

## 블록공중합체를 이용한 나노 박막 제어 및 응용

김진곤, 정운용, 류두열, 김동하\*, T.P.Russell\*  
포항공대 화공과, Univ. MASS.\*

### Control and application of the nanoporous structure in block copolymer thin films

Jin Kon Kim, Unyong Jeong, Du Yeol Ryu, Dong Ha Kim\*, Thomas P. Russell\*

Department of Chemical Engineering and Polymer Research Institute

Electronic and Computer Engineering Divisions

Pohang University of Science and Technology

\*Silvio O. Conte National Center for Polymer Research,

Polymer Science and Engineering Department, University of Massachusetts at Amherst

### 서론

Block copolymers which self-assemble to make periodic structures with well-defined size and spacing on tens of nanometers length scale have attracted a lot of attention due to its potential usage as functional nanostructures.[1-6] The structures are determined by the molecular weight, chemical structure, molecular architecture, and composition of the block copolymers.[7] The controllability of the microdomains dimension as well as the orientation is utmost necessary for possible application. However, the fact that the structures are simply determined by molecular weight and volume fraction for a given block copolymer restricts the range of microdomains size and lateral distance between microdomains. Here, we will present new ways to make nanoholes much smaller than those by block copolymers only, by one way keeping the structure the same, and by the other way control the structure size.

### 본론

An asymmetric P(S-b-MMA), having a styrene weight fraction of 0.70 and a weight average molecular weight (Mw) of 81,000 with a polydispersity of 1.03, was synthesized anionically. A hydroxy terminated random copolymer of styrene and methylmethacrylate denoted P(S-ran-MMA), having a styrene weight fraction of 0.58 and Mw of 11,000 with polydispersity of 1.13, was used to orient vertically PMMA nanodomains to the substrate. Spun-coat random copolymer was covalently bonded to SiO<sub>2</sub> layer at 170 °C for 3 days under vacuum, giving a ~6 nm length of random copolymer brush layer after rinsing with toluene. Thin films (~31 nm) of P(S-b-MMA) were prepared by spin casting on the random copolymer brush. The samples were annealed at 170 °C under vacuum for two days, and then quenched to room temperature.

The block copolymer thin film was exposed to ozone with a flow rate of 0.6 cc/min for various times in air at 17 °C. We found that when the specimen was treated by ozone

at room temperature, PS block was crosslinked to make a hard wall, whereas PMMA block was not affected. The crosslinking of the PS matrix induces volume shrinkage in lateral direction as well as height direction. Finally, when this film is annealed at higher temperature greater than the glass transition temperatures of PS and PMMA blocks ( $\sim 100$  and  $\sim 110$  oC), nanoholes were generated inside the PMMA block. These holes did not change with further annealing. The morphology and size were studied by TEM (Hitachi H-600A), stained with RuO<sub>4</sub> to get better contrast and to get rid of the possibility of PMMA degradation.

Figure 1A, 1B, and 1C are TEM images of specimens treated by ozone for 2 different times (10, 30, and 60 min) at 17oC. It is seen that the nanoholes are formed and these sizes increase from  $\sim 3$  to  $\sim 8$  nm with increasing ozone exposure time. Also, over-focused TEM image without staining with 60 min ozone treatment is added in Figure 1D. This image shows that nanoholes are generated at the center of PMMA block treatment. The TEM images given in Figure 1 indicate that the hexagonally packed cylinder microdomain oriented vertically to the substrate remains the same even though crosslinking degree was varied. Thus, this technique can give a new way to control the nanohole size without changing the original structure.

