Final Report
รายงานฉบับสมบูรณ์

Project Title Syntheses and Characterizations of Acrylamide and Methacrylamide-Functionalized Polyhedral Oligomeric Silsesquioxanes (T_8, T_{10}, and T_{12})

ชื่อโครงการ การสังเคราะห์ และ วิเคราะห์สารประกอบ Acrylamide and Methacrylamide-Functionalized Polyhedral Oligomeric Silsesquioxanes (T_8, T_{10}, and T_{12})

By Associate Professor Dr. Vuthichai Ervithayasuporn

โดย รองศาสตราจารย์ ดร. วุฒิชัย เอื้อวิทยาศุภร

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สนับสนุนโดยสำนักงานกองทุนสนับสนุนการวิจัย

Abstract

Project Code : TRG5780232

Project Title : Syntheses and Characterizations of Acrylamide and Methacrylamide-Functionalized Polyhedral Oligomeric Silsesquioxanes (T_8, T_{10}, and T_{12})

Investigator : Associate Professor Dr. Vuthichai Ervithayasuporn

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Project Period : June 2, 2014 – June 1, 2016

Abstract: The first part of this report focuses on the synthesis and functionalization of polyhedral oligomeric silsesquioxanes (POSS). We first functionalize POSS (e.g. octakis(3-chloropropyl)octasilsesquioxane; T_8) *via* nucleophilic substitution reactions with sodium phenoxide derivatives, leading to the formation of novel T_8 compounds with different aryl functionalities (e.g. aldehyde, nitro, and bromo). Meanwhile, the formation of deca- and dodecasilsesquioxanes (T_{10} and T_{12}) cages was also found during substitution reactions.

The final part of this report, chlorine-containing poly(siloxane/double-decker silsesquioxane) (P-Cl) was prepared in high yield at ambient room temperature *via* dehydrocarbonative polycondensation reaction between di[(3-chloropropyl)isopropoxysilyl]-bridged double-decker octaphenylsilsesquioxane (DDSQ) and hexamethyltrisiloxane. Particular attention for this polymer was also given to its functionalization through substitution reaction, especially due to nucleophilic substitution on the side-chain of polymer at silsesquioxane units. But more important, the use of halogen exchange method with bromine anion allows the formation of more reactive, bromine-containing poly(siloxane/double-decker silsesquioxane) (P-Br), which enables further post-substitution modification reactions in a POSS unit. The glass transition temperatures (T_g ~ 15^{o}C) of both halogenated polymers were significantly higher than poly(dimethylsiloxane) (PDMS). High transparency of polymers with hydrophobic surface could be found from solvent-casting thin film.

Keywords : Cage-rearrangement, Nucleophilic substitution reaction, Polyhedral Oligomeric Silsesquioxane, Copolymerization, Polycondensation, Polysiloxanes

บทคัดย่อ

รหัสโครงการ : TRG5780232

ชื่อโครงการ : การสังเคราะห์ และ วิเคราะห์สารประกอบ Acrylamide and Methacrylamide-Functionalized Polyhedral Oligomeric Silsesquioxanes (T_8, T_{10}, and T_{12})

ชื่อนักวิจัย : รองศาสตราจารย์ ดร. วุฒิชัย เอื้อวิทยาศุภร มหาวิทยาลัยมหิดล

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ระยะเวลาโครงการ : 2 ปี (2 มิ.ย. 2557 ถึง 1 มิ.ย. 2559)

งานวิจัยชิ้นนี้ประกอบด้วยสองส่วนหลักคือ ส่วนแรก เป็นการสังเคราะห์ และเปลี่ยนแปลงหมู่แทนที่ บนสารประกอบพอลิฮีดรอลโอลิโกเมอริกซิลเซสคิวออกเซน ได้แก่สารตั้งต้น octakis(3-chloropropyl)octasilsesquioxane ด้วยปฏิกิริยาแทนที่กับเกลือโซเดียมฟีนอกไซด์ชนิดต่างๆ ทำให้ได้สารประกอบที่มีหมู่แทนที่ชนิดต่างๆได้แก่ แอริลไนโตร อัลดีไฮด์ และ โบรมีน ทั้งนี้ทีมผู้วิจัยยังได้ค้นพบสารผลิตภัณฑ์ข้างเคียงชนิดอื่น ที่มีโครงสร้างสมมาตรทางโมเลกุลที่แตกต่างกันออกไป เช่น แบบรูปทรงกรงสิบเหลี่ยม และ สิบสองเหลี่ยม และ งานวิจัยในส่วนที่สอง เป็นการสังเคราะห์พอลิเมอร์ชนิดใหม่ ที่มีชื่อว่า poly(siloxane/double-decker silsesquioxane) ซึ่งสามารถถูกเตรียมได้ที่อุณหภูมิห้อง โดยผ่านปฏิกิริยา dehydrocarbonative ระหว่างสารประกอบตั้งต้น di[(3-chloropropyl)isopropoxysilyl]-bridged double-decker octaphenylsilsesquioxane และ hexamethyltrisiloxane โดยพอลิเมอร์ใหม่ชนิดนี้มีความสำคัญตรงที่ มีหมู่ฟังก์ชันของคลอรีนเป็นส่วนประกอบ ซึ่งสามารถนำมาใช้ให้ถูกดัดแปลงทางโครงสร้างได้ภายหลัง โดยผ่านปฏิกิริยาการแทนที่ โดยในงานวิจัยนี้ยังได้แสดงถึงการเปลี่ยนแปลงหมู่แทนที่เป็นโบรมีนเป็นองค์ประกอบ ทำให้ได้พอลิเมอร์ชนิดใหม่อีกชนิดหนึ่ง ซึ่งพอลิเมอร์ที่สังเคราะห์ได้เหล่านี้ล้วนมีค่า T_g ที่สูงกว่าซิลิโคนเหลวโดยทั่วไป พร้อมทั้งสามารถขึ้นรูปเป็นฟิมพ์เคลือบผิว มีคุณสมบัติโปร่งแสง และ ความไม่มีขั้วสูง

คำหลัก : การเปลี่ยนแปลงของกรง ปฏิกิริยาแทนที่ พอลิฮีดรอลโอลิโกเมอริกซิลเซสคิวออกเซน โคพอลิเมอไรเซชัน พอลิคอนเดนเซชัน พอลิไซโลเซน

Final report content:

1. Abstract

The first part of this report focuses on the synthesis and functionalization of polyhedral oligomeric silsesquioxanes (POSS). We first functionalize POSS (e.g. octakis(3-chloropropyl)octasilsesquioxane; T_8) *via* nucleophilic substitution reactions with sodium phenoxide derivatives, leading to the formation of novel T_8 compounds with different aryl functionalities (e.g. aldehyde, nitro, and bromo). Meanwhile, the formation of deca- and dodecasilsesquioxanes (T_{10} and T_{12}) cages was also found during substitution reactions.

The final part of this report, chlorine-containing poly(siloxane/double-decker silsesquioxane) (P-Cl) was prepared in high yield at ambient room temperature *via* dehydrocarbonative polycondensation reaction between di[(3-chloropropyl)isopropoxysilyl]-bridged double-decker octaphenylsilsesquioxane (DDSQ) and hexamethyltrisiloxane. Particular attention for this polymer was also given to its functionalization through substitution reaction, especially due to nucleophilic substitution on the side-chain of polymer at silsesquioxane units. But more important, the use of halogen exchange method with bromine anion allows the formation of more reactive, bromine-containing poly(siloxane/double-decker silsesquioxane) (P-Br), which enables further post-substitution modification reactions in a POSS unit. The glass transition temperatures (T_g ~ 15°C) of both halogenated polymers were significantly higher than poly(dimethylsiloxane) (PDMS). High transparency of polymers with hydrophobic surface could be found from solvent-casting thin film.

2. Executive summary

Only a few studies have reported the preparation of silsesquioxane-based aldehyde[1] and bromo functional groups.[2] Moreover, all of them only paid attention to the octameric T_8 cage, but none were found in a larger-cage size. In this study, octakis(3-chloropropyl)octasilsesquioxane (**1**; Cl-T_8),[3] prepared by hydrolytic-polycondensation of the commercially available (3-chloropropyl)trimethoxysilane, has been considered as a promising starting material because of its easy accessibility and facile conversion into other functional groups through nucleophilic substitution reactions.[4-9] Herein, the independent report of cage rearranged T_8 structure (**1**) under one-pot synthesis toward the multi aryl nitro-, aldehyde-, and bromo-functionalized T_8, T_{10}, and T_{12} polyhedral oligomeric silsesquioxanes is presented for the first time. Thus, reactive functional groups could be tolerant under such a condition. In addition, this method is also applicable to gram-scale synthesis and the desired products are easily isolated in their clean and pure forms by practical column chromatography.

Meanwhile, double-decker silsesquioxane is one of POSS structures, considered to be a bifunctional monomer and applicable to prepare silsesquioxane-based polymer.[10,11] We have recently reported the synthesis of a novel double-decker silsesquioxane; named di[(3-chloropropyl)(isopropoxy)silyl]-bridged double-decker octaphenylsilsesquioxane (DDSQ) that has two different functional groups; (*i*-propoxy)silyl and chloropropyl groups.[12] In this report, we actually show that (*i*-propoxy)silyloxy groups can further react with hydrosilane *via* Piers-Rubinsztajn reaction using tris(pentafluorophenyl)borane; $B(C_6F_5)_3$ as a catalyst to form Si-O-Si linkages, leading to the formation of chlorine-containing poly(siloxane/double-decker silsesquioxane) (P-Cl). The Piers-Rubinsztajn reaction between hydrosilane and alkoxysilane is notably rapid and highly efficient.[13,14] Moreover, P-Cl bearing reactively chloropropyl groups on the side chains of polymer can be further functionalized through substitution reaction to obtain bromine-containing poly(siloxane/double-decker silsesquioxane) (P-Br). Our recent reports also suggest that a wide range of functional groups on silsesquioxane materials can be simply done through substitution reaction.[4-9] Herein, we introduce, for the first time, the method for modification on both main and side chains of poly(siloxane/double-decker silsesquioxane).

