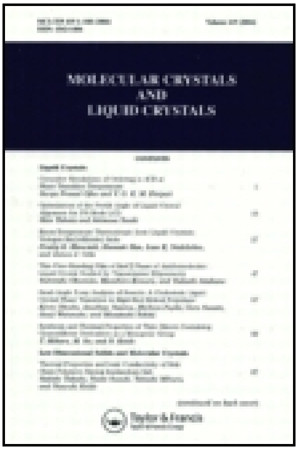

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# Block Copolymer Thin Films from Solutions with Different Solvent Quality

Chansub Lee [a], Hi Jo Youk [a], Han-Yong Jeon [a] & Seung Hyun Kim [a]

[a] Division of Nano-Systems Engineering, Inha University, Incheon, South Korea

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# Block Copolymer Thin Films from Solutions with Different Solvent Quality

**Chansub Lee, Hi Jo Youk, Han-Yong Jeon,**
**and Seung Hyun Kim**
Division of Nano-Systems Engineering, Inha University,
Incheon, South Korea

*Block copolymers composed of chemically different components exhibit unique solution properties depending on the nature of solvent. In this work, by changing the solvent quality from neutral to selective solvent, its effects on the structure of block copolymer thin films are investigated. In a neutral solvent, the cylindrical microdomains exhibit typical morphology with parallel orientation due to selective interaction with substrate, while the micellar solution produces the spherical morphology. Unexpectedly, before the micelle forms, the orientation of cylinders is found to change to perpendicular orientation. Therefore, well-controlled solution processing can provide a very efficient way to produce well-controlled nanostructure without additional processes in practical applications.*

**Keywords:** aggregates; block copolymer; orientation; solvent annealing; solvent quality; thin film

## INTRODUCTION

Block copolymer systems have attracted much attention in the recent research because they can provide a versatile platform for the fabrication of nanostructured materials as a viable alternative to top-down approach such as traditional photolithography [1–3]. The immiscibility between chemically different polymer chains composing block copolymers drives them to phase-separate, like with polymer blends. However, the connectivity of polymer chains in block copolymers restrains them from macroscopically phase-separating, and their phase separation is rather limited to the dimension of the copolymer

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Address correspondence to Seung Hyun Kim, Division of Nano-Systems Engineering, Inha University, Incheon 402-751, South Korea. E-mail: shk@inha.ac.kr

chains, 5 ~ 50 nm in size. Moreover, depending on the volume fraction of the copolymer components and the strength of segmental interactions, various ordered microdomains ranging from spheres to cylinders to lamellae have been predicted theoretically and observed experimentally. Such features of block copolymers make them ideal candidate for applications as templates and scaffolds [4–9]. In thin film state, there exist additional effects due to the presence of interface/surface and geometrical constraints, which sometimes force block copolymers to behavior in a different way from that in the bulk state [10–12]. Therefore, the self-assembly of block copolymer can offer a simple route to fabricate nanometer-scale structure, but the careful control of orientation and order of microdomains in thin films should be required in order to fully utilize the opportunities provided by self-assembly of block copolymers. Much effort has been made in the last decade and some successes have indeed been achieved by the introduction of external fields such as electric fields [5], shear forces [13], temperature gradient [14], graphoexpitaxy [15], crystallization [16], controlled interfacial interactions [17] as well as solvent annealing/evaporation [18,19].

In solution, block copolymers can generate a nanometer-scale object, i.e., form micelles s in a selective solvent, where the insoluble blocks occupy the core of micelle and the soluble blocks are exclusively located in the corona region. The diameter of micelles is controlled by the molecular weight of the block copolymers and the interactions between the copolymer blocks and the blocks with the solvent. Micelle are sometimes used to dissolve otherwise insoluble components in a solvent, which are selectively segregated into the core region of the micelle in the final state. Using this property, the micellar core-shell structure is utilized as a nanoreactor that allows for the selective dissolution of metal precursor salts into the core and the generation of monodisperse metal nanoparticle in a core after an appropriate reduction step [20–23]. In a dry state, thin film with micellar monolayer thickness provides a means to control the arrangement of nanoparticle arrays by self-assembly process [24–26].

