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Preparation, properties and applications of oligomeric and polymeric organosilanes

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Abstract. The studies devoted to methods of preparation of oligomeric and polymeric organosilanes, their properties and their use are reviewed. Industrial sources, as well as processes underlying the laboratory syntheses of these compounds are analyzed. Characteristics of the silicon – silicon σ-bond and electronic interactions in oligoorganosilanes are discussed. Physicochemical properties of oligomeric and polymeric organosilanes and their known and prospective applications are considered. The bibliography includes 336 references.

I. Introduction

Organopolysilanes are silicon analogues of saturated hydrocarbons.† Traditionally, this class of compounds includes all the organic silicon derivatives possessing silicon – silicon bonds, *viz*.: disilanes R_3SiSiR_3, oligosilanes $R_3Si(SiR_2)_n.SiR_3$, cyclosilanes $(R_2Si)_n$ [including polycyclic silanes $(RSi)_n$], polymeric organosilanes of linear $[-(R_2Si)_n-]$, branched $[(RSi)_n]$ and dendritic structure. The formal analogy with saturated hydrocarbons is poorly supported by their chemical properties. Most of reactions proceeding with participation of silicon – silicon σ-bonds are not typical of carbon – carbon σ-bonds. For instance, organopolysilanes readily (*i.e*. at room temperature) react with halogens, chlorides of copper, tungsten, molybdenum, peroxyacids, amine *N*-oxides, while saturated hydrocarbons are inert to these reagents under similar conditions. Organopolysilanes absorb radiation in the UV region and are photochemically active compounds, whereas saturated hydrocarbons are stable to UV light. At the same time the compounds of both classes disproportionate under the action of aluminium chloride.

The literature on the chemistry of oligomeric and polymeric organosilanes is quite extensive. There are more than 100 reviews [1 – 113] considering different aspects of synthesis, physical and chemical properties of these compounds, as well as those of disilenes and silylenes, which are structurally close to them. The main topics of these reviews are the following:

— preparation and properties of oligosilanes (see reviews [3, 5, 7, 9 – 11, 23, 27, 28, 32, 33, 42, 55 – 57, 106, 107]);

— chemistry of inorganic polysilanes;[4 – 8, 22, 23, 25, 56]

— cyclic organopolysilanes (see reviews [1, 2, 24, 27, 29, 30, 34, 61, 87 – 89]);

— spectroscopy and intramolecular interactions in the molecules of oligomeric and polymeric organosilanes (see reviews[18, 19, 31, 34, 43, 44, 58, 60, 77 – 79, 81, 82, 84 – 86]);

— physicochemical properties of the silicon – silicon bond;[18, 23, 26]

— photochemisry of oligomeric[13 – 15, 17, 20, 54, 93] and polymeric [16, 46, 50, 65 – 68, 80] organosilanes;

— thermal reactions of di- and oligosilanes;[53, 59, 90]

— synthesis and properties of polymeric organosilanes;[35, 36, 45 – 49, 66, 70, 73, 83]

— synthesis and properties of polymers including alternating oligosilanyl and organic fragments;[71, 72, 75]

— studies of mechanisms of processes leading to polymeric organosilanes;[74]

— transition metal complexes with oligosilane ligands;[76]

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† The true analogues of saturated hydrocarbons, silicon hydrides Si_nH_{2n+2}, represent compounds highly active to oxygen and alkali. Their activity is determined by the Si – H bonds rather than by the bonds Si – Si. The first member of the series, silane, which has no silicon – silicon bond, but contains four Si – H bonds, is oxidized by oxygen from air with explosion. Introduction of organic substituents significantly stabilizes silicon hydrides, and fully substituted derivatives (like hexamethyldisilane) are much more stable against oxygen, moisture, acids and alkali.

— activation of the silicon–silicon bond by transition metal complexes and bissilylation of organic compounds by organodisilanes;[13, 110]

— polymerization of silicon organohydrides under influence of transition metal complexes with formation of polyorganohydrosilanes;[48, 109, 111, 112]

— reactions of silicon chlorides with alkali metal with formation of four-membered rings with the silicon–silicon bonds $\overline{SiR_2SiR_2CH_2CH_2}$;[62, 91]

— preparation of silyllithium compounds from organodisilanes;[108]

— radical reactions of oligosilanes;[113]

— rearrangements of polysilane chains;[12]

— reactions of oligoorganosilanes with organic peroxides;[106]

— oxidative destruction of the silicon–silicon bond;[107]

— chemistry of disilenes;[37–40]

— chemistry of silylenes;[41, 90, 92–95, 97–105]

— applied aspects of the chemistry of polymeric and oligomeric organosilanes.[51, 52, 63–68, 71, 82]

The studies of oligoorganosilane properties is considered by the authors of the reviews [3, 9] as a part of a general study of homocatenates of Group 14 elements, *i.e.*, of compounds with chains formed by the silicon, germanium, tin or lead atoms.

For the first time high-molecular polydimethylsilane $-(Me_2Si)_n-$ was obtained in 1949 by Burkhard [42, 64, 66] in the course of interaction of sodium with dichlorodimethylsilane. After discovery by Yajima [51–53] of processes of polydimethylsilane transformation into polymethylcarbosilane and then into the final product, high-tensile thermostable silicon carbide fibre, industrial production of polydimethylsilane began. The researches of Yajima stimulated studies in the fields of synthesis of polymeric organosilanes and processes of their thermal decomposition.[51–53, 63] Polymethylcarbosilane $-(SiHMeCH_2)_n-$, which transforms into silicon carbide upon heating, is used not only for the fibre preparation, but also as a binder of SiC powders in the manufacture of monolithic parts by the hot pressing of silicon carbide. In this regard, there had been numerous publications and patents by authors who were trying to obtain polycarbosilane binders with improved properties.

Some fundamental and applied aspects in the chemistry of oligo- and polysilanes relate to their outstanding ability to absorb UV irradiation.[13–17, 54, 65–70] After absorption of a light quantum, the Si_n chain breaks resulting in the formation of two silicon-centred radicals or one silylene. High reactivity of these species was used for photoinitiation of radical polymerization of styrene and other organic monomers [35, 42] and for cross-linking of polyorganosiloxane molecules according to radical [16] or silylene mechanisms. On base plates, polymeric organosilanes form air-stable thin films, which are used in microelectronics for manufacture of printed circuit boards by photolithography.[64–68] Pure polymeric organosilanes are insulators, although upon doping by Lewis acids they become semiconductors. Some conducting materials were obtained by doping. Polymeric organosilanes reveal the photoeffect, their irradiation results in appearance of a charge (*viz*. a hole), which moves fast in the electric field. High photosensitivity of the films and large drift mobility of the holes allow one to use organopolysilanes in electrophotography.[81, 82] Thorough studies of thin films and solutions of various organopolysilanes revealed their photo-, thermo-, piezo-, iono- and solvatochromism.[66, 69, 70]

The silicon–silicon σ-bond (σ_{Si-Si}) is characterized by high polarizability and readily takes part in conjugation with neighbouring σ_{Si-Si}-bonds and also with π- and n-electrons of unsaturated and n-donor (OR, NR_2, SR, F, Cl, Br) substituents. The conjugated system of the σ_{Si-Si}-bonds in oligosilanes is easily polarized by terminal substituents. If electron-withdrawing and electron-donating groups are attached to the different ends of an oligosilane chain, an asymmetric molecule with strong charge displacement is formed. Such compounds show strongly pronounced nonlinear optical properties. The second order optical nonlinearity is also exhibited by polymeric organosilanes.[66] Oligosilanyl hydrides are effective reducing agents, they found their use in the fine organic synthesis.[113] Processes of thermal decomposition of volatile oligosilanes in the gas phase are very important for production of new organosilicon monomers,[97–102] epitaxial films of silicon carbide and silicon nitride and hydrogenated amorphous silicon α-Si:H, the latter is a principal material for transformation of the solar energy into electric one.[114] Oligosilanyl groups are widely used in chemistry of organometallic and coordination compounds.[103]

The chemisty of silylenes,[41, 54, 59, 90, 92–105] disilenes [37–39, 96] and silaethylenes [40, 62, 91, 96] is closely relates to the oligosilane chemistry. A series of both short-lived and relatively stable members of these classes of compounds were obtained from oligosilanes. For instance, dimethylsilylene,[13–15] is formed upon photolysis of permethylated oligomers $Me(Me_2Si)_nMe$ ($n > 3$) and cyclosilane $(Me_2Si)_6$, while dichlorosilylene [92, 94, 97–102, 104] and methylmethoxysilylene [92, 94, 95] are produced upon thermal decomposition of hexachlorodisilane and 1,2-dimethyltetramethoxydisilane, respectively. The first relatively stable compounds with double bonds between silicon atoms (disilenes) and between silicon and carbon atoms (silaethylenes, silenes) were obtained by UV irradiation of oligosilanes.[37–40, 96] For example, photolysis of sterically saturated 2,2-dimesitylhexamethyltrisilane $(Me_3Si)_2SiMes_2$ results in formation of tetramesityldisilene $Mes_2Si{=}SiMes_2$, while tetrasilane $(Me_3Si)_3SiC(O)R$ gives silaethylene $(Me_3Si)_2Si{=}C(OSiMe_3)R$. It follows from the above that oligomeric and polymeric organosilanes have extremely interesting physical and chemical properties.

The aim of the present review consists in analysis of recent publications on chemistry of oligo- and polysilanes and in drawing up a holistic view of the major achievements in this important field of organosilicon chemistry over the past 50 years. In the literature in Russian, the chemistry of compounds containing silicon–silicon bonds is considered in only three reviews,[103, 107, 112] dealing with some particular aspects of this extensive theme. At the same time, there are not only numerous reviews in English (see, for instance, Refs 1–19, 22, 24–27, 30–32, 34–39, 41, 55–57, 64–66, 71, 72, 87, 93, 95, 96, and also Refs 98, 104, 108, 110, 111, 113), but also the monograph,[21] several paper proceedings,[20, 28, 29, 40, 45, 51, 58, 61, 67–70, 88] and some book series,[23, 33, 42, 73, 92, 94] entirely or in part devoted to chemistry of oligo- and polysilanes. The present review pays more attention to achievements of Russian scientists than the reviews listed above.

II. Industrial sources of oligoorganosilanes and oligochlorosilanes

The industrial production of organosilicon monomers [115–117] is based on interaction of methyl chloride with elemental silicon (a mixture of powdered silicon and copper or their alloy, so-called contact mass, is used). Along with the target compounds (Me_2SiCl_2, $MeSiCl_3$, Me_3SiCl, $MeHSiCl_2$), this gives a mixture of high-boiling products (distillation residue). It mainly consists of three types of compounds,[118] those are chloromethyldisilanes, chloromethyldisiloxanes and chloromethylcarbosilanes. Distillation (150–160 °C) of the distillation residues results in easy isolation of a mixture of disilanes [disilane fraction (DSF)] containing 1,2-dimethyltetrachlorodisilane and 1,1,2-trichlorotrimethyldisilane as the major products and 1,1- and 1,2-dichlorotetramethyldisilanes in small amounts.[57] The distillation residues and DSFs are distilled, and the fractions obtained are analyzed by gas-liquid chromatography and chromatography–mass spectrometry.[116,119,120] DSF usually contains 1,2-dimethyltetrachlorodisilane in the largest amount. Of all chloromethyldisilanes $Si_2Me_nCl_{6-n}$ ($n = 1-5$), this compound is most accessible, it can readily be obtained as a pure substance by treatment of DSF with dry hydrogen chloride in presence of aluminium chloride. Under these conditions disilanes with $n = 3-5$ transform into $Si_2Me_2Cl_4$, which is relatively stable against further demethylation and can be easily isolated by distillation.[121] The compounds like $ClMe_2SiSiMeCl_2$ and $ClMe_2SiSiMe_2Cl$ are produced upon treatment of DSF with chlorotrimethylsilane in presence of catalyst ($AlCl_3$) and promotor ($MeHSiCl_2$).[122,123] A suitable method of preparation of chloropentamethyldisilane and 1,2-dichlorotetramethyldisilane is catalytic ($AlCl_3$) disproportionation of the hexamethyldisilane and 1,2-dimethyltetrachlorodisilane mixture.[124] Tetramethylsilane, a side product of the direct synthesis of the organosilicon monomers, can be used as a methylating agent,[125] however its utilization is less convenient than that of Me_3SiCl and Me_6Si_2 as it requires use of an autoclave.

According to the paper [126] there is the only disilane among the products of the direct synthesis of chloroethylsilanes (EtCl + Si/Cu), it is $EtCl_2SiSiEtCl_2$ (25% in the vat residue). Disilanes are practically not formed in the continuous industrial organomagnesium synthesis (EtCl + Mg + $SiCl_4$), the content of the only disilane, $EtCl_2SiSiCl_2H$, in the vat residue is only 0.08%.[127]

The cheapest and most accessible source of hexachlorodisilane is the vat residues of large-tonnage industrial production of tri- and tetrachlorosilanes based on interaction of hydrogen chloride with elemental silicon.[115,117] It is known from the studies [128,129] that the vat residues represent complex mixtures of oligomeric perchlorosilanes (Si_2Cl_6, Si_3Cl_8, Si_4Cl_{10}, Si_5Cl_{12}), perchlorosiloxanes [$Cl_3Si(OSiCl_2)_nOSiCl_3$ ($n = 0-3$)], mixed silanosiloxanes, chlorohydrosilanes and chlorohydrosiloxanes. Twenty compounds containing from two to five silicon atoms were identified in the study,[128] however perchlorooligosilanes Si_nCl_{2n+2} were the major products. Oligomers with $n = 2$ and 3 can be obtained as pure substances. The Si_2Cl_6 purification by distillation was described in details in the work.[130]

According to the studies [131,132] the vat residues of distillation of the mixture $SiHCl_3$–$SiCl_4$ contain predominantly perchlorooligosiloxanes, but not silanes Si_nCl_{2n+2}, as it was found in the studies.[128,129] Apparently, the composition of high-boiling fractions may considerably vary depending on the quality of the initial reactants (siloxanes can be formed in partial hydrolysis of $SiCl_4$).

The products of transformation of polymeric organosilanes to silicon carbide fibre and to binder for manufacture of the silicon carbide parts by hot-pressing can also be attributed to industrial sources of organooligosilanes.[35,52,53,63,133] Polydimethylsilane is heated to 350–400 °C in an inert gas atmosphere to produce polymethylcarbosilane. The escaping volatile products consist of linear and cyclic silanes $Me(Me_2Si)_6Me$, $Me(Me_2Si)_nH$ ($n = 2, 3, 5, 6$), $H(Me_2Si)_nH$ ($n = 2-4$), $(Me_2Si)_n$ ($n = 5-8$).[134,135] Pyrolysis of polyphenylmethylsilane (350 °C, 1 h) results in formation of hydrosilanes $SiPh_2MeH$, $Si_2Ph_3Me_2H$, $Si_2Ph_2Me_3H$.[136] By warming up in the CCl_4 solution, these oligohydrosilanes can easily be transformed to chlorides.[137] It was suggested to utilize the products of the polydimethylsilane pyrolysis as initiators of photolytic curing of liquid siloxane rubber.[138]

It is known[139] that side products of production of high-purity silicon semiconductors by trichlorosilane pyrolysis contain oligomeric chlorosilanes (including pentachlorodisilane). The use of pentachlorodisilane in the synthesis of n-decachlorotetrasilane by the Vyazankin–Razuvaev reaction was suggested.[139]

III. Laboratory methods of synthesis of oligo- and polyorganosilanes

1. The Wurtz reaction

The reaction of organohalosilanes with alkali metals has found its wide use in preparation of oligomeric and polymeric organosilanes.[1–3,9–11,21,23–33,42,45,66] This type of transformation is analogous to the coupling of organic radicals in the interaction of haloalkanes (RX) with sodium discovered by Wurtz in 1855

$$2\,RX + 2\,Na \longrightarrow R-R + 2\,NaX.$$

By virtue of this analogy it is referred as the Wurtz reaction.

