952 Russian Chemical Bulletin, International Edition, Vol. 52, No. 4, pp. 952—957, April, 2003

Synthesis and study of properties of linear permethylpoly(silane-siloxanes)

A. I. Chernyavskii,★ E. G. Kononova, M. I. Buzin, and N. A. Chernyavskaya

A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,
28 ul Vavilova, 119991 Moscow, Russian Federation.
Fax: +7 (095) 135 5085. E-mail: chern@ineos.ac.ru

Heterofunctional polycondensation of α,ω-dichloropermethyloligosilanes $Cl(Me_2Si)_mCl$ (m = 2—6) with 1,5-dihydroxyhexamethyltrisiloxane was used to synthesize linear permethylpoly(silane-siloxanes) with the regular structure $—[(SiMe_2)_mO(SiMe_2O)_3]_n—$, which are soluble, unlike polydimethylsilane, in common organic solvents. The use of Py instead of Et_3N as an acceptor of HCl results in an increase in the yield, molecular weight, and characteristic viscosity of the copolymers. The molecular weight and viscosity characteristics, oxidative and thermal stabilities, and spectral properties of the synthesized copolymers were studied. The dependence of the oxidative and thermal stabilities of the synthesized copolymers on the number of the $SiMe_2$ units in the oligosilane fragment of the main chain was established.

Key words: α,ω-dichloropermethyloligosilanes, 1,5-dihydroxyhexamethyltrisiloxane, heterofunctional polycondensation, permethylpoly(silane-siloxanes), physicochemical and spectral properties.

Poly(dimethylsilane) is the simplest representative of polysilanes. It finds restricted use, mainly as a ceramics-forming polymer,[1] because of its insolubility and infusibility (the melting point is higher than the temperature of decomposition). Recently, the hydrolytic polycondensation of α,ω-dichloropermethyloligosilanes[2—4] or cationic polymerization of oxacyclosilanes containing one or two oxygen atoms, *viz.*, octamethyltetrasilaoxacyclopentane,[2,5] dodecamethylhexasilaoxacycloheptane,[3] and octamethyl-2,3,5,6-tetrasila-1,4-dioxacyclohexane,[2,5—8] made it possible to synthesize linear permethylpoly(oxasilanes) $—[(Me_2Si)_mO]_n—$ (m = 2—4, 6). These polymers retain the capability of absorbing in the UV region, which is inherent in polysilanes, but unlike poly(dimethylsilane), they are soluble in ethers and chlorinated hydrocarbons.[2] Therefore, these compounds are of interest as potential materials for microlithography, electronics, and some other areas of technology.

It can be expected that permethylpoly(silane-siloxanes) with the regular structure also combine, to some extent, the properties of two classes of organosilicon polymers, *viz.*, polysilanes and polysiloxanes. However, few published data on the synthesis of permethylpoly(silane-siloxane) polymers were available up to presently. For example, the synthesis of such a copolymer by the reaction of 1,3-dichlorohexamethyltrisilane (**1b**) with 1,5-dihydroxyhexamethyltrisiloxane (**2**) was reported.[2] However, no characteristics of this copolymer were presented. The reaction[3] of 1,3-dihydroxytetramethyldisiloxane with 1,6-dichlorododecamethylhexasilane (**1e**) afforded the regular silane-siloxane copolymer with a molecular weight of $\sim 4 \cdot 10^3$. The molecular weight was increased to 10^4 by the homofunctional condensation of this copolymer at the terminal hydroxyl groups in the presence of catalytic amounts of CF_3SO_3H. However, this procedure distorted the regular structure of macromolecules. The heterofunctional polycondensation[9] of 1,2-dibromotetramethyldisilane and dichlorohexasilane **1e** with dihydroxytrisiloxane **2** gave silane-siloxane copolymers. However, their molecular weights and physicochemical characteristics were not reported.

In this work, we used the heterofunctional polycondensation of α,ω-dichloropermethyloligosilanes $Cl(Me_2Si)_mCl$ (**1a—e:** m = 2—6, respectively) with dihydroxytrisiloxane **2** to synthesize permethylpoly(silane-siloxanes) $—[(SiMe_2)_mO(SiMe_2O)_3]_n—$ (**3a—e:** m = 2—6, respectively) with the fixed length of the siloxane fragment and variable number of the $SiMe_2$ units in the oligosilane fragment of the macromolecular chain and studied their physicochemical and spectral properties.

