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Highly Porous Polysilsesquioxane Networks via Hydrosilylative Polymerization of Macrocyclic Oligomeric Silsesquioxanes

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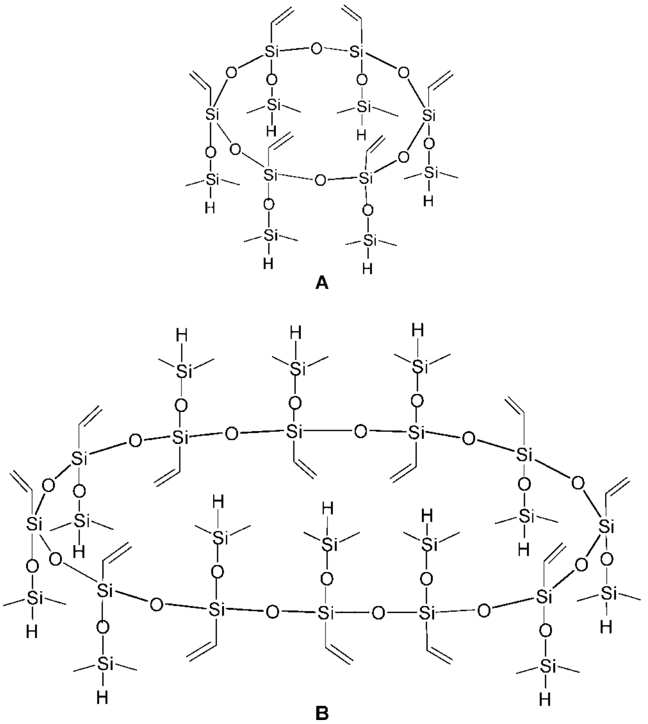
Introduction. Highly porous materials have been attached considerable importance owing to their potential applications in separation, adsorption, catalysis, dielectric, biomaterials engineering and optics devices, etc.[1] During the past years, a variety of approaches have been developed to prepare highly porous materials. Preparation of these materials (e.g., zeolites and nanoporous carbon) usually involves use of organic templates with different shapes and compositions.[1,2] For zeolites, long reaction times, unusual conditions, and large numbers of residual hydroxyl groups in the resulting materials are some major drawbacks to overcome.[3] Recently, it is identified that the control over microporosity in inorganic or organic polymers can be achieved via formation of rigid conjugated networks.[4] Highly rigid, bulky, nanoplanar, and contorted architectures can frustrate efficient packing of polymer chains so that interconnected voids can be formed. Laine et al.[5] utilized several stereo cagelike silsesquioxane macromers and prepared the highly porous polysilsesquioxanes via the binary hydrosilylative polymerization between polyhedral octahydridosilsesquioxanes and octavinylsilsesquioxanes. Nonetheless, the successful application of the above approach to access highly porous materials is only based on the premise that the preparation of functionalized polyhedral oligomeric silsesquioxanes (POSS) becomes convenient and cost-effective. It will be ideal that highly porous polysilsesquioxanes can be alternatively prepared using some readily available oligomeric silsesquioxane macromers if highly rigid, bulky, nanoplanar, and contorted architectures can be also obtained upon polymerization. However, such studies remain largely unexplored.

Polyhedral oligoalkylmetallasiloxanes are a class of novel organometallic compounds, which consist of stereoregular alkylsiloxane macrocycles coordinated to alkaline and/or transition metals (e.g., Mn, Co, Ni, Cu, and trivalent lanthanide metals).[6] These metallasiloxane coordinates can be conveniently derived into macrocyclic oligomeric silsesquioxanes with satisfied yields.[6] Nonetheless, there has been no previous report on the syntheses of polymerizable macrocyclic oligomeric silsesquioxanes using these polyhedral oligoalkylmetallasiloxanes although they have appeared in the 1990s.

In this Communication, we first report the synthesis of the 12- and 24-membered macrocyclic oligomeric silsesquioxanes with the general formula of $[\mathrm{vinylSi(OSiMe_2H)O}]_n$, $n = 6, 12$ (Scheme 1), and then the hydrosilylative polymerization of the macrocyclic oligomeric silsesquioxanes was carried out to access cross-linked polysilsesquioxane networks (Scheme 2). It is expected that the microporosity of polysilsesquioxanes can be achieved with the polymerization of the macrocyclic oligomeric silsesquioxanes containing multifunctional groups since the high rigidity of the cross-linked networks would prevent collapse of micropores formed during in situ polymerization.