However, few systematic study on the effects of solvent quality on the morphology and orientation of microdomains in thin film of block copolymer has yet reported. Here in order to gradually change the solvent quality from neutral to selective solvent, a selective solvent that is favorable for a minor block is systematically added to the block copolymer solution where the block copolymers are initially dissolved in a good solvent for both blocks. The block copolymer film morphology from each copolymer solution is examined by scanning force microscopy (SFM) after film generation and the annealing effects are also investigated.

## EXPERIMENTAL SECTION

Two polystyrene-*block*-poly(ethylene oxide) (PS-*b*-PEO) with different molecular weights used in this work were purchased from Polymer Source, Inc. One (PS-*b*-PEO1) has a molecular weight of 25.3 kg mol$^{-1}$ and the other (PS-*b*-PEO2) a molecular weight of 35.0 kg mol$^{-1}$. Considering the composition of copolymer, both block copolymers self-assembles into hexagonally packed arrays of cylindrical microdomains with PS as a major component and PEO as a minor component. Benzene was used as a neutral solvent, and in order to change the solvent quality, methanol which is a good solvent for PEO but a poor solvent for PS was added stepwise to benzene solution. Therefore, the solvent quality for PS-*b*-PEO was gradually changed from neutral to selective solvent.

Block copolymer thin films were prepared by solution-casting and spin-coating onto the silicon substrate. Film thickness was controlled by the solution concentration and/or spinning speed, and measured by a Filmetrics Interferometer. The structure of block copolymer in solutions was examined by dynamic light scattering and the morphology of block copolymer in thin films by SFM using a Digital Instrument Nanoscope Multimode IVa in a tapping mode. Some of the films were further relaxed to remove the residual stress produced during the film formation by solvent annealing.

## RESULTS AND DISCUSSION

For comparison, all block copolymer solutions are controlled to have a constant copolymer concentration, irrespective of solvent composition. Solvent composition is changed from benzene/methanol 100/0 (v/v) to 60/40 (v/v) to systematically observe the effects of solvent quality. As the concentration of methanol increases in solution, the solvent property is expected to be gradually changed from neutral to selective solvent. This can be directly observed with bare eye for PS-*b*-PEO1 solution, as shown in Figure 1. The solutions of PS-*b*-PEO1 with methanol of lower content ($\leq$30 vol%) look transparent while the solution with methanol of 40 vol% becomes opaque, indicating the micelle formation at this composition due to the increased selectivity. Figure 2 shows SFM phase images of PS-*b*-PEO1 films prepared by solution-casting using the solutions shown in Figure 1. As-cast films from the solutions with methanol of up to 20 vol% exhibit similar morphology

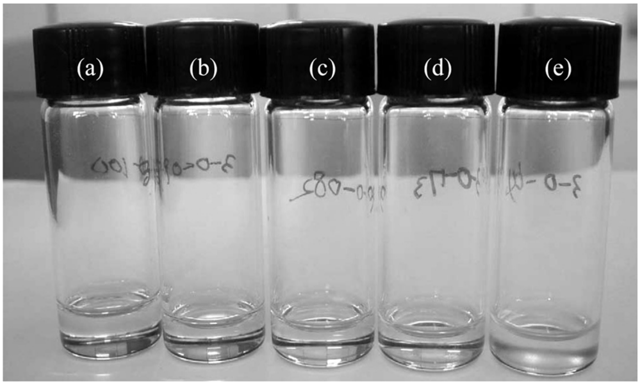

**FIGURE 1** Block copolymer solutions with different composition of benzene and methanol: (a) benzene/methanol 100/0 (v/v); (b) 90/10 (v/v); (c) 80/20 (v/v); (d) 70/30 (v/v); (e) 60/40 (v/v).

