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Dedicated to the 90th Anniversary of Academician M.G. Voronkov

Preparation of Organoalkoxysiloxanes by Partial Acidolysis of Organoalkoxysilanes

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Abstract—Partial polycondensation of $RSi(OMe)_3$ (R = C_6H_5, CH_3) by the reaction with AcOH in the presence of HCl is studied. Oligoorganomethoxysiloxanes are obtained of the average composition $[RSi(OMe)O]_4$, $[RSi(OMe)_{4/6}O_{7/6}]_6$, $RSi(OMe)_{0.5}O_{1.25}]_8$, and $[RSi(OMe)_{0.4}O_{1.3}]_{10}$. Using the method of ^{29}Si NMR spectroscopy they were shown to contain three types of structural fragments: $RSi(OMe)_2O–$, $RSiOMe(O–)_2$, $RSi(O–)_3$. Based on the kinetic data, on the composition, properties, and the ^{29}Si NMR spectroscopy data of the products the conclusion is made that the obtained compounds have polycyclic structure with branched fragments. Using the GLC method the reaction was shown to have an induction period, whose duration can be substantially shortened by addition of HCl or methanol.

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Reactions of organoacetoxysilanes with alcohols [1, 2] and organoalkoxysilanes with organic acids [3–13] are an efficient method of synthesis of organosiloxanes of various composition and structure. A specific feature of these processes is the formation of the siloxane bond upon hydrolytic polycondensation in homogeneous environment due to the presence of water produced in the reaction of an acid with an alcohol. Thus, an industrial method for preparation of organosiloxane resins by the reaction of organoacetoxysilanes with methanol is described [1]. The synthesis of polyethylsiloxane liquids by the reaction of diethyldiethoxysilane with organic mono- and dicarboxylic acids in the presence of sulfuric acid as a catalyst is also described [3]. Depending on the ratio of the reagents cyclic or linear diethylsiloxanes can be obtained in quantitative yield. It was shown that carrying out the reaction of organoalkoxysilanes with acetic acid allows to substantially improve the control of the process, first of all as far as the control of the structure of the formed products is concerned [4]. This is connected with the fact that acetic acid and alcohol are an active medium of the reaction, which dissolve the reagents, the products, and are co-reagents.

In the present work, we have investigated the partial polycondensation of phenyl- and methyltrimethoxysilanes $RSi(OMe)_3$ in the reaction with acetic acid in the presence of hydrogen chloride at different molar ratios of AcOH and $RSi(OMe)_3$. The scheme of the reaction can be represented as follows [Eq. (1)].

$$m\ RSi(OMe)_3 + n\ AcOH \xrightarrow{HCl} n\ AcOMe + (n–x)\ MeOH + [RSi(OH)_xO_y(OMe)_{3–x–2y}]_n \xrightarrow[–MeOH]{HCl} [RSiO_{n/m}(OMe)_{(3m–2n)/4}]_n, \quad (1)$$

R = Me, n:m = 4:4 (**I**), 7:6 (**II**), 10:8 (**III**), 13:10 (**IV**); R = Ph, n:m = 4:4 (**V**), 7:6 (**VI**), 10:8 (**VII**), 13:10 (**VIII**).

The optimal condition of the acidolysis is the starting temperature of 90–95°C. In the course of the reaction the temperature of the reaction mixture decreases to 60°C because of the formation of low-

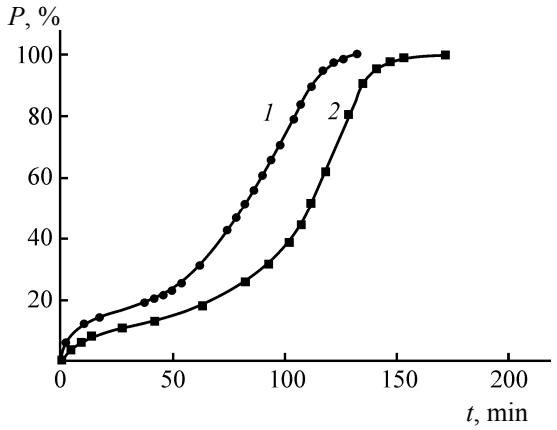


Fig. 1. Conversion curves for the acidolysis of (*1*) $MeSi(OMe)_3$ and (*2*) $PhSi(OMe)_3$ (*n*:*m* = 4:4) in the presence of HCl [$HCl:RSi(OMe)_3$ = 0.007:1].