Scheme 1. Structures of Compound 1 (A) and Compound 2 (B)



Both hexavinylhexa(dimethylhydro)cyclohexasilsesquioxane and dodecavinyldodeca(dimethylhydro)cyclododecasilsesquioxane (compounds **1** and **2**) were synthesized via the two-step routes. In the first step, the coordinates of the metals (e.g., alkaline and copper) with vinylsiloxanolates were prepared via the reactions between vinyltrimethoxysilane [$\mathrm{vinylSi(OMe)_3}$] and copper(II) chloride ($\mathrm{CuCl_2}$) in the basic media (e.g., NaOH or KOH) by following the literature methods reported by Shchegolikhina et al.[6a,e] In this work, the two copper vinylsiloxanolates, $\{\mathrm{K_2[(ViSiO_2)_6K_2Cu_4(O_2SiVi)_6]}\}\cdot n\mathrm{(BuOH)}$ and $\{\mathrm{Na_4[vinylSiO_2]_{12}(Cu)_4}\}\mathrm{(C_2H_5OH)\ (H_2O)_5}$ were synthesized. It was shown that the former has a sandwich structure, in which two cyclohexasiloxanolate ligands [i.e., $\mathrm{vinylSi(O)O^{1-}]_6}$ adopting a *cis* configuration are linked to each other via a layer consisting of four $\mathrm{Cu^{II}}$ ions, whereas the latter has a globular structure, in which the 12-membered organosiloxanolate ligand [i.e., $\mathrm{vinylSi(O)O^{1-}]_{12}}$ in the tris-*cis*−tris-*trans* configuration constitute the saddle conformation, which is fixed by four $\mathrm{Cu^{II}}$ ions. The electroneutrality of the above molecules is provided by external $\mathrm{Na^+}$ or $\mathrm{K^+}$ cations.[6a] These copper vinylsiloxanolates have been used to react with trimethylchlorosilane [$\mathrm{(CH_3)_3SiCl}$] to obtain the derivatives for the purpose of structural analyses.[6a,e] In this work, the reactions of the two copper vinylsiloxanolates with dimethylchlorosilane [$\mathrm{(CH_3)_2SiHCl)}$] were exploited to afford the polymerizable macromers (i.e., compounds **1** and **2**), respectively. To the best of our knowledge, this is the first report on the preparation of polymerizable macrocyclic oligomeric silsesquioxanes. The ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy shows that the polymerizable macromers were successfully obtained with the high yields more than 94%. Both compounds **1** and **2** bear both vinyl groups and silicon−hydrogen bonds (Si−H), which can be employed to promote their self-cross-linking via

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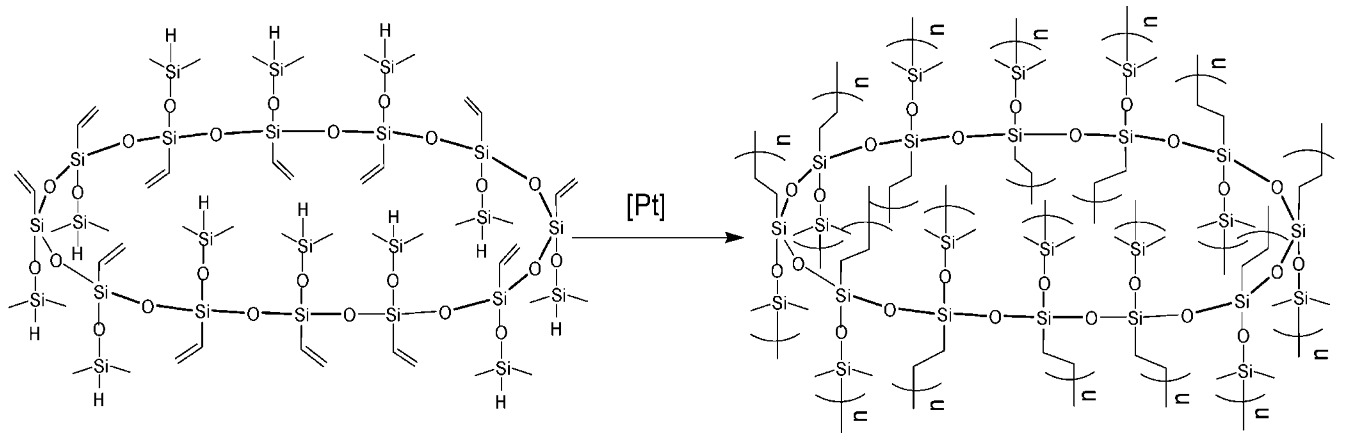
Scheme 2. Hydrosilylative Polymerization of Compound 2