Organochlorosilanes R_3SiX form disilanes R_3SiSiR_3, organodichlorosilanes R_2SiCl_2 produce rings $(R_2Si)_n$ and polymers $-(R_2Si)_n-$, mixtures of R_3SiCl and R_2SiCl_2 result in formation of oligomers $R_3Si(SiR_2)_nSiR_3$. Trifunctional derivatives $RSiX_3$ are not sufficiently active to enter into the reaction under normal conditions, *i.e.* upon heating with the dispersed metal in an organic solvent. However, the reaction of $RSiX_3$ with naphthyllithium results in polycyclic oligosilanes $(RSi)_8$,[30,61,88] and the ultrasonic-mediated interaction of $RSiX_3$ with sodium leads to formation of polymeric organosilanes $(RSi)_n$ with the network structure.[140] Among halogen containing organosilanes, chlorides with methyl, ethyl and phenyl substituents are most often used because of their accessibility. The reactions are usually carried out in tetrahydrofuran (THF) with lithium, in toluene, xylene or nonane with sodium and in THF, toluene, diethyl ether, hexane or nonane with sodium–potassium eutectic. Cyclosilanes $(R_2Si)_n$ are produced upon interaction of R_2SiCl_2 and Li/THF (or Na/K/THF). The reaction with sodium in toluene results in formation of polymers $-(R_2Si)_n-$. The studies [74,141,142] are devoted to investigation of the mechanism of this complex heterogenic reaction. Effects of solvents, additives of crown-ethers,

mercury, naphthalene, anthracene, biphenyl, tetraphenylethylene on the yields of polymers and cyclic compounds were considered, molecular mass distributions were measured,[141, 142] use of yttrium, dispersed lead [141] and samarium iodide [143] was tested in the synthesis. It was shown [144] that bright blue colour of the reaction mixture is determined by the colloid sodium particles. Potassium-graphite KC_8 is turned out a very effective reagent in the coupling reaction.[145] All of three expected products, $R^1_3SiSiR^2_3$, $R^1_3SiSiR^1_3$, $R^2_3SiSiR^2_3$, are formed in syntheses of non-symmetric disilanes from mixtures of chlorides R^1_3SiCl and R^2_3SiCl. Preparation of these compounds from silyllithium or silylpotassium derivatives R^1_3SiM and halides R^2_3SiX seems more reasonable. The silyllithium (silylpotassium) derivatives can easily be prepared by interaction of symmetric phenyl-substituted disilanes $Si_2Ph_nMe_{6-n}$ ($n = 2-6$) with lithium (potassium). Aminosilanes $(R_2N)Ph_2SiCl$ and $(R_2N)PhMeSiCl$ also form the silyllithium derivatives, they are used in syntheses of oligosilanes. The amino group can be replaced by chlorine atom and trifluoromethylsulfonate substituent.[108] The Wurtz reaction has some limitation when applied to vinyl-, allyl-, ethynyl- and alkoxyl-substituted organosilanes. Side processes and lower yields of the target products are observed in the case of the reactions of chlorohydrosilanes. Destruction of the benzene ring of chlorophenylsilanes takes place when the Li–THF system is used.[11, 23, 33, 66]

The coupling reaction of organochlorosilanes under the action of alkali metal vapours and the following fast freezing of the products in a cooled trap can be used to prepare [62, 91] strained cyclosilanes, which cannot be synthesized by conventional methods in the liquid phase. It is worth noting that presently the Wurtz reaction is employed for industrial manufacture of silicone carbide fibre from polydimethylsilane.[133]

2. The Grignard reaction

The Grignard reagents can be used in syntheses of organodisilanes and oligosilanes from corresponding chlorides.[9, 11, 23] In case of perchlorinated compounds Si_2Cl_6 and Si_3Cl_8, the silicon–silicon bonds are partially cleaved by RMgX and monomers SiR_4 are formed along with the target compounds Si_2R_6 and Si_3R_8. The bonds in cyclosilanes $(SiCl_2)_4$ and $(SiCl_2)_5$ are even more prone to destruction. The partially substituted derivatives $Si_2R_nCl_{6-n}$ are more persistent to this side reaction. *tert*-Butylmagnesium chloride is inactive to silicon chlorides, therefore *tert*-butyllithium is used for preparation of disilanes with the *tert*-butyl substituent. Significant difficulties arise when a fourth, fifth or sixth bulk substituent like Pr^i, Bu^t or cyclo-C_6H_{11} has to be added to disilane. Reduction of organochlorodisilane to hydride may occur instead of the chlorine atom replacement.[146] Aryl substituents and unsaturated groups (vinyl, allyl, ethynyl) can easily be introduced *via* the corresponding Grignard and Iotsich reagents.

Intermediate silyl Grignard reagents R_3SiMgX are formed in the reactions of organochlorosilanes with both magnesium and RMgX. Particularly, $Ph_3SiSiMe_3$ was prepared by reaction of the mixture of Ph_3SiCl and Me_3SiCl with both magnesium and n-$C_6H_{13}MgCl$, the product of interaction of Me_3SiCl and Ph_2SiCl_2 in hexamethylphosphorotriamide is $(Me_3Si)_2SiPh_2$.[23] When vinyl chloride (VinCl) is passed through the mixture of Me_2SiCl_2 and magnesium in THF, the mixture of $VinMe_2SiSiMe_2Vin$ and $VinMe_2SiSiMe_2SiMe_2Vin$ is formed instead of Me_2SiVin_2.[147]

3. The Vyazankin–Razuvaev reaction

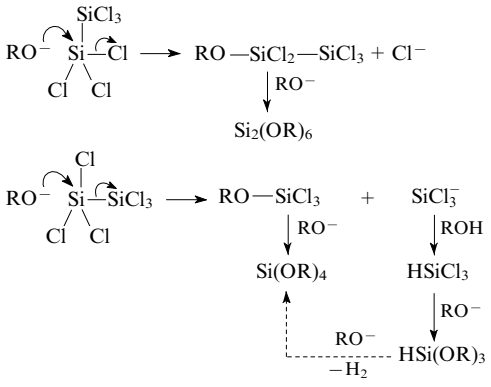
Coupling of silyl radicals upon photolytic or thermal destruction of bis(silyl)mercury represents a convenient method for preparation of oligomeric silanes of various structure:[148]

$$R_3SiHgSiR_3 \longrightarrow R_3SiSiR_3 + Hg.$$

The initial silylmercury derivatives are formed in interaction of silicon hydrides and both diethyl- and di-*tert*-butylmercury. The following compounds were prepared in this way: n-decachlorotetrasilane $Cl(SiCl_2)_4Cl$ from bis(pentachlorodisilanyl)mercury $Cl_3SiSiCl_2HgSiCl_2SiCl_3$, hexakis(trichlorosilyl)disilane $(Cl_3Si)_3SiSi(SiCl_3)_3$ from bis[(tris(trichlorosilyl)silyl]mercury $(Cl_3Si)_3SiHgSi(SiCl_3)_3$,[25] and bis(undecamethylcyclohexasilane) [149] cyclo-$Me_{11}Si_6Si_6Me_{11}$-cyclo from bis(undecamethylcyclohexasilanyl)mercury cyclo-$Me_{11}Si_6HgSi_6Me_{11}$-cyclo. Tris(pentamethyldisilanyl)silane $(Me_5Si_2)_3SiH$ reacts with di-*tert*-butylmercury resulting in formation of $(Me_5Si_2)_3SiHgHgSi(Si_2Me_5)_3$, the latter transforms to hexakis(pentamethyldisilanyl)disilane $(Me_5Si_2)_3SiSi(Si_2Me_5)_3$ upon UV irradiation *via* intermediate formation of compound containing one mercury atom, $(Me_5Si_2)_3SiHgSi(Si_2Me_5)_3$.[150]

4. The nucleophilic substitution at silicon atoms

Silicon chlorides Si_nCl_{2n+2} and $Si_2Me_nCl_{6-n}$, contained in high-boiling fractions of the residues from industrial processes of production of $SiCl_4-SiHCl_3$ and methylsilane monomers, are suitable for synthesis of oligoorganosilanes of different structure. Their chlorine atoms can easily be replaced by organic groups upon interactions with organic derivatives of lithium, magnesium or zinc and by the groups RO, RS, R_2N upon interactions with alcohols, thiols and amines or their derivatives ROM, RSM, R_2NM (M = Li, Na, K). Partial hydrolysis of hexachlorodisilane results in formation of $Cl_3SiCl_2Si-O-SiCl_2SiCl_3$ and $Cl_3SiCl_2Si-O-SiCl_2Cl_2Si-O-SiCl_2SiCl_3$,[25] complete hydrolysis produces silsesquioxane $(Si_2O_3)_n$,[151] treatment with ammonia leads to formation of silsesquiazane $[Si_2(NH)_3]_n$.[152] To prevent destruction of silicon–silicon bonds in perchlorinated oligomers Si_nCl_{2n+2}, the reaction is carried out [23, 25] at subzero temperatures. Besides chlorine atom, trichlorosilyl group can be detached under the action of nucleophiles. Therefore, such processes yield monomeric species $Si(OR)_4$ and $HSi(OR)_3$ together with disilanes $Si_2(OR)_6$.



Methylated disilanes $Si_2Me_nCl_{6-n}$ ($n = 1-5$) are more stable than perchlorinated Si_2Cl_6, however they are actively decomposed by excess of alcohol solution of alkali with release of hydrogen. This reaction underlies the volumetric quantitative method of analysis of silicon in the groups $\equiv Si-Si\equiv$.

5. The disproportionation reaction

The disproportionation reaction with migration of methyl group and chlorine atom catalyzed by aluminium chloride is widely used for synthesis of methylchlorodisilanes. For example, trimethylchlorosilane selectively chlorinates hexamethyldisilane to chloropentamethyldisilane or 1,2-dichlorotetramethyldisilane, octamethyldisilane to 1,3-dichlorohexamethyltrisilane, and tetrakis(trimethylsilyl)silane to tetrakis(chlorodimethylsilyl)silane in the presence of $AlCl_3$.[9-11] When the disilane fraction (or 1,2-dimethyltetrachlorodisilane) is heated with hexamethyldisilane in the presence of aluminium chloride, chloropentamethyldisilane and 1,2-dichlorotetramethyldisilane are formed. Evidently, this approach to synthesis of chloromethyldisilanes is most rational as this excludes loss of methyl groups.[57, 123, 124]

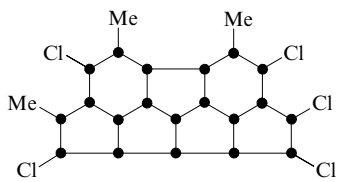
Hexachlorodisilane and chloromethyldisilanes $MeCl_2Si.SiCl_3$, $Cl_2MeSiSiMeCl_2$ disproportionate under the action of trimethylamine, hexamethylposphorotriamide and quaternary ammonium bases.[56, 153-156] Heating of hexachlorodisilane in the presence of trimethylamine in catalytic amounts and removal of tetrachlorosilane formed results in production of dodecachloroneopentasilane [56]

$$4\,Cl_3SiSiCl_3 \xrightarrow{Me_3N} Si(SiCl_3)_4 + 3\,SiCl_4\uparrow.$$

The reaction in closed reactor leads to tetradecachloroneohexasilane precipitating from the reaction mixture in the form of the complex with $SiCl_4$.[154, 155]

$$5\,Cl_3SiSiCl_3 \xrightarrow{Me_3N} [(Cl_3Si)_3SiSiCl_2SiCl_3]\cdot SiCl_4\downarrow + 3\,SiCl_4.$$

The reactivity of disilanes decreases with increase of the number of methyl groups.[56] On heating with Me_3N, methylpentachlorodisilane forms methylundecachloroneopentasilane $(Cl_3Si)_3SiSiCl_2Me$, whereas tris(dichloromethylsilyl)-methylsilane $(MeCl_2Si)_3SiMe$ was obtained from 1,2-dimethyltetrachlorodisilane.[56] 1,2-Dimethyltetrachlorodisilane transforms to a mixture of oligomethylchlorosilanes $Cl(SiMeCl)_nCl$ under the action of hexametapol and quaternary ammonium bases.[156] Heating of disilane fraction with tetrabutylphosphonium chloride produces oligomer of the formula $(Me_2Si)_3(MeSi)_{17}Cl_5$, for which a flat structure consisting of two Si_6 and five Si_5 fused rings was proposed.[156]



● is SiMe group.

A convenient method of synthesis of cyclohexasilanes *via* the anion $[Si_6Cl_{14}]^{2-}$ was proposed.[157] The complex $[(Et_2NCH_2CH_2NEtCH_2CH_2NEt_2)SiH_2Cl_2]_2^+[Si_6Cl_{14}]^{2-}$, in which the doubly charged anion has two hexacoordinated silicon cations as counterions, is obtained by disproportionation of trichlorosilane activated by pentaethyldiethylenetriamine $Et_2NCH_2CH_2NEtCH_2CH_2NEt_2$. The reaction of the complex with $LiAlH_4$ results in cyclohexasilane $(SiH_2)_6$, whereas that with MeMgCl leads to formation of dodecamethylcyclohexasilane $(SiMe_2)_6$. It was also suggested [158] to prepare the latter compound as well as linear oligomers $MeO(SiMe_2)_nOMe$ ($n = 3-6$) by disproportionation of 1,2-dimethoxytetramethyldisilane under the action of sodium methoxide in THF. Network methylalkoxypolysilanes $[MeSi(OR)_m]_n$ ($m < 0.5$) are formed in analogous reactions of alkoxymethyldisilanes $Si_2Me_2(OR)_4$ and $Si_2Me_3(OR)_3$ catalyzed by alkali metalalkoxides and organolithium compounds. Disproportionation reaction enables one to introduce the groups SiR and SiR_2 (R is hexyl, phenyl, ethenyl) into polymer by addition of monomers $RSi(OR)_3$ and $R_2Si(OR)_2$ to alkoxymethyldisilane.[159, 160] The drawback of this method consists in the loss of a part of disilane as a monomer.

6. Reactions with halogenes and halogenides

The silicon–silicon bonds in peralkylated oligoorganosilanes are easily cleaved by halogens.[9, 11, 25, 107] Chlorine atoms strongly retard this reaction, and replacement of the hydrogen atom in methyl group takes place in dimethylterachlorodisilane, $Me_2Si_2Cl_4$, under the action of chlorine under light, resulting in formation of chloromethyl(methyl)-tetrachlorodisilane.[161] The halogen activity decreases in the series

$$Cl_2 > Br_2 > I_2.$$

If the reaction is uncontrolled, permethylated oligomers are transformed by chlorine to dichlorodimethylsilane and trimethylchlorosilane. A mixture of α,ω-dichlorides $Cl(Me_2Si)_nCl$, $n = 2, 3, 4, 6$ can be obtained from dodecamethylcyclohexasilane under cooling and careful passing of chlorine.[162, 163] Polysilanes of lower molecular weight were obtained from action of a pre-determined amount of bromine on polymethylphenylsilane.[164] Clorides of mercury, phosphorus, tin, tungsten and molybdenum are used in preparative syntheses by controlled cleavage of silicon–silicon bonds [most often in cyclosilanes like $(Me_2Si)_6$ and $(Ph_2Si)_4$].[9, 11, 25, 107] Hydrogen chloride and *tert*-butyl chloride react at elevated temperatures only, CCl_4 cleaves the silicon–silicon bond in $(Me_2Si)_6$ under UV irradiation in presence of electron acceptor, 9,10-dicyanoanthracene.[165] Hydrosilanes, tris(trimethylsilyl)silane,[166] pentamethyldisilane and n-heptamethyltrisilane [19, 21] are quantitatively transformed to the corresponding chlorides on heating (50 °C) in CCl_4 solution. It is a radical reaction, it is not observed for triethylsilane. However, the latter compound mixted with $Me_3SiSiMe_2H$ readily forms the corresponding chloride under the action of CCl_4. It was suggested [167] to use copper dichloride to produce organochlorohydrosilanes ClR_2SiSiR_2H and organodichlorodisilanes ClR_2SiSiR_2Cl from dihydrides HR_2SiSiR_2H. The reactions are carried out in diethyl ether with copper(I) iodide as a catalyst.

$$HR_2SiSiR_2H + 2\,CuCl_2 \xrightarrow[Et_2O]{CuI\ (2.5\%)}$$

$$\longrightarrow ClR_2SiSiR_2H + ClR_2SiSiR_2Cl + 2\,CuCl\cdot HCl,$$

$R_2 = Et_2$ (57%); $R_2 = Et_2$ (17%);

$R_2 = PhMe$ (59%) $R_2 = PhMe$ (4%)

$$HR_2SiSiR_2H + 4\,CuCl_2 \xrightarrow[Et_2O]{CuI\ (2.5\%)} ClR_2SiSiR_2Cl + 4\,CuCl\cdot HCl$$