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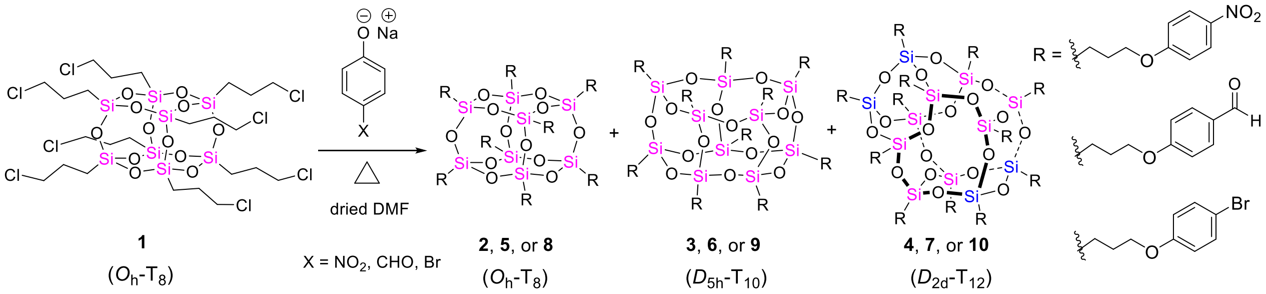
3. Objective

3.1 To prepare multi aryl nitro-, aldehyde-, and bromo-functionalized T_8, T_{10}, and T_{12} polyhedral oligomeric silsesquioxanes

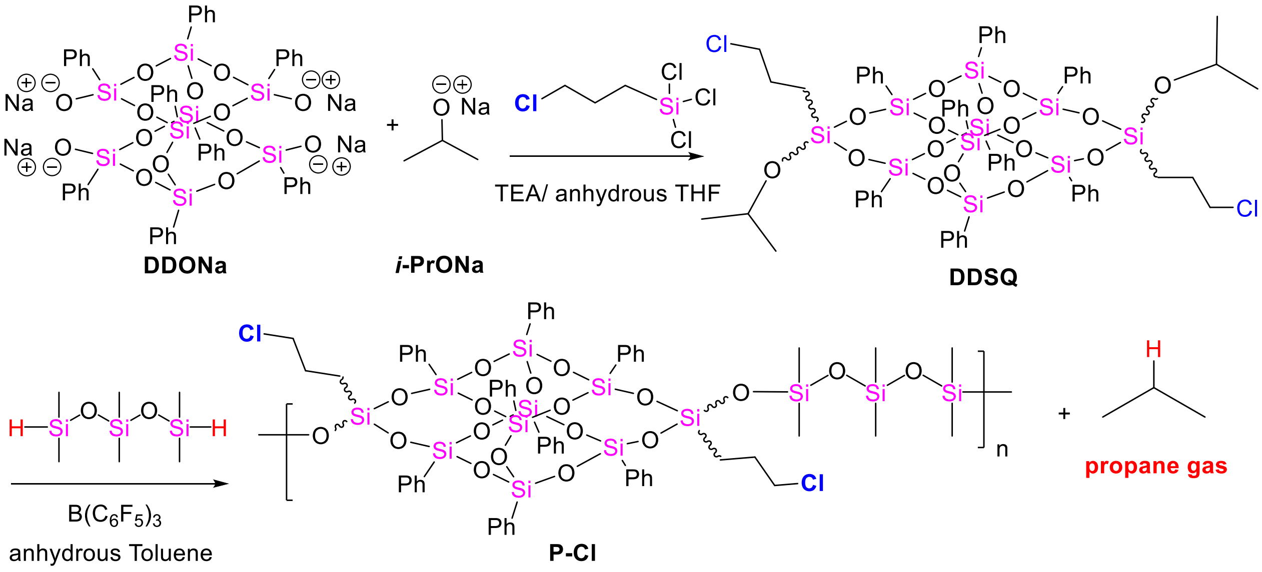
3.2 To prepare chlorine-containing poly(siloxane/double-decker silsesquioxane) (P-Cl). *via* Piers-Rubinsztajn reaction, which could be further functionalized through substitution reaction to obtain bromine-containing poly(siloxane/double-decker silsesquioxane) (P-Br).

4. Research methodology



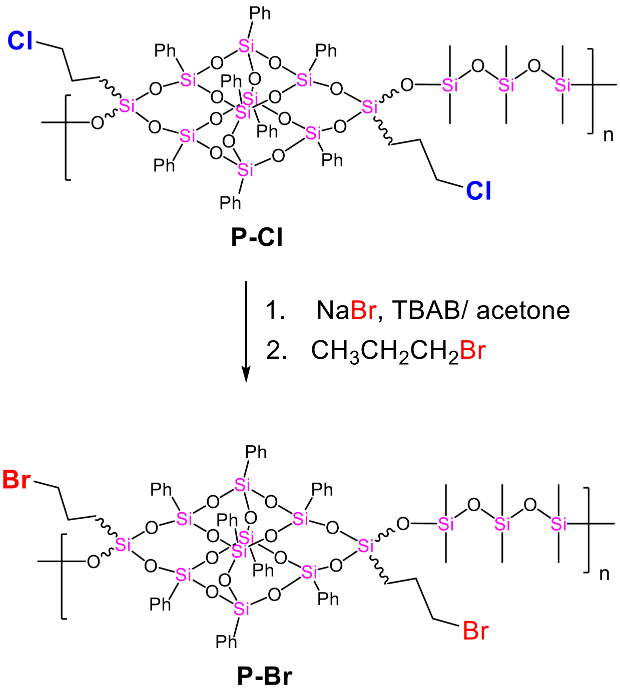
Scheme 1. Cage-rearranged T_8 cage of compound **1** upon introduction of 4-nitrobenzene, 4-oxybenzaldehyde, and 4-bromobenzene functions produced (a) Compounds **2-4**; 70°C, 3 days, 0.15 $mol \cdot L^{-1}$, 1.7 eq. of dried sodium 4-nitrophenoxide/$RSiO_{3/2}$; (b) Compounds **5-7**; 70°C, 1 day, 0.06 $mol \cdot L^{-1}$, 2.0 eq of dried sodium 4-oxybenzaldehyde salt/$RSiO_{3/2}$ and (c) Compounds **8-10**; 55°C, 12 hours, 0.13 $mol \cdot L^{-1}$, 1.5 eq. of dried sodium 4-bromophenoxide salt/$RSiO_{3/2}$.

Organic-inorganic hybrid nano-building blocks of aromatic nitro-, aldehyde-, and bromo-functionalized polyhedral oligomeric silsesquioxanes were easily prepared through nucleophilic substitutions, starting from the reactions between octakis(3-chloropropyl)octasilsesquioxane and phenoxide derivatives. These phenoxide anions not only supplies the substitution functions to a silsesquioxane cage, but can also induce a cage-rearrangement leading to the formation of octa-, deca-, and dodecameric silsesquioxane cages.



Scheme 2. Synthetic approach to prepare double-decker silsesquioxane (DDSQ) monomer and chlorine-containing poly(siloxane/double-decker silsesquioxane) (P-Cl) *via* dehydrocarbonative condensation reaction.

Meanwhile, a mixture of *cis* and *trans*-DDSQ monomers in 1:1 ratio was freshly prepared according to our previous report by using a coupling reaction between tetrasodium salt of double-decker phenylsilsesquioxane (DDONa) and 3-chloropropyltrichlorosilane in the presence of sodium *i*-propoxide (*i*-PrONa).[12] Then, mixed isomers of DDSQ bearing a reactive function of di(i-propoxy)silyl groups were polymerized with hydrosilane groups at terminal chain of hexamethyltrisiloxane using $B(C_6F_5)_3$ as a Lewis acid catalyst through dehydrocarbonative condensation reactionat ambient temperature to obtain P-Cl in 96% yields (Scheme 2).



Scheme 3. Functionalization approach to obtain bromine-containing poly(siloxane/double-decker silsesquioxane) (P-Br) *via* halogen exchange reaction.

The side chains of P-Cl can be modified through substitution reaction at the reactive chloropropyl groups. The treatment of P-Cl with NaBr in the presence of TBAB and 1-bromopropane under acetone solvent smoothly converts the chloro- to bromo functions as shown in Scheme 3.

5. Result

Herein, the independent report of cage rearranged T_8 structure (**1**) under one-pot synthesis toward the multi aryl nitro-, aldehyde-, and bromo-functionalized T_8, T_{10}, and T_{12} polyhedral oligomeric silsesquioxanes is presented for the first time. Thus, reactive functional groups could be tolerant under such a condition. In addition, this method is also applicable to gram-scale synthesis and the desired products are easily isolated in their clean and pure forms by practical column chromatography. Meanwhile, we actually show that (*i*-propoxy)silyloxy groups can further react with hydrosilane *via* Piers-Rubinsztajn reaction using tris(pentafluorophenyl)borane; $B(C_6F_5)_3$ as a catalyst to form Si-O-Si linkages, leading to the formation of chlorine-containing poly(siloxane/double-decker silsesquioxane) (P-Cl). Moreover, P-Cl bearing reactively chloropropyl groups on the side chains of polymer can be further functionalized through substitution reaction to obtain bromine-containing poly(siloxane/double-decker silsesquioxane) (P-Br).