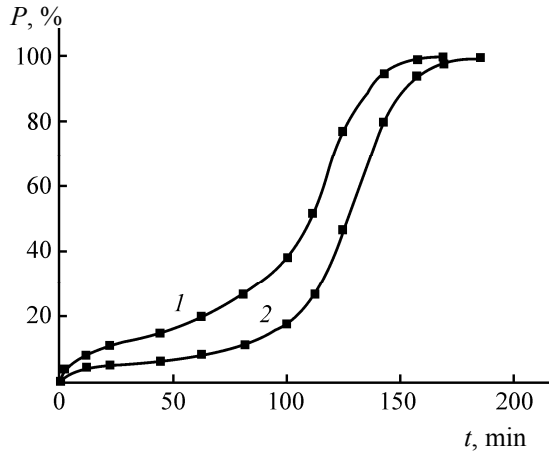


Fig. 2. Conversion curves for the coacidolysis of (*1*) $MeSi(OMe)_3$ and (*2*) $PhSi(OMe)_3$ (*n*:*m* = 14:8) in their mixture (molar ratio 2:1) in the presence of HCl ($HCl:RSi(OMe)_3$ = 0.0035:1.

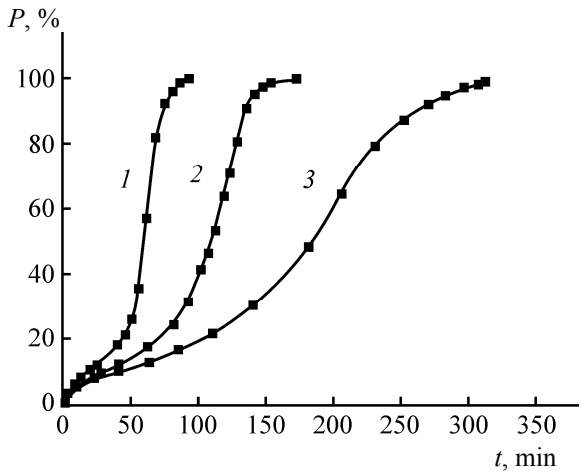


Fig. 3. Conversion curves for the acidolysis of $PhSi(OMe)_3$ (*n*:*m* = 4:4) in the presence of HCl, mol: (*1*) 0.014, (*2*) 0.007, and (*3*) 0.003 [per 1 mol of $RSi(OMe)_3$].

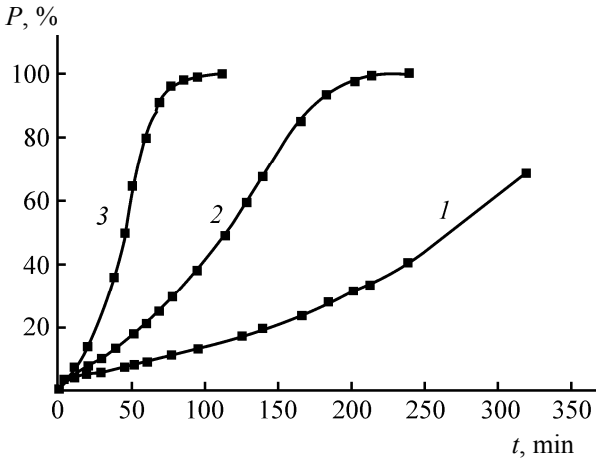


Fig. 4. Conversion curves for the acidolysis of $MeSi(OMe)_3$ (*n*:*m* = 4:4) in the presence of HCl [0.0015 mol per 1 mol of $RSi(OMe)_3$] and MeOH, mol: (*1*) 0, (*2*) 1, and (*3*) 2 [to 1 mol of $RSi(OMe)_3$].

boiling methyl acetate and methanol. The reaction was monitored using the GLC method by measuring the content of the reagents, intermediate and final products of the reaction. In order to complete the process of polycondensation with participation of the SiOH groups after full consumption of acetic acid the low-boiling products were removed from the reaction mixture by gradual increase of the temperature to 135° C. In all cases the acetic acid was fully consumed and stoichiometric amounts of methanol and methyl acetate were distilled off.

The investigation of the kinetics of acidolysis of $RSi(OMe)_3$ has shown that for all reactions at the beginning a small jump in the conversion of alkoxysilane and acetic acid is observed, followed by an inductive period, whose duration is reduced in going from $PhSi(OMe)_3$ to $MeSi(OMe)_3$ in the presence of HCl, CH_3OH, and at the increase in their concentrations (Figs. 1–5).