$R_2 = Et_2$ (90%);

$R_2 = PhMe$ (79%)

7. The reactions of chlorodemethylation and chlorodephenylation

Hexamethyldisilane slowly dissolves in concentrated sulfuric acid with release of methane and formation of sulfates $(Me_3SiSiMe_2O)_2SO_2$ and $O_2S(OSiMe_2SiMe_2O)_2SO_2$. The subsequent treatment with ammonium chloride gives chloropentamethyldisilane and 1,2-dichlorotetramethyldisilane. The terminal methyl groups are demethylated in octamethyltrisilane. Decamethyltetrasilane and heavier homologues cannot be converted to chlorinated derivatives because silicon–silicon bonds are cleaved in the reaction.[10, 11]

When dry hydrogen chloride is passed through hexamethyldisilane in presence of aluminium chloride as catalyst, depending on the reaction conditions the following products are formed: chloropentamethyldisilane (20–25 °C), 1,2-dichlorotetramethyldisilane (50–60 °C) or 1,1,2-trichlorotrimethyldisilane (90 °C).[10, 11] The same chlorides and also 1,2-dimethyltetrachlorodisilane can be obtained by treatment of hexamethyldisilane with acetyl chloride in presence of aluminium chloride.[10, 11] Tetrakis(trimethylsilyl)silane, which is stable to concentrated sulfuric acid, is demethylated to $Si(SiMe_2Cl)_4$ under the action of the mixture $AcCl-AlCl_3$.[10, 11] Phenyl group can be replaced by chlorine atom more readily than methyl group when oligomethylphenylsilanes are treated with both $H_2SO_4-NH_4Cl$ and $HCl-AlCl_3$.[10, 11]

Effective halogenating agents are boron halides and pentachloroantimony. Heating of Me_6Si_2 with BCl_3 (at a ratio of 1 : 3) for 24 h results in production of Me_5Si_2Cl, when BBr_3 is used instead (1 : 1), Me_5Si_2Br is formed.[168] Chloropentamethyldisilane and 1,2-dichlorotetramethyldisilane can be obtained from the action of antimony pentachloride to hexamethyldisilane.[169]

Lately, trifluoromethanesulfonic acid has found its wide use in laboratory syntheses of functional organosilicon compounds. It effectively replaces phenyl group at silicon atom under mild conditions with formation of triflate derivatives containing the fragment $\equiv Si-O-SO_2CF_3$. Yields of the target compounds are often very high and no cleavage of the silicon–silicon bond usually takes place. A large series of organopolysilanes of various structure was prepared using this reagent.[170, 171] The group OSO_2CF_3 at silicon atom can easily be replaced by an organic substituent by the action of Grignard reagents and organic (alkyl and aryl) lithium derivatives. When the organosilicon compound reacts with $LiAlH_4$, the corresponding hydrides are formed, while the corresponding fluorides are obtained from the reaction with potassium fluoride.[171]

8. The substitution of alkoxy and amino groups by chlorine atoms

Chloromethyloligosilanes are products of interaction of alkoxymethyloligosilanes with acetyl chloride. Amino groups at silicon atom are easily replaced by chlorine atoms under the action of hydrogen chloride. This reaction found its use for synthesis of large series of oligomeric organochlorosilanes, its practical meaning was especially increased when the method of production of aminoorganooligosilanes with use of silyllithium reagents like $(Et_3N)_2PhSiLi$ and $(Et_2N)Ph_2SiLi$ was developed. The review of publications on this topic is presented in the work.[108]

9. The reactions of hydrogenation and dehydrocoupling

Silicon hydrides Si_nH_{2n+2} are formed in the reaction of magnesium silicide with hydrochloric acid ($n = 1-8$) and upon reduction of corresponding halides Si_nCl_{2n+2} ($n = 2$, 3) by lithium aluminium hydride.[4–7, 9, 23, 172] A series of cyclosilanes $(SiH_2)_n$ ($n = 4-6$) was also obtained from reaction of halocyclosilanes $(SiX_2)_n$ (X = Cl, Br) with $LiAlH_4$.[173] To prevent cleavage of the silicon–silicon bonds, the reaction is carried out at deep cooling with filtered solutions of $LiAlH_4$. Organohydrosilanes $Si_2R_nH_{6-n}$ ($n = 1-5$) and oligomers with longer silicon chains are easily formed by reduction of chlorides with lithium aluminium hydride. No special precaution is required for these reactions in contrast to the reactions with perchlorinated derivatives because the silicon–silicon bonds in organosilanes are more stable. Less active lithium hydride reduces organochlorosilanes in THF and diglyme in carefully deoxygenated mixtures. The reaction has an inductive period from 1 to 70 min caused by dissolution of passive layer on the LiH surface.[174]

Quite effective method of production of oligoorganosilanes with linear $[H(RHSi)_nH]$ and cyclic $[(HRSi)_n]$ structure was suggested by Harrod.[48, 109] It consists in the action of catalytic amounts of cyclopentadienyl derivatives of titanium, zirconium and hafnium on primary hydrosilanes $RSiH_3$. Initially, dimethylcyclopentadienyltitanium was utilized in this reaction, however some complications originated from low thermal stability of this compound. Therefore, it was started to use catalysts produced *in situ* by alkyllithium (most often, Bu^nLi) addition to a mixture of primary silane and Cp_2MCl_2 (Cp is cyclopentadienyl). Secondary silanes R_2SiH_2 are much less prone to this transformation, nevertheless a series of derivatives of the type $H(R_2Si)_nH$ ($n = 2$, 3) were obtained by this means.[48, 109, 112]

10. Other methods

Compounds containing silicon–silicon bonds are often formed in reactions of oligochlorosilanes under UV light.[14–17] In principle, such reactions can be used in laboratory to obtain di- and oligosilane in moderate amounts. Pyrolytic and free radical processes seem less promising, although there are some examples of sufficiently effective thermal and radical reactions.[11, 23, 42, 59, 102] 1,2-Dimethyltetrachlorodisilane was obtained[175] by hard UV irradiation of dichloromethylsilane vapours under mercury sensitization in a quartz vessel. This method is suitable for production of little amounts of $Si_2Me_2Cl_4$, however it cannot compete with the method of separation of this compound from the disilane fraction.

A mixture of hydrodisilanes $HCl_2SiSiCl_3$ and $H_2ClSi.SiCl_3$ was obtained [176] in 10% yield by passing trichlorosilane and THF vapours through quartz tube heated to 450 °C. The yield of disilanes $Si_2HMe_2Cl_3$ and $Si_2Me_2Cl_4$ from pyrolysis of $MeHSiCl_2$ (600–640 °C) amounted to 3%–5% only.[176] 1,1,2,2-Tetrachloro-1,2-disilaacenaphthene and bis(1,8-naphthylene)dichlorodisilane were prepared [102] by the gas phase pyrolysis of a mixture of trichlorosilane with α-naphtylchlorosilane. Hexakis(trimethylsilyl)disilane $(Me_3Si)_3SiSi(SiMe_3)_3$ is formed [177] on heating of tris(trimethylsilyl)silane $(Me_3Si)_3SiH$ in presence of di-*tert*-butyl peroxide.

The electrochemical method [178] of synthesis is quite promising. A series of organodi-, oligo- and polysilanes was prepared by electrolysis of chlorides R_3SiCl and R_2SiCl_2. A quite attractive method of synthesis of disilanes is based on increased (in comparison with organohydrosilanes) capability to protonation of the only hydrogen atom in trichlorosilane. Interaction of two molecules of $SiHCl_3$ in presence of a hydrogen chloride acceptor gives pentachlorodisilane. The usual acceptors (pyridine, aniline, triethylamine) are unable to absorb hydrogen chloride, therefore the reaction does not proceed. Use [179] of derivatives of trifluoromethanesulfonic acid, Me_3SiOTf, $Me_2Si(OTf)_2$, (TfO)MeClSiSiMeCl(OTf), allowed one to obtain a series of oligochloromethylsilanes, *viz*. $Me_3SiSiCl_3$, $Me_2Si(SiCl_3)_2$ and $Cl_3SiSiMeClSiMeClSiCl_3$. Upon binding of proton from trichlorosilane, the salt $Et_3NH^+(TfO)^-$ is formed. Utilization of more active proton acceptor $(Me_2N)_3P{=}NMe$ instead of triethylamine makes it possible to involve dichloromethylsilane and triphenoxysilane in the transformation of this type.

IV. Properties of the silicon–silicon bond and electronic interactions in molecules of oligoorganosilanes

Some characteristics of the silicon–silicon σ-bond, spectra (UV, photoelectronic, NMR, IR, Raman) and effects of conjugation in oligosilane molecules have been considered in the monograph [180] and the reviews (Refs 9, 11, 18, 23, 34, 44, 46, 58, 60, 65, 66, 77–79, 81, 82, 84–86, 181).

1. The bond energy and the bond length

Values from 40 to 86 kcal mol^{-1} are given for the energy of silicon–silicon bond (see Ref. 181). The self-consisting and most reliable dissociation energies (D) were chosen from large body of data obtained in kinetic, calorimetric and mass-spectrometric measurements in the work.[182] In the series of homocatenates Me_3M-MMe_3 the regular decrease of D takes place:

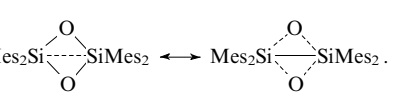
Bond	C–C	Si–Si	Ge–Ge	Sn–Sn	Pb–Pb
D /kcal mol^{-1}	90	81	73	56	55

Table 1 contains silicon–silicon bond lengths (r_{Si-Si}) for compounds **1**–**24**. In non-strained disilanes **1**–**4** and cyclosilanes **21**, **23** the bond length is 2.32–2.34 Å. Small increase of r_{Si-Si} (to 2.36–2.39 Å) is observed in phenyl-substituted oligosilanes **5**, **10**, **22**. Attachment of four trimethylsilyl substituents to the same silicon atom in tetrakis(trimethylsilyl)silane **9** results in their mutual repulsion and remarkable stretching of the bond Si–Si (to 2.36 Å). It is even longer (2.40 Å) in hexakis(trimethylsilyl)disilane **7**. The maximal lengthening (2.69 Å) is observed in hexa-*tert*-butyldisilane **6**. In strained three-membered heterocyclic compounds **11**–**13** the bond is shortened to 2.23–2.29 Å (despite the presence of the bulky mesityl substituents at the silicon atom), whereas it is elongated to 2.40–2.50 Å in hexamesityl-, hexaneopentyl- and hexa-*tert*-butylcyclotrisilanes **15**–**17**. The distance r_{Si-Si} is of 2.36–2.38 Å in four-membered cyclosilanes **18**–**20**, it is somewhat longer than in non-strained (containing non-bulky substituents at silicon atoms) disilanes **1**–**4** and cyclosilanes **21**, **23**.

Tetramesitylcyclodisiloxane **14**, the compound with the smallest ring size of cyclosiloxanes $(R_2SiO)_n$ (n = 2, 3, 4, ...), in fact represents a hybrid of disilane and doubled disilaoxirane because the distance between the two silicon atoms is shorter than the usual silicon–silicon bond

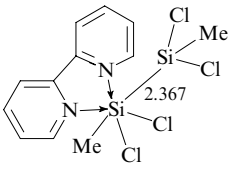
Table 1. The silicon–silicon bond lengths in linear and cyclic oligosilanes.

The number of compound	Formula	r_{Si-Si} /Å	Ref.	The number of compound	Formula	r_{Si-Si} /Å	Ref.
1	H_3SiSiH_3	2.331	181, 183	**13**	$Mes_2\overline{SiSiMes_2}S$	2.289	188
2	F_3SiSiF_3	2.324	181, 183				
3	$Cl_3SiSiCl_3$	2.324	181, 183	**14**	$Mes_2\overline{SiOSiMes_2}O$ [c]	2.310	189
4	$Me_3SiSiMe_3$	2.340	181, 183				
5	$Me_3SiSiPh_3$	2.355	183	**15**	$(Mes_2Si)_3$	2.407	190
6	$Bu^t_3SiSiBu^t_3$	2.697	184	**16**	$[(neo\text{-}C_5H_{11})_2Si]_3$	2.391	190
7	$(Me_3Si)_3SiSi(SiMe_3)_3$	2.400 [a]	185	**17**	$[(Bu^t)_2Si]_3$	2.511	191
8	$Me_3SiSiMe_2SiMe_3$	2.325	183	**18**	$(Me_2Si)_4$	2.363	190
9	$(Me_3Si)_4Si$	2.361	183	**19**	$(Ph_2Si)_4$	2.377	190
10	$Cl(SiPh_2)_5Cl$	2.391,[a] 2.376 [b]	186	**20**	$[(Bu^t)MeSi]_4$	2.377	190
				21	$(H_2Si)_5$	2.342	190
11	$Mes_2\overline{SiSiMes_2}CH_2$	2.272	187	**22**	$(Ph_2Si)_5$	2.396	190
				23	$(Me_2Si)_6$	2.338	190
12	$Mes_2\overline{SiSiMes_2}O$	2.227	188	**24**	$[Bu^t_3Si]_4[Si_4]$	2.320,[a] 2.355 [b]	192

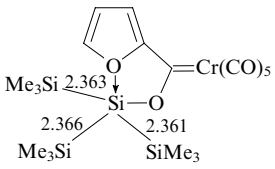
[a] The internal bond; [b] the terminal bond; [c] the structural formula of the compound is the folowing:  .

length. The dual nature of this compound is supported by its reactivity, its interaction with naphthyllithium and then with water gives tetramesitylsilanediol, a product with conserved silicon – silicon bond. The tetrahedron Si_4 in kinetically stable compound **24** is protected from attacks of reagents by four tri-*tert*-butylsilyl ('supersilyl') groups. The distances Si – Si in the tetrahedron have usual (close to the sum of the covalent radii of two silicon atoms) values, while the peripheral supersilyl groups are at the distances of 2.35 Å from the tetrahedron silicon atoms, *i.e.*, these silicon – silicon bonds are slightly elongated.

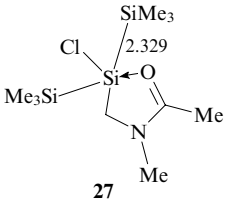
In the compounds, in which one (**25**,[193] **26**,[194] **27**[195]) or both silicon atoms (**28**[195]) are penta- (**26** – **28**) or hexacoordinated (**25**), the distances between silicon atoms may be either close to the 'standard' values ~2.34 Å (2.340, 2.336, 2.345 Å for compound **28**) or appreciably different from them (2.367 Å for compound **25**, 2.366 Å for compound **26**, 2.329 Å for compound **27**).



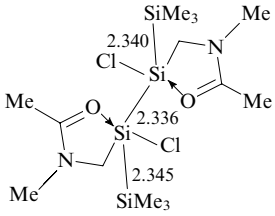
25



26



27



28

Thus, the length of the silicon – silicon σ-bond in linear and cyclic oligosilanes varies from ~2.23 to ~2.70 Å depending on the compound structure and the nature of substituents at its silicon atoms.

2. σ-Delocalization in oligosilanes, σ,π- and σ,n-conjugation

a. The ultraviolet and photoelectron spectra and σ-delocalization

Oligomeric organosilanes were the first representatives of compounds with σ-bonds clearly exhibiting bathochromic (red) shift of the maximum of the long-wavelength absorption band in the UV spectrum with increasing chain length.[196, 197] This effect is similar to the red shift in polyenes determined by delocalization of π-electrons.[58, 198] The absorption band shift (Table 2) for oligosilanes ($n = 2-4$) is as much pronounced as in case of polyenes. However, bathochromic shift in alkane UV spectra is much less pronounced than in oligosilanes. Oligomeric alkylgermanes are close to, while alkylstannanes exceed analogous Si_n-systems in the magnitude of the shifts.

The low-energy absorption bands in UV spectra of permethylated oligosilanes are assigned to the $\sigma \rightarrow \sigma^*$ transitions. Hexamethyldisilane absorbs in the far-UV region (193 nm), however the next member of the homologous series, octamethyltrisilane, has absorption maximum at 216 nm. The extinction coefficient per silicon – silicon bond increases with the increase of n. Elongation of the chain Si_n results in consecutive decrease of the ionization energy for oligosilane molecules. Electron is removed from the highest occupied molecular orbital (HOMO) possessing σ_{Si-Si}-character (the orbital, formed by electrons of two σ-bonded silicon atoms). The contribution from lateral alkyl substituents into the MO energy is marginal. It is assumed[199] that electrons of the Si – Si bonds of the main chain are prone to delocalization, while electrons of Si – C bonds form poorly polarizable shell.