6. Conclusion and Discussion

A complete set of novel polyhedral oligomeric silsesquioxanes; T_n (n = 8, 10, and 12) based aromatic nitro-, aldehyde-, and bromo-functional groups were easily prepared *via* nucleophilic substitution reactions. Cage-rearranged silsesquioxanes (T_8, T_{10}, T_{12}) were simply separated in their pure forms by practical column chromatography. Moreover, physical and thermal properties of the pure silsesquioxane products confirm that the octameric T_8 cage is highly crystalline, while decameric T_{10} and dodecameric T_{12} cages behave like “polymeric or amorphous” materials. We believe that this study serves as a highly useful prototype method for preparation of other reactive aromatic–based silsesquioxanes.

Meantime, copoly(siloxanes/silsesquioxanes) with tunable POSS units on the polymer backbone were synthesized via dehydrocabonative condensation reaction. Therefore, this class of copolymers represents the reactive side chains that can be further functionalized by substitution reaction. Moreover, the halogenated polymers actually exhibit excellent thermal stability, optical transparency, and hydrophobicity. Additionally, the design of multifunctional alternating polysiloxane-based POSS copolymers could be considered for the next generation of a highly versatile silicone in industrial applications.

7. Appendix

8. Output (Acknowledge the Thailand Research Fund)

8.1 International Journal Publication

1. Chimjarn, S.; Kunthom,R.; Chancharone, P.; Sodkhomkhum, R.; Sangtrirutnugul, P.; **Ervithayasuporn, V.*** *Dalton Trans.* **2015**, *44*, 916-919. (IF 2014 = 4.197)

2. Sodkhomkhum, R.; **Ervithayasuporn, V.*** *Polymer* **2016**, *86*, 113-119.
(IF 2014 = 3.562)

8.2 Application

8.3 Others e.g. national journal publication, proceeding, international conference, book chapter, patent

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Synthesis of aromatic functionalized cage-rearranged silsesquioxanes (T_8, T_{10}, and T_{12}) *via* nucleophilic substitution reactions†

Supansa Chimjarn,[a] Rungthip Kunthom,[a] Prapassorn Chancharone,[a] Rapheepraew Sodkhomkhum,[a] Preeyanuch Sangtrirutnugul[a] and Vuthichai Ervithayasuporn*[a,b]

Organic–inorganic hybrid nano-building blocks of aromatic nitro-, aldehyde-, and bromo-functionalized polyhedral oligomeric silsesquioxanes were easily prepared through nucleophilic substitutions, starting from the reactions between octakis(3-chloropropyl)octasilsesquioxane and phenoxide derivatives. These phenoxide anions not only supply the substitution functions to a silsesquioxane cage, but can also induce a cage-rearrangement leading to the formation of octa-, deca-, and dodecahedral silsesquioxane cages.

Aromatic compounds play important roles as intermediates in organic synthesis, as the reactive functional groups (*e.g.* nitro,[1] aldehyde,[2] and bromo[3]) on aromatic rings have been widely utilized for over a century as key chemicals for the synthesis of explosives,[4] dyes,[5] pharmaceuticals,[6] and polymers.[7] Meanwhile, polyhedral oligomeric silsesquioxanes have been well recognized as useful nanosized building blocks in the synthesis of organic–inorganic hybrid materials due to their versatile structure consisting of an inorganic Si–O–Si core and peripheral organic functional groups.[8] Recently, a cage-like silsesquioxane with three-dimensional symmetry with combined organic and inorganic properties has been used for advanced applications such as in the formation of porous materials,[9] polymer nanocomposites,[10] OLEDs,[11] and in catalysis.[12]

For example, silsesquioxane-based nitro functions are promising precursors in many synthetic reactions because of their ability to introduce nitrogen atoms bound to carbons. The first preparation of silsesquioxane-based nitro aromatics and a silsesquioxane cage featuring nitrophenyl substituents was reported by Laine and co-workers in which nitration of octaphenylsilsesquioxane (Ph-T_8) was performed by fuming nitric acid.[13] However, this method suffered from uncontrolled regioselectivity and multiple substitutions of nitro groups on the benzene ring.[14] Subsequent reduction of the nitro groups to yield silsesquioxane-based amino functions, in particular, is highly desirable as the amino derivatives could lead to a wide range of applications.[15] In the meantime, it is well known that phenyl–silicon bonds are capable of electrophilic cleavage. For example, Deans and Eaborn successfully treated 1,3-bis(trimethylsilyl)benzene with fuming nitric acid, which led to the regioselective formation of monosubstituted trimethylsilyl-*para*-nitrobenzene.[16a] Along this line, 4-nitrophenyl-T_8, T_{10}, and T_{12} were successfully prepared by Kawakami and co-workers through nitration of the reactive precursors: 4-trimethylsilylphenyl-T_8, T_{10}, and T_{12} (4-TMSPh-T_8, T_{10}, and T_{12}) at the *ipso*-position.[16b] However, this synthetic approach still possesses several complicated steps (linear synthesis), as the starting precursors of 4-TMSPh-T_8, T_{10}, and T_{12} must be initially prepared through hydrolytic-condensation of the non-commercially available (4-TMSPh)triethoxysilane. Thus, both methods are not synthetically practical since they involve the electrophilic aromatic substitutions, which must be carried out under vigorous conditions with a concentrated acid.

In the meantime, only a few studies have reported the preparation of silsesquioxane-based aldehyde[17a] and bromo functional groups.[17b] Moreover, all of them only paid attention to the octameric T_8 cage, but none were found in a larger-cage size. In this study, octakis(3-chloropropyl)octasilsesquioxane (**1**; Cl-T_8),[18] prepared by hydrolytic-polycondensation of the commercially available (3-chloropropyl)trimethoxysilane, has been considered as a promising starting material because of its easy accessibility and facile conversion into other functional groups through nucleophilic substitution reactions.[8f,19–24] Herein, the independent report of cage rearranged T_8 structure (**1**) under one-pot synthesis toward the multi aryl nitro-, aldehyde-, and bromo-functionalized T_8, T_{10}, and T_{12} polyhedral oligomeric silsesquioxanes is presented for the first time. Thus, reactive functional groups could be tolerant under such a condition. In addition, this method is also applicable to gram-scale

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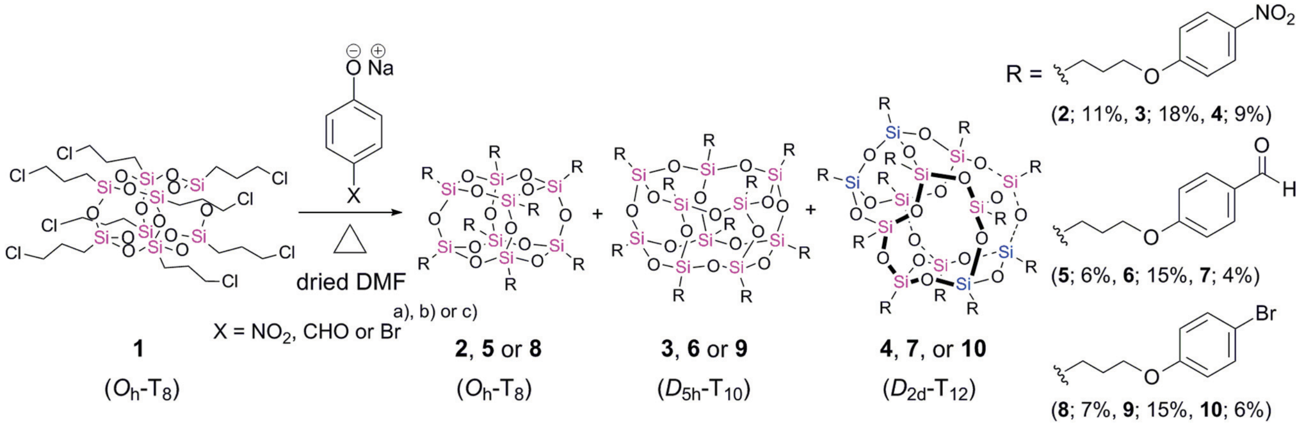
† Electronic supplementary information (ESI) available: Experimental details, ^1H, $^{13}C\{^1H\}$, $^{29}Si\{^1H\}$ NMR, HR ESI–MS, and MALDI-TOF MS spectra of the new compounds **2–10**. See DOI: 10.1039/c4dt02941k



Scheme 1 Cage-rearranged T_8 cage of compound 1 upon introduction of 4-nitrobenzene, 4-oxybenzaldehyde, and 4-bromobenzene functions produced (a) compounds **2–4**; 70 °C, 3 days, 0.15 mol L^{-1}, 1.7 eq. of dried sodium 4-nitrophenoxide/$RSiO_{3/2}$; (b) compounds **5–7**; 70 °C, 1 day, 0.06 mol L^{-1}, 2.0 eq. of dried sodium 4-oxybenzaldehyde salt/$RSiO_{3/2}$ and (c) compounds **8–10**; 55 °C, 12 hours, 0.13 mol L^{-1}, 1.5 eq. of dried sodium 4-bromophenoxide salt/$RSiO_{3/2}$.

synthesis and the desired products are easily isolated in their clean and pure forms by practical column chromatography.