For coacidolysis of the mixture of $MeSi(OMe)_3$ and $PhSi(OMe)_3$ with the excess of acetic acid (*n*:*m* = 14:8) where the final product should correspond the average composition $[RSi(OH)_{0.5}O_{1.25}]_8$, the duration of their inductive periods becomes almost equal (Fig. 2). However, $MeSi(OMe)_3$ reacts faster than $PhSi(OMe)_3$. This allows to assume that in the initial stage of the reaction the copolymer is enriched with methylsiloxane fragments.

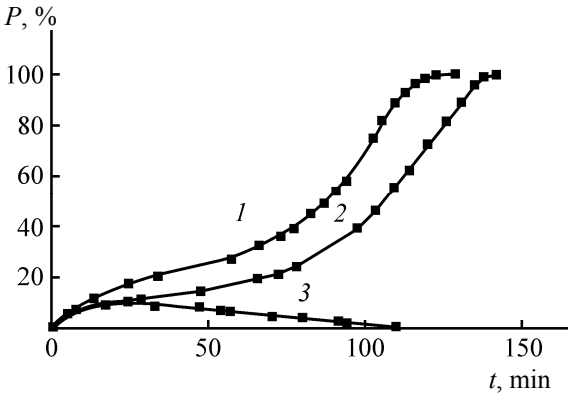


Fig. 5. Conversion curves of (*1*) $PhSi(OMe)_3$, (*2*) AcOH, and (*3*) $Ph(OMe)_2Si(OAc)$ for the acidolysis of $PhSi(OMe)_3$ (n:m = 10:8) in the presence of 0.007 mol HCl per 1 mol of $RSi(OMe)_3$.

The jump of conversion at the beginning of the reaction is caused by the formation of acetoxymethoxy derivatives $RSi(OAc)_n(OMe)_{3-n}$ due to the reaction of $RSi(OMe)_3$ with acetic acid [Eq. (2)].

$$RSi(OMe)_3 + n\text{AcOH} \rightleftarrows RSi(OAc)_n(OMe)_{3-n} + n\text{ MeOH}. \quad (2)$$

To identify the intermediate organo(alkoxy)acetoxysilanes we have prepared the equimolar mixtures [$MeSi(OMe)_3$ + $MeSi(OAc)_3$] and [$PhSi(OMe)_3$ + Ac_2O]. The ^{29}Si NMR spectroscopy has shown that in these mixtures the reactions occur, which result in the formation of all possible organoacetoxymethoxysilanes (Table 1).

$$MeSi(OMe)_3 + MeSi(OAc)_3 \rightleftarrows 2MeSi(OAc)_n(OMe)_{3-n}, \quad (3)$$
$$n = 0, 1, 2, 3.$$

$$PhSi(OMe)_3 + nAc_2O \rightleftarrows PhSi(OAc)_n(OMe)_{3-n} + n\text{AcOM}, \quad (4)$$
$$n = 0, 1, 2, 3.$$

The GLC analysis of the products of the reactions [$MeSi(OMe)_3$ + $MeSi(OAc)_3$] and [$PhSi(OMe)_3$ + Ac_2O] made it possible to identify the monoacetoxyderivatives and to determine their quantitative content.

The analysis by the method of ^{29}Si NMR spectroscopy has shown the presence of $PhSi(OMe)_2(OAc)$ and $MeSi(OMe)_2(OAc)$ in the reaction mixture at the initial stage of the reaction of $RSi(OMe)_3$ with AcOH (Table 1). In Fig. 5 the data on the variation of the molar percentage of $PhSi(OMe)_2(OAc)$ for the acidolysis of $PhSi(OMe)_3$ (n:m = 10:8) in the presence of 0.007 mol of HCl per 1 mol of $PhSi(OMe)_3$ are presented, which show that up to 8% of $Ph(OMe)_2$·Si(OAc) is formed during the reaction.

Therefore, the obtained results prove the conclusion that in the initial stage of the acidolysis of organoalkoxysilanes partial substitution of the alkoxy groups by acetoxy groups occurs [Eq. (5)] [4, 5, 10].

