Double-Decker Silsesquioxane-containing Oligomers for Sub-10 nm Scale Fabricating Materials

Lei Wang¹, Teruaki Hayakawa¹* and Kazuhiro Yoshida²

¹Department of Organic and Polymeric Materials
Graduate School of Science and Engineering, Tokyo Institute of Technology,
2-12-1 O-okayama, Meguro-ku, Tokyo 152-8552, Japan
²Research Laboratory IV, Ichihara Research Center, JNC Petrochemical Corporation
Ichihara, Chiba 290-8551, Japan

Keywords: self-assembly, double-decker silsesquioxane, sub-10 nm scale, fabricating materials

1. Introduction
Reducing the critical dimensions of semiconductor devices is one of the great challenges in microelectronic industry. Photolithography, which is widely used in semiconductor industry, but the feature structure fabricated by photoresist is limited by the wavelength.¹ To further decrease the scale to meet the requirement of industry to get sub-22 nm silicon structure, traditional photolithography reached its physical limits.

In recent years block copolymers (BCPs) are emerging as new candidates for sub-22 nm lithography to meet the requirement of microelectronic industry.² Based on the different chemical segments and differential dissolution rates, organic block copolymers can be utilized as a mask to selective etch the underlying Si substrates. This “bottom-up” method has demonstrated a facile approach to fabricate lithography materials. Higher etching selectivity and higher driving force for microphase separation make organic-inorganic block copolymers excellent alternatives to replace organic-organic BCPs to fabricate periodic structure with feature size at 10 nm scale.³ To meet the requirement of semiconductor industry in the near future, it is still necessary to further shrink the size to achieve sub-10 nm scale. However, due to the Flory-Huggins interaction parameter, BCPs are difficult to provide strong thermodynamic driving force for the formation of nanostructure at single nanometer scale.

On the other hand, the processing for forming the phase-segregated crystal or liquid crystal structure is similar to that for structure based on BCPs; molecules having two or more incompatible segments must undergo microphase segregation.⁴ Amphiphilic low-molecular-weight molecules or oligomers could form layered, cylindrical, cubic and other types of complex segregated structures on the nanometer scale (<10 nm).⁵ These structures are similar in morphology to the self-assembled structures formed by using block polymers;⁶,⁷ the only difference is that, in the former case, the self-aggregated length is larger.⁵ Although well-defined sub-10 nm scale nanostructures can be formed readily, they usually lack the required interdomain etching contrast.

In this study, we explored a new design approach for fabricating self-assembled silsesquioxane-containing oligomers with the feature size at nanometer scale. The basis of these new materials is the combination of the phase-segregation behavior of a small molecule, and the use of the different
property in dry etching resistance to reactive ions. Incorporating the double-decker silsesquioxane (DDSQ)\(^8\)\(^9\) with a strong etch resistance to oxygen plasma into low-molecular-weight molecules may favor the formation of periodic structures for a nanopatternable material. Polystyrene and branched alkyl chains were incorporated into DDSQ via hydrosilylation reaction. The self-assembled structure of these DDSQ-containing oligomers was investigated in here.

**2. Experimental**

**2.1. Materials**

Double-decker silsesquioxane was received as a gift from JNC Petrochemical Corporation. Styrene was purified first by washing with sodium hydroxide (NaOH) solution to remove inhibitor before stirring with calcium hydride (CaH\(_2\)) for 24h and then distilled under vacuum. All other reagents were purchased from Sigma Aldrich or Tokyo Chemical Industry and used without further purification.

**2.2. Synthesis of butene-terminated polystyrene**

![Scheme 1. Synthesis of butene-terminated polystyrene by living polymerization](image)

Firstly 40 ml of THF was transferred to a glass reactor and then the glass reactor was cooled to -78 °C using 2-propanol / dry ice cooling bath. Five minutes later, sec-BuLi was added until color changed to slightly yellow. Then the glass reactor was moved from ice bath to reach room temperature. Few minutes later the solution color changed to colorless. Again the glass reactor was cooled to -78 °C. Five minutes later sec-BuLi was added. After five additional minutes, styrene was added to the reactor. After stirring 30 minutes, excess amount of 4-bromo-1-butene was dropped into the glass reactor to quench the polymerization. The white precipitate was collected and dried under reduced pressure. PS3K: the yield was 95%, GPC gives Mn of 3000 and polydispersity (Mw/Mn) of 1.08. \(^1\)H NMR (400MHZ; CDC\(_13\)): \(\sigma\) 7.50-6.25 (m, 150H), 5.62 (m, 1H), 4.82 (m, 1H), 2.55-0.85 (m, 94H), 0.80-0.60 (m, 9H). \(^1\)C NMR \(\sigma\) 145.6, 127.8, 125.4, 40.4.