To study the reactivity of nucleophilic substitution reactions, ^{1}H NMR spectroscopy was used as an analytical tool to monitor the reaction's progress. For example, the *N*,*N*-dimethylformamide (DMF) solution of a mixture of dried sodium 4-nitrophenoxide and **1** at 70 °C (Scheme 1a) afforded a complete reaction (>99% substitution) within 3 days. Interestingly, under similar conditions with a higher reaction temperature of 100 °C, the substitution reaction remained incomplete (~96% substitution) after 3 days. We suggest that at higher temperatures, the nucleophilicity and leaving ability of chloride anions as a by-product may participate to inhibit a complete substitution. More specifically, the substituent displacement reaches equilibrium at higher temperatures.[22]

In order to evaluate the completion of substitution reactions, the ^{1}H NMR spectrum of the crude product indicates that the proton signals (3.53, 1.82 and 0.75 ppm) of 3-chloropropyl groups are all shifted to 3.98, 1.91 and 0.79 ppm, corresponding to 3-substituted propyl groups, while an additional appearance of signals at 6.91 and 8.05 ppm confirms the regioselective *para*-substitution on the aromatic rings. However, we speculate that the broad ^{1}H NMR signals of the crude product are possibly a result of cage-decomposition. The $^{29}Si\{^1H\}$ NMR spectrum of the crude product shown in Fig. 1 in fact confirms formation of the cage-rearranged products (T_8, T_{10}, and T_{12}). Thin-layer chromatography analysis also reveals three distinct spots at R_f = 0.45, 0.30, and 0.18 along with a broad baseline (R_f = 0–0.15) in a mixed solvent of 1.5% ethyl acetate in CH_2Cl_2. Purification by column chromatography of the crude product (2.74 g) afforded an analytically pure decakis(3-proproxy-4-nitrobenzene)decasilsesquioxane (**3**; 0.81 g, R_f = 0.30, 18% yield) as a major product. The $^{29}Si\{^1H\}$ NMR spectrum of **3** contains a singlet resonance at −68.1 ppm (Fig. 2b), which is characteristic of the decahedral T_{10} cage. On the other hand, octakis(3-proproxy-4-nitrobenzene)octasilsesquioxane (**2**; 0.49 g, R_f = 0.45, 11% yield) and dodecakis(3-proproxy-4-nitrobenzene)dodecasilsesquioxane (**4**; 0.41 g, R_f = 0.18, 9% yield) were isolated as minor products. The $^{29}Si\{^1H\}$ NMR spectra of T_8 and T_{12} cages (Fig. 2a and 2c) show a singlet at −66.7 ppm and two singlet signals at −67.8 and −70.3 ppm (1 : 2 ratio), respectively.

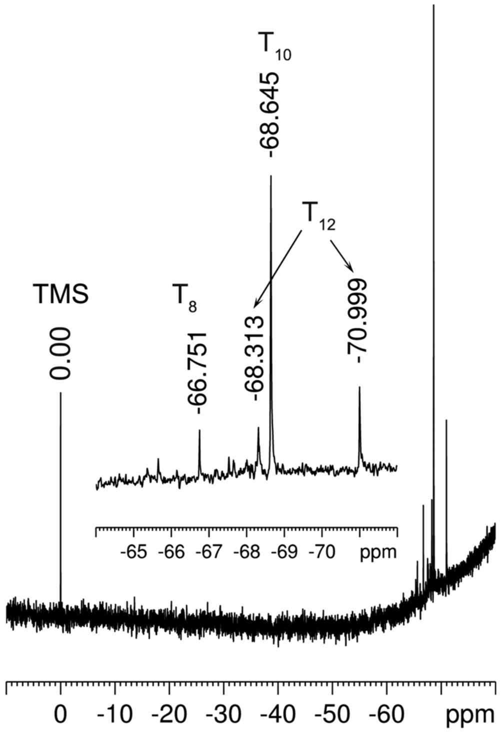


Fig. 1 $^{29}Si\{^1H\}$ NMR spectrum of the crude product of *para*-nitrobenzene-functionalized-polyhedral oligomeric silsesquioxanes in CD_2Cl_2.

Similarly, *para*-oxybenzaldehyde (T_8; **5**, T_{10}; **6**, and T_{12}; **7**) and *para*-bromobenzene (T_8; **8**, T_{10}; **9**, and T_{12}; **10**) functionalized-polyhedral oligomeric silsesquioxanes were prepared *via* nucleophilic substitution reactions of freshly prepared sodium 4-oxybenzaldehyde and 4-bromophenoxide salts, respectively, with **1** (Schemes 1b and 1c). These results are also consistent

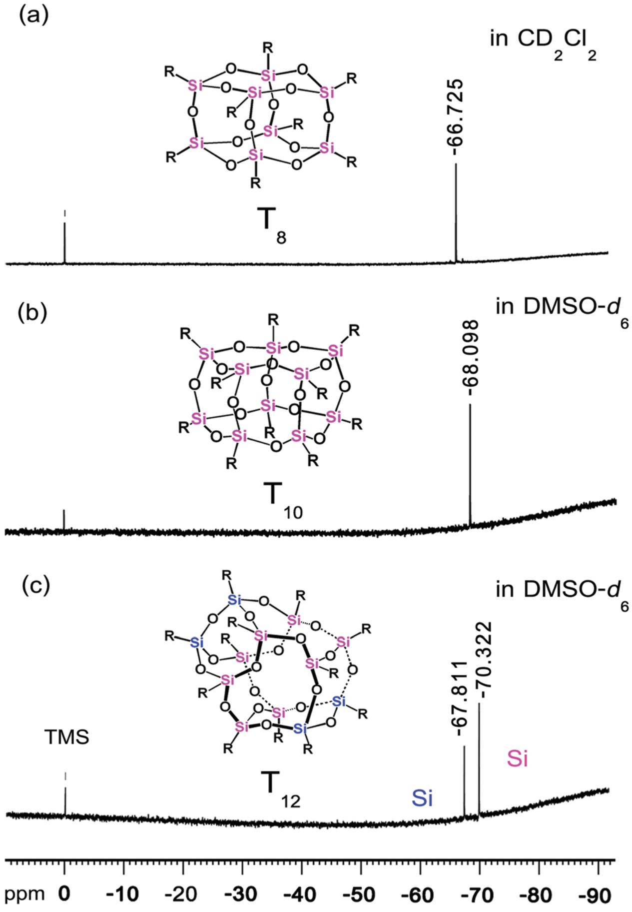


Fig. 2 ^{29}Si{^{1}H} NMR spectra of purified compounds (a) octa-, (b) deca-, and (c) dodeca(*para*-nitrobenzene)-functionalized-polyhedral oligomeric silsesquioxanes (**2**, **3**, and **4**).

with the synthesis of silsesquioxanes-based *para*-nitrobenzene, in which the cage-rearrangement phenomenon of the T_8 cage was promoted under basic reaction conditions[23] with strong nucleophiles including oxygen (*e.g.* acrylate and methacrylate)[24] and nitrogen (*e.g.* azide and phthalimide)[20,21] anions in polar aprotic solvents (*e.g.* DMF and acetone) at high temperatures. In contrast, soft nucleophiles (*e.g.* sulfur, bromine, iodide) appear to leave the T_8 cage completely unperturbed.[19,22] It has also been suggested that this phenomenon could be due to the electronic effect or the electron density of nucleophiles.[20] In this study, we further propose that *para*-nitrophenoxide, *para*-oxybenzaldehyde, and *para*-bromophenoxide anions must play the same role as the anions mentioned above. More specifically, the nucleophilicity on the oxygen atom of a phenoxide anion is strong enough to induce the breakage of the inorganic Si–O bonds of the T_8 cage, yielding various fragments. During the substitution reaction, these fragments can self-assemble to form thermodynamically stable cage-like silsesquioxanes (T_8, T_{10}, and T_{12}). Moreover, we found that substitution and cage-rearranged reactions at higher moisture contents resulted in more unwanted and degraded fragments from cage decomposition. These led to higher amounts of undesired by-products or unidentified polysilsesquioxanes (T_n), as evidenced by broader ^{1}H NMR signals and a longer baseline on the TLC plate.

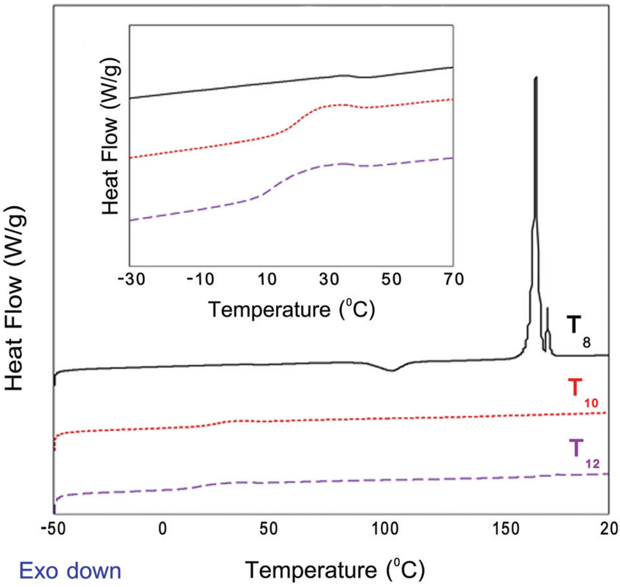


Fig. 3 DSC thermograms of purified octa, deca and dodeca(*para*-nitrobenzene)-functionalized-polyhedral oligomeric silsesquioxanes (**2**, **3**, and **4**) over the temperature range from −50 to 200 °C, at a heating rate of 10 °C min^{-1} under a nitrogen atmosphere.

