Russian Chemical Bulletin, Vol. 46, No. 8, August, 1997

Synthesis of α,ω-dihalopermethyloligosilanes and silane-siloxane copolymers

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α,ω-Dibromopermethyloligosilanes, $Br(SiMe_2)_nBr$ (n = 2—4, 6), were prepared by the reaction of dodecamethylcyclohexasilane with bromine. The reaction of $(Me_2Si)_6$ with MCl_4 (M = Sn, Ti) proceeds with the cleavage of Si—Si- and Si—C-bonds with the formation of α,ω-dichloropermethyloligosilanes, $Cl(SiMe_2)_nCl$ (n = 2—4, 6), and chloro derivatives of cyclohexasilane, $Cl_mSi_6Me_{12-m}$ (m = 1, 2). Silane-siloxane copolymers of regular structure were obtained by heterofunctional copolycondensation of α,ω-dihalopermethyloligosilanes with 1,5-dihydroxyhexamethyltrisiloxane.

Key words: dodecamethylcyclohexasilane, α,ω-dihalopermethyloligosilanes; bromine, tin(IV) and titanium(IV) chlorides; silane-siloxane copolymers.

Dihalosubstituted oligosilanes $Hal(SiR_2)_nHal$ ($n \geq 2$) (**1**) and their derivatives are ideal compounds for the synthesis of different copolymers containing oligosilane moieties. Nowadays, the most widely used method for the synthesis of bifunctional oligosilanes **1** is the reaction of oligocyclosilanes $(R_2Si)_n$ with various halogenating agents. For example, α,ω-dichloropermethyloligosilanes (**1a**) with $n \geq 2$ are synthesized by the reaction of dodecamethylcyclohexasilane $(Me_2Si)_6$ (**2**) with chlorinating agents such as molecular chlorine,[1,2] thionyl chloride,[3] phosphorus pentachloride,[4] and chlorides of metals[5] of III—V groups of the Periodic Table. At the same time, the methods for the synthesis of α,ω-dibromooligosilanes (**1b**) with $n \geq 2$ are studied insufficiently. Compounds **1b** with n = 2—4, 6 were synthesized[6] for the first time by passing Br_2 vapor through a solution of cyclosilane **2** in hexane at 0 °C.

The purpose of this work was to study in detail the synthesis of cyclosilane **2** and its reaction with Br_2, as well as with tin(IV) and titanium(IV) chlorides. In addition, the synthesis of silane-siloxane copolymers by heterofunctional polycondensation of the resulting bifunctional oligosilanes **1a** and **1b** with 1,5-dihydroxyhexamethyltrisiloxane (**3**) was performed.

Results and Discussion

Reaction of dichlorodimethylsilane (4) with lithium. It is known[7] that the reaction of dichlorodimethylsilane (**4**) with a small excess of Li in THF at 0 °C affords cyclosilane **2** in a high yield (90%). With the molar ratio of dichlorodimethylsilane **4** and Li of 1 : 2, cyclosilanes $(Me_2Si)_n$ with n = 5, 7—9 and polydimethylsilane (**5**) are formed in yields up to 45% in addition to cyclosilane **2**. We carried out a series of syntheses of cyclosilane **2** (the starting compound for the preparation of dihalooligosilanes **1**) by the reaction of dichlorosilane **4** with Li and the results obtained differed from those given above (Table 1). Even at 50% excess of the alkali metal, a significant amount of polysilane **5** and a number of cyclosilanes with n = 5, 7—10, along with cyclosilane **2**, were present in the reaction products.