hydrosilylative homopolymerization to access the polysilsesquioxane networks. The hydrosilylative polymerizations were carried out in toluene solutions and were catalyzed with Karstedt catalyst. It was seen that with the polymerization proceeding the systems were gradually gelled and vitrified. After the solvent was eliminated, the white glassy solids were obtained. The solubility tests showed that the solids are no longer soluble in common solvents such as THF, chloroform, toluene, and *N,N'*-dimethylformamide (DMF), suggesting the formation of cross-linked networks. The results of FTIR as well as solid-state ^{13}C and ^{29}Si NMR spectroscopy further proved the occurrence of cross-linking reactions. It is noted that there were still some unreacted Si−H bonds and vinyl groups; i.e., the hydrosilylation reaction did not perform to completion. This observation could be associated with the steric hindrance resulting from the formation of rigid and bulky cross-linking networks.

The above polysilsesquioxane networks were subjected to Brunauer−Emmett−Teller (BET) measurements to evaluate the porosity of the polymers. The nitrogen adsorption−desorption isotherms were volumetrically measured at 77 K after pre-evacuation for 6 h at 150 °C. Shown in Figure 1 are the BET curves of the polysilsesquioxane derived from compounds **1** and **2**. For the polysilsesquioxane network from compound **2**, the adsorption isotherm displayed the intermediate between type I and II and the hysteresis on the desorption arm, indicating a mixed microporous/mesoporous character. The desorption isotherm does not close and is relatively horizontal even when the relative pressure is decreased to a low ratio. This may suggest the pores obtained are narrow and N_2 molecules are trapped in the pores. According to BET calculation, the polysilsesquioxane network has the specific surface area of 308 m^2/g, pore volume of 0.21 cm^3/g, and average pore size of 2.8 nm. The BET measurement was also carried out for the polymer from compound **1**. However, this polysilsesquioxane network showed only little absorption and no significant porosity was displayed, which is in marked contrast to the polysilsesquioxane network resulting from the polymerization of compound **2**. It is plausible to propose that with the hydrosilylative polymerization of macrocyclic oligomeric silsesquioxanes, the difference in porosity is closely associated with the size of the monomers of macrocyclic silsesquioxanes. Compound **1** possesses the macrocyclic structure with 6 Si−O units whereas compound **2** exhibits the macrocyclic structure 12 Si−O units. It seems that the smaller size of macrocyclic oligomeric silsesquioxanes is unfavorable to the formation of highly porous polysilsesquioxane networks. In addition, the configuration of the macrocyclic structures is also an important factor to affect the formation of high porosity (see Supporting Information).

