

## Ultrafine, Highly Ordered Nanostructures from Carbohydrate-Inorganic Hybrid Block Copolymers

Periodic nanostructures obtained through self-assembly of block copolymers (BCPs), known as microphase-separated structure, possesses immense potential as templates for nanofabrication. One of the most important challenges in this field is downsizing of the periodicity (or domain-spacing) of the microphase-separated structure. We here newly synthesized BCPs consisting of oligosaccharide and polydimethylsiloxane segments and investigated their nanostructure by small angle X-ray scattering (SAXS) and grazing incidence SAXS (GISAXS). We found that these BCPs formed ultrafine lamellar and gyroid structures in both the bulk and thin film states. After reactive ion etching, the gyroid thin film was transformed into a gyroid SiO<sub>2</sub> material, demonstrating the material's promising potential as nanotemplates.

Microphase-separated structures of block copolymer (BCP) have found widespread use as templates for creating nanostructured materials. Among different types of BCPs, organic-inorganic hybrid BCPs are highly promising for such applications because of the superior etching resistance of inorganic polymers compared to organic polymers. Specifically, microphase-separated structures derived from silicon-containing BCPs are particularly attractive as nanotemplates because the organic block undergoes decomposition into H<sub>2</sub>O and CO<sub>2</sub>, whereas the silicon-containing block converts to mechanically and thermally stable SiO<sub>2</sub>.

For producing nanoobjects, controlling the domain-spacing ( $d$ ) of microphase-separated structures is critical. In general,  $d$  can be decreased by lowering the degree of polymerization ( $N$ ). However, BCP is required to have a  $\chi N$  (where  $\chi$  means Flory-Huggins interaction parameter) greater than a critical (10.5 for symmetric diblock copolymer) to be microphase separated. Con-

sequently, simply decreasing the  $N$  will eventually result in a disordered state. This fundamental limitation can explain difficulty in fabricating microphase-separated structures with a  $d$  of less than 10 nm [1]. Hence, a significant challenge arises with organic-inorganic hybrid BCPs, as the majority of them formed microphase separated structures with a minimum  $d$  of around 10 nm.

To address this challenge, we have successfully developed an ultrahigh  $\chi$ /low  $N$  carbohydrate-inorganic hybrid BCP system with ABA-type triblock architecture, wherein the A and B blocks consist of maltoligosaccharide (glucose, Glc<sub>1</sub>; maltose, Glc<sub>2</sub>; maltotriose, Glc<sub>3</sub>) and oligodimethyl siloxane (DMS <sub>$n$</sub> ), respectively. Remarkably, our BCPs demonstrated the formation of ultrafine microphase-separated structures in the bulk and thin film states [2].

The BCPs were synthesized via click reaction between  $\alpha,\omega$ -diazido-modified DMS <sub>$n$</sub>  (N<sub>3</sub>-DMS <sub>$n$</sub> -N<sub>3</sub>) and propargyl-modified oligosaccharide (Glc <sub>$m$</sub> -C≡CH;  $m = 1-3$ ) at 60 °C in a mixture of dry-THF/dry-DMF [1/1 (v/v)], in the presence of CuBr and  $N,N,N',N'',N'''$ -pentamethyldiethylenetriamine (PMDETA) as a catalysis and a ligand, respectively (Fig. 1). The successful synthesis of the BCPs were confirmed by <sup>1</sup>H NMR, SEC, FT-IR, and ESI MS analysis.

We next investigated the BCPs nanostructures in the bulk by small angle X-ray scattering (SAXS). All BCPs were thermally annealed at 80 °C for 6 h and then rapidly quenched, which was used for SAXS measurement at ambient temperature. Notably, the SAXS profiles of Glc<sub>1</sub>-*b*-DMS <sub>$n$</sub> -*b*-Glc<sub>1</sub> showed twelve scattering peaks, indicating a highly ordered gyroid (GYR) struc-

