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Crack- and Shrinkage-Free Ethylene-Bridged Polysilsesquioxane Film Prepared by a Hydrosilylation Reaction

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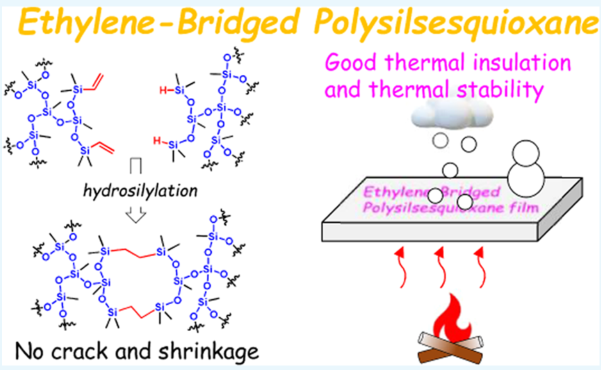
ABSTRACT: With the aim of developing an improved strategy for the preparation of ethylene-bridged polysilsesquioxanes as thermal insulator materials, this paper describes the synthesis of a crack- and shrinkage-free ethylene-bridged polysilsesquioxane film by the hydrosilylation reaction of hydrodimethyl-silylated oligomethylsilsesquioxane (MSQ-SiH) and dimethylvinyl-silylated oligomethylsilsesquioxane (MSQ-SiVi) in the presence of Karstedt's catalyst. Polysilsesquioxane precursors were prepared by the sol−gel reaction of triethoxymethylsilane and the successive capping reaction with chlorodimethylsilane and chlorodimethylvinylsilane. The obtained ethylene-bridged polysilsesquioxane film showed lower density and thermal diffusivity (1.13 g/cm^3 and 1.15 × 10^{-7} m^2/s, respectively) than a polymethylsilsesquioxane film (1.34 g/cm^3 and 1.36 × 10^{-7} m^2/s, respectively). As a result of the introduction of the SiCCSi ethylene bridge, the thermal insulation property of the polysilsesquioxane film was enhanced.



INTRODUCTION

Over the past several decades, sustainable and efficient thermal insulation technology has been demanded for energy saving and reduction in greenhouse gas emission. The efficient use of energy is particularly important in buildings because a large amount of energy is consumed and carbon dioxide is emitted in buildings worldwide. In this context, thermal insulator materials are used in walls and roofs to reduce thermal conductivity for energy saving.[1−3] For example, cellular plastics and fibrous materials such as glass, rock, cellulose, and cotton are conventional thermal insulation materials, which are installed in building envelopes, creating a thick insulation layer. However, the use of thick thermal insulator materials in building envelopes is disadvantageous in terms of space and cost saving. Therefore, the development of enhanced thermal insulation materials is desired for realizing high energy efficiency and cost reduction.

To achieve low thermal conductivity in thermal insulator materials, aerogels have emerged as promising materials.[4,5] Aerogels are highly porous and low-density materials prepared by supercritical drying of a gel, and their high porosity is attractive for good thermal insulation materials.[6] Aerogels are typically classified into inorganic aerogels and organic polymer aerogels. Among the inorganic aerogels, silica aerogels have been extensively studied since Kistler reported the first example in 1931.[7] Silica aerogels have a unique nanostructure that renders them attractive in the field of nanomaterial science. However, most silica aerogels have several disadvantages such as brittleness, low mechanical strength, and high cost, which limit their practical application. Meanwhile, organic polymer aerogels such as polystyrene,[8] polyurethane,[9] cellulose,[10] polyimide,[11] epoxy/amine,[12] and melamine/formaldehyde[13] have also been the focus of research studies. The use of organic polymers in aerogels allows tuning their properties by choosing the appropriate monomer for the polymerization, and a number of organic polymer aerogels with low thermal conductivity have been successfully prepared. However, the thermal durability of organic polymers is generally lower than that of inorganic materials, which limits the application of organic aerogels at high-temperature conditions. For thermal insulation materials in buildings, the nonflammable property is also important because the thermal insulator layer delays heat conduction and prevents flame transfer during a fire.[1] Unfortunately, typical organic polymers are flammable;[14] for example, an organic aerogel based on carboxymethyl cellulose produces a bright flame when placed in a flame.[15] Overall, new thermal insulator materials with high mechanical strength, high thermal property, high flame resistance, and low production cost are required from the viewpoint of practical application.

Owing to the combination of the unique properties of organic and inorganic components, organic−inorganic hybrid

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materials have attracted increased research attention. Among these types of materials, polysilsesquioxane stands out as a representative example.[16−18] Polysilsesquioxanes have the general formula $(RSiO_{1.5})_n$, in which R is an organic group such as alkyl and aryl, typically, methyl, phenyl, and vinyl group, and $SiO_{1.5}$ is the basic unit of the inorganic Si−O−Si network. On the one hand, the organic group is usually selected depending on the application to provide enhanced solubility, compatibility, flexibility, or surface property.[16] On the other hand, the Si−O−Si network enhances the thermal and mechanical properties compared with organic polymers. Polysilsesquioxanes can be easily prepared by the sol−gel reaction of trialkoxysilane via acid- or base-catalyzed hydrolysis and successive polycondensation. Many polysilsesquioxanes have been synthesized so far, and organic−inorganic hybrid materials based on polysilsesquioxanes have been studied as scratch-resistant materials,[19] barrier materials,[20] fire-retardant materials,[21] optical materials,[22] low dielectric constant materials,[23] and insulator materials.[24,25] Since polysilsesquioxane materials are expected to combine the properties derived from the organic moiety and the inorganic oxide, a derivative with high mechanical strength, thermal stability, and high flame resistance can be envisaged as a good thermal insulator material applicable at high-temperature conditions, as long as it also exhibits low thermal conductivity.