Recently, we have reported that the physical state of each silsesquioxane cage was determined by the degree of symmetry at the molecular level.[24] For example, the highly symmetrical T_8 cage (O_h) is crystalline,[18–20,22,24,25] while the less symmetrical T_{10} (D_{5h}) and T_{12} (D_{2d}) cages tend to have a loosely packed structure.[21a,24] Regarding preliminary observations, compound **2** (T_8) is a white solid powder with a melting point (m.p.) of 164.3–165.5 °C, as determined by a melting detector, while compounds **3** (T_{10}) and **4** (T_{12}) appear as fluffy solids at room temperature. In order to better understand the phase-transition of each pure silsesquioxane cage, differential scanning calorimetry (DSC) analyses were performed over temperatures ranging from −50 to 200 °C. As shown in Fig. 3, the cubic T_8 cage (**2**) shows a melting temperature (T_m) at around 166 °C, comparable to what was observed with the melting detector. During the cooling process, there is an exothermic signal at 139 °C (see ESI; Fig. S5†), which corresponds to the crystallization temperature (T_c), always found at lower temperatures compared to the T_m value of the crystalline blocks. In other words, at T_c, the temperature is low enough to slow down the freedom of movement of the otherwise highly mobile and flexible organic chains of the cubic T_8 cage. As a result, the T_8 cages spontaneously align themselves into a closely-packed system. On the other hand, compounds **3** (T_{10}) and **4** (T_{12}) appear to only have the glass transition temperatures (T_g) at 24.5 °C and 22.5 °C, respectively. This evidence, once again, strongly suggests that both deca- and dodecameric silsesquioxanes have a loosely-packed structure or behave like a "polymeric or amorphous" material. It is noted that higher crystallinity of T_8 may explain why only some of the T_8 cubes (and not T_{10} and

T_{12}) could readily precipitate out of the reaction solutions.[18,19,25] X-ray powder diffraction analysis of **2**, **3**, and **4** (see ESI; Fig. S16†) further reveals that the T_8 compound **2** is highly crystalline, whereas compounds **3** (T_{10}) and **4** (T_{12}) are amorphous. Despite these observations, it should be mentioned that highly crystalline T_{10} and T_{12} cages have previously been observed in the presence of rigid phenyl substituents, most likely as a result of better molecular packing from aromatic–aromatic interactions (π–π stacking).[26]

Conclusions

A complete set of novel polyhedral oligomeric silsesquioxanes; T_n (n = 8, 10, and 12) based aryl nitro-, aldehyde-, and bromo-functional groups were easily prepared *via* nucleophilic substitution reactions. Cage-rearranged silsesquioxanes (T_8, T_{10}, T_{12}) were simply separated in their pure forms by practical column chromatography. Moreover, physical and thermal properties of the pure silsesquioxane products confirm that the octahedral T_8 cage is highly crystalline, while decahedral T_{10} and dodecahedral T_{12} cages behave like "polymeric or amorphous" materials. We believe that this study will serve as a highly useful prototype method for the preparation of other reactive aromatic-based silsesquioxanes.

Acknowledgements

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Synthesis of poly(siloxane/double-decker silsesquioxane) *via* dehydrocarbonative condensation reaction and its functionalization

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ABSTRACT

Chlorine-containing poly(siloxane/double-decker silsesquioxane) (**P–Cl**) was prepared in high yield at ambient room temperature *via* dehydrocarbonative polycondensation reaction between di[(3-chloropropyl)isopropoxysilyl]-bridged double-decker octaphenylsilsesquioxane (**DDSQ**) and hexamethyltrisiloxane. Particular attention for this polymer was also given to its functionalization through substitution reaction, especially due to nucleophilic substitution on the side-chain of polymer at silsesquioxane units. But more important, the use of halogen exchange method with bromine anion allows the formation of more reactive, bromine-containing poly(siloxane/double-decker silsesquioxane) (**P–Br**), which enables further post-substitution modification reactions in a POSS unit. The glass transition temperatures (T_g ~ 15 °C) of both halogenated polymers were significantly higher than poly(dimethylsiloxane) (PDMS). High transparency of polymers with hydrophobic surface could be found from solvent-casting thin film.

1. Introduction

Polysiloxanes are considered as one type of synthetic hybrid polymers, wildly used as lubricant, mold release, working media in automobile, and heat transferred oil [1]. The presence of Si–O–Si repeating units in its main chain makes polysiloxanes exhibit several outstanding properties such as high thermal stability, elasticity, and optical transparency [2]. Meanwhile, polyhedral oligomeric silsesquioxanes (POSS) are well-defined nano-sized organic-inorganic materials [3], which are commonly used as a reinforcement enhancer by blending them with polymers [4–6]. Therefore, silsesquioxane-based polymers are much interesting as they are expected to provide several useful properties, such as high thermal stability, enhanced toughness, and low dielectric constant [7–9]. However, as typical silsesquioxanes cages are highly symmetric (e.g. octameric T_8 cage), simply blending them with polymers usually leads to aggregation and poor dispersion of silsesquioxanes molecules in the material [4–6]. One way to overcome these problems is to covalently attach silsesquioxanes molecules to the backbone of polymeric nanocomposite [6,10–13]. Several chemical reactions including hydrosilylation [14–17], Heck [10,11,18], cross-metathesis [14,19], click [6,20], dehydrogenation [21], polycondensation, and ring-opening reaction [22] have been successfully employed to covalently linked POSS molecules into the polymer backbone, resulting in the composite materials with significantly increasing glass transition temperature [7,8,21–24]. Despite several application of dehydrocarbonative condensation in syntheses of siloxane polymers and copolymers [25–29], none has found for the syntheses of covalently linked POSS polymers in main chain. More importantly, the polymerization could be found at ambient temperature due to higher solubility of our starting monomer in organic solvents.

Double-decker silsesquioxane is one of POSS structures, considered to be a bifunctional monomer and applicable to prepare silsesquioxane-based polymer [15,16,19,20]. We have recently reported the synthesis of a novel double-decker silsesquioxane; named di[(3-chloropropyl)(isopropoxy)silyl]-bridged double-decker octaphenylsilsesquioxane (**DDSQ**) that has two different functional groups; (*i*-propoxy)silyl and chloropropyl groups [30]. In this report, we actually show that (*i*-propoxy)silyloxy groups can further react with hydrosilane *via* Piers–Rubinsztajn reaction using tris(pentafluorophenyl)borane; $B(C_6F_5)_3$ as a catalyst to form Si–O–Si linkages, leading to the formation of chlorine-containing

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poly(siloxane/double-decker silsesquioxane) (**P–Cl**). The Piers–Rubinsztajn reaction between hydrosilane and alkoxysilane is notably rapid and highly efficient [31,32,39]. Moreover, **P–Cl** bearing reactively chloropropyl groups on the side chains of polymer can be further functionalized through substitution reaction to obtain bromine-containing poly(siloxane/double-decker silsesquioxane) (**P–Br**). Our recent reports also suggest that a wide range of functional groups on silsesquioxane materials can be simply done through substitution reaction [33–38]. Herein, we introduce, for the first time, the method for modification on both main and side chains of poly(siloxane/double-decker silsesquioxane).

2. Experimental section

2.1. Materials and methods

If not stated, all chemicals were commercially available and used without additional purification. Hexamethytrisiloxane, tris(pentafluorophenyl)borane, tetrabutylammonium bromide (TBAB), 1-bromopropane, anhydrous toluene were purchased from Sigma Aldrich, while **DDSQ** compound was freshly prepared according to our previous report [30]. Fourier transform nuclear magnetic resonance spectra were obtained using a Bruker-AscendTM 400 high-resolution magnetic resonance spectrometer for ^{1}H (400 MHz), ^{13}C{^{1}H} (100 MHz) and ^{29}Si{^{1}H} (79 MHz) nuclei. Chemical shifts were reported in δ units (parts per million) relative to tetramethylsilane (TMS), and residual solvents peaks were used as a reference. Gel permeation chromatography (GPC) analyses were performed on a Waters e2695 instrument equipped with Model 3580 refractive index detectors (Viscotek) and two 10 μm PL Gel columns. Tetrahydrofuran as a solvent was used to elute GPC columns with flow rate of 1.0 mL/min at 35 °C. Molecular weights and molecular weight distributions were also calibrated with polystyrene standards ranging from 500 to 10,000,000 amu. DSC measurements were carried out using a DSC Q200 (TA Instruments). Approximately, 15 mg of the samples were capsulated in aluminum pans. Each experiment was performed under nitrogen atmosphere at a heating rate of 10 °C/min over the temperature range from −50 to 200 °C. TGA experiments were carried out using a TGA/SDTA 851 (Mettler Toledo). Approximately, 8 mg of samples were heated from room temperature to 780 °C at a rate 10 °C/min under nitrogen atmosphere. Fourier transform infrared (FT-IR) spectra were obtained by using Bruker Hong Kong Limited, FT-IR spectrometer model ALPHA. The polymeric films were simply prepared by dropping the polymer solution (82 mg/ml in chloroform) on a glass slide (26 × 26 mm^2). The slide was then left at room temperature for 1 h, subsequently at 70 °C for an additional 1 h to completely remove the solvent. Finally, the solidification of the films was obtained by freezing the films in the refrigerator or freezer, while the thickness of **P–Cl** (22–38 μm) and **P–Br** (16–35 μm) films was measured by Bruker's Dektak XT™ stylus profiler. Contact angles of water on the film surfaces were measured by sessile drop method at 25 °C with the average of five measurements at different positions for one sample.

