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New approaches in silicon production and recycling for sustainable future

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Abstract. Key prerequisites for the accelerated development of chemistry of silicones are considered in the context of the significance of organosilicon polymers for sustainable future. The principal trends in this field during the past two decades are analyzed and the quantum leap that occurred in the control of the structures and selective synthesis of macromolecules is pointed out. The problems of research into silicones are defined and the most promising approaches to the solution of these problems aimed at more active involvement of such systems into various areas of practical activity are demonstrated. The bibliography includes 166 references.

I. Introduction

The role of silicon and its numerous derivatives in the development of the civilization steadily increases. It is impossible to imagine today's life without computers and other semiconductor devices. The modern aircraft and spaceship industry is impracticable without organosilicon polymers, which are suitable for use at extremely low or high temperatures. Without silicones, many modern medical technologies would not be possible. Numerous examples of domestic applications of organosilicon compounds are known. To sum up, the last third of the 20th century and the beginning of the 21th century can be called an era of silicones. The aim of the present review, which was written based on the materials of the presentation at the Russian – German Symposium 'Chemistry Shaping the Future', is to analyze the prospects of the improvement of silicone-based material properties in relation to the global idea of sustainable development. In the context of elaboration of new technologies, the sustainable development is meant to establish environmentally friendly energy- and material-efficient industrial plants providing the total recycling of the produced items.

In recent years, materials based on natural or semi-synthetic polymers, which are either naturally occurring (for example, cellulose, starch, chitin) or are derived as a result of the minimal structural modification of native macromolecules (for example, esters of cellulose, chitosan, polylactide, *etc.*), have found ever-increasing application. However, when switching the polymer material production to renewable resources, one should not forget about the improvement of methods for the preparation of synthetic macromolecules. The modern engineering cannot do without polymer materials. To design such materials, chemists have to compete with the nature. Although the superiority of the nature in the field of biopolymer systems over state-of-the-art research facilities is undeniable, the synthesis methods went far ahead in the qualitative variety of new polymer materials with unique properties. Impressive progress has been achieved in the chemistry of high-molecular-mass compounds. Among numerous examples, silicones should be mentioned in the first place. These organosilicon polymeric systems, which do not occur in the nature, were prepared only in the 20th century. As mentioned above, these compounds play an important role in the development of the modern civilization and have an enormous impact on the technological progress.

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There are several objective reasons for considering the progress particularly in the chemistry of silicones, which are the focus of the present review. First, these polymers are applied in almost all fields of the human activity, from domestic chemicals and cosmetic products to the space development and the production of solar energy.

The second, equally important reason is that the production of silicones is still based on the environmentally unfriendly chlorine cycle, where chlorine is generated in the stage of the production of chlorosilanes and is removed during their processing to polymers.

The third reason is the extensive growth of the production volume of silicones and an increase in the number of developed high-tech countries, which can run the full cycle from the preparation of silicon to the production of a wide range of organosilicon compounds. Until very recently, there were only five such countries (including the USSR). Now, the number of these countries has doubled and it will grow because silicone technologies spread worldwide.

The fourth reason, which is evidently significant, is the presence of inexhaustible resources, primarily, sources of silicon dioxide. At the time of the first oil crisis in the early 1970s, Academician K A Andrianov, who was one of the founders of the chemistry of silicones, reassured his coworkers '...sand will last our time, let us work'.

Finally, the last and probably one of the most important prerequisites is that, together with the quantitative growth, the production of silicones is brought to a new level. Below, we consider different aspects of this issue and make predictions about fundamental changes in this field of chemistry that would be expected in the nearest future.

II. Silicone nanostructures

Nanotechnology came into chemistry of silicones much earlier than it became widely used. Nanotechnology has shown efficiency in the design of particular materials with specific properties. Thus, silicone rubbers and aerogels are true nanomaterials that have come into use long before the emergence of the term nanostructure.

Silicone rubber [1] is the most popular nanomaterial. In the course of the creation of silicone rubber, the nanosized filling material Aerosil was empirically found. The addition of this filler into silicone rubber having a very low tensile strength results in the formation of siloxane rubber. The physico-mechanical properties of the latter are such that this rubber can be used in such practically important fields as medical items, cable insulation, sealing materials and so on. The efficiency of the addition of nanosized filler particles into this material was brought out clearly because the tensile strength of Aerosil-filled silicone rubber increases by almost an order of magnitude.[2] (For comparison, note that, for instance, the tensile strength of carbon black-filled rubber is only twice as high as that of natural rubber.[3])

Silica aerogel is one of the most efficient nanomaterials. Being discovered in 1931,[4] this material is still one of the most efficient heat-insulation materials. It was at least half a century ahead of its time and provided the basis for the rapidly developing branch of industry dealing with the design of heat-insulation materials for different purposes.

So-called MQ resins [5–8] is another example. The development of these copolymers is the story of more than half a century. Until very recently, their molecular structure was not known with certainty. Recent investigations showed that a nanocomposite material is hidden under this name.[9] Earlier, the qualitative term cyclolinear structure has been used to describe such polymers (see Ref. 10, p. 328). This term means only that macromolecules contain both linear and cyclic moieties.

The determination of the molecular structure of homopolymeric systems was a difficult problem as well. For example, a ladder-like structure was assigned to polyphenylsilsesquioxanes,[11–15] while the level of structure imperfection of these ladders is still under study.[16,17] It should be noted that investigations aimed at the directed (and more labour-intensive) synthesis of perfect ladder-like structures were initiated, and the degree of imperfection of ladder-like polyphenylsilsesquioxanes was estimated by comparing them with the latter structures.[18]

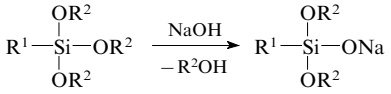
The determination of the structures of related polymethyl and polyvinyl products is even a more difficult task. In these cases, researchers usually restrict themselves to the rough characterization of the structure. This gave rise to the term 'silsesquioxanes', *i.e.*, compounds built of $SiO_{1.5}$ units in a random order. In the preparation of even the simplest linear polysiloxanes, equilibrium processes dominate, resulting in the equilibration and, consequently, in the random distribution of copolymer units along the chain.[19]

III. Development of selective synthesis methods

Organosilicon polymers are unique synthetic systems. The synthesis of these polymers became possible due to advances in heteroorganic and polymer chemistry. These important fields of science and practical activity are characterized not only by a diversity of systems under consideration but also by the accumulation of the most efficient scientific and engineering ideas. The last quarter century has witnessed a quantum leap in organosilicon chemistry, resulting in the elaboration of chemical processes giving polymeric structures with high selectivity. As mentioned above, most of silicon-containing polymers are produced in equilibrium random processes. As a consequence, the composition of these systems is rather well controlled, whereas the structure of macromolecules is difficult to control. The advent of the methods of nonequilibrium polymerization has changed situation for the better.[20,21] This approach is not only suitable for the polymer chain growth *via* the cleavage of cyclic structures, going without interchain exchange reactions, but also offers wide possibilities for the synthesis of star-like polymers and polymer brushes.