The general scheme of the process can be represented as follows [Eq. (5–11)].

$$RSi(OMe)_3 + \text{AcOH} \rightleftarrows RSi(OAc)(OMe)_2 + \text{MeOH}, \quad (5)$$

$$\text{MeOH} + \text{AcOH} \xrightarrow{\text{HCl}} \text{AcOMe} + H_2O, \quad (6)$$

$$RSi(OAc)(OMe)_2 + H_2O \xrightarrow{\text{HCl}} RSi(OH)(OMe)_2 + \text{AcOH}, \quad (7)$$

$$RSi(OMe)_3 + H_2O \xrightarrow{\text{HCl}} RSi(OH)(OMe)_2 + \text{MeOH}, \quad (8)$$

$$RSi(OH)(OMe)_2 + RSi(OMe)_3 \xrightarrow{\text{HCl}} [R(MeO)_2Si]_2O + \text{MeOH}, \quad (9)$$

$$RSi(OH)(OMe)_2 + RSi(OH)(OMe)_2 \xrightarrow{\text{HCl}} [R(MeO)_2Si]_2O + H_2O, \quad (10)$$

$$2\ RSi(OMe)_3 + \text{AcOH} \xrightarrow{\text{HCl}} [R(MeO)_2Si]_2O + \text{AcOMe} + \text{MeOH}. \quad (11)$$

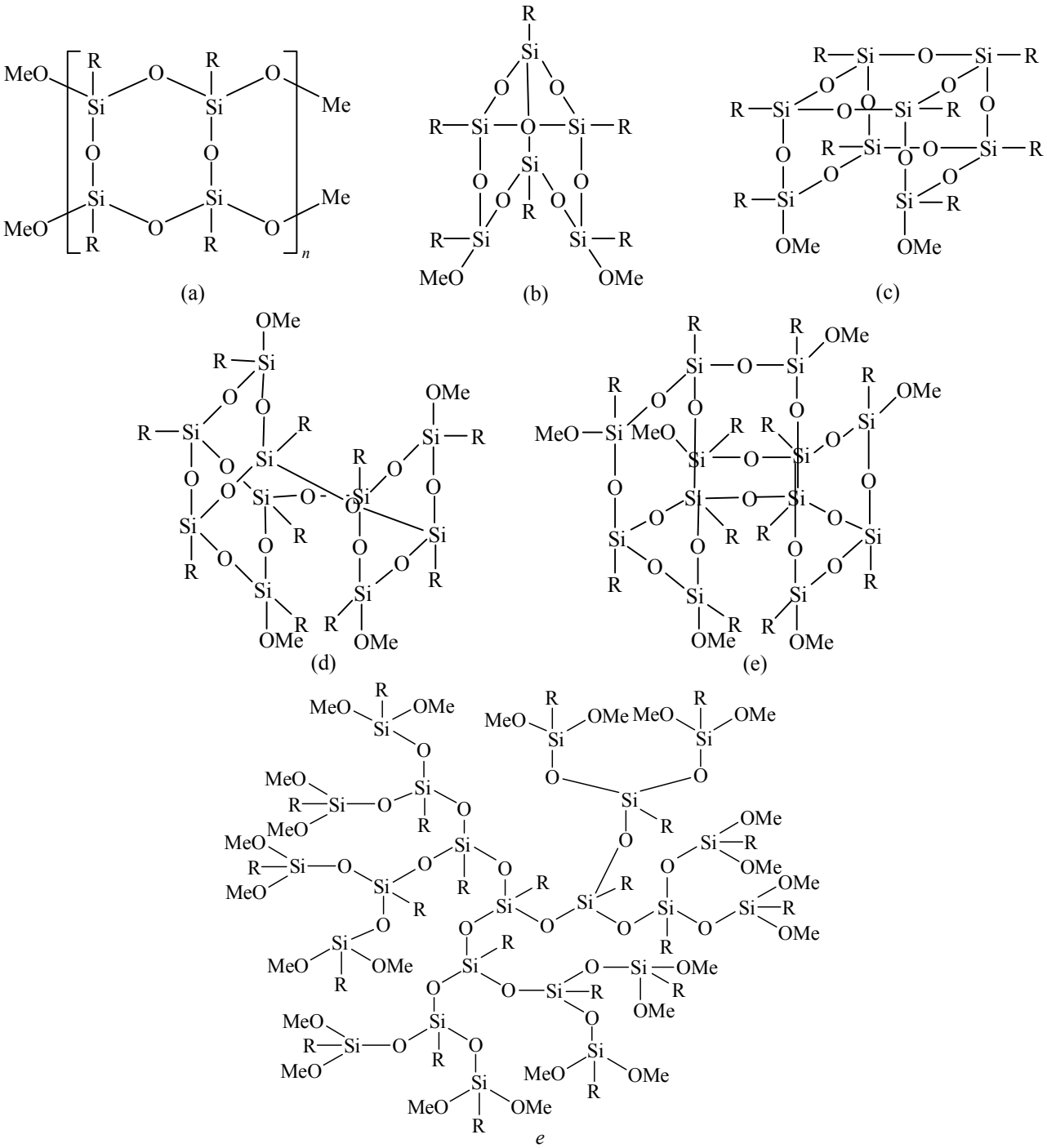
According to this scheme, the eliminated methanol [Eq. (5)] enters the reaction of esterification [Eq. (6)]. With appearance of water in the reaction mixture, reactions (7) and (8) are accelerated, thus enriching it