Results and Discussion

Heterofunctional polycondensation (Scheme 1) was carried out in diethyl ether at −5 to −10 °C in the presence of an acceptor of HCl (triethylamine or pyridine). After benzene was added to the reaction mixture, the reaction was continued on heating (60 °C). The total yield of the reaction products was 85—93%. To separate low-molecular oligo(silane-siloxanes) and cyclic products with the mixed silane-siloxane structure, the high-molecular fraction of the copolymers was precipitated

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 4, pp. 903—907, April, 2003.

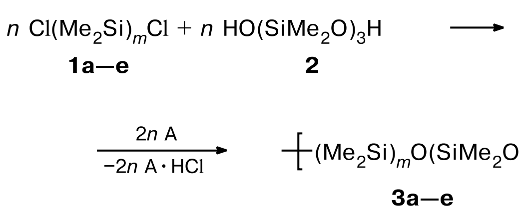
Table 1. Yields and molecular weight and viscous characteristics of poly(silane-siloxanes) **3a—e**

Copolymer	Acceptor of HCl	Yield* (%)	[η] /dL g^{-1}	$M_w \cdot 10^{-3}$	$M_n \cdot 10^{-3}$	M_w/M_n
3a	Et_3N	35.2	0.05	7.6	4.9	1.55
3b	Et_3N	34.4	0.10	11.6	7.7	1.51
3b´	Py	53.3	0.22	43.8	28.9	1.52
3c	Et_3N	34.0	0.06	8.2	4.6	1.78
3c´	Py	57.3	0.11	14.1	8.4	1.68
3d	Et_3N	52.4	0.07	8.6	5.0	1.72
3e	Et_3N	57.9	0.25	31.1	15.3	2.03

* After the copolymer was precipitated.

with methanol from a benzene solution, the yield being 33—57% (Table 1).

Scheme 1



$$n\ Cl(Me_2Si)_mCl + n\ HO(SiMe_2O)_3H \longrightarrow \xrightarrow[-2n\ A\cdot HCl]{2n\ A} -\!\!\left[(Me_2Si)_mO(SiMe_2O)_3\right]_n\!\!-$$

1a—e **2** **3a—e**

A = Et_3N, Py; m = 2—6

Unlike poly(oxasilanes), which are highly crystalline waxy polymers,[2] copolymers **3a—e** containing flexible dimethylsiloxane units in the copolymer chain are viscous colorless liquids. Copolymers **3a—e** are highly soluble in common organic solvents (Et_2O, THF, benzene, toluene, $CHCl_3$, CCl_4, and others). The molecular weight characteristics and characteristic viscosities [η] of the synthesized copolymers are presented in Table 1.

The nature of the HCl acceptor in heterofunctional polycondensation was established to affect the yield, molecular weight, and viscosity of copolymers **3a—e**. We used triethylamine and pyridine as HCl acceptors. It was found that the yield of copolymers was higher (53—57%) in the case of pyridine (*cf.* copolymers **3b** and **3b´**, **3c** and **3c´** in Table 1) than with triethylamine (34%). In addition, when pyridine is used instead of triethylamine, the characteristic viscosity and molecular weight of the copolymers increase by 2—4 times.

Spectroscopic characteristics of copolymers 3a—e. The structures of synthesized copolymers **3a—e** were studied by spectroscopic methods (^{29}Si NMR, IR, UV, and Raman spectroscopies). The ^{29}Si NMR spectra confirm the formation of silane-siloxane copolymers with the regular structure, whose main chain consists of alternating oligosilane and trisiloxane fragments. The parameters of the ^{29}Si NMR spectra for copolymers **3a—e** and (for comparison) above mentioned linear permethylpoly(oxasilanes) $—[(SiMe_2)_mO]_n—$ (**4a—d:** m = 2—4, 6, respectively) are presented in Table 2. The chemical shifts of the Si atoms in the oligosilane fragments are close in the spectra of polymers of both types. For example, for polymers **3a** and **4a** containing two Si atoms in the oligosilane fragment, the signals from the Si_a atoms are observed at δ 0.3—0.8. When the number of consecutively linked Si atoms increase in the macromolecules of polymers **3** and **4**, the signals from the Si_a atoms exhibit a downfield shift and exist at δ ~8—9 for polymers with six Si atoms in the oligosilane fragment (polymers **3e** and **4d**). The signals of the Si_b atom also demonstrate a downfield shift with an increase in the number of the $SiMe_2$ units in the oligosilane fragment (from δ –53.4 for copolymers **3b**, **3b´** and polymer **4b** to δ –45.8 for polymers **3e** and **4d**). At the same time, the chemical shifts of the Si_d and Si_e atoms in the trisiloxane unit of copolymers **3a—e** are virtually independent of the length of the oligosilane fragment and appear at –21.3 and –22.5 ppm, respectively. The chemical shifts of the Si_c atom for polymers **3e** and **4d** are close and lie in the δ region from –40.0 to –40.4 ppm. Thus, the comparative analysis of the ^{29}Si NMR spectra of linear poly(silane-siloxanes) **3** and poly(oxasilanes) **4** shows that the terminal trisiloxane unit linked to the oligosilane fragment in copolymers **3a—e** (instead of the O atom in polymers **4a—d**) has virtually no effect on the chemical shifts of the signals from the Si atoms in the oligosilane fragment of the polymer chain.