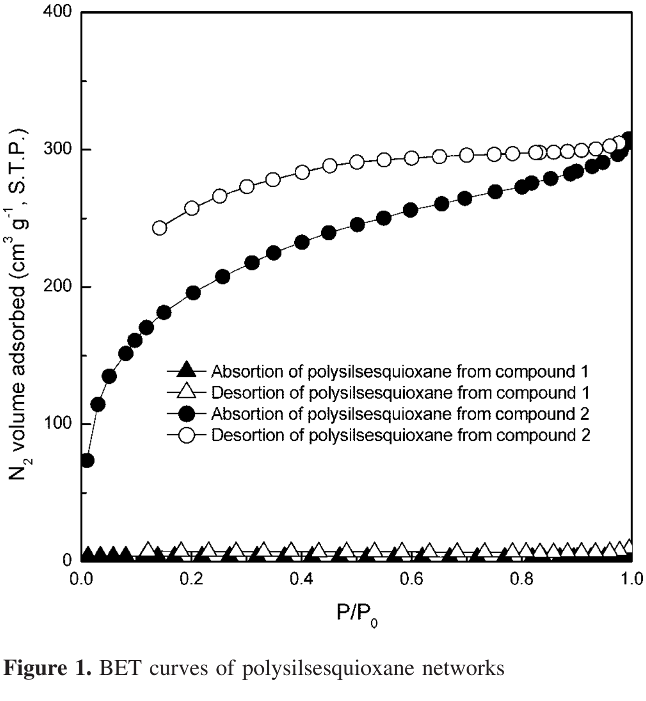


Figure 1. BET curves of polysilsesquioxane networks

The above polysilsesquioxane networks were subjected to thermogravimetric analysis (TGA) to evaluate the thermal stability of the polymers (see Figure 2). Under the identical condition, the polysilsesquioxane networks derived from compound **1** displayed the temperatures of initial decomposition to be 340 °C, which is significantly higher than that (i.e., 210 °C) of the polysilsesquioxane from compound **2**. The difference could be associated with the porosity of the polysilsesquioxane networks. The BET measurements show that the polysilsesquioxane network from compound **1** did not exhibit porosity whereas that from compound **2** is highly porous. It is proposed that to the formation of densely packed cross-linked networks is not favorable for the release of gaseous matters resulting from the thermal decomposition, and thus the initial temperature of decomposition is enhanced. This interpretation is also accounted for the difference in the residue of decomposition for the two networks. For the thermal decomposition of the network from compound **2**, the residue yield is 69%, which is significantly lower than that (79%) of the network from compound **1**. The value of 69% is close to the theoretical yield of ceramic calculated according to the mass fraction of silicon. It is plausible to propose that the decomposition of organic portion

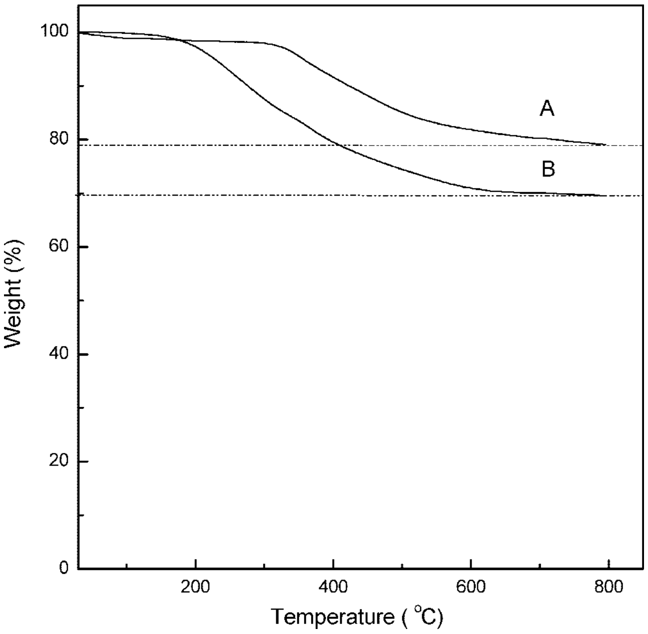


Figure 2. TGA curves of polysilsesquioxane networks from compound **1** (A) and compound **2** (B).

for the polysilsesquioxane network from compound **2** is quite complete, and almost no char was formed with the thermal decomposition.

In summary, the polymerizable macrocyclic oligomeric silsesquioxanes bearing both vinyl groups and Si−H bonds were prepared via the reactions between the metallsilsesquioxanes and dimethylchlorosilane. Both hexavinylhexa(dimethylhydro-)cyclohexasilsesquioxane and dodecavinyldodeca(dimethylhydro)cyclododecasilsesquioxane were characterized by means of FTIR, ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy. The hydrosilylative homopolymerizations of the macrocyclic oligomeric silsesquioxanes were carried out to afford the cross-linked polysilsesquioxane networks. It is identified that the polysilsesquioxane network from dodecavinyldodeca(dimethylhydro)cyclododecasilsesquioxane displayed high porosity in terms of Brunauer−Emmett−Teller (BET) measurement. The cross-linked polymer exhibits specific surface area of 308 m^2/g with the pore volume of 0.21 mL/g. In contrast, the polymer derived from the hydrosilylative homopolymerization of hexavinylhexa(dimethylhydro)cyclohexasilsesquioxane did not exhibit significant porosity. The observation has been interpreted on the difference in size of macrocyclic structures for the silsesquioxane macromers.

