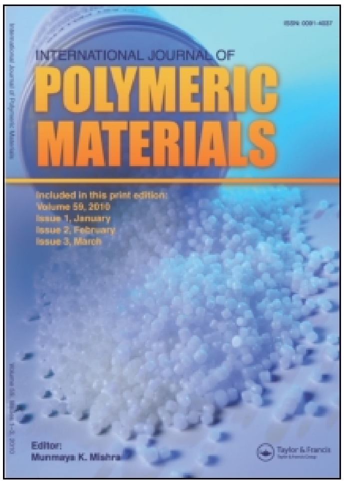

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Organosiloxane Copolymers and Block Copolymers with Cyclolinear Structure of Macromolecules

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Synthesis methods of silicone oligomers and copolymers consisting of flexible linear links of polydimethylsiloxanes and rigid mono- and polycycles, cycloarylens, spirocyclic and spiroladder ladder, etc., are reviewed.

KEY WORDS Organosiloxane copolymers, thermo-oxidative stability, cyclic and polycyclic systems, spirocyclic- spiroladder-polymers.

INTRODUCTION

Today this is a requirement for materials with high heat and thermal stability, freeze resistance, hydrophobicity, high dielectric indices, etc.

Inorganic and, in particular, polyorganosiloxanes fall into this class. Thermal stability of these polymers depends on their structure, while their thermal-oxidative stability depends on the type and number of organic groups surrounding the macrochains. Organic substitution on the silicon atom can lead to variation of vitrification temperature in linear macromolecules over a wide range. Introduction of polyfunctional branching centres, mono-, bi-, tri-, tetra- and polycyclic fragments of another structure, extends the range of possibilities available for the generation of physico-chemical properties.

The largest effect can be expected with the production of cyclochain, ladder and spirocyclic molecular structures.[1-3]

All polyorganosiloxanes with double-stranded chains can undergo rupture of some bond without a decrease in molecular mass. Ladder and spirocyclic polymers do not have elastic properties and because of their high vitrification temperature are characterized by poor processability.[4]

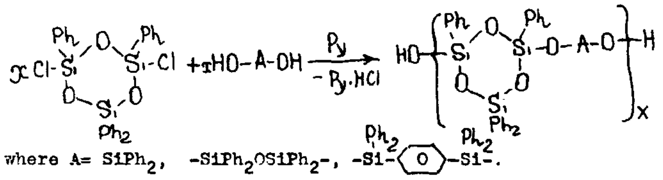
On the other hand, linear polyorganosiloxanes possess good elastic properties and are easily processible, however they have a comparatively low thermal stability. Polydimethylsiloxanes are subject to thermal-oxidative destruction at 260°-270°C and under isothermal conditions at 200-230°C.

One of the most promising methods of obtaining polymers which combine high thermal-oxidative stability with elasticity is the modification of linear polydimethylsiloxanes. It is of interest to develop methods of synthesis of silicone oligomers and copolymers which consist of flexible linear links of polydimethylsiloxanes and rigid mono- and polycycles, cycloarylens, spirocyclic and spiroladder systems as well as bead-like cyclolinear oligomers and copolymers.

1. ORGANOSILOXANE COPOLYMERS WITH CYCLOSILOXANE FRAGMENTS IN THE MAIN CHAIN

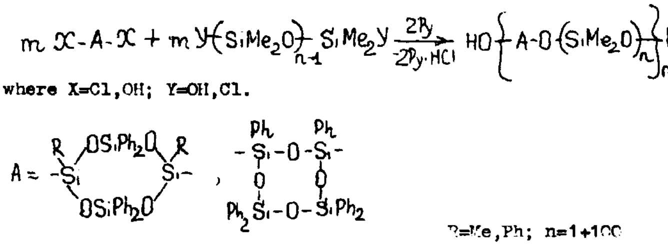
The first papers in the field of cyclolinear oligomers dealt with the reaction of hydrolytic cocondensation of di- and trifunctional silicones.[5] As a result of these reactions at various ratios of the starting components cyclolinear oligomers of irregular statistic structure are obtained with a low yield.

Heterofunctional polycondensation of 1,3-dichloro-1,3,5,5,-tetraphenylcyclotrisiloxane with various silicone diols, in the presence of pyridine as an acceptor of hydrogen chloride, leads to the formation of cyclolinear polyorganosiloxanes with cyclotrisiloxane fragments in the chain[6]:



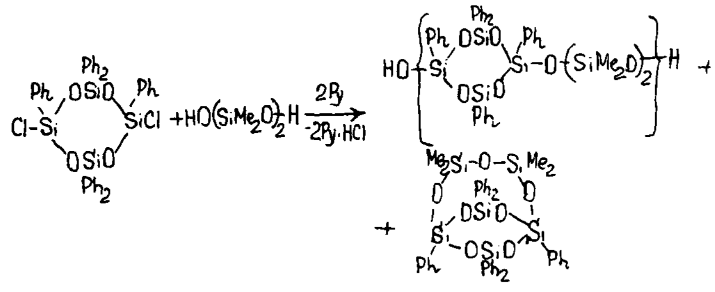
The synthesis of the above copolymers is difficult, consisting of two stages with a low yield. In the first stage a partial hydrolithic condensation of phenyltrichlorosilane results in formation of tetrachlorodiphenyldisiloxane, whose yield does not exceed 30%, except for the paraphase method, when the yield is more than 60%.

Organosiloxane cyclolinear copolymers with eight-member cyclic fragments in the chain were obtained in the reaction of heterofunctional polycondensation of 1,3- and 1,5-dichloro(dihydroxy)-organo-cyclotetrasiloxanes with α,ω-dihydroxy(dichloro)dimethylsiloxanes in the presence of pyridine as an acceptor[7]:

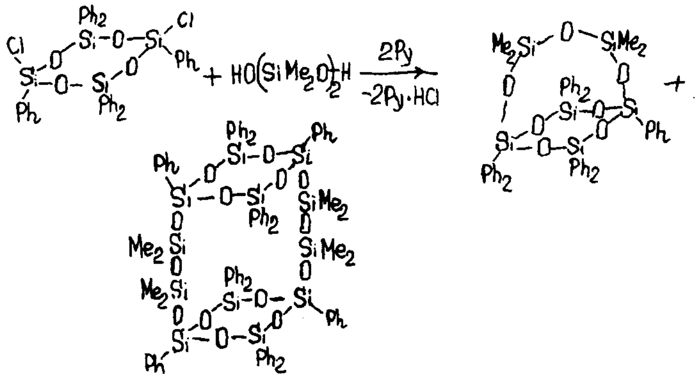


The authors[7] have established that the reaction of organocyclotetrasiloxanes does not depend on the arrangement of functional groups on the silicon atoms.

Heterofunctional condensation of 1,5-dichlorohexaphenylcyclotetrasiloxane with 1,3-dihydroxytetramethyldisiloxane[8] proceeds in two directions, viz., with formation of a cyclolinear copolymer (A) and a bi-cyclic compound (B) by the scheme:



The fact that the reaction proceeds in two directions was proven through deliberate synthesis, viz., by the reaction of condensation of 1,5-dichlorohexaphenylcyclotetrasiloxane with 1,3-dihydroxytetramethyldisiloxane in a 5% solution in the presence of hydrogen chloride as an acceptor which proceeds according to the mechanism of intramolecular condensation, where the cis-form of the starting 1,5-dichlorohexaphenylcyclotetrasiloxane promotes formation of polycyclic structures, while the trans-form is responsible for oligomeric products formation, the ratio of the cis- and trans-forms being 50%. The reaction proceeds according to the scheme:



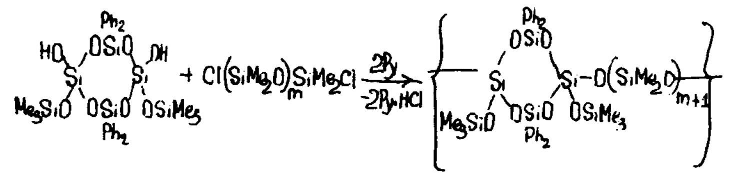
Thus, the method of obtaining cyclolinear organosiloxane copolymers with 1,5-arrangement of the organocyclotetrasiloxane fragment in the chain is promising,[7,8] since the yields of the starting 1,5-dichlororganocyclotetrasiloxanes are equal to 50–60%.

An attractive method for producing cyclolinear copolymers based[9] on the reaction of heterofunctional polycondensation of 1,5-dihydroxycontaining organocyclotetrasiloxanes with α,ω-diamino(bisdimethylamino)dimethylsiloxanes as a solid or solution results in the synthesis of higher molecular cyclolinear copolymers. When α,ω-bisdiethylaminoidimethylsiloxanes is used, the reaction proceeds with formation of a three-dimensional structure. Although the heterofunctional condensation reaction proceeds, it is difficult to guarantee removal of released diethylamine, which in its turn, attacks the siloxane bond in the cyclic grouping, and forms a bipolar zwitterion.[10] The copolymers with 1,5-arrangement of the cyclotetrasiloxane fragment in the diorganosiloxane linear chain were used[11] in chromatography as a fixed phase for gas-chromatographic analysis. The use of the new fixed phase made it possible to increase selectivity of complex mixtures of organic and silicone compounds.

The influence of cyclic groups in cyclolinear copolymers with 1,5-arrangement of the cyclotetrasiloxane fragments on the rigidity parameter are studied.[12] Computer modeling of a macromolecular coil was aimed at using the Monte Carlo method with $n = 1.25$ (where n is the length of the polydimethylsiloxane link). The calculated Kuhn segment A and $\langle h^2_{\text{free}} \rangle/\text{n}M_0$, where M_0 is the molecular mass of the structural unit, $\langle h^2_{\text{free}} \rangle$ is the + ms distance between the ends of the polymer chain at free rotation about virtual bonds. The influence of the cycles on the conformation characteristics is only revealed when $n = 1$. In case of the transition from $n = 5$ to $n = 25$, saturation takes place, and an increase in the number of the Si—O groups does not influence the coil size. In practice, however, when there is some retardation in the rotation about the virtual bonds, eight-member cycles start to exert their influence.[12]

Thermomechanical studies of copolymers with organocyclotetrasiloxane fragments in the chain have revealed[7,13] that 1,5- or 1,3-arrangement of the cyclotetrasiloxane fragment does not produce affects on the thermomechanical properties of the copolymers. A similar conclusion was drawn when studying the thermal-oxidative stability of copolymers. Introduction of an eight-member cycle into the chain changes the character of copolymer decay, i.e. destruction proceeds accompanied by formation of oligomer products with simultaneous structurization which prevents the main chain from decaying. With an increase in thermodynamic rigidity, one can observe an increase in thermal stability.

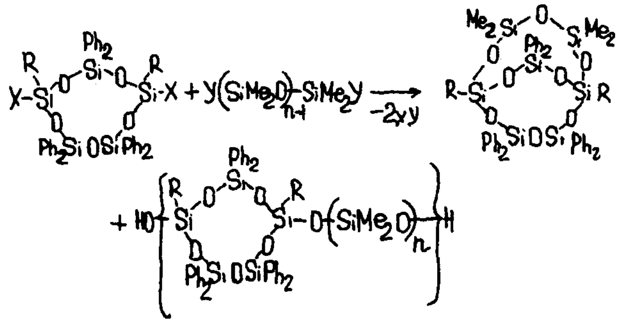
In the reaction of heterofunctional polycondensation of dihydroxyorganocyclotetrasiloxanes with surrounding trimethylsiloxy-groups with α,ω-dichlorodimethylsiloxanes the cyclolinear copolymers are synthesized with regular arrangement of cyclotetrasiloxane fragments in the chain[14]:



where $m = 0,1,2,10$.

