Synthesis of nanofibers organosiloxane structures under hydrothermal conditions

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Abstract. The paper presents the possibility of producing polyhedral oligomeric silsesquioxanes (POSS) under hydrothermal conditions in a high-pressure reactor. POSS was prepared by hydrolytic polycondensation of cyclohexyl trichlorosilane under conditions of elevated temperature and pressure. Morphology and structure of the final products were characterized by X-ray diffraction (XRD), thermal analysis (TGA and DTA) in an atmosphere of argon, Fourier transform infrared spectrum (FT-IR) and scanning electron micrograph (SEM). The resulting compound is a nanofibers of a polyhedral oligomeric silsesquioxane. The diameter of the obtained nanofibers is 50 ... 150 nm, and the length is from 200 nm to 30 μm.

1. Introduction
Organosiloxane materials are widely used as a filler to create various functional polymer composites [1,2]. Composites with additives of organosiloxane structures were widely used in the space industry [3-6]. Due to their chemical nature, organosiloxanes are highly resistant to the flow of atomic oxygen in outer space [7–9]. The Si atom, which is part of organosiloxanes, plays the main role in creating stable protective structures in the form of non-volatile oxides or glass-like substances on the surface when such materials are in an aggressive environment. The improved resistance of these materials to the action of strong oxidizing agents (including atomic oxygen in outer space) is based on the surface conversion mechanism, i.e. the formation of a new dense oxide protective layer.

One of the most promising organosiloxane fillers for space composites is polyhedral oligomeric silsesquioxanes (POSS), the chemical structure of which can be represented by the general formula (RSiO₁.₅)ₙ with n = 6, 8, 10, ..., where R is an organic radical [10-11]. The term "silsesquioxanes" indicates the ratio between the number of oxygen and silicon atoms: $\text{sesqui} = 1.5$. The most accessible and widely used are octahedral compounds (n = 8).

POSS synthesis is the subject of many works [12-14]. One of the main methods for producing POSS is the hydrolytic polycondensation of trifunctional monomers of the XSiY₃ type at room temperature [15–16]. However, the reaction time is several days, and the product yield reaches 70%. To increase the reaction rate, it is possible to use catalysts or increase the temperature of the process. In [17], to accelerate the course of the reaction for obtaining POSS-N₃, the process temperature was increased to 80 °C.
This paper presents the possibility of obtaining POSS structures by hydrolytic polycondensation of cyclohexyl trichlorosilane under conditions of elevated temperature and pressure.

2. Materials and methods

2.1. Materials

Cyclohexyl trichlorosilane $\text{C}_6\text{H}_{11}\text{SiCl}_3$ (manufacturer PJSC Khimprom, Novocheboksarsk, Russia) was used as a reagent. Cyclohexyl trichlorosilane is a colorless liquid with a boiling point of 206 °C and a density of 1.23 g/cm$^3$ (99.2% purity).

Silicon tetrachloride with the chemical formula $\text{SiCl}_4$ was produced by KHORST LLC, Moscow, Russia. $\text{SiCl}_4$ is a colorless liquid with a boiling point of 57 °C and a density of 1.48 g/cm$^3$ (99.9995% purity).

POSS synthesis was carried out in acetone solution. The chemical formula of acetone is $\text{C}_3\text{H}_6\text{O}$, boiling point 56 °C, density 0.79 g/cm$^3$. Acetone was produced by Component-Reagent LLC, Moscow, Russia (99.75% purity).

Distilled water was used for the reaction according to GOST 6709-72 "Distilled water - Technical specifications" (pH = 6.6).

2.2. Synthesis POSS

To obtain silsesquioxanes of a fully condensed structure (POSS), at the first stage, the synthesis of polyhedral oligosilsesquioxanes of a partially condensed structure was carried out. Scheme (1) shows the reaction of the formation of polyhedral oligosilsesquioxanes of a partially condensed structure by hydrolytic condensation of cyclohexyltrichlorosilane at room temperature (20 °C) for 24 hours:

$$n\text{C}_6\text{H}_{11}\text{SiCl}_3 + 1.5n\text{H}_2\text{O} \rightarrow (\text{C}_6\text{H}_{11}\text{SiO}_{1.5})_n + 3n\text{HCl}$$

Figure 1 shows the structural formulas of partially condensed oligosilsesquioxanes, which can be obtained as a result of the reaction according to scheme (1).

![Structural formulas of partially condensed oligosilsesquioxanes](image)

**Figure 1.** Structural formulas of partially condensed oligosilsesquioxanes

The resulting partially condensed oligosilsesquioxanes are a white precipitate. The resulting precipitate was washed from acetone. For this, centrifugation was used at high speeds of 6000 rpm to
separate the solid phase from the starting reaction products, followed by washing. The washing and centrifugation operation was repeated several times.

The synthesis of monofunctional polyhedral condensed oligosilesesquioxanes was carried out according to the sol-gel technology according to scheme (Fig. 2) by the interaction of partially condensed oligosilesesquioxanes with silicon tetrachloride in a GSA-0.3 high-pressure reactor for 4 hours.