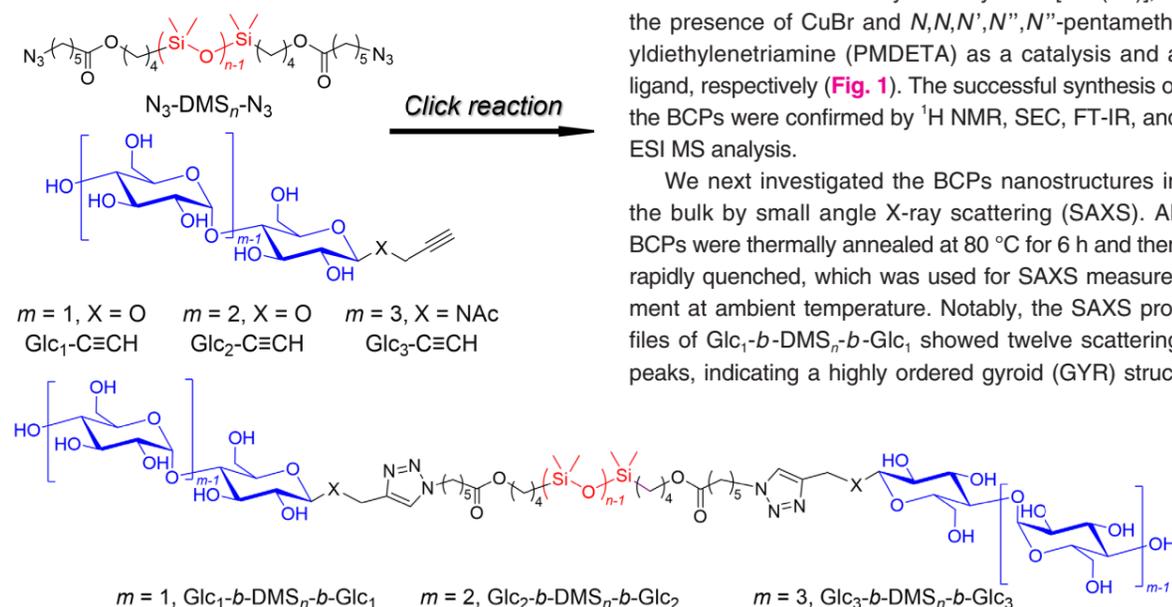


Figure 1: Synthesis of Glc <sub>$m$</sub> -*b*-DMS <sub>$n$</sub> -*b*-Glc <sub>$m$</sub>  ( $m = 1-3$ ).