Among polysilsesquioxanes, bridged polysilsesquioxanes composed of an organic bridging group between two silanes have a unique structure. Bridged polysilsesquioxanes containing methylene, ethylene, ethenylene, ethynylene, and benzene as organic bridging spacers have been prepared by a sol−gel method.[26] Interestingly, bridged polysilsesquioxanes have been applied as adsorption materials,[27,28] separation membranes,[29−31] and low dielectric materials[32−34] by taking advantage of the characteristics of the organic bridging spacer. Considering these backgrounds, we reported a reverse osmosis (RO) membrane based on bridged polysilsesquioxane for water purification.[35] The rigidity of the organic bridging spacer increased the membrane pore size, and RO membranes prepared from bis(triethoxysilyl)ethane, -ethene, and -ethyne showed improved water permeability as the rigidity of the bridging units increased in the order ethane <ethene <ethyne. Bridged polysilsesquioxanes are promising materials for thermal insulation because the organic bridging spacer provides porosity and the polysilsesquioxane framework enhances the mechanical strength and the thermal property.[26,35,36] We previously reported the preparation of bridged polysilsesquioxane by the nitrogen flow method,[37] and the molecular weight of ethylene-bridged polysilsesquioxane was controlled by changing the amount of water, according to a reported procedure.[37−40] A gel film of ethylene-bridged polysilsesquioxane was obtained by heating at 80 °C for a week. However, when subjecting the gel film to heat treatment at 200 °C over 20 min, many cracks appeared because the elimination of unhydrolyzed ethoxy groups in ethylene-bridged polysilsesquioxane caused serious shrinkage of the film (unpublished data). Unfortunately, isolation of ethylene-bridged polysilsesquioxane without ethoxy groups was hindered by the tendency of the ethylene-bridged silane monomer having six ethoxy groups to form a gel during the sol−gel reaction. Using bis(trimethoxysilyl)ethane instead of bis(triethoxysilyl)ethane may improve the shrinking problem. However, the gel formation still seems to be difficult to control.

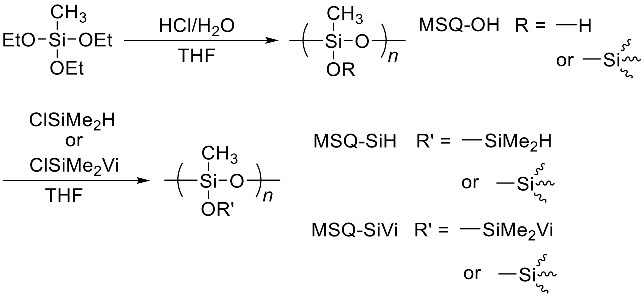
Therefore, a new strategy for the preparation of ethylene-bridged polysilsesquioxanes for various applications including thermal insulator materials is highly desired. In this paper, we report a new synthetic method for crack- and shrinkage-free ethylene-bridged polysilsesquioxanes that involves the hydrosilylation reaction of polysilsesquioxane precursors. The thermal insulation property of the resulting ethylene-bridged polysilsesquioxane is investigated.

■ RESULTS AND DISCUSSION

Synthesis of Silylated Oligomethylsilsesquioxane. As mentioned in Introduction section, the preparation of an ethylene-bridged polysilsesquioxane without ethoxy groups was difficult because the ethylene-bridged silane monomer has six ethoxy groups, and multifunctional polysilsesquioxanes tend to form a gel. Therefore, we focused on the preparation of an ethylene-bridged polysilsesquioxane film by hydrosilylation as a powerful tool for the formation of SiCCSi bonds.[41]

We designed a synthetic route shown in Scheme 1 for the preparation of oligomethylsilsesquioxanes having hydrosilyl and vinyl groups as precursors of the ethylene-bridged polysilsesquioxane film. First, according to a modified reported procedure,[42,43] the sol−gel reaction of triethoxymethylsilane was performed to achieve the complete hydrolysis of the ethoxy groups and to ensure a high content of silanol groups for the capping reaction. The hydrolysis of triethoxymethylsilane was conducted using excess hydrochloric acid and water to completely hydrolyze the ethoxy groups, and the polycondensation was maintained for 3 h at 0 °C to prevent excess polycondensation and gel formation. Despite being a highly sticky product, the obtained oligomethylsilsesquioxane (MSQ-OH) showed high solubility in polar organic solvents such as tetrahydrofuran (THF), acetone, and chloroform.