**2.3. Synthesis of allyl 3,4-bis(octadecyloxy)benzoate**

\[\text{Scheme 2. Synthesis route of allyl 3,4-bis(octadecyloxy)benzoate}\]

3,4-Bis(octadecyloxy)benzoic chloride was synthesized according to the literature\(^10\). To a solution of 3,4-bis(octadecyloxy)benzoic chloride (8.0 mmol) in 130 ml THF, allylachol (4.646 g, 80 mmol) and triethylamine (1.619 g, 16 mmol) were added at room temperature. Then, the mixture was stirred at 50 °C for overnight. Solvent and unreacted reagents were removed by reduced pressure distillation. Hexane was used as the solvent for recrystallization to purify the product affording allyl 3,4-bis(octadecyloxy)benzoate (yield: 84%) as white solid. \(^1\)H NMR (400MHZ; CDC\(_13\)): \(\sigma\) 7.64 (s, 1H), 7.54 (s, 1H), 6.84 (s, 1H), 6.00 (m, 1H), 5.36 (b, 2H), 5.25 (b, 2H), 4.78 (b, 2H), 4.02 (m, 4H ), 1.81 (m, 4H), 1.46 (m, 4H), 1.24-1.31 (m, 56H), 0.86 (m, 6H). \(^1\)C NMR \(\sigma\) 165.9, 155.0, 149.2, 132.1, 122.3, 118.2, 111.4, 69.0, 67.0, 31.9, 29.6, 29.3, 25.9, 22.7, 14.1.

**2.4. Synthesis of DDSQ-PS**

\[\text{Scheme 3. Hydrosilylation reaction of DDSQ}\]

DDSQ dimer (0.115 g, 0.048 mmol) and butene-terminated polystyrene (0.384 mmol) were added to a Schlenk tube. 1ml toluene and 10 \(\mu\)L Pt(dvs) were injected to the tube after degassing and refilling with argon three times. After the reaction was stirred at 100°C for 12 hours, 300ml methanol was used to precipitation. DDSQ-(PS3K) the yield was 65%, GPC gives Mn of 15000 and polydispersity (Mw/Mn) of 1.06. \(^1\)H NMR (400MHZ; CDC\(_13\)): \(\sigma\) 7.46-6.28 (m, 690H), 2.32-0.80 (m, 376H), 0.79-0.60 (m, 36H), 0.60-0.40 (m, 94H), 5.62 (m, 1H), 4.82 (m, 1H), 2.55-0.85 (m, 94H), 0.80-0.60 (m, 9H).
0.20-0.41 (m, 24H). $^{13}$C NMR $\sigma$ 146.2, 134.0, 128.0, 127.6, 127.4, 40.2, 40.1, 0.3.

2.5. Synthesis of DDSQ-(C18-2A)

DDSQ dimer (0.115 g, 0.048 mmol) and allyl 3,4-bis(octadecyloxy)benzoate (0.384 mmol) were added to a Schlenk flask. 1ml toluene and 10 μL Pt(dvs) were injected to the tube after degassing and refilling with argon three times. After the reaction was stirred at 100°C for 12 hours, 300ml methanol was used to precipitation. Recycling preparative HPLC was used to remove any unreacted 3,4-bis(octadecyloxy)benzoate and byproducts. DDSQ-(C18-2A) the yield was 38%.

1H NMR (400MHZ; CDCl$_3$): $\sigma$ 7.36-6.38 (m, 102H), 3.82 (m, 16H), 3.21 (m, 8H), 1.65 (m, 16H), 1.40 (m, 168H), 1.28 (m, 16H), 1.09 (m, 24H), 0.71 (m, 16H), 0.46 (m, 8H), 0.00 (m, 24H). $^{13}$C NMR $\sigma$ 134.3, 127.5, 58.0, 35.6, 31.9, 29.7, 17.2, 14.2, 3.6.