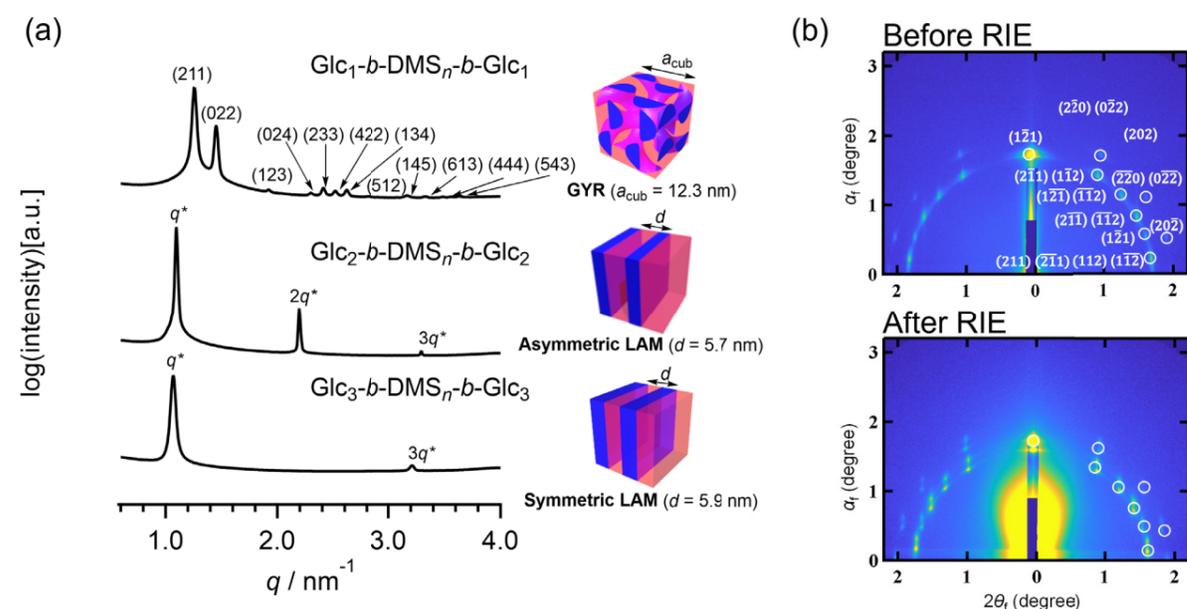


Figure 2: (a) Bulk SAXS profiles of Glc<sub>1</sub>-*b*-DMS <sub>$n$</sub> -*b*-Glc<sub>1</sub> (upper), Glc<sub>2</sub>-*b*-DMS <sub>$n$</sub> -*b*-Glc<sub>2</sub> (middle), and Glc<sub>3</sub>-*b*-DMS <sub>$n$</sub> -*b*-Glc<sub>3</sub> (lower). (b) GISAXS images of Glc<sub>1</sub>-*b*-DMS <sub>$n$</sub> -*b*-Glc<sub>1</sub> thin films before (upper) and after the RIE (lower).

tures (Fig. 2(a)). The cubic lattice parameter ( $a_{\text{cub}}$ ) was determined to be 12.3 nm using the slope of a plot of  $q_{hkl}$  versus  $(h^2 + k^2 + l^2)^{1/2}$  [ $a_{\text{cub}} = 2\pi(h^2 + k^2 + l^2)^{1/2}/q_{hkl}$ ], where  $h, k, l$  are Miller indices. Besides, the lamellar (LAM) structures with domain-spacing ( $d = 2\pi/q^*$ ) of 5.6–5.9 nm were discovered in Glc<sub>2</sub>-*b*-DMS <sub>$n$</sub> -*b*-Glc<sub>2</sub> and Glc<sub>3</sub>-*b*-DMS <sub>$n$</sub> -*b*-Glc<sub>3</sub> (Fig. 2(a)) as indicated by the higher ordered scattering peaks at the integer multiple positions relative to the primary peak ( $q^*$ ). Notably, the even-ordered peak ( $2q^*$ ) was absent (or suppressed) in the SAXS profiles of Glc<sub>3</sub>-*b*-DMS <sub>$n$</sub> -*b*-Glc<sub>3</sub>, corroborating the formation of a symmetric LAM structure.

The BCP thin film were prepared by spin-coating 5.0 wt% DMF solutions onto silicon wafer to investigate the microphase separation in the thin film state by grazing incidence SAXS (GISAXS) measurement. We here focused on GISAXS analysis of the GYR-forming Glc<sub>1</sub>-*b*-DMS <sub>$n$</sub> -*b*-Glc<sub>1</sub>. It is well established that GYR thin film exhibit a scattering pattern that varies depending on their orientation. However, the Glc<sub>1</sub>-*b*-DMS <sub>$n$</sub> -*b*-Glc<sub>1</sub> thin film exhibited a uniformly oriented GYR structure with the (121) plane parallel to the silicon wafer (Fig. 2(b)). GISAXS analysis determined the  $a_{\text{cub}}$  to be 12.5 nm, which is consistent with the result of the bulk SAXS analysis. Furthermore, the GYR's morphology, dimension, and orientation remained stable over eight-month period.

Finally, we attempted to prepare a nanoporous materials by utilizing the GYR nanostructures in the Glc<sub>1</sub>-*b*-DMS <sub>$n$</sub> -*b*-Glc<sub>1</sub> thin film. To convert the DMS <sub>$n$</sub>

block to SiO<sub>2</sub> and selectively remove the saccharide block, reactive ion etching (RIE) processes were used. The progress of the reaction was characterized by the ATR FT-IR. Although the characteristic broad absorption bands due to the hydroxyl group at approximately 3,000 cm<sup>-1</sup> and Si-CH<sub>3</sub> at approximately 1,250 cm<sup>-1</sup> were observed before the RIE, these absorption bands vanished after the RIE. Interestingly, the GISAXS images of the thin film after the RIE revealed a distinct pattern similar to that observed prior to the RIE. This demonstrates that the GYR structures, in which the (121) plane is parallel to the silicon wafer, was maintained throughout the etching process (Fig. 2(b)). These findings indicated that a GYR-structured nanoporous SiO<sub>2</sub> material could be synthesized by simply applying the RIE process to a BCP thin film.

### REFERENCES

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### BEAMLINE

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T. Nishimura and T. Isono (Hokkaido Univ.)