Scheme 1. Synthetic Route for the Precursors of Ethylene-Bridged Polysilsesquioxane Films



To investigate the chemical structure of MSQ-OH, ^1H nuclear magnetic resonance (NMR), ^{29}Si NMR, and attenuated total reflection-Fourier transform infrared spectroscopy (ATR-FTIR) measurements were conducted. As shown in Figure 1a, multiple signals attributed to the silylmethyl groups were observed in the ^1H NMR spectrum at ∼0.18 ppm after hydrolysis and polycondensation of triethoxymethylsilane. Besides, three main signals were observed at 1.24, 1.85, and 3.73 ppm, which can be attributed to unhydrolyzed ethoxy groups of the product, ethanol as a byproduct, and THF as the reaction solvent, respectively. The integral ratio of the silylmethyl signal at 0.18 ppm and the total methyl protons from the ethoxy groups in the product and ethanol at 1.24 ppm was determined to be 3:0.52. Considering the integral ratio, the ethoxy groups were considerably hydrolyzed and

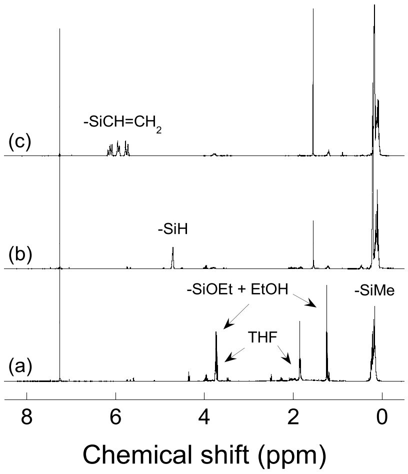


Figure 1. ^{1}H nuclear magnetic resonance spectra of the precursors (a) MSQ-OH, (b) MSQ-SiH, and (c) MSQ-SiVi. Chemical shifts are referenced to residual chloroform in $CDCl_3$ (7.26 ppm).

consumed. However, the accurate estimation of the remaining ethoxy groups in the product was hindered by overlapping of the signals of the ethoxy groups in the product and in ethanol as a byproduct at 1.24 ppm in the ^{1}H NMR of MSQ-OH. Moreover, the amount of silanol in the product could not be determined because the signal for the silanol group is usually weak and broad. Meanwhile, as shown in Figure 2a, the ^{29}Si NMR spectrum of MSQ-OH mainly showed multiple sharp signals at ∼−56.7 ppm, corresponding to a T^2 structure, along with small signals at ∼−65 ppm, corresponding to a T^3 structure, where T^n refers to $(MeSi(OSi)_n(OR)_{3-n})$. Therefore, MSQ-OH had the T^2 structure $MeSi(OSi)_2(OR)$ containing two siloxane bonds, indicating that MSQ-OH was a linear and/or cyclic structure containing silanol or ethoxy groups in the side chain. The weight-average molecular weight (M_w) and the polydispersity index (M_w/M_n) were estimated to be 450 and 1.34 by gel permeation chromatography (GPC) (Table 1), respectively, suggesting an oligomeric structure for MSQ-OH with 5−7 repeating units. In the ATR-FTIR spectrum of MSQ-OH (Figure 3a), clear peaks at 1269 and 1049 cm^{-1} corresponding to the silylmethyl group and the siloxane bond were observed, respectively. Furthermore, a broad peak assigned to silanol groups was observed at 3285 cm^{-1}. Therefore, it can be concluded that MSQ-OH was a linear and/or cyclic oligomer having many silanol groups.

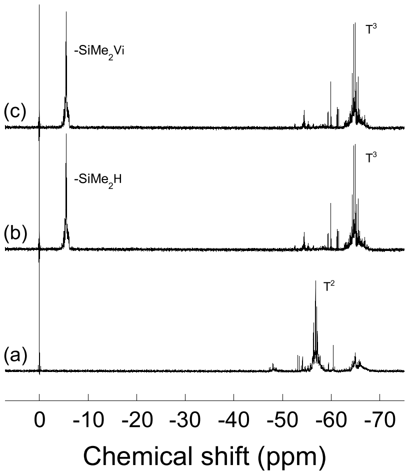


Figure 2. ^{29}Si nuclear magnetic resonance spectra of the precursors (a) MSQ-OH, (b) MSQ-SiH, and (c) MSQ-SiVi. Chemical shifts are referenced to tetramethylsilane (0 ppm).

Table 1. Results on the Synthesis of Oligomethylsilsesquioxanes for the Hydrosilylation Reaction

	M_w[a]	M_w/M_n[a]	residual OEt (%)[b]	SiH (mol %)[b]	SiVi (mol %)[b]
MTES-OH	450	1.34	n.d.[c]		
MTES-SiH	760	1.37	<1	48	
MTES-SiVi	860	1.40	<1		52

[a] Estimated by gel permeation chromatography employing a polystyrene standard as a reference. [b] Determined by ^{1}H NMR relative to the $SiCH_3$ group in the oligomethylsilsesquioxane backbone. [c] Not determined.