Methods analogous to the calculations of π-systems with the Hückel method are used to obtain MO energies in oligosilanes.[58, 198] The molecular orbital of the oligosilane is represented as a linear combination of single bonds orbitals. A parameter of interaction of two neighbouring σ_{Si-Si}-bonds is introduced, that is the resonance integral β. The dependence of the MO energy on n for linear oligomers $R(R_2Si)_nR$ has the form

$$E_j = E_{Si-Si} + 2\beta\cos\left(\frac{\pi j}{n}\right), \quad j = 1, 2, 3, \ldots, n-1,$$

where E_{Si-Si} is the energy of σ-orbital in disilane R_3SiSiR_3.

In the Sandorfy C-method, there are two parameters of orbital interaction, those are β_{vic}, a parameter of overlap of the sp^3-orbitals of two neighbouring silicon atoms, and β_{gem}, a parameter of overlap of the sp^3-orbitals centered at the same silicon atom. Each sp^3-orbital has the same Coulomb integral α. To calculate α and β, a procedure of fitting of transition energies (obtained from electronic spectra) or ionization potentials (measured by photoelectron spectroscopy) is used in solving the secular equation.

The ratio β_{vic}/β_{gem} determines the ability of the linear chain to conjugation and the size of energetic gap, *i.e.*, the difference between energies of the lowest unoccupied and highest occupied MOs at the given $n \rightarrow \infty$.

A good agreement is obtained between calculated and observed values of transition energies and ionization potentials for oligomers with $n = 2-5$, when the Sandorfy C-method is used. Starting from $n = 6$ discrepancy is observed, which increases for longer chains (till $n = 16$).[199] This method is unable to explain why the energies of the $\sigma \rightarrow \sigma^*$-transitions are very different for different conform-

Table 2. The low-energy bands in the absorption spectra of alkanes, alkenes and silanes.[58, 196 – 198]

n	$H(CH_2)_nH$		$H(CH{=}CH)_{n/2}H$		$Me(Me_2Si)_nMe$		$Ph(Me_2Si)_nPh$		$Cl(Me_2Si)_nCl$	
	$\nu \times 10^{-3}/cm^{-1}$	λ/nm	$\nu \times 10^{-3}/cm^{-1}$	λ/nm	$\nu \times 10^{-3}/cm^{-1}$	λ/nm	$\nu \times 10^{-3}/cm^{-1}$	λ/nm	$\nu \times 10^{-3}/cm^{-1}$	λ/nm
2	75	133	55.6	180	51.7	193	42.4	236	49.0	204
3	72	139	–	–	46.2	216	41.2	243	45.7	219
4	70	143	43.9	228	42.5	235	39.9	251	42.6	235
5	68	147	–	–	40.0	250	38.8	258	40.0	250
6	67	149	31.9	314	38.5	260	37.7	265	38.6	259

ers. For example, the experimentally measured excitation energy for the *gauche*-form of octamethyltetrasilane is 48 100 cm^{-1}, that for the *anti*-form is 43 900 cm^{-1}, the Sandorfi C-method gives the value 43 200 cm^{-1} close to that for the *anti*-form. When a modified method is used, two additional parameters, $\beta_{1,3}$ and $\beta_{1,4}$ (Fig. 1), are introduced, and the calculated transition energies coincide with the experimental ones for linear oligomers till $n = 16$. The parameter $\beta_{1,4}$ is a resonance integral depending on the dihedral angle, the value of $\beta_{1,3}$ is close to zero. This modification is called 'ladder' because the topology of interacting hybrid sp^3-orbitals resembles a ladder.[199] A good correspondence between calculated and measured transition energies is obtained when $\beta_{vic} = -3.32$, $\beta_{gem} = -0.62$, $\beta_{1,3} = 0$, $\beta_{1,4}(90°) = -0.40$, $\beta_{1,4}(165°) = +0.75$, $\alpha = -2.63$ eV.

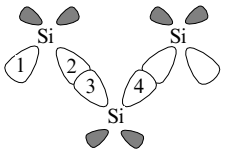


Figure 1. Overlapping of sp^3-orbitals in trisilane. (1, 2) β_{gem}; (2, 3) β_{vic}; (1, 3) $\beta_{1,3}$; (1, 4) $\beta_{1,4}$.

Table 3 shows ionization potentials for electrons from the silicon–silicon σ-bonds of hydro- and methyl-substituted oligosilanes of linear and cyclic structure. The first ionization potentials (IP_1) of alkanes C_2-C_6 are also shown there for comparison. It is seen that IPs of silanes are smaller than those of alkanes. At the same time, IPs of hydrosilanes are larger than those of permethylated analogues. It can be explained by larger donor ability of CH_3 substituents in comparison with H atoms. The first ionization potential regularly decreases with the increase of n in series of linear derivatives. In case of cyclic derivatives the dependence is more complicated. It is due to more rigid fixation of silicon atoms in the molecules resulting in that relative arrangement of Si–Si bonds is often not suitable for the σ,σ-conjugation. In the case of linear molecules, in which there is free (or nearly free) rotation of particular fragments around silicon–silicon bonds, the latter can hold positions favourable for interaction of σ_{Si-Si}-orbitals.

Table 3. The ionization potentials of oligosilanes of linear and cyclic structure, assigned to the ionization of σ-electrons of silicon–silicon bonds.[58, 200]

Formula	IP /eV	Formula	IP /eV
Oligosilanes			
Si_2H_6	10.53	Si_2Me_6	8.69
Si_3H_8	9.87, 10.72	Si_3Me_8	8.19, 9.14
Si_4H_{10}	9.62, 10.32, 10.85	Si_4Me_{10}	7.98, 8.76, 9.30
Si_5H_{12}	9.36, 10.06, 10.56, 10.86	Si_6Me_{14}	7.70
Cyclosilanes			
$(SiH_2)_5$	9.4, 10.35	$(SiMe_2)_4$	7.60, 8.15, 8.50
$(SiH_2)_6$	9.6, 10.8	$(SiMe_2)_5$	7.94, 8.91
		$(SiMe_2)_6$	7.79, 8.16, 9.12
Alkanes			
C_2H_6	11.65	C_4H_{10}	10.63
C_3H_8	11.07	C_5H_{12}	10.35
		C_6H_{14}	10.18

Note. The values of IP_1, IP_2, IP_3 and so on are given for oligosilanes, while only the values of IP_1 are shown for alkanes.

Substituents with π- and n-electrons (Ph, Cl) at the ends of the Si_n chain induce bathochromic shift of the absorption maximum in the UV spectrum because of interaction of σ-electrons of the silicon–silicon bonds with the π-system of benzene ring or with lone electron pairs of chlorine atom (see Table 2). In case of phenyl-substituted oligomers, the shift is quite substantial, whereas for chloro-substituted oligomers it is much less pronounced and was observed for the first members (with $n = 2, 3$) of the series only. The damping of the effect (observable for phenylated derivatives also) with the increase of n is explained by increasing difference in energy levels of frontal orbitals of interacting fragments.

For the first time, Hague and Prince[201] observed effective interaction of two π-systems separated by two silicon atoms for 1,2-diphenyltetramethyldisilane. The intensive absorption band of this compound at around 240 nm is absent in the spectrum of dimethyldiphenylsilane, despite the phenyl groups are separated by a single silicon atom in the latter compound. It was shown in the subsequent studies of Gilman *et al.*,[202] Sakurai and Kumada,[203] Shoryguin *et al.*,[197] and Pitt[204] that the observed band is a result of predominant interaction of π-electrons of phenyl groups with σ-electrons of the silicon–silicon bond (σ,π-conjugation). Investigations of permethylated oligosilanes $Me(Me_2Si)_nMe$ showed that the system of σ_{Si-Si}-bonds is a chromophore, while the π-substituent shifts the absorption maximum (σ–σ* transition) to red. Ionization energies of σ-electrons of the silicon–silicon bond and π-electrons of benzene ring are of 8.69 ($Me_3SiSiMe_3$) and 9.24 eV (PhH). This moderate difference in the energy levels causes effective interaction of σ- and π-electrons in pentamethylphenyldisilane and lowering its IP_1 to 8.39 eV. The highest occupied MO of this compound represents the σ_{Si-Si}-orbital of disilane perturbed by interaction with the benzene π-orbital. Contribution from the σ_{Si-Si}-orbital in HOMO of $PhMe_2SiSiMe_3$ is equal to 72%, and that from the π-system is 28% only. The ionization potentials of large set of substituted di- and trisilanes, containing substituents like ROC_6H_4, $R_2NC_6H_4$, $CH_2{=}CH$, $RC{\equiv}C$, RO, RS, were measured by means of the photoelectron spectroscopy and the electronic absorption spectroscopy of the charge-transfer complexes. Some of these IP_1 values are shown in Table 4. In almost all cases, ionization of Si_n-derivatives is easier than that of their Si_1-analogs. The only exclusion is represented by benzyltrimethylsilane, IP_1 of which is slightly lower than that of pentamethylphenyldisilane. Nevertheless, this fact does not mean that the ability of the $Me_3SiSiMe_2$ group to the resonance interaction with benzene ring is lower than that of the Me_3SiCH_2 group. Pentamethyldisilyl group acts as a highly effective electron donor according to the mechanism of σ,π-conjugation and an acceptor by the mechanism of d,π-conjugation, whereas the group Me_3SiCH_2 is unable to act as an acceptor because the silicon atom is separated from the ring by the methylene fragment.

Thus, quantum chemical calculations and data of UV and photoelectron spectroscopy show that the HOMO of

Table 4. The first ionization potentials for substituted oligosilanes and some related compounds.

Compound	IP_1 /eV	Ref.	Compound	IP_1 /eV	Ref.
$SiMe_4$	10.29	44	Me_3SiPh	9.00	207
$Me_3SiSiMe_3$	8.69	44	$Me_3SiSiMe_2Ph$	8.39	208
Me_3SiVin	9.86	205	$Me_3SiSiMe_2SiMe_2Ph$	8.12	208
$Me_3SiSiMe_2Vin$	8.56	205	$(Me_3Si)_2SiMePh$	8.15	208
$VinMe_2SiSiMe_2Vin$	8.63	205	$Me_3SiSiMe_2SiMe_2SiMe_2Ph$	7.88	208
$SiCl_4$	12.12	205	Me_3SiBn	8.35	209
$Cl_3SiSiCl_3$	10.91	205	$3\text{-}Me_3SiSiMe_2C_6H_4SiMe_2SiMe_3$	8.39	209
Me_3SiSMe	8.91	206	$4\text{-}Me_3SiSiMe_2C_6H_4SiMe_2SiMe_3$	8.06	209
$Me_3SiSiMe_2SMe$	8.43	206	$4\text{-}Me_3SiSiMe_2C_6H_4CH_2SiMe_3$	7.98	209
Me_3SiSBu^n	8.76	206	$PhSiMe_2Ph$	8.98	207
$Me_3SiSiMe_2SBu^n$	8.28	206	$PhSiMe_2SiMe_2Ph$	8.23	207

peralkylated oligosilanes represents a linear combination of σ-orbitals of the silicon–silicon bonds characterized by a large integral of the exchange interaction.

The presence of π- and n-donor substituents elongates the conjugation chain and cause the bathochromic shift of the absorption maximum and lowering the first ionization potential of the compound. Much less is known about the nature of the lowest unoccupied molecular orbitals in organosilanes. The data of the electron transmission spectroscopy demonstrate[210] that there is strong delocalization of the lowest unoccupied MO (LUMO) along the Si_n chain, but not on substituents. Ionization energies and electron capture energies of di-, tri- and tetramers, which correspond to the energy levels of HOMO and LUMO, are presented in Table 5.

Table 5. The energies of the frontier orbitals in oligosilane molecules according to data of the photoelelectron and electron transmission spectroscopies.[210]

Oligo-silane	E /eV		ΔE /eV
	the occupied MO	the unoccupied MO	
Si_2Me_6	−8.69	+2.30	10.90
Si_3Me_8	−8.19, −9.14	+1.58	9.77
Si_4Me_{10}	−7.98, −8.76, −9.30	+1.12, +2.90	9.10

The lowest unoccupied molecular orbitals belong to MOs of the σ^*_{Si-Si}-type, while energies of MOs of the σ^*_{C-Si}-type lie higher by ~1.5 eV. The energy level of LUMO decreases from 2.30 to 1.12 eV with lengthening the Si_n chain, and the HOMO–LUMO energy gap also decreases.

b. Radical-anions of cyclosilanes and σ-delocalization

The electrolytic reduction of decamethylcyclopentasilane in a mixture of ethers (dimethyl ether : 1,2-dimethoxyethane = 3 : 1) at −75 °C results in formation of dark-blue radical-anion $(Me_2Si)_5^{-\bullet}$ (Ref. 211). The EPR spectrum of this species consists of 15 equally spaced signals at intervals of 0.53 G. This picture corresponds to the expected splitting by 30 equivalent protons on the 10 methyl groups in $(Me_2Si)_5$. The analysis of the spectrum shows that the unpaired electron equally interacts with each of the hydrogen atoms, *i.e.*, the electron is delocalized over all five silicon atoms of cyclosilane as it does in typical aromatic radical-anion. The electrolytic reduction of dodecamethylcyclohexasilane into yellow radical-anion $(Me_2Si)_6^{-\bullet}$ proceeds at −120 °C. In its EPR spectrum there are 19 signals with hyperfine splitting of 0.49 G. Tetradecamethylcycloheptasilane cannot be reduced by electrolysis into radical-anion at temperatures from −80 to −130 °C.

When treated with Na–K alloy, three cyclosilanes $(Me_2Si)_n$ ($n = 5-7$) and linear silanes $Me(Me_2Si)_nMe$ with $n \geqslant 6$ produce the same radical-anion $(Me_2Si)_5^{-\bullet}$. The electron affinity of cyclosilane $(Me_2Si)_5$ seems to be high. $(Me_2Si)_5^{-\bullet}$ is predominantly formed in both chemical and electrochemical reduction in presence of large excess of benzene. At the same time, benzene radical-anion is produced under analogous conditions in solution of $(Me_2Si)_6$ in PhH. High electron affinity of $(Me_2Si)_5$ is explained by its flat structure, favourable for overlapping of orbitals of neighbouring silicon atoms. Six-membered and especially seven-membered rings are not flat, and formation of a σ-delocalized molecular orbital is hampered. The electronic absorption spectra of radical-anions $(Me_2Si)_5^{-\bullet}$ and $(Me_2Si)_6^{-\bullet}$ are characterized by intensive bands at 645 and 425 nm, respectively.[211]

An action of Li, Na, K, MeLi, Me_3SiK, MeONa, MeOK on $(Me_2Si)_6$ in hexamethylphosphorotriamide results in cleavage of the Si–C bond, but not Si–Si bond, and formation of stable anion $Si_6Me_{11}^-$, which can be used for synthesis of derivatives of dodecamethylcyclohexasilane.[212]

3. The refraction of the silicon–silicon bond, the dipole moments and conformations of oligo- and polyorganosilanes

The molecular refraction of the silicon–silicon bond is equal to 5.87 cm^3, it is considerably larger than the molecular refractions of Si–O (1.80), $Si-C_{Alk}$ (2.47), Si–N (2.16) and Si–H (3.2) bonds.[213] The molecular refractions and the dipole moments (μ) of silyl-substituted benzenes were measured[214, 215] (Table 6). The exaltation of the molecular refraction (the excess of the experimental value over the calculated value) for the substituents $Me_3SiSiMe_2$ and $(Me_3Si)_2MeSi$ is larger than for Me_3Si. This evidences of high polarizability of Si–Si σ-bond and its inclination to conjugation with benzene ring. The dipole moment increases on going from Me_3Si-substituted to $Me_3SiSiMe_2$-substituted benzenes with any other substituents (of considered: H, F, Cl, NMe_2). On going further to the group $(Me_3Si)_2MeSi$, increase in μ is observed for fluoro-substituted benzenes only. The dipole moments of hexamethyldisilane and hexachlorodisilane are equal to zero, the dipole moment of benzylpentamethyldisilane is of −0.43 D.[215]

