

# Synthesis and Nanostructural analysis of Hybrid Materials Composed of Oligosaccharides and POSS

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## Introduction

### Microphase separation

Polymer A Polymer B

coupling

Self-assembly

Block Copolymer (BCP)

Application

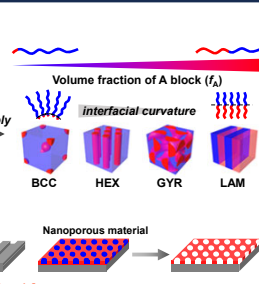
Nanofabrication

Lithography

Nanoporous material

① Downsizing of domain-spacing ( $d$ )

② Fabrication of various morphologies



### Downsizing of domain-spacing ( $d$ )

Molecular weight of BCP

$\chi$ : Flory-Huggins interaction parameter

$N$ : Degree of polymerization of BCP

$\chi N \rightarrow 10.5$

Control of molecular weight distribution ( $D$ )

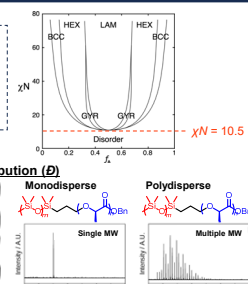
$D \rightarrow$  interfacial roughness,  $d \uparrow$

orderliness  $\downarrow$

Monodisperse BCP Polydisperse BCP

LAM ( $d = 7.1$  nm) disorder

Monodisperse BCP ( $D = 1.00$ ) is ideal



### Conformational Asymmetry

General BCP

$a_A = a_B$

$a_A > a_B$

Conformationally asymmetric BCP

$\chi N$

Disordered

Ref. E. W. Meijer et al., J. Am. Chem. Soc. 2016, 138, 4210-4218.

Ref. Masten, M. W.; Bates, F. S.; J. Polym. Sci. Part B: Polym. Phys., 1997, 35, 945

## This Work

### Previous Work (Inorganic-Oligosaccharide)

reacted

reacted

$-N_3$  &  $-CH=CH_2$ : CuAAC

(Cu(I)-catalyzed azide-alkyne cycloaddition)

$-SH$  &  $-CH=CH_2$ : Thiol-ene reaction

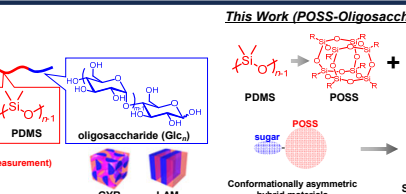
✓ Ultrafine domain-spacing ( $d = 3.5 \sim 6.0$  nm)

✓ LAM, GYR structures (HEX is observed by in-situ SAXS measurement)

✓ Sufficient etching selectivity (Selective removal)

Ref. Nishimura, T.; Satoh, T.; Isono, T. et al. Nanomaterials 2022, 12, 1653.

Ref. Nishimura, T.; Chen, H.-L.; Satoh, T.; Isono, T. et al. Macromolecules 2022, 55, 266-278.



### This Work (POSS-Oligosaccharide)

Reaction Scheme

Allyl oligosaccharide ( $Glc-CH=CH_2$ ;  $n = 1-4$ )

Propargyl oligosaccharide ( $Glc-C\equiv CH$ ;  $n = 1-4$ )

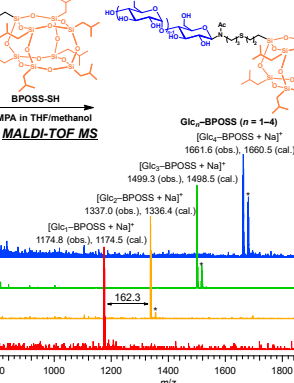
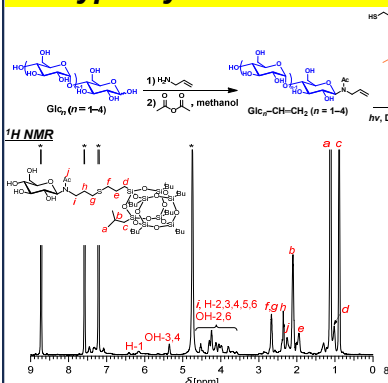
Thiol-ene reaction

