Orientation Control of Microphase Separated Nanocylinders in Confined Volume Fabricated by Inkjet Printing

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Amphiphilic liquid crystalline diblock copolymer, PEO-ₙ-PMA(Az), forms highly ordered microphase separated film with perpendicular PEO cylinders on various substrate just by thermal annealing. Parallel oriented PEO cylinders film can be also obtained by surface covering method with poly(dimethylsiloxane) (PDMS) which inhibits the surface induced perpendicular cylinder formation. Herein, we present a simple procedure for alignment control of microdomains in micron-scale confined volume by high resolution inkjet printing (SUJ Technology) without patterned substrate. The PEO₁₁₄₋ₙ-PMA(Az)₄₃ lines with a several-micron width were prepared by the inkjet printing and subsequent PDMS top-coating and annealing. We found that PEO cylinders were oriented along the line just by the simple method. On the other hand, perpendicular PEO cylinders were obtained in the line without the top-coating. This method will afford several applications such as metallic nanowires, wire grid arrangement etc, because of the simple process without substrate patterning and desired shapes drawn by the printing system.

Key words: Mirophase-separation, Liquid crystal, Inkjet printing, Orientation control

1. INTRODUCTION

Fabrication of macroscopic domain of periodic nanoscale structures using self-organizing systems has attracted increasing attention because of the simplicity and low cost of the method. Block copolymers are self-assembling materials that spontaneous microphase separate into the densely packed periodic arrays of nanodots, nanowires, and interconnected networks. The feature size of nanostructure is restricted to molecular scale because of the chemical link between the incompatible blocks. When confined in thin films, microphase-separated structure can serve as lithographic masks with feature sizes and densities that are difficult to achieve with conventional optical lithography systems. Nevertheless, practical applications of block copolymer thin films are limited because, in general, the microdomains in thin films have no preferred orientation with poor long-large order. Therefore, many efforts have been made for fruition of macroscopic alignment of micromdomains. For example, applications of the external field, e.g., shear forces, electric fields, magnetic fields, or light irradiation and alignment via confinement of chemically or topologically surface patterned substrates have successfully been performed. The techniques using patterned substrates can produce impressive density multiplication and fabricate nanostructure at a target position with pin-point accuracy. However, the major drawback of these approaches is that every substrate must be prepatterned to direct the alignment of microdomains, which requires costly lithographic steps. Furthermore, another drawback in topologically surface is that the topographic pattern created to drive the alignment must be incorporated or eliminated with additional processing steps from the final nanofabricated structure.

The amphiphilic liquid crystalline block copolymer, PEO-ₙ-PMA(Az) (Fig. 1), forms highly ordered microphase separated film with perpendicular PEO cylinders on various substrate just by thermal annealing. Substrate modifications such as surface neutralization are not necessary, because the perpendicular cylinder forms from a film surface. The formation process of the microdomain in thin film was visualized by temperature controlled atomic force microscopy (AFM). The micropase-separated film with hydrophilic PEO cylinders can be easily applied to several block copolymer templating processes because of its amphiphilic properties. In addition, parallel oriented PEO cylinders film can be also obtained by surface covering method with poly(dimethylsiloxane) (PDMS) which inhibits the surface induced perpendicular cylinder formation. However, the parallel cylinders in thin films had no preferred orientation.

![Fig. 1 Chemical structure of PEO₁₁₄₋ₙ-PMA(Az)₄₃ diblock copolymer.](image-url)
In this paper, we present a simple procedure for alignment control of microdomains in micron-scale confined volume prepared by high resolution inkjet printing (SIJ Technology) without patterned substrate. We demonstrate in-plane uniaxial orientation of parallel oriented PEO cylinders by inkjet printing and PDMS top-coating.

2. EXPERIMENTAL SECTION
PEO$_{114}$-b-PMA(Az)$_{43}$ was synthesized by atom transfer radical polymerization (ATRP) according to our previous work. The characteristics of this sample were as follows: the weight-averaged molecular weight was $2.4 \times 10^4$, polydispersity index was 1.14, and PEO weight fraction of the block copolymer was 0.19.

Silicon wafers were modified by self-assembled monolayer (SAM) using chemical vapor deposition (CVD) with octadecyltrimethoxysilane (ODS) as shown in our previous work. First, an as-purchased silicon wafer was cleaned by ultra-sonication in acetone. Then, vacuum ultraviolet (VUV, $\lambda = 172$ nm) irradiation for 30 min caused the wafer surface hydrophilic (static water contact angle < 5$\degree$). In addition, the CVD of ODS was carried out at 140 $\degree$C for 2 h. The static water contact angle of SAM-modified silicon wafer was > 80$\degree$.