Table 6. The exaltations of the molecular refractions (ΔR_D) and the dipole moments (μ) of silyl-substituted benzenes 4-XC_6H_4Y.[214]

X	Y	ΔR_D /cm^3	μ /D
Me_3Si	H	0.70	0
Me_3Si	Cl	0.87	1.81
Me_3Si	F	0.40	1.67
Me_3Si	NMe_2	2.78	1.76
$Me_3SiSiMe_2$	H	3.07	0.28
$Me_3SiSiMe_2$	Cl	3.58	1.84
$Me_3SiSiMe_2$	F	3.03	1.74
$Me_3SiSiMe_2$	NMe_2	4.40	1.83
$(Me_3Si)_2MeSi$	H	6.20	0
$(Me_3Si)_2MeSi$	F	5.92	1.83
$(Me_3Si)_2MeSi$	NMe_2	8.23	1.82

Populations of the *gauche*-conformations for a series of 1,2-disubstituted tetramethyldisilanes are calculated from the temperature dependence of the dipole moments measured in the range 20–90 °C in a neutral solvent (cyclohexane).[216] The *trans*-form ($\varphi = 180°$) is energetically more favourable for disilanes $XMe_2SiSiMe_2X$ than the *gauche*-form ($\varphi = 60°$). According to the calculations, the dipole moments of *trans*-conformers aree equal to zero when X = H, F, Cl, Br, I, whereas for *gauche*-conformers they are equal to 1.533, 2.809, 3.429, 3.854, 4.017 D. The experimental data shown in Table 7 demonstrate that the part of

Table 7. The dipole moments, differences between the enthalpies of the *trans*- and *gauche*-conformers (ΔH) and the population of the *gauche*-conformations (p) for 1,2-disubstituted tetramethyldisilanes $XMe_2SiSiMe_2X$.[216]

X	μ /D	ΔH /kJ mol^{-1}	p (%)
H	1.25	–	–
F	1.91	2.09	46
Cl	1.96	2.17	33
Br	1.78	4.16	21
I	1.47	6.54	13
OMe	1.38	10.15	0
SMe	1.86	2.93	8

molecules in less stable *gauche*-conformation is substantial and increases with increasing temperature. The population of this conformation decreases in the series F > Cl > Br > I, *i.e.*, with increase of the substituent size. It is accompanied by regular increase in differences between enthalpies of the *trans*- and *gauche*-forms. The experimentally measured dipole moment of tetramethyldisilane is equal to that calculated on assumption of free (barrierless) rotation of the $SiMe_2H$ groups. This implies that there is no steric hindrance for rotation in this compound.

Energetic barriers for rotation around the Si–Si bond in disilanes are much lower than the barriers of rotation around the C–C bond in the corresponding carbon derivatives (Table 8). They are small in unhindered hydrides, fluorides and chlorides ($\sim$1 kcal mol^{-1}). In compounds X_3CCX_3 the relative rotation of the groups CX_3 becomes more hampered on going from X = H to X = F and then to X = Cl. In contrast, no appreciable hindrance to free rotation of two silyl groups in disilanes X_3SiSiX_3 is produced by even chlorine atoms (the rotation barriers are practically equal for Si_2H_6 and Si_2Cl_6). This difference is explained by longer distances between substituents X in disilanes (r_{Si-Si} = 2.34 Å) in comparison with the ethane derivatives (r_{C-C} = 1.54 Å). The increase in size of organic substituents at silicon atoms leads to a sharp increase in the activation energy of the internal rotation. It is equal to 13.7 kcal mol^{-1} for symmetric tetra-*tert*-butyldisilane. However the carbon analogue of this disilane has much higher rotation barrier (> 23 kcal mol^{-1}).

According to data of the X-ray diffraction analysis, ^{1}H and ^{13}C NMR spectroscopy, and quantum chemical calculations, in the liquid phase organodisilanes can exist in the form of only *trans*- or *gauche*-conformer or as their mixture. They crystallize in *trans*-, *gauche*- or even in eclipsed conformation, however usually in the first-mentioned one (Table 9).

Calculations of conformations of $(SiX_2)_n$ (n = 4–6; X = H, Me, Cl, Br, I) showed[227,228] that the folded conformation is the most favourable for the four-membered cyclosilanes, the envelope and twist conformations are preferable for the five-membered rings, and the chair conformation is favourable for the six-membered rings. According to the X-ray diffraction analysis, cyclic tetrasilanes $(SiR_2)_n$ can exist in both folded [R = Pr^i (Ref. 229), R_2 = $MeBu^t$ (Ref. 230)] and flat [R = Me (Ref. 231), $SiMe_3$ (Ref. 232)] conformations, *i.e.* conformational flexibility is characteristic of these compounds. Experimental data for cyclohexasilane $(SiH_2)_6$ (Ref. 233) and dodecamethylcyclohexasilane $(SiMe_2)_6$ (Ref. 234) supported the results of calculations. The chair conformation is characteristic of both of them. Two hydroxyl groups in decamethylcyclohexasilane-1,4-diol $Me_{10}Si_6(OH)_2$ are in equatorial positions (*trans*-configuration),[235] while in the 1,3-isomer they are in axial positions (*cis*-configuration).[236] Permethylated cycloheptasilane $(SiMe_2)_7$ has the twisted chair conformation, molecular mechanics calculations with the MM2 method predicted that the twisted–chair–chair conformation is the most stable for eight-membered ring $(SiMe_2)_8$.[237] In the solid state the conformations of large rings $(SiMe_2)_{13}$ and $(SiMe_2)_{16}$ are appreciably different from those of corre-

Table 8. The energy barriers of rotation (U) around the Si–Si bond in disilanes and the C–C bond in their carbon analogues.

Disilanes	U /kcal mol^{-1}	Ref.	Ethane derivatives	U /kcal mol^{-1}	Ref.
$H_3Si-SiH_3$	1.22	217	H_3C-CH_3	2.93	221
$H_3Si-SiH_2F$	1.05	218	H_3C-CH_2F	3.33	221
$H_3Si-SiHF_2$	0.85	23	H_3C-CHF_2	3.21	221
$H_3Si-SiF_3$	0.81	23	H_3C-CF_3	3.15	221
$Cl_3Si-SiCl_3$	1.0	219	Cl_3C-CCl_3	10.8	219
$Me_3Si-SiMe_3$	1.05	220	Me_3C-CMe_3	8.8	222
$Bu^t_2HSi-SiHBu^t_2$	13.7	218	$Bu^t_2HC-CHBu^t_2$	> 23	218

Table 9. Conformations of oligoorganosilanes according to quantum chemical calculations, the X-ray diffraction analysis and the NMR spectroscopy.

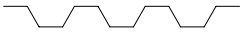
Oligoorganosilane	Method	Conformation	Ref.
$HMe_2SiSiMe_2H$	EFF [a]	*gauche*/*trans*	216, 223
$HCy_2SiSiCy_2H$ [b]	EFF	*gauche*	223
	X-ray	*gauche*	223
$HBu^t_2SiSiBu^t_2H$	EFF	*gauche*	218, 223
	NMR [c]	*gauche*	218, 223
$HPh_2SiSiPh_2H$	EFF	*gauche*/*trans*	224
	X-ray	*trans*	224
	NMR [c]	*gauche*/*trans*	224
$HMes_2SiSiMes_2H$	EFF	*trans*	224
	X-ray	*trans*	224
	NMR [c]	*trans*	224
$HBu^t_2SiSiMes_2H$	X-ray	*trans*	225
	NMR [d]	*trans*	225
$HAr_2SiSiAr_2H$ [e]	X-ray	eclipsed	226
n-Si_4H_{10}	EFF	*gauche*/*trans*	220
n-Si_4Me_{10}	EFF	*gauche*/*trans*	220

[a] EFF are the empirical force field calculations; [b] Cy is cyclohexyl; [c] in CD_2Cl_2; [d] in $CDCl_3$; [e] Ar = 2-$Me_2NCH_2C_6H_4$.

sponding cycloalkanes. Authors of the study [232] noticed greater conformational flexibility of oligosilane chains as compared with oligoalkane ones.[238]

Experimental and theoretical data concerning conformations of di- and oligosilanes [239] have special importance for analysis of conformational states in polymers with silicon backbone. Discovery of thermochromism for polymeric organosilanes stimulated quantum chemical calculations and experimental investigations of solutions containing such polymers and films formed by them.[46, 65–68, 77–82, 86] Because of lower barriers of the internal rotation around the silicon–silicon bond than around the carbon–carbon bond, molecules of polysilanes possess higher conformational flexibility than molecules of alkanes. The dispersion interactions between long alkyl substituents at the silicon atoms are sufficient for formation of extensive areas with highly ordered conformational structure in the polymer. This order can also be induced by bulky substituents, resulting in higher energetic preference of the *trans*-configuration of the Si_n backbone over the *gauche*-configuration.

It is known that molecules of organic polymers tend to coil. It was shown in the experiment and calculations [240] that the long chain Si_n of real polymeric organosilane splits into segments with $n \approx 10-30$, having a uniform conformational structure and separated from one another by sections with non-uniform structure. The strict order is created because of regular reiteration of one of conformations (*gauche*- or *trans*-) of the main silicon chain. If the *gauche*-conformation is repeated ($\varphi = 60°$, *gauche*–*gauche*–*gauche*–...), polymer twists in a spiral. If the *trans*-conformation is repeated ($\varphi = 180°$, *trans*–*trans*–*trans*–...), a rectilineal segment is formed (with all silicon atoms lying in a single plane), which has a form of regularly repeated zigzags when viewed laterally



Such configuration is called *syn*-periplanar (and also flat *trans*-zigzag and rod-shaped). Some data of the absorption and emission spectroscopy indirectly confirm the existence of the conformationally uniform and non-uniform segments in polymeric organosilanes. Particularly, broadening of UV bands is explained [241] by existence of such segments. Because energies of the frontal orbitals (and hence, of the $\sigma \rightarrow \sigma^*$-transitions) depend on the chain conformation, the absorption bands are broadened. The quantum yields of photoluminescence of polymeric organosilanes usually increase with increasing excitation wavelength. It is because the quanta with lower energy excite chain segments with greater delocalization, larger oscillator strengths, and therefore, with larger capability to emission, exceeding that to intersystem crossing and other processes.[242]

The molecular orbital calculations of the spiral segments showed that HOMO of this segment is stabilized, while LUMO is destabilized, and therefore the HOMO–LUMO energy gap increases.[240, 243, 244] In contrast, destabilization of HOMO and stabilization of LUMO take place for the flat *trans*-zigzag segment, and therefore the energy gap decreases. Thus, the best conditions for σ-delocalization are available in *syn*-periplanar segments. Even insertion of a single *gauche*-fragment into the *syn*-periplanar Si_n chain results in its curling and interruption of the conjugation chain.

If any external influence causes reorganization of all segments from the spiral to the rod-shaped conformation, the UV band will be replaced by a new band in the red region. If the external influence leads only to increase of the *syn*-periplanar segments, the absorption band will undergo bathochromic shift.

Thermochromism of polymeric organosilanes was studied for solutions [245] and films.[246] The nature of substituents at the silicon atom has crucial effect on the temperature dependence of the UV spectrum. Poly(n-hexylmethylsilane) has one lengthy and one short alkyl substituents. The UV spectrum of this polymer at 25 °C (in isooctane) contains a broad band at 306 nm. Cooling of the solvent to −67 °C causes its bathochromic shift to 330 nm and some increase of its intensity. Below −67 °C polymer precipitates from the solution. These spectral changes were explained [245] by the increasing number of the *syn*-periplanar segments at low temperatures.

In the molecule of polydi-n-hexylsilane, two long alkyl substituents are attached to each silicon atom. Cooling of the dilute solution results first in a little bathochromic shift of the broad absorption band at 318 nm and then, at −23.5 to −24.2 °C, in its abrupt transformation into a new narrow band red shifted to 354 nm. This saltatory transformation of the spectrum is caused by the monomolecular conformational transition 'the spiral'–'the rod'.[245, 247]

Thermochromic behaviour of the polydi-n-hexylsilane film is somewhat different [246] from the behaviour of this compound in solution. The UV spectrum of a heated and then cooled film has an absorption band at 317 nm. On storage of this film, the intensity of this band decreases and a new longer wavelength band at 371 nm appears with time. When the film is heated to 100 °C and then is cooled back, the spectrum takes its initial appearance. This transition is completely reversible and can be repeated many times. A phase transition proceeding at 42 °C was revealed by the differential scanning colorimetry. Heating does not result in melting of the polymer to give an isotropic liquid, and thus,

the changes of UV spectrum take place in the solid state of the compound. This allowed studies of the film by means of the X-ray and electron diffraction analysis,[248,249] solid state NMR, IR and Raman spectroscopy.[246,249–251] On the basis of the results obtained, the thermal transitions in polydi-n-hexylsilane responsible for changes in the UV spectrum are well interpreted. The content of the regular segments is minimal in a freshly prepared film. At room temperature the polymer crystallizes to monoclinic form, this results in conformational ordering of the Si_n chain and in appearance of the absorption band in the red region of the spectrum. The heating causes the first-order phase transition from the crystalline to mesomorphic state; as a result, the Si_n chain becomes conformationally disordered. The higher temperature phase was identified as a 2*D*-pseudohexagonal condiscrystalline phase. The position of the absorption band (371 nm) indicates that the length of the regular Si_n chain segment formed in crystallization is larger than in the case of the thermochromic transition in solution (λ = 354 nm). The ionization potentials of polydi-n-hexylsilane were measured[252] at two temperatures, above (50 °C) and below (20 °C) the phase transition temperature (42 °C). It was found that in high-ordered crystalline state IP is lower (5.78 eV) than in the mesomorphic state (5.94 eV).

Polymeric organosilanes with bulky substituents at silicon atoms do not exhibit thermochromic effect, probably, because of existence of higher barriers for rotation around the silicon–silicon bonds, making the thermally initiated conformational transitions unattainable.

Another type of the thermochromism phenomenon was observed for polydiarylsilanes, containing long alkoxy substituents in the *para*-positions of the benzene rings.[253] There are two absorption bands at 325 (strong) and 409 nm (weak) in the UV spectrum of polybis(*p*-butoxyphenyl)silane in *tert*-butoxybenzene solution at room temperature. On warming up, the shorter wavelength band disappears, while the longer wavelength band becomes more intensive. This change in the UV spectrum is reversible (not only for the solution, but also for a film) and is not accompanied by any phase transitions in the polymer. It is believed that the thermochromism of this sort is due to transformation of the silicon chain from the spiral state to the rod-shaped state. In the case under consideration, the spiral state is turned out to be more energetically favourable. The examples discussed above illustrate the variety of forms in which polymeric organosilanes exist, caused by conformational changes in the Si_n chain.

4. The σ-constants of oligosilanyl substituents

The electrophilic (σ_p^+) and nucleophilic (σ_p^-) constants (Table 10) are studied best of the σ-constants of oligosilanyl groups. They reflect the total effect (resonance and inductive) of substituents on the benzene ring when the electron withdrawing and electron donating groups, respectively, are placed at *para*-position.[180] The analysis of σ_p^+ showed that the electron donating effect increases in the series Me_3Si, $Me_3SiSiMe_2$, $Me_3SiSiMe_2SiMe_2$, $(Me_3Si)_2MeSi$. The absolute values for the constants obtained by different methods can vary significantly. However, if measured by the same method, they strictly follow the same regularity. For example, the constants σ_p^+ obtained from kinetic measurements[257] and from ^{13}C NMR data[256] have small negative values (from −0.01 to −0.05, a weak electron donating effect), whereas the constants σ_p^+ calculated[255] from data of the electronic absorption spectroscopy of the charge-transfer complexes (EAS CTC) between oligosilanes and tetracyanoethylene are much larger in their absolute values (from −0.62 to −0.81), demonstrating larger donating capabilities of the Si_n substituents. The general increase of the electron donating capability of oligosilanyl groups can be related to withdrawing the electron density from the π-stystem of the benzene ring by tetracyanoethylene. It is known that the latter forms complexes with both benzene and its derivatives and oligoorganosilanes.[180]

When there is electron deficiency in the benzene ring, enhancement of the σ_{Si-Si}–π-conjugation takes place, which causes the increase of the σ_p^+ constants of oligosilanyl substituents in comparison with those measured by ^{13}C NMR spectroscopy. The higher electron donating capability of the substituents Me_3SiO ($\sigma_p^+ = -0.60$) and Me_5Si_2O ($\sigma_p^+ = -0.60$) as compared with Me_3Si ($\sigma_p^+ = 0$) and Me_5Si_2 ($\sigma_p^+ = -0.23$) is due to the oxygen atom, the lone pairs of which play the crucial role in interactions with the π-system of the benzene ring. The constants σ_p^+ of the substituents Me_3SiO and Me_5Si_2O coincide. Therefore, the perturbations caused by the Si–Si σ-bond in the conjugation system $Si-Si-O-C_6H_4$ are minimal.