As can be concluded from the literature data, these facts indicate that the amount of Li in the reaction system was insufficient. Since metallic Li practically always contains an admixture of Na, which is known[8] to have a substantial effect on the composition and yield of the products of the reaction of Li with chlorosilanes, we assumed that the deviation of the reaction from the expected course resulted from an increased amount of Na in Li. In fact, ~9.5% of Na was present in the Li used by us. First, such a high content of Na in Li violates the necessary ratio between dichlorosilane **4** and Li and, second, it promotes the increase in the yield of polysilane **5**, since Na, unlike Li, readily reacts with dichlorosilanes to give polysilanes.[9] The results obtained also indicate (see Table 1, entries *1*—*5*) that the duration of the addition of dichlorosilane **4** and the duration of subsequent keeping of the reaction mixture have a noticeable effect on the composition of the reaction products. For example, rapid addition of dichlorosilane **4** increases the yield of polymer **5** and the relative content of cyclosilane **2** in the cyclooligosilane mixture (*cf.* entries *2* and *3*, and *4* and *5* in Table 1). On the other hand, as mentioned earlier,[10] longer stirring of the reaction mixture after the addition of dichlorosilane **4**

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 8, pp. 1513—1517, August, 1997.

1066-5285/97/4608-1449 $18.00

Table 1. Effect of conditions of the reaction of dichlorosilane **4** with Li on the composition of the reaction products

Entry	Ratio **4** : Li	Time/h		Product composition (%)		Total yield (%)	$(Me_2Si)_n/\sum_{n=5}^{10}(Me_2Si)_n$ (%) at different n					
		addition of **4**	stirring	$(Me_2Si)_n$	5		5	6	7	8	9	10
1	1 : 2.3[a]	0.5	10	26.4	73.6	78	5.4	71.1	6.6	14.4	2.7	—
2	1 : 2.3[a]	1.5	7	33.5	66.5	82	2.3	64.6	8.4	20.2	4.4	0.1
3	1 : 2.3[a]	2.5	2.5	47.2	52.8	84	2.1	32.8	15.5	41.0	8.0	0.5
4	1 : 3.0[a]	1.5	9	38.3	61.7	82	2.2	87.6	4.4	5.8	—	—
5	1 : 3.0[a]	3.0	9	49.4	50.6	83	3.4	77.7	6.5	9.7	2.7	—
6	1 : 2.0[b]	1.0	10	54.3	45.7	86	12.1	33.4	14.2	31.7	8.6	—
7	1 : 2.3[b]	1.0	10	100	—	89	1.1	98.9	—	—	—	—

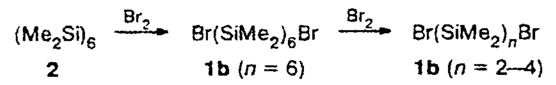
Content of Na in Li: [a] 9.5%; [b] <1%.

with excess alkali metal favors an increase in the content of cyclohexasilane **2** as compared with other cyclooligosilanes (entries *2* and *3* in Table 1). When Li containing <1 % of Na was used in the reaction, the results obtained were close to those published previously (entries *6* and *7* in Table 1).[7,11]

Cyclosilane **2** was also synthesized in this work in 75% yield by the modified procedure from Ref. 10, involving depolymerization of the resulting polysilane **5** with a K/Na alloy in the presence of catalytic amount of naphthalene (see Experimental).

Synthesis of α,ω-dibromopermethyloligosilanes 1b by the reaction of cyclosilane 2 with Br_2. The reaction of cyclosilane **2** with liquid Br_2 (molar ratio 1 : 1) was carried out in petroleum ether at −10 °C. A GLC analysis showed that, along with unreacted cyclosilane **2** (45%) and α,ω-dibromooligosilane **1b** with $n = 6$ (15%), the lower homologs of oligosilane **1b** with $n = 4$ (15%), $n = 3$ (10%), and $n = 2$ (15%) were present in the reaction mixture, indicating that Br_2 was consumed not only for opening of the cycle in cyclosilane **2** but also in a reaction with the initially formed oligosilane **1b** with $n = 6$ (Scheme 1).