Table 1. ^{29}Si NMR parameters (δ_{Si}, ppm) of organo(alkoxy)acetoxysilanes, detected in the reaction mixtures

Reaction mixture	$RSi(OMe)_3$	$RSi(OMe)_2(OAc)$	$RSi(OMe)(OAc)_2$	$RSi(OAc)_3$
$MeSi(OMe)_3$+ $MeSi(OAc)_3$	–40.09	–41.85	–42.86	–43.27
$MeSi(OMe)_3$+ 2AcOH	–39.7	–41.66	–	–
$PhSi(OMe)_3$ + Ac_2O	–55.15	–58.12	–60.8	–63.13
$PhSi(OMe)_3$ + 2 AcOH	–54.78	–57.90	–	–

with methanol and acetic acid and shifting the equilibrium reaction (6) to the right. The catalytic effect of HCl on reactions (6)–(10) accelerates them when its concentration increases. Thus, it becomes clear why the introduction of methanol and HCl into the reaction mixture results in a substantial decrease in the duration of the inductive period.

From the reaction with the chosen ratios of the reagents the oligoorganomethoxysiloxanes were obtained with the average composition corresponding to formulas $[RSi(OMe)O]_4$ (**I, V**), $[RSi(OMe)_{4/6}O_{7/6}]_6$ (**II, VI**), $RSi(OMe)_{0.5}O_{1.25}]_8$ (**III, VII**), and $[RSi(OMe)_{0.4}O_{1.3}]_{10}$ (**IV, VIII**). All compounds, except for **VIII**, are readily soluble in organic solvents.



(a) (b) (c) (d) (e)

e

R = Me, Ph; *n* = 1, 2, 3, 4.

Table 2. Parameters of ^{29}Si and ^{1}H NMR spectra of the starting silanes $RSi(OMe)_3$ and their structural fragments in compounds **I–VIII**

Compound/fragment	Chemical shift, ppm
δ_{Si}	
$MeSi(OMe)_3$	–40.2
$–OSiMe(OMe)_2$	–48.2÷–49.7
$(–O)_2SiMe(OMe)$	–55.5÷–59.5
$(–O)_3SiMe$	–63.0÷–68.0
$PhSi(OMe)_3$	–71.4
$–OSiPh(OMe)_2$	–60.5÷–64.0
$(–O)_2SiPh(OMe)$	–66.0÷–72.5
$(–O)_3SiPh$	–76.0÷–81.0
δ_H	
$Si–CH_3$	0.03–0.23
$Si–OCH_3$	3.07–4.18
$Si–C_6H_5$	7.55–8.33

The molecular structure of these compounds, depending on the conditions of synthesis, can be ladder (a), three-dimensional polyhedral cluster having three-, tetra-, penta- and hexasiloxane rings (b–e), and branched dendrimeric (f).

Branched organosilsesquioxanes can also include the fragments of the ladder, three-dimensional, and polycyclic structures [11–17].

The degree of polycondensation (α) calculated by the formula $\alpha = 100\times(2n/3m)$ [n and m are molar amounts of AcOH and $RSi(OMe)_3$, respectively] is 66.67% for compounds **I** and **V**; 77.78% for compounds **II** and **VI**; 83.33% for compounds **III** and **VII**; 86.67% for compounds **IV** and **VIII**. The critical degree of polycondensation for the three-functional monomers at which the gel formation is beginn-ing (α_{cr}) calculated by the formula $\alpha_{cr} = 100\times(1/[f-1])^{0.5}$, must be 70.71%. Therefore, except for **I** and **V**, all other products in the case of branched dendrimeric structure should exist in the form of a cross-linked gel product. High solubility of the obtained products at high degrees of polycondensation allows an assumption that they have polycyclic structure and include branching. This is also confirmed by the ^{29}Si NMR spectroscopy data.