The IR spectra of poly(silane-siloxanes) **3a—e** contain intense broad adsorption bands at 1080—1030 cm^{-1} characteristic of stretching vibrations of the Si—O—Si bonds. The Raman spectra of these compounds exhibit lines corresponding to stretching vibrations of the Si—Si bonds at 360—400 cm^{-1} (symmetric vibrations) and 440—500 cm^{-1} (antisymmetric vibrations).

Poly(silane-siloxanes) **3a—e** (similarly to poly(oxasilanes) **4a—d**) retain the capability of absorbing in the UV region, which is inherent in oligo- and polysilanes[1] due to the presence of oligosilane fragments in their polymeric chain. The position of the absorption maximum λ_{max} depends on the number of the $SiMe_2$ groups in the oligosilane fragment of the copolymer. An increase in this number results in the appearance of the bathochromic shift of the absorption maximum (see Table 2). Note that the position of the absorption maximum in the spectra of poly(silane-siloxanes) **3** and poly(oxasilanes) **4** at the same number of the $SiMe_2$ groups in the oligosilane fragment is virtually the same (see Table 2).

Oxidative and thermal stabilities of copolymers 3a—e. Oxidative and thermal stabilities of the copolymers were studied by thermogravimetric (TGA) and differential thermal (DTA) analyses. The oxidative destruction of copolymers **3a—e** in air (Fig. 1) occurs in two stages: at 200—300 °C (I) and 300—560 °C (II). At higher tempera-

Table 2. ^{9}Si NMR and UV spectroscopic data for poly(silane-siloxanes) **3a—e** and poly(oxasilanes) **4a—d**

Polymer[a]	^{29}Si NMR[b]						UV, λ_{max}/nm	Refs.
	δ					$I_{SiSi} : I_{SiO}$[c], found / calculated		
	Si_a	Si_b	Si_c	Si_d	Si_e			
—$(Si_aSiOSi_dOSi_eOSiO)_n$— (**3a**)	0.28	—	—	−21.28	−22.41	1 : 1.41 1 : 1.50	201[d]	[e]
—$(Si_aSi_bSiOSi_dOSi_eOSiO)_n$— (**3b**)	7.39	−53.22	—	−21.27	−22.39	1.17 : 1 1.00 : 1	222[d]	[e]
—$(Si_aSi_bSiOSi_dOSi_eOSiO)_n$— (**3b´**)	7.21	−53.39	—	−21.41	−22.50	1.12 : 1 1.00 : 1	223[d]	[e]
—$(Si_aSi_bSiSiOSi_dOSi_eOSiO)_n$— (**3c**)	8.16	−47.90	—	−21.29	−22.55	1.51 : 1 1.33 : 1	238[d]	[e]
—$(Si_aSi_bSiSiOSi_dOSi_eOSiO)_n$— (**3c´**)	8.18	−47.93	—	−21.19	−22.41	1.45 : 1 1.33 : 1	238[d]	[e]
—$(Si_aSi_bSi_cSiSiOSi_dOSi_eOSiO)_n$— (**3d**)	7.91	−45.95	−42.71	−21.37	−22.63	1.82 : 1 1.67 : 1	258[d]	[e]
—$(Si_aSi_bSi_cSiSiSiOSi_dOSi_eOSiO)_n$— (**3e**)	7.99	−45.81	−40.38	−21.35	−22.65	2.17 : 1 2.00 : 1	265[d]	[e]
—$(Si_aSiO)_n$— (**4a**)	0.80	—	—	—	—	—	201[f]	5
—$(Si_aSi_bSiO)_n$— (**4b**)	8.3	−53.5	—	—	—	—	224[f]	2
—$(Si_aSi_bSiSiO)_n$— (**4c**)	8.92	−48.11	—	—	—	—	241[f]	5
—$(Si_aSi_bSi_cSiSiSiO)_n$— (**4d**)	9.03	−45.67	−40.00	—	—	—	264[f]	3

[a] Methyl groups at the Si atoms are not shown.

