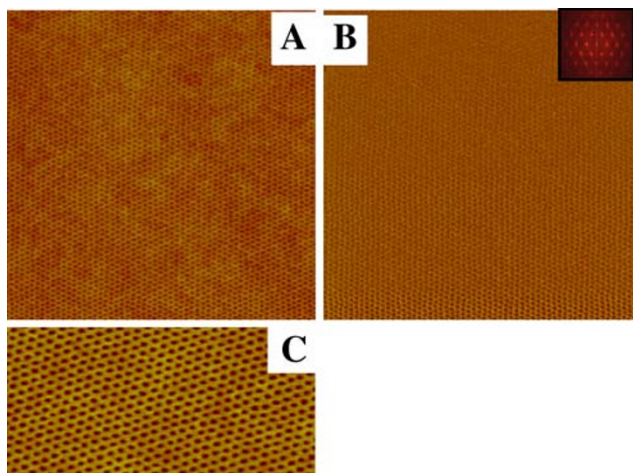
The as-deposited PS-PVP/HABA thin film form cylindrical phase separation normal to the substrate, with poor lateral ordering. Due to the thermal liability of hydrogen bonding, solvent vapor annealing is an elegant approach to promote BCP ordering, in the previous study, dioxane was chosen as the annealing solvent, here we dedicating chosen a 1,4-dioxane/nitromethane mixture solvent annealing in order to further enhances the long-range ordering in relatively short time. After being annealed in a dioxane/nitromethane mixture solvent for about 24 h, the films were taken out and rinsed in methanol for 5 min to destroy the hydrogen bonding and removes selectively HABA from thin film, and resulted a nanoporous thin film, the AFM revealed the orientation order is only of short-range, this is also apparent from a smashed ring in the FFT plot (Fig. 2).

However, further prolonging solvent annealing time to about 72 h in mixture atmosphere lead to a dramatically increase in the long-range ordering of the thin film, AFM image clearly identified a near-defect-free ordered arrays of highly ordered hexagonal structure with all pores oriented perpendicular to the substrate (Fig. 3), the Fourier transform plot of the corresponding AFM phase image is shown in the inset, the six sharp first-order peaks clearly indicate the presence of a highly ordered hexagonal structures, this higher order peaks attest to the high degree of order within the thin film. The mean center-to-center distance of the nanopores based on the AFM image is about 30 nm. During solvent annealing, PS, and P4VP/HABA, blocks are swelled by dioxane vapor and tend to organize into a



**Fig. 2** AFM images of nanoporous thin films **a** height image, **b** phase image. Mixture solvent annealing for 24 h, and washed with methanol. Thin film 45 nm thick, lateral scale 1500 nm × 1500 nm. The inset is the FFT plot of the image

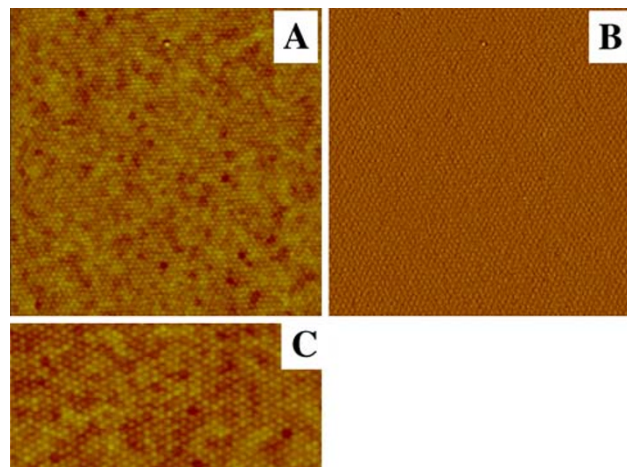




**Fig. 3** AFM images of the nanoporous thin films **a** height image, **b** phase image, **c** enlarged height image. Mixture solvent annealing 72 h, and washed with methanol. Thin film 45 nm thick, lateral scale 1500 nm  $\times$  1500 nm. The inset is the FFT plot of the AFM image

ordered structures, however, this process is restrained by dioxane in a certain extent due to the good solubility of dioxane for all the blocks, with the addition of nitromethane which is a good solvent only for the minor PVP/HABA block, the repulsion between the PS and P4VP/HABA domains is enhanced, a fast and highly ordered defect-free microphase separation structure is achieved.

These nanoporous thin films can be used as scaffolds for fabricating organic, inorganic, and metal nanostructures. Compared with the well studied inorganic and metal nanostructures, organic (polymeric) nanostructures remains less researched, despite their great potential in catalysis and membrane separation. Here, we demonstrated that highly ordered phenolic resin nanodot and nanowire arrays can be prepared through perfect replication of the ordered nanotemplate with the direction of hydrogen bonding and the capillary action of nanopores [27]. The above prepared nanoporous thin films were immersed in the phenolic resin precursor/ethanol solution, the nanopores were immediately filled by phenolic precursors due to the capillary action of cylindrical nanopores the formation of inter-polymer hydrogen bonding complex between the PVP in the inner pore surface of the nanotemplate and the phenolic resin. As ethanol is just a good solvent for minor component PVP, while is a nonsolvent for the matrix composed of PS, thus, the nanoporous templates are maintained during the dip coating process. When the template was drop from the precursor solution, the ethanol vaporized and the phenolic resin precursor were maintaining inside the nanopores. After curing with formaldehyde, the filled nanotemplates were then pyrolysed at middle temperature (heating to 450 °C in 2 h and keep 2 h), this temperature is enough to degrade PS-PVP nanotemplate, while the phenolic resin can still maintained. AFM height image