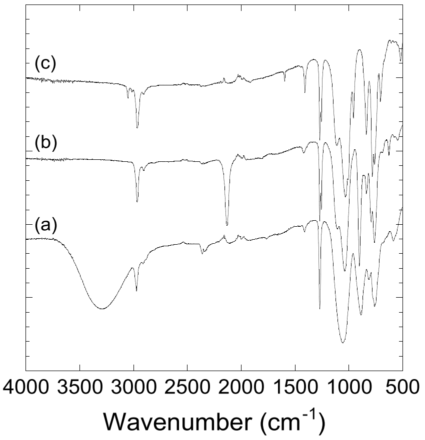


Figure 3. Attenuated total reflectance Fourier transform infrared spectra of the precursors (a) MSQ-OH, (b) MSQ-SiH, and (c) MSQ-SiVi.

Next, the capping reaction of MSQ-OH was performed using chlorodimethylsilane and chlorodimethylvinylsilane, as shown in Scheme 1. Since MSQ-OH was a sticky product, it was dissolved in THF for the capping reaction with the chlorosilanes. After the reaction with chlorodimethylsilane, the morphology of the product changed to a colorless liquid. Figure 1b shows the ^{1}H NMR of hydrodimethyl-silylated oligomethylsilsesquioxane (MSQ-SiH) after the capping reaction with chlorodimethylsilane. New signals corresponding to hydrosilyl and silylmethyl groups appeared at 4.71 and 0.08−0.22 ppm, respectively. Although the sharp signals attributed to the silylmethyl group in the dimethylsilyl capping agent were almost overlapped with those of the silylmethyl group in the oligomethylsilsesquioxane backbone, the integral ratio of the hydrosilyl group and the total number of silylmethyl groups was 1:12.3, namely, the molar percentage of the silylmethyl group was 48% per repeat unit of $-MeSiO_{1.5}-$ (Table 1). The ^{29}Si NMR spectra of MSQ-OH changed dramatically after the capping reaction. As shown in Figure 2b, a new signal attributed to the dimethylsilyl group was observed at −5.51 ppm. Then, multiple sharp signals at −56.7, corresponding to the T^2 structure, shifted to −64.9 ppm, which can be assigned to a T^3 structure of $MeSi(OSi)_3$ after the capping reaction. This shows that the silanol groups in

MSQ-OH were converted to $SiOSiMe_2H$. Indeed, as shown in Figure 3b, the broad peak attributed to the silanol group completely disappeared after the capping reaction, and a shoulder peak ascribed to a siloxane bond and a peak attributed to the hydrosilyl group appeared at 1105 and 2131 cm^{-1}, respectively, in the ATR-FTIR spectrum of MSQ-SiH. These results indicate that the capping reaction of MSQ-OH with chlorodimethylsilane proceeded quantitatively. The M_w and M_w/M_n of MSQ-SiH were estimated to be 760 and 1.37 by GPC (Table 1), respectively. Apart from the expected increase due to the introduction of the dimethylsilyl group as a capping agent, no substantial increase in the molecular weight was observed, further supporting that the capping reaction proceeded quantitatively without the occurrence of intermolecular reactions of MSQ-OH. It was concluded that the capping reaction was controlled using excess chlorodimethylsilane at 0 °C to complete the capping reaction avoiding the siloxane formation. Furthermore, although slightly observed in the ^1H NMR of MSQ-SiH, the presence of ethoxy groups was almost negligible. Therefore, it can be concluded that the obtained MSQ-SiH had a hydrosilyl group per two repeating units of the siloxane bond and should be a good oligomer for the preparation of the ethylene-bridged polysilsesquioxane film by the hydrosilylation reaction.

The capping reaction of MSQ-OH with chlorodimethylvinylsilane was conducted in a similar way, affording dimethylvinyl-silylated oligomethylsilsesquioxane (MSQ-SiVi) as a colorless liquid. The M_w and M_w/M_n of MSQ-SiVi were estimated to be 860 and 1.40, respectively (Table 1). As shown in Figure 1c, new signals corresponding to vinyl and silylmethyl groups appeared at 5.72−6.18 and 0.07−0.20 ppm, respectively. The integral ratio of the vinyl group and total silylmethyl groups was 3:11.7, and the molar percentage of the vinyl group was determined to be 52% per repeat unit of $-MeSiO_{1.5}-$ (Table 1). The calculated molar ratio of vinyl and silylmethyl groups in the oligomethylsilsesquioxane backbone was roughly 1:2, which was in agreement with the capping reaction of MSQ-OH with chlorodimethylsilane. Moreover, the signals corresponding to the T^2 structure were shifted to −64.6 ppm in the ^{29}Si NMR spectrum of MSQ-SiVi (Figure 2c), and the broad peak of silanol completely disappeared in the ATR-FTIR spectrum of MSQ-SiVi (Figure 3c). Therefore, MSQ-SiVi could be also considered a good precursor of ethylene-bridged polysilsesquioxane by the hydrosilylation reaction.