Scheme 1



$$\underset{\mathbf{2}}{(Me_2Si)_6} \xrightarrow{Br_2} \underset{\mathbf{1b}\ (n\,=\,6)}{Br(SiMe_2)_6Br} \xrightarrow{Br_2} \underset{\mathbf{1b}\ (n\,=\,2-4)}{Br(SiMe_2)_nBr}$$

We studied the influence of the amount of Br_2 added on the composition of the reaction products. The reaction was carried out until complete disapearance of cyclosilane **2**; the reaction course was monitored by GLC (Fig. 1). The absence of oligosilane **1b** with $n = 5$ in the reaction products indicates that the probability of cleavage of different Si—Si bonds in 1,6-dibromohexasilane is different, since otherwise dibromooligosilanes **1b** with $n = 5$, 4, 3 would be obtained from oligosilane **1b** with $n = 6$ in equal amounts. At the same time, oligosilanes **1b** with $n = 4$ and 3 are formed rapidly and approximately in equimolar amounts, which indicates that the cleavage of the $—SiMe_2—SiMe_2Br$ bond in oligosilane **1b** with $n = 6$ in the reaction with Br_2 occurs substantially more slowly than the cleavage of the $—SiMe_2—SiMe_2—$ bond. This is also confirmed by the fact that the main reaction product after consumption of the initial cyclosilane **2** is dibromodisilane **1b** with $n = 2$ (yield 76% with respect to the compound **2** taken into the reaction), in which the Si—Si bond is rather resistant to the action of bromine, which, in turn, is proven by the absence of dimethyldibromosilane in the reaction products. Thus, according to the rate of the reaction with Br_2 depending on the number of the $SiMe_2$ groups, bromooligosilanes **1b** ($n = 2$—4, 6) can be arranged in the following series: $n = 6 \geq n = 4 \geq n = 3 >> n = 2$.

Similar results have been obtained earlier[2] in a study of the reaction of cyclosilane **2** with Cl_2.

Synthesis of α,ω-dichloropermethyloligosilanes 1a by the reaction of cyclosilane 2 with MCl_4 (M = Sn, Ti). As a continuation of a number of previous works,[5,12,13] in which chlorides of metals of III—IV groups of the Periodic Table were used for the replacement of alkyl substituents in cyclic and linear oligosilanes with chlorine atoms, we studied the reaction of cyclosilane **2** with $SnCl_4$ and $TiCl_4$. It has been shown previously[5] that the reaction of cyclosilane **2** with $SnCl_4$ in CH_2Cl_2 gives not

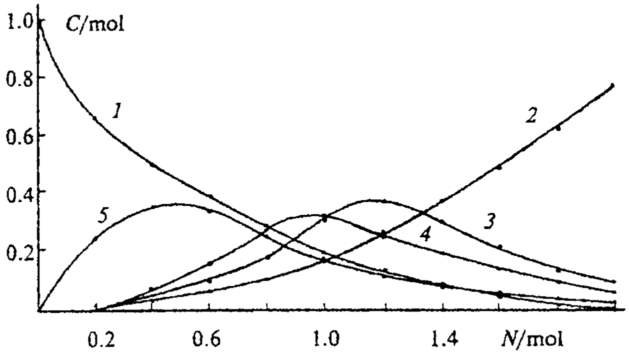


Fig. 1. Dependence of the degree of conversion of cyclosilane **2** and composition of the products of the reaction of **2** with Br_2 (*C*) on the amount (*N*) of Br_2 added: *1* — **2**; *2*—*5* — **1b**, $n = 2$, 3, 4, 6, respectively.

Table 2. Conditions and composition of the products of the reaction of cyclosilane **2** with MCl_4

MCl_4	**2** : MCl_4 ratio	Reaction time /h	Product composition (%)							
			2	$Cl(SiMe_2)_nCl$ at different n				$Cl_mSi_6Me_{12-m}$ at different m	
				2	3	4	6	1	2
$SnCl_4$	1 : 1	30	6.4	9.1	26.0	15.7	34.8	3.5	1.3
$TiCl_4$	1 : 0.5	100	33.2	2.1	3.7	7.5	51.1	2.4	—

only dichlorohexasilane **1a** (n = 6) as a main product, but also its lower homologs (n = 2—4) as a result of the cleavage of its Si—Si bonds. When studying this reaction, we found (Table 2) that not only cleavage of the Si—Si bonds in cyclosilane **2** and dichlorooligosilane **1a** (n = 6), but also cleavage of the Si—Me bonds in the starting cyclosilane **2** occur upon the reaction of cyclosilane **2** with $SnCl_4$ to form its mono and dichloro derivatives $Cl_mSi_6Me_{12-m}$ (**2a**) (Scheme 2).