[b] In $CDCl_3$.

[c] The ratio of integral intensities of signals from the Si atoms in the oligosilane and trisiloxane fragments of the copolymer.

[d] No solvent.

[e] Data of this work.

[f] In *n*-heptane.

tures (up to 1000 °C) the weight of the samples remains unchanged. A comparison of the TGA curves (see Fig. 1, *a*) shows that at the first stage of destruction the weight loss of the copolymers with the even number of the $SiMe_2$ units in the oligosilane fragment (copolymers **3a,c,e** with $m = 2$, 4, and 6: curves *1*, *3*, and *5*, respectively) is ~9 wt.%, which is almost twofold lower than that for the copolymers with the odd number of the $SiMe_2$ units (copolymers **3b,d** with $m = 3$ and 5: curves *2* and *4*, respectively). Evidently, this results in a greater amount of the coke residue in the copolymers with the even number of the $SiMe_2$ units after the second stage of destruction: 50—60 wt.% compared to 40 wt.% (*cf.* curves *1*, *3*, *5* and *2*, *4* in Fig. 1, *a*). In addition, in the series of copolymers with both even and odd numbers of the $SiMe_2$ units, the stability of the copolymers decreases with an increase in the *m* value. According to their oxidative stability that depends on the number of the $SiMe_2$ units (*m*) in the oligosilane fragment, polymers **3a—e** ($m = 2$—6, respectively) can be arranged in the following order: $2 > 4 > 6 > 3 > 5$.

The DTA curves of copolymers **3a—e** are presented in Fig. 1, *b*. As can be seen, the weight loss in the copolymers is accompanied by exothermic effects, indicating that air oxygen participates in chemical reactions in the copolymers at elevated temperatures. The character of the observed exothermic peaks is almost the same for the copolymers with $m = 2$, 3, and 4 (curves *1—3*, respectively, in Fig. 1, *b*). In the case of the copolymers with $m = 5$, 6 (curves *4* and *5*), an intense exothermic effect appears at 460 °C, which can be a consequence of a decrease in the oxidative stability of the copolymers with an increase in the length of the dimethylsilane fragment to five or six units.

The TGA curves of copolymers **3** in argon are presented in Fig. 2. The main weight loss of the copolymers occurs in the temperature interval from 350 to 550 °C, and at higher temperatures the weight of the samples remains virtually unchanged. Note that the thermolysis of copolymers **3** exhibits the same regularities that their oxidative destruction: a decrease in the thermal stability of the copolymers with an increase in the number of the $SiMe_2$ units in the polymeric chain and a decrease in the thermal stability on going from the copolymers with the even *m* number to those with the odd *m* number (see Fig. 2). Similar effects have been observed previously[4] for thermolysis of poly(oxasilanes) **4a—c**.

Evidently, the processes that occur during thermolysis of copolymers **3** are rather complicated. Using copolymer **3c** as an example, we compared the IR spectrum (Fig. 3)

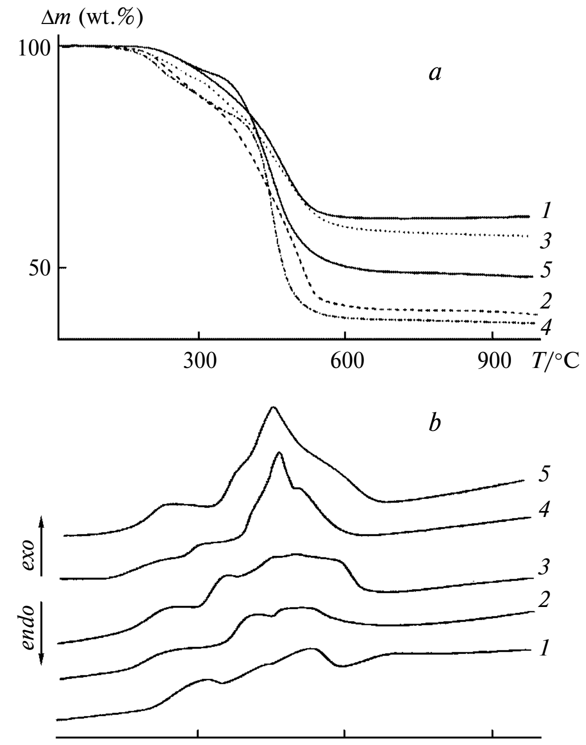


Fig. 1. TGA (*a*) and DTA (*b*) curves for poly(silane-siloxanes) **3a—e** in air (*1—5*, respectively); Δ*m* is the weight of the residue.