Depending on the value of m, the polymers are crystalline ($T_{\text{vit}} = 100°\text{C}$, $T_{\text{melt}} = 440°\text{C}$, $m = 0$), highly elastic ($T_{\text{vit}} = 30°\text{C}$, $E_{\text{str}} = 400\%$) and rather strong ($\sigma_{\text{rupt}} = 40\ \text{kG/cm}^2$ at 24°C) products. It should be noted that the dielectric permeability of this polymer decreases linearly with increase in temperature.

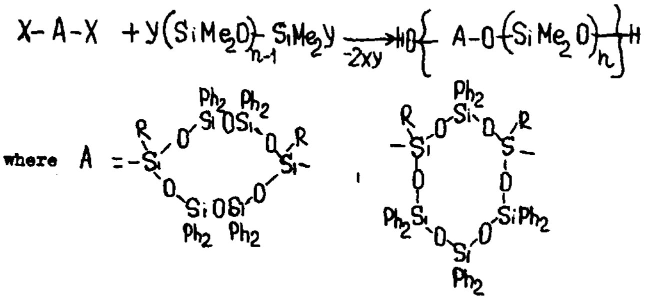
Copolymers with a regular arrangement of organocyclopentasiloxane fragments in the chain were synthesized in the reaction of heterofunctional polycondensation of difunctional organocyclopentasiloxanes with α,ω-dihydroxy(dichloro)(bisdimethylamino)dimethylsiloxanes[15] according to the scheme:



where R = Me, Ph; X = Cl, OH; Y = OH, Cl, Me$_2$N; $n = 2 \div 51$.

At small lengths of the linear dimethylsiloxane link the reaction runs both intermolecularly with formation of copolymers and intramolecularly with formation of bicycloorganosiloxanes. The polycondensation rate depends, to a great extent, not only on the steric effect of the surrounding radicals, but also on the inductive influence of the surrounding radicals in the silicon atoms of the silsesquioxane link. By means of fractionation of copolymers and elementary analysis it is proved that the reaction proceeds directionally with formation of copolymers having regular arrangement of cyclopentasiloxane fragments in the chain.

Cyclolinear copolymers with 1,5- or 1,7-arrangement of organocyclohexasiloxane fragments in the dimethylsiloxane chain were synthesized[16] in the reaction of heterofunctional polycondensation of organocyclohexasiloxanes with 1,5- and 1,7-arrangement of functional groups in silicon with α,ω-dihydroxy(dichloro)(bisdimethylamino)dimethylsiloxanes, according to the scheme:



where R = Me, Ph; X = Cl, OH; Y = OH, Cl, Me$_2$N; $n = 2 \div 51$.

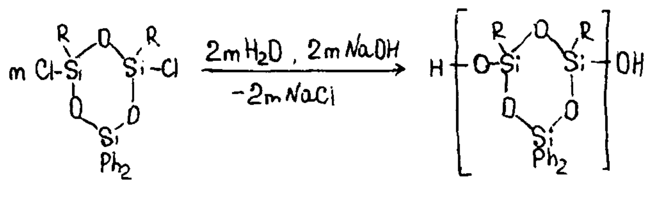
At short lengths of the linear dimethylsiloxane link the copolymer yield is low, since the condensation reaction can proceed not only intermolecularly, but also intramolecularly.[8,15] Replacement of a methyl radical by a phenyl in the silsesquioxane atom of silicon in copolymers leads to a rise in vitrification temperature by ~10°C. The arrangement of the cyclohexasiloxane fragment in the chain does not produce noticeable effect on the vitrification temperature. The presence of any chemical inclusions in the polydimethylsiloxane chain[17,18] (surrounding groups other than the methyl one, branching sites) results in a loss of ability to crystallize at distances of 30 Si—O— links between the inclusions in the chain. The copolymers under study do not crystallize at lengths of $n < 25$. The temperature region corresponding to the process of vitrification of copolymers with cyclotetra-, -penta-, and -hexasiloxane fragments in the chain rises towards higher temperatures with a decrease of the value of n and with an increase in the volume of the cycle (i.e. the number of phenyl groups). This is explained by the influence in three-dimension of the phenyl groups, whose presence in the polymethylsiloxane chain involves a rise in the vitrification temperature.[19]

Comparative estimation of the thermal-oxidative stability of copolymers shows that with an increase in the volume of cyclic fragments, i.e. in the case of transition from the copolymers containing cyclotetrasiloxane fragments to those containing organocyclopenta- and -cyclohexasiloxane fragments in the linear chain; the thermal-oxidative stability of the copolymers regularly decreases.

Introduction of cyclic fragments into the polydimethylsiloxane chain hinders the chain transfer which proceeds with release of oligomer products of the D_n type.

The copolymers with cyclolinear structure, the so called "bead-like" copolymers, were synthesized by reaction of homofunctional polycondensation of 1,3-dihydroxytetraphenylcyclotrisiloxane.[20]

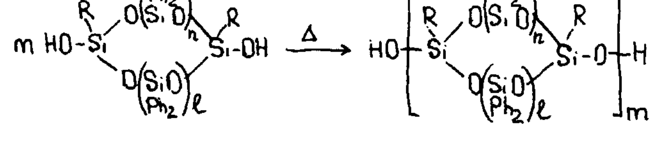
Oligomers of similar structure were also synthesized from 1,3-dichlorotetraorganocyclotrisiloxane in the presence of NaOH in the xylol solution according to the scheme:



where R = Ph, —$C_6H_4CH_3$; $m = 3 \div 50$.

Oligomers obtained are slightly soluble.

Homofunctional polycondensation of a mixture of cis- and trans-isomeric dihydroxyhexaorganocyclotetrasiloxanes in various solvents at their boiling temperatures in the presence of activated carbon as a catalyst and without it, the oligomers of a "bead-like" structure were obtained with organocyclotetrasiloxane fragments in the chain.[21] Similarly, the reactions of homofunctional polycondensation of 1,5-dihydroxy-1,5-diorganohexaphenylcyclopentasiloxane and 1,7-dihydroxy-1,7-diorganooctaphenylcyclohexasiloxane were studied.[22–24] The reaction of homofunctional polycondensation proceeds according to the scheme:



where R = Me, Oh; h = l = 1; n = 1; l = 2; n = l = 2; m = 3 ÷ 28.

It is shown that the polycondensation depth increases with rise of boiling temperature of the solvent used and increase in the amount of catalyst.[21-24] The same authors[25] obtained cyclolinear oligomers from heterofunctional condensation and showed that the heterofunctional polycondensation depth exceeds that of the homofunctional condensation.

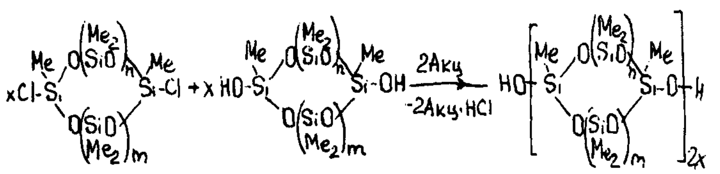
Comparative estimation of thermal-oxidative stability revealed that with an increase in the cyclic fragments volume the thermal oxidative stability of oligomers decreases.

Soluble polycyclic oligomers of linear structure are obtained in the reaction of heterofunctional polycondensation of 1,5-dihydroxyorganocyclotetrasiloxanes with 1,5-dichloro- or 1,5-diaminorganocyclotetrasiloxanes.[25] Depending on the three-dimensional structure of the cycles, heterofunctional polycondensation the oligomers of atactic or syndiotactic structure can be obtained, with T_{vit} of the syndiotactic oligomers not differing from that of atactic ones. This class of polymers is intermediate between the well-known flexible linear polydiorganosiloxanes, whose statistic segment is 10 Å and rigid ladder polyorganosilsesquioxanes with Kuhn segment on the order of 80–300 Å.

The influence of the size of the organocyclosiloxane link,[27] the character of substituents in the organosilsesquioxane fragment as well as geometric isomerism of the link on the behaviour of macromolecular chains in the solution has been studied.

For copolymers with hexamethylcyclotetrasiloxane fragments in the chain, thermogravimetric analysis was conducted.[28] The main products of destruction are polymethylbicyclo- and polymethyltricyclosiloxanes of the T_2D_n and T_4D_n composition (where D and T are the siloxane and silsequioxane links, and n = 2,3,4). In addition to methycyclosiloxanes, D_3 and D_4 were found, with D_4 not exceeding 3–4%. The data indicated that destruction proceeds by depolymerization. Among the volatile products of destruction, benzene, methane, and hydrogen were discovered. The volatile product composition in the presence of methyl and phenyl substituents suggests a more complicated process of destruction.

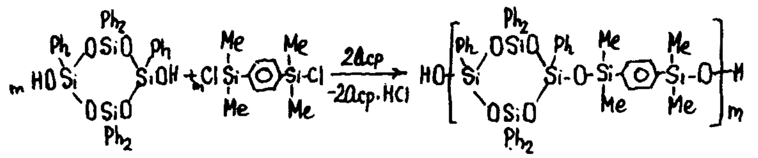
As a result of the reaction of heterofunctional condensation of dichloromethylcyclosiloxanes with corresponding dihydroxymethylcyclosiloxanes, the methylsiloxane polycyclic oligomers of the following structure were obtained[28]:



where $n = m = 1,2,3$; $n = m$.

Only two oligomers: polymethylcyclotetra- and polymethylcyclohexasiloxanes enriched with trans-isomeric links are able to crystallize. The vitrification temperature does not depend on the ratio of cis- and trans-isomeric links and decreases linearly with an increase of the number of dimethylsiloxane links. Polymethylcyclohexasiloxane is capable of exhibiting a liquid crystal state. Calorimetric data, in the regions of 380 and 500 K indicates small endothermal peaks peculiar to mesophase transitions, and observations under polarized light indicates in the first region appearances and in the usual disappearances of birefringence characteristic for mesophase transitions. X-ray analysis shows a broad diffraction maximum at 3.9–4.1 Å, indicative of a liquid crystal phase.

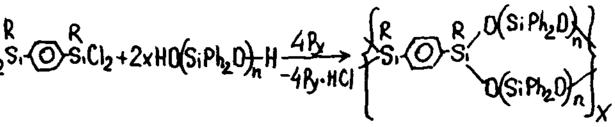
Arylencyclosiloxane oligomers with atactic structure were synthesized in the reaction of heterofunctional condensation of 1,4-bis(dimethylchlorosilyl)benzene with 1,5-dihydroxyhexaphenylcyclotetrasiloxane in a mole ratio 1:0.9 and 1:1. The process was carried out in a 60–70% solution of anhydrous toluene in the presence of an amine acceptor[29]:



where $m = 4 \div 16$.

These oligomers are attractive for block-copolymer synthesis.

Arylencyclosiloxane oligomers were also synthesized by heterofunctional condensation of 1,4-bis(dichlororganosilyl)-benzenes with diphenylsilandiol and 1,3-dihydroxytetraphenyldisiloxane in a 50% solution in dry toluene, the starting components being in the ratio 1:2 in the presence of pyridine. On the basis of the quantitative yield and ready solubility of the reaction products it was proposed that the reaction proceeds intermolecularly with formation of organocyclotetra- and organocyclohexasiloxane fragments between the arylenegroups in the chain[30]:



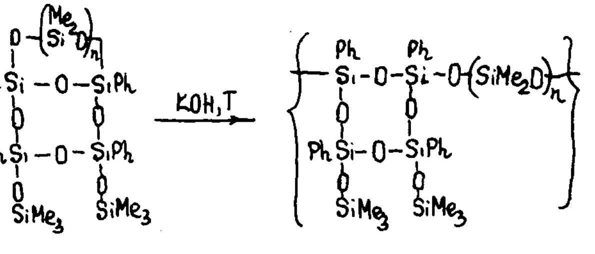
where R = Me, Ph; $n = 1,2$.