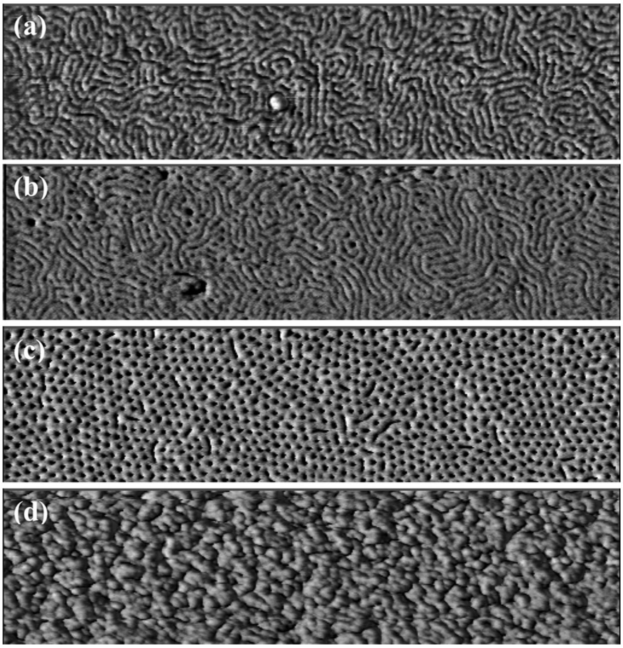

**FIGURE 2** SFM phase images of PS-*b*-PEO1 films prepared by solution-casting the solutions with different solvent composition: (a) benzene/methanol thanol 100/0 (v/v); (b) 80/20 (v/v); (c) 70/30 (v/v); (d) 60/40 (v/v).

where the cylindrical microdomains are oriented parallel to the surface. 60/40 (v/v) solution produces a typical morphology generated from the micellar solution.

On the other hand, unexpectedly, for the film made from 70/30 solution, the cylindrical morphology with perpendicular orientation to the surface is produced which is in most cases more desirable from the point of view of applications. Similar results were observed in case of films prepared by spin-coating, as shown in Figure 3. Solutions with up to 20 vol % methanol produce the films with a mixed orientation of cylindrical microdomains. The micellar solution with 40 vol% methanol content (Fig. 3d) generates the film with small spherical objects characteristic of the aggregates in a solution, which is very similar to that in Figure 2d.

To investigate the solution properties, the dynamic light scattering experiments were conducted. As expected, no scattering was detected

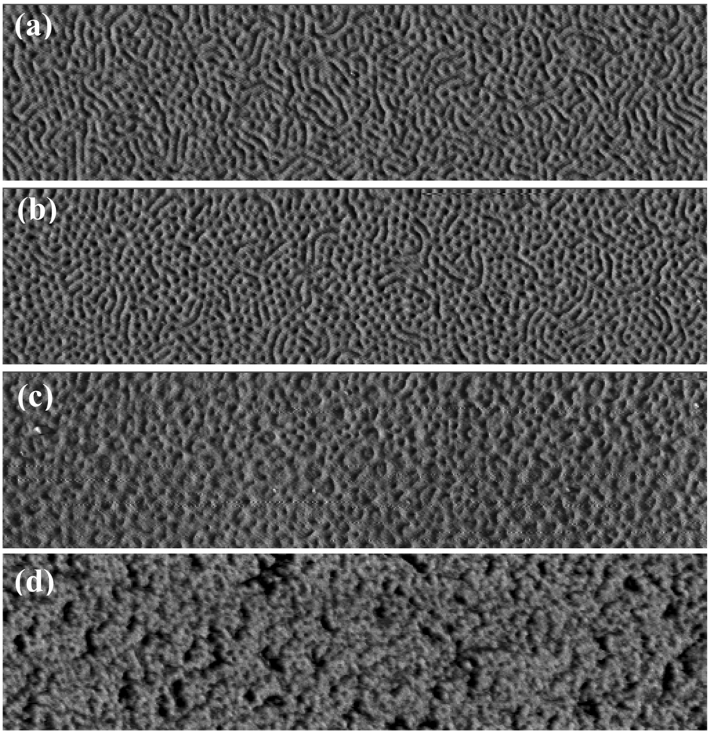

**FIGURE 3** SFM phase images of PS-*b*-PEO1 films prepared by spin-coating the solutions with different solvent composition: (a) benzene/methanol 100/0 (v/v); (b) 80/20 (v/v); (c) 70/30 (v/v); (d) 60/40 (v/v).