![Figure 2. The synthesis of monofunctional polyhedral condensed oligosilesesquioxanes](image)

### 2.3. Research Methods

The Fourier transform IR spectrum was recorded using a IR spectrometer VERTEX 70. The specimen was pressed using a spectroscopically pure KBr matrix.

X-ray phase analysis was performed using the DRON-3 diffract meter (CuKα radiation, Ni filter) according to the standard method. The tube voltage amounted to 20 kV, the anode current was 20 mA, and the detector rotation rate was 2.4 degrees per minute with 1° angular pitch. The measurement rate limit reached 1000–4000 pulses per second. Data analysis and preliminary processing was performed with PDWin software (DrWin, Qual) using the PDF JCPDS database (version 2.02 1999).

Microphotography was performed using electronic microscope Tescan Mira 3 LMU. A thermal analyzer, STA 449 F1 Jupiter (NETZSCH), was used for thermal analysis. The materials were investigated in the temperature range from 20 to 1000° C. The heating rate was 5 K/min.

### 3. Result and discussion

The FT-IR spectra of the hydrothermally prepared compound are presented in Fig. 3. The very strong and predominant absorbance peak at 1080 cm\(^{-1}\) can be assigned to Si–O–Si asymmetric stretching vibrations. The IR band at 450–470 cm\(^{-1}\) is due to O–Si–O bending vibrations. The IR band at 780–800 cm\(^{-1}\) is assigned to Si–OH group. The IR band at 1440–1480 cm\(^{-1}\) corresponds to the C–H bond in the cyclohexane radical (–C\(_6\)H\(_{11}\)). The IR band at 2950–2970 cm\(^{-1}\) corresponds to the –CH\(_2\)– structural fragment in the structure of the cyclohexane radical. It should be noted that on the IR band of the obtained substance there are no bands at 3450–3500 cm\(^{-1}\), which indicates the absence of physically adsorbed water (H\(_2\)O). Also, there is no IR band at 1650–1680 cm\(^{-1}\) in the IR band responsible for the –OH bond. Thus, it can be argued that the chemical bonds in the IR band of the obtained substance correspond to the bonds that must be present in the IR band of the polyhedral oligomeric silsesquioxane. The absence of physically adsorbed water and the –OH bond indicates the production of a fully condensed polyhedral oligomeric silsesquioxane.

![Image of chemical structure](image)
The X-ray powder diffractogram of the obtained substance is shown in Figure 4. Analysis of the diffraction pattern showed that the synthesized substance has a pronounced crystalline structure. There is no information (card) in the PDF2 database about polyhedral oligomeric silsequioxanes. However, the obtained diffraction pattern results are consistent with the known literature data indicated in [17]. The characteristic crystal features of synthesized compound show four main reflections at $2\theta=9^\circ$, $12^\circ$, $12.5^\circ$, $19^\circ$ corresponding to the lattice spacing of $10.4 \, \text{Å}$, $7.9 \, \text{Å}$, $6.9 \, \text{Å}$, and $4.3 \, \text{Å}$, respectively.

Figure 5 shows a SEM image of a substance synthesized under hydrothermal conditions. An analysis of the data in Figure 5 showed that the resulting substance is a nanofibers. The diameter of nanofibers is from 50 to 150 nm. The length of the nanofibers varies from 200 nm and can reach 30 μm.
Figure 5. SEM image of substance synthesized under hydrothermal conditions.

Thermal analysis of the synthesized substance was carried out in the temperature range from 20 to 800 °C in an argon atmosphere. The Al₂O₃ hitch served as a reference. Figure 6a shows the obtained TGA curve of the synthesized substance. Figure 6a shows that the synthesized substance is thermostable to a temperature of 300 °C without loss of mass on the TGA curve. The temperature at which mass loss ends is 580 °C. After a temperature of 580 °C, the residual mass of the sample did not change and amounted to 40%.

Figure 6. TGA curve (a) and DTA curve (b) of substance synthesized under hydrothermal conditions.

Figure 6b shows the DTA curve of the synthesized substance. The DTA curve in Figure 6b is characterized by a long exothermic effect with a pronounced maximum at 420 °C. The peak at a given temperature corresponds to the maximum weight loss of the test substance. Thus, the resulting substance has high thermal stability. The obtained results on the thermal analysis of the obtained substance are consistent with published data on the thermal stability of the polyhedral oligomeric silsesquioxane in [18].

4. Conclusion
The hydrolytic polycondensation of cyclohexyl trichlorosilane was synthesized under hydrothermal conditions. It was found that the compound obtained is a nanofibre of a polyhedral oligomeric
silsesquioxane. The diameter of the obtained nanofibers is 50 ... 150 nm, and the length is from 200 nm to 30 μm.

It was established that the obtained POSS nanofibers have a pronounced crystalline structure. The characteristic crystal features of synthesized compound show four main reflections at 2θ=9°, 12°, 12.5°, 19° corresponding to the lattice spacing of 10.4 Å, 7.9 Å, 6.9 Å, and 4.3 Å, respectively.

The resulting nanofibers are thermostable to a temperature of 300 °C. The temperature at which mass loss ends is 580 °C. After a temperature of 580 °C, the residual mass of POSS does not change and remains 40%.

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