However, the probability of incomplete cyclization with formation of a branched structure is not excluded.

The oligomers with atactic macromolecular structure were synthesized by reaction of catalytic dehydrocondensation of dihydroxyorganocyclotetra(penta, hexa)siloxanes with the corresponding dihydride derivatives in 60–70% solution in dry toluene in the presence of platinahydrochloric acid or catalytic amounts of anhydrous KOH in the temperature interval from 20° to 40°C.

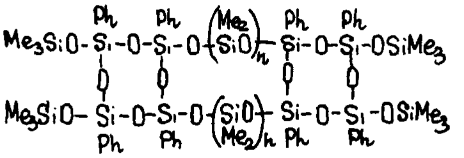
The above reaction is second order and the rate constants and activation energy of the dehydrocondensation reaction were calculated. It was established that in the case of potassium hydroxide as a catalyst no opening of the siloxane skeleton takes place[31] and completely soluble polymers are formed.

Organosiloxane copolymers with monocyclic fragments in the dimethylsiloxane chain were obtained not only in the reaction of heterofunctional condensation, but via the polymerization reactions in the presence of various amounts of nucleophilic potassium hydroxide at different temperatures.[32] In all cases the reaction proceeds with formation of soluble copolymers of cyclolinear structure, according to the scheme:



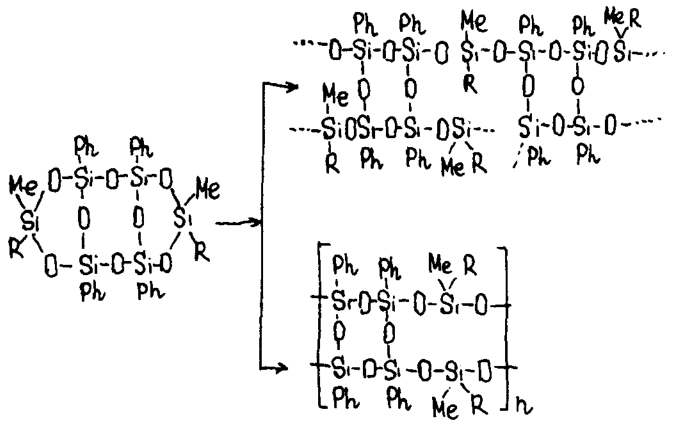
where $n = 1,2$.

Polymerization of tricyclic compounds with tetrakistrimethylsiloxy-groups at the ends of the molecule having the structure:



proceeds in a similar way.

When studying anionic polymerization of 1,7-dimethyl-1,7-diorgano-3,5,9,11-tetraphenyltricyclohexasiloxanes in toluene solution in the presence of 1,5-dipotassiumoxytrimethyltriphenyltrisiloxane as an initiator it was shown[33] that in all cases polymerization leads to formation of structurized products which later on rearrange into soluble cyclolinear polymers, according to the scheme:



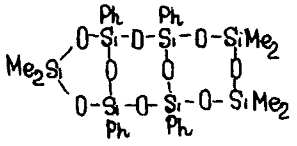
R = Me, Ph.

This general scheme is realized due to sequential and parallel elementary reactions: a) of interchain interaction finally resulting in three-dimensional cross-linked products and b) of intrachain cyclization with formation of polymers.

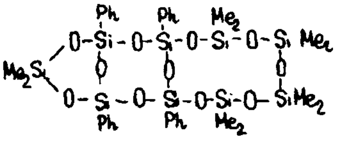
Cyclolinear organosiloxane copolymers with bicyclic fragments in the chain were synthesized in the reaction of heterofunctional polycondensation of 5,7-bis-(chlorodimethoxy)-1,1-dimethyl-3,5,7,9-tetraphenylbicyclohexasiloxane and 5,7-bis-(chloromethylphenylsiloxy)-1-methyl-1-phenyl-3,5,7,9-tetraphenylbicyclohexasiloxane with α,ω-dihydroxydimethylsiloxanes in the 70–80% solution of dry benzene at a gradual rise of temperature from 25°C to 75°C. The conversion of hydrogen chloride was not more than 60%, while the polymer yield after reprecipitation was 40–50%.

Considering the fact that the hydrogen chloride produced cannot be instantly eliminated from the reaction mixture by argon flow, the authors[34] do not exclude side reactions of homocondensation of α,ω-dihydroxydimethylsiloxanes. As a result, in addition to organocyclosiloxane formation, the length of diols can increase, and hence, blocks of different lengths can form.

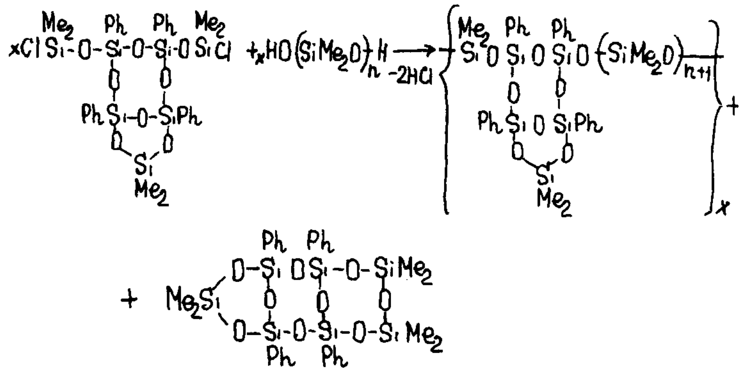
By means of a detailed analysis of the reaction mixture obtained as a result of the interaction of 5,7-bis(chlorodimethyloxy)-1,1-dimethyl-3,5,7,9-tetraphenylbicyclohexasiloxane with 1,3-dihydroxytetramethyldisiloxane it was established[34] that 45% of polymers is formed with $\eta_{red} = 0.20$. Chromatographic analysis confirmed the lack of octamethylcyclotetrasiloxane in the reaction products. On distillation of the products remained after the benzene-methanol mixture was extracted from the mother solution, a compound was released with $T_{boil} = 220–222°C$ ($P = 1 \times 10^{-3}$ mmHg). On the basis of elementary analysis data, NMR-spectra and molecular mass analysis, the compound was assigned the following structure:



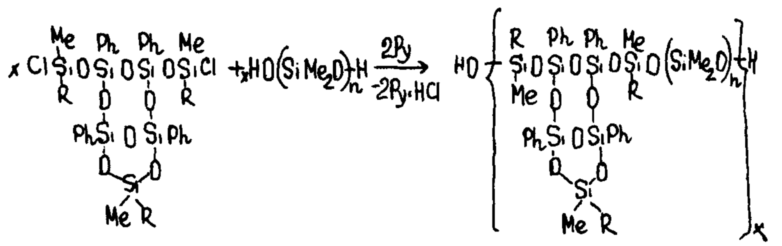
Besides, about 13% of the reaction product was obtained in which the proportion of protons in the methyl and phenyl groups is 1.37:1.00, i.e. it is close to the proportion that is required for the diol formed at intramolecular cyclization with a bicyclic compound (calculated as 1.52:1.00), however, it was not possible to isolate an individual compound, because a cross-linked system was formed. In a diluted solution of diethyl ether a deliberate synthesis of tricyclic compound was carried out. The compound had the structure:



However, on distillation the reaction mixture also transformed to a three-dimensional cross-linked polymer. Thus, proceeding from experimental data, the authors[35] put forward the following scheme of the reaction:



To eliminate the reaction of homocondensation of α,ω-dihydroxydimethylsiloxanes, further investigations of heterofunctional polycondensation were made in the presence of pyridine as an acceptor of hydrogen chloride. As a result rubber-like substances or viscous liquids were obtained whose yield was equal to 70–90% depending on the length of the dimethylsiloxane link. Therefore, the reaction of heterofunctional condensation of dichlorobicyclohexasiloxanes with α,ω-dihydroxydimethylsiloxanes in the presence of pyridine proceeds by the scheme:

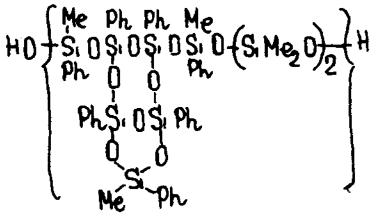


where R = Me, Ph; $n = 2 \div 70$.

The foregoing schemes of reaction did not allow the authors[35] to study kinetics of the polycondensation process: in the first case because of side reactions of homocondensation and intramolecular cyclization. In the second case, due to poor reproducibility of the characteristics of viscosity after elimination of hydrochloric pyridine both on washed and unwashed samples, since when the mass of the samples became constant, further polycondensation took place.

To obtain kinetic characteristics at heterofunctional polycondensation of 5,7-bis(diethylaminodimethylsiloxy)-1,1-dimethyl-3,5,7,9-tetraphenylbicyclosiloxane with 1,3-dihydroxytetramethyldisiloxane, it was shown that the reaction is accompanied by release of diethylamine, but after conversion of diethylamine was 15–17%, a three-dimensional cross-linked polymer was formed. This was explained by nucleophilic attack on a silicon atom in labile six-member cycle compounds.[36]

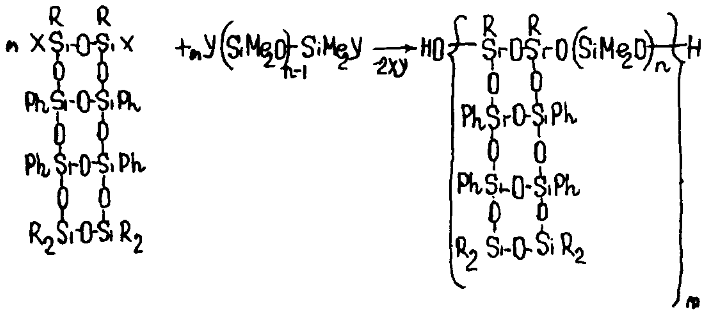
The investigations of hydrodynamic properties (characteristic viscosity, coefficients of progressive diffusion and sedimentation) as well as bifurcation in the flow for copolymer with bicyclic fragments in the chain have proved its linear structure:



In the case of the sample of molecular mass M_{SD} = 57000, the characteristic viscosity is comparatively small $[\eta] = 0.22$ dl/g, which is not typical for rigid-chain polymers.[37] Bifurcation for this polymer is also small: $\Delta h/\Delta\tau = 7 \times 10^{-10}$, practically coinciding with the value of bifurcation for a linear polymethylphenylsiloxane.[38]

Copolymers with tricyclic fragments in the dimethylsiloxane chain were synthesized by the interaction of 1,3-dichloro(dihydroxy)-organotricyclodecasiloxanes with α,ω-dihydroxy(dichloro)dimethylsiloxanes both in the presence of pyridine as an acceptor and without it.[8,13]

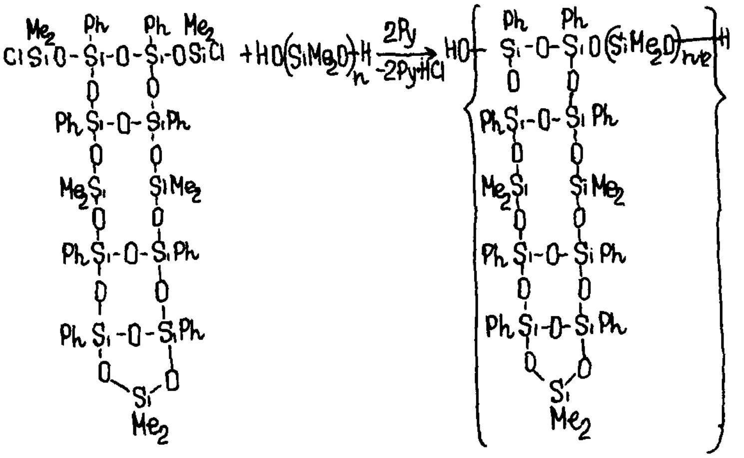
Based on the data for the HCl release rate and amount, it is shown in Reference 8 that the functional group reactivity depends both on inductive and steric effects of the surrounding groups. The reaction proceeds by the scheme:



where R = Me, Ph; X = Cl, OH; Y = OH, Cl; $n = 1 \div 70$.