The most substantial achievement in the chemistry of organosilicon compounds is the use of sodium salts of organo(alkoxy)silanes for the preparation of polymers (Scheme 1).[22,23]

Scheme 1

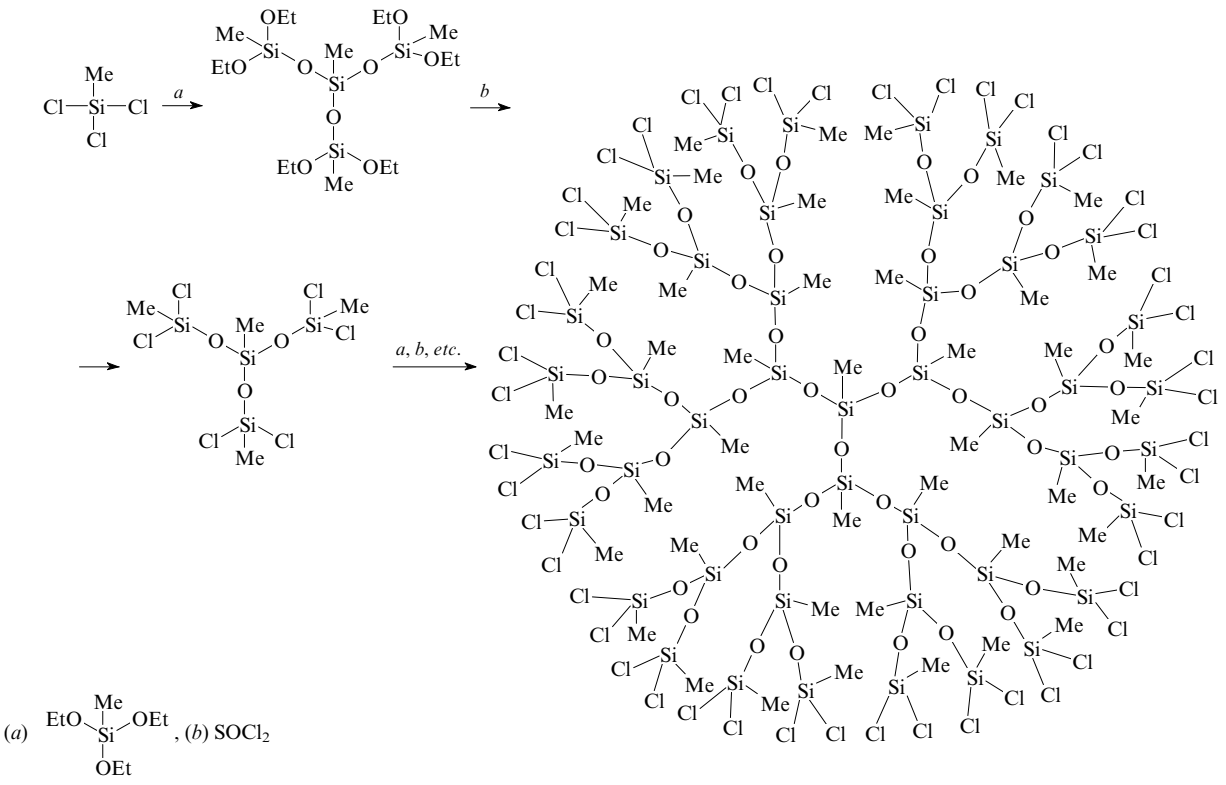


R^1, R^2 = Alk

Being constructed as new multifunctional monomers, these compounds little by little led to a considerable architectural revival in the field of siloxane polymers.†

† Ealrier, sodium salts have been also used for the synthesis of polymers with a specified structure.[24] For example, these salts were widely used in the chemistry of cage metallosiloxanes,[25,26] which are beyond the scope of the present review.

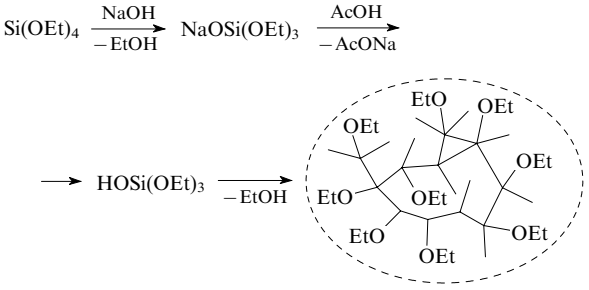
Scheme 2



It is sodium oxy(organo)alkoxysilanes that were the first reagents that made it possible to control the structures of various siloxane macromolecules. These reagents can be considered as compounds with independent functional groups. First organosilicon dendrimers were synthesized by successive reactions with the participation of each type of groups taken separately (Scheme 2).[27–29]

First inorganic hyperbranched polymers were synthesized in a similar way (Scheme 3).[30,31] In the resulting product (the shape of the polymer is shown by a dashed line), a silicon atom acts as a unit; the line between the units stands for the Si–O–Si bond; OEt groups are located at the free ends of the bonds (for simplicity, only some of them are shown).