*2.1.1. Synthesis of chlorine-containing poly(siloxane/double-decker silsesquioxane) (**P–Cl**)*

The starting material of *cis*- and *trans*-**DDSQ** in 1:1 ratio was freshly prepared according to our previous report [30]. **DDSQ** (1.0 g, 0.863 mmol) and tris(pentafluorophenyl)borane (8.8 mg, 2% mol) were transferred into a vial under nitrogen atmosphere. 2.50 mL of anhydrous toluene was then added into a reaction mixture. The mixture was kept stirring at room temperature until the solid was completely dissolved. Then, an equivalent molar ratio of 1,1,3,3,5,5 hexamethyltrisiloxane (219 μL, 0.863 mmol) was slowly added into the reaction solution at room temperature. The reaction was allowed to proceed at room temperature for 3 days. The reaction was stopped by adding it into methanol (10 mL) where polymeric gel was immediately formed. This polymeric gel was washed several times with methanol and finally dried under vacuum to obtain 1.06 g (96% yield) of dried **P–Cl**.

FT-IR (cm^{-1}) 3074, 2960, 1594, 1431, 1261, 1089, 1010, 842, 801, 726, 695, 577; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ −0.097 to 0.077 (m, 18H, O–Si($\mathit{CH_3}$)$_2$–O), 0.85 (m, 4H, –Si–$\mathit{CH_2}$–CH_2–), 1.90 (m, 4H, –CH_2–$\mathit{CH_2}$–CH_2), 3.38 (m,4H, –CH_2–$\mathit{CH_2}$–Cl) 7.12-7-59 (m, 40H, –C_6H_5) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 °C): δ 0.96, 11.23, 26.61, 47.28, 127.60, 127.73, 127.86, 130.42, 130.59, 131.54, 134.01, 134.11 ppm; ^{29}Si{^{1}H} NMR (79 MHz, $CDCl_3$, 25 °C, TMS): $\delta = -79.76, -79.43, -77.27, -79.10, -67.65, -19.84$ ppm.

*2.1.2. Synthesis of bromine-containing poly(siloxane/double-decker silsesquioxane) (**P–Br**)*

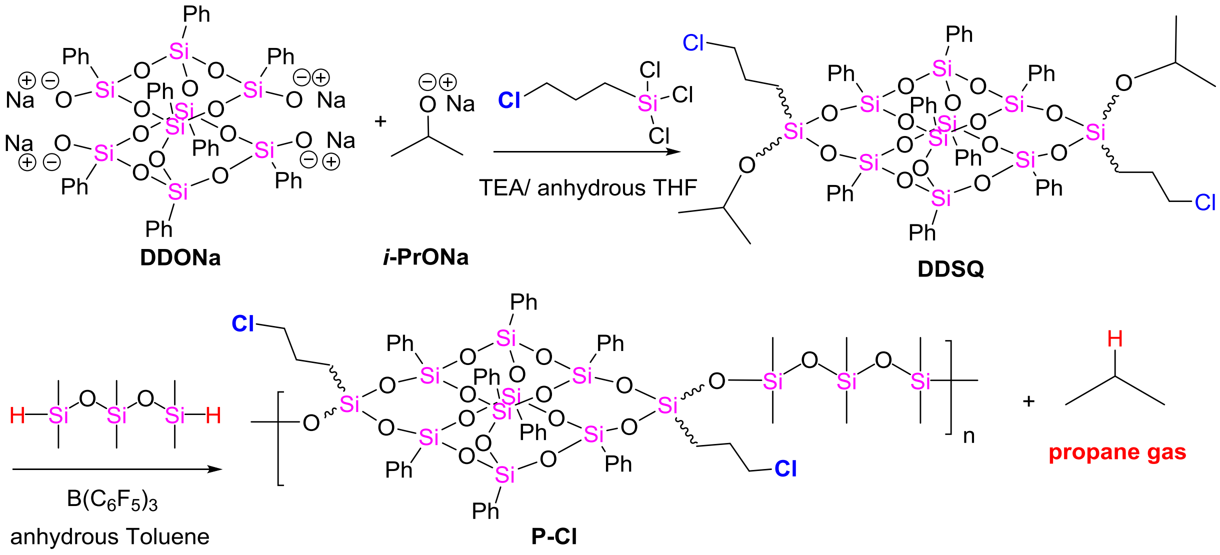
0.50 g of **P–Cl**, sodium bromide (0.24 g, 2.3 mmol), and TBAB (0.038 g, 0.12 mmol) were transferred into thick-wall tube. Then, the mixture was evacuated under vacuum for 10 min and sealed properly. Then, 2.5 mL of acetone was added into the mixture *via* syringe. The solution mixture was stirred at 70 °C for 2 days. The solution mixture was then cooled down to ambient temperature, and was added with 0.7 mL of 1-bromopropane. The temperature was then elevated back to 70 °C and the reaction proceeded at this temperature for another 3 days. The solvent was then evaporated to yield a crude mixture, which was then washed with 25 mL deionized water to remove the soluble salt. And 25 mL of CH_2Cl_2 was additionally added to redissolve the crude product. Two phases separation between water and CH_2Cl_2 was used to further purify the product. Evaporation of CH_2Cl_2 layer yielded 0.53 g of **P–Br** as a yellow viscous gel (99% yields).

FT-IR (cm^{-1}) 3073, 3052, 2961, 1594, 1431, 1261, 1240, 1089, 1010, 843, 801, 726, 695, 577; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ −0.093 to 0.151 (m, 18H, O–Si($\mathit{CH_3}$)$_2$–O), 0.86 (m, 4H, Si–$\mathit{CH_2}$–CH_2), 1.96 (m, 4H, –CH_2–$\mathit{CH_2}$–CH_2), 3.25 (m, 4H, –CH_2–$\mathit{CH_2}$–Br) 7.14-7-59 (m, 40H, –C_6H_5) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 °C): δ 0.97, 12.72, 26.80, 36.35, 127.60, 127.74, 127.88, 128.02, 130.42, 130.54, 130.60, 131.51, 134.01, 134.12 ppm; ^{29}Si{^{1}H} NMR (79 MHz, $CDCl_3$, 25 °C, TMS): $\delta = -79.76, -79.43, -79.26, -79.10, -67.96, -19.84$ ppm.

3. Results and discussion

Firstly, a mixture of *cis* and *trans*-**DDSQ** monomers in 1:1 ratio was freshly prepared according to our previous report by using a coupling reaction between tetrasodium salt of double-decker phenylsilsesquioxane (**DDONa**) and 3-chloropropyltrichlorosilane in the presence of sodium *i*-propoxide (***i*-PrONa**) [30]. Then, mixed isomers of **DDSQ** bearing a reactive function of di(*i*-propoxy) silyl groups were polymerized with hydrosilane groups at terminal chain of hexamethyltrisiloxane (Scheme 1) using $B(C_6F_5)_3$ as a Lewis acid catalyst through dehydrocarbonative condensation reaction at ambient temperature to obtain **P–Cl** in 96% yields. Previously, Kawakami et al. prepared the poly(siloxane/silsesquioxane) at higher temperature (60 °C) *via* dehydrocoupling condensation reaction between reactively silanol and hydrosilane groups [21,23], because of poorer solubility in organic solvents of their **DDSQ** monomer. Therefore, during the polymerization progress, their double-decker silsesquioxane monomer containing a higher polarity of silanol groups may need a higher temperature to be solubilized.

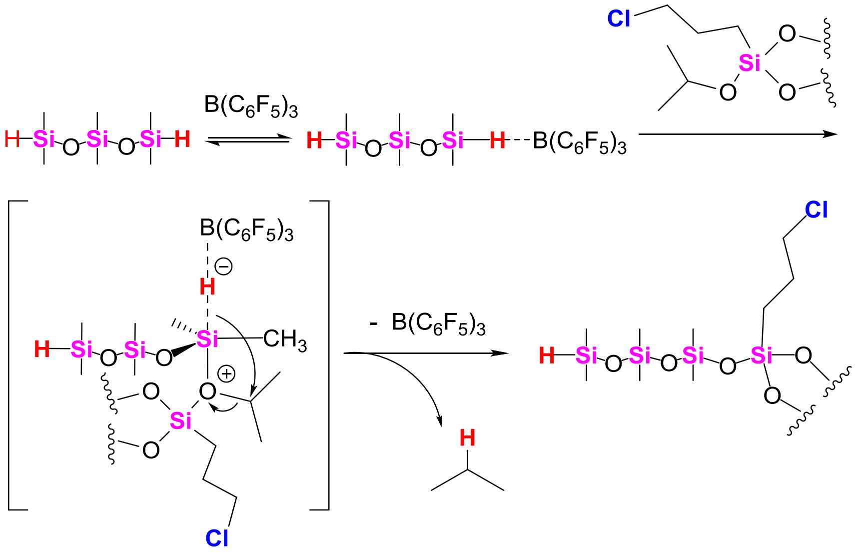
In contrast, our polymerization can be performed at ambient temperature due to the presence of highly soluble (*i*-propoxy)silyl groups in our **DDSQ** monomer. The evolution of bubbles was immediately observed upon the addition of hexamethyltrisiloxane



Scheme 1. Synthetic approach to prepare double-decker silsesquioxane (**DDSQ**) monomer and chlorine-containing poly(siloxane/double-decker silsesquioxane) (**P–Cl**) *via* dehydrocarbonative condensation reaction.