Preparation of the Ethylene-Bridged Polysilsesquioxane Film by the Hydrosilylation Reaction. The appropriate reaction temperature for the hydrosilylation reaction was determined by performing a thermogravimetric and differential thermal analysis (TG-DTA) of a mixture of MSQ-SiH and MSQ-SiVi in the presence of a 5 wt % Karstedt's catalyst solution (10 times diluted with toluene) at a heating rate of 10 °C/min under an air flow of 100 mL/min. Upon increasing the temperature from room temperature to 1000 °C, three exothermic peaks were observed at ~80 °C, 280 °C, and 480 °C, as shown in Figure 4. The first strong exothermic peak at 80 °C can be attributed to the reaction heat of the hydrosilylation of MSQ-SiH and MSQ-SiVi, and thus, we considered that the hydrosilylation reaction would effectively proceed at 80 °C. Meanwhile, second and third exothermic peaks were observed at 280 and 480 °C, along with a weight loss that started at ~250 and 400 °C, respectively. According to the literature, in polyhedral oligomeric silsesquioxanes having vinyl groups, the decomposition of the vinyl groups due to peroxidation and polymerization starts at ~200 °C in air.[44] Bearing this in mind, we performed the hydrosilylation reaction of MSQ-SiH and MSQ-SiVi in the presence of Karstedt's catalyst as follows: First, the mixture was heated at 80 °C for 1 h to start the hydrosilylation reaction efficiently, followed by heating at 160 °C for 4 h to complete the hydrosilylation reaction below the decomposition temperature of 200 °C. For the preparation of the ethylene-bridged polysilsesquioxane film, a mixture of MSQ-SiH and MSQ-SiVi with a feed molar ratio of 1:1 was added in a poly(tetrafluoroethylene-*co*-perfluoroalkylvinyl ether) (PFA) vial together with Karstedt's catalyst. The mixture was heated at 80, 120, and 140 °C for 1 h at each temperature and then heated at 160 °C for 4 h to obtain a colorless and sufficiently stiff ethylene-bridged polysilsesquioxane film with a MSQ-SiH/MSQ-SiVi ratio of 1:1 (hereafter, denoted as EBSQ-1). It was noted that the remaining Karstedt's catalyst did not influence the color of EBSQ-1 because the amount of Karstedt's catalyst was low.

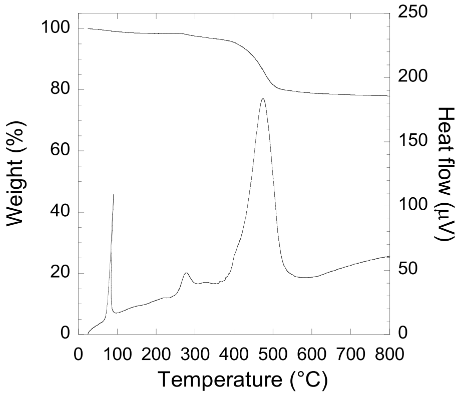


Figure 4. Thermogravimetric analysis of MSQ-SiH and MSQ-SiVi in the presence of a 5 wt % Karstedt's catalyst solution (10 times diluted with toluene) at a heating rate of 10 °C/min under an air flow of 100 mL/min.

Figure 5 shows the ATR-FTIR spectra before and after the hydrosilylation reaction of MSQ-SiH and MSQ-SiVi using Karstedt's catalyst. In a mixture of MSQ-SiH and MSQ-SiVi before the hydrosilylation reaction, a clear peak corresponding to hydrosilyl groups was observed at 2131 cm^{-1}, along with

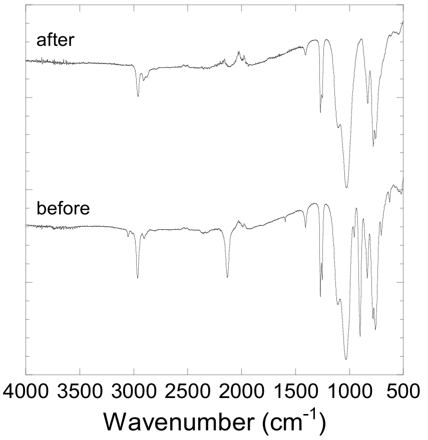


Figure 5. Attenuated total reflectance Fourier transform infrared spectra of a mixture of MSQ-SiH and MSQ-SiVi before and after the hydrosilylation reaction.

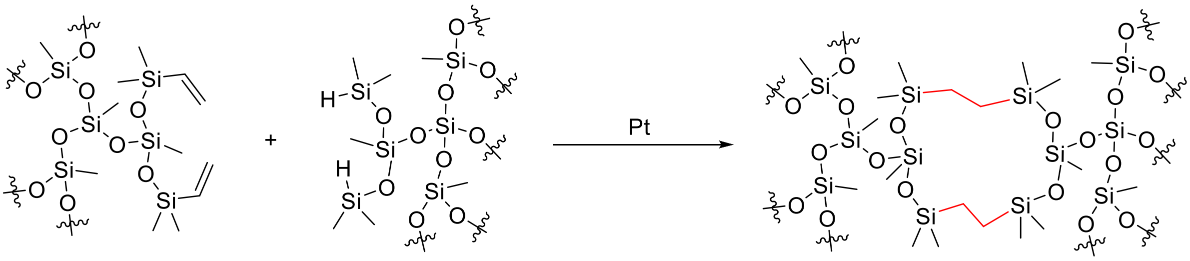


Figure 6. Schematic illustration of the hydrosilylation of MSQ-SiH and MSQ-SiVi.

small peaks of vinyl groups at 3053 and 1595 cm^{-1}. These three peaks almost disappeared after heating at 160 °C for 4 h, indicating that the hydrosilylation reaction of MSQ-SiH and MSQ-SiVi proceeded quantitatively to form EBSQ-1 in the film state, as shown in Figure 6. No signal attributed to ethylene was detected in the ATR-FTIR spectrum of EBSQ-1 because the peak of SiCCSi was overlapped with that of the silylmethyl groups in the oligomethylsilsesquioxane backbone and the capping agent.