for solutions with up to 20 vol% methanol, indicating no formation of any aggregates over such range of methanol concentration in mixed solvent. On the other hand, 40 vol% methanol solution clearly exhibits the aggregation formation whose average size is estimated as around 41 nm from their size distribution, as shown in Figure 4. Interestingly, the solution with 30 vol% methanol shows different behavior from those with other concentrations of methanol, where week scattering signal, although not so strong as the one for micellar solution with 40 vol% methanol, was detected, and based on that, the size distribution can be calculated, as shown in Figure 4. This behavior is also different from those with lower content of methanol, where any reliable size distribution could not be generated from the light scattering. The exact structure of a solution with 30 vol% methanol is not clear at this point, but very tiny aggregates in solution induce the orientation change of cylindrical microdomains from parallel to perpendicular direction. Therefore, this method can provide much easier and more efficient route to manipulate the orientation of cylindrical microdomains than different methods for the control of perpendicular cylindrical orientation in consideration of practical applications.

The same result is observed for PS-*b*-PEO2 with higher molecular weight. Figure 5 shows the SFM phase images of PS-*b*-PEO with 35 kg mol$^{-1}$. The films made from the solutions with lower content of methanol (up to 20 vol%) show parallel orientation of PEO cylinders,

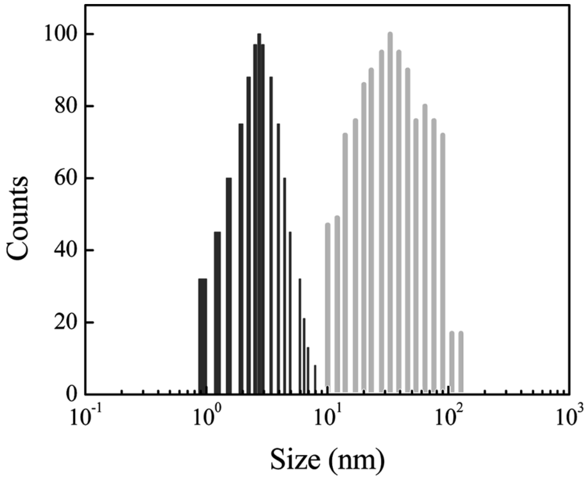

**FIGURE 4** Size distribution of aggregates in a solution with 30 vol% methanol (in red, left) and 40 vol% methanol (in yellow, right) measured by light scattering.

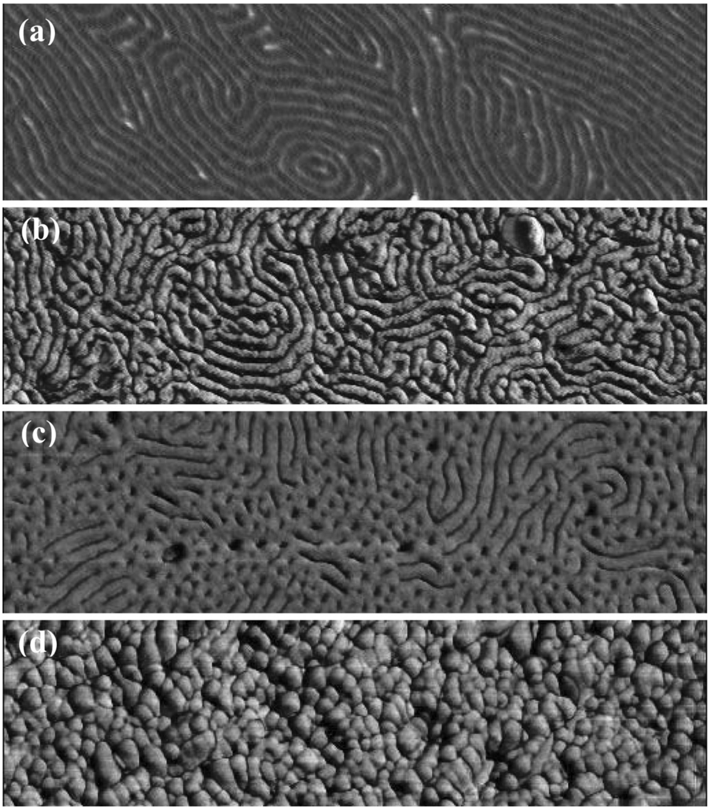

**FIGURE 5** SFM phase images of PS-*b*-PEO2 films prepared by solution-casting the solutions with different solvent composition: (a) benzene/methanol thanol 100/0 (v/v); (b) 80/20 (v/v); (c) 70/30 (v/v); (d) 60/40 (v/v).