For the copolymer fraction with $n = 1$ (28% of the whole mass), $[\eta] = 0.12$ dl/g, M_{SD} = 7400, and bifurcation of this copolymer is $\Delta h/\Delta\tau = 5 \times 10^{-10}$, which practically coincides with anisotropy of a copolymer with bicyclic fragments in the chain. At small lengths of the dimethylsiloxane link the interchain distance in the amorphous copolymer reaches its maximum $d_1 = 11.1$ Å ($n = 1$). It is shown that the changes in interchain distances directly relate to the polydimethylsiloxane link length, because at $n = 25$ a second maximum appears on diffractograms which characterizes the interchain distance in the dimethylsiloxane chain with $d_1 = 7.8$ Å.

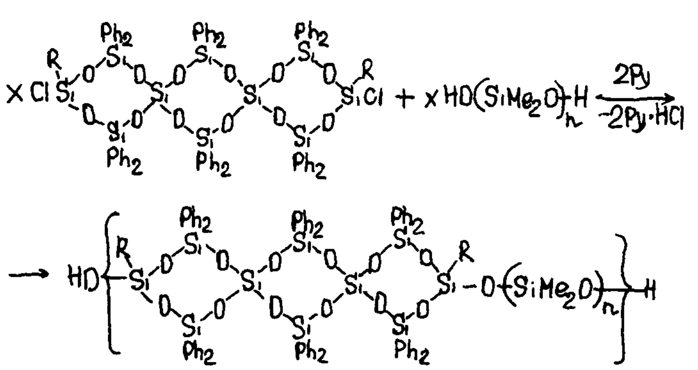
For further investigations of the influence of the polycyclic blocks volume on the properties of copolymers,[35] synthesized with tetracyclic fragments in the linear chain, viz., the reaction of heterofunctional polycondensation of dichlororganotetracyclosiloxane with α,ω-dihydroxydimethylsiloxane was studied in the presence of pyridine according to the scheme[35]:



$n = 2 \div 70$.

A comparative X-ray analysis revealed that the interchain distances are close to those in the copolymers with bi- and tricyclic fragments in the chain. At small lengths no significant increase in d_1 is observed, since the minimum length of the one-chain link was equal to octamethyltetrasiloxane.

In References 39 and 40 the reaction of heterofunctional polycondensation of α,ω-dichloroorganospirotricyclotetrasiloxanes with α,ω-dihydroxydimethylsiloxanes is studied. As a result of the reaction cyclolinear copolymers with spirotricyclic fragments in the dimethylsiloxane chain were obtained. The reaction runs according to the scheme:

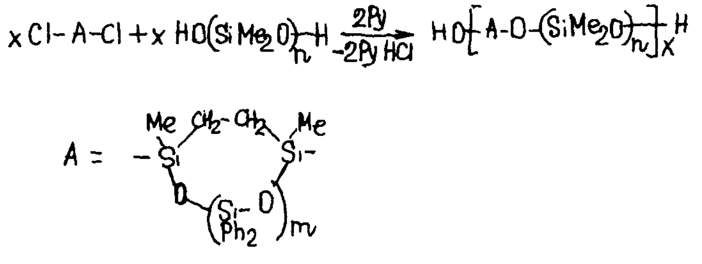


where R = Me; $h = 8$; R = Ph; $n = 70242$; $x = 20 \div 60$.

It is shown that an increase of the dimethylsiloxane fragment length, mass losses also increase, while T_{vit} of the copolymers decreases.

2. ORGANOSILOXANE COPOLYMERS WITH CYCLOCARBOSILOXANE AND CARBOCYCLOSILOXANE FRAGMENTS IN THE CHAIN

Copolymers with monocyclic carbosiloxane fragments in the chain were also synthesized in the reaction of heterofunctional condensation of 1,3-dichloro-1,3-dimethyl-2-ethylen-5,5-diphenylcyclocarbosiloxane or 1,3-dichloro-1,3-dimethyl-2-ethylen-5,5,7,7-tetraphenylcyclocarbosiloxane with α,ω-dihydroxydimethylsiloxane both without an acceptor and in the presence of pyridine as an acceptor.[41] The reaction proceeds by the scheme:



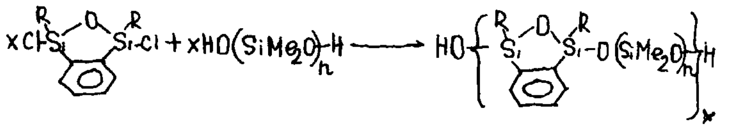
where $m = 1{,}2$; $n = 2 \div 50$.

The copolymers are transparent or slightly opalescent products very easily soluble in various organic solvents. As in the case of polydimethyldiphenylsiloxane copolymers, the effect of the links other than dimethylsiloxane ones on T_{vit} of the copolymers starts showing up even when the content of the latter is ~3% mole.

The effect of the cyclocarbosiloxane fragment on T_{vit} with $m = 2$ is more evident than that of the same fragment with $m = 1$.

With an increase in the cyclic fragments volume as well as with an increase in the length of the linear dimethyloxane links, thermal-oxidative stability of copolymers decreases.[42] Cyclolinear copolymers with organocyclocarbosiloxane fragments in the chain with $m = 1$ do not differ in their thermal stability from copolymers with cyclotetrasiloxane fragments in the chain. Besides, as the authors point out, the yield of the starting dichloroorganocyclocarbosiloxane ($m = 1$) is higher.

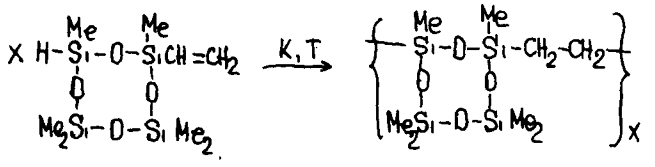
Copolymers with disilaoxaindane fragments in the chain were synthesized in the reaction of heterofunctional polycondensation of 1,3-dichloro-1,3-dimethyl(diphenyl)-1.3-disila-2-oxaindanes with α,ω -dihydroxydimethylsiloxanes in the presence of amine as an acceptor.[43,44] As a result, transparent or slightly opalescent products completely soluble in organic solvents were synthesized by the scheme:



where R = Me, Ph; $n = 2 \div 37$.

For a nonfractionated sample of the copolymer R = Me, $n = 2$, $M_{\text{SD}} = 36400$ is found. The synthesized copolymers are amorphous systems. As thermogravimetric investigations show, the main process of destruction for the above copolymers starts at temperatures of 560–600°C.

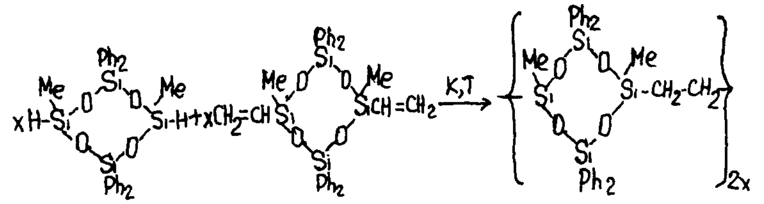
Copolymers with ethylene bridges between the cyclic fragments in the chain were synthesized in the reaction of addition of 1-hydrid-3-vinylhexamethylcyclotetrasiloxane in the presence of the Spyer catalyst, by the scheme[45]:

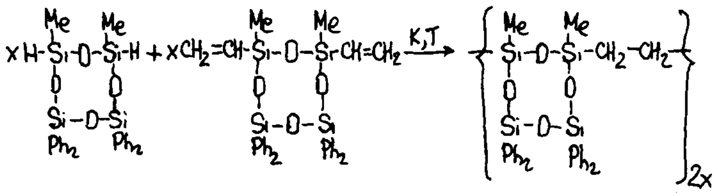


As a result of polyaddition completely soluble polycarbosiloxanes are obtained bound along the ridge.

Cyclolinear polyorganocarbosiloxanes containing organocyclotetrasiloxane fragments in the chain were synthesized by reaction of hydrid polyaddition of α,ω-dihydriddimethylsiloxanes to divinylhexamethylcyclotetrasiloxanes.[46] However, the starting divinylhexamethylcyclotetrasiloxane was obtained by a joint hydrolysis of dimethyldichlorosilane and methylvinyldichlorosilane. In spite of using effective rectification columns and an analytical chromatograph with a preparative attachment, the authors failed to separate isomeric 1,3- and 1,5-divinylhexamethylcyclotetrasiloxanes which are formed during hydrolysis. Therefore, copolymers contain isometric cycles along the ridge (1,3-arrangement) and by the diagonal (1,5-arrangement). Heating reprecipitated polymers at 100–110°C in the presence of 0.001–0.01 wt% catalysts of anionic polymerization there occurs an abrupt increase of viscosity and gel formation. Changing the length of alkylensiloxane ridge between the organocyclotetrasiloxane fragments in the chain one can change the average distance between the cross-link sites.

The polymers with 1,5-arrangement of the cyclotetrasiloxane in the chain were synthesized by reaction of hydrid polyaddition of 1,5-dihydridorganocyclotetrasiloxanes to 1,5-divinylchlororganocyclotetrasiloxanes.[47] Hydrid polyaddition of 1,3-dihydrid-1,3-dimethyltetraphenylcyclotetrasiloxane to 1,3-divinyl-1,3-dimethyltetraphenylcyclotetrasiloxane in the presence of platinahydrochloric acid as a catalyst (0.01 M of the solution in tetrahydrofuran), according to the scheme:

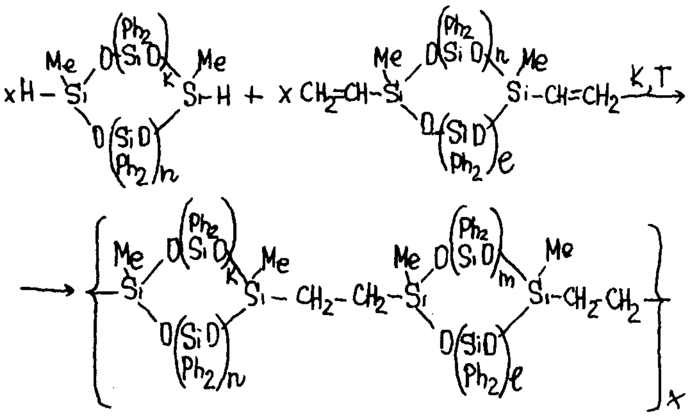




The polyaddition reaction proceeds with formation of a β-adduct. Reactivity of the groups in tetracyclosiloxanes by reaction of hydrid addition depends on their position in the cycle. Polymers with a higher molecular mass are formed by interaction of the cycles with functional groups in the 1,5 position.