The substituents Me_3SiCH_2 ($\sigma_p^+ = -0.66$) and $Me_5Si_2CH_2$ ($\sigma_p^+ = -0.72$) are characterized by larger electron donating capability than Me_3Si ($\sigma_p^+ = -0.22$) and Me_5Si_2 ($\sigma_p^+ = -0.62$). The group $(Me_3Si)_3Si$ bound to the benzene ring shows appreciably weaker electron donating effect ($\sigma_p^+ = -0.11$) than the group $(Me_3Si)_3C$ ($\sigma_p^+ = -0.51$).

The analysis of the known constants σ_p^- shows that the group Me_5Si_2 is in general more electropositive than Me_3Si. This means that the electron density transfer according to the mechanism of the direct polar conjugation from the lone electron pair of nitrogen and oxygen atoms to the group Me_5Si_2 is more difficult than to the group Me_3Si. Deviation from this trend in the series of the sulfur derivatives is insignificant and can be caused by an experimental error in evaluation of the σ_p^- constants.

The Hammett constant of the pentamethyldisilanyl group measured by the classical method[258] is equal to +0.028. The Taft constant for tris(trichlorosilyl)silyl substituent $(Cl_3Si)_3Si$ [$\sigma^* = +1.36$ (Ref. 259)] lies within the range of the values known for the trichlorosilyl group (1.32, 1.55, 1.77, 2.40).[260]

5. Complexes with the Lewis acids and bases

Oligosilanes form charge-transfer complexes with both the Lewis acids and the Lewis bases. If there are organic substituents at silicon atoms, the ionization energy of the oligosilane decreases and it becomes able to form complexes with electron acceptors. In contrast, the halogen substituents withdraw the electron density from the silicon atoms. Upon addition of nitrogen containing bases, complexes with the Si←N bonds are formed and the silicon atoms change their state from tetracoordinated to penta- or hexacoordinated. The complex formation usually represents an initial stage of more complicated processes, which proceed in presence of electron donors or acceptors under heating or irradiation by UV light and result in cleavage of silicon–silicon bonds.

Table 10. The σ-constants of oligosilanyl and some related substituents.

Substituent	Compound	Method	σ_p^-	σ_p^+	Ref.
Me_3Si	4-$Me_3SiC_6H_4OH$	^1H NMR [a]	+0.06	–	254
	4-$Me_3SiC_6H_4Ac$	IR [b]	–	0	254
Me_5Si_2	4-$Me_5Si_2C_6H_4OH$	^1H NMR [a]	+0.02	–	254
	4-$Me_5Si_2C_6H_4Ac$	IR [b]	–	−0.23	254
Me_3Si	4-$Me_3SiC_6H_4Ac$		–	−0.60	254
Me_5Si_2O	4-$Me_5Si_2OC_6H_4Ac$		–	−0.60	254
Me_3Si	4-$Me_3SiC_6H_4NMe_2$	NTN [c]	+0.06	–	255
	Me_3SiPh	EAS CTC [d]	–	−0.22	255
Me_5Si_2	4-$Me_5Si_2C_6H_4NMe_2$	NTN [c]	+0.04	–	255
	Me_5Si_2Ph	EAS CTC [d]	–	−0.62	255
	Me_5Si_2Ph	^{13}C NMR [e]	–	−0.01	256
	4-$Me_5Si_2C_6H_4SnMe_3$	see [f]	–	−0.03	256, 257
1-Me_7Si_3	$Me(Me_2Si)_3Ph$	EAS CTC [d]	–	−0.77	255
	$Me(Me_2Si)_3Ph$	^{13}C NMR [e]	–	−0.01	256
2-Me_7Si_3	4-$(Me_3Si)_2MeSiC_6H_4NMe_2$	NTN [c]	+0.04	–	255
	$(Me_3Si)_2MeSiPh$	EAS CTC [d]	–	−0.81	255
	$(Me_3Si)_2MeSiPh$	^{13}C NMR [e]	–	−0.07	256
	4-$(Me_3Si)_2MeSiC_6H_4SnMe_3$	see [f]	–	−0.05	256, 257
Me_3SiCH_2	Me_3SiCH_2Ph	EAS CTC [d]	–	−0.66	255
$Me_5Si_2CH_2$	$Me_5Si_2CH_2Ph$	"	–	−0.72	255
$(Me_3Si)_2CH$	$(Me_3Si)_2CHPh$	"	–	−0.76	255
Me_3SiS	4-$Me_3SiSC_6H_4NMe_2$	NTN [c]	+0.14	–	206
Me_5Si_2S	4-$Me_5Si_2SC_6H_4NMe_2$	"	+0.17	–	206
$(Me_3Si)_3Si$	$(Me_3Si)_3SiPh$	^{13}C NMR [e]	–	−0.11	256
	4-$(Me_3Si)_3SiC_6H_4SnMe_3$	see [f]	–	−0.06	256, 257
$(Me_3Si)_3C$	$(Me_3Si)_3CPh$	^{13}C NMR [e]	–	−0.51	256
$PhMe_2Si$	$PhMe_2SiPh$	"	–	+0.08	256
$Ph(Me_2Si)_2$	$Ph(Me_2Si)_2Ph$	"	–	+0.01	256
$Ph(Me_2Si)_3$	$Ph(Me_2Si)_3Ph$	"	–	0.00	256
cyclo-Me_9Si_5	cyclo-$Me_9Si_5SiMe_2Ph$	"	–	0.00	256
	cyclo-Me_9Si_5Ph	"	–	−0.07	256
cyclo-$Me_{11}Si_6$	cyclo-$Me_{11}Si_6Ph$	"	–	−0.05	256

[a] The values were calculated by the equation $\sigma_p^- = 0.7\Delta\delta$, where $\Delta\delta$ is a difference between the chemical shifts in substituted and unsubstituted phenols. [b] The values of σ_p^+ were calculated by the equation $\sigma_p^+ = 0.085\Delta\nu$, where $\Delta\nu$ is difference between the wave numbers of the carbonyl group vibrations in substituted and unsubstituted acetophenones. [c] The values of σ_p^- were calculated from basisity of nitrogen atoms determined by non-aquous titration in nitromethane (NTN). [d] The values of σ_p^+ were calculated from the equation $\nu_{CT} = 26200 + 9300\,\sigma_p^+$, where ν_{CT} is the band frequency of the charge-transfer complex with tetracyanoethylene. [e] The values of σ_p^+ were calculated from the equation $\sigma_p^+ = -0.1081(128.24 - \delta^p)$, δ^p is the chemical shift of a carbon atom located in *para*-position to the substituent. [f] The values of σ_p^+ were calculated from rate constants for the Sn−C bond cleavage by perchloric acid.

a. Complexes with the Lewis acids

Formation of coloured charge-transfer complexes by permethylated oligosilanes $Me(Me_2Si)_nMe$ ($n = 2-5$), $Si(SiMe_3)_4$ with teracyanoethylene in solutions in $CHCl_3$ and CH_2Cl_2 was demonstrated in the studies.[261,262] Broad asymmetric charge-transfer bands are observed in the region 400–600 nm and consist of two overlapping poorly resolved bands. The electron is transferred from HOMO of oligosilane, which has the σ-nature, to LUMO of teracyanoethylene of π-symmetry. The doublet form of the bands means that the electron density transfer occurs from both HOMO and a lower lying MO of oligosilane. Even in the first study [261] devoted to the charge-transfer complexes of oligosilanes, it was noticed that dodecamethylcyclohexasilane forms charge-transfer complexes with chloranil (2,3,5,6-tetrachloro-*p*-benzoquinone) (yellow) and with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (violet). For a series of donors of the same type interacting with the same acceptor, the energy of the charge-transfer band relates to the first ionization potential of the donor by the linear dependence

$$h\nu_{CT} = a\,I_1 + b.$$

This dependence enables determining of IP_1 (sometimes, also IP_2) of new compounds with a reasonable precision, without use of the photoelectron spectroscopy. This method was repeatedly used for studies of conjugation effects in derivatives of oligosilane with aryl,[209,255,263–265] vinyl,[266] allyl,[266] alkoxyl, phenoxyl, and thiol [206] substituents. The basis of this method and results of its application are considered in the review.[267]

The complexes do not produce an EPR signal, however a strong nine-line signal of tetracyanoethylene radical-anion appears after irradiation of the solution with light of a mercury lamp at −70 °C;[262] the longer the chain from silicon atoms, the higher the intensity of this signal (tetramethylsilane does not produce a signal under analogous conditions). Thus, the complete transfer of an electron from

σ_{Si-Si}-orbital to tetracyanoethylene proceeds easier for long-chained silanes.

Hexamethyl- and hexaethyldisilanes form weak complexes with bromine and iodine in hexane, CCl_4, CH_2Cl_2, $ClCH_2CH_2Cl$.[268] Tetramethyl- and tetraethylsilanes also form charge-transfer complexes with halogens, but their charge-transfer bands have maxima at lower wavelengths.

Compound	$SiMe_4 \cdot I_2$	$Si_2Me_6 \cdot I_2$	$SiEt_4 \cdot I_2$	$Si_2Et_6 \cdot I_2$
λ/nm	262	297	273	300

The complexes of disilanes with halogens are then transformed to the corresponding halides. When disilane is taken in excess, the rates of consumption of the charge-transfer complexes and halogens are equal, *i.e.*, the system disilane–halogen quickly reaches equilibrium.

$$Si_2R_6 + X_2 \rightleftarrows Si_2R_6 \cdot X_2 .$$

b. Complexes with the Lewis bases

Hexafluorodisilane, hexachlorodisilane, hexabromodisilane, octachlorotrisilane, chloromethyldisilanes ($Cl_2MeSi.SiMeCl_2$, $ClMe_2SiSiMeCl_2$, $Me_3SiSiCl_3$), and fluoromethyldisilanes ($F_2MeSiSiMeF_2$, $F_2MeSiSiMe_2F$) form colored complexes with 2,2′-bipyridine and 1,10-phenanthroline quite stable at room temperature and poorly soluble.[269,270] Even with an excess of the base, they have a composition of 1 : 1. The base is coordinated by its two sites to the same silicon atom (to the middle one in case of octachlorotrisilane). The plane of the base is oriented perpendicularly to the Si—Si bond. If there are silyl substituents, electron withdrawing capability of the silicon atom increases, the following series illustrate this trend:

$$SiMe_3 < SiMe_2Cl < SiMeCl_2 < SiCl_3.$$

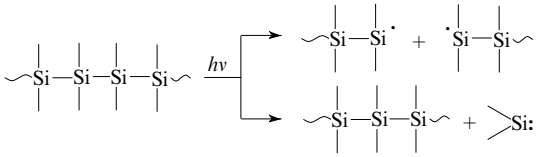
The effect of the $SiMe_3$ group is comparable with the influence of chlorine atom. Octachlorotrisilane is the strongest acceptor in the studied series of compounds. Fluorosilanes are less prone to complexation than the corresponding chlorinated derivatives. Formation of the complexes is the first stage of complex processes in interaction of di- and trisilanes with amines, proceeding on heating and resulting in preparation of oligosilanes and monomers $SiCl_4$ and $MeSiCl_3$.[56,154–156]

V. Applications of oligomeric and polymeric organosilanes

At present, the practical use of oligomeric and polymeric organosilanes in technology is based on two fundamental properties of these compounds, those are the ability to undergo photochemical transformation under UV irradiation and the capability to transform to polycarbosilane and then, when heated, to silicon carbide.

1. The photolithography processes

The photochemical activity of the compounds with silicon–silicon bonds allows their use in processes of photolithography.[64–68] Polymeric organosilanes easily form thin transparent films stable in air. UV irradiation results in cleavage of the Si_n chains, the irradiated areas acquire capability to faster dissolution in organic solvents than non-irradiated areas. The processes of photolytic decomposition of polymeric organosilanes[35,36,46,65,66] are very complex. Two major directions of these processes consist in cleavage of silicon–silicon bonds with formation of silicon-centred radicals and elimination of silylenes.



Then, silyl radicals can abstract hydrogen atoms forming silicon hydride groups or react with oxygen with formation of the groups $\equiv SiOO^{\bullet}$, which eventually transform to hydroperoxide, silanol and disiloxane moieties.

Atmospheric oxygen actively participates in the process of photochemical decomposition. The molecules in the irradiated areas often become cross-linked and hence insoluble. Therefore polymeric organosilanes can act not only as positive but also as a negative photoresist. On exposure, a spectral bleaching due to photodecomposition of the polymer occurs, therefore uniform irradiation of the layer takes place at the whole depth. Due to high content of silicon, polymeric organosilanes are stable to oxygen plasma etching. It is because of fast formation of the surface silicon oxide layer, preventing removal of the lower lying layers. This effect is especially important for manufacturing the schemes with multilayer resists. In the case of a two-level version, a thin (0.1–0.5 μm) layer of polymeric organosilane is applied on top of quite thick (1–3 μm) planarizing layer of organic polymer, which is not photosensitive, but is readily etched by plasma. A high-resolution image is formed in the upper thin layer and then it is transferred into thick planarizing layer by the reactive ion etching. The latter stage results in production of topological elements with almost vertical wall profiles.

2. Optical imaging systems

It was suggested to use[271–274] films of polymeric organosilanes for imaging. The device[271] consists of a layer (1 μm) of titanyl phthalocyanine (TiOPc) dispersed in polyvinylbutyryl rubber and applied on a plate of aluminium or silicate glass; on top of it a layer (3 μm) of transparent colourless poly(phenylmethylsilane) (PPMS) is applied. Under UV irradiation, active species (radicals, silylenes) are formed in PPMS, which interact with TiOPc, bleaching the lower lying blue layer. Development of the hidden image occurs upon heating the plate at 250 °C only. Another version of the process[272] consists in that the PPMS film is applied to a glass plate coated with a conducting indium tin oxide layer. After exposure, the plate is rinsed with an organic solvent. Development of the hidden image is carried out by electrochemical polymerization of thiophene derivatives, using the plate as an electrode. Fokushima *et al.*[273] used for the imaging the layers of PPMS and polyphenylhydrosilane (PPHS) of thickness of 0.2 μm and solution of $AgBF_4$ in EtOH as a developer. When the PPMS film is irradiated, a positive image is formed, irradiated areas (siloxanes) are removed by alcohol. Upon exposure of the PPHS film, a negative image is formed, the polymer becomes cross-linked and loses solubility, unirradiated areas are removed with toluene. The developer reacts with the polymer with formation of colloid silver.

3. Light-emitting diodes

PPMS was used [274, 275] for manufacture of diodes emitting light in the UV (see Ref.[274]) and visible [275] regions. The pure polymer emits in the UV region (electroluminescence), the polymer doped with the complex $[Eu(TTFA)_3]$ (TTFA is 2-thenoyltrifluroacetone) emits in the red region. These materials are suggested for use in manufacture of colour displays.

4. The offset printing

The possibility of use of polymeric organosilanes in the offset printing was shown.[276] Formation of a hidden image in the PPMS film is carried out by photochemical oxidation of the polymer under UV light. Hydroxyl and siloxane groups are accumulated in the irradiated areas resulting in increase in their wettability by the ink. Unexposed areas remain hydrophobic and after spraying the ink, they do not stain.

5. The electrophotography

Pure polymeric organosilanes are dielectrics. Upon doping with antimony pentafluoride or arsenic pentafluoride, some of them become semiconductors.[36, 42] It was suggested [81, 82, 277] to use PPMS as a photoacceptor in the electrophotography. This usage is ensured by high photosensitivity of the polymer and its strong hole conduction of 10^{-4} cm^2 V s^{-1}, this figure is significantly larger than that for poly(*N*-vinylcarbazole), which is usually used in xerography. Polymethylphenylsilane can be combined with the charge photogenerators like selenium or phthalocyanine pigment. The charge mobility is practically independent of the nature of substituents at silicon atoms in the polymeric organosilane. This fact indicates that the hole transport occurs *via* the σ-electronic states of the silicon chain rather than by hopping between the substituents.[66, 80, 81] The drift mobility depends on the applied electric field and the temperature. The activation energy for PPMS is 0.25 eV, this value is one of the lowest of the known for amorphous solids.