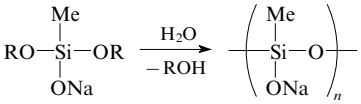
Scheme 3



In all these cases, the synthesis strategy based on the independence of functional groups was employed, sodium oxy groups and then alkoxy groups being involved in the reaction. Various combinatorial possibilities of these compounds have been discussed in our earlier review.[32] This approach was used, in particular, to synthesize acyclic polymethylsilsesquioxanes, which can be called regularly branched polymers. Later on, irregularly branched polymers containing a minimum number of cyclic moieties, so-called hyperbranched polyethoxysiloxanes, were prepared.[33,34]

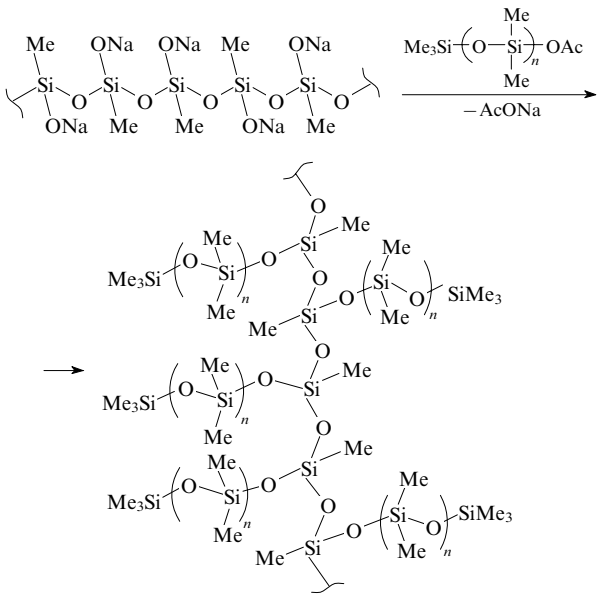
More recently, it was shown that the reverse order of the participation of functional groups in the reaction (first alkoxy groups and then sodium oxy groups) also results in

Scheme 4



R = Alk

Scheme 5

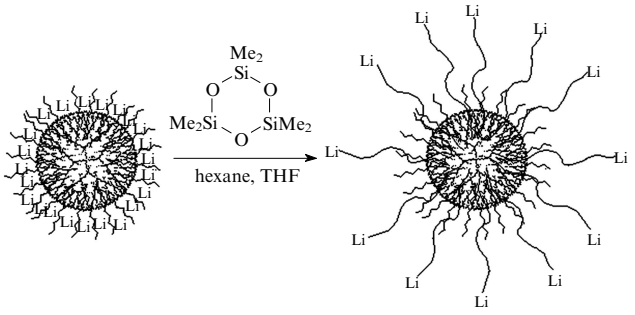


the controlled formation of the polymeric structure. This approach was used to synthesize linear polymethylsilsesquioxanes in the form of polysodium salts (Scheme 4)[35, 36] and numerous comb-type polymethylsiloxanes with different-length arms (Scheme 5).[37, 38]

It should be noted that new synthetic strategies are not only suitable for the preparation of linear polymethylsilsesquioxanes but also made it possible to carry our systematic studies on the assessment of the influence of the molecular structure on the properties of polymers. A number of compounds, which have an absolutely identical chemical composition but differ both in the structure of the macromolecules as a whole and the structural set of individual units, were synthesized. The range of isomeric polymers continues to expand, resulting in a database of polymeric model systems. An investigation and comparison of their properties will ultimately lead to the elucidation of detailed structure–property relationships for the most common polymethylsiloxane polymers.

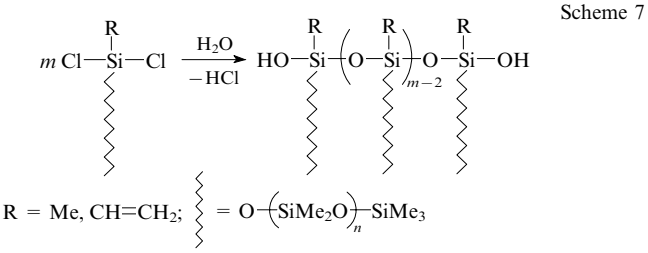
The use of the nonequilibrium polymerization of strained hexamethylcyclotrisiloxane with the participation of lithium initiators made yet another breakthrough in the control of the architecture of polydimethylsiloxanes. This method was employed to synthesize multiarm star-shaped siloxanes and dense polymer brushes. Various approaches were developed for the construction of dense macromolecules. Let us mention the 'grafting from' technique with the use of multicentre polylithium initiators, which were designed due to achievements in the chemistry of organosilicon dendrimers (Scheme 6)[39] and the synthesis based of macromonomers (Scheme 7).[40, 41]

Scheme 6



In these siloxane systems, important changes in the structure of multiarm star-shaped polymers were observed. An increase in the number of star arms is initially accompanied by the transition from the coil (12 and 16 arms) to globular (48 arms) conformation of macromolecules in solution,[39] which is manifested in fundamental changes in the dependence of the branching factor on the molecular mass of the polymer. A further increase in the number of

Scheme 7



star arms (to 128) results in the formation of a mesophase of polydimethylsiloxane chains with a melting point of 61 °C. The formation of this mesophase is caused by the stretching and interpenetration of polydimethylsiloxane arms in dense multiarm structures.[42] Therefore, a qualitative change was found in the molecular organization of the polymer in a block form.

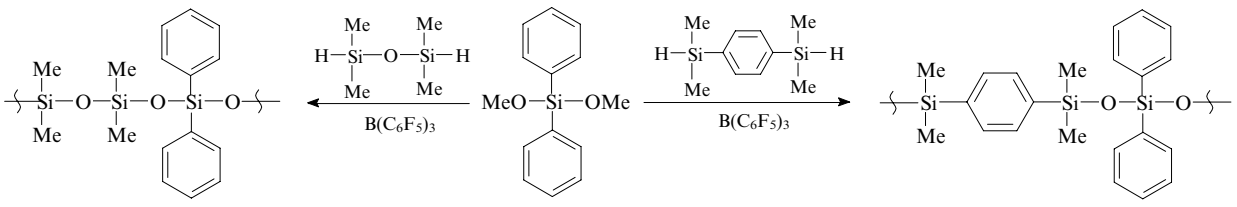
The recently discovered condensation of hydridosilanes with alkoxysilanes in the presence of catalytic amounts of $B(C_6F_5)_3$ (Scheme 8)[43] is an important achievement from the point of view of an increase in the selectivity of the synthesis of molecules with a siloxane backbone. A new promising method for the synthesis of siloxanes was developed[44–48] using the side reaction, which results in the formation of the siloxane bond and is accompanied by the release of alkane, as the main reaction. The possibility of the introduction of different silanes into this reaction was studied by Chojnowski *et al*.[49] It appeared that the steric effect plays an important role. Thus, the presence of bulky groups in the alkoxy substituent and at the silicon atom decreases the efficiency of the process and requires more drastic conditions for its initiation.[46]

This reaction is a real alternative to the conventional acid- and base-catalyzed nucleophilic substitution used for the formation of the siloxane bond. This reaction can be employed to develop new selective methods for the construction of a wide range of complex siloxane structures — linear, branched and three-demensional (Scheme 9).[48]

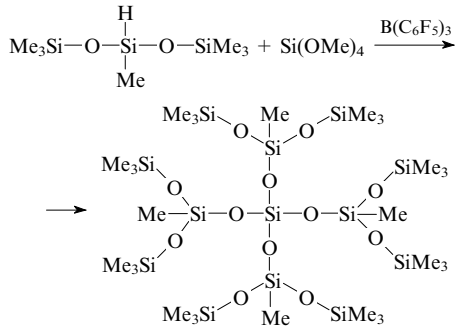
Although there are numerous methods for the formation of the siloxane bond, the latter approach seems very promising. Despite the occurrence of the side reaction (metathesis),[46] the level of control of the structure is rather high, and the choice of available reagents with desired functional groups is enormous. It should be noted that this reaction is environmentally friendly. Thus, alkanes that are released can be easily trapped and utilized. The only drawback of this reaction is that it requires an exotic catalyst, tris(perfluorophenyl) borate. However, since modern catalytic systems are rapidly put in the industry, this catalyst is now commercially available.