Fabrication procedure of PEO$_{114}$-b-PMA(Az)$_{43}$ thin lines is shown in Fig. 2. First, thin lines were printed by subfemtolitre inkjet printing apparatus (SIJ Technology Co.) from the 0.1 - 1 wt% anisole solutions onto the SAM-modified silicon wafer or glass substrate. The applied electric voltages to eject the anisole solution were DC 500 V and AC 500 V. The frequency of the applied AC voltage was 100 Hz. Second, the lines were coated with 2 wt% PDMS solution and thermally annealed at 140 $\degree$C for 2 h in vacuum oven. After annealing, PDMS was rinsed by hexane.

Thin films of PEO$_{114}$-b-PMA(Az)$_{43}$ were prepared by spin-coating from the 3 wt% toluene solution onto the unmodified silicon wafer at 2000 rpm for 30 s for comparison with the line experiments. The orientations of azobenzene mesogens in the lines and films were evaluated by polarized optical microscopy (POM). The surface morphologies were observed by atomic force microscopy (AFM).

3. RESULT AND DISCUSSION
The POM image of PEO$_{114}$-b-PMA(Az)$_{43}$ thin film annealed without PDMS top-coating showed dark field image, which indicates the azobenzene mesogens were oriented perpendicular to the substrate. Hexagonally arranged dot pattern corresponding to a (001) plane of the microphase-separated hexagonal cylinder structure was observed in AFM observation (Fig. 3a). The fast Fourier transformed (FFT) image shows six peak spots, which indicates the image has a single grain structure without grain boundary.

On the other hand, the bright field image was observed in POM observation when PEO$_{114}$-b-PMA(Az)$_{43}$ thin film was annealed with PDMS top-coating. Furthermore, stripe patterns were observed in AFM observation (Fig. 3b). The dark and bright regions indicate PEO cylindrical microdomains and PMA(Az) matrix, respectively. These results suggest that PDMS top-coating inhibited the surface induced perpendicular cylinder formation and induced parallel orientation of cylinders. However, the film shows the multi-grains of parallel cylinders having no preferred orientation with poor long-large order. The FFT image in Fig. 3b suggests that their alignment directions were random. The periodic
distance between the cylinders was 23 nm determined from the FFT image. Fig. 4a and 4b show AFM phase images of PEO114-b-PMA(Az)43 thin line on the SAM-modified silicon wafer without PDMS top-coating. Fig. 4b is enlarged image of Fig. 4a. The hexagonally arranged dot pattern corresponding to a (001) plane of the microphase-separated hexagonal cylinder structures were observed in the whole line. The perpendicular cylinders would be freely formed from the top-surface of the line in the characteristic manner of the block copolymer. Fig. 4c and 4d show AFM phase images of the PEO114-b-PMA(Az)43 line with the PDMS top-coating. Surprisingly, the PEO cylinders are aligned along the line direction just by drawing of the line without substrate patterning. Fig. 4e and 4f show POM images of PEO114-b-PMA(Az)43 line on the glass substrate under the crossed polarizer (P) and analyzer (A) with a sensitive color plate (S). The color change depends on the angle between the directions of S and azobenzene mesogen with positive birefringence. The blue and red colors in the configuration in Fig. 4e and 4f suggest that the azobenzene mesogens were parallel and perpendicular to the directions of S, respectively. These results indicate that azobenzene mesogens were aligned along the line in wide-range area.

3D AFM topographic image of a PEO114-b-PMA(Az)43 line in which PEO cylinders were aligned parallel along the line (Fig. 4c) is shown in Fig. 5a. The line had a high curvature of 0.20 μm⁻¹ at polymer-air interface. When a PEO114-b-PMA(Az)43 line was drawn on hydrophilic silicon wafer irradiated by VUV light, the line had a low curvature of 0.006 μm⁻¹ due to higher wettability between the block copolymer and the substrate than the SAM-modified substrate. PEO cylinders in the line with low curvature was randomly aligned same as the film case.

We considered cylinder orientation mechanism in the case of the high curvature as follows. If the PEO cylinders were not oriented parallel to the line direction, they would bend along a surface curvature of the line as shown in Fig. 5b. However, it is inferred that the high curvature of line at polymer-air interface disturbed growth of perpendicular or tilted PEO cylinder to the line direction due to the resulting bending elastic energy and induced formation of parallel PEO cylinder to the line (Fig. 5c).

4. CONCLUSION

In summary, we have presented a simple procedure for alignment control of microphase separated cylindrical microdomains in micron-scale confined volume by high resolution inkjet printing (SIJ Technology) without patterned substrate. In-plane uniaxial orientation of parallel oriented PEO cylinders were realized by inkjet printing and PDMS top-coating. High curvature of the line at polymer-air interface would induce formation of PEO cylinder parallel to the line. The aligned PEO cylinders can be applied to template for metallic nanowires17, wire grid arrangement18, etc. In addition, we expect that this orientation control approach can be applied to other block copolymer chemistries and morphologies.

5. REFERENCES

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