of the initial copolymer and the IR spectra obtained after heating this copolymer in Ar at 450 and 1000 °C and made several conclusions about chemical transformations that occur in the oligosilane fragment of copolymers **3** during their thermolysis. The main weight loss of copolymer **3c** upon its thermolysis (see Fig. 2) observed in the 350—550 °C temperature interval along with the destruction of the copolymer is accompanied by its cross-linking and transformation into the insoluble state. This is likely related to the elimination of the Me groups from the Si atoms in the polymeric chain and rearrangement of the framework of the polymeric chain itself, which is indicated, on the one hand, by a decrease in the intensity of absorption bands of the C—H and Si—C bonds and Me group and, on the other hand, by the appearance of absorption bands of stretching vibrations of the Si—H (at 2110 cm^{-1}) and Si—CH_2—Si* bonds (at 1040—1080 and 800 cm^{-1}) in the IR spectrum of copolymer **3c** after it was heated at 450 °C for 0.5 h. The formation of the Si—H and Si—CH_2—Si bonds in the polymeric chain is obviously related to the fact that the Yajima rearrangement[10] occurs in the oligosilane fragment at 450 °C (Scheme 2).

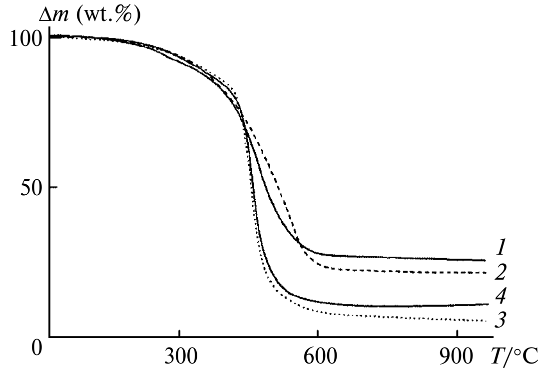


Fig. 2. TGA curves for poly(silane-siloxanes) **3a,c—e** in argon (*1—4*, respectively); Δ*m* is the weight of the residue.

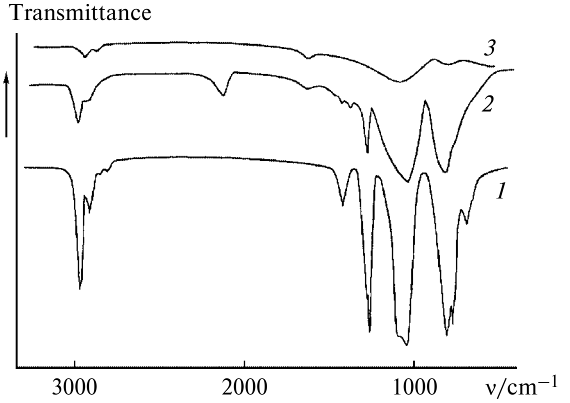
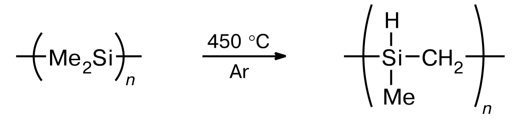


Fig. 3. IR spectra of poly(silane-siloxane) **3c** before (*1*) and after heating at 450 (*2*) and 1000 °C (*3*).

Scheme 2



$$\left(\mathrm{Me_2Si}\right)_n \xrightarrow[\text{Ar}]{450\ ^\circ\text{C}} \left(\overset{\mathrm{H}}{\underset{\mathrm{Me}}{\mathrm{Si}}}-\mathrm{CH_2}\right)_n$$

Being heated at 1000 °C for 2 h, copolymer **3c** loses the most part of Me groups and is transformed into a silicon-hydroxycarbide material: the IR spectrum (see Fig. 3) contains absorption bands of the residual Me groups at 2960 and 2900 cm^{-1}, a broad band at 1070 cm^{-1}, which is the sum of absorption bands corresponding to vibrations of the Si—CH_2—Si and Si—O—Si bonds, and an absorption band at 800 cm^{-1}, while the spectrum does not contain the absorption band of the Si—H bonds at 2100 cm^{-1}.

