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Heterofunctional oligoorganylsilsesquioxanes

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Abstract

The results of studies of the synthesis processes and some physico-chemical properties of heterofunctional octa(methylvinyl)silsesquioxanes of the general formula $R_nR'_{8-n}[SiO_{1.5}]_8$, where $n = 0$–8, $R = CH_3$, $R' = C_2H_3$, are reported. It has been shown that the directed synthesis of the investigated oligoorganylsilsesquioxanes accomplished by homo- and hetero-functional copolycondensation of three-functional derivatives of organylsilanes. The technique has been developed for the synthesis of octamethyl or octavinyl-silsesquioxanes by combined polycondensation of tetramethyltetrachlorotetracyclosiloxane with vinyltrichlorosilane, providing a set of products with $n = 4$ to 6. On the basis of the results of studies of the dependence of vapour pressure on temperature for some $(CH_3)_n(C_2H_3)_{8-n}[SiO_{1.5}]_8$ compounds, the conditions of purification of the compounds obtained have been found. Data of complex thermoanalytical studies of octa(methyl, vinyl)silsesquioxanes are presented.

In our earlier work we reported on the synthesis and studies of oligoorganylsilsesquioxanes containing saturated and unsaturated radicals near a silicon atom [1–3]. Despite the fact that the possibility of producing these compounds was demonstrated by Olsson in 1956 [4], interest in them has recently arisen again. This is explained by the determination of the area of practical use of such substances as initial reactants during the synthesis of thermostable polymers [5], as well as in some fields of microelectronics [2,6]. In this respect, of no less interest are the heterofunctional oligomers containing simultaneously saturated and unsaturated radicals near the silicon atoms of a silicon-oxygen framework, which allows practical applications of the materials to be extended by combining the properties of individuals compounds.

The present paper describes the synthesis and study of the properties of octa(methyl, vinyl)silsesquioxanes and generalizes the results obtained earlier [7–9]. The simplest method of synthesis of this kind of compound is hydrolytic copoly-

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condensation of the relevant organyltrichlorosilanes according to eq. 1, where $n = 0$–8.

$$CH_3SiCl_3 + C_2H_3SiCl_3 + H_2O \xrightarrow{ROH} (CH_3)_n(C_2H_3)_{8-n}[SiO_{1.5}]_8 + HCl \qquad (1)$$

The synthesis gives a mixture of nine compounds; in this case, no correspondence of the ratio of the initial reactants to the composition of the prepared product is observed [8,10]. The main requirement of this kind of material is reproducibility of their composition.

It has been established empirically that the quantitative ratio of oligomers in the mixture depends on the following factors: the concentration and ratio of the initial reactants, the synthesis time and the method of cleaning. We suppose that non-reproducibility of the composition of the synthesized products is due to their regrouping in a reaction mixture that occurs under the action of HCl evolving during the synthesis. To confirm this supposition, we carried out a series of experiments in which we changed the ratio of the initial reactants methyltrichlorosilane/vinyltrichlorosilane (w) from 1/7 to 7/1, the time of synthesis and the concentration of HCl in the reaction medium. It was found that with a synthesis time of 21 h the obtained mixture of reproducible composition is enriched with a compound in