Considerable progress was achieved in the last two decades in the research on carbosilane systems. Although the production volume of carbosilane systems is traditionally smaller than that of siloxane polymers, the former

Scheme 8



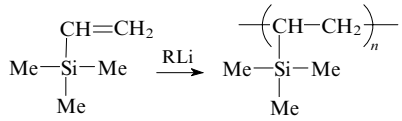
Scheme 9



systems are used in some high-tech fields, primarily, for the preparation of silicon carbide fibres and highly efficient membranes. Presently, studies of silicon carbide materials concern primarily the specificity of their molecular organization. Investigations of the products of the known rearrangement of polymethylsilane into polymethylcarbosilane [50–52] showed that these systems are dense globular molecular systems.[53]

In the design of carbosilane membrane materials, attention was focussed on the control of the properties by the directed changes in the structure and the expansion of their range. Methods were developed in detail for the synthesis of poly(vinyltrimethylsilane) (Scheme 10) [54] and poly(trimethylsilyl)propyne, as well as of their copolymers.[55–59]

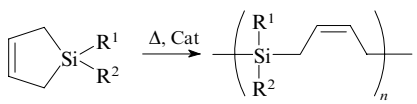
Scheme 10



The route from poly(vinyltrimethylsilane) to poly(trimethylsilyl)propyne was very long and took more than 30 years. However, the last decade has witnessed the preparation of a series of new carbosilane polymers. These polymers were synthesized by the polymerization of strained silacyclobutanes and disilacyclobutanes and by the ring-opening metathesis polymerization (ROMP).[60, 61] The latter method experiences a new birth associated with the design of new highly efficient catalysts.[62]

The metathesis of carbosilane rings, which was already known at the end of the 20th century (Scheme 11),[63, 64] has attracted attention of synthetic chemists as an efficient method for the preparation of carbosilane polymers.[65–67]

Scheme 11



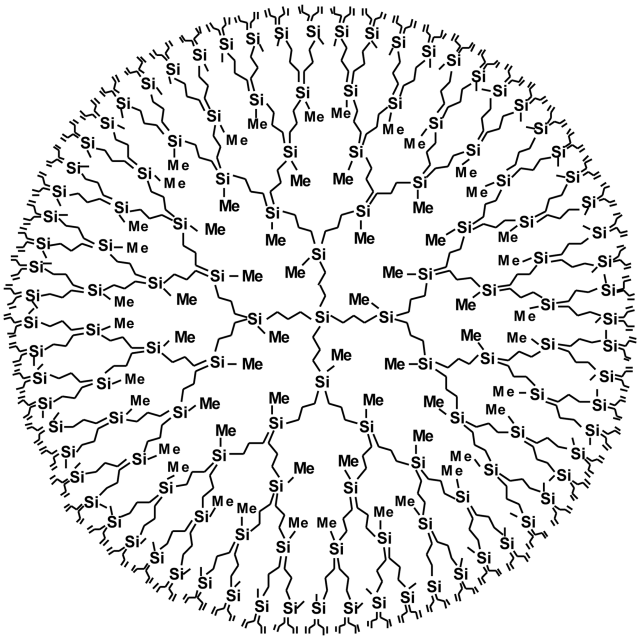
R^1, R^2 = Alk; Cat is a catalyst

This reaction was employed to prepare cyclolinear carbosilane polymers containing disilacyclobutane units.[68] The ring-opening polymerization of mono- and disilacyclobutane derivatives afforded a series of polysiltrimethylenes containing different substituents at the silicon atom and polydimethylsilmethylene.[69] An analysis of the permeability coefficients of the synthesized polysilalkylenes and data on the solubility and diffusion coefficients of different gases in these polymers showed that these compounds are promising for practical application as membrane materials in the separation of gaseous hydrocarbons.

When considering the advances in the chemistry of carbosilanes, note the progress in the research on the hydrosilylation reaction. Taking into account the importance of this process, researchers have focussed on the elucidation of the mechanism of the catalysis and the development of new catalyst systems. Let us mention the design of an efficient non-platinum catalyst as an intermediate result.[70, 71]

Equally important achievements were made in the targeted synthesis of complex molecular structures, such as carbosilane dendrimers and hyperbranched polymers. The strategies for the synthesis of both types of organosilicon polymers are based on a combination of the hydrosilylation and the use of an organometallic reactant. Among numerous original chemical schemes, the latter combination proved to be the most efficient for the synthesis of high-generation carbosilane dendrimers (structure **1**).[72–75] Important results of the studies of such dendrimers are the discovery and establishment of the nature of the second relaxation transition caused by the formation of the entanglements of dendrimer branches and the formation of a strong physical network.[76–80]