Thus, the heterofunctional polycondensation of α,ω-dichloropermethyloligosilanes with dihydroxytrisiloxane afforded permethylpoly(silane-siloxanes) with the regular structure, which are of interest as potential polymeric photoinitiators of structurization of organosilicon rubbers, cross-linking agents of composite materials, and

---

* The band of vibrations of the Si—CH_2—Si bonds overlaps with the bands of vibrations of the Si—O—Si and Si—Me bonds, which is indicated by their significant broadening compared to the spectrum of the initial copolymer.

pre-ceramic polymers for preparation of Si—O—C-ceramic materials.

Experimental

^{29}Si NMR spectra were recorded on a Bruker WP-400 SY spectrometer (79.46 MHz) using Me_4Si as internal standard. IR spectra in a region of 400—3700 cm^{-1} and UV spectra at 200—335 nm were recorded on Specord M-82 and Specord M-40 spectrophotometers, respectively. Raman spectra in the region from 200 to 4000 cm^{-1} were obtained on a T-64000 spectrometer (Jobin Yvon) equipped with a CCD detector (the wavelength of the exciting line was 514.5 nm).

The characteristic viscosity [η] of copolymers **3a—e** was determined in benzene at 25 °C using an Ubbelohde viscometer with the hanging level. Molecular weight characteristics of copolymers **3a—e** were determined by gel chromatography on a Bruker LC21 liquid chromatograph (refractometer as detector, columns packed with polystyrene-divinylbenzene gel, toluene as eluent, calibration by the polystyrene standard).

Thermal tests of copolymers **3a—e** were carried out in air and argon in the 20—1000 °C temperature interval (rate of temperature elevation 10 °C min^{-1}, weight of samples 60—80 mg) on a Q-1500D derivatograph.

Dichlorooligosilanes **1a—e** were synthesized using a previously described procedure.[11] 1,5-Dihydroxytrisiloxane (**2**) was synthesized using a known procedure.[12] Diethyl ether and benzene were dehydrated by refluxing followed by distillation in an N_2 flow above metallic sodium in the presence of benzophenone, and Et_3N and Py were distilled above NaOH granules in an N_2 flow. All reactions were carried out in an atmosphere of dry argon.

Permethylpoly(disilane-trisiloxane) — copolymer 3a. A mixture of dihydroxytrisiloxane **2** (1.44 g, 6 mmol) and Et_3N (1.21 g, 12 mmol) in anhydrous diethyl ether (10 mL) was added dropwise at –5 to –10 °C with vigorous stirring by a solution of dichlorodisilane **1a** (1.12 g, 6 mmol) in anhydrous diethyl ether (5 mL). The reaction mixture was stirred for 2 h at –5 to –10 °C and for 15 h at ~20 °C and then added by anhydrous benzene (20 mL). The resulting mixture was brought to boiling and stirred for 10 h. A precipitate of $Et_3N \cdot HCl$ was filtered off, and the filtrate was washed with water to the neutral reaction and dried with Na_2SO_4. The copolymer was isolated by precipitation with a threefold excess of MeOH and dried in a desiccator (60 °C) to a constant weight. Copolymer **3a** (0.75 g) was obtained. Found (%): C, 33.97; H, 8.78; Si, 39.12. $C_{10}H_{30}O_4Si_5$. Calculated (%): C, 33.86; H, 8.52; Si, 39.58. IR (KBr), ν/cm^{-1}: 2958, 2902 (ν(CH)); 1410, 1260 (δ(CH_3)); 1085, 1028 (ν(SiOSi)); 802, 694, 662 (ν(SiC)). Raman, Δν/cm^{-1}: 2966, 2906 (ν(CH)); 1407, 1262, 1253, 861 (ρ(CH_3)); 787, 768, 709, 687, 661 (ν(SiC)); 492, 426, 378 (ν(SiSi)).