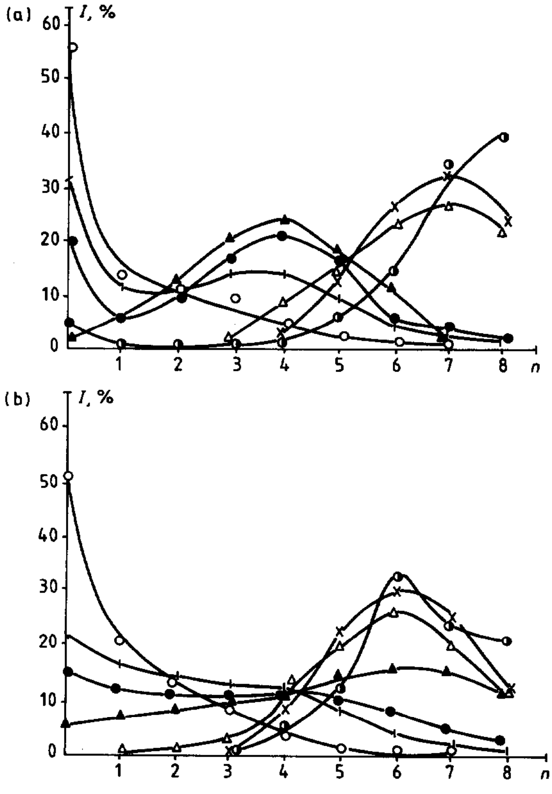


Fig. 1. Dependence of the composition of the products of hydrolytic copolycondensation of $MeSiCl_3$ and $VinSiCl_3$ on the ratio w: ○, $w = 1/7$; $w = 2/6$; ●, $w = 3/5$; ▲ $w = 1/1$; △, $w = 5/3$; ×, $w = 6/2$; ◑, $w = 7/1$; |, $w = 2/6$; *a*, Time of exposure of the reaction mixture: 72 h; *b*, 168 h.

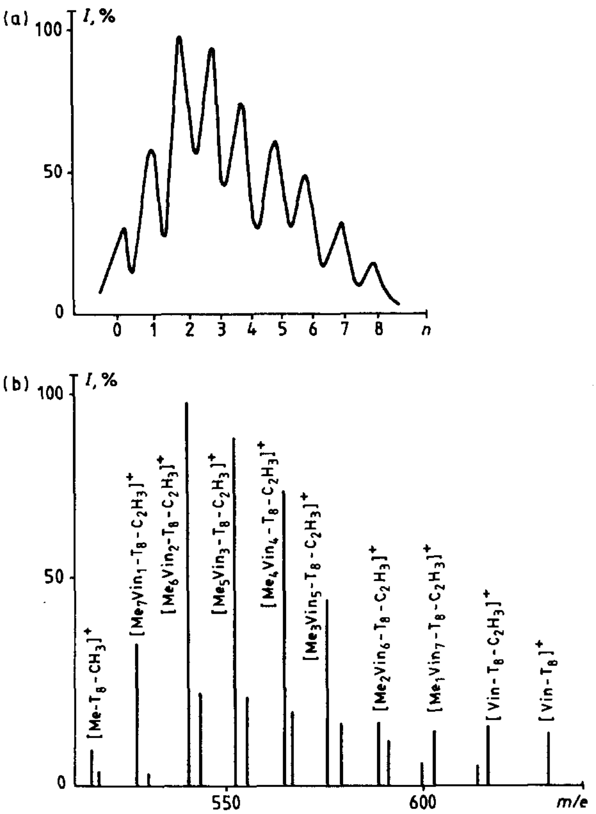


Fig. 2. Chromatogram (a) and mass spectrum (b) of the mixture of octa(methyl,vinyl)silsesquioxanes.

which the ratio of methyl (Me) and vinyl (Vin) radicals corresponds to *w*. The yield of the product (~ 5%) increases with increasing synthesis time; however, the composition of the mixture changes randomly (Fig. 1).

The composition of the products obtained was determined from the data of GLC and mass spectrometric analyses. The chromatograms obtained under the same conditions reveal nine maxima, the position of the first and last maxima corresponding to octamethylsilsesquioxane (methyl-T_8) and octavinylsilsesquioxane (vinyl-T_8); this was established by comparison with the chromatograms of reference substances. The remaining seven maxima correspond to the compounds $(CH_3)_4(C_2H_3)_{8-n}$-$[SiO_{1.5}]_8$, where $n = 1$ to 7. As the methyl radicals in the molecule of methyl-T_8 are replaced by vinyl ones, the molecular weight of the substance and the time of its confinement in the chromatographic column increase (Fig. 2a).