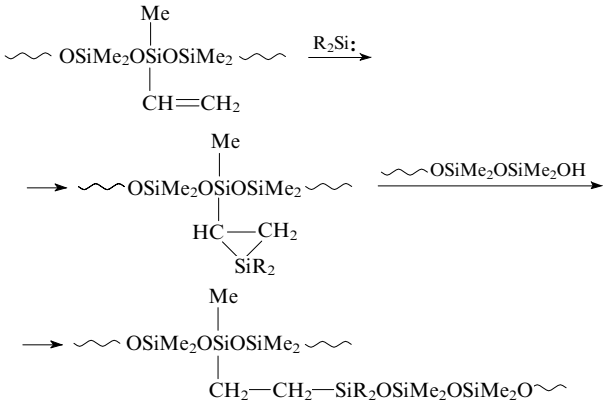
6. Initiation of the free radical polymerization

The capability of polymeric organosilanes to generate free radicals is used [278, 279] in photopolymerization processes with participation of various organic monomers, those are acrylic acid and its methyl, ethyl, n- and *tert*-butyl, and cyclohexyl esters, methacrylic acid and its methyl ester, styrene and its 2-chloro- and 2,4-dichloro-substituted derivatives, acrylamide, acrylonitrile and so on. Polymeric organosilanes were added in an amount of 0.015 – 0.032 g per 8 – 10 ml of the monomer, the mixture was irradiated by solar light (12 – 19 h) or the mercury lamp light (10 – 50 min) in pyrex tubes. The efficiency of initiation (f) by poly(phenylmethylsilane) is equal to 1×10^{-3} only (for comparison f is equal to 1.0 for di-*tert*-butylperoxide, 0.28 for α,α-dimethoxydihydrobenzoin, 1×10^{-4} for acetone). The low initiation efficiency is obviously explained by proceeding of the competitive disproportionation of the silyl radicals as well as by steric hindrances. It was shown by means of UV and ^{29}Si NMR spectroscopy that during the styrene polymerization polysilane fragments $(PhMeSi)_n$ ($n = 4 – 6$) become embedded into the polymer carbon chain. The authors also noticed absence of oxygen inhibition, unusual for typical radical polymerization processes.

7. Vulcanization of silicon rubbers

In the studies [16, 280] the fragments $\rangle SiPhSiMe_3$ were inserted into chains of polyorganosiloxanes containing methylvinyl-, methylallyl- and methylbut-3-enylsiloxane groups in addition to dimethylsiloxane groups by catalytic co-polymerization of octamethylcyclotetrasiloxane $(Me_2SiO)_4$ with organocyclosiloxanes $(RMeSiO)_n$ ($n = 3, 4$; R = vinyl, allyl, but-3-enyl) and $(Me_3SiSiPhO)_3$. The 2 – 10 μm thick films were cured by irradiation with a 500 W xenon – mercury lamp for 5 min in air or in nitrogen atmosphere. The cross-linking of the polysiloxane chains occurs due to sequentially occurring reactions of radical cleavage of silicon – silicon bonds and homolytic aromatic substitution by silyl radicals. Thick (up to 100 μm) films are only cured if the liquid rubber contains methylbut-3-enylsiloxane groups. The authors explained this fact by higher inclination of the latter groups to the radical polymerization in comparison with methylvinyl- and methylallylsiloxane groups.

Minor additives of soluble oligoorganosilanes (1 mass % – 3 mass %) to liquid siloxane rubbers cause their curing in air under UV light.[281 – 284] Both permethylated and methylvinyl derivatives undergo vulcanization. The necessary requirement of good polymerization consists in presence of terminal hydroxyl groups in the polysiloxane molecules. Oxygen has no inhibitory effect on this reaction. Initiating effect is only exhibited by compounds known as good photolytic sources of silylenes, *viz*. dedecamethylcyclohexasilane $(Me_2Si)_6$, linear permethylated oligomers $Me(Me_2Si)_nMe$ ($n = 4 – 6$), 2-phenylheptamethyltrisilane $(Me_3Si)_2SiMePh$ and 2,2-diphenylhexamethyltrisilane $(Me_3Si)_2SiPh_2$. Phenylsilanes $Me_3SiSiBu^n_2Ph$, $Me_3SiSiMePh_2$, $Ph_2MeSiSiMePh_2$ do not initiate photopolymerization despite their large extinction coefficients. Addition of organic peroxides also did not result in curing even upon prolonged irradiation. Octamethyltrisilane $Me(Me_2Si)_3Me$ and 1-phenylheptamethyltrisilane, known as not good sources of silylenes, have lower initiation activity. Replacement of the hydroxyl groups in the rubber molecules causes abrupt deceleration of the vulcanization. On the basis of these facts, it was assumed, that active compounds responsible for vulcanization effect are silylenes $R_2Si:$. This mechanism of this process was proven in photochemical reactions with model compounds.[282] It consists in addition of diorganosilylene to vinyl group with formation of strained silirane ring. Cross-linking occurs by subsequent addition of a terminal OH group of polysiloxane to this silirane.



In the case of permethylated rubbers, silylene generated by UV irradiation inserts into the SiO–H bond with formation of hydrosilane $SiOSiR_2H$. Upon irradiation, the latter undergoes the condensation reaction with a compound containing silanol group with formation of disiloxane fragment and release of hydrogen.

$$\sim OSiMe_2O{-}H + R_2Si: \longrightarrow \sim OSiMe_2OSiR_2H$$

$$\sim OSiMe_2OSiR_2H + HOSiMe_2O\sim \xrightarrow[-H_2]{} \sim OSiMe_2OSiR_2OSiMe_2O\sim$$

The study of kinetics of the photopolymerization[283] by means of laser interferometry, as well as the study of characteristics of the cured elastomers showed the following things. The vulcanization rates differ strongly depending on the photoinitiator used. There is no full parallelism between the rates of the oligosilane destruction and the rubber structurization, although in the limiting cases there is coincidence, *i.e.* the most slowly decomposing compound (dodecamethylcyclohexasilane) causes slow structurization, extending to the great depth (determining high quality of the film formed). 2,2-Diphenylhexamethyltrisilane decomposes most rapidly resulting in fast structirization to small depth (determining low quality of the coating). Thus, the structurization of the matrix either occurs synchronously with the photoinitiator decomposition or drops behind it.

The rates of generation of the active species and cross-linking of the polysilane molecules caused by these species depend on each other in a complicated manner. At low concentrations (0.5%) of dodecamethylcyclohexasilane, the decomposing photoinitiator is effectively used in the process of cross-linking of the matrix. With increasing concentration, the rate of the rubber structurization starts to drop behind the organosilane decomposition rate, *i.e.* not all of the generated species participate in cross-linking of the polymeric molecules. The part of the efficiently used species increases with the increase of the concentration of a light-sensitive component from 0.5% to 2.0%. On further increase of the concentration to 4.0%, the structurization rate remains constant, however the process proceeds to a greater depth due to increasing the content of active particles. An approximate equality of the initiator decomposition and rubber structurization rates is attained at some initial concentrations of the photoinitiator. The structurization rate dropping behind the organosilane decomposition rate is explained by the fact that not every species able to cause cross-linking finds a fragment (a multiple carbon–carbon bond) of the polymeric molecule that can participate in the cross-linking reaction.

The minimal time of curing is 45 s for the layer thickness of 30 μm. Content of the gel fraction in thick films (150–200 μm) increases from 27% to 72% with increasing irradiation time. The visually observed fast vulcanization (absence of stickiness) is reached at larger content of sol fraction (up to 70%) and provided by polymerization of the upper layer of the film. Further irradiation causes increase in cross-links and hardening of the film. At thickness in 300 μm, curing to a sufficient depth cannot be reached in 3 min, therefore no film of good quality can be produced (the deepest layers remain non-cured).

8. Film-forming materials cured under UV irradiation

Oligomeric organic allyl esters are applied as film-forming substances.[285] To create thermostable coatings, organosilicon compounds are used.[286] The basis of industrial silicone coatings are most often polyorganosiloxanes, thermally cured by a mechanism of hydrolytic polycondensation. Allyloxy-substituted oligosilanes are promising compounds for preparation of new film-forming materials.[287] Of four studied compounds, containing vinyl, allyl or allyloxyl substituents at silicon atoms [$Vin_2MeSiSiMeVin_2$, $All_2MeSiSiMeAll_2$, $(AllO)_2MeSiSiMe(OAll)_2$, $H(AllO..SiMe)_n(SiMe_2)_mH$], the best capacity for photocuring in a thin layer was demonstrated by oligomer with hydride groups at silicon atoms.

These groups are formed in the course of synthesis of the oligomer from polymethylchlorosilane $(ClSiMeCl)_m..(SiMe_2)_nCl$ (Ref. 156) and allyl alcohol in presence of triethylamine by partial cleavage of silicon–silicon bonds. The structurization occurs by hydrosilylation reaction initiated by UV irradiation. Curing happens under irradiation in 5 min.

9. Regulators of molecular weight of polymers

Chain transfer to solvent or a specially added compound (a chain transfer agent)[288] is used in industry to control the polymer molecular weight. Good chain transfer agents are the compounds, containing hydrogen or chlorine atoms active in radical reactions. Thiols and tetrachloromethane found their wide application as regulators of molecular weight. The more chain transfer agent is introduced to the system, the smaller the molecular weight of polymer. The regulator activity is characterized by the chain transfer constant (C_s), which is equal to the ratio of rate constants for chain transfer and chain propagation. For instance, $C_s \times 10^3$ for CCl_4 in polymerization of vinyl acetate (VA), methyl methacrylate (MMA) and styrene is equal to 1000, 0.24 and 9.0, respectively.[288] Silicon hydrides **29**–**43** of different structure were used as chain transfer agents in the radical polymerization of these monomers (Table 11) in the studies.[289–294]

The C_s values for all organohydrosilanes (with the only exception) in polymerization of VA are larger than those in

Table 11. The constants for chain transfer *via* organohydrosilanes in the bulk polymerization of vinyl acetate, methyl metacrylate and styrene at 60 °C.

The number	Organohydrosilane	$C_s \times 10^3$		
		VA	MMA	styrene
29	$Me_3SiSiMe_2H$	216	56	14
30	$H_2MeSiSiMeH_2$	1387	234	37
31	$Bu^i_2MeSiSiBu^iMeH$	134	13	7
32	$HPr^iMeSiSiMePr^iH$	420	72	14
33	$HMe_2SiSiMe_2H$	550	175	18
34	$(Me_3Si)_3SiH$	4120	8300	550
35	$(Me_3Si)_2SiMeH$	2264	706	92
36	$H_3SiCH_2CH_2SiH_3$	386	9	7
37	$(Me_3SiCH_2)_3SiH$	13	20	16
38	$(Me_3SiO)_3SiH$	2	–	–
39	$(Me_3SiO)_2SiMeH$	9	1	5
40	$(HMe_2SiO)Me_2Si..SiMe_2(OSiMe_2H)$	30	7	22
41	$(HMe_2SiO)Me_2Si..SiMe(OSiMe_2H)_2$	16	4	17
42	Pr^i_3SiH	13	3	5
43	Et_3SiH	16	4	7

polymerization of MMA and styrene. A strong dependence of the chain transfer constant on structure of the organosilicon compounds was ascertained. The most active compounds are those containing hydrogen atom at di-, tri- or tetrasilanyl fragment. The constant C_s significantly increases on going from the compounds of normal structure to the iso-derivatives and then to the tertiary compounds. Tris(trimethylsilyl)silane is more active than CCl_4 in vinyl acetate, methyl methacrylate and styrene polymerizations by 4, 35 000 and 60 times, respectively. Carbosilane (**36**, **37**), siloxane (**38**–**41**) and silane (**42**, **43**) hydrides are much less active than oligosilanes. If disilanyl fragment is separated from the silicon hydride group by an oxygen atom (**33**, **40**), the activity of this compound as a chain transfer agent is substantially decreased.

A linear dependence of $\log C_s$ on the sum of the inductive constants (σ_i) of substituents at the silicon atom bound to a hydrogen atom was revealed for monofunctional hydrides **29**, **34**, **35**, **38**, **39**.

In the case of vinyl acetate polymerization:

$$\log C_s = -(5.5 \pm 0.4)\,\Sigma\sigma_i - (1.7 \pm 0.1);$$

for methyl methacylate polymerization:

$$\log C_s = -(7.6 \pm 0.7)\,\Sigma\sigma_i - (2.7 \pm 0.2).$$

The large negative values of the reaction constants indicate substantial charge separation in the transition state of the chain transfer. The oligoorganohydrosilane molecule acts as a nucleophile, whereas the radical species is an electrophile. The higher nucleophilic activity of oligosilane hydrides can be explained by donation of the electron density by the trimethylsilyl groups to the silicon atom and to the hydrogen atom bound to it. Obviously, the latter is attacked by the growing macroradical first of all. The low activity of siloxane hydrides **38**, **39** is explained by electron withdrawing properties of the Me_3SiO group.

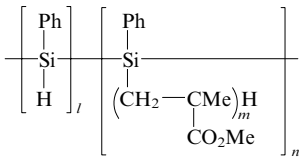
Poly(methyl methacrylate) obtained with use of oligoorganosilanes in the polymerization process was tested as a positive electron-beam and X-ray resist and demonstrated increased sensitivity while maintaining high contrast coefficient.[289]

Polyfunctional compounds containing 2–4 hydrogen atoms (**30**, **32**, **33**) were used[294] to introduce the Si–H group into the macromolecule. 1,2-Dimethyldisilane (**30**) proved to be most suitable for this goal. Polymerization in presence of this compound leads to the polymer molecules containing silicon hydride junctions and ends, due to which they undergo further transformations by the hydrosilylation reaction.

10. Graft copolymers of polyphenylsilane with methyl methacrylate

Oligomers $H(RHSi)_nH$ consisting of organosilicon hydride groups have special importance for the above processes because each group can take part in the chain transfer step. The study of polymerization of MMA in presence of oligophenylsilane $H(PhHSi)_nH$ ($n = 6$–10) showed[295] that the reactants taken in the ratio 1 : 1 (one molecule of MMA per PhSiH group) are copolymerized even in absence of free radical initiators. The reaction slowly proceeds in the cold (from −5 to 8 °C, 15 days), and faster at ambient temperature (20 h). Heating in the presence of organic peroxides accelerates the process resulting in light yellow non-transparent glassy co-polymer of poly(phenylsilane) (PPS) with MMA.

The addition of hydroquinone results in pronounced slowing down of the polymerization process. Copolymers were obtained from mixtures of MMA and PPS at initial molar ratios from 50 : 50 to 94 : 6. After reprecipitation they represent white glassy materials soluble in acetone, THF, ether, benzene, CCl_4, CH_2Cl_2 and poorly soluble in saturated hydrocarbons and methanol. All the copolymers are unimodal and characterized by small molecular weights (1 600–4 000) and polydispersity indexes (1.3–1.4). Formation of graft polymer



in the reaction of PPS and MMA can proceed according to two mechanisms: the mechanism with initial generation of silyl radicals initiating the fast terminating polymerization and the free radical mechanism of MMA polymerization with chain transfer to PPS.

11. Catalysts of olefin metathesis

Permethylated linear ($Me(Me_2Si)_4Me$) and cyclic ($(Me_2Si)_6$) oligosilanes were applied[296] for preparation of catalyst of α-alkene metathesis. Tungsten hexacarbonyl and oligodimethylsilane were irradiated with UV light. The reduced tungsten subcarbonyl products containing dimethylsilylene coordinated by an atom of the transition metal catalyzed transformation of hex-1-ene to dec-5-ene. Exchange of tungsten hexacarbonyl by tungsten hexachloride results in sharp decrease in the yield of dec-5-ene despite increase in conversion of hex-1-ene.

12. Reducing agents

Tributylstannane is often utilized as a reducing agent in the fine organic synthesis.[297] Its activity is due to easy hydrogen atom abstraction by the radical mechanism. Simple silicon hydrides [both organic R_3SiH (R = Et, Ph, EtO) and inorganic X_3SiH (X = Cl)] are less active reducing agents. According to the study[298] one of the reasons of this fact consists in higher strength of the Si–H bond as compared with the Sn–H bond (by ~10 kcal mol^{-1}). Oligoorganohydrosilanes are more active in free radical reactions. A vivid demonstration of this fact is transformation of pentamethyldisilane into pentamethylchlorodisilane[137] by heating at 50 °C in CCl_4 in absence of free radical initiators. Triethylsilane remains unchanged under similar conditions.