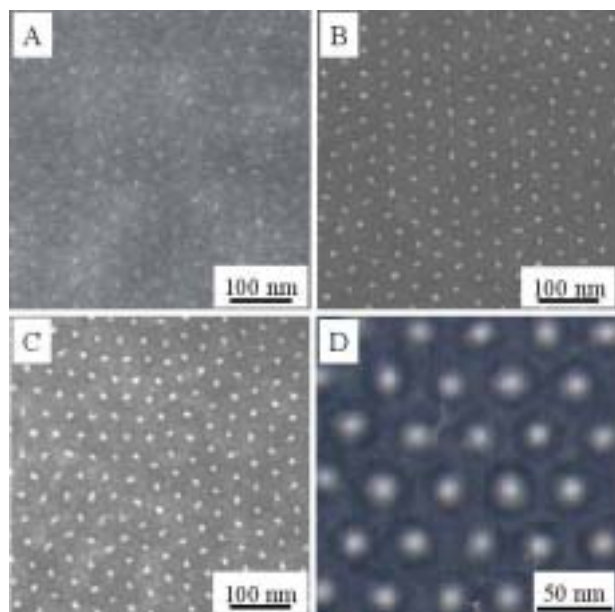


Figure 1. TEM images with different ozone exposure times, followed by annealing at 170 oC for 4 hr in vacuum oven. (A) 10 min ozone exposure, (B) 30 min ozone exposure, (C) 60 min ozone exposure, (D) over-focused image of 60 min

Thin films ( $\sim 31$  nm) of P(S-b-MMA)/PMMA mixtures with 1.5 ~ 22 wt % PMMA homopolymer relative to PMMA block were prepared by spin casting on the random copolymer brush. The samples were annealed at 170 C under vacuum for two days, and then quenched to room temperature. After crosslinking, the sample was dipped into acetic acid for over 4 hr to remove completely PMMA homopolymer. Then, the sample was annealed at 170 oC for 4 hr in order to get the final holes. These holes did not change with further annealing at higher temperatures. Figure 2 shows the resultant holes with varying homopolymer content. It ranged from a few nanometers to over 20 nm. The insets in Figure

2 are Fourier Transformation (FT) of the TEM images, in which the FT images are complete circles in all cases. The lattice distance which is inverse proportional to the distance in the FT image, increases with increasing content of PMMA homopolymer (34 nm for neat PS-*b*-PMMA and 44 nm for 22 wt % of PMMA homopolymer). These results indicate that the cylindrical morphology took simple expansion in lateral direction, without skewing the structure, with increasing PMMA homopolymer content.

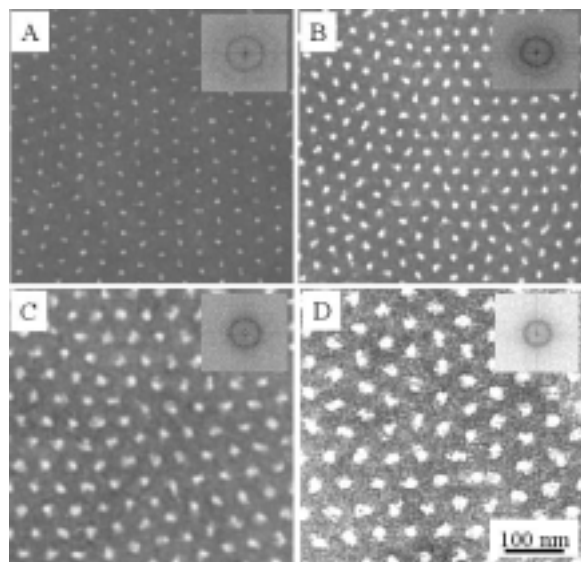


Figure 2. TEM images after selective removal of PMMA homopolymer.