In addition to methyl-T_8 and vinyl-T_8, the mass spectrum of the products shows seven peaks of molecular ions formed by elimination of the methyl and vinyl radicals from the parent one, the first way being more preferable for substances enriched with methyl substituents. Less intense are the peaks of doubly charged ions formed by the simultaneous elimination of two radicals, which is typical of oligoorganylsilsesquioxanes (Fig. 2b) [11].

No less typical are the IR spectra of the products which may be used for product identification. For instance, the band in the region of 514 cm^{-1} for methyl-T_8,

Table 1

	Ratio of the initial reactants	Compound with maximum content in the mixture
1	1/7	$(CH_3)_1(C_2H_3)_7[SiO_{1.5}]_8$
2	2/6	$(CH_3)_2(C_2H_3)_6[SiO_{1.5}]_8$
3	3/5	$(CH_3)_3(C_2H_3)_5[SiO_{1.5}]_8$
4	4/4	$(CH_3)_4(C_2H_3)_4[SiO_{1.5}]_8$
5	5/3	$(CH_3)_5(C_2H_3)_3[SiO_{1.5}]_8$
6	6/2	$(CH_3)_6(C_2H_3)_2[SiO_{1.5}]_8$
7	7/1	$(CH_3)_7(C_2H_3)_1[SiO_{1.5}]_8$

typical of deformation vibrations of the silicon-oxygen framework in heterofunctional oligomers, is shifted to high values of wavenumbers down to 586 cm^{-1} for pure vinyl-T_8 upon replacement of the methyl radicals by vinyl ones. Using GLC data of some of the obtained mixtures with different ratios of compounds with $n = 1$ to 7, we plotted the dependence of the wavenumber on the content of methyl radicals in the mixture. This plot, which is used as a calibration plot, allows the position of the absorption band of interest to be calculated for individual octa(methyl,vinyl)silsesquioxanes.

The most appropriate initial reactants for the synthesis of heterofunctional oligoorganylsilsesquioxanes are organylsilanes containing no chlorine. In this respect, organyltriacetoxysilanes are promising; during their hydrolysis, acetic acid is evolved which is less active than HCl and is required as a catalyst for the condensation of the products of hydrolysis, eq. 2 where $n = 0$–8.

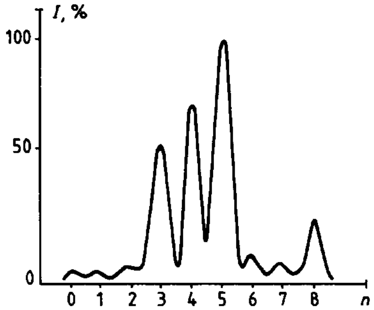
$$CH_3Si(OCOCH_3)_3 + C_2H_3Si(OCOCH_3)_3 + H_2O \xrightarrow{ROH} (CH_3)_n(C_2H_3)_{8-n}[SiO_{1.5}]_8 + CH_3COOH \quad (2)$$

When the reaction proceeds according to eq. 2, no changes in the ratio of the components in the mixture with increasing synthesis time occur. In this case, coincidence of the ratio of the initial reactants and of the composition of the material obtained is observed (Table 1). For instance, with $w = 6/2$ the mixture contains a maximum amount of $(CH_3)_6(C_2H_3)_2[SiO_{1.5}]_8$; with $w = 1/1$, the mixture is enriched with the symmetric compound $(CH_3)_4(C_2H_3)_4[SiO_{1.5}]_8$, and so on. It is evident that processes of rearrangement of the products in the reaction mixture under the action of acetic acid occur more slowly. For instance, with $w = 1/1$ and exposure of the reaction mixture for 5 and 10 days, only the total yield of the product (up to 30%) increases with an increase in time, the composition remaining unchanged.