The cross-sectional field emission scanning electron microscopy (FE-SEM) image depicted in Figure S1 revealed that EBSQ-1 was an entirely uniform and crack-free film. Therefore, it was demonstrated that a crack- and shrinkage-free ethylene-bridged polysilsesquioxane film can be successfully prepared by the hydrosilylation reaction of oligomethylsilsesquioxanes containing hydrosilyl and vinyl groups.

Thermal Diffusivity of the Ethylene-Bridged Polysilsesquioxane Films. As mentioned in Introduction section, the SiCCSi ethylene bridge affords sufficient porosity to the previously reported ethylene-bridged polysilsesquioxane to be used as a membrane for water desalination.[35] Therefore, we expected it to be a good thermal insulating material because of its porosity. Unfortunately, when the ethylene-bridged polysilsesquioxane film, which was prepared by hydrolysis and polycondensation of bis(triethoxysilyl)ethane with water, was heated at 200 °C over 20 min, many cracks appeared in the film due to the shrinkage arising from the elimination of ethoxy groups. In EBSQ-1, owing to the lack of shrinkage during the formation of the film, the SiCCSi ethylene bridge could be expected to improve the thermal insulating property. Consequently, the thermal diffusivity of EBSQ-1 was measured to reveal the effect of SiCCSi on the thermal insulating property. To provide a comparison, the thermal diffusivity of a film prepared from MSQ-OH without SiCCSi was also evaluated.

To obtain the film from MSQ-OH for the thermal diffusivity measurements, a 20 wt % MSQ-OH solution in THF was heated at 160 °C for 4 h in a PFA vial. However, many holes were observed in the freestanding film due to the rapid evaporation of THF and the water produced by the polycondensation of silanol groups. Therefore, the 20 wt % MSQ-OH solution in THF was first heated at 80 °C overnight to slowly remove THF and water, followed by heating at 160 °C for 4 h. The resulting film prepared from MSQ-OH (denoted as MSQ) was uniform and colorless, with a thickness of ~600 μm, similar to that of EBSQ-1 (~700 μm). The averaged thermal diffusivity of MSQ was 1.36 × 10^{-7} m^2/s, which was higher than that of EBSQ-1 (1.15 × 10^{-7} m^2/s), as shown in Table 2. This indicates that, as expected, the thermal insulating property of the ethylene-bridged film was superior to that of the MSQ film, demonstrating the key role of the SiCCSi ethylene bridge in providing sufficient void space. The thermal diffusivity of EBSQ-1 was also lower than that of organic polymers such as polyvinylchloride, nylon, low-density polyethylene, high impact polystyrene, and polypropylene.[45]

Table 2. Thermal Diffusivity and 5 wt % (T_d^5) and 10 wt % (T_d^{10}) Loss Temperature for MSQ-OH, EBSQ-1, EBSE-2, and EBSQ-3

	MSQ-SiH	MSQ-SiVi	thermal diffusivity (10^{-7} m^2/s)[a]	density (g/cm^3)	T_d^5 (°C)[b]	T_d^{10} (°C)[b]
EBSQ-1	1	1	1.15	1.13	302	285
EBSQ-2	2	1	1.18	1.15	298	383
EBSQ-3	4	1	1.28	1.16	364	418
MSQ			1.36	1.34	436	481

[a] The measurements for thermal diffusivity were repeated at least three times, and the averaged thermal diffusivity was calculated. [b] Measured at a heating rate of 10 °C/min under an air flow of 100 mL/min.

If the void space provided by the ethylene-bridged structure is essential for the thermal insulating property, the thermal diffusivity of the ethylene-bridged polysilsesquioxane film can be expected to depend on the amount of SiCCSi units. To understand the effect of the SiCCSi ethylene bridge, ethylene-bridged polysilsesquioxanes having different amounts of SiCCSi units were prepared by changing the feed molar ratio of MSQ-SiH and MSQ-SiVi to 2:1 and 4:1, respectively. The hydrosilylation reaction of MSQ-SiH and MSQ-SiVi at feed molar ratios of 2:1 and 4:1 also proceeded, affording ethylene-bridged polysilsesquioxane films with a thickness of ~700 μm denoted as EBSQ-2 and EBSQ-3, respectively. Again, complete disappearance of the small peaks of the vinyl groups of the precursors was evidenced in the ATR-FTIR spectra (Figure S2). Surprisingly, hydrosilyl peaks were not observed even under an excess of hydrosilyl groups, which might be due to the side reaction of hydrosilyl groups with ambient moisture. The averaged thermal diffusivity of EBSQ-2 and EBSQ-3 were determined to be 1.18 × 10^{-7} and 1.28 × 10^{-7} m^2/s, respectively (Table 2), indicating that the thermal diffusivity of the ethylene-bridged polysilsesquioxane films decreased with increasing the amount of SiCCSi units (in the order EBSQ-1 > EBSQ-2 > EBSQ-3). Therefore, EBSQ-1 with the largest amount of SiCCSi units exhibited the lowest thermal diffusivity. On the other hand, EBSQ-3 showed the highest thermal diffusivity because EBSQ-3 prepared from a feed molar ratio of MSQ-SiH and MSQ-SiVi of 4:1 contained the lowest amount of SiCCSi units. This trend confirms that the SiCCSi ethylene bridge improves the thermal insulating property by providing the void space that ensures sufficient porosity, even though the void space was too small to analyze by FE-SEM. As shown in Table 2, the densities of the films decreased with increasing the amount of SiCCSi units (the amount of SiCCSi units followed the order EBSQ-1 > EBSQ-2 > EBSQ-3 > MSQ). This supports that sufficient void space was created by the formation of SiCCSi bonds.

