

# Density Multiplication by Directed Self-assembly of Block Copolymer Binary Blends

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Density multiplication of chemically patterned templates by self-assembly of block copolymer (BCP) stands out as a promising alternative to overcome the limitation in conventional lithographic techniques<sup>1-3</sup>. However, equilibrium formation of perpendicularly oriented cylinders to complete the density multiplication of hexagonally closed-packed pattern is confined within a narrow BCP film-thickness range<sup>2,3</sup>. In this paper, we show binary blending of BCPs is an effective way to promote perpendicular orientation of the cylindrical domains and to expand the thickness window for the density multiplication.

Two asymmetric poly(styrene-*block*-methyl methacrylate)s, (PS-*b*-PMMA)s,  $\alpha$  and  $\beta$  with total molecular weight of 47.7kg/mol and 67.2kg/mol were used. Thin films of neat  $\alpha$  and binary blend of  $\alpha$  and  $\beta$  (fraction of  $\alpha$ : 80wt%) were self-assembled on chemically pre-patterned templates to form PMMA cylinders. The templates used were prepared by patterning PS grafted Si wafer by ebeam lithography, to form hexagonal lattice of circular areas having higher affinity to the PMMA cylinders. The lattice spacings of the patterned PS layers,  $d_s$ , were two times larger than those of microphase separated BCPs in bulk,  $d_0$ , which were  $d_0=24\text{nm}$  for neat  $\alpha$  and  $d_0=27\text{nm}$  for  $\alpha\beta$  binary blend.

Figures 1(a) and 1(b) show the SEM images of the microdomain structures of neat  $\alpha$  with thickness  $t_f$  of 38nm and 23nm, self-assembled on the templates with  $d_s = 48 \text{ nm}$ , respectively. For  $t_f = 38\text{nm}$ , the PMMA cylinders formed a hexagonal array with lattice spacing  $d=24\text{nm}$ , completing interpolation of the cylinders in between the chemically patterned lattice underneath. On the other hand, for  $t_f = 23\text{nm}$ , the PMMA cylinders were registered perpendicularly only on the chemically patterned lattice points. Figures 1(c) and 1(d) show the SEM images for  $\alpha\beta$  binary blend films on the templates with  $d_s = 54\text{nm}$ . As was the case for neat  $\alpha$ , complete density multiplication with  $d = 27\text{nm}$  was observed for  $t_f = 38\text{nm}$ , but the degree of interpolation became worse for  $t_f = 24\text{nm}$ . However, comparison of Figure 1(b) and 1(d) reveals that the degree of interpolation was better for the binary blend system.

The result suggests that addition of BCP with longer-chain promotes the stability of the hexagonally packed cylindrical morphology with perpendicular orientation. The stabilization can be attributed to the conformational entropy effects. The longer PS-block chains relax the conformation of the PS-block chains by their selective occupation of the interstitial regions in the matrix<sup>4,5</sup>.

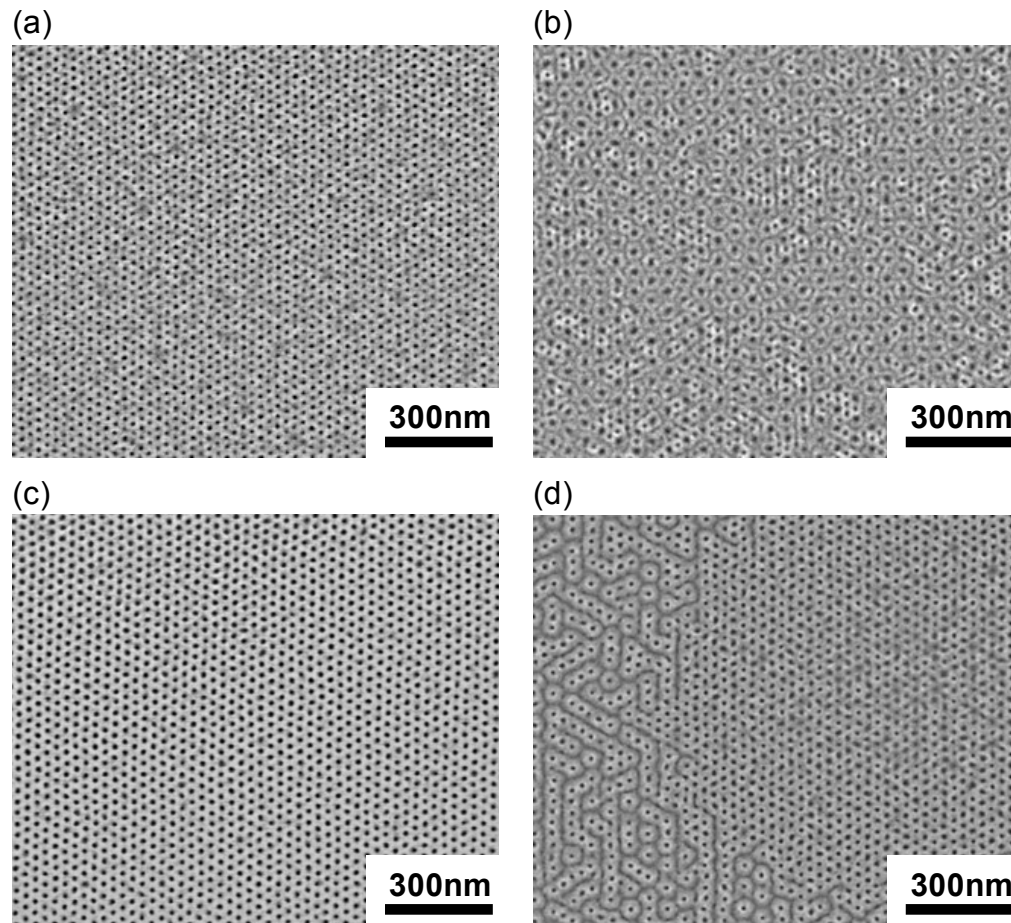


Figure 1 Top-view scanning electron micrographs of microdomain structures of PS-*b*-PMMA thin films self-assembled on the chemically-patterned templates with  $d_s = 2d_0$ . (a) Neat  $\alpha$  with  $t_f = 38$  nm. (b) Neat  $\alpha$  with  $t_f = 23$  nm. (c)  $\alpha\beta$  binary blend with  $t_f = 38$  nm. (d)  $\alpha\beta$  binary blend with  $t_f = 24$  nm. Weight average molecular weight of PS-*b*-PMMA and weight fraction of PS block of  $\alpha$  and  $\beta$  are 47.7 kg/mol and 0.25, and 67.2 kg/mol and 0.31, respectively.

#### References

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