Another possibility of obtaining substances with reproducible composition is the heterofunctional polycondensation reaction of organyltrichloro- and organyltriacetoxy-silanes with a synthesis time of not more than 80 h (eq. 3, $X = Cl$, $Y = OCOCH_3$, $n = 0$–8).

$$CH_3Si(X)Y_3 + C_2H_3Si(Y)X_3 + H_2O \xrightarrow{ROH} (CH_3)_n(C_2H_3)_{8-n}[SiO_{1.5}]_8 + H(X)Y \quad (3)$$

Copolycondensation of CH_3SiCl_3 and $C_2H_3Si(OAc)_3$ with $w = 2/6$ and exposure of the reaction mixture for 3 days results in products enriched with



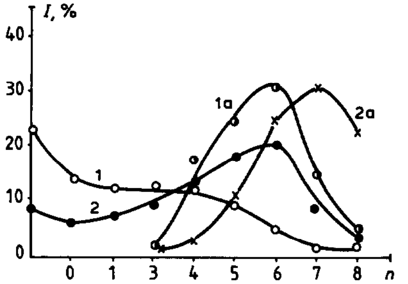


Fig. 3. Chromatogram of the product prepared by combined hydrolytic polycondensation of $D_4^{CH_3Cl}$ with vinyltrichlorosilane.

Fig. 4. Products of the hydrolytic polycondensation of $MeSiX_3$ and $VinSiX_3$ before (1, 2) and after (1a, 2a) sublimation at 100–120 °C.

$(CH_3)_2(C_2H_3)_6[SiO_{1.5}]_8$. With an increase in the synthesis time, its content decreases and becomes comparable with the content of $(CH_3)_3(C_2H_3)_5[SiO_{1.5}]_8$.

There is another way of synthesizing heterofunctional oligomers that allows a narrower set of products to be obtained. In the case given, this is the combined hydrolytic polycondensation of tetramethyltetrachlorotetracyclosiloxane ($D_4^{CH_3,Cl}$) with vinyltrichlorsilane (eq. 4, where $n = 4–6$).

$$[CH_3ClSiO]_4 + C_2H_3SiCl_3 \xrightarrow{ROH} (CH_3)_4(C_2H_3)_{8-n}[SiO_{1.5}]_8 + HCl \qquad (4)$$

As can be seen from eq. 4, besides the symmetrical product with $n = 4$, compounds with $n = 5$, 6 are formed. This means that in the course of the reaction, cleavage of the Si–O bonds of the silicon–oxygen cycle occurs with subsequent rearrangement of the intermediate products into three-dimensional oligomers. The mixture composition was found to be unchanged independently of the synthesis conditions (Fig. 3), unlike the products of hydrolytic copolycondensation of the mixture of methyl- and vinyl-trichlorosilane.

The substances obtained were cleaned by vacuum sublimation, and as a result it was found that the cleaning conditions affect the composition of the sublimate obtained: in the temperature range 100 to 120 °C in a vacuum of 10^{-3} mmHg, the composition of the mixture of initial components is varied and enriched with oligoorganylsilsesquioxanes $(CH_3)_6(C_2H_3)_2[SiO_{1.5}]_8$ (Fig. 4); at temperatures from 180 to 200 °C, the composition of the mixture obtained is practically the same as the initial one.

Since with long exposure of the reaction mixture of the products prepared by eq. 1 the mixture is also enriched with a compound corresponding in composition to $(CH_3)_6(C_2H_3)_2[SiO_{1.5}]_8$, one can assume that this compound is the most thermodynamically stable.

Complex thermoanalytical investigation of the products obtained was done. Figure 5 shows the dependence of the weight reduction on the temperature calculated from the thermogravimetric curves. From these data it follows that the volatility and thermal stability of the individual compounds (methyl-T_8 and vinyl-T_8) and the volatility of the mixtures (methyl,vinyl-T_8) are close; however, there is a