2.6. Measurement

Small angle X-ray scattering (SAXS) was performed using a Bruker NanoSTAR (Bruker AXS K.K., Kanagawa, Japan, 50KV per 100 mA) with a 2d-PSPC detector. Bright field Transmission Electron Miscope (TEM) images were taken by using Hitachi H7650 zero A under 80KV accelerating voltage. Bulk samples were pasted onto epoxy resin for handling. The samples were then microtomed by Diamote diamond knife at room temperature into a preset thickness of 70 nm using Reicheut-Jung Ultracut E Microtome. Ruthenium oxide was utilized for the staining of samples.

3. Results and Discussion

3.1 Self-assembly of DDSQ-PS

Butene-terminated polystyrene with different molecular weight, namely PS1.5k, PS2.3K and PS3K, were synthesized by anionic polymerization and terminated by 4-bromo-1-butene. And then, butene-terminated PS reacted with DDSQ dimer via hydrosilylation reaction. These obtained DDSQ-PS samples were purified by washing with hexane to remove any unreacted butane-terminated polystyrene. DDSQ-PS exhibits well-defined chemical structure with polydispersity index less than 1.10.

SAXS was employed to investigate the self-assembly structure of DDSQ-PS. However, as shown in Figure 1, there is no diffraction peak appears on the SAXS profile. It suggests microphase structure was not formed in the bulk sample of DDSQ-(PS3K). In addition, similar results are also observed from other DDSQ-PS samples. A possible explanation may lies on the repulsive force between PS segment and DDSQ is insufficient to form microphase separation structure due to the chemical structure similarity of polystyrene and the side group of double-decker silsesquioxane.

3.2 Self-assembly of DDSQ-(C18-2A)

In order to form microphase nanostructures, branched alkyl chains were considered as an alternative to replace polystyrene. Allyl 3,4-bis(octadecyloxy)benzoate was synthesized as described in the experimental section. Next, this wedge-shape building block was incorporated into DDSQ via hydrosilylation reaction and the obtained product was carefully purified by recycling preparative HPLC.

Alkylated DDSQ, DDSQ-(C18-2A), exhibits hydrophobic amphiphilic structure which endows it strong driving force to form self-aggregation nanostructure with long-range order. In addition, according to the simulation result obtained by Spartan software, the molecular size of allyl 3,4-bis(octadecyloxy)benzoate in the extended conformation is around 2.3 nm. Thus, alkylated DDSQ exhibits a comprehensively smaller molecular size and is expected to form sub-10 nm scale periodic structure.

The SAXS pattern of DDSQ-(C18-2A) shows well-defined diffraction peaks with ratio 1:2, suggesting a lamellar structure with a $d$-spacing value of 8.2 nm. Figure 3 shows a well-organized lamellar pattern consisting of alternating arranged bright and dark streaks. These dark and bright
domains are supposed to correspond to the POSS molecules and the long alkyl chain domains, respectively.

Figure 2. SAXS pattern of DDSQ-(C18-2A)

The self-assembled structure of the bulk sample suggests that alkylated DDSQ has potential for application in the thin film nanopatterning. Since DDSQ exhibit excellent oxygen plasma etching contrast and well-organized periodic structure at nanometer scale, this alkylated DDSQ molecular material with self-assembling ability may provide a platform for the nanometer engineering.

Figure 3. TEM image of DDSQ-(C18-2A)

4. Conclusion
In this article, two series of DDSQ-containing oligomers were synthesized and their self-aggregation behaviors were investigated. Result shows that DDSQ-(C18-2A) could form well-organized lamellar structure with a d-spacing 8.2 nm. Considering the demand of microelectronic industry, this branched alkylated DDSQ may serve as an excellent candidate for the next generation fabricating materials.

5. Acknowledgement
This work was supported by Chinese Scholarship Council. We thank Ryohei Kikuchi (Tokyo Institute of Technology) for the assistance with TEM. L.W. appreciate the great help from Ying Shi (Tokyo Institute of Technology).

References