into the reaction mixture, indicative the formation of propane gas as a by-product from condensation polymerization. We suggest that highly acid catalyst of $B(C_6F_5)_3$ rapidly reacts with hydrosilane groups at a terminal chain of hexamethyltrisiloxane to form the boron-hydrosilane complex in equilibrium. Subsequently, zwitterionic oxonium ion was formed after the oxygen atom at (*i*-propoxy) silyl group donates its pair of electron to the more electrophilic silicon atom. Finally, hydride transfer released a propane gas from the complex while new Si–O–Si linkages were formed. Our proposed mechanism of cross-coupling reaction, developed by Chonowski et al. [39], is shown in Scheme 2. The polymerization progress is also monitored by NMR spectra. In ^{1}H NMR, the proton signals of (*i*-propoxy)silyl groups at 1.18 and 4.49 ppm from **DDSQ** units in **P–Cl** were completely disappeared, whereas the proton signals of hexamethyl groups from siloxane moiety were instead appeared at −0.1–1.0 ppm. The relative ratio of proton integration between hexamethyl groups from linear siloxane and choropropyl and phenyl groups from **DDSQ** units in Fig. 1b provides the correct information about the perfect alternating copolymer in 20:12:40 ratio, compared to theoretical value of 18:12:40. The repeating units ($n = 11$) of **P–Cl** copolymer with narrow polydispersity index (PDI = 1.89) was estimated by GPC result as shown in Table 1. From comparable ^{29}Si{^{1}H} NMR spectra in Figs. S3 and S6, there is a signal shift of silicon atoms at terminal **DDSQ** unit from −61.25 to −67.65 ppm, further confirming the formation of new Si–O–Si linkage. The ^{29}Si{^{1}H} NMR spectrum (Fig. S6) in the region from −19 to −20 ppm is assigned for hexamethyltrisiloxane linkages in the **P–Cl**. FT-IR spectrum in Fig. S10 ensured the formation of the product as there were observable signals for siloxane and silsesquioxane at 1010 and 1089 cm^{-1}, respectively.

The side chains of **P–Cl** can be modified through substitution reaction at the reactive chloropropyl groups. The treatment of **P–Cl** with NaBr in the presence of TBAB and 1-bromopropane under acetone solvent smoothly converts the chloro- to bromo functions as shown in Scheme 3, developed method by our previous report [40]. In order to complete a bromine substitution, 1-bromopropane



Scheme 2. Suggested mechanism of **P–Cl** formation.

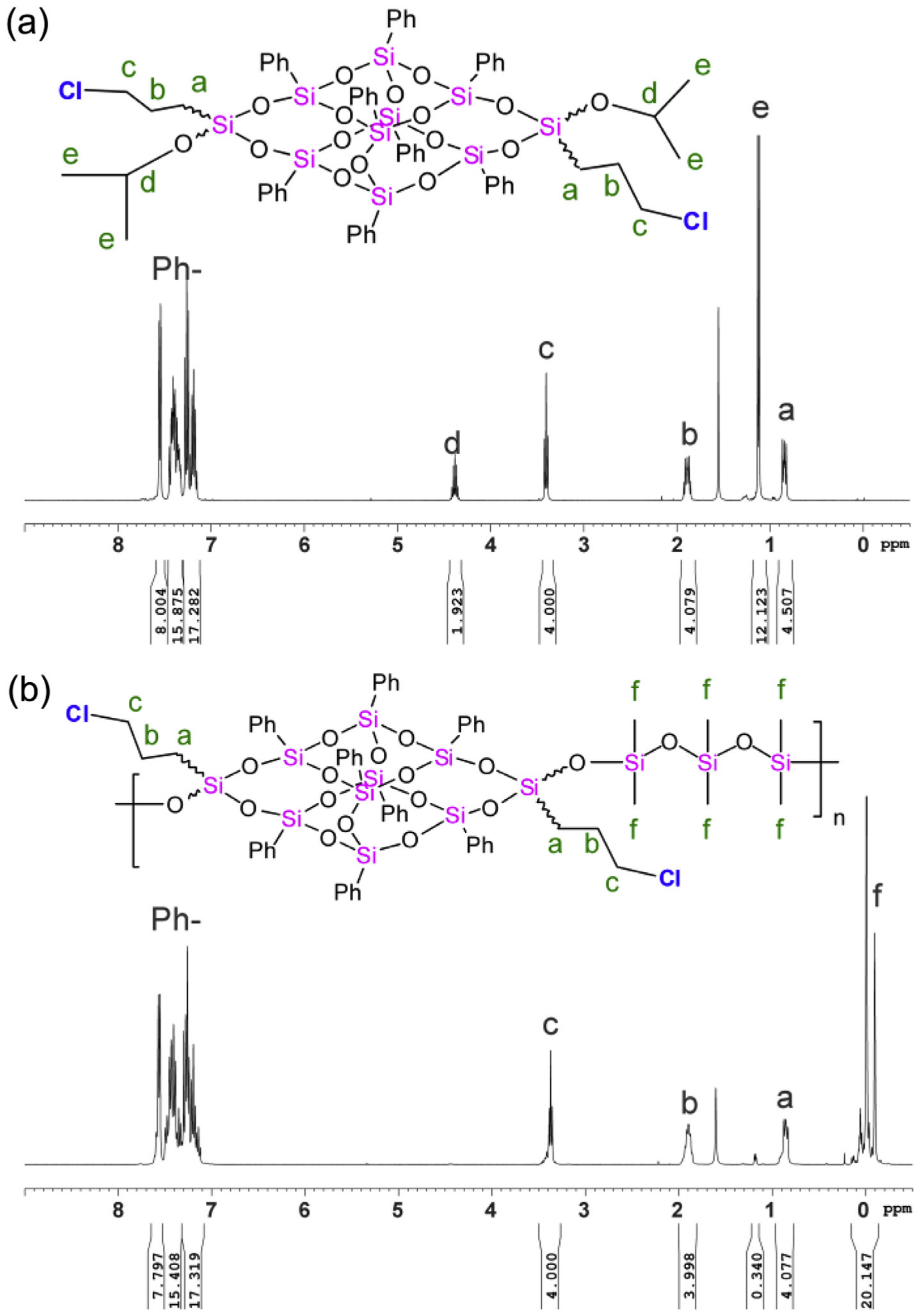


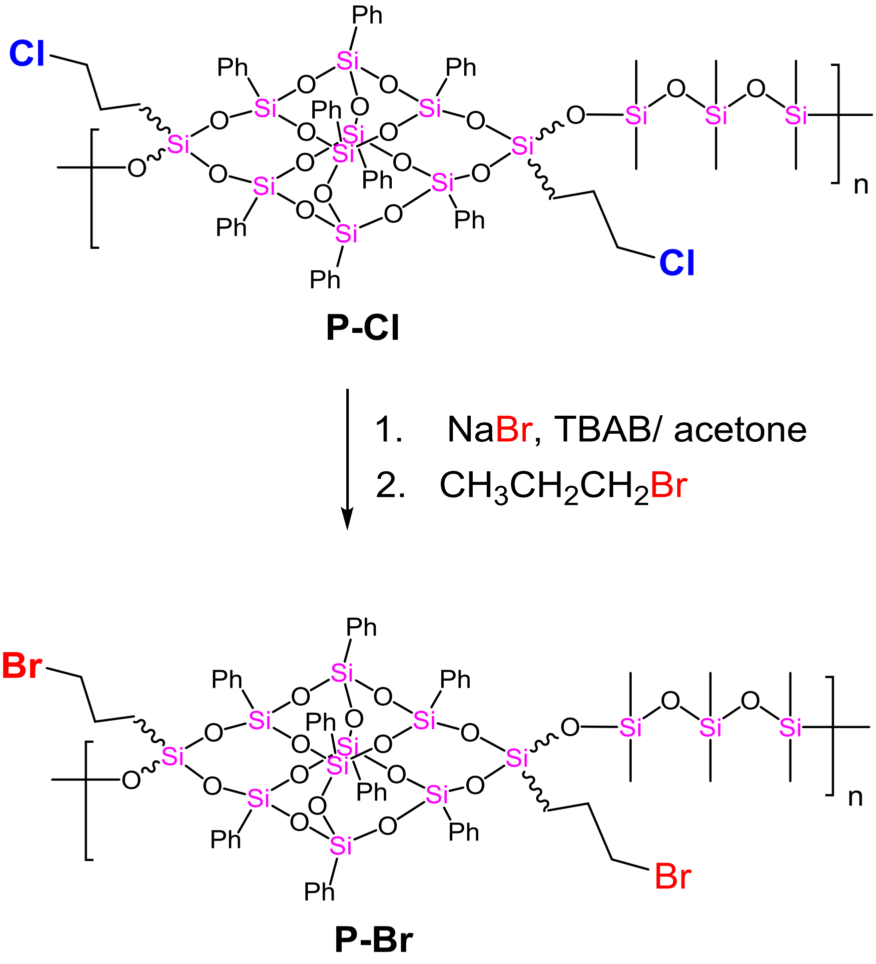
Fig. 1. ^{1}H NMR spectra of (a) **DDSQ** and (b) **P–Cl**.

Table 1
Polymerization of **DDSQ** with hexamethyltrisiloxane catalyzed by $B(C_6F_5)_3$ at room temperature, its functionalization through halogen exchange reaction, thermal and physical properties of polymer films.

