

## Deca-nanometer Ordered Structures in Amphiphilic Diblock Copolymer Thin Films as Reliable Nanotemplates

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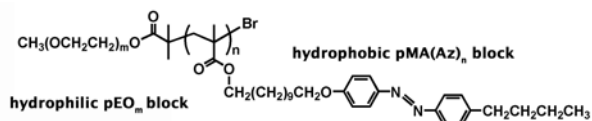
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### Introduction

Microphase separation found in polymer alloys including well-designed block copolymers and polymer blends has fascinated polymer physicists for a long time and recently draw much attention in wider research fields. One of the recent motivations is the application of a variety of such ordered nanostructures toward bottom-up-type nanotechnology and nanoscience. We have set to develop a reliable fabrication method of highly ordered and oriented cylinder array structures in a deca-nanometer level as polymer nanotemplates, through which the nanostructures can be transferred into and hybridized with various kinds of materials to be nanostructured, such as polymers, metals, metal oxides, and so on. Recently, we



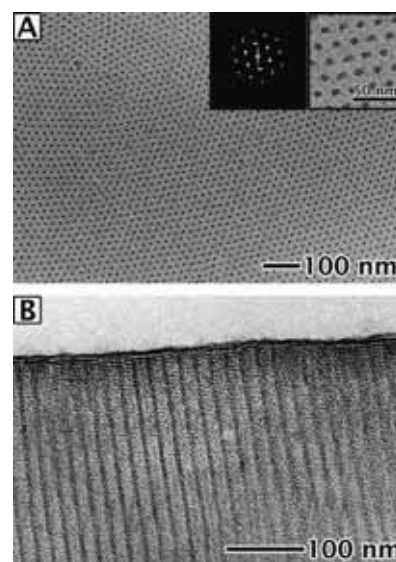
have succeeded in fabricating normally oriented cylinder array (NOCA) structures in thin films of newly designed amphiphilic diblock copolymers comprised by poly(ethylene oxide) (pEO) segment and poly(methacrylate) segments bearing azobenzene mesogen in the side chain (pMA(Az)). Emphasis should be placed on the normal orientation of the hexagonally arranged pEO cylinders in pMA(Az) matrices, quite different from multi-domain structures consisting of randomly oriented cylinder array domains found in bulk samples of conventional block copolymers. Here, we report the fabrication methods of the NOCA structures with respect to size and orientation controllability.

### Experimental

A series of amphiphilic diblock copolymers, pEO<sub>m</sub>pMA(Az)<sub>n</sub>, were prepared by using atom transfer radical polymerization of methacrylate bearing azobenzene mesogen in the side chain from pEO-based macroinitiators [1]. The resulting copolymers have narrow polydispersity ( $M_w/M_n = 1.12-1.24$ ) and a wide range of composition ( $m = 40, 114, \text{ and } 454, n = 10-152$ ) corresponding to 46-96 % of volume fraction on pMA(Az). The TEM sample was prepared by exposure of the thin film to RuO<sub>4</sub> vapor, which is known to stain hydrophilic region of the sample.

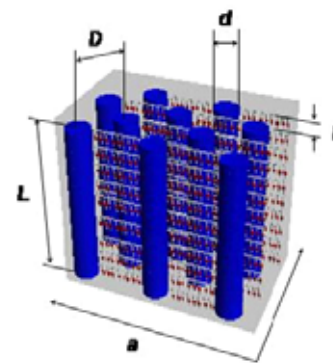
### Results and discussion

The SAXS measurement indicated that all the copolymers studied here have highly ordered and hexagonally arranged cylinder structures due to microphase separation even in a wide range of volume fraction on pMA(Az), quite different from a narrow cylinder phase lying between sphere and lamella phases found in a conventional phase diagram of diblock copolymers. The periodicity of the hexagonal cylinder structures could be widely and precisely controlled in 10-50 nm by copolymer compositions. For example, the pEO<sub>454</sub>pMA(Az)<sub>n</sub> polymers show 43.5 nm, 47.0 nm, and 50.2 nm of periodicity for  $n = 35, 90, \text{ and } 135,$



**Figure 1** TEM images as (A) top-view of pEO<sub>114</sub>pMA(Az)<sub>45</sub> thin film and (B) cross-section of pEO<sub>114</sub>pMA(Az)<sub>35</sub> thin film. Both samples were annealed at 140 °C and then stained with RuO<sub>4</sub> vapor.

respectively. **Figure 1A** shows a TEM image of pEO<sub>114</sub>pMA(Az)<sub>45</sub> thin film prepared by spin coating. Black dots of pEO domain stained by RuO<sub>4</sub> were hexagonally arranged with 7 nm of diameter and 20 nm of periodicity, corresponding to the (001) face of the hexagonal cylinder array structure. Higher order peaks in FFT image implied that the pEO cylinder array structure was formed over several micrometer region. **Figure 1B** shows a TEM cross sectional image of pEO<sub>114</sub>pMA(Az)<sub>45</sub> thin film. To our knowledge, this image is one of the best TEM images directly confirming a NOCA structure in several hundreds nanometer thick film. Note that the NOCA structure spans from one surface to the other, sometimes over 2 μm thick film, which has never been demonstrated so far. Furthermore, a 3nm-periodic layered structure between the pEO cylinders, assignable to smectic phase as liquid crystalline property of pMA(Az) segment, was clearly observed, like steps in a ladder. AFM topographic and phase images of pEO<sub>114</sub>pMA(Az)<sub>45</sub> spin-coated film showed hexagonally arranged hydrophilic pEO dot array in hydrophobic pMA(Az) matrix as the (001) face of NOCA structure. As **Scheme** shows, various structural parameters in NOCA can be controlled by polymer design and film



**Scheme** Structural parameters to be controlled by block copolymer design.

preparation with thickness and area.

We conclude that the present block copolymers have well-balanced amphiphilicity and liquid crystalline property to form highly ordered NOCA structure, which drives one to apply as nanostructured templates.

### References

- [1] Y. Tian, K. Watanabe, X. Kong, J. Abe, and T. Iyoda, *Macromolecules*, **35**, 3739 (2002).
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