Structure 1

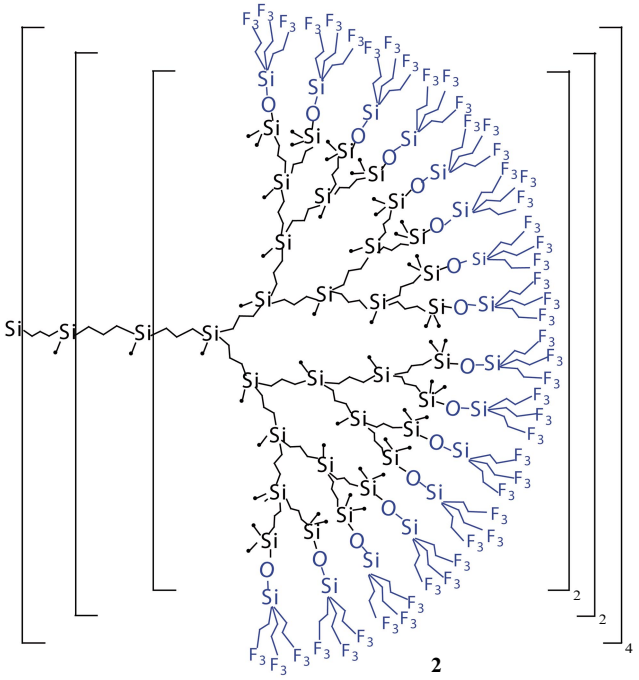


1

Dendrimers synthesized by the mixed carbosilane–siloxane method [81–83] were used for the preparation of a wide range of functional derivatives. Since these dendrimers contain a large and exactly known number of functional groups at the branch ends, they can be employed in the synthesis of derivatives with an outer shell of different nature. An important result of these studies is the conclusion that the outer shell has a key effect on the properties of dendritic macromolecules, primarily, on the glass-transition temperature.[84] Other properties of the polymers can also be controlled by changing the outer shell. Thus, the introduction of fluorinated moieties into the outer shell of the

dendrimers (structure **2**, the points at the ends of the bond stand for methyl groups) results in its low surface energy responsible for the hydrophobic and oleophilic properties of such dendrimers, *i.e.*, the dendrimers acquire specific properties dictated by the structure of the fluorine atom and the electronic structure of the C–F bond.[85–87]

Structure 2



2

The fluorine atom can be present at the periphery of the dendrimer in tris(perfluorophenyl)borate groups.[88,89] A dendrimer with this periphery is an active polyanionic cocatalyst for metallocenes, which are employed in the olefin polymerization. This system is characterized by high stability and is efficient in the reactions performed in aliphatic hydrocarbons, as well as in a block form and in the gas phase. The application of the strategy of spacer elongation made it possible to synthesize carbosilane dendrimers containing carborane clusters at the ends of the branches,[90–92] which are widely used in medicine, catalysis and the synthesis of liquid crystals and heat-resistant polymers. Carbosilane dendrimers containing hydroxyl[93–95] and phenylphosphine[96,97] functional groups were synthesized.

In recent years, numerous studies were performed on the synthesis of metal-containing catalyst systems based on carbosilane dendrimers.[98–101] Here the structure of the dendritic matrix carrier plays a key role because the accessibility of metal centres is of great importance for the catalytic activity of metallodendrimers. In addition, due to the definite sizes and shapes of such macromolecules, catalysts based on these compounds can be easily extracted from the reaction mixture by ordinary nanofiltration.

Considerable progress was achieved also in studies of hyperbranched carbosilane systems. It was shown that the properties of branched systems are influenced not only by the purely geometric factors[102] but also by the regularity of the molecular structure organization.[103–105] Since the chemical compositions of regular and irregular analogues are completely identical, these studies are very important because they provide an objective comparison of the properties of such systems.

Therefore, the control of the properties of new carbosilane polymers is related to the possibility of the fine control of their molecular structure. The employment of purely organic systems usually does not ensure such a high level of control. This fact should be considered as incontrovertible evidence for a considerable qualitative changes in the synthesis of organosilicon polymers.

IV. Aerogels

The improvement of the processes that form the basis of the industrial production of silicones entails considerable progress in the practical applications of organosilicon polymers. The above-mentioned aerogels provide one of the most striking examples.

Aerogels are porous ultralight materials derived from a gel, in which the liquid component is completely replaced by a gas with retention of the structure (Fig. 1). Since the creation of first aerogels by Kistler,[106] these materials have attracted sustained attention from researchers because of a complex of unique properties. They are characterized by the record low density and low values of the heat conductivity ($\sim$0.01 W mK^{-1}), dielectric constant ($\sim$1.0–2.0) and reflectivity ($\sim$1.05), as well as by high values of the porosity ($\sim$99%), transparency in the visible region of the spectrum (90%) and specific surface area (1.000 m^2 g^{-1}).

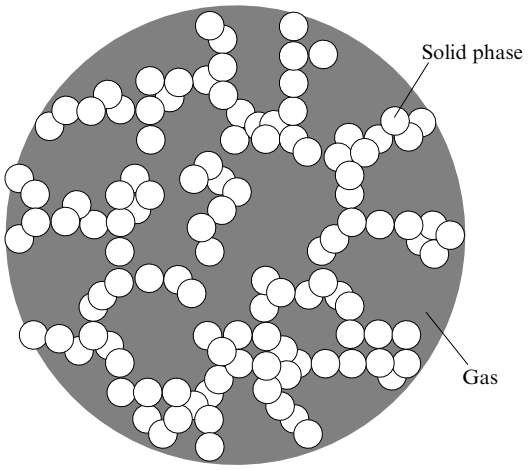


Figure 1. Structure of aerogel.

Aerogels were long employed only in special fields, for example, in space exploration, for the detection of elementary particles,[107] in catalysis,[108] in aerospace engineering and electronics.[109–111] The major shortcomings of aerogels that prevent them from being more widely used are their extreme brittleness and other unsatisfactory mechanical characteristics.[112] Other disadvantages are the hydrophilicity of traditional purely silica aerogels, the relatively high cost of production and the difficulties of the preparation of large samples because of the necessity of supercritical drying.

In the last two decades, many approaches were proposed for the improvement of mechanical properties of aerogels.

They are based mainly on the introduction of additional (most often, polymer) components. For example, Novak *et al.*[113] have succeeded in increasing the tensile strength of aerogels by the addition of polyvinylpyridine into the reaction medium and cross-linking of the aerogel with a small amount of $CuCl_2$. The resulting interpenetrating organic and inorganic networks are linked to each other by hydrogen bonds between pyridine and free silanol groups on the silica surface. Silica aerogels can be reinforced by introducing a polymer precursor in the course of their preparation.[114] The precursor forms a film, which covers the silica backbone of the gel and is covalently bound to it. Diisocyanate polymer cross-linking agents capable of forming bonds with silanol groups on the surface of the silica backbone were employed to prepare composite aerogels, which showed a 300-fold increase in the tensile strength at a three-fold increase in the density.[115] In this case, another problem was simultaneously solved: due to high tensile strength, composite aerogels did not require supercritical drying and were more hydrophobic.

Similar results were obtained for epoxide[116] and styrene[117] cross-linking agents. These agents were used to coat the aerogel, which was prepared by the copolymerization of tetramethylsiloxane with aminopropyl(triethoxy) silane containing aminopropyl groups.