Permethylpoly(trisilane-trisiloxane) — copolymer 3b. Similarly to the synthesis of copolymer **3a**, the reaction of dihydroxytrisiloxane **2** (1.20 g, 5 mmol), dichlorotrisilane **1b** (1.23 g, 5 mmol), and Et_3N (1.01 g, 10 mmol) afforded copolymer **3b** (0.71 g). Found (%): C, 35.25; H, 8.97; Si, 40.26. $C_{12}H_{36}O_4Si_6$. Calculated (%): C, 34.90; H, 8.79; Si, 40.81. IR (KBr), ν/cm^{-1}: 2958, 2891 (ν(CH)); 1408, 1260 (δ(CH_3)); 1074, 1028 (ν(SiOSi)); 802, 774, 689, 660, 643 (ν(SiC)). Raman, Δν/cm^{-1}: 2963, 2900 (ν(CH)); 1404, 1263, 1253, 1246, 854 (ρ(CH_3)); 790, 760, 707, 685, 662, 640 (ν(SiC)); 502, 396 (ν(SiSi)).

Permethylpoly(trisilane-trisiloxane) — copolymer 3b´. Similarly to the synthesis of copolymer **3a**, the reaction of dihydroxytrisiloxane **2** (1.20 g, 5 mmol), dichlorotrisilane **1b** (1.23 g, 5 mmol), and Py (0.79 g, 10 mmol) gave copolymer **3b´** (1.10 g). Found (%): C, 34.65; H, 8.67; Si, 40.35. $C_{12}H_{36}O_4Si_6$. Calculated (%): C, 34.90; H, 8.79; Si, 40.81. IR (KBr), ν/cm^{-1}: 2958, 2891 (ν(CH)); 1408, 1260 (δ(CH_3)); 1074, 1028 (ν(SiOSi)); 802, 774, 689, 660 (ν(SiC)). Raman, Δν/cm^{-1}: 2961, 2902 (ν(CH)); 1405, 1260, 1251, 851 (ρ(CH_3)); 787, 763, 738, 704, 683, 660, 641 (ν(SiC)); 497, 396 (ν(SiSi)).

Permethylpoly(tetrasilane-trisiloxane) — copolymer 3c. Similarly to the synthesis of copolymer **3a**, the reaction of dihydroxytrisiloxane **2** (1.20 g, 5 mmol), dichlorotetrasilane **1c** (1.52 g, 5 mmol), and Et_3N (1.01 g, 10 mmol) afforded copolymer **3c** (0.80 g). Found (%): C, 35.98; H, 9.27; Si, 41.39. $C_{14}H_{42}O_4Si_7$. Calculated (%): C, 35.70; H, 8.99; Si, 41.73. IR (KBr), ν/cm^{-1}: 2958, 2891 (ν(CH)); 1408, 1260 (δ(CH_3)); 1085, 1034 (ν(SiOSi)); 802, 768, 689 (ν(SiC)). Raman, Δν/cm^{-1}: 2960, 2895 (ν(CH)); 1406, 1252, 1243, 850 (ρ(CH_3)); 788, 764, 741, 706, 684, 661, 647 (ν(SiC)); 503, 470, 378 (ν(SiSi)).

Permethylpoly(tetrasilane-trisiloxane) — copolymer 3c´. Similarly to the synthesis of copolymer **3a**, the reaction of dihydroxytrisiloxane **2** (1.20 g, 5 mmol), dichlorotetrasilane **1c** (1.52 g, 5 mmol), and Py (0.79 g, 10 mmol) afforded copolymer **3c´** (1.35 g). Found (%): C, 35.84; H, 9.13; Si, 41.11. $C_{14}H_{42}O_4Si_7$. Calculated (%): C, 35.70; H, 8.99; Si, 41.73. IR (KBr), ν/cm^{-1}: 2958, 2891 (ν(CH)); 1408, 1260 (δ(CH_3)); 1085, 1040 (ν(SiOSi)); 808, 774, 689 (ν(SiC)). Raman, Δν/cm^{-1}: 2961, 2895 (ν(CH)); 1408, 1252, 854 (ρ(CH_3)); 786, 763, 705, 686, 662, 650 (ν(SiC)); 503, 471, 378 (ν(SiSi)).