Tris(trimethylsilyl)silane was suggested[113,299] to be used as the most effective reducing agent, comparable in its activity with tributylstannane. Absolute rate constants of the hydrogen abstractions by carbon- and oxygen-centred radicals are commensurable for $(Me_3Si)_3SiH$ and Bu^n_3SnH. Tris(trimethylsilyl)silane is easily accessible as it can be prepared[300] in one stage from the industrial products, *viz*. trichlorosilane, trimethylchlorosilane and lithium. It readily reduces many organic compounds, *viz*. chlorides, bromides, iodides, acyl chlorides, isocyanides, thioethers, with good yield (80%–99%). Addition of the $(Me_3Si)_3Si$ group is observed in case of interactions with unsaturated organic compounds and ketones. For instance, β-[tris(trimethyl-

silyl)silyl]styrene and tris(trimethylsilyl)silyloxycyclohexane are formed from phenylacetylene and cyclohexanone, respectively [113, 298] The hydride $(Me_3Si)_3SiH$ is oxidized by air oxygen to $(Me_3SiO)_2(Me_3Si)SiH$.

The advantages of application of another easily accessible oligosilanyl reducing agent, 1,4-dihydrooctaphenyltetrasilane $H(SiPh_2)_4H$, were demonstrated in the study.[301] Its reaction with alkyl halides is carried out in presence of $AlCl_3$. The mechanism of this reaction is not radical, it consists in the transfer of hydride anion from silane to the carbocation formed in the interaction of the Lewis acid with RCl.

It was suggested to utilize hexachlorodisilane as a reducing agent in syntheses of organic derivatives of nitrogen,[302] phosphorus [303–305] and sulfur.[304] The products are obtained in good yields. The reduction occurs fast and under mild conditions. For example, 4-methylpyridine oxide is transformed to 4-methylpyridine in chloroform at 25 °C in 1 h in 95% yield, diphenyl sulfoxide is converted to diphenyl sulfide in benzene at 25 °C in 1 h in 91% yield, methylphenylallylphosphine oxide gives methylphenylallylphosphine (of 100% optical purity) in benzene at 80 °C in 5 min in 73% yield. The mild conditions of the reaction are especially important for preparation of optically active phosphines from their oxides, because increasing temperature results in racemization of the phosphine and the optically pure product cannot be obtained. Reduction of acyclic phosphine oxides proceeds with inversion of the configuration and is highly stereospecific. It is interesting to note that the reaction with trichlorosilane results in retention of the configuration. If a mixture of $SiHCl_3$ with a strong base like triethylamine is used instead of $SiHCl_3$ itself, inversion of the configuration at the phosphorus atom takes place. This fact was explained [305] by presence of perchloropolysilanes $Cl(SiCl_2)_nCl$ in the reaction mixture, which are formed under the base influence by trichlorosilane disproportionation and reduce phosphine oxides to the inverted products. Phosphetane oxides and phosphine sulfides are reduced by hexachlorodisilane with complete retention of the configuration of substituents at the phosphorus atom.[306]

13. Chemosensors for nitroaromatic compounds

There have been attempts to create sensors for explosive compounds on basis of polymeric organosilanes.[307–309] The detection is based on the effect of quenching of the polymer photoluminescence due to formation of complexes between the polymer molecule and nitroaromatic compound. Two types of polymers show high chemosensing activity, those are polytetraphenylsiloles [307, 308] and poly(3,3,3-trifluoropropylmethylsilanes).[309] A broad absorption band and a narrow emission band are presented in the UV spectra of polymeric organosilanes. The emission band of fluorinated polymer [309] lies at 335 nm (excitation at $\lambda_{exc} = 280$ nm) and has half-width of 20 nm. Formation of complexes with 1,3-dinitrobenzene, 2,4-dinitrotoluene, 1,3,5-trinitrobenzene and 2,4,6-trinitrophenol (picric acid) results in quenching of the luminescence. Dependence of the fluorescence intensity on the concentration of the quenching agent follows the Stern–Volmer equation for all tested compounds. High values of the Stern–Volmer constant ($0.84–4.15 \times 10^4$ mol litre^{-1}) indicate effective quenching of luminescence of polymeric organosilane by nitroaromatic compounds. Poly(n-propylmethylsilane), a non-fluorinated analogue of the fluorinated organosilicon polymer, shows lower sensitivity to the quenching. It is explained [309] as it follows.

Trifluoroproyl substituents stabilize both HOMO and LUMO of the polymer relative to the non-fluorinated analogue, causing approach of the polymer LUMO energy to that of nitroaromatic compound. Thereby, the electron transfer from polysilane LUMO to quenching agent LUMO becomes easier. Transition of the complex to the ground state occurs by a radiationless deactivation. Low efficiency of fluorescence quenching in case of poly(n-propylmethylsilane) is due to its inability to form complexes with nitroaromatic compounds. Because of withdrawing effect of trifluoropropyl substituents in molecules of the fluorine containing polymer, the silicon atoms of this polymer are more capable to coordination with oxygen atoms of nitro groups. Using poly(3,3,3-trifluoropropylmethylsilane) as an example, the possibility of creation of chemosensors was demonstrated,[309] as the quenching effect operates not only in solutions but also in thin polymeric films.

14. Chemical vapour deposition processes

The chemical vapour deposition (CVD) processes are widely used in production of materials for electronic engineering,[310] particularly, for formation of polycrystalline silicon and silicon thin-layer materials. The base compound for silicon microelectronics is monosilane of high purity. Depending on the conditions, the method of its thermal decomposition can be directed either to production of polycrystalline silicon or to formation of films of amorphous hydrogenated or epitaxial crystalline silicon. Deposition of crystalline materials occurs at high temperatures (700–1000 °C), while formation of amorphous products proceeds at lower temperatures (400–500 °C). Amorphous hydrogenated silicon [114, 311] α-Si:H, a realtivelly new semiconducting material, contains up to 50 at.% of hydrogen. The increased interest in this species is caused, first of all, by an opportunity of manufacturing cheap convertors of the solar energy to the electric one on the basis of this material. It is because of effective absorption of the solar light by this material, facility of deposition of its films on large substrates from differen materials, high photoconductivity and adjustable electroconductivity, and the possibility of doping by carbon, nitrogen, oxygen, fluorine, chlorine, germanium and tin. Plasmochemical methods utilizing direct current and high-frequency gas discharges are widely used for deposition of amorphous hydrogenated silicon.

Disilane Si_2H_6 and its heavier homologues (Si_3H_8, Si_4H_{10}, *etc.*) are less accessible and more expensive compounds than monosilane SiH_4, large-scale production of which is well established.[312] Despite of this, the studies of thermal decomposition of higher silanes are quite numerous. First of all, it is dictated by the fact that the oligosilanes are decomposed at temperatures lower than those necessary for monosilane decomposition and give films with variable electrophysical characteristics.[313–315] It is found that use of Si_2H_6 enables to reach larger rates of film growth both in thermal and photochemical processes. Disilane is utilized as a pure substance or in mixture with helium or argon (5 vol.%–10 vol.%). The substrate temperature is of 400–500 °C in the thermal process. With increasing temperature, the hydrogen concentration in the α-Si:H layer decreases to 5 at.%. The portion of the Si_3SiH moieties in comparison with the $Si-SiH_2-Si$ moieties

increases simultaneously The substantial advantage of the disilane utilization consists in possibility to realize photochemical method of film deposition,[315] it is because its absorption edge is shifted to the longer wavelength region (to 200 nm). Molecules of Si_2H_6 are decomposed by the excimer ArF laser emission at 193 nm.

Epitaxial silicon layers are grown from disilane by molecular-beam epitaxy.[316] It was noted that application of Si_2H_6 in place of SiH_4 allows one to decrease significantly the temperature of the process (to 630 °C) and to increase the rate of film growth, simultaneously reducing the number of defects in the film.

The CVD method is quite promising for production of silicon nanoparticles doped with cations of rare-earth metals.[317] Formation of aerosols[311,318] from α-Si:H is often observed in thermal or plasmochemical decomposition of mono- and disilane and represents a negative factor, breaking structural perfection of films of amorphous hydrogenated silicon. Conduction of the process at ~1000 °C results in formation of superdispersed particles of elemental silicon instead of the α-Si:H phase. Nanoparticles of this sort of 11–15 nm size doped with erbium were obtained[317] by high-temperature decomposition of the gas mixture of disilane with volatile erbium β-diketonate, erbium tris(2,2,6,6-tetramethylhepta-3,5-dionate), $Er(tmhd)_3$. The choice of this metal is dictated by its capability to emit light at 1.5 nm,[319] the wavelength that is used in modern fibre-optic lines of communication for transmission of the light signal.[320] Amplification of intensity of the emission of erbium(III) cation present in transparent glass or semiconducting material is a relevant problem, its solution is highly important for improvement of a principal components of telecommunicational systems, erbium fibre-optic amplifiers of light signals.[321] Cations of rare-earth metals have low extinction coefficients (ε), therefore light of quite high intensity is required for their excitation. Pumping of erbium cation[320] is carried out *via* its short-lived level $^4I_{11/2}$ by light of 980 nm. When excited at 488 nm, the nanoparticles of Si : Er obtained in the study[317] show broad intensive emission band centred at 1550 nm. Intensity of the emission decreases with increase of the excitation wavelength λ_{exc} from 475 to 514 nm. This fact together with absence of the pronounced band of the silicon nanoparticle emission, always observable in the visible region,[310] indicates that transmission of the absorbed energy from the silicon component of the ultradispersed particle to the cation Er^{3+} occurs, further transition of the cation from its metastable level $^4I_{13/2}$ to the ground level $^4I_{15/2}$ results in emission of photon with energy of 0.83 eV. Thus, a problem of low value of ε for Er^{3+} is overcome and an effective amplification of the light pulse is achieved.

15. Fibres, coupling agents and coatings made of silicon carbide

In 1975 Yajima[322] obtained firm thermostable silicon carbide fibre by pyrolysis of polydimethylsilane. The latter was initially transformed to soluble gumlike polymethylcarbosilane[323] by heating at 450 °C in autoclave. Thin fibres were pulled through a fibre die, conserved from surfaces in air and then heated under nitrogen from 400 to 1300 °C in accordance with a specially developed procedure. The conservation consists in formation of a thin protective cross-linked polycarbosiloxane layer on the fibre surface.

$$\text{—(SiMe}_2\text{)}_n\text{—} \xrightarrow{450^\circ,\ 14\ \text{h, autoclave}} \text{—(SiMeH—CH}_2\text{)}_n\text{—} \xrightarrow[\text{conservation}]{200^\circ,\ O_2} \text{(60\%, } M_n = 1750\text{)}$$

$$\longrightarrow \cdots \xrightarrow[\text{annealing}]{1300^\circ,\ N_2} \beta\text{-SiC (Nicalon)}$$

The silicon–carbide fibre NICALON obtained in this way has the following characteristics: it is resistant to stretching up to 2500 MPa, diameter of fibres is 13–15 μm, elongation is ~2%, density is 2.55 g cm^{-3}, number of threads in a bundle is 500.

The gum used to obtain the fibre is a binder agent ready for use.[323] It is applied as a coupling agent in forming high-temperature composite products with ceramic matrix[324] by hot pressing,[325] including the following stages:

— mixing of ultradisperse or fibrous silicon carbide with solution of polycarbosilane gum in an organic solvent;

— drying (solvent removal);

— crushing;

— screening, after which powder of silicon carbide coated by polycarbosilane is obtained;

— cold pressing;

— sintering.

Polycarbosilane is an excellent coating for devices and individual parts working at high temperatures and in corrosive media. Foreign manufacturers offer a wide range of silicon carbide fibres, coupling agents and coatings on the basis of polycarbosilane. Well-known companies like 'COI Ceramics' and 'UBE Industries' produce the following widely used sorts of fibres and coatings: Hi-NICALON TM Type S Ceramic fibre, SYLRAMIC TM SiC Fiber, Tyrannoxes Fiber, SA-Tyrannoxes Fiber, Tyranno Fiber S (High Temperature Grade), Tyranno Fiber LoxM (High Temperature Grade), Tyranno Fiber ZMI (High Temperature Grade), Tyranno Fiber SA3 (High Temperature Grade), Tyranno Fiber (Semi-Conductive Grade) Types A, C, D, F, G, H, Tyranno Coat Types ST-100, CT-100, HD-100, EI-100, MR-100, PM-100, VN-100, UI-100, Starfire SMP-10 (Liquid precursor to SiC-ceramics).

In the USSR, production of silicon carbide fibre was developed by researchers of the State Research Institute for Chemistry and Technology of Organoelement Compounds.[133] At present, the silicon carbide fibre is not produced in Russia.

Later, the method of Yajima was improved by both Yajima himself and other researchers.[51–53,63,133,326] To increase the yield of silicon carbide, many polymeric organosilanes and other organosilicon compounds like polysilylenethylenes $(R_2Si-C\equiv C)_n$ and polydisilanylenethylenes $(R_2SiSiR_2-C\equiv C)_n$ were tested.[133,313] Oligo- and polyorganohydrosilanes $(RHSi)_n$ produced by catalytic disproportionation of primary silanes $RSiH_3$ are considered as very promising sources.[111] The performance characteristics of silicon carbide fibre is significantly improved when it is doped with nanodispersed particles of titanium or zirconium carbonitrides. Introduction of these dopants is achieved by addition of alkylamides of these metals to polycarbosilane[327–333] at the stage of its pyrolytic decomposition. The initial product for production of the fibre and coupling agent is obtained with use of sodium dispersion in toluene. This process presents a high fire hazard. A new relatively safe method of production of polydimethylsilane was suggested.[334] It consists in interaction of dichlorodimethylsilane with sodium deposited on the surface of a solid

inflammable inorganic material (sodium or calcium chloride). Processes of thermal decomposition of precursors of ceramic silicon-containing materials are considered in details in the studies.[51–53, 63, 133–135]

VI. Conclusion

Oligo- and polyorganosiloxanes represent the largest class of organosilicon compounds, on the basis of which various materials having numerous applications in life and technology are produced. In their chemical structure, they represent chains of silicon atoms separated by oxygen atoms. For the first time, the idea of production of thermostable dielectrics consisting of silicon oxide chains with organic groups attached to their silicon atoms was expressed by academician K A Andrianov in 1935.[335] The modern industry of organosilicon materials is mainly based on utilization of methyl derivatives, and thus, on the direct method of synthesis of dichlorodimethylsilane suggested by Rohow and Müller in 1940. The chemistry of oligo- and polyorganosilanes was developing in the early 20th century in parallel with the chemistry of polyorganosiloxanes, which are very useful for electrical engineering.

An idea of synthesis of organosilicon analogs of saturated hydrocarbons was formulated and fulfilled by Kipping.[336] However the synthesized polyorganosilanes did not find practical application. The syntheses with use of alkali metals were laborious, while the obtained organosilicon gums could not compete with polyorganosiloxanes. As it was mentioned in the introduction, polydimethylsilane, an oxygen free analog of polydimethylsiloxane, prepared by Burkhard in 1949, proved to be non-melting polycrystalline polymer, hardly suitable for transformation to practically useful products. For many years, this work was overlooked by researchers. Only in 1975, owing to studies of Yajima[322] the polymer obtained by Burkhard found its application for production of high-temperature composites with ceramic matrix.

Thus, as in the case of polysiloxanes, just the simplest polysilane found its practical use. The examples of search for new practical applications discussed above are not exhaustive. New studies concerning new directions of use of compounds containing silicon–silicon bonds are regularly published in domestic and international journals. All of them are based on combination of unique properties typical of oligoorganosilanes:

— pronounced delocalization of σ-bonds and consequent ability to absorb and emit in the UV region, as well as occurrence of non-linear optical and semi-conducting properties;

— high photochemical activity, production of radicals and silylenes under UV irradiation;

— inclination to thermal rearrangements and silylene formation, lower thermal stability in comparison with monomeric analogues;

— formation of charge-transfer complexes.

Microlithography and synthesis of silicon carbide are now the most developed processes in chemistry of organosilanes.

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