An important line for the expansion of the spectrum of practical application of aerogels was supported by studies on the preparation of flexible aerogels. Different-density aerogels coated with a hexamethylene diisocyanate-based polymer were documented.[118] Capadona *et al.*[118] systematically investigated the dependence of the bending modulus on the parameters of the synthesis, which are responsible for the density of the silica backbone (the concentration of silanes), and the degree of cross-linking (the concentration of diisocyanates and the temperature). It was noted that aerogels with a density lower than 0.1 g cm^{-3} have certain flexibility, their tensile strength remaining by at least an order of magnitude higher than that of non-modified (totally inorganic) aerogels.

Another approach to the preparation of flexible aerogels is based on a decrease in the functionality of alkoxysilyl precursors. The two-step acid-base-catalyzed sol – gel process with the use of methyl(trimethoxy)silane as the precursor affords flexible (the compressibility is up to 60%) and superhydrophobic (the wetting angle is 164°) aerogels.[119]

Kanamoru *et al.*[120] also synthesized methylsilsesquioxane aerogels based on methyl(trimethoxy)silane. A surfactant was added into the reaction mixture to prevent the phase separation; urea was added as a catalyst for the condensation. Samples of this aerogel showed the uniaxial compression up to 80%, and they recovered their original shape after the removal of the load. Kanamoru *et al.* explained this increase in elasticity compared with inorganic tetraalkoxysilane-based aerogels by the following factors: 1) the lower density of the network; 2) the smaller number of residual silanol groups favouring irreversible shrinkage; 3) the uniform distribution of methyl groups in the bulk of the gel. All these factors, taken together, are responsible for the recovery of the original shape after the temporary compression.

It should be noted that the use of methyl(trialkoxy)silanes instead of tetraalkoxysilanes marked the transition from inorganic silica structures to organosilicon polymethylsilsesquioxanes. This transition confirms the main ides of the present review: an increase in both the selectivity and the control of the chemical reactions is important not by itself but as a means for improving the properties of materials and simplifying methods for their preparation. The employment of alkoxysilanes made it possible to improve the properties of aerogels, making the latter less brittle and more hydrophobic. These compounds, unlike their chlorosilyl analogues, make the process totally chloride-free.

Before turning to the prospects of chloride-free methods for the production of silicones, let us consider universal approaches of chemistry of organosilicon compounds developed in the past decade. We lump all these methods under the term active medium.

V. Active medium

The term 'active medium' is applied, in particular, to the condensation of alkoxysilanes in acetic acid. First attempts to perform the reaction of alkoxysilanes with acetic acid were made as early as in 1868.[121] After these experiments, in the 20th century chemists repeatedly turned to this reaction with different aims. The main goal was to prepare acetoxy derivatives having different structures. These compounds are widely used as components of cold vulcanizing systems for sealing materials and certain binding materials. However, condensation processes in the presence of acetic acid as the catalyst or the reactant have found little use because the reaction involves many steps and its mechanism is unclear.

The interest in acetic acid as a promising reactant was renewed in the course of the development of the chemistry of sol – gel processes. Here AcOH acts not only as the catalyst for the main condensation reaction of alkoxy groups with silanol groups but also serves as a reactant providing the generation of water in the system. This factor is particularly important for highly reactive titanium and other metal alkoxides.

The systematic investigation of this reaction with the participation of different organo(alkoxy)silanes showed that a typical cascade process proceeds in the presence of an excess of anhydrous acetic acid, resulting in the complete conversion of alkoxysilyl groups and the formation of siloxane products having different structures.[122]

It was shown that the following three reactions play a key role in the multistep process (Scheme 12): the acidolysis of alkoxysilyl groups [(reaction (1)], the esterification of acetic acid with the resulting alcohol [reaction (2)] and the hydrolysis of acetoxysilyl groups [reaction (3)]. The siloxane bond can be formed in two ways [reactions (4) and (5)]; however, the contribution of the homocondensation is insignificant.[123] Since water is generated in the slowest of the three steps (in the reaction giving ester), this process exhibits unique features, such as the molecular character of water consumption and full homogeneity. Numerous experiments with alkoxysilanes having different structures, which gave various products, show the versatility of this method. It can be applied on the industrial scale for the production of rubbers and liquids, branched polymer systems, hyperbranched polymers and nanogels.

Scheme 12

$$Me_2Si(OMe)_2 + AcOH \overset{(rapid)}{\rightleftharpoons} Me_2Si\begin{matrix}OMe\\Ac\end{matrix} + MeOH \quad (1)$$

$$AcOH + MeOH \overset{(slow)}{\rightleftharpoons} AcOMe + H_2O \quad (2)$$

$$Me_2Si\begin{matrix}OMe\\Ac\end{matrix} + H_2O \overset{(rapid)}{\rightleftharpoons} Me_2Si\begin{matrix}OMe\\OH\end{matrix} + AcOH \quad (3)$$

$$Me_2Si\begin{matrix}OMe\\Ac\end{matrix} + Me_2Si\begin{matrix}OMe\\OH\end{matrix} \overset{(rapid)}{\rightleftharpoons} \rightleftharpoons \begin{matrix}Me_2Si-O-SiMe_2\\|\quad\quad|\\MeO\quad\quad OMe\end{matrix} + AcOH \quad (4)$$

$$Me_2Si\begin{matrix}OMe\\OH\end{matrix} + Me_2Si\begin{matrix}OMe\\OH\end{matrix} \overset{(slow)}{\rightleftharpoons} \rightleftharpoons \begin{matrix}Me_2Si-O-SiMe_2\\|\quad\quad|\\MeO\quad\quad OMe\end{matrix} + H_2O \quad (5)$$

Anhydrous acetic acid plays a key role in this procedure, where it acts as a reactant (in the step giving ester), a catalyst (in the acidolysis and subsequent heterofunctional condensation of silanol and an acetoxy derivative accompanied by elimination of acetic acid) and a solvent ensuring the homogeneity of the process. The term active medium adequately reflects the multifunctionality of acetic acid in this process.

The condensation under active medium conditions has advantages over the commonly used hydrolytic polycondensation (HPC) of chlorosilanes.[124] A very important fact is that this method is oriented towards alkoxysilanes. In addition, the method has the following engineering benefits:

— the homogeneity provides a high level of composition uniformity even in the case of complex multicomponent systems;[125, 126]

— due to the cascade character, the process can be performed in a one-pot fashion;

— the separation of the product does not require washing out and, consequently, does not give large volumes of wash water, which are produced in most of HPC reactions.