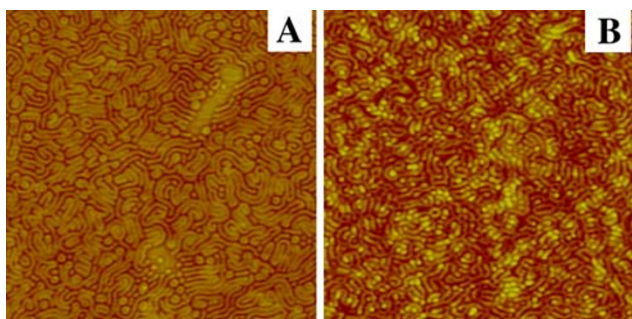


**Fig. 4** AFM images of highly ordered polymeric nanodots arrays from nanoporous thin film after pyrolysis. **a** Height image, **b** Phase image. Lateral scale 1500 nm  $\times$  1500 nm. **c** Enlarged height image

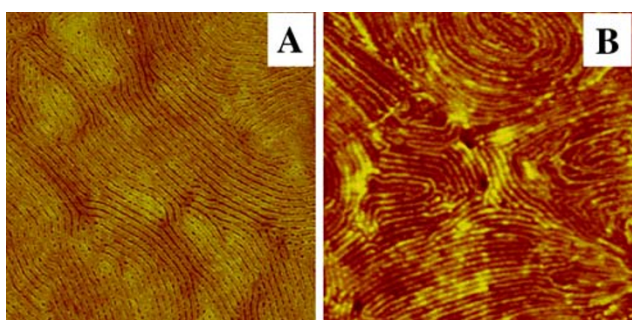
revealed, after pyrolysis, highly ordered discrete phenolic resin nanodots arrays with uniform diameter can be observed (Fig. 4), of special interest is that the original highly ordered structure of nanoporous thin film was almost maintained throughout the nanotemplate transfer process and thus resulted a perfect nanotemplate transformation; the average center-to-center distance between the nanodots was 30 nm, which was identical to that of the original porous nanotemplate.

In addition to preparation of nanodots arrays, we further extend this facile nanotemplate replica method to fabricate polymeric nanowire arrays. A special advantage of the supramolecular assembled PS-PVP/HABA system we used here is that the orientation of the phase separation can be reversibly switched from the perpendicular to parallel orientation and vice versa upon exposure to 1,4-dioxane or chloroform vapor, respectively. Thus, instead of dioxane vapor, the PS-PVP/HABA supramolecular assembly thin film was annealed in a saturated chloroform vapor for short time of 15 min to achieve re-alignment. After rinsing with methanol, the AFM revealed that most of cylindrical microdomains orientation was re-alignment parallel to the substrate, still it was clear that 15 min is not enough to fulfill the re-alignment process and thus the coexistence of normal and parallel alignments of nanodomains were observed (Fig. 5a). Followed the same template transfer process, this nanotemplate was dip coating from phenolic resin precursor solution, and followed by curing and middle temperature pyrolysis, large areas of short polymeric nanowires with nanodots mixture were formed (Fig. 5b), which was similar to the original nanotemplate.

Further prolonging the chloroform solvent annealing time to 30 min is enough to fulfill the re-alignment transformation process, after rinsing with methanol, the AFM



**Fig. 5** **a** AFM height images of thin film nanotemplate, after re-alignment using chloroform annealing for 15 min. **b** Height images of the resulted short polymeric nanowire arrays replica after pyrolysis. Lateral scale 2000 nm × 2000 nm



**Fig. 6** **a** AFM height images of thin film nanotemplate, after re-alignment using chloroform annealing for 30 min. **b** AFM height images of polymeric nanowire arrays replica after pyrolysis. Lateral scale 2000 nm × 2000 nm

revealed that all the cylindrical microdomains were oriented parallel to the substrate (Fig. 6a), and thus after deposition and middle temperature pyrolysis, a longer nanowire arrays which was identical to that in the original nanotemplate can be achieved (Fig. 6b).

## Conclusion

In summary, we have provided a general route to fabricate highly ordered polymeric nanodot and nanowire arrays using supramolecular assembled block copolymer thin film as nanotemplates through the interpolymer hydrogen bonding capillary action. The as-deposited PS-PVP/HABA thin film formed randomly hexagonally packed cylindrical phase separation structures, with the dedicating choosing of mixture solvent annealing atmosphere (dioxane as good solvent for both blocks and an additional nitromethane as a selective solvent only for the minor component PVP/HABA), a near-defect-free nanoporous thin film with long-range ordering over a broader range of length scales can be achieved, extraction of HABA microdomains resulted in

highly ordered nanoporous thin films. Under the direction of interpolymer hydrogen bonding and the capillary action of nanopores, the nanotemplate can be properly filled with phenolic resin precursor, followed by curing and pyrolysis at middle temperature which will selectively degrade the PS-PVP block copolymer nanotemplate, a perfect ordered nanodot arrays replication was obtained, thus resulted in an excellent and efficient transformation of the nanoporous template to functional polymeric nanodot arrays. The orientation of the supramolecular assembly thin films can be readily re-alignment from the perpendicular to parallel the substrate upon exposure to chloroform vapor, and thus this facile nanotemplate replica method can be further extend to generate large areas of polymeric nanowire arrays. Thus, we have achieved a successful sub-30 nm patterns nanotemplates transfer methodology for fabricating polymeric nanopattern arrays with tunable morphology and lateral spacings.

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