Scheme 2

$$\mathbf{2} + SnCl_4 \longrightarrow \underset{\mathbf{1a}}{Cl(SiMe_2)_nCl} + \underset{\mathbf{2a}}{Cl_mSi_6Me_{12-m}}$$

n = 2—4, 6; m = 1, 2

The reaction of cyclosilane **2** with $TiCl_4$ was studied under similar conditions. According to the GLC data (Fig. 2), the reaction of $TiCl_4$ with cyclosilane **2** is more complicated than described in the previous work.[5] According to the previous data, dichlorooligosilane **1a** (n = 6) in the only reaction product, and the ratio between **1a** and the unreacted cyclosilane **2** is ~1 : 1. We have found that in addition to the main product of the reaction of cyclosilane **2** with $TiCl_4$, dichlorooligosilane **1a** with n = 6, its homologs, dichlorooligosilanes **1a** with n = 2—4, and monochlorosubstituted cyclosilane **2a** are formed, *i.e.*, similarly to the reaction with $SnCl_4$, not only cleavage of the Si—Si bonds in cyclosilane **2** and dichlorooligosilane **1a** (n = 6) but also replacement of the methyl group in cyclosilane **2** with a chlorine atom take place. However, the content of dichlorooligosilanes **1a** (n = 2—4) and monosubstituted cyclosilane **2a** in the reaction products is much lower than that in the reaction with $SnCl_4$ (see Table 2). It should also be noted that the reaction of cyclosilane **2** with $TiCl_4$ occurs at a substantially lower rate but more selectively than that with $SnCl_4$. This allows one to monitor reliably the course of the reaction and to find its optimal conditions in order to reach the highest yield of the target product.

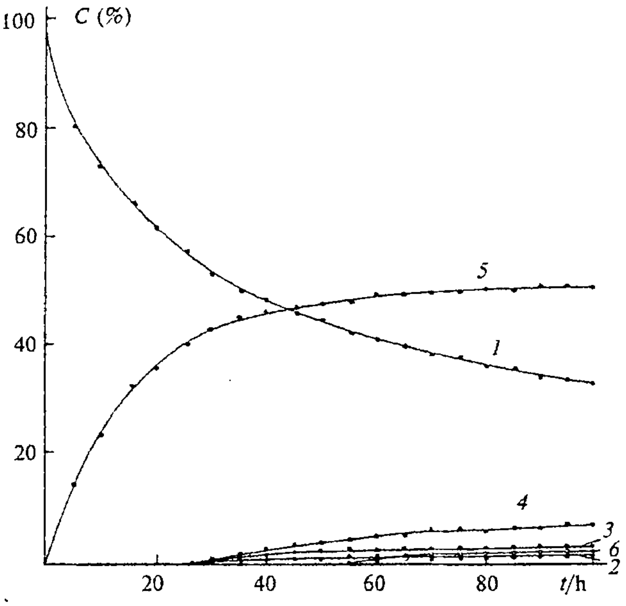


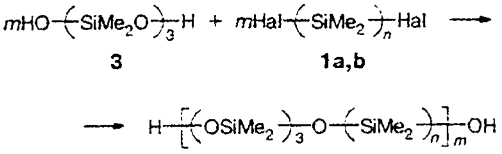
Fig. 2. Dependence of the composition of the reaction mixture on the time of the reaction of cyclosilane **2** with $TiCl_4$: *1* — **2**; *2*—*5* — **1a**, n = 2, 3, 4, 6, respectively; *6* — **2a**, m = 1.