Experimental Section. Synthesis of Compound **1**. The synthesis of copper and potassium vinylsiloxanolate $\{K_2[(ViSiO_2)_6K_2Cu_4(O_2SiVi)_6]\}\cdot n(BuOH)$ was carried out according to the procedure of Shchegolikhina.[6a] Copper and sodium vinylsiloxanolate (1.6 g) was added to the mixture composed of toluene (24 mL), dimethylchlorosilane $[(CH_3)_2SiHCl)]$ (10.00 g, 92.20 mmol), and pyridine (5.95 g, 73.75 mmol) at room temperature. The reaction was allowed to carry out at 35 °C for 24 h with vigorous stirring. After cooling to room temperature, the system was filtered to isolate the precipitates, and the solution was washed with deionized water until no chlorine ions were detected with aqueous silver nitrate ($AgNO_3$). After drying with $MgSO_4$, all the solvents were eliminated with rotary evaporation to afford 1.56 g of viscous liquid with the yield of 96%. ^{1}H NMR (400 MHz, $CDCl_3$): 5.81−5.97 (m, 3H, O_3SiVi), 4.76 (sept, 1H, SiH), 0.24 (d, 6H, $OSiMe_2$). ^{13}C NMR (100 MHz, $CDCl_3$, 22 °C): 134.94, 132.38, 0.80. ^{29}Si NMR (99 MHz, $CDCl_3$, 22 °C): −4.75 (O**Si**Me$_2$H), −80.35 (O$_3$**Si**vinyl).

Synthesis of Compound **2**. Copper and sodium vinylsiloxanolate $\{Na_4[vinylSiO_2]_{12}(Cu)_4\}(C_2H_5OH)\ (H_2O)_5$ was synthesized by following the method reported by Shchegolikhina et al.[6e] The above copper and sodium vinylsiloxanolate (3.50 g, 2.29 mmol) was added to the mixture composed of toluene (48 mL), dimethylchlorosilane $[(CH_3)_2SiHCl)]$ (20.00 g, 184.39 mmol), and pyridine (11.90 g, 147.50 mmol) at room temperature. The reaction was allowed to carry out at 35 °C for 24 h with vigorous stirring. After cooling to room temperature, the system was filtered to isolate the precipitates, and the solution was washed with deionized water until no chlorine ions were detected with aqueous silver nitrate ($AgNO_3$). After drying with $MgSO_4$, all the solvents were eliminated with rotary evaporation to afford 3.79 g of viscous liquid with the yield of 94.5%. ^{1}H NMR (400 MHz, $CDCl_3$): 5.86−6.01 (m, 3H, O_3SiVi), 4.72 (sept, 1H, SiH), 0.178 (d, 4H, *cis*−*trans*-SiMe$_2$) 0.175 (d, 2H, *cis*-*cis*-SiMe$_2$). ^{29}Si NMR (99 MHz, $CDCl_3$): −6.21 (*cis*−*cis*-OSiMe$_2$H), −6.32 (*cis*−*trans*-OSiMe$_2$H), −81.8 (*cis*−*trans*-O$_3$Si vinyl), −81.9 (*cis*−*cis*-O$_3$Si vinyl).

Hydrosilylative Polymerization. To a 50 mL flame-dried flask, 1.0 g of compound **1** (or compound **2**) dissolved in 15 mL of anhydrous toluene was charged. The system was connected to a standard Schlenk line and was cooled to 0 °C and purged with N_2 for three times. Then, 50 μL of Karstedt catalyst (in the solution of toluene) was injected into the mixture using a syringe and the temperature was gradually raised to 80 °C. It was observed that, with the proceeding of reaction, the solutions were gradually transformed into the transparent colorless gels. With the polymerization being carried out for 12 h, the solvent was removed with rotary evaporation. The obtained brittle, glassy solids were grounded into white powders and were further dried in vacuo at 60 °C for 24 h.

Specific Surface Area Analyses. Surface areas and pore size distributions were determined by nitrogen sorption at 77 K using the volumetric technique on a Micromeritics ASAP 2010 instrument (Norcross, GA). The polysilsesquioxane solids were grounded and sieved through a 200 mesh sieve and degassed at 150 °C, 3 μmHg for at least 6 h before measurements. Specific surface areas were calculated using the multipoint Brunauer−Emmett−Teller (BET) method using DeltaGraph graphics software. Pore size distributions were determined by density functional theory (DFT) using nitrogen on carbon at 77 K with the slitlike pore model.

Thermal Gravimetric Analysis (TGA). A Perkin-Elmer thermal gravimetric analyzer (TGA-7) was used to investigate the thermal stability of samples. The samples (about 10 mg) were heated in a nitrogen atmosphere from ambient temperature to 800 °C at the heating rate of 20 °C/min in all cases.

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Supporting Information Available: Selected FTIR spectra; ^{1}H, ^{13}C, and ^{29}Si NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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