Thermal Stability of the Ethylene-Bridged Polysilsesquioxane Films. Similar to the thermal insulating property, thermal stability is also a main concern for thermal insulating materials to be applicable at high temperatures over 200 °C. The thermal stabilities of the ethylene-bridged polysilsesquioxane films in air were evaluated by TG-DTA, and the results are summarized in Table 2. The MSQ film showed high thermal stability, with 5% weight loss temperature (T_d^5) and 10% weight loss temperature (T_d^{10}) of 436 and 481 °C, respectively. For EBSQ-1, EBSQ-2, and EBSQ-3, strong exothermic peaks were observed at ~300 °C (Figure S3), which prevented accurately determining their T_d^5 and T_d^{10} values; however, the thermal stabilities of EBSQ-1, EBSQ-2, and EBSQ-3 were apparently lower than that of the MSQ film, decreasing with increasing the amount of SiCCSi units, as shown in Table 2. This is due to the degradation of the organic network, which is similar to periodic mesoporous organosilicas.[46] Unfortunately, it was concluded that the SiCCSi ethylene bridge decreased the thermal stability in the air condition.

Compared with a gel film of ethylene-bridged polysilsesquioxane prepared by heating at 80 °C for a week, the thermal stability of EBSQ-1 was quite higher than that of a previously reported gel film.[37] In the TG curve of the gel film prepared by the sol−gel method, a rapid weight loss was observed at 240−300 °C due to the decomposition of the SiCCSi bonds and the ethoxy groups. Interestingly, the decomposition temperature of EBSQ-1 shifted to ~300 °C because EBSQ-1 has no ethoxy groups. Compared with the organic polymer, EBSQ-1 showed high thermal stability.[45] The ethylene-bridged polysilsesquioxane film prepared by the hydrosilylation reaction exhibited high thermal stability, and cracks were not observed after heating at 200 °C for at least 5 h. These results demonstrate the feasibility of our synthetic route to ethylene-bridged polysilsesquioxane films for the preparation of thermal insulating materials.

■ CONCLUSIONS

We have developed a synthetic route for the preparation of ethylene-bridged polysilsesquioxane films as thermal insulating materials, which consists of the hydrosilylation reaction of the oligomeric precursors MSQ-SiH and MSQ-SiVi in the presence of Karstedt's catalyst. MSQ-SiH and MSQ-SiVi were prepared by the capping reaction of MSQ-OH, which was in turn obtained by the sol−gel reaction of triethoxymethylsilane with chlorodimethylsilane and chlorodimethylvinylsilane. ^{1}H and ^{29}Si NMR and GPC analyses revealed that MSQ-SiH and MSQ-SiVi were linear and/or cyclic oligomers having hydrosilyl and vinyl groups, respectively.

The hydrosilylation reaction of MSQ-SiH and MSQ-SiVi proceeded quantitatively, according to the disappearance of hydrosilyl and vinyl groups as confirmed by ATR-FTIR. The resulting ethylene-bridged polysilsesquioxane film was uniform and free of cracks, as revealed by a cross-sectional FE-SEM image.

The ethylene-bridged polysilsesquioxane film EBSQ-1 showed lower density (1.13 g/cm^3) and thermal diffusivity (1.15 × 10^{-7} m^2/s) than the polymethylsilsesquioxane film MSQ, whose density and thermal diffusivity were 1.34 g/cm^3 and 1.36 × 10^{-7} m^2/s, respectively. The density and thermal diffusivity of ethylene-bridged polysilsesquioxane films with different contents in SiCCSi units was found to decrease by increasing the amount of SiCCSi, which proved that the thermal insulating property of the films was enhanced by introducing the SiCCSi ethylene-bridged structure. Although the ethylene-bridged structure decreased the thermal stability, EBSQ exhibited high thermal stability, with T_d^5 and T_d^{10} exceeding 280 °C.