Synthesis of silane-siloxane copolymers. One of the methods most widely used in polymer chemistry for the preparation of copolymers with regular structure is heterofunctional polycondensation. However, at present there is a lack of literature data on the synthesis of silane-siloxane copolymers by this method. The synthesis of this kind of copolymers by the reaction of trisiloxanediol **3** with dichlorooligosilane **1a** (n = 3) has been reported[14] but no characteristics of the copolymer obtained have been given. Recently,[15] a silane-siloxane copolymer of regular structure with a molecular mass of $\sim 4 \cdot 10^3$ was synthesized by the reaction of 1,3-dihydroxytetramethyldisiloxane with dichlorooligosilane **1a** (n = 6). Homofunctional polycondensation of the resulting copolymer at the terminal hydroxy groups in the presence of a catalytic amount of CF_3SO_3H resulted in an increase in the molecular mass of the copolymer to 10^4; however, in this case the regularity of the macromolecular structure was violated.

Heterofunctional polycondensation of trisiloxanediol **3** and difunctional oligosilanes **1** synthesized (Scheme 3) was studied in the present work.

The reaction was carried out in ether at −5 to −10 °C in the presence of Et_3N as an HHal acceptor. The yields of copolymers **6a,b** were 90—95%. The copolymers are viscous light yellow liquids readily soluble in common organic solvents. The molecular masses (determined from the ^{29}Si NMR spectra by the ratio of

Scheme 3



1a: Hal = Cl, n = 6
1b: Hal = Br, n = 2

integral intensities of the signals of the terminal silanol groups and oligosilane fragments) were ~5200 ($m \approx 9$) for copolymer **6a** and ~3500 ($m \approx 10$) for copolymer **6b**. The ^{29}Si NMR spectra (see Experimental) confirm the formation of silane-siloxane copolymers of regular structure. After thermal homocondensation of the synthesized copolymers at the terminal OH-groups, IR and NMR spectroscopy did not detect any remaining terminal groups, but in this case the copolymers (**6'a,b**) retained a regular structure (according to the ^{29}Si NMR spectroscopy data). Molecular masses and some physicochemical characteristics of the silane-siloxane copolymers synthesized will be reported elsewhere.

Thus, heterofuctional copolycondensation of α,ω-dihydroxypermethyloligosiloxanes and α,ω-dihalopermethyloligosilanes afforded the regular silane-siloxane copolymers.

Experimental

GLC analysis was carried out on a LKhM-8MD chromatograph (stainless steel 0.3×100 cm column, 5% SE-30 on Chromaton N-AW-DMCS; katharometer as the detector, the temperature was programmed to rise from 30 to 300 °C at a rate of 12 deg min^{-1}; helium was the carrier gas).

^{1}H and ^{29}Si NMR spectra were recorded on a Bruker WP-200SY spectrometer with $SiMe_4$ as the internal standard.

Chloro-substituted cyclosilanes **2a** (m = 1, 2) were identified by comparison with standard samples synthesized by the known procedures.[16,17]

All reactions were carried out in an atmosphere of dry argon.

Synthesis of dodecamethylcyclohexasilane 2. *A*. The reaction of dichlorosilane 4 with Li. A solution of dichlorosilane **4** (13 g, 0.1 mol) in dry THF (40 mL) was added dropwise to a suspension of finely cut Li (Na content ~9.5%) (1.6 g, 0.23 g-at) in dry THF (150 mL) over a period of 1.5 h. The reaction mixture was stirred at 0 °C for 6 h and at ~20 °C for 1 h. Hexane (80 mL) was added to the mixture, the precipitate was filtered off, and the solvents were distilled off. Crystallization of the residue from EtOH gave 1.4 g (28%) of a mixture of cyclosilanes $(Me_2Si)_m$ (m = 5—10). ^{29}Si NMR (CCl_4), δ: −42.06 (m = 5); −41.82 (m = 6); −41.64 (m = 7); −39.85 (m = 8); −38.43 (m = 9); −37.61 (m = 10).

After filtration of the reaction mixture, the residue was consecutively washed with THF, EtOH, and water, and the insoluble residue was washed with an EtOH—H_2O (1 : 1) mixture until negative reaction for chloride ion and dried in a vacuum oven (75 °C) to yield 2.6 g (53.2%) of polysilane **5** as a white powder. UV, λ_{max}/nm: 344. IR (KBr), ν/cm^{-1}: 2990, 2940 (C—H); 1245, 835 (Si—Me).

Entries *1* and *3—7* (see Table 1) were carried out in a similar way.

