

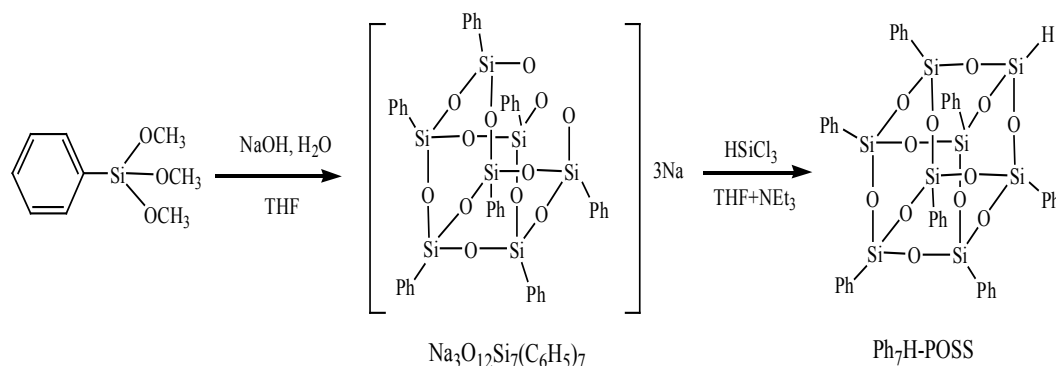
Synthesis of H-POSS

Synthesis of Heptaphenyltricycloheptasiloxane trisodiumsilanolate [$\text{Na}_3\text{O}_{12}\text{Si}_7(\text{C}_6\text{H}_5)_7$, the Intermediate]

Phenyltrimethoxysilane (91.08g, 0.46mol), tetrahydrofuran (500ml), deionized water (10.5g, 0.58mol) and Sodium hydroxide (7.9g, 0.2mol) were charged into a three-necked flask equipped with a reflux condenser and a magnetic stirrer in oil bath. After stirring and refluxing at 70 °C for 5 hours, the mixture was cooled down to room temperature and stirred during the following 15 hours. Then, volatile matter was evaporated with the help of rotary evaporator, and a kind of white powder was obtained. The white powder was immediately filtrated three times with tetrahydrofuran as the solution and dried in a vacuum oven at 70 °C for 5h. In the end, we gained the intermediate with a yield of 98.9% (65g).

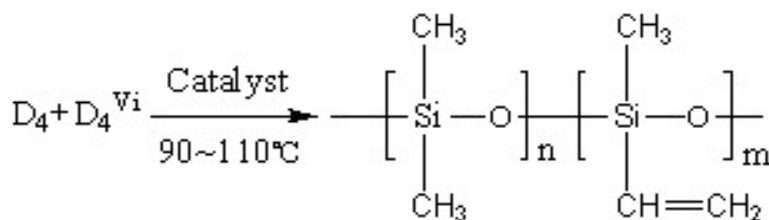
Synthesis of POSS

The reaction is called “corner-capping” reaction whose whole process should be conducted under dried nitrogen atmosphere. In a three-necked flask which was in an ice bath and equipped with a magnetic stirrer, the intermediate obtained above (20g, 20mmol) and triethylamine (3.04g, 30mmol) were dissolved in distilled tetrahydrofuran (400ml). After stirring vigorously for 30min, trichlorosilane (2.9ml, 30mmol) was injected into the flask. The mixture was stirred at 0 °C for 3 hours and then at room temperature for another 3 hours. Afterwards, the solvent in the flask was eliminated by rotary evaporating, and a raw product was obtained. Then the raw product was dissolved in chloroform (200ml), washed with deionized water three times to get the organic phase, dried over anhydrous magnesium sulfate and precipitated with anhydrous methanol (2000ml). At last, the precipitate suffered suction filtration and was dried in a vacuum oven at 60 °C for 48 hours. POSS we obtained was 12g with a yield of 84.8%. The whole reaction was carried out as follows:



Synthesis of PDMS

Predetermined amount of D₄ (octamethylcyclotetrasiloxane) and D₄^{vi} (tetramethyltetravinylcyclotetrasiloxane) were charged into a dried three-necked flask equipped with a nitrogen inlet, a thermometer, a mechanical stirrer and a condenser which was connected with a round-bottom flask and an oil pump. Firstly, water in the D₄ and D₄^{vi} were removed at 65 °C for about 1 hour with the help of high purity nitrogen and the oil pump. Then catalyst, 1% TMAOH [tetramethylammonium hydroxide, (CH₃)₄NOH] and definite content of MM^{vi} (1,3-divinyltetramethylsiloxane) as end-capping reagent were added. Subsequently, the reaction mixer was heated to 110 °C in an oil bath for 3-4 hours. When the viscosity was large enough, the temperature was elevated to 150 °C for 1-1.5 hours to decompose the catalyst and then was raised to 180 °C, accompanied by vacuumizing to remove the low molecular weight polymers and residual monomers. The reaction equation is shown as follows:



Characterization of H-POSS

Fourier transform infrared spectrometer (FT-IR) was recorded by a Nicolet Magna 560 infrared analyzer using KBr pellet technique. The spectrum was recorded in 4000~500 cm^{-1} region using 32 scans. With tetramethylsilane (TMS) as an internal reference at room temperature, ^1H (600 MHz) and ^{29}Si (400 MHz, decoupled from H) NMR spectra were obtained on a Bruker AV 11-400 spectrometer linked to a computer running WIN-NMR software in CDCl_3 , respectively. X-ray photoelectron spectroscopy (XPS) was conducted on a XSAM 800 of Kratos Company in a current of 15mA with Aluminum target. Wide angle X-ray diffraction (WAXD) spectra was obtained on a Philips X'Pert Graphics and Identify at a scanning rate of 2.4 deg/min from 5 to 45 $^\circ$ (2 θ), operating at 35 kV, 25 mA, using Ni-filtered Cu K α radiation.

In FT-IR, Si-O-Si of POSS cages shows a peak at 1134.7 cm^{-1} which is the characteristic absorption peak of H-POSS, 2251.9 cm^{-1} and 881.5 cm^{-1} belong to Si-H, 3074.3 cm^{-1} and 1595.5 cm^{-1} are attributed to benzene ring. In ^{29}Si NMR spectra, the proportion of peak intensity at -78.2, -78.5 and -82.9 ppm is 4:3:1, meaning the formation of the structure T ($\text{O}_{3/2}\text{Si-R}$) and the number of Si atoms in three chemical environment is 1,3 and 4 respectively, which is consistent with the theoretical structure of H-POSS as shown in the reaction equation. As to ^1H NMR spectra, peaks between 7ppm and 8ppm are for H atoms of benzene, and 4.49ppm belongs to the H atom directly connecting with Si. XPS indicates that the molar contents of C, O and Si are 67.5%, 20.1% and 12.4% respectively, which is in accord with theoretical results that the value is 67.7%, 19.4% and 12.9% severally. Thus, there is a plenty of evidences that H-POSS was successfully synthesized.

Characterization of PDMS

Gel permeation chromatography (GPC) analysis of PDMS was performed on a AGILENT-1100 system consisting of a 5 $\mu\text{m} \times 10,000 \text{ \AA}$ and 5 $\mu\text{m} \times 100 \text{ \AA}$ two PLgel columns and a refractive-index detector. The eluting solvent was tetrahydrofuran at a flow rate of 1.0 mL/min. The retention times were calibrated against polystyrene standards.

It is indicated in the GPC curves of PDMS that only one large peak exits in the graph, which proves that residual monomers, mainly octamethylcyclotetrasiloxane (D_4) and tetramethyltetravinylcyclotetrasiloxane (D_4^{vi}), and low molecular weight polymers (or called oligomers) has been almost removed. The GPC results show that the PDMS has a relative molecular weight of 528,429 g/mol, and its polydispersity index (PDI) is 1.681.