■ EXPERIMENTAL SECTION

Materials. Triethoxymethylsilane, chlorodimethylsilane, and chlorodimethylvinylsilane were purchased from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan) and used as received. THF, toluene, diethyl ether, and 6 mol/L hydrochloric acid were purchased from FUJIFILM Wako Pure Chemical Co., Ltd. (Osaka, Japan). THF and toluene were distilled over calcium hydride before use. Diethyl ether and 6 mol/L hydrochloric acid (HCl) were used as received without further purification. Platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane (Karstedt's catalyst) was purchased from Sigma-Aldrich and used as received. Water was purified by Millipore Mill-Q UV system, which had a resistance of 18.2 MΩ·cm and a total organic carbon content of <10 ppb.

Measurements. ^{1}H NMR (400 MHz) measurements were performed on a Varian 400 MHz spectrometer, and ^{29}Si NMR (100 MHz) measurements were performed on a Varian 500 MHz spectrometer. The samples were dissolved in deuterium chloroform ($CDCl_3$), and residual chloroform was used as an internal standard (7.26 ppm) for chemical shift reference in ^{1}H NMR. In ^{29}Si NMR, tetramethylsilane was used as an internal standard (0 ppm). GPC was performed on Shimadzu LC-20AD system equipped with an RID-10A detector and triply connected TSKgel G6000H/G4000H/G2000H columns. THF was used as an eluent at 40 °C at a flow rate of 1 mL/min, and polystyrene standards were used for calibration. FTIR spectra were recorded on a Shimazu IR Affinity-1 spectrometer equipped with an ATR unit. Thermogravimetric analysis (TGA) was performed on an SII EXSTAR TG-DTA6200 thermal analyzer at a heating rate of 10 °C/min under an air flow of 100 mL/min. FE-SEM was performed on a Hitachi S-4800 field emission scanning electron microscope. The samples were attached to the holder with carbon tape, and the surface was coated with platinum. Thermal diffusivity measurements were performed on ai-Phase Mobile M3 type 1 (ai-Phase Co., Ltd., Japan). The measurements were repeated at least three times, and the averaged thermal diffusivity was calculated. The density of the film was measured using a helium gas pycnometer on AccuPyc 1340 Series Pyconometers (Micromeritics, U.S.).

Synthesis of MSQ-OH. Triethoxymethylsilane (10.698 g, 60 mmol) and THF (24.33 mL, 300 mmol) were added to a 100 mL flask and stirred in an ice bath for 10 min. Then, 6 mol/L HCl (2.188 g, 12 mmol) and water (14.468 g, 900 mmol) were added dropwise over 5 min at 0 °C, and the mixture was stirred at this temperature for 3 h. The reaction mixture was extracted with 30 mL of diethyl ether and washed with 30 mL of water three times. The organic layer was dried over anhydride magnesium sulfate for 10 min and evaporated under reduced pressure. Finally, the residue was dried under vacuum for 1 h at room temperature to prevent the gel formation, and MSQ-OH (4.492 g) was obtained as a highly sticky product.

Synthesis of MSQ-SiH by the Capping Reaction of MSQ-OH with Chlorodimethylsilane. In a 100 mL twonecked flask, 4.215 g of MSQ-OH was dissolved in 10 mL of THF and stirred at 0 °C for 10 min. Chlorodimethylsilane (33.33 mL, 300 mmol) was added dropwise over 1 h at 0 °C. After being allowed to warm to room temperature, the reaction mixture was stirred overnight. The reaction mixture was then evaporated under vacuum for several hours at room temperature to remove THF and unreacted chlorodimethylsilane. The residue was passed through a poly(vinylidene difluoride) (PVDF) membrane filter with a pore size of 0.45 μm, and MSQ-SiH (4.974 g) was obtained as a colorless liquid.

Synthesis of MSQ-SiVi by the Capping Reaction of MSQ-OH with Chlorodimethylvinylsilane. MSQ-SiVi was synthesized as described above for MSQ-SiH except using 4.056 g of MSQ-OH and 40.5 mL of chlorodimethylvinylsilane (300 mmol) as precursors. MSQ-SiVi (5.264 g) was obtained as a colorless liquid.

Preparation of the Ethylene-Bridged Polysilsesquioxane Film by the Hydrosilylation Reaction. In a typical preparation, 0.21 g of MSQ-SiH and 0.19 g of MSQ-SiVi in a molar ratio of ~1:1 were mixed by a rotation/revolution vacuum mixer (V-mini300, EME corporation) for 10 min at 1600 rpm. Then, a 5 wt % Karstedt's catalyst solution (10 times diluted with toluene) was added to the mixture, followed by mixing again with the rotation/revolution vacuum mixer for 10 min at 1600 rpm. For the preparation of the film, the mixture was poured into a PFA vial and heated at 80, 120, and 140 °C for 1 h at each temperature. Then, the mixture was heated at 160 °C for 4 h and was removed from the PFA vial. Finally, a freestanding film with a thickness of ~700 μm was obtained.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c00183.

> Field emission scanning electron microscopy micrograph; attenuated total reflectance Fourier transform infrared spectra; and thermogravimetric analysis traces (PDF)

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. Individual author contributions are as follows: T.H. directed this study and wrote the manuscript with contributions from all of the authors. Y.N. and K.O. contributed to all of the experimental work. J.O. directed this study and edited the manuscript.

Notes

The authors declare no competing financial interest.

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