***B*. Depolymerization of polydimethylsilane 5.** A mixture of a K/Na alloy (0.1 g, 0.004 g-at. Na and 0.45 g, 0.012 g-at. K) and naphthalene (0.06 g, 1.2 mmol) in dry THF (80 mL) was stirred until the dark green color persisted, and then polysilane **5** (8.5 g, 0.15 mol) was added. The reaction mixture was heated to boiling and kept for 1 h with vigorous stirring. Then EtOH (5 mL) was carefully added dropwise to the cooled reaction mixture, and after that water (5 mL) was added. The unreacted polymer (1.2 g) was filtered off, the solvent was evaporated, and hexane (30 mL) was added to the residue. The solution was washed with water until neutral reaction and dried with Na_2SO_4. The solvent was removed on a rotary evaporator, and the residue was crystallized from an EtOH—THF (5 : 1) mixture to yield 6.5 g (75%) of cyclosilane **2**, m.p. 252—253 °C. ^{29}Si NMR (CCl_4), δ: −41.84.

Reaction of cyclosilane 2 with Br_2. A solution of Br_2 (1.08 *M*) in petroleum ether was added dropwise with vigorous stirring to a solution of cyclosilane **2** (3.75 g, 11 mmol) in petroleum ether (40 mL) cooled to −10 °C. The reaction was continued until complete consumption of cyclosilane **2**; the course of the reaction was monitored with GLC. The reaction mixture was heated to ~20 °C, and the solvent was distilled off (95—100 °C). Fractionation of the residue afforded 6.8 g (76%) of dibromodisilane **1b** (n = 2), b.p. 64—65 °C (10 Torr), m.p. 42 °C (*cf.* Ref. 18: b.p. 79 °C (30 Torr), m.p. 40 °C). ^{1}H NMR (CCl_4), δ: 0.73.

The residue, a brown oil with a strong smell, was a mixture of dibromooligosilanes **1b** (n = 3, 4, 6). ^{1}H NMR (CCl_4), δ: n = 3: 0.68 (s, 12 H, $SiMe_2Br$); 0.30 (s, 6 H, $SiMe_2$); n = 4: 0.64 (s, 12 H, $SiMe_2Br$); 0.28 (s, 12 H, $SiMe_2$); n = 6: 0.61 (s, 12 H, $SiMe_2Br$); 0.25 (s, 12 H, Si_bMe_2); 0.27 (s, 12 H, Si_cMe_2).

Reaction of cyclosilane 2 with MCl_4 (M = Sn, Ti). A solution of $TiCl_4$ (10 g, 5 mmol) in dry CH_2Cl_2 (2 mL) was added dropwise to a solution of cyclosilane **2** (3.5 g, 10 mmol) in dry CH_2Cl_2 (30 mL). The reaction mixture was vigorously stirred for 100 h; the reaction was monitored by GLC. The residue was filtered off, and the solvent was removed. The lower dichlorooligosilanes **1a** (n = 2—4) were distilled off *in vacuo*, and the starting cyclosilane **2** and monochlorosubstituted cyclosilane **2a** were removed by sublimation. The residue was distilled to give 1.7 g (61%) of dichlorooligosilane **1a** (n = 6), b.p. 166—167 °C (1 Torr), m.p. 45—46 °C (*cf.*, Ref. 4: b.p. 160—162 °C (0.8 Torr), m.p. 43.5—45 °C). ^{29}Si NMR (C_6D_6), δ: 26.63 ($SiMe_2Cl$); −40.81 (Si_bMe_2); −39.65 (Si_cMe_2).