Methyl acetate that is formed as a result of the condensation cannot be considered as a waste product since it is a commonly used solvent. Besides, the advantages of this method are that it requires simple apparatus and proceeds with high selectivity. The condensation of difunctional alkoxysilanes in an active medium can be forced to afford either linear or cyclic compounds as the major products in yields of up to 90% by slightly changing the reaction conditions.[127] In the case of highly functional systems, the molecular mass of the resulting polymers can be controlled rather efficiently.[128] The stabilization of the silanol groups in the final steps plays an important role, because it considerably decreases the risk of the gel formation.

VI. Prospects of the chloride-free synthesis of alkoxysilanes

An analysis of the prospects of the chloride-free synthesis of alkoxysilanes is a reasonable continuation of the present review. The preparation of organosiloxane polymers in an active medium is promising only if it is possible to perform the efficient direct synthesis of alkoxysilanes. Thus, the pathway of the development of global organosilicon industry was determined for a long period of time once the problem of the synthesis of methylchlorosilanes was successfully solved.[129] However, growing production volumes of silicones and a further expansion of the scope of their practical application, along with increasing environmental regulations, make the research on the development of chloride-free methods for the synthesis of organosilicon monomers quite important.

In 1946 Rochow[130] implemented the idea of the chloride-free direct synthesis of organo(alkoxy)silanes by passing gaseous methanol over a copper silicon alloy (the ratio Si : Cu = 9 : 1) by analogy with the direct synthesis of chlorosilanes. Tetramethoxysilane was obtained as the major product. The reaction mixture contained also small amounts of methyl(hydrido)silanes, but attempts to isolate individual products failed. Under similar conditions, the conversion of ethanol was only 10%;[131] the reaction gave condensed ethyl silicates. Attempts to find an appropriate catalyst for the selective formation of organo(alkoxy)silanes according to this method were unsuccessful.

More recently, three- and tetramethoxysilanes were synthesized in 48% and 40% yields, respectively, by the reaction of methanol with a copper silicon alloy in a liquid phase (in a suspension in the high-boiling-point solvent, silicone oil[132]).

Currently, the reactions of silicon with alcohols are studied mainly in the liquid phase.[133, 134] Polyaromatic oils,[135, 136] alkylated aromatic compounds,[137] condensed orthosilicates[138] and so on are used as solvents. Copper and the following organic and inorganic copper compounds serve as catalysts: metal copper powder, colloidal copper, CuO, $Cu(OH)_2$, alkoxides, carboxylates, *etc*. These reactions generally give alkenes and aldehydes as by-products deactivating the catalyst. The introduction of reducing additives (hydrogen, CO or monosilanes) contributes to the stabilization of the process.[137] It should be noted that the reaction is characterized by high and stable reaction rate; the selectivity with respect to trialkoxysilane is higher than 80%, the conversion of silicon reaches 70%.[139] Suzuki and co-workers[140] found that the catalyst can be activated by the addition of a $Si-CuCl_2$ mixture at 260 °C. This led to the complete conversion of silicon and high selectivity (89%) with respect to trimethoxysilane.

The search for efficient promoters, which would increase the conversion of silicon and the selectivity and stability of the process, is currently under-way. It appeared that in the presence of copper(I) chloride, the main reaction pathway leads to the formation of trialkoxysilanes.[134] Han *et al.*[133] used additives of an activator as a suspension of CuCl in dibenzyltoluene at 200–320 °C. The overall yield of methoxysilanes reached 95%; the selectivity was 81% and the conversion of silicon was 85%. In the presence of alkaline catalysts (alkali metal alkoxides,[141] calcium oxide or hydroxide[142]), the reactions give tetraalkoxysilane as the major product.

Promoting high-boiling-point cyanide and nitrile additives, in particular, $[NC(CH_2)_x]_2SiY_2$, where $x = 2-8$; Y = Alk, cyclo-Alk, Ar, ArAlk, OR (R = Me, Et, Pr^n), are employed to increase the conversion of silicon and the selectivity of the formation of trialkoxysilane in the direct synthesis of alkoxysilanes with the participation of ethanol and higher alcohols. These promoters slow down the deactivation of the catalyst, thus stabilizing the process.[143]

The publications cited above show that the authors and big companies they represent have serious commercial ambitions. Attempts to apply nanotechnology to the direct synthesis of alkoxysilanes are documented. Thus, nanosized (0.1 – 100 nm) particles of copper and its compounds were proposed as catalyst precursors.[144] In the authors' opinion, the use of such particles provides a high degree of dispersion of the catalytic sites, thus increasing the rate and selectivity of the reaction, as well as the conversion of silicon, resulting in a substantial decrease in the necessary amount of copper.

Ensuring of the steady-state conditions of the reaction also contribute to the optimization of the process. The efficiency of the addition of surfactants (fluorine derivatives of silicones) to the reaction suspension was reported.[136] This leads to a decrease in the time required for the establishment of steady-state conditions, improves the control of foaming and increases the selectivity of the reaction and the yield of the product. This process affords trialkoxysilane as the major product (the ratio trialkoxysilane : tetraalkoxysilane > 9; on the average, this ratio is 15). A similar effect was observed in the reaction with the use of different silicone derivatives as promoters: hydrophobized silica sol particles, polyorganosiloxanes, cyclic and branched oligomers and polymers.[139] In the presence of antifoaming agents, the conversion of silicon reaches 92% – 94%. Two hours after the beginning of the process, the selectivity with respect to trimethoxysilane is higher than 85%.

To prepare ethoxy derivatives under similar conditions, methanol was pre-added as a promoter to a suspension of an activated catalytic system. In the beginning of the reaction, the temperature of the reaction mixture was lowered to 230 °C to suppress side reactions with the participation of alcohols (dehydrogenation and dehydration). In the presence of antifoaming additives, the triethoxysilane : ethanol ratio in liquid products is 80 : 20 after 60 min; in the absence of these additives, the ratio is ~ 60 : 40.

As can be seen from the available data, the further development of chloride-free methods for the synthesis of tri- and tetraalkoxysilanes holds promise, and these methods should be highly competitive with conventional processes.

The above-considered examples refer to the synthesis of alkoxysilanes other than organo(alkoxy)silanes. Hence, it cannot be said that there is a strategic breakthrough in chloride-free methods. However, first examples of the chloride-free synthesis of organo(alkoxy)silanes were described. Okamoto *et al.*[145 – 147] published a series of studies on the direct synthesis of alkyl(alkoxy)silanes at elevated pressure. The reaction of methanol with silicon in an autoclave at 160 °C with the simultaneous addition of ethylene into the reaction zone[145] gave methoxy(ethyl)silanes with a selectivity of 26% [4% of dimethoxy(ethyl)silane and 22% of trimethoxy(ethyl)silane] at the conversion of silicon equal to 59%. In the reaction in a high-pressure flow reactor,[146] the selectivity with respect to dimethoxy(ethyl)silane increased to 30%; the yield of the target product was 20%.