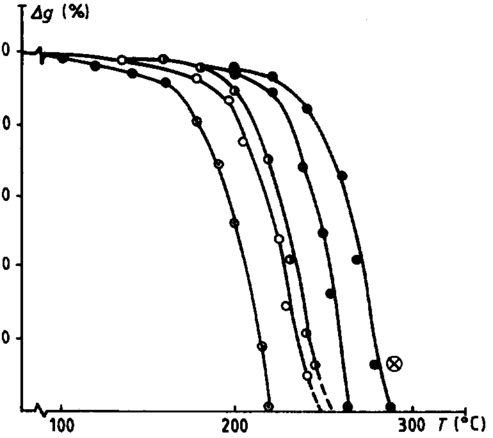


Fig. 5. Dependence of the weight reduction on the temperature for octa(methyl,vinyl)silsesquioxanes: ◑, $w = 6/2$; ○, $w = 1/1$; ⊙, $w = 7/1$; ⊗, methyl-T_8; ●, vinyl-T_8.

quantitative difference caused by the prevalence of this or that component. For instance, with a decrease in the number of methyl substituents in the substances their volatility grows; for mixtures enriched with individual methyl-T_8 or products with a large number of methyl group, the volatility decreases and approaches the values for pure methyl-T_8. An exception is the mixture enriched with $(CH_3)_6(C_2H_3)_2[SiO_{1.5}]_8$, which is explained by the very low temperature of sublimation of this product. The latter is in conformity with the regular enrichment of substances prepared under low-temperature sublimation by this product (Fig. 4).

As is known [2,7], oligoorganylsilsesquioxane films are deposited by vacuum thermal evaporation and the film composition is required to be reproducible. In order to identify the conditions of deposition, we investigated the dependence of the vapour pressure of octa(methyl,vinyl)silsesquioxanes on the temperature. Measurements were made by the Knudsen method with mass-spectrometric recording for the following compounds: $(CH_3)_4(C_2H_3)_4[SiO_{1.5}]_8$, $(CH_3)_5(C_2H_3)_3[SiO_{1.5}]_8$, and $(CH_3)_6(C_2H_3)_2[SiO_{1.5}]_8$. Enrichment of the mixture by the above compounds was performed by repeated gradient sublimation and recrystallization. For quantitative calculation of the vapour pressure of individual compounds at a fixed temperature, we carried out several experiments with different weighed amounts of substances and then solved the system of equations describing the number of components in the mixture. From our estimations, the calculation error is 15%, the experimental error 3–4%. It should be noted that the highest equilibrium vapour pressure at a temperature of 104°C is observed for $(CH_3)_6(C_2H_3)_2[SiO_{1.5}]_8$; hence it is this compound that should enrich the mixture under low-temperature sublimation, which agrees with the data gained above.

The plots of $\log p - 1$ versus T for $(CH_3)_4(C_2H_3)_4[SiO_{1.5}]_8$, $(CH_3)_5(C_2H_3)_2$-$[SiO_{1.5}]_8$ and $(CH_3)_6(C_2H_3)_2[SiO_{1.6}]_8$ (Fig. 6) have different slopes (ΔH_{subl} 23.8 ± 1.0, 25.2 ± 1.0 and 27.5 ± 1.0 kcal/mole, respectively) and intersects at points corresponding to temperatures of 160 and 230°C. It is evident that the optimal temperature range within which the product sublimation proceeds with no variation in the composition is 160–200°C, as at these temperatures the difference between the vapour pressures of individual compounds is minimum.