It is shown that polymers with disilaethylene groups have lower thermal-oxidative stability, but higher thermal stability in the absence of oxygen in comparison with their polyorganosiloxane analogues.[48]

In the reaction of hydrid polyaddition of dihydridorganocyclotetra(penta,hexa)-siloxanes to divinylorganocyclopenta(hexa)siloxanes in the presence of 0.01 M solution of platinahydrochloric acid in tetrahydrofuran the carbosiloxane copolymers with cyclic fragments in the chain were synthesized.[49]

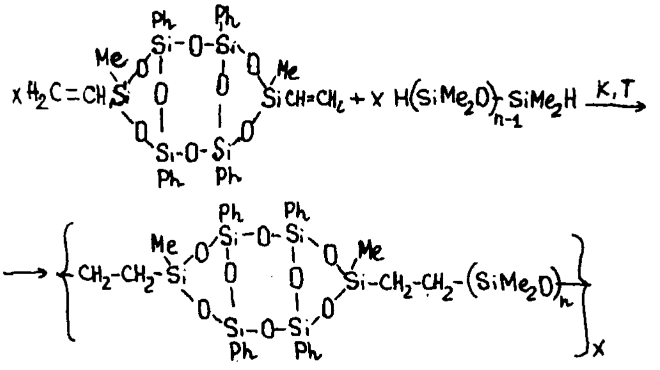


where $k = h = 1;\ m = 1;\ l = 2;\ m = l = 2.$

$k = 1;\ n = l = 2;\ m = 1;\ k = 1;\ n = m = l = 2;\ k = n = m = l = 2.$

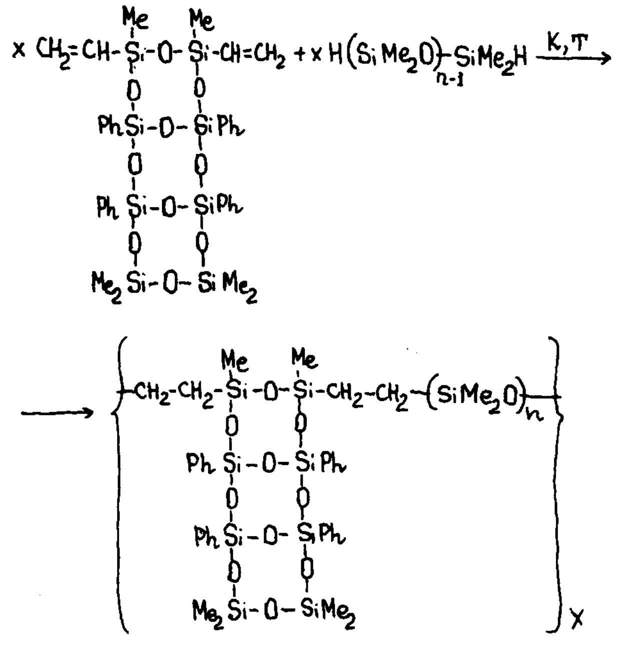
Constant rates and activation energy of the polyaddition reaction are calculated. It is found that with an increase of the cycle volume the polyaddition rate decreases. It is also shown that with an increase in the volume of cyclic fragments in the chain thermal stability decreases.

Polyorganosiloxanes with linear and cyclic fragments in the chain were obtained by addition of 1,7-divinyl-1,7-dimethyl-3,5,7,9-tetraphenyltricyclohexasiloxane to α,ω-dihydrodimethylsiloxanes in the presence of 0.1 M solution of platinahydrochloric acid in tetrahydrofuran. As a result carbosiloxane copolymers with regular arrangement of tricyclohexasiloxane fragments along the chain were obtained[50] by the scheme:



where $n = 2 \div 5O$.

Cyclolinear copolymers with tricyclosiloxane fragments in the chain were synthesized in the reactions of hydrid polyaddition of organotricyclosiloxane with vinyl groups in silicon with α,ω-dihydriddimethylsiloxanes in the presence of platinahydrochloric acid or rhodium complexes as a catalyst[51] according to the scheme:



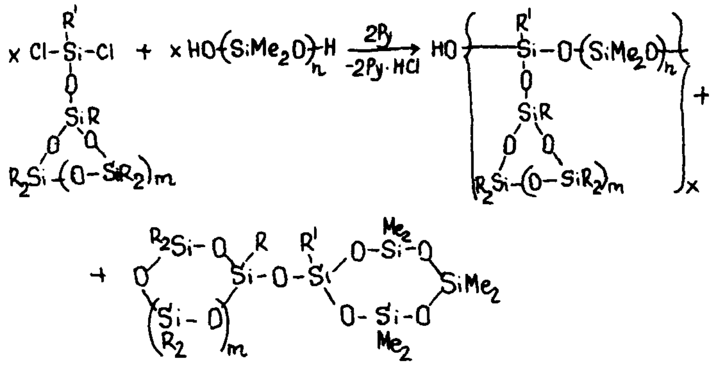
where $n = 2 \div 37$.

Thus, the reaction of hydrid polyaddition can be successfully used to synthesize copolymers with cyclolinear structure.

3. ORGANOSILOXANE COPOLYMERS WITH CYCLOSILOXANE FRAGMENTS IN THE SIDE CHAIN

Cyclolinear dimethylsiloxane copolymers are considered in which in the organosisesquioxane link with branching structure there are diorganocyclosiloxane fragments instead of linear dimethylsiloxy-links.[52-54]

Organosiloxane copolymers with regular arrangement of organocyclotri-, -tetra-, and -pentasiloxane fragments in the side chain were synthesized in the reactions of heterofunctional polycondensation of dichlororganosiloxydiorganocyclosiloxanes with α,ω-dihydroxydimethylsiloxanes in the presence of pyridine as an HCl acceptor. At small lengths of the linear dimethylsiloxane link the copolymer yield is low. When studying heterofunctional polycondensation of dichlororganosiloxydiorganocyclosiloxanes with 1,5-dihydroxyhexamethyltrisiloxane after polymer reprecipitation in the mother solution low-molecular products were found which correspond to a bicyclic compound by their structure and composition[54]:

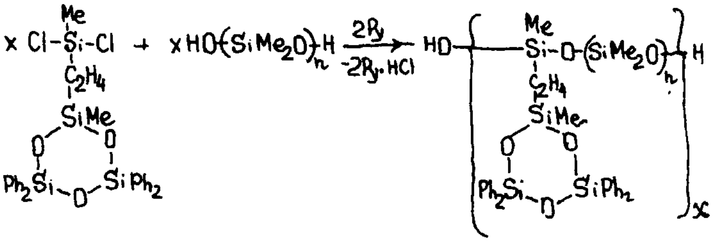


where R = R' = Me = Ph, R ≠ R', $m = 1,2,3$; $n = 1 \div 51$.

Depending on surrounding groups in silicon, the polymers obtained are transparent or slightly opalescent substances soluble in ordinary organic solvents with $\eta_{\text{spec.}} = 0.03 \div 0.2$. The yield is 75–92%. Low yields at small lengths of the dimethylsiloxane link are explained by the fact that, besides the reaction of intermolecular condensation, there takes place intramolecular cyclization with formation of bicyclic compounds.[35] The structure of the synthesized copolymers is identified by the IR and ^{29}Si spectra. Molecular masses, molecular mass distribution, characteristic viscosities, hydrodynamic and conformation characteristics are found. For copolymer with R = R' = Me, $m = 3$, $n = 1$, the polydispersion coefficient is estimated: $\varepsilon = \bar{M}_w/\bar{M}_n = 1.23$. For the same copolymer the value of the constant K in the Mark-Kuhn-Howinck equation is calculated: $K = (2.38 \pm 0.1) \times 10^{-4}$ as well as the value of the parameter $\alpha = (0.5579 \pm 0.004)$. Comparison of the equilibrium rigidity parameter of the copolymer with that of polydimethylsiloxane showed that the three-dimensional cyclic substituent in a molecule results in an increase in equilibrium rigidity ($A_0 = 27$ Å) compared to that of polydimethylsiloxane ($A_0 = 10$ Å).

Analysis of thermomechanical properties of copolymers[55] showed that replacement of one methyl group by a phenyl one in the silsesquioxane link leads to a rise in vitrification temperature by ~10°C.

Organosiloxane copolymers with regular arrangement of carbocyclotrisiloxane fragments in the side chain were synthesized in the reaction of heterofunctional polycondensation of methyldichlorosilylcarbocyclotrisiloxane with α,ω-dihydroxydimethylsiloxanes in the presence of pyridine by the scheme[56]:



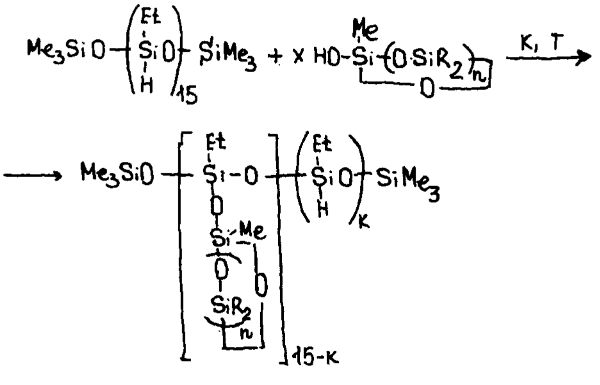
where $n = 2 \div 51$.

Comparison of thermal-oxidative stability of the copolymers with organosiloxane fragments in the side chain showed[52–54] that replacement of a part of methyl groups by phenyl ones both in a silsesquioxane atom of silicon and in a cycle results in a rise of decomposition starting temperature up to 280–300°C which is associated with a high resistance of phenyl groups to oxidation as well as with their inhibiting effect on oxidation of methyl groups.[57] Replacement of an oxygen bridge by an ethylene group results in slight decrease of thermal-oxidative stability of the copolymer.

With an increase in the volume of a cycle fragment, by replacement of a pentaphenylcyclotrisiloxane fragment by a heptaphenylcyclotetrasiloxane a slight decrease of thermal-oxidative stability takes place. A similar phenomenon is observed when a heptamethylcyclotetrasiloxane fragment is replaced by a nonamethylcyclopentasiloxane.

Comparison of thermal-oxidative stability of copolymers with phenylcyclosiloxane fragments in the side chain and copolymers containing cyclotetra-, -penta-, and -hexasiloxane fragments along the chain showed that they are characterized by approximately one and the same thermal-oxidative stability, since introduction of cyclic fragments in the side chain hinders the chain transfer reactions that proceed with release of the D-type cycles. Therefore, the authors claim that cyclic fragments in the side chain in the case of destruction behave like copolymers with cyclic fragments along the dimethylsiloxane chain.

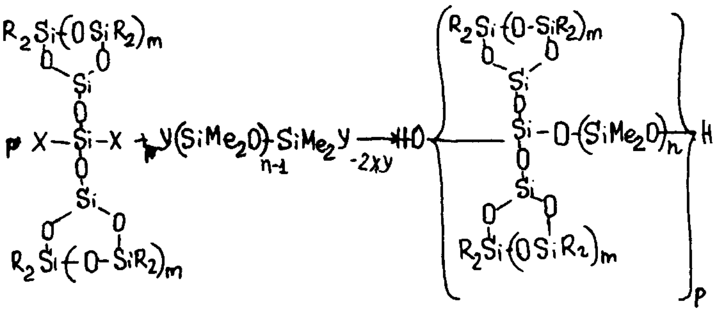
Ethylsiloxane oligomers with organocyclosiloxane fragments in the side chain were synthesized in the reaction of catalytic dehydrocondensation of oligoethylhydridsiloxane with end trimethylsiloxy-groups with hydroxyorganocyclosiloxanes in the presence of platinahydrochloric acid or anhydrous powdered potassium hydroxide as a catalyst at various proportions of the starting components at 40–60°C.[58] It was shown that at a starting component proportion of 1:15, the dehydrocondensation reaction does not run to the end, and dehydrocondensation of all the active centres is impeded (80%) which might be explained by steric difficulties due to organocyclosiloxane fragments at macromolecular chain formation. At the ratio of 1:7.5 the conversion of hydrogen is ~96%. The reaction proceeds according to the scheme:



where R = Me, Ph; n = 2,3.

Depending on surrounding groups, the products are transparent or slightly opalescent liquids, soluble in ordinary organic solvents. The reaction order, the rate constants of the catalytic dehydrocondensation reaction are determined, and it is shown that every time the temperature rises by 10°C, the reaction rate constants increase by a factor of 1.7.