Polymers	M_w[a] (g mol^{-1})	M_n[a] (g mol^{-1})	PDI[a]	n[a]	Contact angle (°)	T_g[b] (°C)	T_{d5}[c] (°C)	Residual[d] (%wt)
P–Cl	2.72×10^4	1.44×10^4	1.89	11	113 ± 1.6	15	431	79
P–Br	1.94×10^4	1.16×10^4	1.78	8	106 ± 0.8	15	364	74

[a] By SEC with polystyrene standard.
[b] Determined by DSC (10 °C/min).
[c] 5% weight loss by TGA (10 °C/min) under nitrogen atmosphere.
[d] Residual under nitrogen atmosphere at over 780 °C.

was introduced as an alkylating reagent. Because, undesired chloride ions were still remained in the reaction equilibrium and its amount can be simply removed by reacting with 1-bromopropane. Consequently, the highly volatile compound of 1-chloropropane could be formed instead, suppresses the amount of chloride anions, while increasing the concentration of bromide anions. Thus, the



Scheme 3. Functionalization approach to obtain bromine-containing poly(siloxane/double-decker silsesquioxane) (**P**—**Br**) *via* halogen exchange reaction.

chemical equilibrium will be driven toward the desired **P**—**Br** with a complete substitution. Moreover, organobromine compound has been already found to be more reactive precursor than organochloride because of favorable leaving ability in nucleophilic substitution reactions. In Fig. 2, $^{13}C\{^1H\}$ NMR spectra show a significant shift of $-CH_2$-X moieties from 47.28 to 36.05 ppm, indicating a complete conversion from **P**—**Cl** to **P**—**Br**. The specificity of this substitution reaction is also notable as the reaction occurs only at the side chain. The silsesquioxane linkage of **DDSQ** units in a main chain is left intacted as evidence by the sharp and unshifted ^{29}Si $\{^1H\}$ NMR signals. However, some minor degradation of polymer in a substitution reaction can be still found as result of the reduction of repeating units from 11 to 8, shown in Table 1. We suggest that some alkali metal halides [41–43], trace amounts of water [44,45], and the thermal degradation [46,47] during substitution reactions may cause a cleavage of polysiloxane linkages, especially to hexamethyltrisiloxane unit leading to silanol formation.

Thermal properties of **P**—**Cl** were evaluated by DSC and TGA (Table 1). **P**—**Cl** exhibits a great thermal stability up to 431 °C at 5% weight loss temperature (T_{d5}) in nitrogen atmosphere. The residue weight of **P**—**Cl** at 780 °C still remained 79% as shown in Fig. S12. The glass transition temperature (T_g) of **P**—**Cl** appears to be at 15 °C, therefore the polymer is in a rubbery state at room temperature (Fig. S13). However, T_g of **P**—**Cl** is highly greater than linear poly(dimethylsiloxane) or PDMS ($T_g \sim -123$ °C), because double-decker silsesquioxane is bulkier and more rigid than highly flexible methyl siloxane linkages. Judging from a decreasing in its T_{d5}, the thermal stability of brominated polymer of **P**—**Br** is lower than **P**—**Cl**. We suggest that hydrogen bromide is more favorable released than hydrogen chloride by the thermal decomposition at higher temperature due to a lower dissociation energy of C—Br than C—Cl bondings [48,49]. Thus, the thermal properties of double-decker silsesquioxane polymer can be adapted by changing the rigidity and steric hindrance of the co-monomer's side chain. For example, polymer with higher T_g can be achieved by incorporating a more rigid phenyl ring in the side chain, while the one with lower T_g can be attained by using a more flexible alkyl side chain monomer [20].

Apparently, **P**—**Cl** film can be casted like a thin film at room temperature. The **P**—**Cl** film is highly transparent and hydrophobic as shown in Fig. 3, having of water contact angle due to the presence of organic moieties (e.g. phenyl, methyl groups) in the polymer backbone. As expected, water contact angle of **P**—**Br** film shows no significant difference. We suggest that their equilibrium contact angles and surface energies can be further tuned through either surface roughness processing or introducing difference of polar interfacial functional groups. The transparency of coating slide with polymeric films was studied by UV–Vis spectra as shown in Fig. S14. Both **P**—**Cl** and **P**—**Br** films exhibit excellent transparency, showing the cutoff wavelength at 296 nm and transmittance over 80% at visible region (400–800 nm).

4. Conclusions

Copoly(siloxanes/silsesquioxanes) with tunable POSS units on

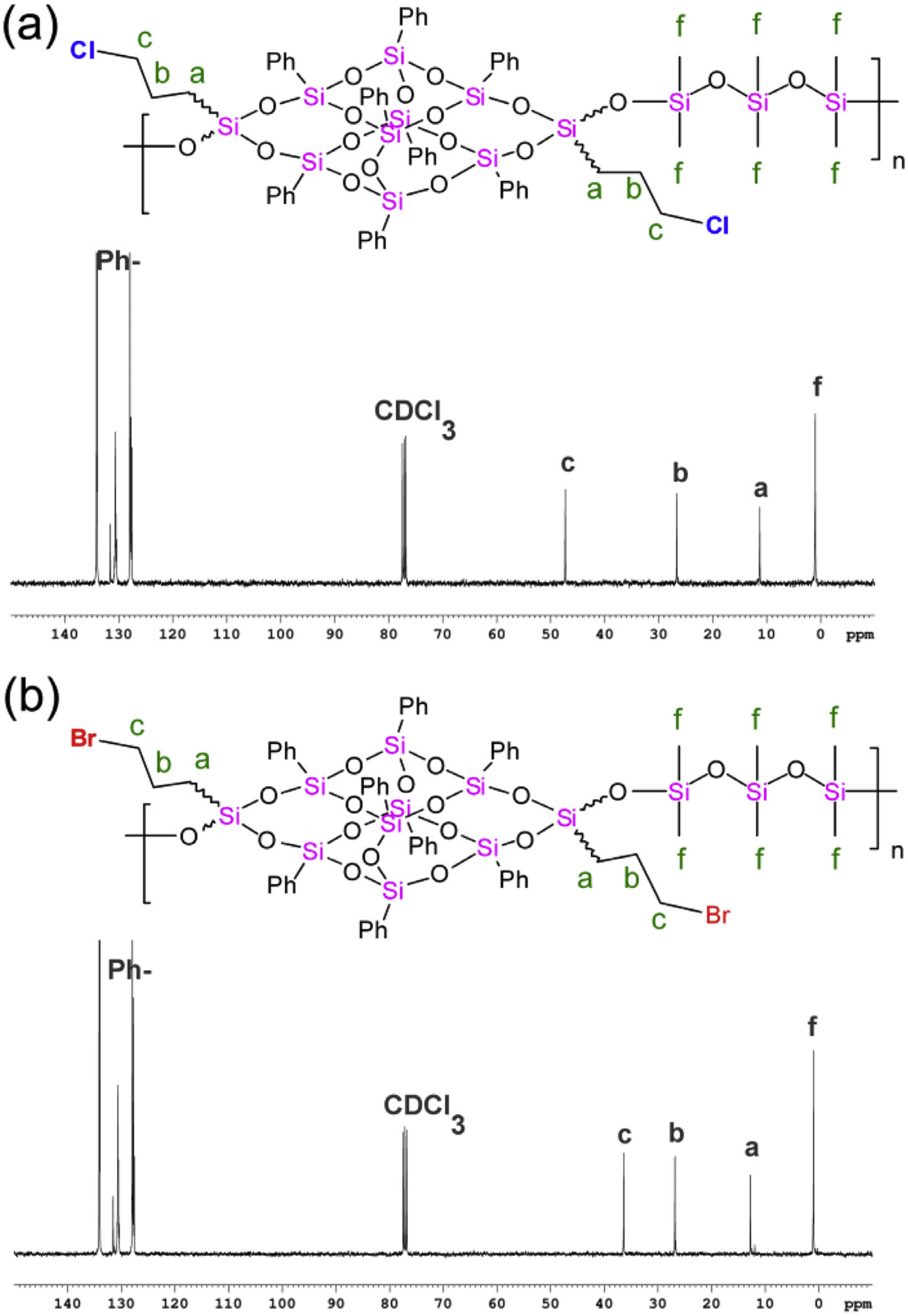


Fig. 2. $^{13}C\{^{1}H\}$ NMR spectra of (a) **P–Cl** and (b) **P–Br**.

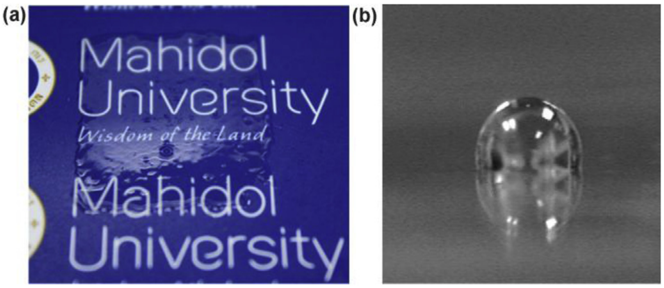


Fig. 3. (a) Casted **P–Cl** film at room temperature and (b) a water droplet on **P–Cl** film.

the polymer backbone were synthesized *via* dehydrocabonative condensation reaction. Therefore, this class of copolymers represents the reactive side chains that can be further functionalized by substitution reaction. Moreover, the halogenated polymers actually exhibit excellent thermal stability, optical transparency, and hydrophobicity. Additionally, the design of multifunctional alternating polysiloxane-based POSS copolymers could be considered for the next generation of a highly versatile silicone in industrial applications.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.polymer.2016.01.044.

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