Similarly, starting from a solution of cyclosilane **2** (3.5 g, 10 mmol) in CH_2Cl_2 (35 mL) and a solution of $SnCl_4$ (2.6 g, 10 mmol) in CH_2Cl_2 (5 mL), stirring of the reaction mixture for 30 h, filtration, and removal of the solvent gave a mixture (3.9 g). According to GLC data, it contained unreacted cyclosilane **2**, mono- and dichlorosubstituted cyclosilane **2a**, as well as dichlorooligosilanes **1a** (n = 2—4, 6). ^{29}Si NMR (CCl_4), δ: $(Me_2Si)_6$: −41.81; $ClSi_6Me_{11}$: 16.87 (SiMeCl); −41.22 (Si_bMe_2); −41.33 (Si_cMe_2); −41.74 (Si_dMe_2); $Cl_2Si_6Me_{10}$: 16.12 (SiMeCl); −39.56 ($SiMe_2$); **1b**: n = 2: 17.53; n = 3: 24.95 ($SiMe_2Cl$); −43.71 ($SiMe_2$); n = 4: 26.57 ($SiMe_2Cl$); −42.52 ($SiMe_2$); n = 6: 26.64 ($SiMe_2Cl$); −40.73 (Si_bMe_2); −39.56 (Si_cMe_2).

Synthesis of silane-siloxane copolymers 6a,b. A solution of dibromodisilane **1b** (n = 2) (2.76 g, 10 mmol) in anhydrous ether (10 mL) was cooled to −10 °C, and a mixture of diol 3 (2.40 g, 10 mmol) and Et_3N (2.02 g, 20 mmol) in anhydrous ether (10 mL) was added dropwise. The reaction mixture was vigorously stirred at −5 to −10 °C for 2 h and at ~20 °C for 20 h. The precipitate of $Et_3N \cdot HBr$ was filtered off and washed with anhydrous ether (2×10 mL). The ethereal solution was concentrated, washed with water to neutral reaction, and dried with Na_2SO_4. The ether was distilled off to give 3.36 g (95%) of copolymer **6b** as a viscous liquid. ^{29}Si NMR (CCl_4), δ: 0.35 (OSiSiO); −11.78 (SiOH); −21.83 (SiSiO$\underline{\mathrm{Si}}$O); −21.95 (OSiO$\underline{\mathrm{Si}}$OSi). The resulting copolymer was heated on an oil bath at 75—80 °C in a high vacuum (0.05 Torr) for 40 h to induce its homocondensation at the terminal OH-groups. The reaction mixture was dissolved in CH_2Cl_2 and precipitated with excess MeOH to yield 2.16 g (61%) of copolymer **6'b**. Found (%): C, 34.41; H, 8.11; Si, 39.25. $C_{10}H_{30}O_4Si_5$. Calculated (%): C, 33.89; H, 8.54; Si, 39.50. ^{29}Si NMR (CCl_4), δ: 0.39 (OSiSiO); −21.78 (SiSiO$\underline{\mathrm{Si}}$O); −22.02 (OSiO$\underline{\mathrm{Si}}$OSi). The integral intensity ratio, $I_{SiSi} : I_{SiO}$: found 1 : 1.61, calculated 1 : 1.50. UV, λ_{max}/nm: 205.

Similarly, starting from dichlorooligosilane **1a** (n = 6) (4.19 g, 10 mmol) and diol **3** (2.40 g, 10 mmol) (after thermal homocondensation and precipitation), copolymer **6'a** (3.76 g, 64%) was obtained. Found (%): C, 36.21; H, 8.93; Si, 42.54. $C_{18}H_{54}O_4Si_9$. Calculated (%): C, 36.81; H, 9.26; Si, 43.03. ^{29}Si NMR (CCl_4), δ: 9.01 (O$\underline{\mathrm{Si}}$Si); −21.67 (O$\underline{\mathrm{Si}}$OSiSi); −22.02 (OSiO$\underline{\mathrm{Si}}$OSi); −39.78 (OSiSi$\underline{\mathrm{Si}}$); −45.34 (OSi$\underline{\mathrm{Si}}$Si). Integral intensity ratio, $I_{SiSi} : I_{SiO}$: found 2.15 : 1, calculated 2.00 : 1. UV, λ_{max}/nm: 262.

The authors express their gratitude to T. V. Strelkova (A. N. Nesmeyanov Institute of Organoelement Compounds of the RAS) for recordng the NMR spectra.

This study was financially supported by the Russian Foundation for Basic Research (Project No. 97-03-32689a.

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Received January 21, 1997;
in revised form March 25, 1997