Organosiloxane copolymers with bicyclic fragments in the side chain were synthesized in the reactions of heterofunctional condensation of organobicyclosiloxydichlorosilanes with α,ω-dihydroxydimethylsiloxanes at the starting components proportion of 1:1 in the presence of pyridine.[59,60] In this case the reaction proceeds by the scheme:



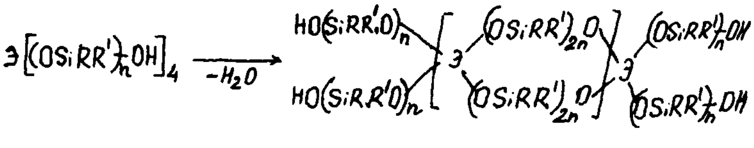
where $m = 1,2$; R = Me, Ph; $n = 1 \div 51$.

At small lengths of the dimethylsiloxane link the copolymer yields are low which can be explained by the fact that besides intermolecular condensation, there takes place intramolecular cyclization with subsequent formation of a tricyclic structure.

4. ORGANOSILOXANE OLIGOMERS AND COPOLYMERS CONTAINING SPIROCYCLIC FRAGMENTS IN THE CHAIN

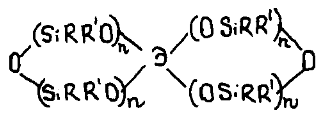
Synthesis of organosiloxane oligomers and polymers with spirocyclic molecular structure has been demonstrated.[61] During condensation of cross-like elementorganic oligomers with hydroxyl groups at the ends of the branches $\ni [(OSiR_2)_n\text{—}OH]_4$ the polymers with a net structure of molecules are formed only when the distance between the central atom of the oligomer and the functional group is long enough.

Condensation of tetrakis(diorganosiloxanehydroxy)silane or titanium with small values of n, soluble polymers are formed which points to the fact that the reaction of polycondensation of the mentioned compounds proceeds intermolecularly with formation of copolymers with spirocyclic structure.[62]:



where $n = 2,3$; $\ni$ = Si, Ti; R = R′ = Me; R = Me, R′ = Ph.

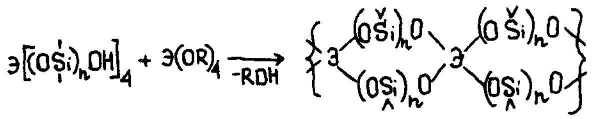
Soluble polymers with spirocyclic structure, low-molecular spirocyclic compounds are formed in small amounts with the following structure:



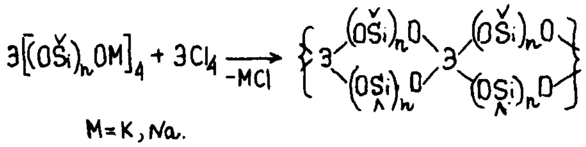
where $n = 2,3$; R = R = MEPh; R = R′; $\ni$ = Si, Ti.

The reaction partially proceeds by the mechanism of intramolecular cyclization. To obtain spirocyclic polymers, other types of the reaction were used,[63] in particular:

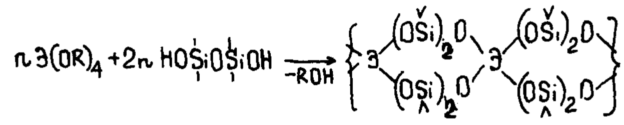
1. Polycondensation of tetrafunctional compounds:



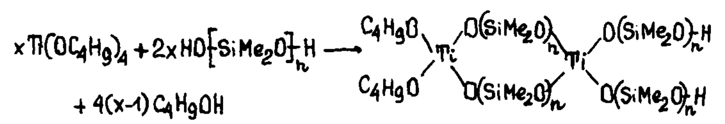
2. Exchange decomposition reaction:



3. Polycondensation of difunctional compounds with tetrafunctional ones:



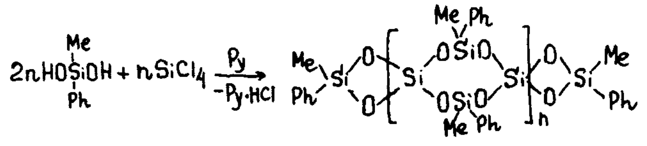
Polycondensation of tetrabutoxytitanium with α,ω-dihydroxydimethylsiloxanes is a particular case of the last reaction[64]:



where $n = 2 \div 4$.

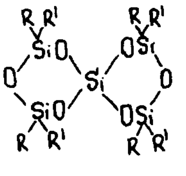
On completion of the reaction, soluble polymer products of spirocyclic structure are formed whose molecular mass does not exceed 3150. Low molecular mass polymers are explained by difficulties which arise of the approach of the reagent to the functional groups as well as the side reaction of etherification of hydroxyl groups released by butyl alcohol in the course of the reaction.

The problems of thermal treatment[65] and chemical conversions of methylphenylspirocyclosiloxane obtained in the reaction of silicon tetrachloride with methylphenyldihydroxysilane in the presence of pyridine as an acceptor by the following scheme:



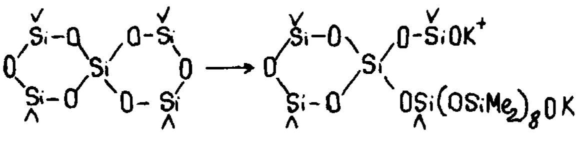
Thermal polymerization of methyphenylspirocyclosiloxane at various temperatures showed that a rise in the polymerization temperature does not change the dependence of the gel fraction content on polymerization time, but produces an effect only on the rate at which the maximum content of the gel fraction is achieved.

Polymerization of organospirobicyclosiloxanes having the following structure[66]:

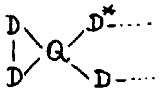


where R = R′ = Me, Ph; R = R′, indicated that in the case of polymerization of such bicycles at 150°C in the presence of a homogeneous nucleophilic initiator of α,ω-dipotassiumoxydimethylsiloxane ($n = 8$) depends on the groups surrounding in a silicon atom, they form either three-dimensional products insoluble in organic solvents or completely soluble products, octamethylspiro-5,5-pentasiloxane transforms to gel completely.

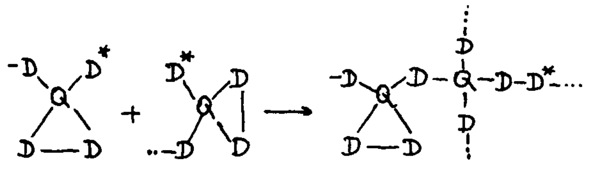
Replacing a methyl groups in silicon in the bicycle by phenyl groups, along with the formation of a product having a three-dimensional cross-linked structure, a soluble polymer is also formed, with the gel-fraction content in the polymerization products decreasing. When the bicyclic group has R = R′ = Ph, then only soluble polymers are obtained with $\eta_{sp} = 0.1$. In the process of polymerization of a spirane bicyclic compound the growing polymeric chain enters into two competitive reactions, according to the schemes:



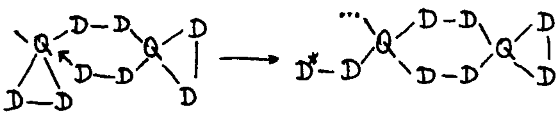
or



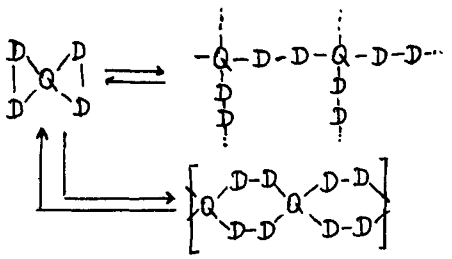
The interchain interaction is



The internal polymerization is

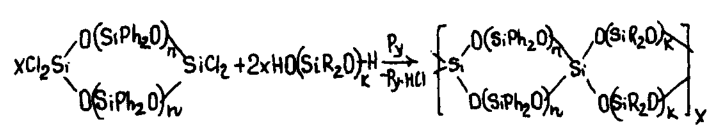


The polymerization process develops in two directions[65] and that is of equilibrium character:



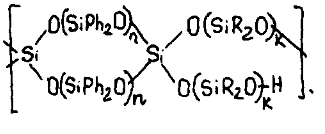
For spirocyclic structures tetrafunctional cyclic fragments prepared in advance in which one cyclic grouping is always preserved.

Heterofunctional polycondensation of tetrachlororganocyclotetra- and -hexasiloxanes with dihydroxydiphenylsilanes or 1,3-dihydroxytetraphenyldisiloxane in the presence of pyridine in the solution of anhydrous toluene, oligoorganospirocyclosiloxanes were synthesized which completely dissolve in ordinary organic solvents according to the scheme[67,68]:

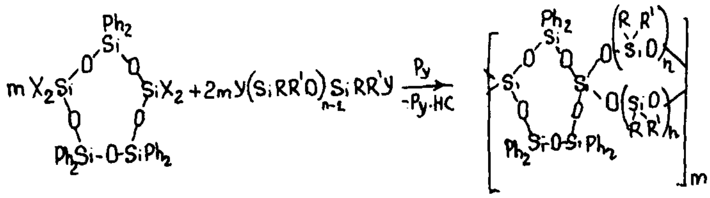


where $n = m = 1$; $n \neq m$; $k = 1,2,3$; R = Me, Ph.

When constructing a spirocyclic structure the authors do not exclude formation of a defect structure due to i.e. formation of incomplete cyclization:



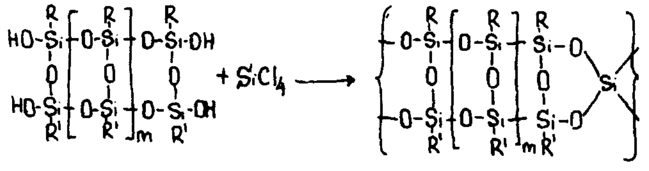
Similarly, in case of the polymerization of 1,1,5,5-tetrachloro- and 1,1,5,5-tetrahydroxyhexaphenylcyclopentasiloxanes with α,ω-dihydroxy and α,ω-dichlorodiorganosiloxanes with the starting component ratio of 1:2 in the 60% solution of anhydrous toluene in the presence of pyridine, the reaction proceeds, according to the scheme[69]:



X = OH, Y = Cl; R = R′ = Me, Ph; *n* = 1,2,3.
X = Cl, Y = OH; R = Me, R′ = Ph.

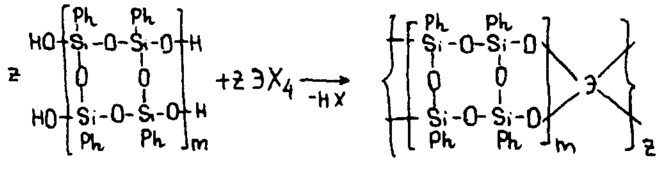
A comparative estimation of thermal-oxidative stability of oliorganospirocyclosiloxanes has shown that the oligomers consisting of only cyclotetrasiloxane fragments have the highest stability (5% mass losses for these oligomers are observed at 480°C). Introduction of large cyclic fragments into the chain results in decrease of their thermal-oxidative stability.

The compounds, containing fragments of spiro- and ladder structures in the chain simultaneously, represent rather an interesting group. Such polymers are obtained by heterofunctional condensation of tetrafunctional polycyclic (ladder) compounds with silicon tetrachloride, the most favourable conditions for spiroladder structure formation are created when in the initial period the reaction proceeds at low temperature in concentrated solutions[70,71]:



where R = Ph, R′ = iso-C_4H_9, *m* = 2.