The addition of small amounts of thiophene into the reaction mixture of metallic silicon and methanol at 380 °C, made it possible to prepare, along with tri- and tetramethoxysilanes, methyl(dimethoxy)silane with a selectivity of 22%.[147] The addition of formaldehyde trimers also leads to an increase in the selectivity of the reaction. Under similar conditions, the use of ethanol resulted in 14% selectivity with respect to ethyl(diethoxy)silane; the conversion of silicon was 43%.

Different methods for the synthesis of alkyl(alkoxy)silanes were covered by U.S patents: the reaction of activated silicon with ethers in the presence of catalytic amounts of a halogen-containing catalyst in an autoclave at 200 °C;[148] the reaction of silicon with alcohol, acetal or carboxylic ester in the presence of a copper catalyst in a high-boiling-point solvent for 90 – 100 h;[149] the reaction of tetraalkoxysilane with activated carbon at 250 °C in the presence of bases (metal hydroxides, amides, alkoxides).[150] In all cases, the resulting organo(alkoxy)silanes were not isolated and were only detected in the reaction mixture, whose composition was analyzed by GLC, NMR spectroscopy and GC-mass spectrometry.

The available data are of no commercial interest as yet. However, they give hope that that studies aimed at developing of chloride-free process for the production of organo(alkoxy)silanes will lead to success.

VII. Processing of siloxane wastes

The waste safety and recycling of the produced items are the next important factors in the route of bringing the production of silicone to the platform of sustainable development. From this point of view, silicone materials have considerable prospects. The silicone industry has given little attention to this aspect primarily because the production volumes of silicones and organic polymers are non-comparable. However, at all times there were prerequisites for the solution of the problem of the silicone waste processing. Thus, silicone rubber easily undergoes thermal catalytic depolymerization and the siloxane bond is rather reactive towards electrophilic and nucleophilic agents. Studies on the thermal decomposition of silicone rubber wastes to produce the so-called 'silicone oil' consisting of dimethylcyclosiloxanes of different ring size, which are suitable for recylcing,[151, 152] can be mentioned as an illustration. Another line of the processing is based on the chemical decomposition of siloxane polymers to low-molecular-mass products. In this case, the efficient contact of the reactant with pulverized wastes is provided with the use of either solvents or water emulsions,[153 – 157] including in supercritical media.[158, 159] An approach based on the treatment of pulverized rubbers with a solution of tetraethoxysilane was described;[160] however, this method is of little use for rubber mixtures. Scientific publications on this issue are scarce due, to a large extent, to the well-known theoretical fundamentals of all methods mentioned above. However, as the requirements for recycling become more stringent, versatile technologies would be expected to be developed. For example, let us mention recent reports on the utilization of wastes in the production of organosilicon rubbers and rubber mixtures at high temperatures (140 – 190 °C) using a mixture of alkali metal hydroxide and water,[161, 162] as well as on the employment of an organosilicon solvent followed by the chemical decomposition in an alkaline medium at 50 – 60 °C.[163, 164] The latter method served as the basis for the development of an efficient scheme for the recycling of wastes of organosilicon rubbers giving a liquid product, which can serve as a silicon-containing raw material for the production, for example, of different rubber mixtures and

compounds. The recycling of wastes of siloxane rubbers giving the starting monomers and a filler is even more promising.[165]

Therefore, versatile methods for the processing of silicone materials, including filled composite materials, would be expected to be developed in the nearest future, because all necessary prerequisites are available for this.

VIII. Conclusion

The above brief analysis of the prospects for the development of the chemistry of organosilicon polymers shows that this field of research is in a very important stage of evolution. Being objects of research in both heteroorganic and polymer chemistry, silicones have certain highly specific features. Thus, there are inexhaustible resources of these materials, and efficient procedures of the recycling of their wastes are available. Taking into account the advances of the last years in the control of the structures and properties of macromolecules and in the development of selective methods of their synthesis, one would expect a breakthrough in this field of chemistry with all traits of the transition from quantitative changes to a quantum leap. Actually, the transition to chloride-free production can occur in the foreseeable future. As was shown above, there are serious prerequisites to this transition, such as progress in the direct synthesis of alkoxysilanes, which can serve as the basis for the preparation of various organosilicon products, from liquids to rubbers, binders, inorganic and hybrid materials.

We also mention the bottleneck to the transition to new environmentally more friendly methods with the participation of organosilicon systems, that is the direct synthesis of dimethyl(dialkoxy)silanes. However, there will be no need in chloride-free methods as applied to the available organosilicon products for a long time, because there is an abundance of industrial plants in the world for the production of organosilicon oligomers and polymers prepared based on chlorosilanes according to the traditional process. For technologies of tomorrow to find use and for serious research teams to be interested in their development, the properties of the main types of organosilicon products should be qualitatively changed. From this point of view, a high degree of control of the structure and, consequently, properties of organosilicon polymers, which is considered in the present review, is of great importance. A comparison of these diverse problems and approaches to their solution makes us to conclude that the joint consideration of these problems allows one to easily reveal their relationships and correlations. Actually, an increase in the selectivity of chemical reactions and the advent of efficient methods for the control of the polymeric structures[166] would be expected to lead to the design of new efficient materials necessary for a significant growth in the global silicone market. This, in turn, will ultimately stimulate the transition to chloride-free methods for the synthesis of main monomers and related polymers. Besides, these relationships also include the possibility of the efficient regeneration of spent materials.

Therefore, the ideology of sustainable development as referred to the organosilicon production shows considerable promise and would be expected to be realized in the nearest future. The sum of internal and external factors, which determine the vector of the development of the organosilicon complex as a whole, attests' to the prospects of this field as regards the expansion of structural diversity and an increase in the quality of the available products, the transition to chloride-free technologies and a high degree of the recycling of these materials. Examples which most completely correspond to the model of sustainable development are scarce in materials science.

In conclusion, let us mention that the analysis of the literature in the present review is not claimed to be complete and does not include the detailed consideration of particular aspects. Only the main trends which seem to be most promising and which reflect the main vectors of the development of the chemistry of silicones are considered.

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