and on the other hand, the film from 40 vol% methanol solution exhibits the feature of micellar solution. As in the case of PS-*b*-PEO1, the film from 30 vol% methanol solution shows the orientational change (Fig. 5c), although it still has parallel orientation over small region. As the molecular weight of block copolymer increases, the critical micellar concentration (CMC) at which the micelle starts to form is usually expected to decrease. However, in this work, the CMC does not change much over the molecular weight we have changed, although the increase in the size of microdomains can clearly be observed in Figure 5.

Figure 6 shows the SFM phase images of solvent-annealed films of PS-*b*-PEO1 which were initially produced by spin-coating. In spite of

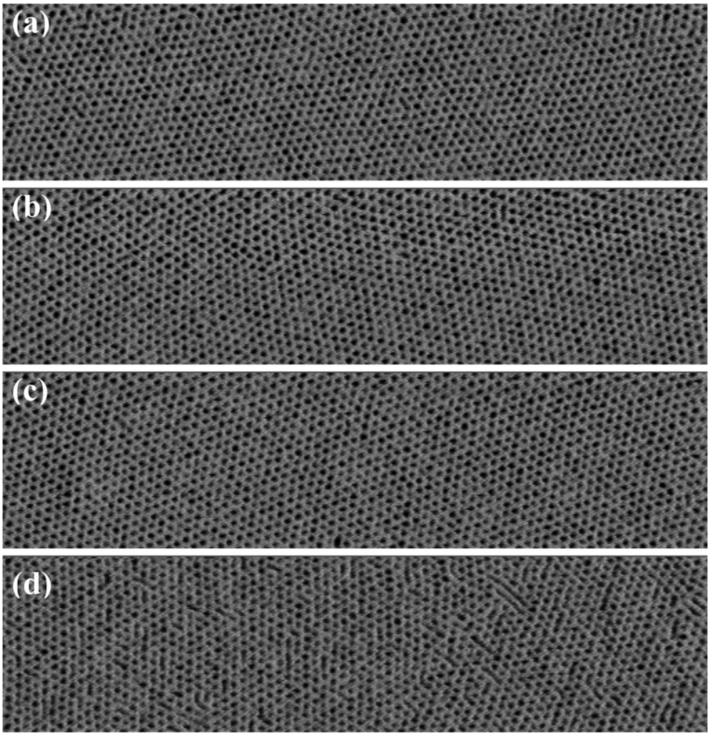

**FIGURE 6** SFM phase images of solvent-annealed PS-*b*-PEO1 films that were initially prepared by solution-casting the solutions with different solvent composition: (a) benzene/methanol 100/0 (v/v); (b) 80/20 (v/v); (c) 70/30 (v/v); (d) 60/40 (v/v).

different morphologies with different methanol content in solution, as shown in Figure 3, the annealed films show the similar morphology after solvent annealing. As shown in the previous works [18,19,27], solvent vapors are absorbed into the block copolymer films and the films are swollen during the solvent annealing. Thus the order generated by the microphase separation disappears and the films are in the disordered state. On solvent evaporation, ordering is initiated at the surface of the film and propagates through the entire film, leading to a high degree of lateral order with perpendicular orientation, as shown in Figure 6. Therefore, the memory for initial morphology before solvent annealing has been lost, and the films with the same morphology are generated after solvent annealing, irrespective of the methanol content in solution of block copolymer.

## CONCLUSION

The structure and morphology of as-cast and as-spun films of block copolymer were shown to strongly depend on the solvent quality. In this work, the solvent quality was gradually changed from neutral to selective for the minor block. For solutions with lower content of methanol, no aggregates are formed in solution and the films made from such solutions have parallel orientation through the solution-casting process and mixed orientations through spin-coating process. In the case of solution with much higher content of methanol, the micelle are formed in solution due to the increased selectivity of solvent, and the film made from such solution exhibits the micellar feature at the surface. Just before micelle formation, however, the morphological change is observed due to the change of solution state. Therefore, well-controlled solution processing can provide a very simple but robust way to produce well-controlled nanostructure without additional processes.

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