Similarly, copolymers[72] with a spiroladder structure were synthesized by polycondensation of oligotetrols with cis-anti-cis-tactic structure with silicon tetrachloride at low-temperature in the presence of an acceptor. At high temperature, polycondensation of oligotetrols with tetraethoxysilane and tetrabutoxytitanium, copolymers of a similar structure were synthesized by the scheme:



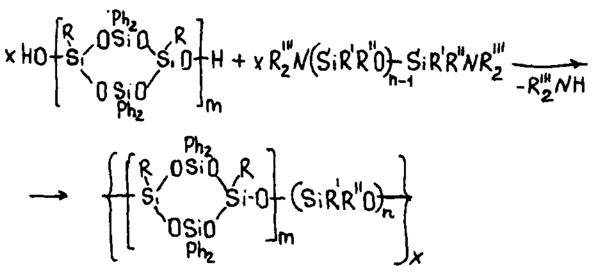
where X = Cl, CC_2H_5, OC_4H_9. Э = Si, Ti. *m* = 5 ÷ 46.

In all cases, both at low- and high-temperature polycondensation, completely soluble copolymers are obtained which preserve the cis-anti-cis-tactic structure of the polycyclic ladder block.

Copolymers of similar structure were also obtained by heterofunctional polycondensation of phenethylcontaining oligotetrols of various degrees of condensation with tetrachlorosilane and tetrabutoxytitanium.[73]

5. ORGANOSILOXANE BLOCK-COPOLYMERS OF CYCLOLINEAR STRUCTURE

Organosiloxane block-copolymers of cyclolinear structure were obtained in the reaction of heterofunctional polycondensation of dihydroxycontaining oligomeric prepolymers with α,ω-diamino(bisdimethylamino)diorganosiloxanes at the starting components ratio of 1:1, according to the scheme[74]:



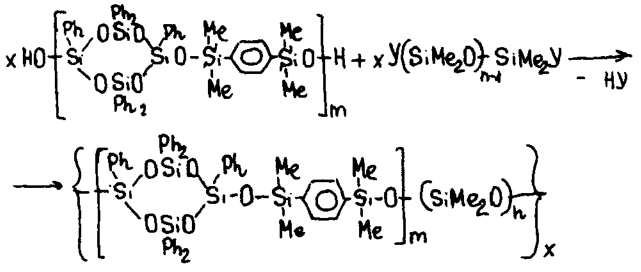
where R = Me, Ph, $m = 10 \div 28$; $R' = R'' =$ Me, Ph; $R' = R''$, $R''' =$ H, Me.

The reaction in solution or solid in the temperature range from 20 to 100°C, at $m < n$. When $m \geq n$, the reaction takes place at 100–150°C. Ammonia or diethylamine released in the course of the reaction is distilled in the process of vacuum synthesis. As is pointed out in References 74 and 75, the suggested method of synthesis of cyclolinear block-copolymers is simple and does not require any additional purification of by-products formed during the reaction.

Occurrence of a block structure (phase incompatibility) in copolymers must be connected with the value (m, n) of rigid and flexible fragments in the block-copolymer. In the copolymers consisting of dimethylsiloxane and cyclosiloxane blocks,[13] the value of n for the dimethylsiloxane block from which flexible block properties start to reveal, must be higher than 20, while in polycyclic blocks even with $m = 3 \div 5$ there occur properties characteristic of rigid block systems. Therefore, at certain values of m and n segregation processes take place resulting in formation of domains for rigid and flexible blocks separately.

The block structure formation established by thermogravimetric and X-ray analyses.[75] The former has shown that block-copolymers are stable up to 350–400°C.

Arylencyclosiloxane block-copolymers were synthesized by heterofunctional condensation of dihydroxycontaining arylencyclosiloxanes with α,ω-dichlo(bisdimethylamino)dimethylsiloxanes. As a result transparent or slightly opalescent hard or viscous (depending on the value of n) copolymers were obtained which easily dissolve in various organic solvents.[76] The depth of arylencyclosiloxane polycondensation with α,ω-bis(dimethylamino)dimethylsiloxanes is somewhat greater than that with α,ω-dichlodimethylsiloxanes. The reaction proceeds by the scheme:

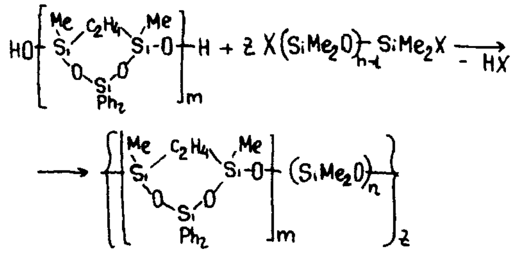


where Y = Cl, Me_2N; $m = 4 \div 16$, $n = 2 \div 66$.

Comparative thermogravimetric studies showed that 5% mass losses in such copolymers are observed at temperatures from 400 to 450°C. With an increase of the arylensiloxane fragment length, the thermal-oxidative stability of the block-copolymers increases.

Thermomechanical and X-ray analyses showed that at small lengths of the dimethylsiloxane link the polymers are monophased, and the maximum distance is observed at small lengths of the dimethylsiloxane link ($n = 2$). With $n = 32$ and more and with $m \approx 4$ there is a phase separation in the copolymers. This transformation into a two-phase structure is explained by the arylencyclosiloxane fragments being isolated into a separate phase. For the first time arylencyclosiloxane block-copolymers of the $(AB)_mC_n$-type[76] were synthesized and a possibility of regular alternation of arylencyclosiloxane and dimethylsiloxane fragments in the chain was shown.

Organosiloxane block-copolymers with cyclocarbosiloxane fragments in the chain were similarly synthesized by heterofunctional polycondensation of dihydroxycontaining organocyclocarbosiloxane oligomers with α,ω-dichloro(bisdimethylamino)dimethylsiloxanes by the following scheme[77]:



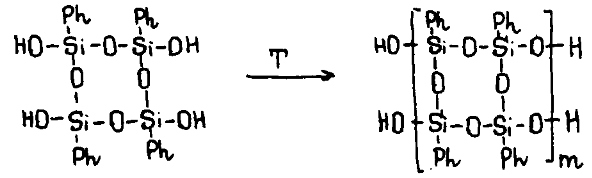
where X = Cl, Me_2N; $m = 5 \div 16$; $n = 2 \div 61$.

At small values of ($m \leq 5$) and with $n = 25$ no phase separation in the block-copolymers is observed. Only at certain values of $m \geq 10$, it is possible to observe phase separation in copolymers which can be revealed from thermomechanical and X-ray data.

Ladder polymers are characterized by high thermal stability, their application in technology is associated with certain difficulties due to high vitrification temperatures. To improve their properties, plasticization of ladder polymers with linear diorganosiloxane is carried out.

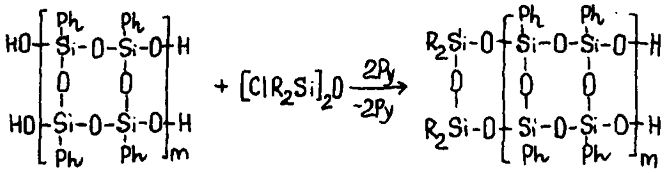
Organosiloxane block-copolymers with ladder fragments in the form of suspensions in the dimethyloxane chain were synthesized by heterofunctional polycondensation of difunctional polyphenylsiloxanes containing the *T* links (C_6,H_5,$SiO_{1.5}$) with α,ω-dichlorodimethylsesquioxanes containing *D* links (Me_2SiO) which radically differ in type of chains formed persistent length for polydimethylsiloxane is 10 Å and that for polyphenylsilsesquioxane - 150 Å.

Difunctional polyphenylsilsesquioxanes were obtained by homofunctional polycondensation of cis-1,3,5,7-tetrahydroxy-1,3,5,7-tetraphenylcyclotetrasiloxane (tetrol) in the solution by the scheme:



where $m = 3 \div 40$.

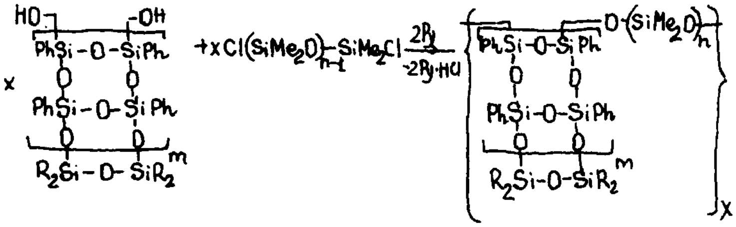
When the product of tetrol thermal condensation is boiled over activated carbon, the polycondensation reaction depth increases ($m > 10$). Then a partial blocking of the residual hydroxyl groups was conducted with 1,3-dichlorotetraorganodisiloxanes in 5% diluted solution by the scheme:



where R = Me, Ph; $m = 3 \div 37$.

The starting components proportion is violated after partial blocking, compounds without functional groups could be formed.[78] However, the presence of these compounds does not prevent the use of the main products in the further reaction of polycondensation.

During polycondensation of dihydroxypolyphenylsilsesquioxane with α,ω-dichlorodimethylsiloxanes in the 60–70% of dry benzene at 20 ÷ 40°C, white powdered polymers were obtained completely soluble in organic solvents with $\eta_{spec.} = 0.05 \div 0.35$ and T_{vit} ranging from −123 to −300°C, depending on the length of the linear component *n*. Hydrodynamic studies of copolymers showed they resembled regular linear structure. The reaction proceeds by the scheme:



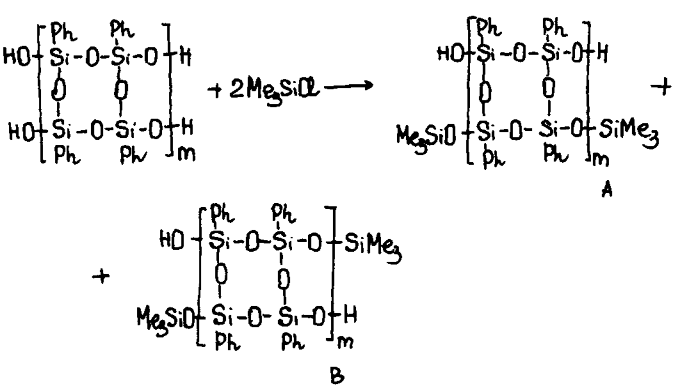
where R = Me, Ph; m = 3,10,37; n = 1 ÷ 108.

In the IR spectra of the copolymers there is a wide absorption band with a pronounced maximum at 1140 cm^{-1}, while in the products of thermal condensation of tetrol in the presence of anionic catalysts in this region one can always observe splitting of the maximum and for the compounds with molecular mass of 3000–5000 these maximums are arranged at 1045–1155 cm^{-1}; with an increase of molecular mass of polyorganosilsesquioxane the first maximum rises with respect to the second one.[79]

At small lengths of the dimethylsiloxane link (n = 1 ÷ 10) the copolymers are monophased regardless of the polycyclic block. As is shown, with an increase of $n \geqslant 25$, phase incompatibility starts showing up in the diffractograms. In addition to the diffraction maximum d_1 = 11.0 ÷ 13.0 Å a diffraction maximum at 7.8 Å appears. With an increase of n, the intensity of this maximum characterizing the interchain distance between linear dimethylsiloxane links increases, thus pointing to the fact that in the block copolymers under study there can take place packing both of the main chains and side branches from the main one. One of the phases is represented by structures consisting of densely packed, placed in parallel side branches of the ladder structures of mesomorphic character, while the second phase is represented by an amorphous structure which is similarly observed in polydimethylsiloxane.

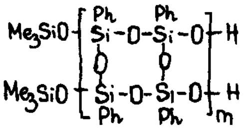
Thermogravimetric analysis showed[75] that the synthesized block-copolymers are characterized by a high thermal stability. The beginning of the main destruction process, as a result of introduction of polycyclic fragments into the dimethylsiloxane chain shifts by ~100°C towards higher temperatures compared to linear polydimethylsiloxanes. With an increase of the polydimethylsiloxane link length, mass losses increase, and an increase of the polycyclic block length from 3 to 37 does not lead to a noticeable rise of thermal stability. The authors of Reference 75 come to a conclusion that thermomechanically the optimal version of plasticized polyphenylsilsesquioxane corresponds to a copolymer with a small value of dimethylsiloxane links and polycyclic blocks which are blocked by organic groups and consist of three ladder links.