Permethylpoly(pentasilane-trisiloxane) — copolymer 3d. Similarly to the synthesis of copolymer **3a**, the reaction of dihydroxytrisiloxane **2** (0.96 g, 4 mmol), dichloropentasilane **1c** (1.45 g, 4 mmol), and Et_3N (0.81 g, 8 mmol) afforded copolymer **3d** (1.11 g). Found (%): C, 36.02; H, 9.03; Si, 41.92. $C_{16}H_{48}O_4Si_8$. Calculated (%): C, 36.31; H, 9.14; Si, 42.46. IR (KBr), ν/cm^{-1}: 2958, 2891 (ν(CH)); 1408, 1260 (δ(CH_3)); 1070, 1034 (ν(SiOSi)); 802, 768, 689, 660, 638 (ν(SiC)). Raman, Δν/cm^{-1}: 2958, 2893 (ν(CH)); 1405, 1262, 1252, 1238, 850 (ρ(CH_3)); 787, 761, 738, 704, 684, 661 (ν(SiC)); 502, 478, 441, 366 (ν(SiSi)).

Permethylpoly(hexasilane-trisiloxane) — copolymer 3e. Similarly to the synthesis of copolymer **3a**, the reaction of dihydroxytrisiloxane **2** (0.72 g, 3 mmol), dichlorohexasilane **1a** (1.26 g, 3 mmol), and Et_3N (0.61 g, 6 mmol) afforded copolymer **3** (1.02 g). Found (%): C, 36.44; H, 9.19; Si, 42.71. $C_{18}H_{54}O_4Si_9$. Calculated (%): C, 36.81; H, 9.27; Si, 43.03. IR (KBr), ν/cm^{-1}: 2958, 2891 (ν(CH)); 1408, 1260 (δ(CH_3)); 1085, 1034 (ν(SiOSi)); 802, 762, 734, 689, 660, 638 (ν(SiC)). Raman, Δν/cm^{-1}: 2955, 2894 (ν(CH)); 1404, 1260, 1251, 1236, 848 (ρ(CH_3)); 761, 740, 706, 682, 661 (ν(SiC)); 502, 480, 454, 416, 363 (ν(SiSi)).

The authors thank E. V. Vorontsov and L. A. Mikhalitsyn for recording ^{29}Si NMR and Raman spectra, respectively.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 00-03-33189).

References

1. (a) R. West, *J. Organomet. Chem.*, 1986, **300**, 327; (b) R. D. Miller and J. Michl, *Chem. Rev.*, 1989, **89**, 1359; (c) R. West, in *Comprehensive Organometallic Chemistry*, Eds. G. Wilkinson, A. G. F. Stone, and E. W. Abel, Elsevier, Amsterdam, 1995, **2**, 95.
2. J. Chojnowski, J. Kurjata, S. Rubinsztajn, and M. Ścibiorek, in *Frontiers of Organosilicon Chemistry*, Eds. A. R. Bassindale and P. P. Gaspar, The Royal Society of Chemistry, Cambridge, 1991, 70.
3. J. Chojnowski, W. Fortuniak, N. Gladkova, M. Pluta, M. Ścibiorek, and B. Zavin, *J. Inorg. Organomet. Polym.*, 1995, **5**, 7.
4. J. Kurjata, M. Ścibiorek, W. Fortuniak, and J. Chojnowski, *Organometallics*, 1999, **18**, 1259.
5. J. Chojnowski, J. Kurjata, and S. Rubinsztajn, *Makromol. Chem., Rapid Commun.*, 1988, **9**, 469.
6. J. Kurjata and J. Chojnowski, *Makromol. Chem.*, 1993, **194**, 3271.
7. J. Chojnowski and J. Kurjata, *Macromolecules*, 1994, **27**, 2302.
8. J. Chojnowski, J. Kurjata, S. Rubinsztajn, M. Ścibiorek, and M. Zeldin, *J. Inorg. Organomet. Polym.*, 1992, **2**, 387.
9. A. I. Chernyavskii and B. G. Zavin, *Izv. Akad. Nauk, Ser. Khim.*, 1997, 1513 [*Russ. Chem. Bull.*, 1997, **46**, 1449 (Engl. Transl.)].
10. (a) S. Yajima, J. Hayashi, and M. Omori, *Chem. Lett.*, 1975, 931; (b) S. Yajima, K. Okamura, and J. Hayashi, *Chem. Lett.*, 1975, 1209.
11. A. I. Chernyavskii and N. A. Chernyavskaya, *Izv. Akad. Nauk, Ser. Khim.*, 2002, 1607 [*Russ. Chem. Bull., Int. Ed.*, 2002, **51**, 1751].
12. K. A. Andrianov, V. V. Astakhin, and V. K. Pyzhov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1962, 2243 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1962, **11** (Engl. Transl.)].

Received March 20, 2002;
in revised form June 28, 2002