(A) 0 wt%, (B) 1.5 wt%, (C) 9 wt%, (D) 22 wt%

Now, we estimate the nanohole size. Since the PMMA homopolymer used in this study has 2.5 times the molecular weight of PMMA block chain, localization of PMMA homopolymer in the central area within PMMA cylinders is a reasonable assumption. In this case, simple mathematics gives the final radius as following.

$$\pi R_f^2 = \left( \frac{fw}{1-w+fw} \right) \frac{2}{\sqrt{3}} D_m^2 \left[ 1 + \left( \frac{1-f}{f} \right) \left( \frac{1-w}{w} \right) \frac{A_o}{S_{o,PS}} \right] \quad (1)$$

Here,  $f$  is the volume fraction of block PMMA in the block copolymer and  $w$  is the weight fraction of homopolymer PMMA to that of PMMA block. The diameters calculated by eq (1) (solid line) and measured by TEM (solid circles) according to the amount of PMMA homopolymer are given in Figure 3. The results are in good agreement. This supports the assumption of localization of homopolymer near the center of PMMA block is reasonable. The nanoholes with the diameters spanning from ~6 nm to ~18 nm were successfully achieved.

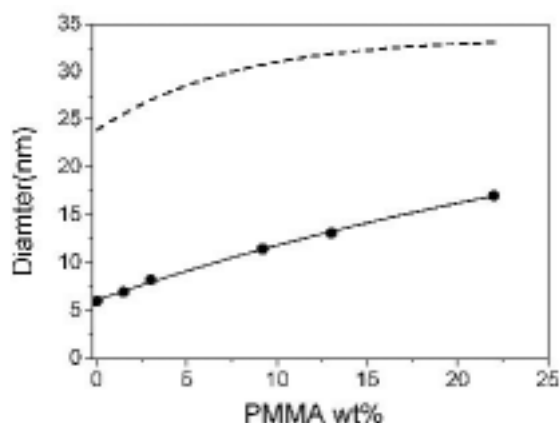


Figure 3. Hole diameters after selective removal of PMMA homopolymer : from calculation using eqn.(1) (solid line) and from measurement with TEM images in Figure 2 (solid circle). For comparison, calculated hole diameters after UV etching are also given (dotted line).

In summary, these simple processes make possible to overcome the restriction in domain size and lateral dimension of manholes in block copolymer thin films.

## References

- [1] M. Park, C. K. Harrison, P. M. Chaikin, R. A. Register, D. H. Adamson, *Science* 1997, 276, 1407.
- [2] A. Averopoulos, V. Z.-H. Chan, V. Y. Lee, D. No, R. D. Miller, N. Hadjichristidis, N. L. Thomas, *Chem. Mater.* 1998, 10, 2109.
- [3] T. Thurn-Albrecht, J. Schotter, A. Kästle, N. Emley, T. Shibauchi, L. Krusin-Elbaum, K. Guarini, C. T. Black, M. T. Tuominen, T. P. Russell, *Science* 2000, 290, 2126.
- [4] T. Thurn-Albrecht, R. Steiner, J. DeRouchey, C. M. Stafford, E. Huang, M. Ball, M. Tuominen, C. J. Hawker, T. P. Russell, *Adv. Mater.* 2000, 12, 787.
- [5] C. T. Black, K. W. Guarini, K. R. Milkove, S. M. Baker, M. T. Tuominen, T. P. Russell, *Appl. Phys. Lett.* 2001, 79, 409
- [6] P. Mansky, C. K. Harrison, P. M. Chaikin, R. A. Register, N. Yao, *Appl. Phys. Lett* 1996, 68, 2586.
- [7] F. S. Bates, G. H. Fredrickson, *Annu. Rev. Phys. Chem.* 1990, 41, 525.
- [8] U. Jeong, H. C. Kim, R. L. Rodriguez, I. Y. Tsai, C. M. Stafford, J. K. Kim, C. J. Hawker, T. P. Russell, *Adv. Mater* 2002, 14, 274

## 결론

Novel routes by which the size scale of nanostructures can be extended beyond the bounds achievable with the block copolymers alone. One of them is using block copolymer and homopolymer mixture, and the other is by crosslinking the matrix by ozone exposure. Diameter of the generated manholes ranges from a few nanometers to tens of nanometers with good ordering regularity. The nanohole size and lateral distribution are well controlled and predictable with high reproducibility.