The analysis of the ^{29}Si NMR spectra has shown that the products of partial polycondensation of $RSi(OMe)_3$ contain three types of basic fragments: $–OSiR(OMe)_2$, $(–O)_2SiR(OMe)$, and $(–O)_3SiR$ (Table 2). Compound **I** contains trace amounts of the starting $MeSi(OMe)_3$. The molar fractions of the organic groups (Ph or Me) and methoxy groups bound to the silicon atom, determined from integral intensities of the signals in the ^{1}H NMR spectra, are close to the calculated values (Tables 3, 4).

The absence of the starting monomer in most cases and low content of the $–OSiR(OMe)_2$ fragment (1.5–3 times less than the statistical content) is indicative of their high reactivity in acidolysis. The content of the structural fragments $(–O)_2SiMe(OMe)$ and $(–O)_3SiMe$ is somewhat higher, of $(–O)_2SiPh(OMe)$ substantially higher, and of $(–O)_3SiPh$ lower than calculated. This means that fragment $(–O)_2SiPh(OMe)$ has the lowest reactivity.

As follows from the obtained data, the molecular structure of the products includes a large number of branches due to structural fragments $(–O)SiR(OMe)_2$.

Table 3. Degree of polycondensation and molar fractions[a] of the basic structural fragments in compounds **I–IV**

Comp. no.	α, %	Found (calculated), %					
		$MeSi(OMe)_3$	$–OSiMe(OMe)_2$	$(–O)_2SiMe(OMe)$	$(–O)_3SiMe$	$Si–CH_3$	$Si–OCH_3$
I	66.67	0.11 (3.72)	14.71 (22.22)	54.69 (44.44)	30.48 (29.63)	51.4 (50.0)	48.9 (50.0)
II	77.78	0 (1.11)	4.93 (11.52)	43.67 (40.33)	51.40 (47.05)	62.8 (60.0)	37.2 (40.0)
III	83.33	0 (0.46)	3.11 (6.95)	37.37 (34.73)	59.52 (57.86)	68.4 (66.7)	31.6 (33.3)
IV[b]	86.67	0 (0.24)	– (4.62)	– (30.04)	– (65.10)	– (71.4)	– (28.6)

[a] Calculated from the integral intensities of the signals in the ^{29}Si NMR spectra. [b] Insoluble.

Table 4. Degree of polycondensation and molar fractions[a] of the basic structural fragments in compounds **V–VIII**

Comp. no.	α, %	Found (calculated), %					
		$PhSi(OMe)_3$	$–OSiPh(OMe)_2$	$(–O)_2SiPh(OMe)$	$(–O)_3SiPh$	$Si–C_6H_5$	$Si–OCH_3$
V	66.67	0 (3.72)	17.12 (22.22)	63.43 (44.44)	19.45 (29.63)	61.8 (62.5)	38.2 (37.5)
VI	77.78	0 (1.11)	2.60 (11.52)	69.55 (40.33)	27.85 (47.05)	68.7 (71.4)	31.3 (28.6)
VII	83.33	0 (0.46)	3.62 (6.95)	57.89 (34.73)	38.49 (57.86)	76.3 (76.9)	23.7 (23.1)
VIII	86.67	0 (0.24)	1.77 (4.62)	57.73 (30.04)	40.50 (65.10)	79.8 (80.7)	20.2 (19.4)

[a] Calculated from the integral intensities of the signals in the ^{29}Si NMR spectra.

EXPERIMENTAL

The reaction mixtures were analyzed by GLC method using decane or dodecane as an internal standard on a LKhM-80 chromatograph; column 2 m of diameter 4 mm, stationary phase 10% of polydimethylsiloxane SE-30 on silanized chromosorb W, carrier gas helium. ^1H, ^{29}Si NMR spectroscopic study of the products was performed on a AM 360 Bruker spectrometer with working frequency 360.13 MHz.

Acidolysis of $PhSi(OMe)_3$. A round-bottom four-neck flask of 500 ml capacity equipped with a stirrer, a thermometer, a condenser with calcium chloride drying tube, was charged with 56.99 g of glacial acetic acid, 2.6 g of acetic anhydride, 0.72 g of hydrochloric acid, and 198.37 g of $PhSi(OMe)_3$. After stirring of the reaction mixture at room temperature for 15 min an aliquot was taken for analysis, and the reaction mixture was heated to 90°C. Aliquots were taken intermittently, which were dissolved to 50% in *p*-xylene and the composition was determined by GLC method. After the conversion reached ~100% the distillation of low-boiling products was started by gradual heating of the reaction mass to 140°C.

The acidolysis of $MeSi(OMe)_3$ and the mixture of $MeSi(OMe)_3$ with $PhSi(OMe)_3$ was performed similarly.

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