In contrast to Reference 75, a partial blocking of hydroxyl groups of oligotetrols is carried out by heterofunctional condensation of oligotetrol with trimethylchlorosilane at the starting components ratio of 1:2 in the presence of pyridine by the scheme:

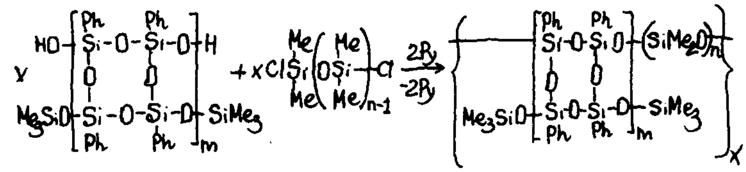


where $m = 3 \div 20$.

The blocking proceeds in two directions. However, the authors do not exclude that the reaction can proceed differently with formation of the following products:

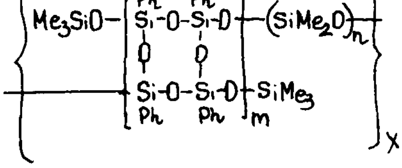


Polycondensation of difunctional polyphenylsilsesquioxanes with α,ω-dichlorodimethylsiloxanes in the presence of pyridine leads to formation of block-copolymers,[76] according to the scheme:



where $m = 3, 10, 20$; $n = 2 \div 35$.

The possibility of reaction of heterofunctional polycondensation leading to formation of block-copolymers, in which, apart from the block-copolymers of the above-mentioned structure, there can also exist block-copolymers of the following structure:

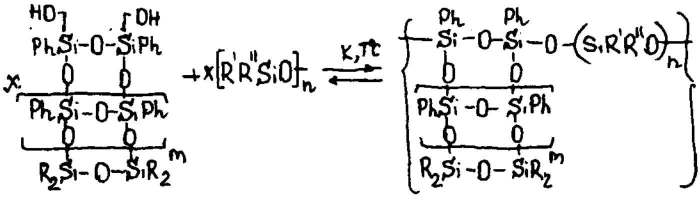


It is known that 1,3- and 1,5-arrangement of monocyclotetrasiloxane fragments[7] in the dimethylsiloxane chain does not have a marked influence on physico-mechanical properties and thermal stability of copolymers. In the case of block-copolymers containing polycyclic fragments the arrangement either along the ridge or along the diagonal in the linear chain does not produce any serious influence on the properties of such block-copolymers. The copolymers preserve cis-anti-cis-tactic structure of polyphenylsilsesquioxane blocks. Comparative estimates of thermal-oxidative stability of the copolymers showed that arrangement of the ladder fragment in the chain, along the chain or in the form of suspension does not produce any marked effect on thermal stability of the copolymers. Neither does the length of the polycyclic fragments.

The length of the dimethylsiloxane fragment has a certain influence on the phase state of the synthesized block-copolymers. As is shown,[76] at a small length of the dimethylsiloxane link ($n = 2 \div 15$) the copolymers represent a monophase system with one T_{vit}. An increase in the length n leads to formation of a two-phase system which points to a microdomain structure of these block-copolymers.

At a high content of ladder blocks they represent a continuous phase in which discrete aggregates of dimethylsiloxane fragments are distributed. Formation of the microdomain structure is observed only at certain values of m and n. X-ray analyses, too, proved that the system is two-phase. It was shown[75] that the interchain distance d_1 in the block-copolymers is comparable with that of the block-copolymers containing polycyclic fragments in the form of a suspension.[78]

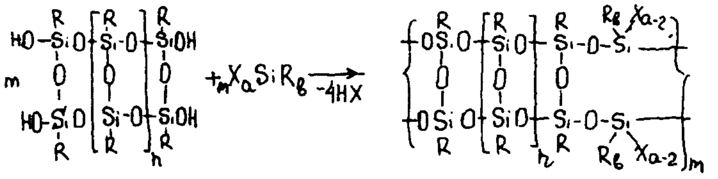
Copolymers containing polyphenylsilsesquioxane fragments in the chain in the form of a suspension are also obtained by a polymerization-exchange reaction of polycyclic diols of different lengths with organosiloxanes by the scheme[80]:



where R = MePh; R′ = R″ = Me, Ph; m = 2,20,40.

Investigation of the reaction has revealed that polycyclic diol is a part of the macromolecule. The organic surrounding of cyclotri- and cyclotetrasiloxanes as well as the size of the polycyclic blocks have an effect on the course of polymerization and the properties of the cyclolinear polymers. However, it should be noted that unlike the results of Reference 78, irregular copolymers are obtained.

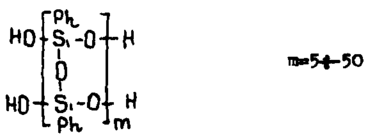
Block-copolymers were obtained as a result of condensation of tetrafunctional ladder alkyl(aryl)silsesquioxanes with silandiols and organochlorosilanes, according to the scheme[81,82]:



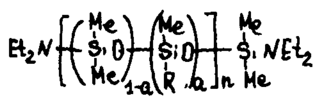
where R = Me, Ph; X = Cl, OH; a = 2–3, b = 1–2.

Since in the process of homofunctional condensation the probability of the reaction between siloxandiols of the same structure is rather high, regulation of the exact number of siloxane links in the blocks is rather complicated. During heterofunctional condensation in the conditions when homofunctional condensation does not take place, it is possible to obtain block-copolymers with exactly predetermined structure without homopolymer impurities.

Polycondensation of phenylsilsesquioxanes with the general formula:

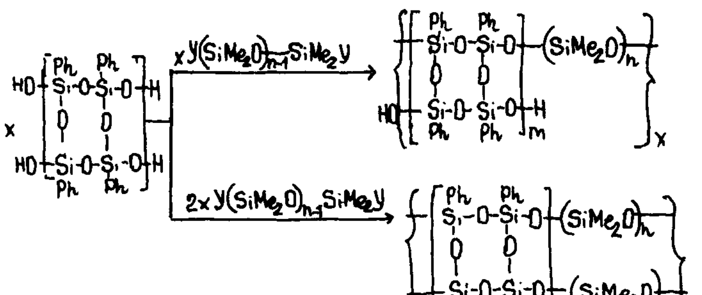


with α,ω-bis(diethylamino)- or α,ω-dichlorodiorganosiloxanes[83]



where $a = 0 \div 0.33$; $h = 20 \div 250$; R = MePh in a mole ratio of the components from 1:1 to 1:3.1, respectively, at certain stages of conversion leads to gel-formation. It was established that the maximum tendency to gel-formation was revealed at the mole ratio of polyphenylsilsesquioxane to α,ω-bis(diethylamino)diorganosiloxane of 1:2. It was also found that the gel-formation time increases with an increase of n in the linear organosiloxane.

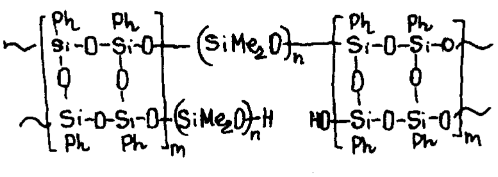
Heterofunctional condensation of tetrahydroxyoligophenylsilsesquioxanes with α,ω-bis(diethylamino)- or α,ω-dichlorodiorganosiloxanes[84] in a mole ratio of 1:1 and 1:2 result in copolymers with one- and two-strand diorganosiloxane fragments in the chain, according to the scheme:



where Y = Cl, Me_2N; $n = 1 \div 66$; $m = 5 \div 46$.

The polycondensation results in completely soluble copolymers,[83] which is explained by cis-anti-cis-tactic structure in the copolymers obtained in which the cis-syndiotactic configuration prevails.

Copolymers with two-strand dimethylsiloxane fragments in the chain there exist defect structures as:



Thermogravimetric studies have shown that an increase of the polycyclic block length from $m = 10$ to $m = 46$ does not lead to a significant rise in the thermal-oxidative stability. The latter increases at transition of copolymers with one-strand dimethylsiloxane fragments to copolymers with two-strand dimethylsiloxane fragments.

Thermomechanical investigations have shown that at small lengths of dimethylsiloxane fragments, the copolymers with two-strand dimethylsiloxane links are characterized by an elevated vitrification temperature. Increase of the length of the dimethylsiloxane fragment $n \geqslant 32$ results in the occurrence of a two-phase structure and, hence, on the thermomechanical curves there appear two vitrification temperatures: for rigid and flexible phases.

Data from X-ray analyses agree with thermomechanical studies. Only at certain values of the dimethylsiloxane link n a third diffraction maximum appears on the diffractograms characterizing the interchain distance in polydimethylsiloxane indicating that the system is two-phase, i.e. that the block-copolymer structure has been formed.

In contrast to the above mentioned methods, in which blocks of different character are formed in advance, and block-copolymer formation takes place via heterofunctional polycondensation of the oligomer blocks, the authors of Reference 85 used another principle of block copolymer synthesis consisting in that formation of rigid copolymers took place directly in the process of copolymer formation. Using polyfunctional oligomers of the formula $Cl_xR_{3-x}SiO[SiMe_2O]_nSiR_{3-x}Cl_x$, obtained under controlled conditions as well as $PhSiCl_3$, it is possible to grow rigid phenylsilsesquioxane blocks in a block-copolymer at hydrolythic condensation. However, the hydrogen chloride released in the process of synthesis can lead to splitting of the siloxane bond, and, besides, it is very difficult to regulate the polycyclic block length at hydrolithic condensation.

Some of the organosiloxane copolymers and block-copolymers were tested as binders for glass reinforced plastics and antifriction materials, carbo- and heterochain polymer modifiers, hydrophobization of various materials, corrosion-resistant coatings, etc.

Oligomethylsiloxane copolymers of cyclolinear structure with cyclic diphenylsiloxy- and vinylsilsesquioxane fragments in the chain can be used as modifying ingredients (0.5–2% of the rubber mass) of rubber mixtures based on carbochain elastomers.

Organosiloxane oligomers and copolymers of cyclolinear structure due to their high thermal-oxidative stability and good processibility into products are recommended as binders for producing coatings and composite moulding materials,[85] carbon-filled plastics,[9] composite plastics[21] and for the fixed phase in chromatography.[11]

Organosiloxane block-copolymers with polycyclic fragments in the macromolecular chain have a high thermal stability in air and can be used as binders in solid lubricants.

Polyphenylsilsesquioxanes with polycyclic chains of molecules were used as binders for new heat resistant glass-cloth-base laminates. Comparative tests of the latter have shown that they have a higher bending strength after ageing at 350°C during 1000 hours (σ_{bend} = 100 ÷ 130 MPa) than glass-cloth-base laminates based on well-known polyphenylvinylsilsesquioxanes (63 MPa).

Polyorganosiloxanes with bicyclic and polycyclic fragments in the linear diorganosiloxane chain presented themselves in a good light for development of antifriction self-lubricating materials. It is established that the developed materials have more stable friction coefficient and can be used as materials for plain bearings.

The introduction of a titanium atom into spiroladder polyphenethylsilsesquioxanes increases their adhesion to various materials which predetermines application of synthesized titaniumcontaining polyphenethylsilsesquioxanes for production of thermoplastic coatings on a triacetate photographic film, china, glass[73] as well as film-forming materials for temporary corrosion-resistant coatings for copper, steel, brass. Such coatings are characterized by high impact strength.[86]

Thus, as one can see from the review, modification of linear diorganosiloxane copolymers with cyclic and polycyclic fragments in the chain is a promising trend in organosilicon chemistry and has found a wide application in practice. In cyclolinear copolymers one can vary the linear chain length, thus regulating the network density at their transformation into a three-dimensional structure without the release of volatile substances.

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