Thiol-yne reaction

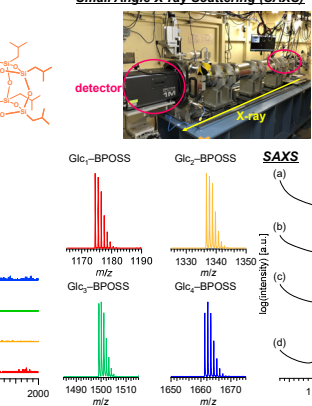
AB-type hybrid materials

AB<sub>2</sub>-type hybrid materials

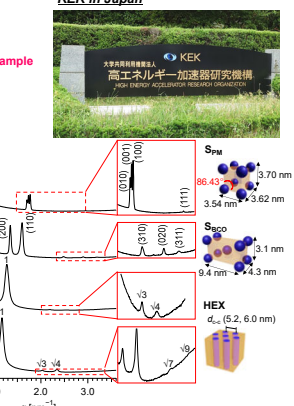
## AB-type Hybrid Materials



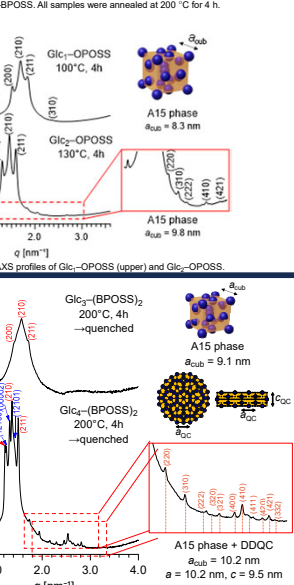
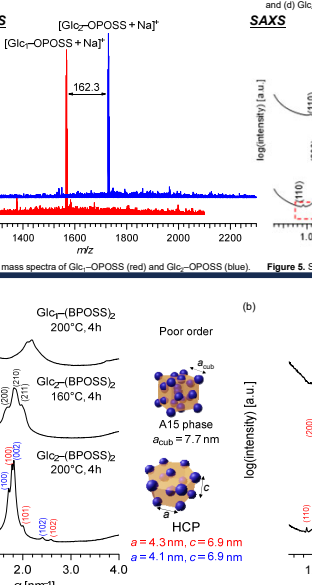
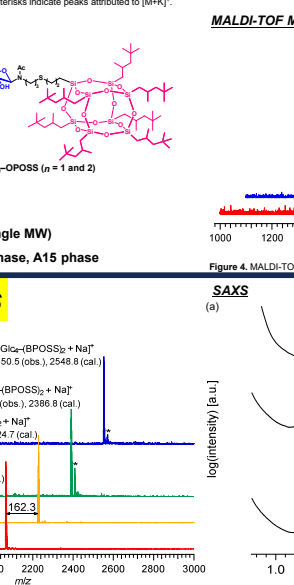
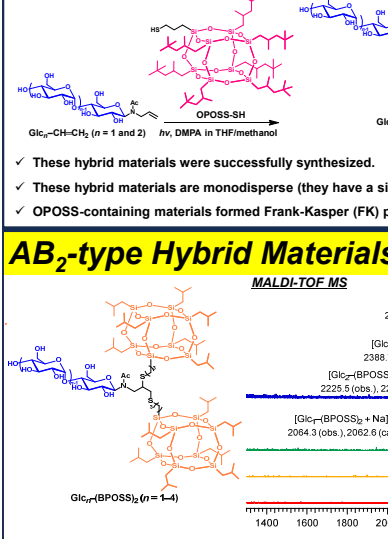
### Small Angle X-ray Scattering (SAXS)



### KEK in Japan



## AB<sub>2</sub>-type Hybrid Materials



## Conclusion

- A facile synthesis method was established for hybrid materials composed of POSS and oligosaccharides.
- Through this method, spherical and cylindrical domains, which unobserved in conventional PDMS and oligosaccharide systems, were successfully formed.
- The alkyl-chain in the POSS segments was found to have a significant impact on the self-assembly behavior, enabling the construction of high interfacial curvature morphologies.
- AB<sub>2</sub>-type hybrid materials were readily formed various spherical packing structures, including FK phases and DDQC.
- Accordingly, molecular design guidelines were established for achieving diverse spherical morphologies in inorganic-sugar hybrid materials.