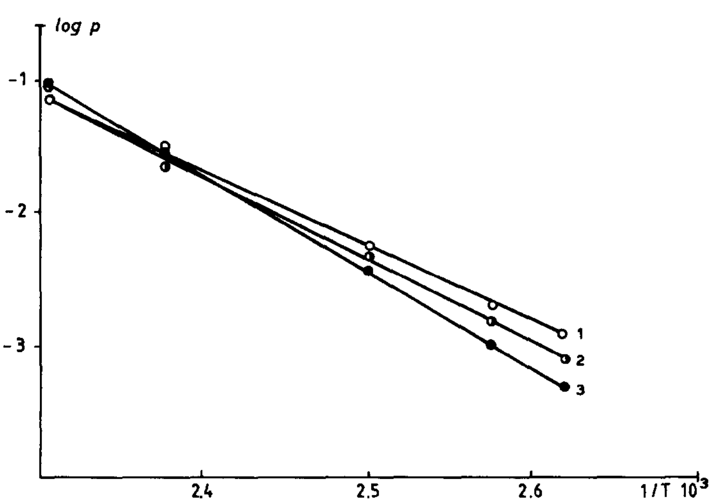


Fig. 6. Dependence of the vapour pressure on the temperature for 1, $Me_4Vin_4[SiO_{1.5}]_8$; 2, $(CH_3)_5(C_2H_3)_3[SiO_{1.5}]_8$; and 3, $(CH_3)_6(C_2H_3)_2[SiO_{1.5}]_8$.

The results of experimental tests showed that the third resublimation of the material in a vacuum of 10^{-3} mmHg in the temperature range 180–200 °C gives substances with reproducible composition corresponding to the initial product.

Thus, the above-described experiments with (methyl,vinyl-T_8) demonstrated the possibility of obtaining heterofunctional oligomers in four ways: homofunctional copolycondensation of alkyl- and alkenyl-trichlorosilanes as well as of alkyl- and alkenyl-triacetoxysilanes (equations 1 and 2); heterofunctional copolycondensation of organyltrichloro- and organyltriacetoxy-silanes (eq. 3); and the interaction reaction of chlorine-containing cyclosiloxanes and alkenyltrichlorosilanes (eq. 4).

The influence of the conditions of synthesis and cleaning on the composition of the materials obtained was investigated. Complex thermoanalytical studies of the substances obtained were made and the dependence of the vapour pressure on the temperature was examined; this made it possible to determine the optimal conditions of material sublimation with no variation in the composition.

We used methyl- and vinyl-trichlorosilanes of the "*p*" qualification sublimated preliminary at temperatures of 65 and 91 °C, respectively. The reaction of hydrolytic copolycondensation of methyl- and vinyl-trichlorosilane was carried out at temperatures ranging from 0 to 10 °C with $MeSiCl_3/ViSiCl_3/C_2H_5OH$ ratios from 7/1/132 to 1/7/132. The reaction mixture was kept at room temperature and the precipitate was filtered off 72 and 168 h after the beginning of the reaction.

Organyltriacetoxysilanes were obtained by the technique described in ref. 12. Combined hydrolytic polycondensation of methyl- and vinyl-triacetoxysilane was performed in ethyl alcohol medium with $MeSi(OAc)_3/VinSi(OAc)_3/C_2H_5OH$ ratios from 1/7/40 to 7/1/40 and the exposure times of the reaction mixture ranging from 120 to 240 h. Then the precipitate was filtered off.

Combined hydrolytic polycondensation of tetramethyltetrachlorotetracyclosiloxane with vinyltrichlorosilane was carried out in a mixture of ethanol and ether (ratio 1/3). 22.4 ml of $D_4^{CH_3Cl}$ was added to this mixture at room temperature, the mixture was stirred for 30 min, than 41.5 ml of vinyltrichlorosilane was introduced and the mixture was stirred for 1 h. After that, water (10 ml) was added drop by drop and the mixture was kept at room temperature for 168 h. The precipitate was filtered off, treated with ethanol and dried.

Chromatographic analysis of the finite products was performed with an LHM-72M chromatograph equipped with a column (1.5 m long and 3 m in diameter) packed with Chromosorb with an immovable liquid phase (SE-30). The column temperature was programmed at a rate of 11°/min. Mass spectra were recorded in an MS-902 spectrometer at ionization energies of 60 eV. IR spectra of the pellets of the examined products pressed in KBr were recorded on a UR-20 spectrometer. Thermogravimetric investigations were performed on a Setaram microanalyzer with a symmetrical furnace in a flowing inert atmosphere. The gas flow rate was 100 to 110 ml/min; the furnace heating rate was 5°/min. The specific surface of the samples under investigation was 2–3 m^2/g and was measured by the method of thermal desorption of argon.

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